

Measurements of Hazardous Organic  
Chemicals in the Ambient Atmosphere

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**MEASUREMENTS OF HAZARDOUS ORGANIC CHEMICALS  
IN THE AMBIENT ATMOSPHERE**

by

H.B. Singh, L.J. Salas  
R. Stiles, and H. Shigeishi  
Atmospheric Science Center  
SRI International  
Menlo Park, California 94025

Cooperative Agreement  
805990

Project Officer

L. Cupitt  
Atmospheric Chemistry and Physics Laboratory  
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY  
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## ABSTRACT

Analytical methods were refined and applied to the ambient analysis of 44 organic chemicals, many of which are bacterial mutagens or suspected carcinogens. On-site field collection programs, based on single site studies of 9 to 11 days duration each, were conducted in 10 U.S. cities. Field studies were performed with an instrumented mobile laboratory. A round-the-clock measurement schedule was followed at all sites. The field measurements allowed a determination of atmospheric concentrations, variabilities, and mean diurnal behaviors of the chemicals. The data were analyzed relative to theoretically estimated removal rates. Typical diurnal profiles show highest concentrations of the primary pollutants during nighttime or early morning hours, with minimum concentrations in the afternoon hours. Chemistry plays only a nominal role in defining this diurnal behavior in most cases. Except for aromatic hydrocarbons and aldehydes, average concentrations of the measured species were in the 0- to 5-ppb range. The average concentration range observed for aromatics and aldehydes was 0- to 20-ppb.

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## SECTION 1

### INTRODUCTION

A recent report from the Office of the U.S. Surgeon General concluded that "toxic chemicals are adding to the disease burden of the United States in a significant, although as yet not precisely defined way" (U.S. SG, 1980). Estimates suggesting that 50 to 90 percent of human cancer is of chemical origin continue to persist (LaFond, 1978; U.S. SG, 1980). The degree to which the general ambient environment contributes to human cancer is a matter of both active research and debate (Peto, 1980). There is little doubt, however, that over the last three decades large amounts of a growing number of synthetic organic chemicals have been released into the ambient environment. In many cases, virtually the entire quantity of synthetic organic chemicals manufactured is released into the environment as a necessary outcome of use (ADL, 1975; Singh et al., 1979a). Urban atmospheres contain a complex mixture of a large number of chemicals, many of which are known to be toxic at concentrations significantly higher than those encountered in typical ambient atmospheres. The process of understanding the risks associated with exposure to potentially hazardous chemicals requires a determination of the ranges of concentrations that can be found in the ambient air.

This study was initiated primarily to examine the range of concentrations of a variety of potentially hazardous gaseous organic chemicals\* at selected urban locations under varying meteorological and source-strength conditions. These chemicals were measured and analyzed on-site in ambient air using a suitably outfitted mobile laboratory. The overall program of analytical methods development, field measurements, data collection, and data analysis is expected to provide information that will permit a better assessment of the atmospheric abundance and chemistry of this potentially harmful group of chemicals.

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\*The term "hazardous chemicals" as used here is not intended to imply that a proven human health hazard exists. In most cases toxicity studies are incomplete or inconclusive and involve extrapolation of animal data to humans.

## SECTION 2

### OVERALL OBJECTIVES

The overall objective of the study was a survey of the ranges of concentrations of selected hazardous organic chemicals which may be found in urban atmospheres within the United States.

To achieve this general objective, the following approach was used:

- Develop procedures for the sampling and analysis of selected organic chemicals, at expected ambient concentrations.
- Equip and prepare a mobile environmental laboratory to conduct on-site and around-the-clock measurements of chemical species of interest.
- Conduct field measurements at several locations with the primary purpose of developing a reliable data base that could be used to better understand the concentrations and diurnal behavior of these chemicals.
- Develop and synthesize information from the literature on sources, fates, and effects of these potentially hazardous chemicals.
- Prepare a final report that combines information developed from the preceding tasks.

### SECTION 3

#### ANALYTICAL METHODOLOGY

##### TRACE CONSTITUENTS OF INTEREST

The chemicals targeted for this study were those suspected of being hazardous and chemicals structurally similar to these. Although toxicity data in many cases were insufficient to prove a human health hazard, they were adequate to merit inclusion of the chemical in our measurement plan. Many selected chemicals were either bacterial mutagens or suspected of being carcinogens. Some nontoxic chemicals, such as chlorofluorocarbons, were measured primarily because of their ability to act indicators of anthropogenic pollution. The final list of chemicals to be measured was based on further discussions with the project officer; our ability to satisfactorily measure a trace constituent at its expected ambient concentration was an essential requirement.

A total of 45 trace chemicals were targeted and are categorized in Table 1. The categories include chlorofluorocarbons, halomethanes, haloethanes, halopropanes, chloroalkenes, chloroaromatics, and oxygenated species. In addition to the chemicals of Table 1, other important meteorological parameters (wind speed, wind direction, temperature, pressure, relative humidity, and solar flux) were also measured.

Table 1 also identifies more than two dozen chemicals as bacterial mutagens (BM) or suspected carcinogens (SC). This information is obtained from literature and studies that have evaluated large bodies of available data (Helmès et al., 1980; Albert, 1980; U.S. SG, 1980). Information about bacterial mutagenicity is based largely on the "Ames Salmonella Microsome Assay" (McCann and Ames, 1977). In some cases other bacterial tests have also been utilized [BM(O)]. It is relevant to add that nearly 90 percent of tested animal chemical carcinogens are also found to be mutagens in the "salmonella/microsome" test, while an equal percentage of tested noncarcinogens are found to be nonmutagens (McCann and Ames, 1977). Mutagenic tests are direct and simple, but the carcinogenicity information is based on epidemiology, animal tests, and a critical and a comprehensive evaluation of carcinogenic, mutagenic, and other toxicological data (Albert, 1980; U.S. SG, 1980). Evidence for the mutagenicity of toluene (U.S. SG, 1980; Albert, 1980) and carcinogenicity of trichlorethylene (Albert, 1980) is currently in some dispute for lack of sufficient data.

TABLE 1. LIST OF TARGET CHEMICALS

Chemical Name*	Chemical Formula	Toxicity†
<b>Chloro-Fluorocarbons</b>		
Trichloromonofluoromethane (F11)	$\text{CCl}_3\text{F}$	These chlorofluorocarbons are nontoxic but have excellent properties as tracers of urban air masses
Dichlorodifluoromethane (F12)	$\text{CCl}_2\text{F}_2$	
Trichlorotrifluoroethane (F113)	$\text{CCl}_2\text{FCClF}_2$	
Dichlorotetrafluoroethane (F114)	$\text{CClF}_2\text{CClF}_2$	
<b>Halomethanes</b>		
Methyl chloride	$\text{CH}_3\text{Cl}$	BM‡
Methyl bromide	$\text{CH}_3\text{Br}$	BM
Methyl iodide	$\text{CH}_3\text{I}$	SC‡, BM
Methylene chloride	$\text{CH}_2\text{Cl}_2$	BM
Chloroform	$\text{CHCl}_3$	SC, BM
Carbon tetrachloride	$\text{CCl}_4$	SC, NBM‡
<b>Haloethanes and halopropanes</b>		
Ethyl chloride	$\text{C}_2\text{H}_5\text{Cl}$	-
1,1 Dichloroethane	$\text{CHCl}_2\text{CH}_3$	BM(0)‡
1,2 Dichloroethane	$\text{CH}_2\text{ClCH}_2\text{Cl}$	SC, BM
1,2 Dibromoethane	$\text{CH}_2\text{BrCH}_2\text{Br}$	SC, BM
1,1,1 Trichloroethane	$\text{CH}_3\text{CCl}_3$	Weak BM
1,1,2 Trichloroethane	$\text{CH}_2\text{ClCHCl}_2$	SC, NBM
1,1,2,2 Tetrachloroethane	$\text{CHCl}_2\text{CHCl}_2$	SC, BM
1,2 Dichloropropane	$\text{CH}_2\text{ClCHClCH}_3$	BM
<b>Chloroalkenes</b>		
Vinylidene chloride	$\text{CH}_2=\text{CCl}_2$	SC, BM
(cis) 1,2 Dichloroethylene	$\text{CHCl}=\text{CHCl}$	NBM
Trichloroethylene	$\text{CHCl}=\text{CCl}_2$	SC, BM
Tetrachloroethylene	$\text{CCl}_2=\text{CCl}_2$	SC
Allyl chloride	$\text{ClCH}_2\text{CH}=\text{CH}_2$	SC
Hexachloro-1,3 butadiene	$\text{Cl}_2\text{C}=\text{CCl}-\text{CCl}=\text{CCl}_2$	BM
<b>Chloroaromatics</b>		
Monochlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	BM(0)
o-Chlorotoluene	$\text{C}_6\text{H}_4\text{CH}_3\text{Cl}$	BM
o-Dichlorobenzene	$\text{o-C}_6\text{H}_4\text{Cl}_2$	BM(0)
m-Dichlorobenzene	$\text{m-C}_6\text{H}_4\text{Cl}_2$	BM(0)
p-Dichlorobenzene	$\text{p-C}_6\text{H}_4\text{Cl}_2$	BM(0)
1,2,4 Trichlorobenzene	$\text{1,2,4-C}_6\text{H}_3\text{Cl}_3$	-
<b>Aromatic hydrocarbons</b>		
Benzene	$\text{C}_6\text{H}_6$	SC
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	BM(0)
Ethyl benzene	$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$	-
m/p-Xylene	$\text{m/p-C}_6\text{H}_4(\text{CH}_3)_2$	-
o-Xylene	$\text{o-C}_6\text{H}_4(\text{CH}_3)_2$	-
4-Ethyl toluene	$\text{4-C}_6\text{H}_4\text{C}_2\text{H}_5\text{CH}_3$	-
1,2,4 Trimethyl benzene	$\text{1,2,4-C}_6\text{H}_3(\text{CH}_3)_3$	-
1,3,5 Trimethyl benzene	$\text{1,3,5-C}_6\text{H}_3(\text{CH}_3)_3$	-
<b>Oxygenated and nitrogenated species</b>		
Formaldehyde	$\text{HCHO}$	SC, BM
Acetaldehyde	$\text{CH}_3\text{CHO}$	-
Phosgene	$\text{COCl}_2$	-
Peroxyacetyl nitrate (PAN)	$\text{CH}_3\text{COOONO}_2$	Phytotoxic
Peroxypropionyl nitrate (PPN)	$\text{CH}_3\text{CH}_2\text{COOONO}_2$	Phytotoxic

\*In addition to chemical species, meteorological parameters were measured. These were: wind speed, wind direction, temperature, pressure, relative humidity, and solar flux.

†Toxicity information obtained from reviews by Helmes et al. (1980); Albert (1980); U.S. SG (1980). Additional references are contained within these reviews.

‡BM: Positive mutagenic activity based on Ames salmonella mutagenicity test (Bacterial Mutagens).

NBM: Not found to be mutagens in the Ames salmonella test (Not Bacterial Mutagens).

SC: Suspected Carcinogens.

BM(0): Bacterial Mutagen (Other microbial tests).

## FIELD INSTRUMENTATION

One primary motivation of our study was to conduct on-site analysis to minimize the many problems that are encountered when air samples are collected in bags, vessels, or in tubes filled with solid sorbents.

It is widely recognized that the integrity of an air sample is best maintained when:

- Nominal amounts of air samples are collected on inert surfaces
- Time between collection and analysis is kept to an absolute minimum
- Prior to analysis, trace volatile chemicals are exposed to as low a temperature as possible.

Our on-site field analysis program was devised to take maximum advantage of these desirable features. All field work was conducted using a suitably instrumented mobile environmental laboratory. Table 2 summarizes the equipment that was available on our mobile laboratory for the conduct of this study. This laboratory was air-conditioned for temperature control and operated on a 220-V, 80-A circuit. Provision was also devised for operating on 110-V input. A 200-m electrical cord was always used to station the laboratory away from the electrical source or a power pole. The sampling manifold was all stainless steel with a variable inlet height. (In all cases, the sampling manifold was adjusted to be higher than nearby structures: A typical manifold inlet height was 5 m above ground.) For pumping and pressurizing air samples, a special stainless-steel metal bellows compression pump (Model MB 158) was always used. For the analysis of aldehydes, surface air was sampled in an all-glass apparatus.

## EXPERIMENTAL PROCEDURES

For all the halogenated species and organic nitrogen compounds shown in Table 1, electron-capture detector (ECD) gas chromatography (GC) was the primary means of analysis. The aromatic hydrocarbons were measured using flame-ionization detector (FID) gas chromatography. Formaldehyde was measured by the spectrographic chemical analysis technique utilizing the chromotropic acid procedure (U.S. Public Health Service, 1965). In the third year of this research, formaldehyde and acetaldehyde were also measured by analyzing the 2,4 dinitrophenylhydrazine derivatives, formed by reaction of 2,4 dinitrophenylhydrazine (DNPH) with aldehydes, with high-performance liquid chromatographic (HPLC) methods (Kuwata et al., 1979; Hull, 1980; Fung and Grosjean, 1981; Salas and Singh, 1981).

For the aldehyde DNPH-HPLC analysis, the sampling reagent was prepared by dissolving 0.25 g of purified DNPH in 1.0 liter of HPLC-grade acetonitrile and adding 0.2 ml of concentrated sulfuric acid to this solution. DNPH was purified by repeated recrystallization (at least three times) from HPLC-grade acetonitrile. A 7-ml aliquot of this reagent solution was transferred into a bubble and cooled with the help of an icewater Dewar flask. An air flow rate of 0.5 l/min was maintained for a typical sampling period of 2 hours. After

TABLE 2. ENVIRONMENTAL MOBILE LABORATORY INSTRUMENTATION\*

Instrument	Features	Analysis
Perkin Elmer 3920 GC1	2 ECD <sup>†</sup> , 1 dual FID <sup>‡</sup>	Trace constituents
Perkin Elmer 3920 GC2	2 ECD, 1 dual FID	Trace constituents
Perkin Elmer 3920 GC3 (capillary column GC)	2 ECD, 1 dual FID	Trace constituents
Coulometric dual EC-Gc	Coulometric ECD	Halocarbons, PAN, PPN, COCl <sub>2</sub> ; calibration
Spectraphysics HPLC 8700 (variable wavelength SP3400 detector)	HPLC <sup>§</sup>	Aldehydes
Beckman 6800	FID	CO-CH <sub>4</sub> -THC
Horiba AIA-24	NDIR <sup>**</sup>	CO, CO <sub>2</sub>
Bendix 8101-B	Chemiluminescent	NO, NO <sub>2</sub>
Monitor Labs Model 8440E	Chemiluminescent	NO and NO <sub>2</sub>
Dasibi Model 1003 AH	Photometric principle	O <sub>3</sub>
AID Model 560	Chemiluminescent	O <sub>3</sub>
Bendix 8002	Chemiluminescent	O <sub>3</sub>
Eppley pyranometer		Solar flux
Eppley UV radiometer		Ultraviolet radiative flux
Miscellaneous meteorological equipment		Wind speed, wind direction, temp, pressure, dew point, relative humidity
Auto Lab IV Data System (No. 1)		GC data
SP-4000 Multichannel Data System (No. 2)		GC data
HP-3390 printer plotter		
Digitem Data System (No. 3)		All continuous air quality and meteorological data

\*Note: Sampling of all trace organics is performed from a stainless-steel manifold. A Teflon® manifold is used for inorganics (e.g., O<sub>3</sub>, NO, NO<sub>x</sub>).  
Finnigan 3200 GC/MS available to this project at SRI.

<sup>†</sup>Electron capture detector.

<sup>‡</sup>Flame ionization detector.

<sup>§</sup>High performance liquid chromatograph.

<sup>\*\*</sup>Nondispersive infrared.



sampling, a 2.0 ml aliquot of the exposed reagent solution was transferred into a heavy-walled reaction flask with Teflon® cap, warmed at 75°C for 20 minutes, and subsequently cooled to room temperature. The DNP hydrazone derivatives were analyzed with a Spectra Physics HPLC (Model 8700) equipped with a variable wavelength detector (Model 3400) set at 360-nm wavelength. The HPLC was used in an isocratic mode with a solvent flow rate of 1.5 ml/min. A 36 percent H<sub>2</sub>O; 64 percent acetonitrile solvent gave the most desired resolution of the two hydrazones of interest. A 10 microliter sampling loop was used for HPLC analysis. Typical analysis time was less than 10 minutes.

Under normal operating conditions, five GC channels were operated with ECDs and only one with FID. Although the exquisite sensitivity of the ECD would allow the determination of several species in Table 1 with a direct 5-ml injection of air, preconcentration of air samples was necessary for efficient operation. All six GC channels were equipped with stainless-steel sampling valves and could be operated either with a direct sampling loop or with a preconcentration trap. In no instance was a sample size of greater than 1 liter used: In most cases, sample volumes of 500 ml or less were satisfactory. Sample preconcentration was conducted on a 4-inch-long bed of 100/120 mesh glass beads packed in 1/16-inch diameter stainless-steel tubing maintained at liquid oxygen temperature. The glass beads could be replaced with an equivalent length of SE-30 packing (3 percent SE-30 on 100/120 mesh acid-washed chromosorb W) or glass wool with completely satisfactory results. Desorption of chemicals from the preconcentration traps was accomplished by holding the trap at boiling-water temperature and purging with carrier gas. Additional details have also been earlier provided by Singh et al. (1979a,b; 1980).

Because the use of liquid oxygen is tedious at best, we attempted to preconcentrate air samples on Tenax® traps at room temperature. Considerable testing indicated that Tenax® suffers from serious artifact problems. A number of "ghost peaks" were seen, particularly on our ECD systems. In addition, we encountered serious difficulties in quantitatively absorbing and desorbing specific species that were tested. Because of the possibility of confusing artifacts (sometimes present in significant amounts) with real pollutants, we have discontinued the use of Tenax® as a column pretrap. It appears that oxygen or ozone can oxidize Tenax® monomer to produce electron-absorbing oxygenated species; therefore, all preconcentrations in this study have been performed on glass beads, glass wool, or SE-30 packing surfaces. These artifact problems have also been observed by other investigators (Sievers, 1981).

The sampling for GC analysis was achieved by pressurizing a 1-liter SUMMA® polished stainless-steel canister to 32 psi. The sampling line and the pretrap (maintained at 90°C) were flushed with ambient air and the canister pressure brought to 30 psi. Sampling then began. The preconcentration trap was immersed in liquid oxygen and an air volume sampled from pressure  $p_1$  to  $p_2$ . A high-precision pressure gauge ( $\pm 0.05$  psi) was used to measure the canister pressure. A typical setting was  $p_1 = 30.0$  psi and  $p_2 = 24.0$  psi. Ideal gas laws were found to hold excellently at these pressures and were used to estimate sample volumes. The pressure range of 30 to 20 psi assured smooth flow through the preconcentration traps without problems of plugging. All

other sampling was accomplished by using sampling loops that were flushed with all-glass syringes of 100-ml volume. A 10- $\mu$ l direct syringe injection of the sampled DNPH solution was injected into the HPLC for aldehyde analysis.

Table 3 summarizes methods used for the analysis of trace species. The GC and the HPLC conditions used are also stated. Because of the dominant water response of the ECD, a post-column Ascarite trap was inserted to remove water from halocarbon analysis. No water trap was used for the analysis of aromatic hydrocarbons, PAN, PPN, and phosgene. The latter three did not require any preconcentration step and were measured with a direct 5-ml air injection.

The identity of trace constituents was established by using the following criteria:

- Retention times on multiple GC columns (minimum of two columns)
- EC thermal response
- EC ionization efficiency

Details of these comparisons for halocarbon species, organic nitrogen compounds, and aromatic hydrocarbons have already been published (Singh et al., 1979a,c; 1980). Figures 1-8 provide representative chromatograms of the atmospheric analysis of selected trace chemicals.

## CALIBRATIONS

### Primary Standards

Calibrations for all species were performed using three basic methods:

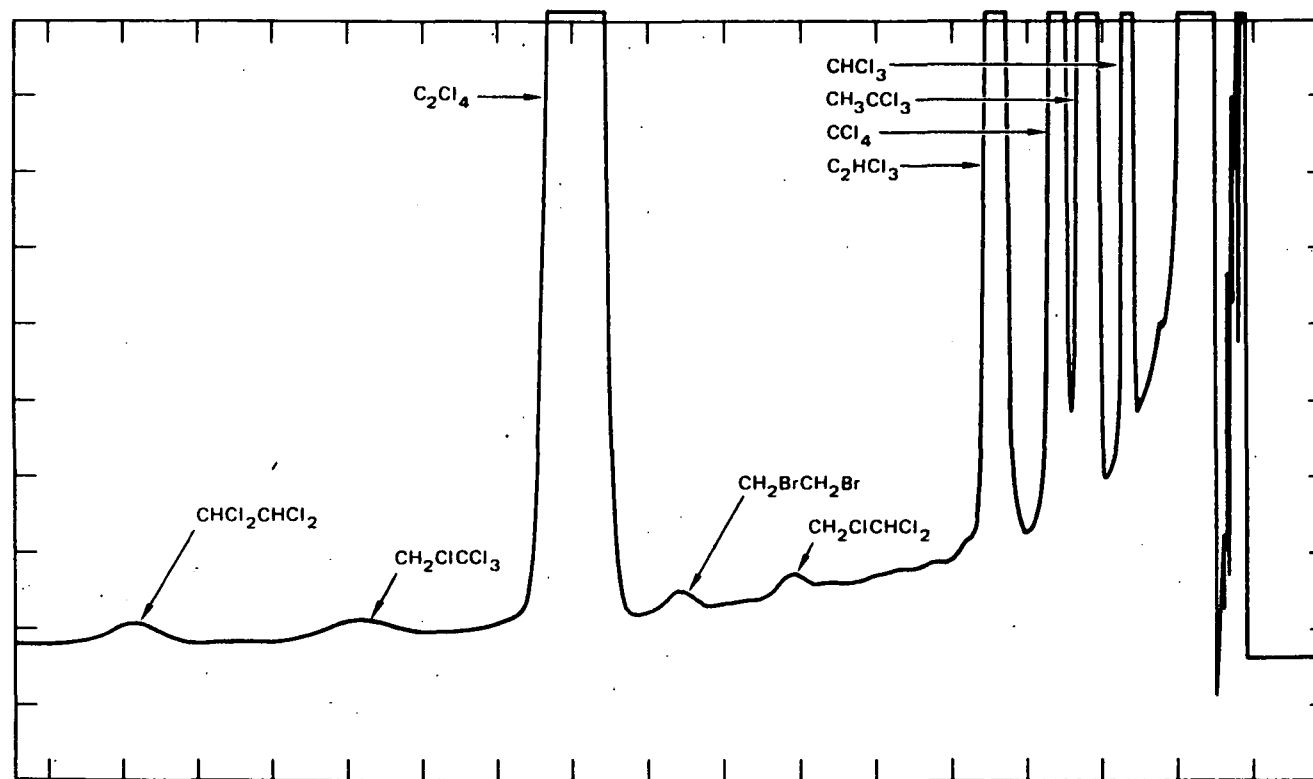
- Permeation tubes
- Multiple dilutions
- Gas-phase coulometry.

As reported earlier (Singh et al., 1977b; 1980), permeation tubes provide a reliable means to generate low-ppb primary standards for a significant number of chemicals listed in Table 1. Permeation tubes (8- to 10-cm long) for many trace constituents of interest, constructed from standard FEP or TFE Teflon® tubing of varying thicknesses, were obtained commercially. Each permeation tube was contained in a specialized glass holder (Figure 9). Based on our previous experience, we concluded that some permeation tubes could operate satisfactorily only at high temperatures. Therefore, two temperature baths maintained at  $30.0^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$  and  $70.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$  were installed. The  $30^{\circ}\text{C}$  bath was a water bath, and the  $70^{\circ}\text{C}$  bath was an oil bath. All permeation tubes were contained in specialized holders and were purged continuously with a prepurified gas (helium, air, or nitrogen) flowing at 50 to 80 ml/min. Permeation tubes were weighed roughly once a week on a semimicro ( $10^{-5}\text{g}$ ) balance. These weighings were done before, during, and after the field experiments. The constancy of permeation rate over a period of many months could be

TABLE 3. ANALYTICAL CONDITIONS FOR THE ANALYSIS OF SELECTED TOXIC CHEMICALS

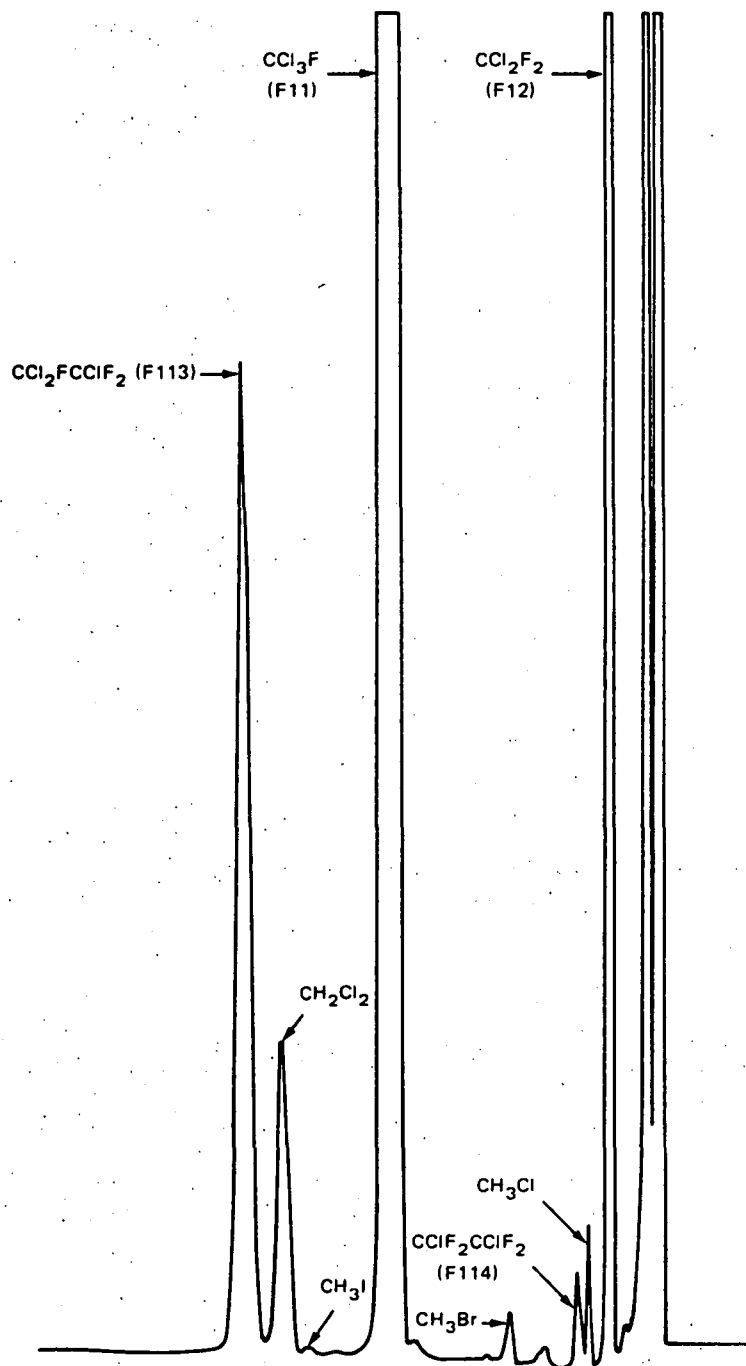
GC or HPLC Column			Species Measured	Detector		Typical Carrier Flow Rate (ul/min)	Typical Sample Size (ul)	Remarks
No.	Description	Temp. (°C)		Type	Temp. (°C)			
1	6 ft x 1/8 in, SS,* 20% SP2100, 0.1% DC 1500 on 100/120 mesh Supelcoport	45	CHCl <sub>3</sub> ; CH <sub>2</sub> CCl <sub>3</sub> ; CCl <sub>4</sub> ; cis-CHClCHCl, C <sub>2</sub> HCl <sub>3</sub> ; CH <sub>2</sub> ClCHCl <sub>2</sub> ; CH <sub>2</sub> BrCH <sub>2</sub> Br; C <sub>2</sub> Cl <sub>4</sub> ; CH <sub>3</sub> CHCl <sub>2</sub> ; CH <sub>2</sub> ClCCl <sub>3</sub> ; CHCl <sub>2</sub> CHCl <sub>2</sub> ; CH <sub>2</sub> ClCHClCH <sub>3</sub>	Electron capture	275	40	500	No water trap
2	33 ft x 1/8 in, SI, 20% DC 200 on 80/100 mesh Supelcoport	45	CH <sub>3</sub> Cl; CH <sub>3</sub> Br; CH <sub>2</sub> CCl <sub>2</sub> ; CH <sub>3</sub> I; CCl <sub>3</sub> F; CCl <sub>2</sub> F <sub>2</sub> ; CClF <sub>2</sub> CCl <sub>2</sub> F; CClF <sub>2</sub> CClF <sub>2</sub>	Electron capture	275	25	500	Ascarite water trap
3	6 ft x 1/8 in, SS, 10% N, N, -bis (2-cyanoethyl) Formamide on Chromosorb P (A/W)	65	C <sub>6</sub> H <sub>6</sub> ; C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> ; m/p/o-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> ; 4-C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5</sub> ; 1,3,5 C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> ; 1,2,4 C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub>	Flame ionization	275	45	500	No water trap
4	3 ft x 1/8 in, SI, 5% SP 1200 -5% Bentone on 100/120 mesh Supelcoport	65	C <sub>6</sub> H <sub>5</sub> Cl; n-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> ; o-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> ; 1,2,4 C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub> ; C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl; CCl <sub>2</sub> CClCClCCl <sub>2</sub>	Electron capture	275	45	750	No water trap
5	15 ft x 1/8 in, SS, 10% SP 1000 on 100/120 mesh Supelcoport	45	CH <sub>2</sub> ClCH <sub>2</sub> Cl	Electron capture	265	25	100	Ascarite water trap
6	10 ft x 1/8 in, SS, 0.2% CW 1500 80/100 mesh on carboxpack C	45	CH <sub>2</sub> Cl <sub>2</sub> ; CCl <sub>3</sub> F; cis-CHClCHCl; CH <sub>3</sub> I; CCl <sub>3</sub> FCClF <sub>2</sub> ; CH <sub>3</sub> CCl <sub>3</sub> ; CCl <sub>4</sub> ; C <sub>2</sub> H <sub>5</sub> Cl; CH <sub>2</sub> CHCH <sub>2</sub> Cl	Electron capture	265	40	10	Ascarite water trap; also used for CH <sub>2</sub> CCl <sub>2</sub> measurement with preconcentration
7	10 in x 1/4 in, Teflon, 5% CS 400, on 60/80 mesh Chromosorb P (A/W)	30	PAH, PPH	Electron capture	30	60	5	No water trap; direct injection
8	5 ft x 1/4 in, SS, 30% didecyl phthalate, 100/120 mesh, Chromosorb P (A/W)	30	CoCl <sub>2</sub>	Electron capture	30	70	5	No water trap; direct injection
9	1 ft x 1/4 in SS, sphersorb QUS-10	30	HCHO, CH <sub>3</sub> CHO	Variable wave-length detector set at 360 nm	30	1.5	0.01	Isocratic mode, 36% H <sub>2</sub> O, 64% acetonitrile SP mode 8700, SP 3400 detector

\*Stainless steel



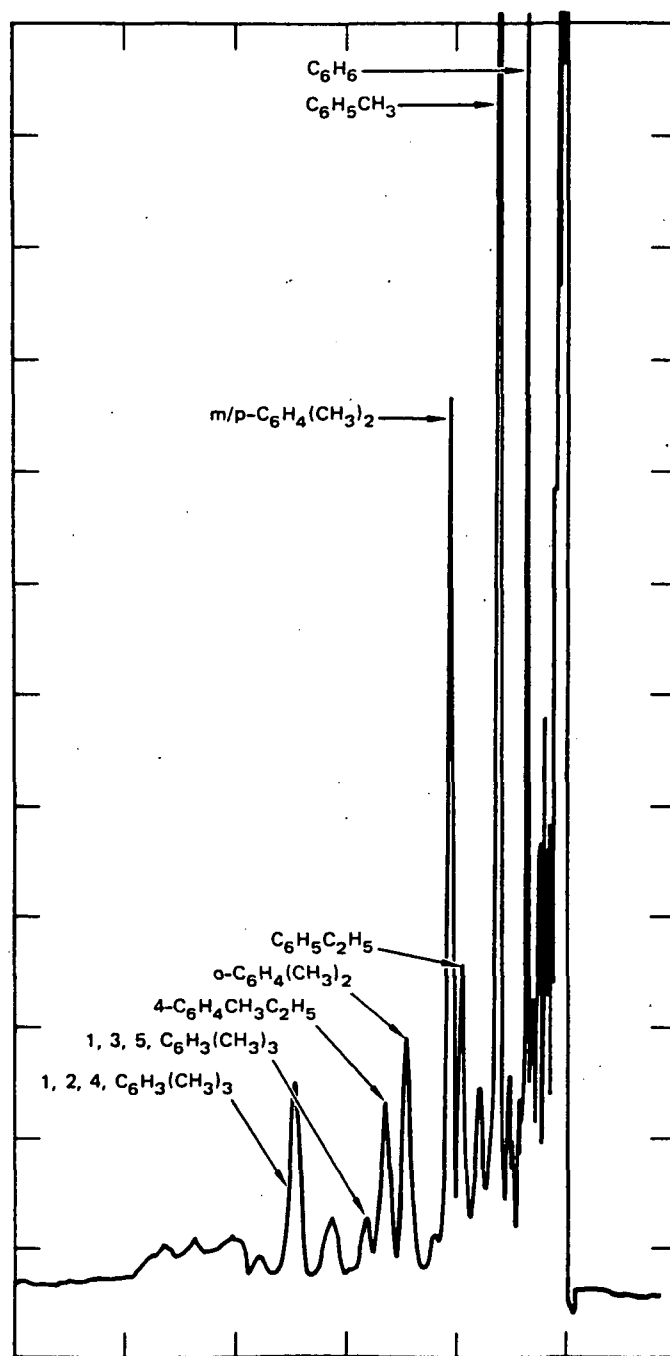
Note: Menlo Park air; Attenuation 16; 300-ml sample; Column No. 1.

Figure 1. Chromatogram showing ambient analysis of selected chlorinated and brominated toxic chemicals.



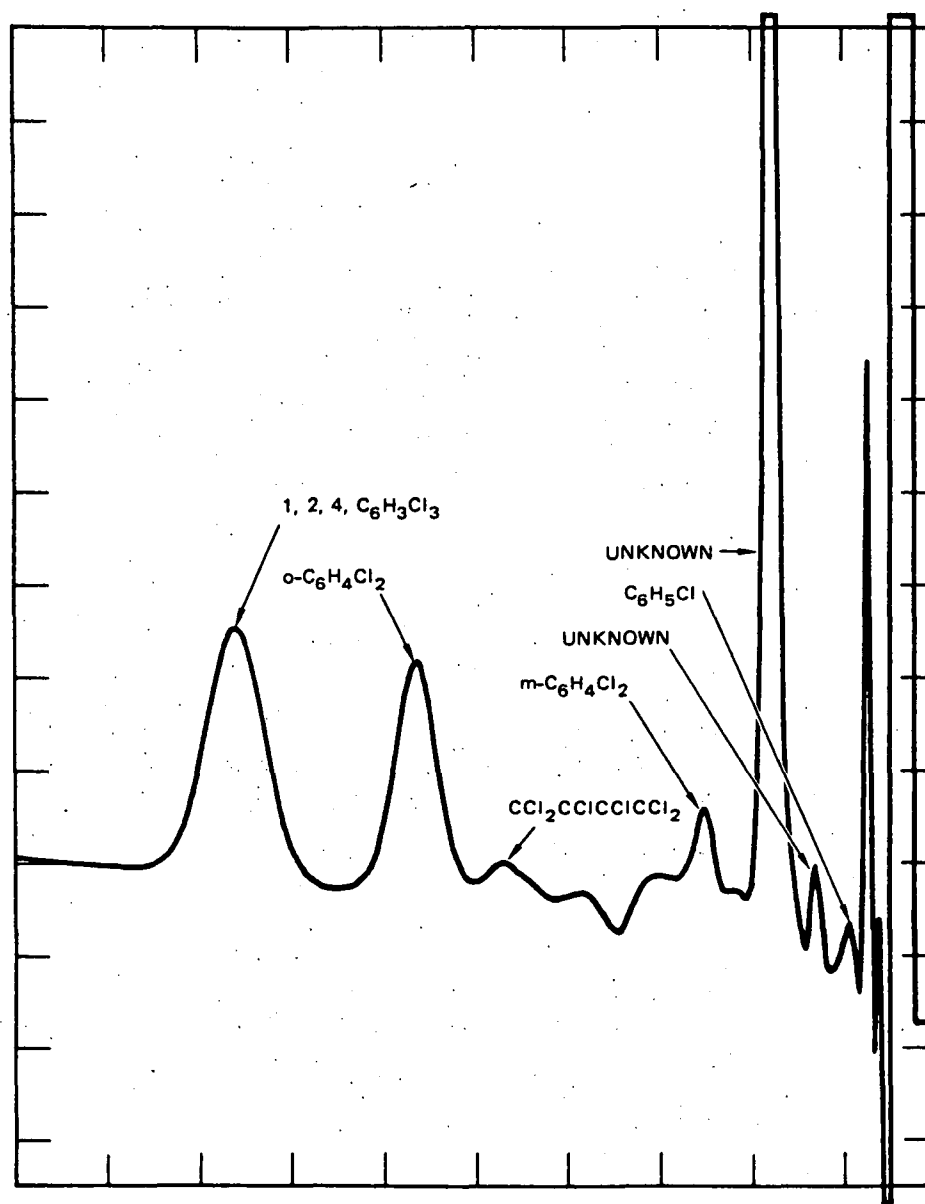
Note: Chicago air; Attenuation 8; 300-ml sample; Column No. 6.

Figure 2. Chromatogram showing separation of methyl halides and chlorofluorocarbons from ambient air.



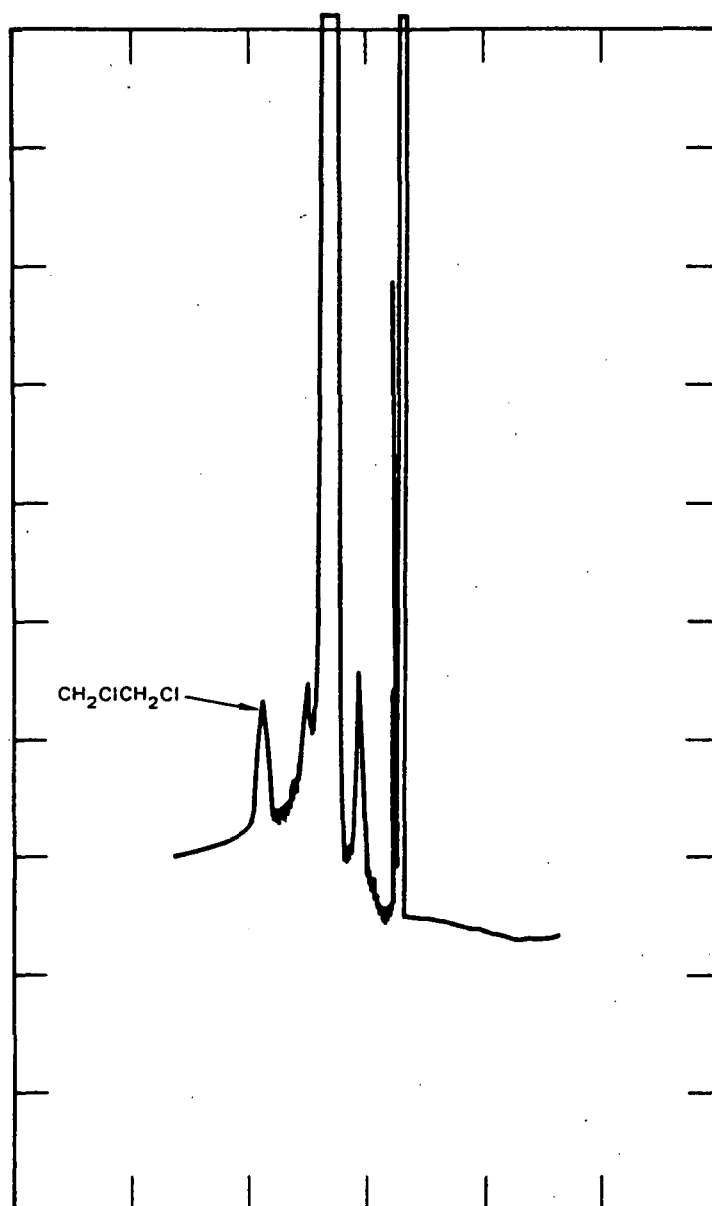
Note: Menlo Park air; Attenuation 8; 400-ml sample; Column No. 3.

Figure 3. Analysis of aromatic hydrocarbons in ambient air.



Note: Menlo Park air; Attenuation 2; 800-ml sample; Column No. 4.

Figure 4. Halogenated aromatics in the air.



Note: Menlo Park air; Attenuation 4; 50-ml sample; Column No. 5.

Figure 5. Analysis of 1,2 dichloroethane.



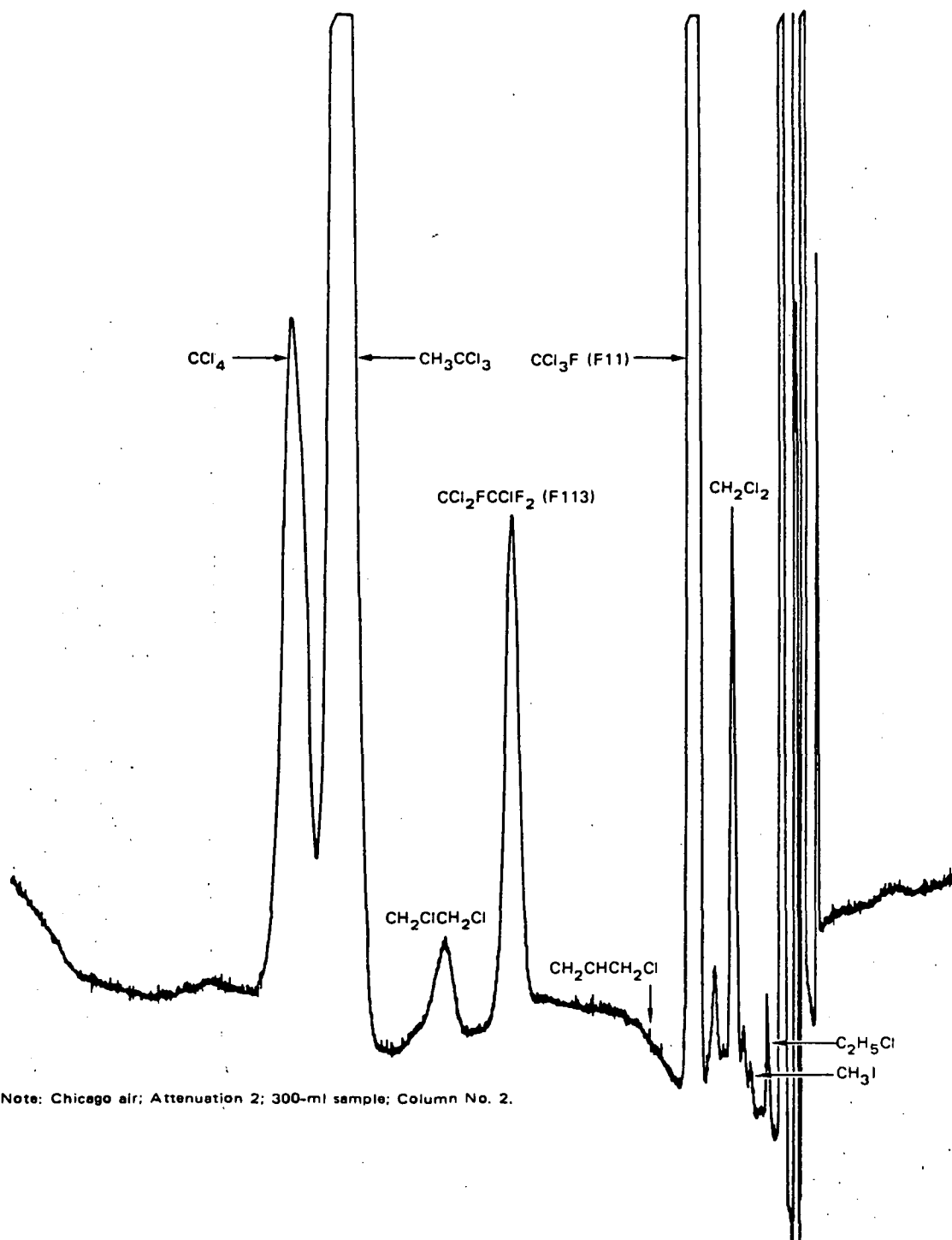


Figure 6. Chromatogram showing methyl chloride separations from other halocarbons.

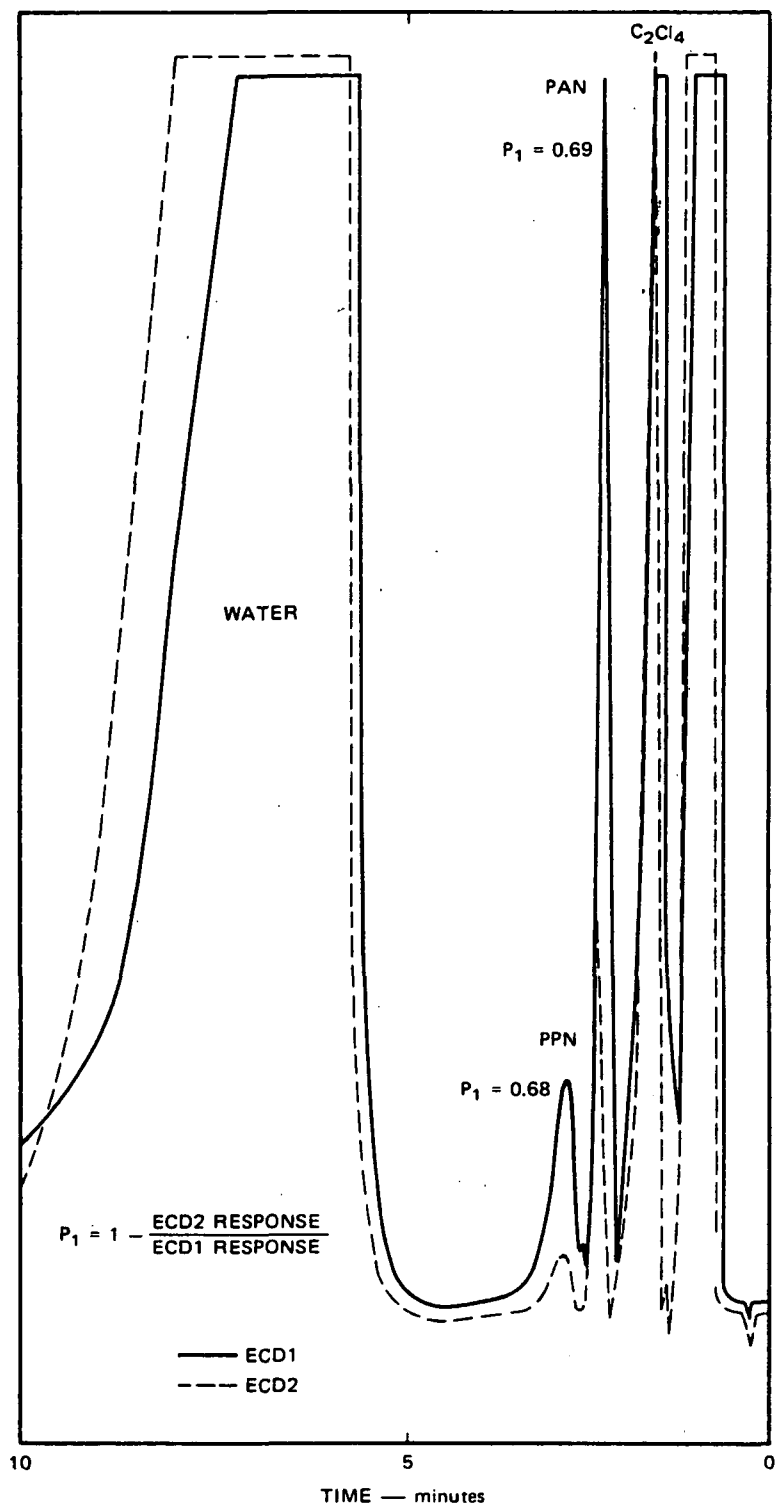


Figure 7. PAN and PPN separation from the air.

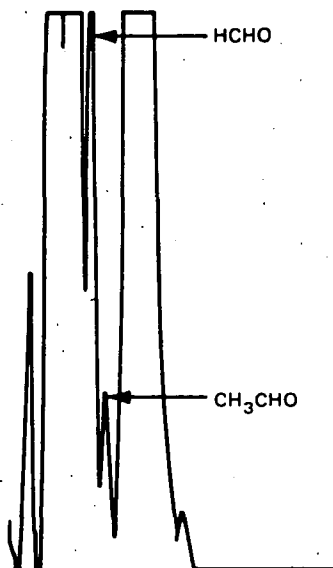


Figure 8. Separation of dinitrophenyl hydrazones of formaldehyde and acetaldehyde on HPLC.

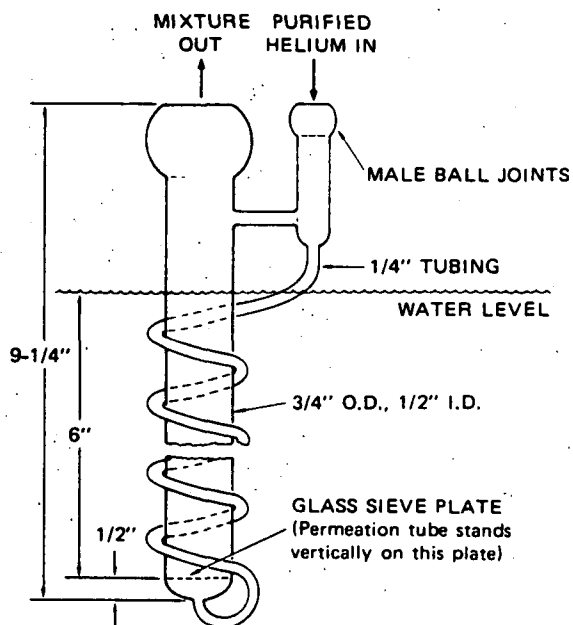


Figure 9. Permeation tube holder.

established. A large-volume mixing chamber was installed at the permeation tube exit to allow for complete mixing. Syringe samples were withdrawn from the mixing chamber using all-glass syringes.

With the installation of the 70°C bath, all permeation tubes performed excellently. Table 4 reports the measured permeation-rate data for each of the chemical constituents of interest. It is clear from Table 4 that many species for which permeation tubes could not be used earlier (Singh et al., 1979c) are now giving excellent results. Figures 10 and 11 demonstrate the excellent linearity of the permeation rate for some of these chemicals. It is also clear from Table 4 and Figure 11 that the formaldehyde permeation tube could be further improved. Overall, we believe that this method is a reliable means to generate primary standards.

It is also clear from Table 4 that most of these permeation tubes can be used to prepared standards directly at parts per billion (ppb) concentration levels. Batch dilutions were carried out to reduce these concentrations by a factor of  $10^2$  to  $10^3$ . These were performed by injecting a known volume (typically 10.0 ml) of the high concentration mixture into an evacuated precleaned electropolished stainless steel container of 1- to 5-liter size, followed by pressurization with diluent gas to 40 psi. Over a wide range of concentration levels of low ppb's and low ppt's (parts per trillion), the frequency-modulated ECDs that we used were linear (Singh, et al., 1977b). The linearity of the FID over a much larger concentration range is well known.

In addition to permeation tubes, standards were obtained from Scott-Marrin (Riverside, California). These were obtained at higher concentrations (5 to 10 ppm) for long-term stability. Table 5 lists the chemicals, the standard concentrations, and the cylinder materials. All of the chemicals were stored in aluminum cylinders except those containing  $\text{CH}_3\text{Cl}$ , which were contained in stainless-steel cylinders. Extreme care was required in selecting cylinder materials; some of the chemicals (e.g., methyl chloride) form unknown chemical complexes that might react explosively with aluminum (Private Communication--Scott-Marrin Inc.).

All of the commercially obtained standards were rechecked with our permeation-tube standards when this was possible. The comparisons were found to yield excellent results ( $\pm 10$  percent). The aromatic hydrocarbon standards were checked for carbon response against those available from the National Bureau of Standards (NBS) and found to agree within  $\pm 5$  percent. For other aromatic hydrocarbons, carbon response derived from benzene and toluene responses was used.

For the chlorinated aromatics, the Scott-Marrin standards were found to deteriorate over a period of several months. In the case of PAN and PPN, only gas-phase coulometry was used, and the data must be considered preliminary until the confirmation of the reliability of PAN and PPN determination using gas-phase coulometry can be established.

TABLE 4. PERMEATION RATE DATA FOR GENERATING PRIMARY STANDARDS

Compound	Permeation Tube Number or I.D.	Temperature (°C*)	Permeation Rate		Quality†
			ng/min	ppb/l/min (25°C, 1 atm)	
HCHO	MET8	70.0	326	266	F
CH <sub>2</sub> =CHCHO	2356	30.0	969	423	E
CH <sub>2</sub> OCH <sub>2</sub>	1908	30.0	1120	618	E
CH <sub>3</sub> CHO	MET9	30.0	3300	1837	E
CH <sub>3</sub> COCH <sub>3</sub>	MET10	30.0	615	260	G
C <sub>2</sub> H <sub>5</sub> CHO	MET11	30.0	2604	1100	E
C <sub>6</sub> H <sub>5</sub> CHO	MET12	30.0	95	23	F
CCl <sub>2</sub> F <sub>2</sub> (F12)	6138	30.0	615	123	E
CCl <sub>3</sub> F (F11)	1911	30.0	1680	299	E
CHCl <sub>2</sub> F (F21)	2347	30.0	942	224	E
CHClF <sub>2</sub> (F22)	2348	30.0	80	23	E
CCl <sub>2</sub> FCClF <sub>2</sub> (F113)	1238	30.0	715	93	E
CClF <sub>2</sub> CClF <sub>2</sub> (F114)	2345	30.0	6254	894	E
CH <sub>3</sub> Cl	2355	30.0	1915	927	E
C <sub>2</sub> H <sub>5</sub> Cl	2350	30.0	480	182	E
CH <sub>2</sub> CHCl	2352	30.0	1270	497	E
ClCH <sub>2</sub> CH=CH <sub>2</sub>	7497	30.0	142	45	E
CH <sub>3</sub> Br	1893	30.0	2477	638	S
CH <sub>3</sub> I	1239	30.0	109	19	G
CH <sub>2</sub> Cl <sub>2</sub>	2354	30.0	523	150	E
(cis) CHClCHCl	1939	30.0	2564	646	E
(trans) CHClCHCl	1898	30.0	1696	428	E
CCl <sub>2</sub> CH <sub>2</sub>	1897	30.0	731	184	G
CH <sub>2</sub> ClCH <sub>2</sub> Cl	1907	70.0	2622	648	E
CH <sub>2</sub> ClCH <sub>2</sub> Cl	1899	30.0	125	31	G
CHCl <sub>2</sub> CH <sub>3</sub>	2353	30.0	71	18	G
CH <sub>2</sub> ClCHClCH <sub>3</sub>	MET1	70.0	2456	531	E
(trans) CHCl=CHCH <sub>2</sub> Cl	MET2	70.0	7806	1720	E
COCl <sub>2</sub>	2351	30.0	942	233	E
CHCl <sub>3</sub>	1229	30.0	174	36	G
C <sub>2</sub> HCl <sub>3</sub>	1253	30.0	314	58	E
CCl <sub>3</sub> CH <sub>3</sub>	1896	70.0	980	179	E
CCl <sub>3</sub> CH <sub>3</sub>	1589	70.0	3450	632	E
CHCl <sub>2</sub> CH <sub>2</sub> Cl	1901	30.0	129	24	G
CCl <sub>4</sub>	1894	70.0	1983	315	E
C <sub>2</sub> Cl <sub>4</sub>	1902	70.0	3352	494	E
C <sub>2</sub> Cl <sub>4</sub>	1590	30.0	706	104	E
CH <sub>2</sub> BrCH <sub>2</sub> Br	1237	70.0	1220	160	E
CHBr <sub>3</sub>	1895	70.0	1316	127	E
C <sub>6</sub> H <sub>5</sub> Cl	MET3	70.0	4507	980	E
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	MET4	70.0	1528	295	E
o-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	MET5	70.0	1359	226	E
m-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	MET6	70.0	2515	418	E
p-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	MET7	70.0	3571	593	E

Note: All permeation tubes were given a 2 week or longer conditioning time.

\*Temperature maintained to  $\pm 0.05^\circ\text{C}$ .

†E=Excellent (errors in permeation rate  $< \pm 10\%$ ); G=Good (errors in permeation rate  $< \pm 15\%$ ); F=Fair (errors in permeation rate  $< \pm 25\%$ ).

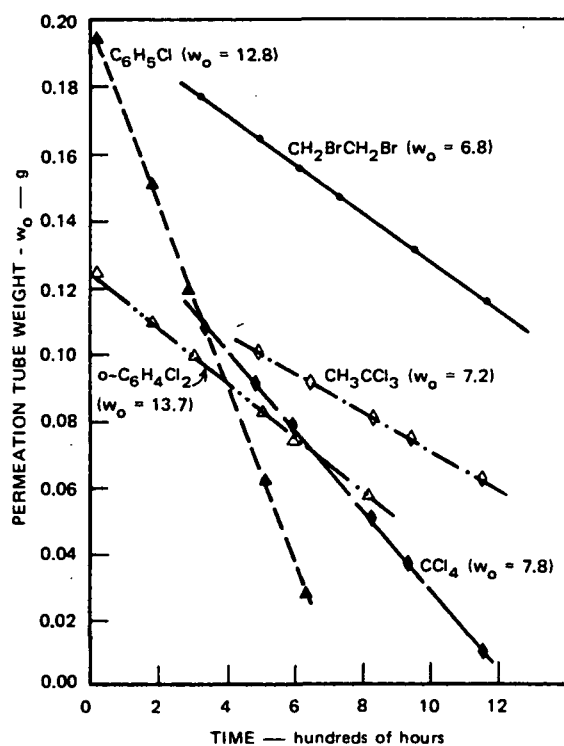


Figure 10. Permeation tube weight-time relationship for selected halogenated chemicals.

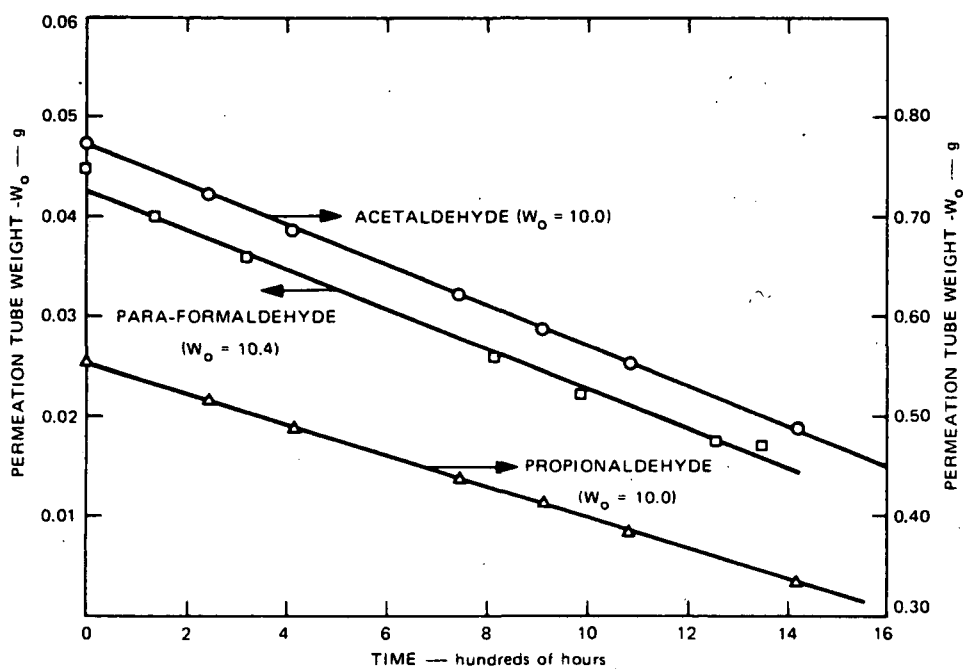


Figure 11. Permeation tube weight loss of selected oxygenated chemicals.

TABLE 5. PPM LEVEL PRIMARY STANDARDS IN AIR\*

Standard and Compound†	Concentration (ppm)	Long-term Stability‡ (2-year period)	Cylinder	
			Type	Size (ft <sup>3</sup> )
S1				
1,1,1 Trichloroethane	5.0	E	Aluminum	30
Carbon tetrachloride	5.2	E		
1,2 Dibromoethane	5.0	E		
Hexachloroethane	0.8	U		
S2				
Monochlorobenzene	5.0	P	Aluminum	150
o-Dichlorobenzene	5.0	P		
S3				
Benzene	5.0	E	Aluminum	150
Toluene	5.0	E		
S4				
Methyl chloride	10.0	E	Stainless steel	30
Methylene chloride	10.0	E		
1,2 Dichloroethane	10.0	E		
S5				
Trichloroethylene	10.0	E	Aluminum	30
Tetrachloroethylene	10.0	E		
Chloroform	10.0	E		
S6				
Ethane	4.07	E	Aluminum	150
Propane	5.03	E		
n-Butane	4.95	E		
S7				
Methyl chloride	10.0	E/S	Stainless steel	30
Methyl bromide	10.0	E/S		
Methyl iodide	5.0	E/S		

\*Obtained on order from Scott-Marrin, Inc., Riverside, California.

†For all of these chemicals (except  $C_6H_6$  and  $C_6H_5CH_3$ ) satisfactory permeation tubes were also operational. Therefore, a majority of these standards were used more as secondary standards than as primary ones. For aromatic hydrocarbons, the Scott-Marrin standards were used as primary standards.

‡E: Excellent; P: poor; U: unknown; E/S: Excellent over the short term; long-term tests have not been made.

## Secondary Standards

Except for the aromatic hydrocarbons, it was not possible to use primary standards during field operation. Therefore, an optimal scheme that depended on the use of secondary standards was devised.

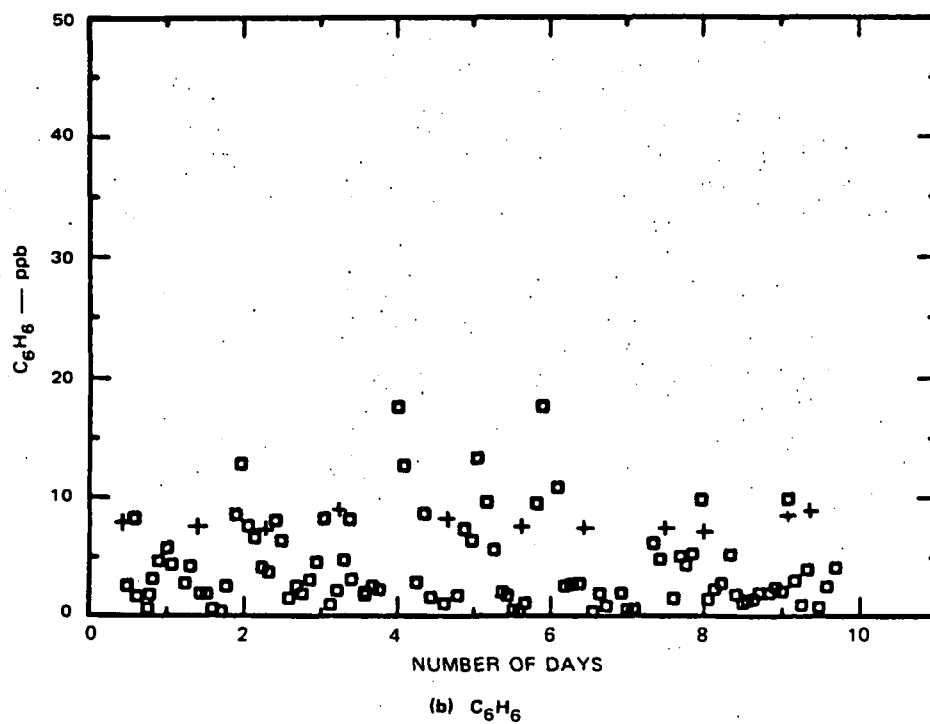
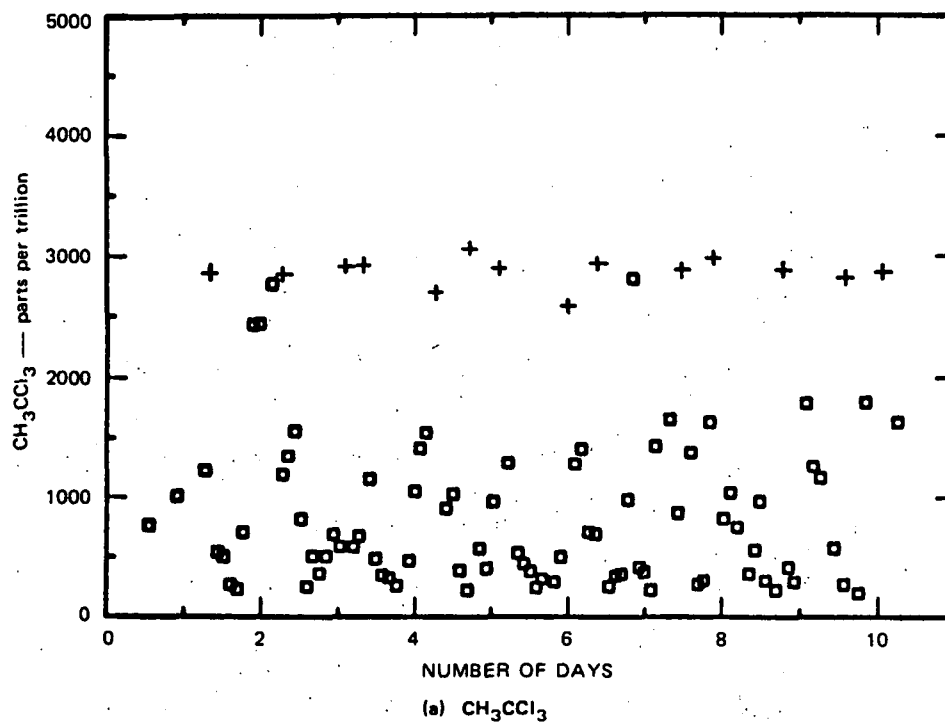
A 35-liter and several 5-liter (as backups) SUMMA<sup>®</sup> polished stainless-steel samplers were filled with urban air samples to a pressure of 35 to 40 psi. These were allowed to stabilize for one to two days and then analyzed by comparing them against the primary standards. The 35-liter pressurized secondary standard was then used for field operation: Each GC channel was calibrated about three times a day with this secondary standard. The stability of nearly all species over a period of several days was found to be excellent. Figure 12 shows an example of the stability of a secondary standard during the course of a field experiment. Some species, such as PAN, PPN, or COCl<sub>2</sub>, could not be stored for any reasonable length of time. This was not a serious hindrance since other chemicals could be used to ascertain the constancy of the ECD and the FID responses during field operations. All of the Scott-Marrin standards were also carried on board after these had been diluted to low-ppb levels. These were also used as secondary standards (in addition to the collected air samples). The stability of the diluted Scott-Marrin cylinders (in polished 1- to 5-liter stainless-steel vessels) was found to be excellent. Analysis of these before field experimentation, during field studies, and after the completion of field studies did not show a change from the measurement precision under field conditions.

In the case of aldehydes, all calibrations had to be performed in the field. The repeatability of the acetaldehyde-hydrozone calibration with HPLC is clearly shown in Figure 13.

## QUALITY CONTROL

Two major factors were critical in establishing the quality of the acquired data: the accuracy of primary standards and the precision and repeatability of measurements. As stated earlier in this section, the primary standards commercially obtained were compared with our permeation tubes, which can be routinely used to obtain reliable standards within errors of  $\pm 5$  to 10 percent. The aromatic hydrocarbon standards were compared with NBS propane standards and found to be accurate to within  $\pm 5$  percent. The cross-calibrations between SRI-generated standards and Scott-Marrin standards typically resulted in differences of about  $\pm 10$  percent or less. The use of secondary standards nearly three times a day clearly demonstrated the excellent precision that was obtainable during field studies: The precision of reported field measurements is estimated to be better than  $\pm 15$  percent. In order to assess the overall accuracy of field measurements further, we conducted two programs of interlaboratory comparisons. The results from one of these programs conducted in early 1981 are shown in Table 6. The measurement errors were found to be less than  $\pm 10$  percent. A similar program was also conducted under the auspices of the U.S. Environmental Protection Agency (EPA). Four laboratories participated in this program. The results of this intercomparison were inconclusive because of uncertainties associated with the





□ AMBIENT DATA  
 + SECONDARY STANDARD

Figure 12. Secondary standard response for 1,1,1 trichloroethane and benzene in Phoenix — Site 2.

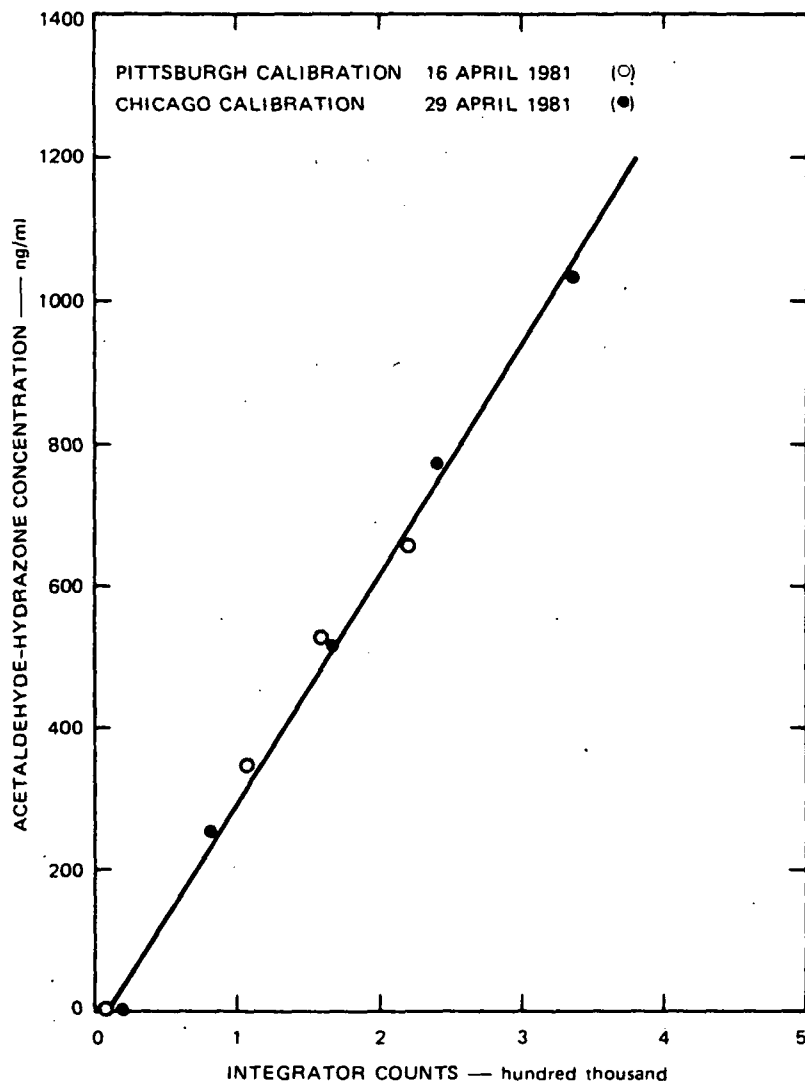


Figure 13. Calibration curve for dinitrophenyl hydrazones of acetaldehyde and its repeatability.

procedures used to prepare standard mixtures that were sent for analysis to the four laboratories (Arnts, 1980). For the analysis of aldehydes, the methods are still in a development stage, and accuracies of  $\pm 30$  percent can be expected. (It should be possible to reduce these errors in the near future.) Further details on the quality control aspects of the research plan have been presented separately (Singh et al., 1981). It is noted that interlaboratory comparisons provide one of the best means to test the quality of new data. These comparisons to date have been performed only on an extremely limited basis.

TABLE 6. INTERLABORATORY COMPARISON OF SELECTED TRACE CONSTITUENTS\*

Chemicals	Sample 1		Sample 2	
	SRI	OGC	SRI	OGC
N <sub>2</sub> O	312 ppb	336 ppb	309 ppb	335 ppb
CCl <sub>2</sub> F <sub>2</sub>	315 ppt	330 ppt	285 ppt	298 ppt
CCl <sub>3</sub> F	280 ppt	278 ppt	175 ppt	175 ppt
CH <sub>3</sub> CCl <sub>3</sub>	180 ppt	183 ppt	131 ppt	138 ppt

\*Samples of unknown composition ("blind samples") analyzed at SRI; same samples analyzed by Oregon Graduate Center (OGC).

## SECTION 4

### PLAN OF FIELD MEASUREMENTS

After the measurement methodology was developed, field studies were conducted at ten selected urban sites in the continental United States. In consultation with the project officer, the following cities were chosen:

- Los Angeles, California
- Phoenix, Arizona
- Oakland, California
- Houston, Texas
- St. Louis, Missouri
- Denver, Colorado
- Riverside, California
- Staten Island, New York
- Pittsburgh, Pennsylvania
- Chicago, Illinois.

Within the above cities, specific sites were chosen that represented an open urban area. Large point sources or topographical features that could affect the representativeness of the measurements were avoided. Every attempt was made to select sites that can be expected to be indicative of general pollution levels prevalent in the area. Practical constraints such as power and shelter availability also played a role in the selection of sites. It must be emphasized that only one site within each of the selected cities was monitored. The data collected here, while perhaps typical of general ambient environment, are truly representative only of the specific site monitored.

The site locations, and the periods of field measurements, are shown in Table 7. Each field study was of roughly two weeks' duration. Actual field data was collected from 9 to 11 days on an around-the-clock basis (Table 7). Preliminary literature search clearly indicated that available data on hazardous organic chemicals were highly limited and virtually all were obtained during daytime hours. Based on our past experience (Singh et al., 1979a), we believed that significant night and daytime differences in the abundance of organic chemicals were likely. Thus we concluded that despite the logistical difficulty, a 24-hour measurement schedule offered the most efficient means to collect the maximum amount of data to characterize the burden of toxic organic chemicals in the ambient air. In addition, night abundances of trace

TABLE 7. FIELD SITES AND MEASUREMENT SCHEDULE

No. Data	Field Site			Experiment Period	Days of Actual Data Collection	Site Address
	City Name	Latitude (°N)	Longitude (°W)			
1	Los Angeles, CA	34°04'	118°09'	9 Apr 79 - 21 Apr 79	10	Los Angeles State University
2	Phoenix, AZ	33°28'	112°06'	23 Apr 79 - 6 May 79	11	19th and Adam St. at state capitol
3	Oakland, CA	37°45'	122°11'	28 Jun 79 - 10 Jul 79	9	Hegenberger and 14th St.
4	Houston, TX	29°47'	95°15'	14 May 80 - 25 May 80	10	Mae St. and I-10 Front- age Road (Florissant Valley College)
5	St. Louis, MO	38°46'	90°17'	29 May 80 - 9 Jun 80	10	3400 Pershall Rd. (Florissant Valley College)
6	Denver, CO	39°45'	104°59'	15 Jun 80 - 28 Jun 80	11	Marion St. and E. 51st
7	Riverside, CA	33°59'	117°18'	1 Jul 80 - 13 Jul 80	11	Big Spring Rd. and Perimeter Road (U.C. Riverside campus)
8	Staten Island, NY	40°35'	74°12'	26 Mar 81 - 5 Apr 81	9	Wild Ave. and Victory Blvd. (Consolidated Edison Power Plant)
9	Pittsburgh, PA	40°26'	79°56'	7 Apr 81 - 17 Apr 81	9	Carnegie Mellon Institute (campus)
10	Chicago, IL	41°45'	87°42'	20 Apr 81 - 2 May 81	9	79th St. and Lawndale

chemicals were likely to provide important information about the sources and sinks of measured species. Therefore, a 24-hour-per-day, seven-days-a-week measurement schedule was followed during all field programs.

## SECTION 5

### ESTIMATED LOSS RATES OF MEASURED CHEMICALS IN POLLUTED ATMOSPHERES

A knowledge of the atmospheric loss rate of a chemical is essential for the interpretation of field data and for the eventual prediction of the fate of an organic chemical. It is well known that hydroxyl radical (HO) plays a central role in depleting atmospheric organics, both in the polluted and the clean atmospheres. For the halogenated (except methyl iodide) and aromatic hydrocarbons of interest here, we have concluded that no significant error in loss rates is incurred when reactions with species other than HO, such as  $O(^3P)$ ,  $O_3$ ,  $HO_2$ , are neglected. In the case of the aldehydes and methyl iodide both reaction with HO and photolysis are important.

The residence times of PAN and PPN are largely controlled by their thermal decomposition and are estimated from mechanisms suggested by Hendry and Kenley (1979). For the purposes of these calculations an average daytime HO radical abundance of  $2 \times 10^6$  molecule/cm<sup>3</sup> is assumed. [These HO levels are well supported by HO estimates from available field data (Calvert, 1976; Singh et al., 1981a) and are probably typical of summer months within the boundary layer of polluted urban environments. In winter months the HO levels can be lower by a factor of about two, but no direct wintertime estimates are available.] The kinetic and photolytic data utilized in Table 8 are taken from Atkinson et al. (1979), Hampson (1980), Hudson and Reed (1980), and estimated from Hendry and Kenley (1979) and Hendry et al. (1980).

Table 8 provides these data and estimates the percentage loss due to chemical reaction in one day (12 sunlit hours). For virtually all species of Table 8, nighttime loss rates are negligibly small. This percentage loss is defined as:

$$\text{percent loss} = [1 - \exp(-4.32 \times 10^4 K)] \times 100 \quad ,$$

where  $K = k_{HO}(HO) + k_{hv} + k_{thermal}$ .

It is clear from Table 8 that the daily loss rate of HOCs ranges from near-zero to 100 percent per day. Chloromethanes and chloroethanes, collectively a dominant group, are relatively unreactive, and a daily loss rate of 0 to 3 percent per day is estimated. In the entire haloalkane group, methyl iodide is the only species that is relatively rapidly removed by photolytic decomposition ( $\approx 12$  percent/day loss rate). The daily loss rate of aromatic hydrocarbons, aldehydes, and PAN is quite substantial.

TABLE 8. ESTIMATED DAILY LOSS RATES (%) OF SELECTED TRACE CHEMICALS

Chemical Name	Dominant Removal Mechanism (reaction with)	Rate Constant at 300K* (k x 10 <sup>12</sup> )	Percentage Loss in One Day (12 sunlit hours)†
Methyl chloride	HO	0.05	0.4
Methyl bromide	HO	0.04	0.4
Methyl iodide	photolysis	$\approx 3 \times 10^6 \ddagger$	12.2
Methylene chloride	HO	0.15	1.3
Chloroform	HO	0.10	0.9
Carbon tetrachloride	Strat. photolysis	<0.0001	$\approx 0.0$
Ethyl chloride	HO	0.39	3.3
1,1 Dichloroethane	HO	0.26	2.3
1,2 Dichloroethane	HO	0.22	1.9
1,2 Dibromoethane	HO	0.25	2.2
1,1,1 Trichloroethane	HO	0.01	<0.1
1,1,2 Trichloroethane	HO	0.33	2.8
Tetrachloroethane (isom)	HO	<0.01	<0.1
1,2 Dichloropropane	HO	1.3 <sup>§</sup>	10.2
Vinylidene chloride	HO	4.0 <sup>§</sup>	29.2
(cis) 1,2 Dichloroethylene	HO	4.0	29.2
Trichloroethylene	HO	2.2	17.2
Tetrachloroethylene	HO	0.17	1.5
Allyl chloride	HO	28 <sup>§</sup>	91.1
Hexachloro-1,3 butadiene	HO (?)	-	-
Chlorobenzene	HO	0.9 <sup>§</sup>	7.4
o-chlorotoluene	HO	3.0 <sup>§</sup>	22.8
Dichlorobenzene (o,m,p)	HO	0.3 <sup>§</sup>	2.6
Trichlorobenzene (isom)	HO	0.1 <sup>§</sup>	0.9
Benzene	HO	1.4	11.4
Toluene	HO	6.0	40.9
Ethyl benzene	HO	8.0	51.0
m-Xylene	HO	23.4	86.5
p-Xylene	HO	12.3	67.0
o-Xylene	HO	13.9	71.3
4-Ethyl toluene	HO	12.9	67.0
1,2,4 Trimethyl benzene	HO	33.2	96.4
1,3,5 Trimethyl benzene	HO	49.2	99.3
Formaldehyde	HO, photolysis	11.0, 2.8 x 10 <sup>7</sup> ‡	88.2
Acetaldehyde	HO, photolysis	15.0, 1.4 x 10 <sup>7</sup> ‡	85.1
Phosgene	-	-	-
Peroxyacetyl nitrate (PAN)	Thermal	-	99.9**
Peroxypropionyl nitrate (PPN)	Thermal	-	99.9**

\*Rate constant with hydroxyl radical (HO) in units of cm<sup>3</sup>molec<sup>-1</sup>s<sup>-1</sup>.

†Calculated based on an estimated daytime (12 hour) average HO abundance of 2 x 10<sup>6</sup> molec/cm<sup>3</sup>.

‡Rate constant due to photolysis in units of s<sup>-1</sup>.

§Estimated from Hendry and Kenley (1979).

\*\*Thermal degradation in the presence of HO and HO<sub>2</sub>.



In all cases listed in Table 8, the loss rate should be reduced in winter months because of reduced temperatures and solar flux. In the case of PAN the effect of temperature is extremely dominant and could very substantially reduce its loss rate (Hendry and Kenley, 1977; Cox and Roffey, 1977).

## SECTION 6

### ANALYSIS AND INTERPRETATION OF FIELD DATA

The field operations, which entailed onsite measurement studies, were conducted around-the-clock on a seven-day-per-week basis, allowing the collection of a large body of ambient data on hazardous organic chemicals. This body of data supplements and considerably expands the highly limited data previously available.

The data collected during these studies have been compiled, validated, and statistically treated. A computer-compatible master data file has been created. In addition to computer processing of field data, we have also analyzed data to study the diurnal variations that are typically observed. Further interpretation of these data was beyond the available resources of this study because of the lack of daily city-based emissions information for these chemicals. The data generated in this study, however, when further analyzed in the context of prevailing meteorology and source inventories, have the potential to add significantly to our knowledge of urban atmospheric chemistry.

Table 9 is presented to give a general idea of the yearly U.S. production, average emissions, and typical use patterns of important chemicals. A major source term for each of the chemicals has also been assigned, based on available information. Table 9 provides a preliminary basis for comparing the relative abundance of chemicals in the ambient atmospheres.

#### ATMOSPHERIC CONCENTRATIONS AND VARIABILITIES OF MEASURED SPECIES

Tables 10, 11, and 12 summarize the ambient data collected at ten sites. Average concentrations\* (arithmetic averages) and standard deviations (one sigma) in units of parts per trillion (ppt =  $10^{-12}$  v/v) and  $\text{ng}/\text{m}^3$  are provided. This redundancy is often convenient, because exposures are invariably expressed in mass concentration units. Maximum and minimum concentration levels are also provided. A dash is used to show instances where no data were obtained or data obtained were such that standard deviations could not be computed. In addition, mean diurnal profiles have been plotted. These are based

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\*"Concentration" as used here includes "volumetric mixing ratio" (e.g. concentration in parts per trillion).

TABLE 9. PRODUCTION, EMISSION AND USAGES OF SELECTED CHEMICALS

Compound	Source*	U.S. Production for Indicated Year† (million metric tons)	Emissions† (percent)	Usage and Remarks
Methyl chloride	A; N(O)	0.20 (1978)	5 - 10	85 percent of production used for manufacture of silicones and tetramethyl lead intermediates; large natural source (23 million tons/yr) identified in the ocean
Methyl bromide	A; N(O)	0.02 (1977)	250	Soil fumigant; oceanic source significantly larger than man-made emissions is possible
Methyl iodide	N(O)	20.0	-	A natural oceanic source of 20.5 million tons/yr is estimated
Methylene chloride	A	0.30 (1978)	80 - 90	55 percent of production used for paint removing and solvent degreasing
Chloroform	A	0.16 (1978)	5 - 10	Manufacture of fluorocarbon-22
Carbon tetrachloride	A	0.34 (1978)	5 - 10	Manufacture of fluorocarbons-11 and -12
Ethyl chloride	A	0.3 (1978)	25	85 percent consumed in the manufacture of tetraethyl lead
1,2 Dichloroethane	A	4.8 (1978)	22	87 percent used for vinyl chloride monomer synthesis; also used for the production of chloroethylenes and chloroethanes; about 0.4 million tons per year used for lead scavenging in automobiles
1,2 Dibromoethane	A	0.1 (1976)	5 - 25	Major gasoline additive for lead scavenging; also used as a fumigant
1,1,1 Trichloroethane	A	0.3 (1978)	295	70 percent of production used for metal cleaning; most other applications also result in direct release
Vinyl chloride	A	3.2 (1978)	2 - 5	Used for polymer synthesis
Vinylidene chloride	A	0.2 (1974)	2 - 5	Used for polymer synthesis
Trichloroethylene	A	0.14 (1978)	>90	70 to 80 percent used for metal cleaning
Tetrachloroethylene	A	0.33 (1978)	>90	60 percent used for dry cleaning and textile processing; another 15 percent used for metal cleaning
Monochlorobenzene	A	1.5 (1978)	>50	50 percent used in solvent applications, remainder in the production of nitrobenzene, DDT, diphenyl oxide
o-Dichlorobenzene	A	0.04 (1976)	>25	About 25 percent of production used in solvent applications
p-Dichlorobenzene	A	0.03 (1976)	>90	90 percent of production used for space deodorizing and moth control
1,2,4 Trichlorobenzene	A	0.01 (1973)	No data	70 percent used as a dye carrier and a herbicide intermediate
Benzene	A	5.0 (1978)	2 - 5	Auto exhaust is the major emission source; estimated U.S. total emissions approach 0.5 million metric tons per year
Toluene	A	4.2 (1978)	2 - 5	Auto exhaust is the major emission source; estimated U.S. total emissions approach 1 million metric tons per year
o-m-p Xylenes	A	2.9 (1978)	2 - 5	Auto exhaust is the major emission source; estimated total U.S. emissions approach 0.5 million metric tons per year
Formaldehyde	A, N	2.6 (1979)	-	Auto exhaust is a major primary source; significant secondary photochemical sources also exist. A major natural source from methane oxidation is likely.

\*A=anthropogenic, N=natural, O=oceanic.

†Source: Singh et al. (1979a, 1980); U.S. Tariff Commission reports.

TABLE 10. ATMOSPHERIC CONCENTRATIONS OF MEASURED CHEMICALS (SITE 1-3)

Chemical Group and Species	Los Angeles--Site 1 (9-21 April 1979)						Phoenix--Site 2 (23 April - 6 May 1979)						Oakland--Site 3 (28 June - 10 July 1979)					
	ppt			ng/m <sup>3</sup>			ppt			ng/m <sup>3</sup>			ppt			ng/m <sup>3</sup>		
	Mean*	S.D.†	Maximum	Minimum	Mean	S.D.	Mean	S.D.	Maximum	Minimum	Mean	S.D.	Mean	S.D.	Maximum	Minimum	Mean	S.D.
Chlorofluorocarbons																		
Trichlorofluoromethane (F11)	473	197	1070	221	2653	1105	249	138	722	110	1396	774	239	151	1477	108	1340	847
Dichlorofluoromethane (F12)	-‡	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Trichlorotrifluoroethane (F113)	305	667	4160	49	2333	5102	151	225	1251	12	1155	1721	49	5	309	16	375	451
Dichlorotetrafluoroethane (F114)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Halonethanes																		
Methyl chloride	3001	1759	7761	1038	6188	3626	2391	940	5685	1231	4928	1938	1066	781	5000	484	2197	1610
Methyl bromide	244	174	894	13	946	752	67	47	190	4	260	182	55	24	108	26	213	93
Methyl iodide	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methylene chloride	3751	2620	12029	601	13014	9090	894	989	5155	86	3102	3431	416	315	2406	86	1443	1093
Chloroform	88	40	224	24	427	194	111	106	514	27	539	515	32	12	60	13	155	58
Carbon tetrachloride	215	107	995	97	1351	673	277	114	855	131	1741	717	169	133	987	94	1062	836
Haloethanes and halopropanes																		
Ethyl chloride	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1,1 Dichloroethane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1,2 Dichloroethane	519	233	1353	173	2097	942	216	220	1450	39	873	889	83	106	842	38	335	428
1,2 Dibromoethane	33	26	187	5	252	198	40	38	204	2	305	290	16	13	85	2	122	99
1,1,1 Trichloroethane	1028	646	3144	224	5602	3520	824	597	2814	198	4490	3253	291	161	967	143	1586	877
1,1,2 Trichloroethane	9	6	45	4	49	33	16	10	42	<1	87	54	8	4	29	4	44	22
1,1,1,2 Tetrachloroethane	4	2	12	<1	27	14	9	4	16	<1	62	27	4	1	8	<1	27	7
1,1,2,2 Tetrachloroethane	17	11	96	4	117	75	17	6	31	<1	117	41	7	3	13	3	48	21
1,2 Dichloropropane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chloroalkenes																		
Vinylidene chloride	5	3	10	1	20	12	30	16	150	<1	119	63	13	5	24	5	51	20
(cis) 1,2 Dichloroethylene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Trichloroethylene	399	302	1702	36	2142	1621	484	587	3070	12	2598	3151	188	270	1558	14	1009	1449
Tetrachloroethylene	1480	446	2065	174	10028	3022	994	716	3697	129	6735	4851	308	292	1450	53	2087	1978
Allyl chloride	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hexachloro-1,3 butadiene	3	2	8	1	32	21	7	9	58	1	75	96	1	0	3	1	11	0
Chloroaromatics																		
Monochlorobenzene	-200	-	-500	<50	918	-	-200	-	-500	<50	918	-	-100	-	-300	<50	459	-
o-Chlorotoluene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
o-Dichlorobenzene	13	10	50	2	78	60	23	35	236	1	138	210	4	5	33	1	24	30
m-Dichlorobenzene	8	6	25	2	48	36	9	6	28	1	54	36	7	3	15	3	42	18
p-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1,2,4 Trichlorobenzene	7	5	34	2	52	37	3	2	10	1	22	15	3	2	15	1	22	15
Aromatic hydrocarbons																		
Benzene	6040	4580	27870	720	19229	14581	4740	6750	59890	390	15091	21490	1550	1220	4630	60	4935	3884
Toluene	11720	9070	53380	1140	44010	34059	8630	9090	38730	540	32407	34134	3110	3180	16940	150	11678	11941
Ethyl benzene	2250	4470	27660	100	9735	19340	2000	2870	16640	60	8653	12417	600	670	4580	60	2596	2899
m/p-Xylene	4610	6140	49960	530	19945	26565	4200	4660	26970	210	18171	20162	1510	1420	8260	100	6533	6144
o-Xylene	1930	1810	12740	90	8150	7918	1780	1880	9190	40	7701	8134	770	730	4050	80	3331	3158
4-Ethyl toluene	1510	1450	10150	100	7396	7102	1510	1500	7370	200	7396	7347	660	620	3400	20	3233	3037
1,2,4 Trimethyl benzene	1880	2380	13290	170	9208	11657	1740	1910	10090	20	8522	9355	-	-	-	-	-	-
1,3,5 Trimethyl benzene	380	680	5020	<40	1861	3331	400	370	1520	<40	1959	1812	-	-	-	-	-	-
Oxygenated species																		
Formaldehyde	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Acetaldehyde	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Phosgene	-	-	-	-	-	-	-	-	-	-	-	-	50	5	57	42	202	20
Peroxyacetyl nitrate (PAN)	4977	4483	16820	30	24580	22141	779	767	3720	<30	3847	3788	356	422	1850	50	1758	2084
Peroxypropionyl nitrate (PPN)	722	673	2740	<30	3978	3708	93	77	330	<30	512	424	149	118	500	<30	821	650

\* Arithmetic mean.

† One standard deviation.

‡ Dashes indicate that chemical was not measured and/or standard deviations could not be computed.

TABLE 11. ATMOSPHERIC CONCENTRATIONS OF MEASURED CHEMICALS (SITE 4-7)

Chemical Group and Species	Houston--Site 4 (14-25 May 1980)						St. Louis--Site 5 (29 May - 9 June 1980)						Denver--Site 6 (15-28 June 1980)						Riverside--Site 7 (1-13 July 1980)						
	ppt			ng/m <sup>3</sup>			ppt			ng/m <sup>3</sup>			ppt			ng/m <sup>3</sup>			ppt			ng/m <sup>3</sup>			
	Mean <sup>a</sup>	S.D. <sup>b</sup>	Maximum	Minimum	Mean	S.D.	Mean	S.D.	Maximum	Minimum	Mean	S.D.	Mean	S.D.	Maximum	Minimum	Mean	S.D.	Mean	S.D.	Maximum	Minimum	Mean	S.D.	
Chlorofluorocarbons																									
Trichlorofluoromethane (F11)	476	178	1105	305	2658	998	374	105	905	217	2097	589	637	255	1246	289	3572	1430	671	318	1860	201	3763	1793	
Dichlorodifluoromethane (F12)	897	474	2817	482	6430	2341	622	182	1156	383	3072	899	1005	565	3178	471	4963	2790	1056	401	2804	667	5215	1980	
Trichlorotrifluoroethane (F113)	199	190	1604	37	1522	1453	132	171	1791	22	1010	1308	275	245	1608	28	1690	1798	274	262	2311	26	2096	2004	
Dichlorotetrafluoroethane (F114)	28	20	58	12	195	70	25	6	37	13	174	42	34	9	60	17	237	63	29	9	62	13	202	63	
Halomethanes																									
Methyl chloride	955	401	2284	531	1968	831	732	138	1015	531	1508	284	763	132	1157	519	1573	272	703	179	1593	437	1449	369	
Methyl bromide	100	58	278	45	388	225	81	25	125	7	314	97	124	51	227	23	481	198	259	167	1033	43	1004	648	
Methyl iodide	3.6	2.2	11.2	0.6	21	13	2.4	1.6	7.2	0.2	15	9	1.8	1.0	4.8	0.6	10	6	2.8	1.2	6.2	0.6	16	7	
Methylene chloride	574	153	3606	49	1991	1919	421	583	6402	82	1441	702	967	926	4874	108	3355	3213	1949	1406	9428	478	6762	4878	
Chloroform	623	749	5112	38	2055	3638	73	30	191	25	355	144	185	206	1636	19	899	1001	703	798	4747	109	3415	3876	
Carbon tetrachloride	404	449	2934	126	2539	2822	129	6	148	112	811	38	174	19	274	116	1094	119	175	23	267	151	1100	145	
Haloothenes and haloethanes																									
Ethyl chloride	227	273	1248	10	598	719	45	29	182	10	121	76	41	24	125	10	108	63	87	65	312	16	229	171	
1,1-Dichloroethane	63	20	126	9	255	81	60	14	105	26	242	57	65	31	142	11	263	125	66	22	147	8	267	89	
1,2-Dichloroethane	1512	1863	7300	50	6110	7528	124	101	607	45	501	408	241	297	2088	54	974	1200	357	325	2505	63	1442	1313	
1,2-Dibromoethane	59	22	368	10	650	550	16	4	26	8	122	31	31	15	78	10	217	314	22	7	47	10	168	53	
1,1,1-Trichloroethane	553	263	1499	134	1925	1453	235	136	886	132	1281	741	313	553	2499	151	3085	3013	747	257	1549	205	4070	1490	
1,1,2-Trichloroethane	32	24	129	45	174	131	15	6	45	6	82	33	27	10	56	7	147	54	41	21	89	4	223	114	
1,1,1,2-Tetrachloroethane	42	15	80	2	82	103	6	3	18	4	41	21	10	12	89	5	69	82	9	3	18	4	62	21	
1,1,2,2-Tetrachloroethane	11	9	77	2	75	67	6	2	12	4	41	14	10	3	17	3	69	21	12	9	77	5	82	62	
1,2-Dichloropropane	81	37	253	22	374	171	53	12	88	22	244	55	48	14	99	20	221	65	57	15	88	11	263	89	
Chloroalkenes																									
Vinylidene chloride	25	36	136	44	99	143	9	5	34	44	36	20	31	49	224	44	123	194	9	6	56	44	36	24	
(cis) 1,2-Dichloroethylene	71	59	429	21	281	234	39	8	66	25	154	32	76	61	605	25	301	242	60	14	173	33	238	55	
Trichloroethylene	144	195	940	5	773	1047	112	154	1040	8	401	827	198	313	2483	7	1063	1680	118	55	236	15	633	295	
Tetrachloroethylene	401	598	3215	34	2717	4052	328	955	2804	67	2209	6471	394	158	1130	99	2670	1071	484	236	1626	173	3279	1599	
Allyl chloride	45	9	45	45	416	1	45	45	45	45	416	1	45	45	45	45	416	1	45	45	45	45	416	1	
Hexachloro-1,3-butadiene	11	20	154	1	117	213	3	2	10	1	32	21	2	1	7	0.4	21	11	4	3	16	1	43	32	
Chloroaromatics																									
Monochlorobenzene	309	517	2785	9	1619	2374	240	243	1167	5	1102	1116	290	217	1114	33	1332	996	—	—	—	—	—	—	
p-Chlorotoluene	45	—	58	45	26	—	45	—	25	45	26	—	45	—	111	45	26	—	45	—	39	45	26	—	
m-Dichlorobenzene	7	8	67	1	42	54	6	11	95	1	36	66	26	34	227	2	156	204	10	8	76	3	60	48	
o-Dichlorobenzene	7	8	47	1	42	48	4	8	55	1	24	48	8	7	36	1	48	42	6	4	21	1	36	24	
p-Dichlorobenzene	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
1,2,4-Trichlorobenzene	2	2	13	1	15	15	1	1	6	1	7	7	6	4	35	1	44	30	10	7	40	2	74	52	
Aromatic hydrocarbons																									
Benzene	5780	5880	32700	860	18402	18120	1410	1190	5820	160	4489	3789	4390	3940	21910	110	13976	12544	3950	1910	10980	520	12576	6081	
Toluene	10130	10850	65450	1040	38780	40743	1520	1250	6450	101	5708	4494	6740	5280	24600	290	23432	19827	5800	3670	20970	450	21780	11781	
Ethyl benzene	1380	1400	7280	50	5971	6052	640	460	2100	50	2768	1940	2220	1130	18520	90	9605	13542	1330	870	4080	250	5754	3548	
m/p-Tylene	3840	4270	23780	270	16614	18474	950	703	3210	110	4110	3042	2840	3320	20850	150	12374	14384	2731	1513	7340	260	9652	6555	
o-Tylene	1307	1440	9790	80	5655	6317	310	300	1440	60	1341	1298	1280	1210	6000	410	5538	5235	1100	450	3140	80	4758	2812	
n-Ethyl toluene	870	1030	2670	60	4261	5045	240	180	1240	80	1176	892	900	760	4380	70	4408	3722	870	460	2650	70	4016	2253	
1,2,4-Trimethyl benzene	1150	1410	9160	50	5633	7300	370	370	2540	60	1812	1812	1410	2310	5540	130	6906	11314	740	500	3120	100	3674	2448	
1,3,5-Trimethyl benzene	460	800	5350	70	2253	3918	530	490	1360	80	7596	2600	340	240	1290	30	1665	1176	230	170	1260	70	1127	833	
Oxygenated species																									
Formaldehyde	—	—	—	—	—	—	11300	4500	18700	8100	13836	5510	12300	5900	28700	6600	15061	7274	19000	7600	41000	10400	23265	9306	
Acetaldehyde	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Phosgene	<20	—	<20	—	81	—	<20	—	<20	—	81	—	<20	—	<20	—	81	—	<20	—	—	—	—	202	—
Peroxyacetylnitrate (PAN)	438	835	4350	<10	2163	777	203	890	40	1368	1003	443	1264	11647	12	2188	6154	1196	1249	5760	120	5907	6149	—	
Peroxypropionynitrate (PPN)	110	140	630	<10	406	771	64	93	250	<10	353	512	45	47	318	<10	248	259	193	197	900	<10	1063	1086	

<sup>a</sup> Arithmetic mean.<sup>b</sup> True standard deviation.

Dashes indicate that chemical was not measured and/or standard deviations could not be computed.

TABLE 12. ATMOSPHERIC CONCENTRATIONS OF MEASURED CHEMICALS (SITE 8-10)

Chemical Group and Species	Staten Island--Site 8 (26 March-5 April 1981)				Pittsburgh--Site 9 (7-17 April 1981)				Chicago--Site 10 (20 April-2 May 1981)			
	ppt		ng/m <sup>3</sup>		ppt		ng/m <sup>3</sup>		ppt		ng/m <sup>3</sup>	
	Mean <sup>a</sup>	S.D. <sup>b</sup>	Maximum	Minimum	Mean	S.D.	Maximum	Minimum	Mean	S.D.	Maximum	Minimum
Chlorofluorocarbons												
Trichlorofluoromethane (F11)	360	143	909	175	2019	802	333	45	486	279	1811	252
Dichlorofluoromethane (F12)	519	190	1028	318	2563	938	496	178	976	306	2450	879
Trichlorotrifluoroethane (F113)	129	78	359	59	987	597	68	27	162	42	520	207
Dichlorotetrafluoroethane (F114)	39	33	204	21	272	230	30	5	43	22	209	35
Halomethanes												
Methyl chloride	701	186	1208	446	1445	383	665	105	852	450	1371	216
Methyl bromide	84	108	671	27	326	419	41	6	62	27	159	23
Methyl iodide	2	1	4	1	12	6	1	1	3	0	6	2
Methylene chloride	1605	2947	18476	226	5846	10224	390	244	1308	152	1353	847
Chloroform	146	117	872	38	709	568	97	41	238	31	471	199
Carbon tetrachloride	309	202	1200	125	1942	1270	331	107	691	131	2081	673
Halooethanes and halopropanes												
Ethyl chloride	110	64	312	10	290	168	84	45	229	42	221	118
1,1 Dichloroethane	13	5	37	3	53	20	12	15	105	3	48	61
1,2 Dichloroethane	256	520	4312	55	1034	2101	121	35	237	66	489	141
1,2 Dibromoethane	20	6	36	12	153	46	16	10	59	6	122	76
1,1,1 Trichloroethane	468	248	1427	221	2550	1351	486	272	1595	158	2648	1482
1,1,2 Trichloroethane	7	2	11	3	38	11	6	2	11	3	33	11
1,1,1,2 Tetrachloroethane	- <sup>c</sup>	-	-	-	-	-	4	1	5	4	27	7
1,1,2,2 Tetrachloroethane	-	-	-	-	-	-	4	<1	4	3	27	7
1,2 Dichloropropane	26	15	79	10	120	69	23	8	50	4	106	37
Chloroalkenes												
Vinylidene chloride	-	-	-	-	-	-	-	-	-	-	-	-
(cis) 1,2 Dichloroethylene	18	6	41	8	71	24	13	5	25	4	51	20
Trichloroethylene	167	199	1005	26	896	1068	96	93	420	13	515	499
Tetrachloroethylene	292	200	1034	79	1978	1355	409	357	1657	80	2771	2419
Allyl chloride	-	-	-	-	-	-	-	-	-	-	-	-
Hexachloro-1,3 butadiene	-	-	-	-	-	-	6	7	19	<1	64	75
Chloroaromatics												
Monochlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
o-Chlorotoluene	-	-	-	-	-	-	-	-	-	-	-	-
o-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
m-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
p-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
1,2,4 Trichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
Aromatic hydrocarbons												
Benzene	4204	4287	19034	82	13384	13648	5003	9818	64619	392	15928	31257
Toluene	8975	10638	67304	623	33707	39947	3928	7286	46313	386	14750	27360
Ethyl benzene	1742	2472	17230	9	7537	10695	765	1564	10465	69	3310	6767
m/p-Xylene	4088	8352	54638	170	17687	36135	1551	2357	10783	110	6710	10198
o-Xylene	1288	2194	16189	47	5573	9492	573	828	3787	43	2479	3582
4-Ethyl toluene	411	468	2778	13	2013	2292	309	416	2881	39	1513	2038
1,2,4 Trimethyl benzene	831	917	4682	62	4070	4451	1034	1349	24722	39	5064	16403
1,3,5 Trimethyl benzene	210	273	1621	51	1029	1337	121	128	797	45	593	627
Oxygenated species												
Formaldehyde	14300	9100	45900	7000	17510	11143	20600	5200	35100	12900	25224	6367
Acetaldehyde	-	-	-	-	-	-	1400	600	2600	200	2514	1978
Phosgene	-	-	-	-	-	-	-	-	-	-	-	-
Peroxyacetylnitrate (PAN)	747	718	3888	65	3689	3546	266	121	648	65	1314	598
Peroxypropylnitrate (PPN)	204	527	3110	32	1124	2904	45	8	65	32	248	44

<sup>a</sup> Arithmetic mean.<sup>b</sup> One standard deviation.<sup>c</sup> Dashes indicate that chemical was not measured and/or standard deviations could not be computed.

on two-hour averages and one sigma ( $\sigma$ ) standard deviation. Where raw data are plotted, the day of the week is also shown.

Because many of the chemicals measured here are also ubiquitous components of the global troposphere, Table 13 has been prepared to define this background (Singh et al., 1981c; Singh and Hanst, 1981). To facilitate discussion, chemicals in Tables 10-12 have been divided into seven categories. Much of the information presented in Tables 10-12 is self-explanatory, so only the salient features will be discussed in the next section. Some additional details can also be found in interim reports (Singh et al., 1979c; 1980).

#### INTERPRETATION OF FIELD DATA BY CHEMICAL CATEGORY

##### Chlorofluorocarbons (CFCs)

As indicated earlier, CFCs are not considered or expected to be toxic. They can, however, act as useful indicators of polluted air masses, and their possible involvement in stratospheric ozone destruction (Molina and Rowland, 1974) is well known. A maximum of four CFCs (fluorocarbons 11, 12, 113, and 114) were measured. Fluorocarbons 12 and 11 are the dominant CFCs. The average F12 and F11 concentrations were typically in the 0.5 to 1 ppb and 0.3 to 0.7 ppb range respectively (Tables 10 through 12). Maximum concentrations of 3.2 ppb for F12 and 1.2 ppb for F11 were measured. Average concentrations of F113 and F114 were significantly lower, although a high F113 level of 4.2 ppb was measured in Los Angeles (Site 1). Typical average concentrations at all sites were 2 to 10 times the geochemical background concentrations (Table 13).

The mean F12/F11 concentration ratio at all sites (Sites 4-10) was between 1.5 and 1.9. The highest value of 1.9, measured at Houston (Site 4), may be due to a greater use of air conditioned automobiles, which use F12 as a refrigerant. The F12 and F11 emission ratio for the United States is not available for 1981, but is determined to be approximately between 1.5 to 1.7 for the previous two years (CMA, 1981; CIS, 1981). In the clean troposphere and at midlatitudes, an F12/F11 concentration ratio of about 1.6 has been measured (Table 13). It is clear, therefore, that the F12/F11 ratio measured in the urban environment is consistent with the expected values. A much greater variability in the F12/F113 ratio (3 to 9) is observed probably indicative of the difference in use patterns of these fluorocarbons.

Although a considerable data base on the background concentrations of these fluorocarbons is available, relatively little urban data have been published. Typical F12 and F11 levels from several cities (Simmonds et al., 1973; Lillian et al., 1975; Singh et al., 1979a) are not inconsistent with measurements in this study. Because of the rapidly changing use patterns of fluorocarbons in recent years (CMA, 1981) urban measurements obtained at different times cannot be quantitatively compared.

TABLE 13. AVERAGE BACKGROUND CONCENTRATION  
OF TRACE SPECIES AT 40°N FOR YEAR 1981

Chemical Group and Species	Concentration	
	ppt	ng/m <sup>3</sup>
<b>Chlorofluorocarbons</b>		
Trichlorofluoromethane (F11)	190	1066
Dichlorofluoromethane (F12)	300	1481
Trichlorotrifluoroethane (F113)	25	191
Dichlorotetrafluoroethane (F114)	15	105
<b>Halomethanes</b>		
Methyl chloride	650	1340
Methyl bromide	10	39
Methyl iodide	2	12
Methylene chloride	50	173
Chloroform	20	97
Carbon tetrachloride	135	848
<b>Haloethanes and halopropanes</b>		
Ethyl chloride	10	26
1,1 Dichloroethane	-*	-
1,2 Dichloroethane	40	162
1,2 Dibromoethane	2	15
1,1,1 Trichloroethane	180	981
1,1,2 Trichloroethane	-	-
1,1,1,2 Tetrachloroethane	-	-
1,1,2,2 Tetrachloroethane	-	-
1,2 Dichloropropane	-	-
<b>Chloroalkenes</b>		
Vinylidene chloride	-	-
(cis) 1,2 Dichloroethylene	-	-
Trichloroethylene	15	80
Tetrachloroethylene	50	337
Allyl chloride	-	-
Hexachloro-1,3 butadiene	-	-
<b>Chloroaromatics</b>		
Monochlorobenzene	-	-
o-Chlorotoluene	-	-
o-Dichlorobenzene	-	-
m-Dichlorobenzene	-	-
p-Dichlorobenzene	-	-
1,2,4 Trichlorobenzene	-	-
<b>Aromatic hydrocarbons</b>		
Benzene	-	-
Toluene	-	-
Ethyl benzene	-	-
m/p-Xylene	-	-
o-Xylene	-	-
4-Ethyl toluene	-	-
1,2,4 Trimethyl benzene	-	-
1,3,5 Trimethyl benzene	-	-
<b>Oxygenated species</b>		
Formaldehyde	400	490
Acetaldehyde	40†	72†
Phosgene	-	-
Peroxyacetylnitrate (PAN)	20†	99†
Peroxypropionynitrate (PPN)	-	-

\*Dashes indicate absence of available data.

†Estimated from mechanistic models.



## Halomethanes

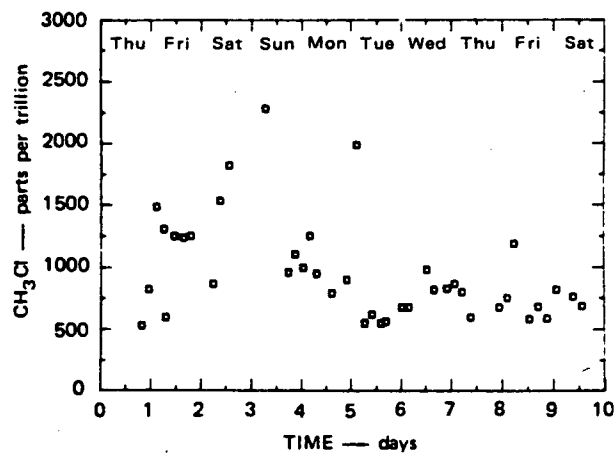
Six halomethanes--methyl chloride, methyl bromide, methyl iodide, methylene chloride, chloroform, and carbon tetrachloride--were measured. As can be seen from Table 1, all six of these are bacterial mutagens or suspected carcinogens. Three methyl halides have dominant natural (oceanic) sources (Table 9).

Methyl Chloride--The dominant natural halocarbon in the atmosphere is methyl chloride. A nearly uniform background concentration of 0.6 to 0.7 ppb has been measured around the globe (Table 13), and no temporal trend is evident (Singh et al., 1981c). Urban levels of methyl chloride have not been reported in the literature, although Lovelock (Watson et al., 1979) did report methyl chloride levels of over 2 ppb in Kenya. The methyl chloride urban data base presented here is the most extensive available to date, because solid sorbents such as Tenax®, which are used for routine data collection, do not appear to collect methyl halides (Pellizzari and Bunch, 1979;\* Bozzelli et al., 1980). Based on our measurements, it appears that although typical methyl chloride levels in urban areas are close to or only slightly elevated above background levels, concentrations an order of magnitude higher than the background can be encountered. Thus average methyl chloride levels of 0.60 to 0.85 ppb measured at Sites 5-10 are indistinguishable from the background. Average levels approaching 3 ppb at Los Angeles and 1 ppb at Houston are clearly elevated. As is clear from Table 9, methyl chloride from man-made sources is extremely small compared with its natural (oceanic) source. However, unidentified primary or secondary sources of methyl chloride must exist at least in some of the cities. Methyl chloride is slowly decomposed (Table 8) in the atmosphere (daily loss rate <0.5%), and its global residence time is estimated to be between 1 and 2 years. Figure 14 shows the actual measured concentrations of methyl chloride at six selected urban sites.

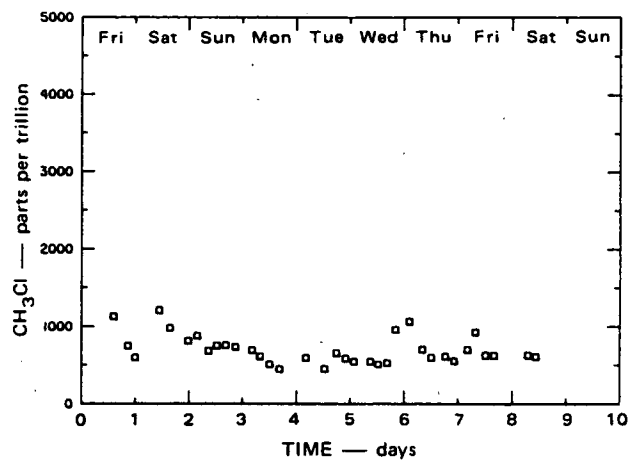
Methyl Bromide--Methyl bromide levels as high as 1 ppb were measured in Los Angeles (Site 1). At Staten Island (Site 8), a concentration as high as 0.67 ppb was measured--but only once. The highest average levels of 0.25 ppb were measured in southern California (Sites 1 and 8), perhaps because of the application of methyl bromide as a fumigant in this area (Table 9). At all other sites, average levels were approximately of 0.1 ppb or less. In almost all cities, however, methyl bromide levels were significantly elevated above the background of 10 to 15 ppt (Table 13). Substantial natural sources contributing to this background must exist (Lovelock, 1975). Suggestions have been made that such gasoline additives as 1,2 dibromoethane could be decomposed to form methyl bromide (NAS, 1978). Data to support this suggestion are currently limited: other than data reported by us and a few isolated measurements reported in NAS (1978), very few methyl bromide measurements exist. Pellizzari and Bunch (1979) noted traces of methyl bromide on some of their Tenax® cartridges but did not quantify these. Figure 15 shows the variability of methyl bromide at three selected sites. Both primary and secondary sources of methyl bromide may exist in urban areas, but the actual nature of these

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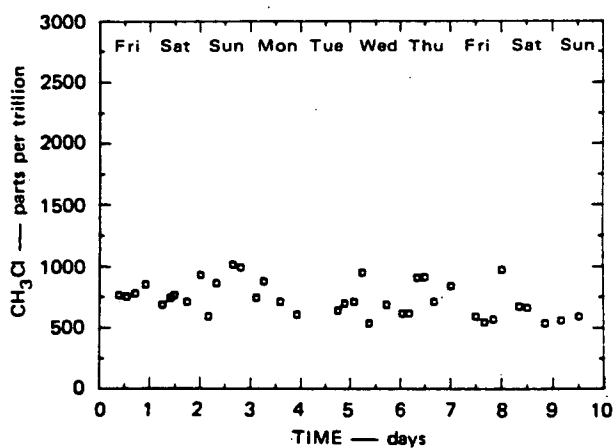
\*This reference summarizes data from a number of studies conducted over a period of several years under several different contracts from EPA.



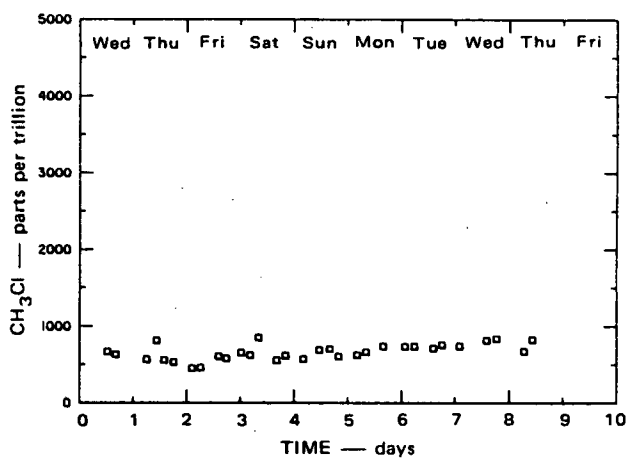
(a) HOUSTON, TX



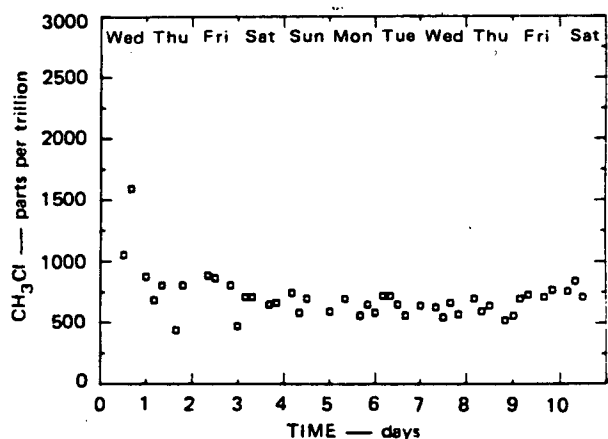
(d) STATEN ISLAND, NY



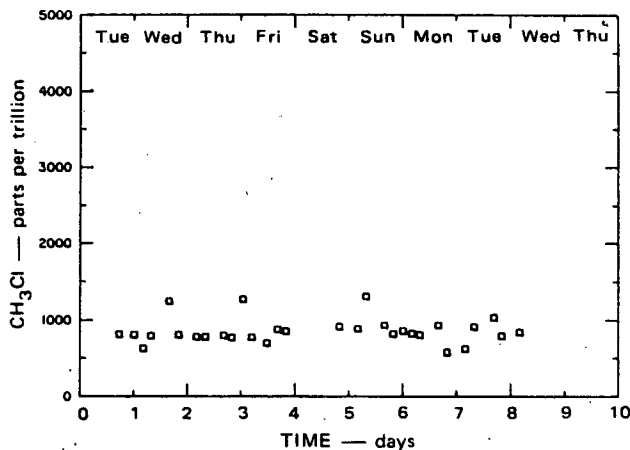
(b) ST. LOUIS, MO



(e) PITTSBURGH, PA

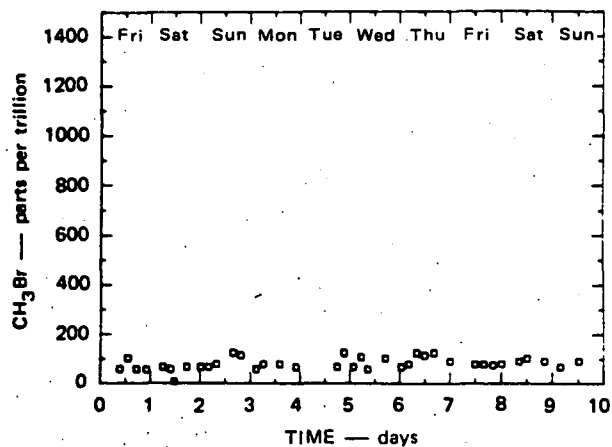


(c) RIVERSIDE, CA

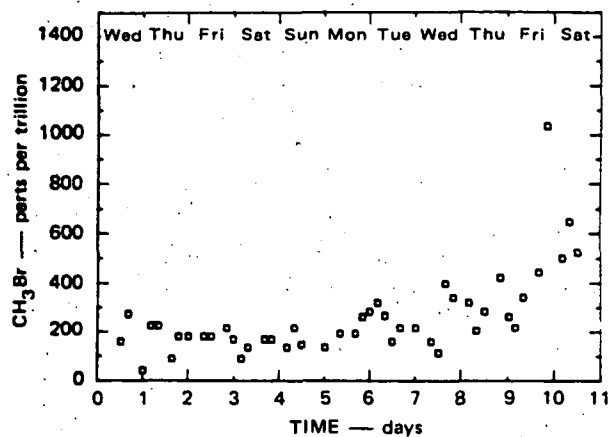


(f) CHICAGO, IL

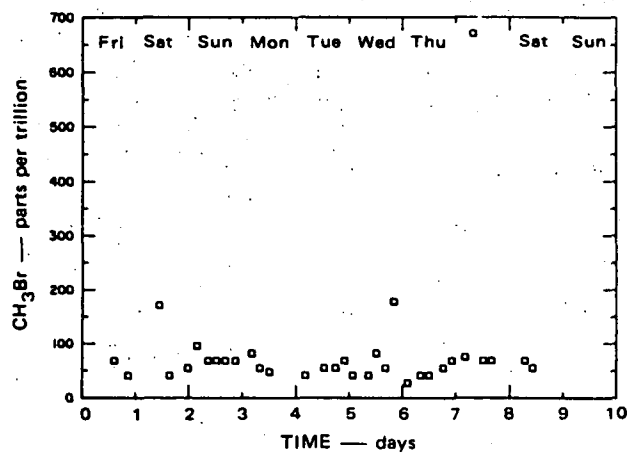
Figure 14. Methyl chloride in the ambient air of selected cities.



(a) ST. LOUIS, MO



(b) RIVERSIDE, CA



(c) STATEN ISLAND, NY

Figure 15. Atmospheric concentrations of methyl bromide.

sources has not yet been characterized. Methyl bromide is chemically removed from the atmosphere at a slow rate (Table 8) that is comparable to the removal rate of methyl chloride.

Methyl Iodide--Methyl iodide was carefully measured to avoid interference or contamination from other pollutants. It was resolved on two different GC columns (columns 2 and 6 in Table 3): The results were very nearly identical. As indicated in Table 1, methyl iodide is both a suspected carcinogen and a mutagen. It is different from methyl chloride and methyl bromide primarily because of its rather exclusive natural source. Our measurements at all urban sites point to average methyl iodide levels in the 1- to 4-ppt range, with 2 ppt perhaps a typical average value. These concentrations are very nearly the same as or slightly less than those measured near marine environments (Table 13 and Singh et al., 1981). This is not surprising, because methyl iodide is primarily of oceanic origin (Lovelock, 1975) and is significantly less stable than either methyl chloride or methyl bromide. Methyl iodide is decomposed by sunlight in the troposphere, and a daily loss rate of approximately 12 percent is estimated (Table 8). Limited atmospheric concentration data from clean as well as polluted environments, as summarized by Chameides and Davis (1980), point to a considerable variability. A substantial part of this variability, we believe, is associated with earlier measurement problems. Significantly elevated methyl iodide levels at Bayonne, New Jersey, reported by Lillian et al. (1975), appear anomalous. Measurements at Bayonne should be repeated. Our findings, based on measurements conducted at several cities, point to very low methyl iodide levels, with an average value of about 2 ppt and a maximum value of less than 11 ppt. Figure 16 shows the diurnal variation of methyl iodide at two selected sites. A slight dip in the afternoon is indicative of photochemical loss as well as of possible vertical gradients in the concentration of methyl iodide.

Although methyl iodide is a major carrier of organic iodine in the biosphere, its sources and its atmospheric role are currently not well understood. A certain marine algae known to concentrate iodine from sea water has been identified as one source of methyl iodide (Lovelock, 1975; Watson et al., 1980). It has also been postulated that methyl iodide could react with chloride ions in sea water to form methyl chloride (Zafirou, 1975). Chameides and Davis (1980) have postulated that methyl iodide could photolyze to form iodine atoms, which could lead to some ozone destruction within the boundary layer. However, their calculations are based on average methyl iodide levels of 10 to 50 ppt, rather than 1 to 4 ppt.

Methylene Chloride--Methylene chloride is clearly a large-volume chemical of exclusively anthropogenic origin (Table 9). To the best of our knowledge no natural sources of methylene chloride have been identified. Maximum concentrations of 12 ppb, 9 ppb, 18 ppb, and 56 ppb were measured at Los Angeles (Site 1), Riverside (Site 7), Staten Island (Site 8) and Chicago (Site 10), respectively. Average levels were highest in southern California, with concentrations of 3.7 ppb and 1.9 ppb at Los Angeles and Riverside, respectively. Concentration levels at Staten Island and Chicago were about 1.7 ppb each; at all other sites, average concentrations ranged between 0.4 and 1 ppb. Background levels of methylene chloride are about 50 ppt at 40°N (Table 13); thus a significant elevation above background levels is evident. Average urban

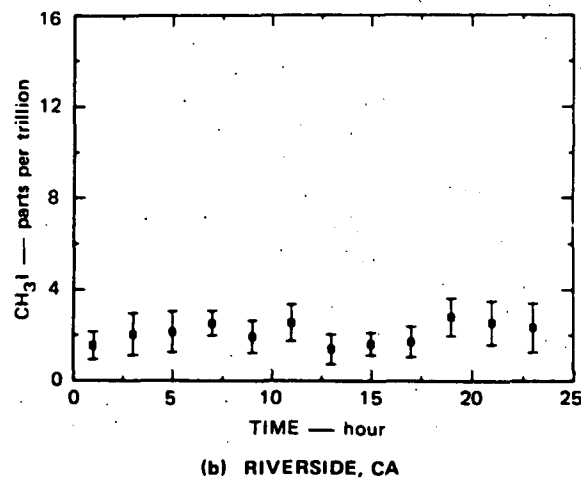
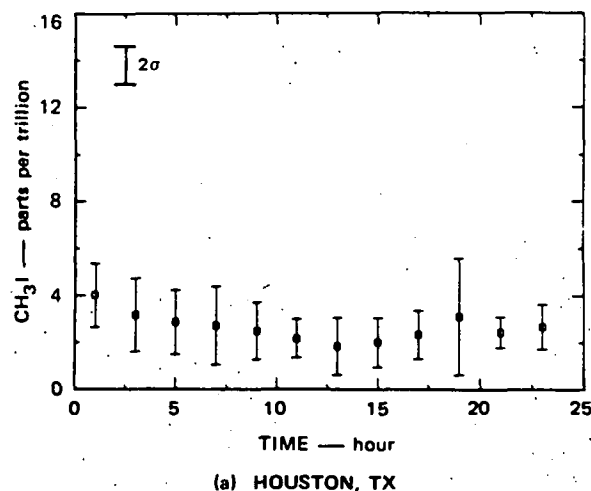


Figure 16. Mean diurnal variation of methyl iodide.

concentrations are one or two orders of magnitude higher than the background environment. The highest average levels were typically encountered at night. Figure 17 shows typical diurnal variations at six selected sites.

Methylene chloride is relatively unreactive, and a daily chemical loss rate of less than 2 percent is estimated (Table 8). The diurnal variation of methylene chloride is therefore primarily determined by its source strength and the atmospheric mixing processes. The afternoon minimum observed at several sites (e.g. Figure 17) can only be attributed to dilution caused by deep vertical mixing. In the absence of local emissions inventories and detailed meteorological analysis, further conclusions would be premature.

Pellizzari and Bunch (1979) have also reported methylene chloride concentrations from several locations within the United States. Although our data are not necessarily inconsistent with their results, certain discrepancies are

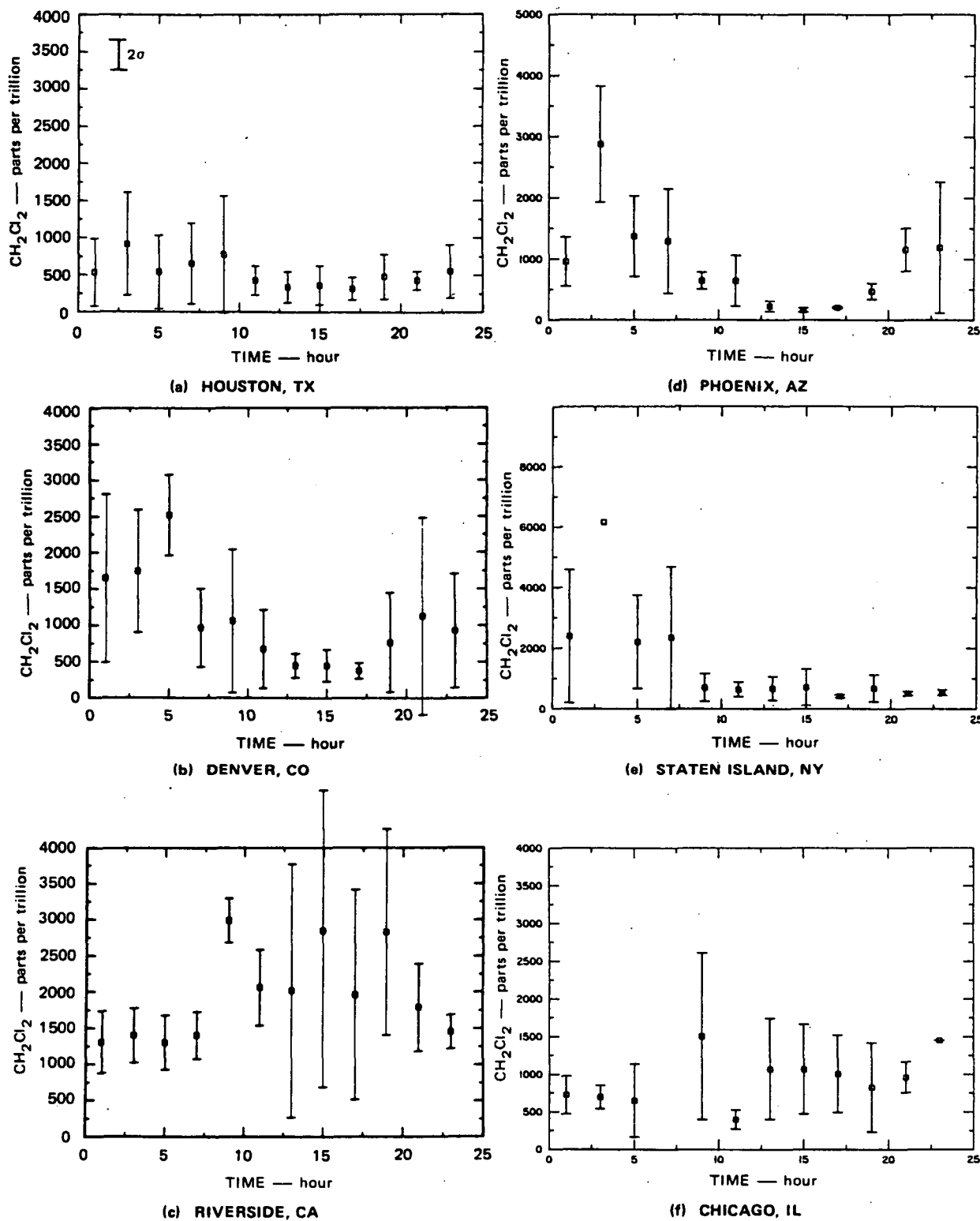


Figure 17. Mean diurnal variation of methylene chloride at selected sites.

evident. For example, they report many concentrations significantly below the geochemical background that has been relatively well characterized (Cox et al., 1976; Singh et al., 1979a, 1981c; Cronn et al., 1977). A maximum concentration of slightly over 300 ppb was also reported from an industrial site in Edison, New Jersey.

Chloroform--Chloroform, a mutagen and a suspected carcinogen (Table 1), has received a great deal of attention in recent years because of high concentrations that have been found to be present in drinking water (Symons et al., 1975). The background of chloroform is in the 10- to 20-ppt range (Table 13). Tables 10 through 12 clearly show that urban levels are significantly elevated. Highest concentration levels approaching 5 ppb were measured at more than one site. At Houston and Riverside, average concentrations were found to be 0.4 ppb and 0.7 ppb respectively. At most other sites typical average concentrations were in the vicinity of 0.1 ppb.

The direct emissions of chloroform appear to be too small (Table 9) to account for its pervasiveness in urban environments. Figure 18, showing the diurnal variation of chloroform at Phoenix (Site 2), and Figure 19, showing raw data from Staten Island (Site 8), leave little doubt that high chloroform levels are typical for geographically widely separated areas. The urban sources of chloroform are probably secondary in nature and also complex. In a recent review (Batjer et al., 1980), chlorination of water and possibly automobile exhaust were identified as two important sources. The reactivity of chloroform is comparable to that of methylene chloride (Table 8), and its diurnal variation is therefore not chemically controlled.

Although chloroform levels in several urban environments have been reported by Pellizzari and Bunch (1979), a wide variability does not allow useful comparisons. Pellizzari and Bunch (1979) report concentrations that

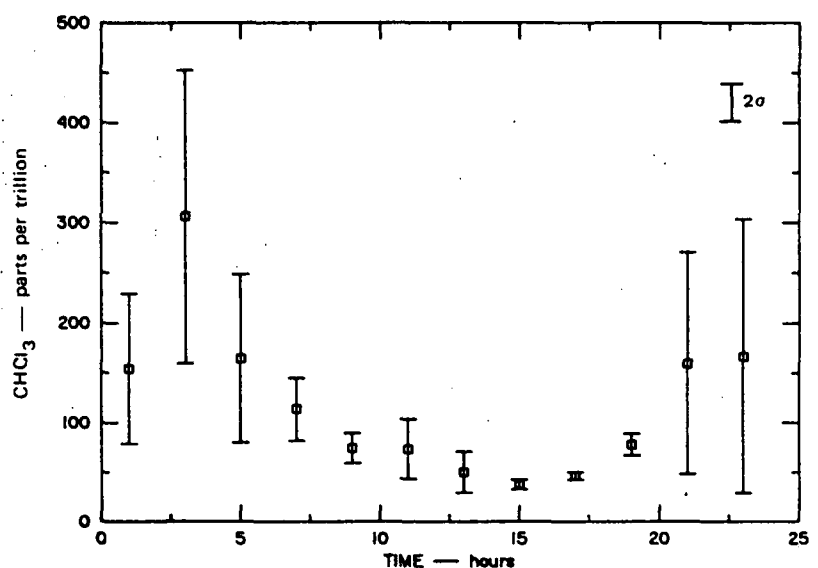


Figure 18. Mean diurnal variation of chloroform at Phoenix, AZ.

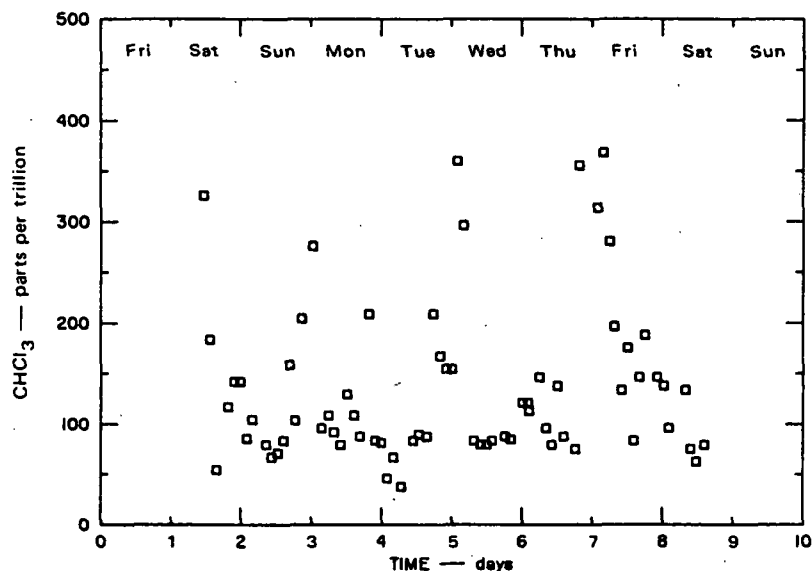


Figure 19. Atmospheric concentrations of chloroform at Staten Island, NY.

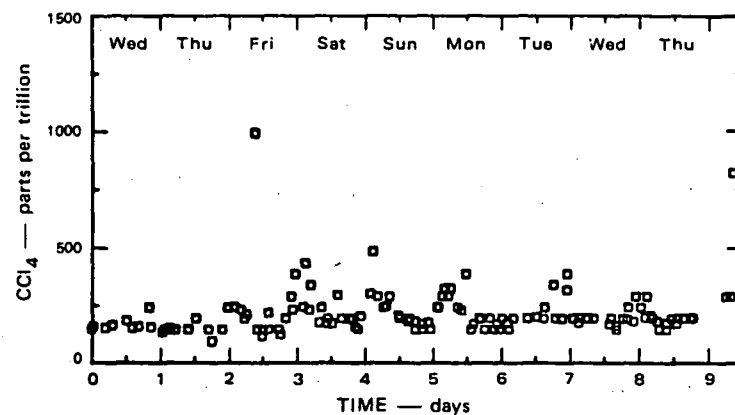
vary from unquantifiable levels to about 7 ppb, a range comparable to that found during this study.

Carbon Tetrachloride--Carbon tetrachloride, a suspected carcinogen, has been found to be nearly uniformly distributed around the globe at a background concentration of about 125 to 150 ppt (Table 13 and Singh et al., 1979a). Considerable evidence suggests that this background reservoir of carbon tetrachloride is of man-made origin (Singh et al., 1976; Altshuller, 1976). Urban carbon tetrachloride levels are higher than the background levels by about a factor two or three. The highest levels, approaching 3 ppb, were measured in Houston (Site 4), but the average concentration was still only 0.4 ppb. At most other sites, average carbon tetrachloride levels were between 0.2 to 0.3 ppb.

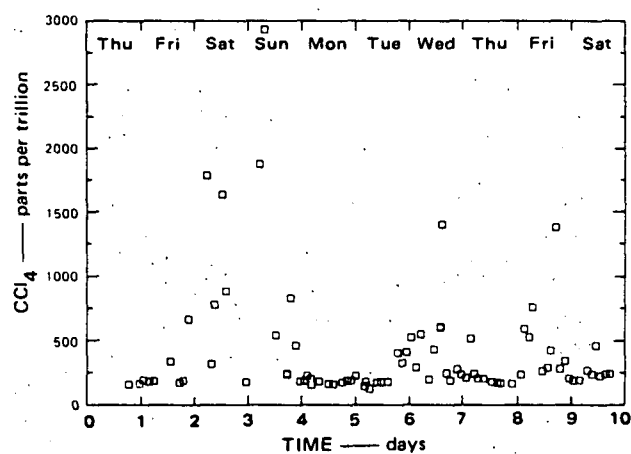
Figure 20 shows the kind of scatter typically observed at three different sites. The mean diurnal variation at Staten Island (Site 8) is shown in Figure 21. The afternoon minimum is comparable to the background carbon tetrachloride levels, a condition accomplished by deep vertical mixing during the afternoon hours. In a manner somewhat similar to that observed for chloroform, the highest levels are encountered during stagnant night hours.

The carbon tetrachloride levels measured here are not only in good agreement with our earlier published data (e.g. Singh et al., 1977a, 1979a), but also agree well with a three-day study conducted in Los Angeles by Simmonds et al. (1974). They measured carbon tetrachloride levels in the range of 0.1 to 2 ppb, with an average of 0.22 ppb [compared with our results of 0.1 to 1 ppb and an average of 0.22 ppb at Los Angeles (Site 1)]. In addition, Pellizzari and Bunch (1979) and Bozzelli et al. (1980) have both reported carbon tetrachloride data from several locations using the Tenax® collection process. (It appears that there are serious problems associated with the use of Tenax® for carbon tetrachloride measurement. The bulk of the data presented by these two investigators is almost a factor of 10 lower than the geochemical background

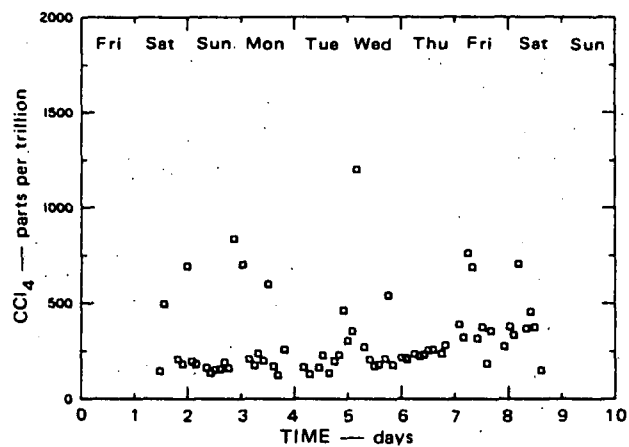




(a) LOS ANGELES, CA



(b) HOUSTON, TX



(c) STATEN ISLAND, NY

Figure 20. Atmospheric concentrations of carbon tetrachloride at selected sites.

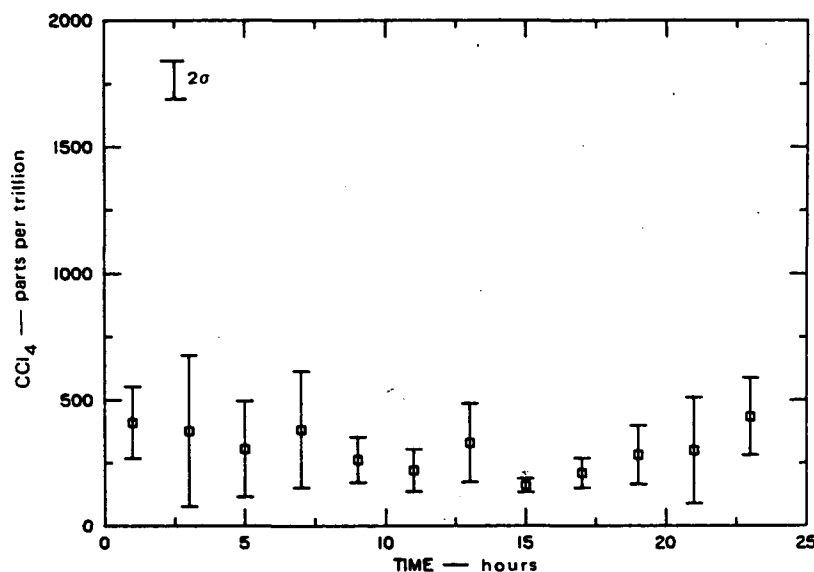


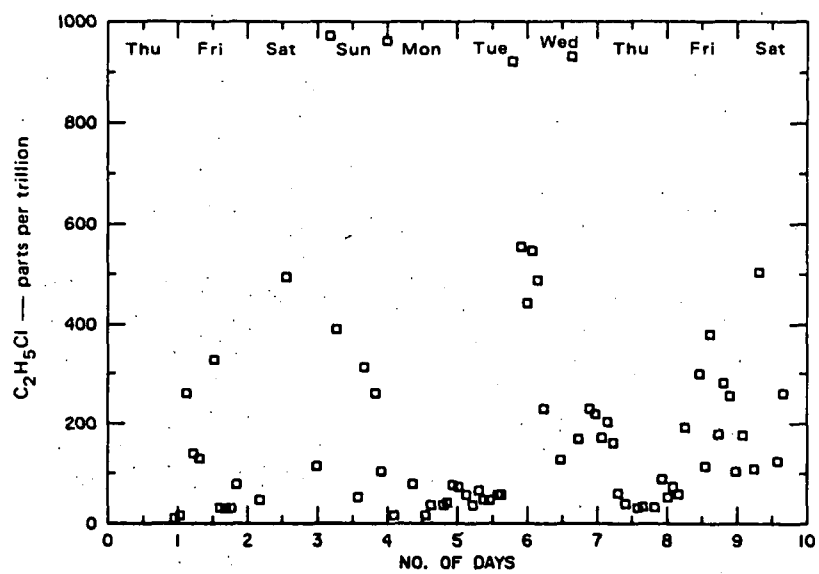
Figure 21. Mean diurnal variations of carbon tetrachloride at Staten Island, NY.

of carbon tetrachloride.) Ohta et al. (1976) report unusually high carbon tetrachloride concentrations from Tokyo: The average concentration level of 1.4 ppb is a factor of three to six higher than typical averages found during this study.

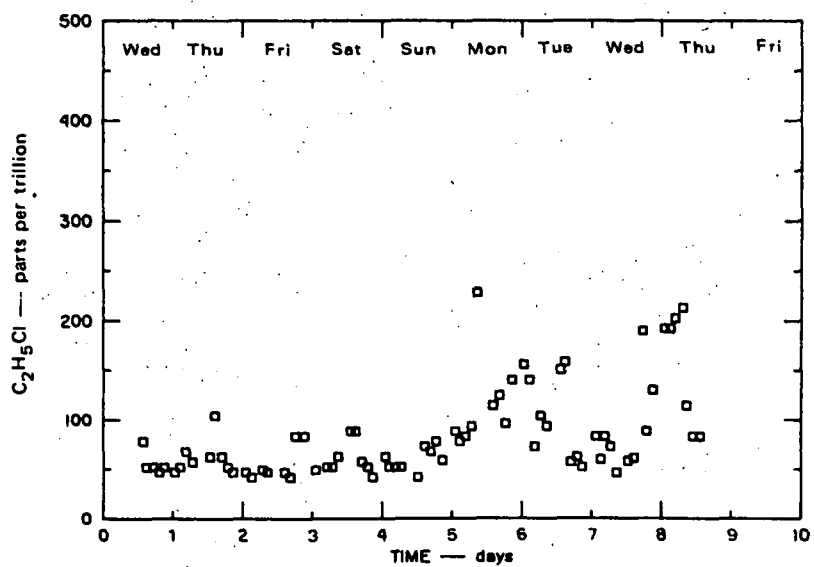
#### Haloethanes and Halopropanes

Nine important chemicals in this category were measured: ethyl chloride; 1,1 dichloroethane; 1,2 dichloroethane; 1,2 dibromoethane (or ethylene dibromide); 1,1,1 trichloroethane; 1,1,2 trichloroethane; 1,1,1,2 tetrachloroethane; 1,1,2,2 tetrachloroethane; and 1,2 dichloropropane. Seven of these (excluding ethyl chloride and 1,1,1,2 tetrachloroethane) are either bacterial mutagens or suspected carcinogens (Table 1).

Ethyl Chloride--Ethyl chloride is a commonly used chemical intermediate (Table 9). It is estimated that about 0.01 million tons of ethyl chloride are released into the atmosphere every year in the United States. A daily chemical loss rate of about 3 percent is estimated (Table 8). Average ethyl chloride concentrations at all sites were 0.1 ppb or less. [Houston (Site 4), whose average and maximum levels were 0.23 ppb and 1.3 ppb, respectively was an exception (Figure 22). At no other site did the maximum concentration ever exceed 0.32 ppb.] Background concentration of ethyl chloride (at 40°N) is found to lie between 10 to 15 ppt (Table 13), clearly suggesting that significant urban sources exist. No atmospheric data on ethyl chloride could be found in the literature. Part of the reason may be its poor collection efficiency on Tenax®, which has been frequently used for urban monitoring of toxic chemicals.



(a) HOUSTON, TX



(b) PITTSBURGH, PA

Figure 22. Atmospheric concentrations of ethyl chloride.

Dichloroethanes--At all sites monitored, 1,1 dichloroethane was present in relatively low concentrations. Average concentrations at any of the sites did not exceed 0.07 ppb; the maximum measured concentration did not exceed 0.15 ppb. At Sites 8-10, extremely low average levels (10 to 15 ppt) were encountered (Table 12); comparable concentration levels have been reported by Pellizzari and Bunch (1979) from parts of New Jersey and Los Angeles. Figure 23 shows the mean diurnal variation of 1,1 dichloroethane at Denver (Site 6) and Riverside (Site 7). A daily loss rate of only about 2 percent is estimated (Table 8).

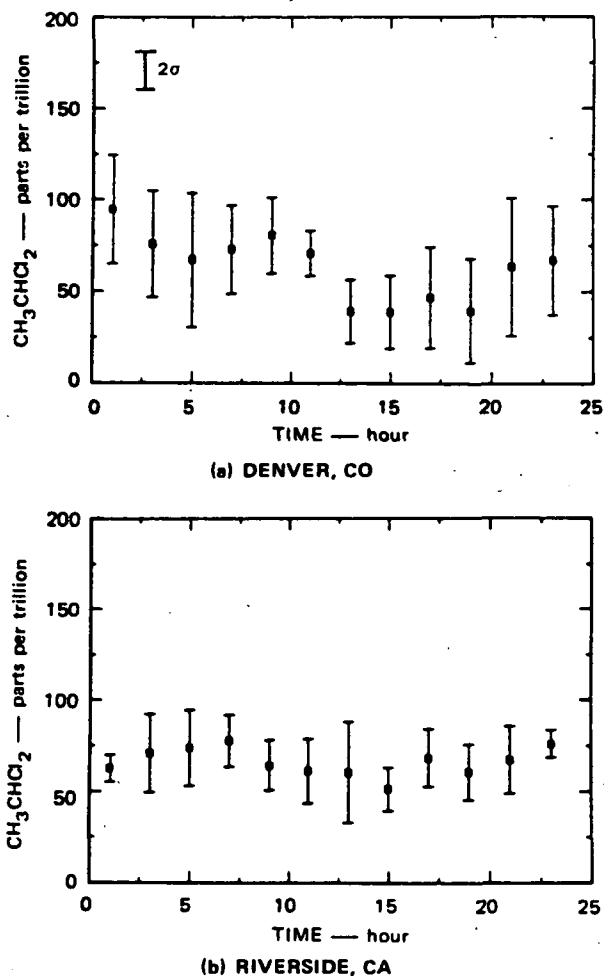
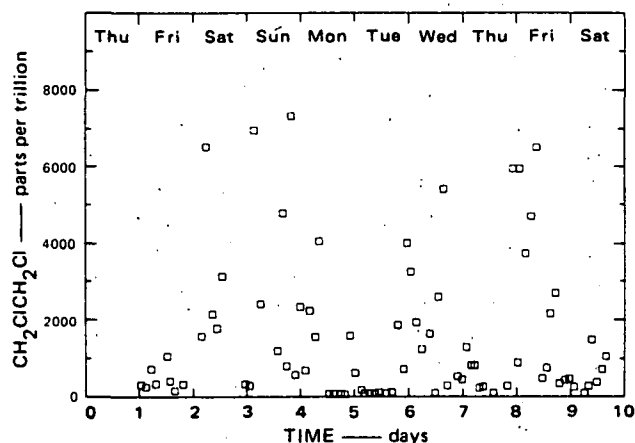


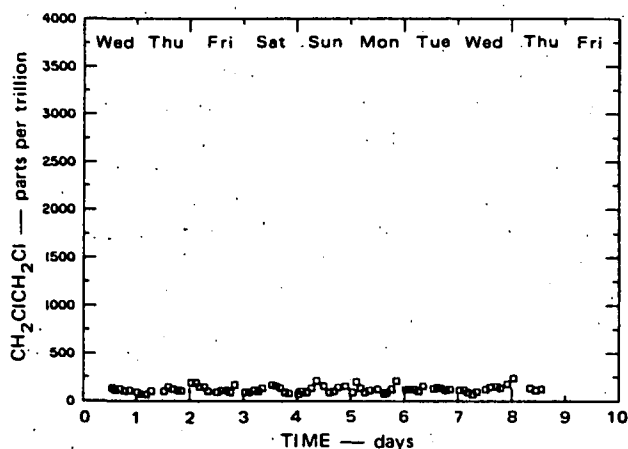
Figure 23. Mean diurnal variation of 1,1 dichloroethane.

1,2 dichloroethane is a large-volume chemical (Table 9) that is a bacterial mutagen and a suspected carcinogen (Table 1). Estimated yearly U.S. emissions exceed 0.2 million tons. It is an exclusively man-made chemical that has also become a part of our global environment. Singh et al. (1981c) report a background concentration of about 40 ppt at 40°N (Table 13). It is obvious from Tables 10-12 that urban levels are significantly elevated. The

highest average concentration (1.5 ppb) was measured in Houston, compared with average levels of 0.1 ppb to 0.5 ppb at all other sites. The maximum concentration (7.3 ppb) was also measured at Houston (Site 4), followed by Staten Island (Site 8), where a maximum of 4.3 ppb was measured. Figure 24 provides a comparison of the atmospheric concentrations of 1,2 dichloroethane at Houston (Site 4) and Pittsburgh (Site 9). Figure 25 shows the mean diurnal variation at Houston and Riverside.



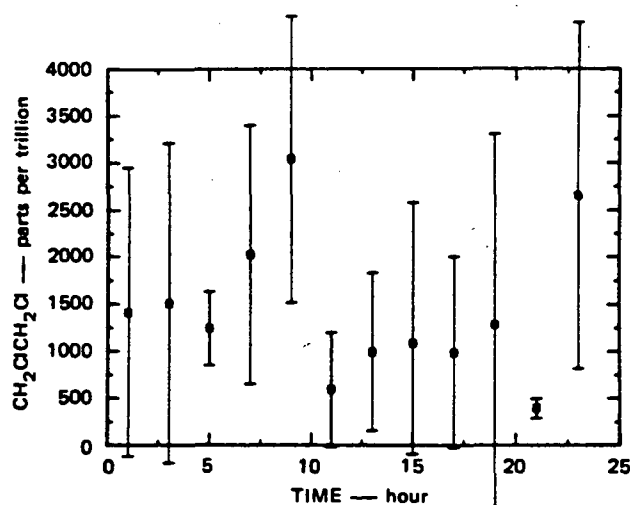
(a) HOUSTON, TX



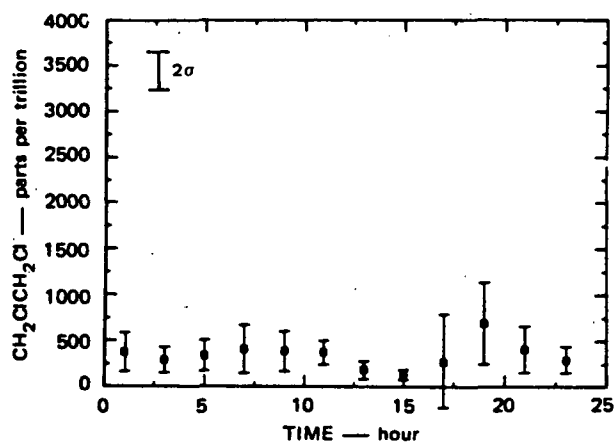
(b) PITTSBURGH, PA

Figure 24. Atmospheric concentration of 1,2 dichloroethane.

The measurements of 1,2 dichloroethane conducted by Bozzelli et al. (1979) and Pellizzari and Bunch (1979) provide a great deal of data that appear to be well below the measured (as well as estimated) background of this chemical (Singh et al., 1981c; Altshuller, 1980). While higher numbers



(a) HOUSTON, TX — 15-24 MAY 1980



(b) RIVERSIDE, CA — 7-12 JULY 1980

Figure 25. Mean diurnal variation of 1,2 dichloroethane.

reported by Pellizzari and Bunch (1979) are comparable to those measured here, in the case of Bozzelli et al. (1979), of the nearly 250 samples collected at various sites in New Jersey, quantification was possible for only two samples.

Ethylene Dibromide--1,2 dibromoethane (also commonly known as ethylene dibromide) is a suspected carcinogen (Table 1). The estimated risk associated with exposure to 1,2 dibromoethane is nearly 50 times that due to 1,2 dichloroethane for equal exposure (Albert, 1980). About 0.1 million tons of this chemical is manufactured in the United States every year (Table 9). It is primarily used as a gasoline additive and a fumigant. Its atmospheric reactivity is comparable to that of 1,2 dichloroethane (Table 8).

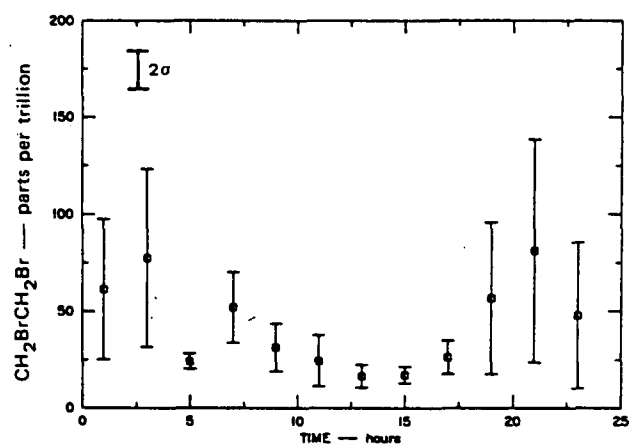
Although it is highly toxic, 1,2 dibromoethane is present in urban atmosphere at relatively low concentrations. The average concentration at none of the sites exceeded 0.06 ppb. The typical range of average concentrations was from 0.015 ppb to 0.06 ppb. The highest concentrations of 0.37 ppb were measured in Houston (Site 4); highest levels in Los Angeles, Phoenix, and Chicago were in the vicinity of 0.2 ppb. Figures 26 and 27 show the distribution and the mean diurnal variation of ethylene dibromide at selected sites.

Limited ethylene dibromide data from U.S. cities is available from the literature. Ambient levels in the 15- to 30-ppt range were reported by Going and Spigarelli (1976). Leinster et al. (1978) have reported ambient levels of between 0 and 20 ppt in London air. Bozzelli et al. (1980) report rather high levels from several New Jersey cities, with maximum concentrations of about 6 ppb. [Quantifiable samples indicate average concentrations of 0.5 to 1 ppb. These results are clearly in disagreement with ours.] Data reported by Pellizzari and Bunch (1979) away from the highways are also in the 0 to 0.3 ppb range, although highway air concentrations as high as 8 ppb are reported. The discrepancies that currently appear to exist should be resolved, because 1,2 dibromoethane is expected to be a potent carcinogen.

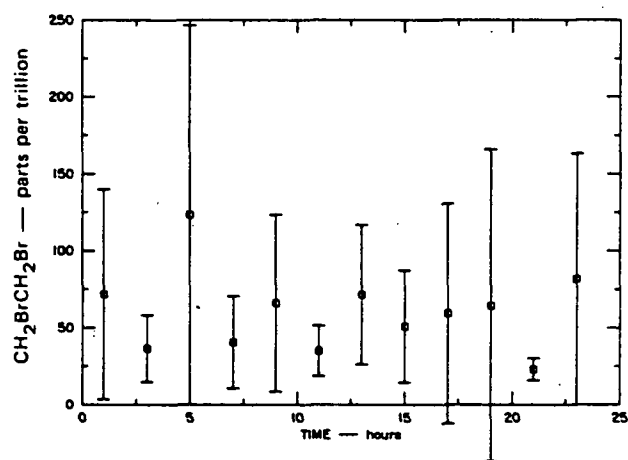
Trichloroethanes--1,1,1 trichloroethane is another large-volume chemical that is released in significant quantities to the atmosphere (Table 9). The chemical has a long atmospheric lifetime and is globally distributed (Singh et al., 1979a). Its atmospheric residence time is estimated to be about eight years (Singh, 1979b); thus about 15 percent of all 1,1,1 trichloroethane released at ground level enters the stratosphere, where it can interact with ozone in a way similar to fluorocarbons. 1,1,1 trichloroethane is suspected to be weakly mutagenic (Table 1), although considerable disagreement on its mutagenic and carcinogenic potential persists (Farber, 1979; Lapp et al., 1979). The background burden of this chemical is constantly increasing; background concentration is now reported to be about 0.18 ppb (Table 13).

The highest 1,1,1 trichloroethane concentration, 5.1 ppb, was measured in Los Angeles. Average concentration at all sites ranged between 0.2 and 1 ppb. Typical diurnal variations at selected sites are shown in Figure 28. Figure 29 shows the raw data as well as the mean diurnal profile at Staten Island: Although nighttime averages are typically high, the associated higher standard deviations at Staten Island are easily explained from raw data. Indeed, high midnight values were encountered on only three of the days monitored (Figure 29).

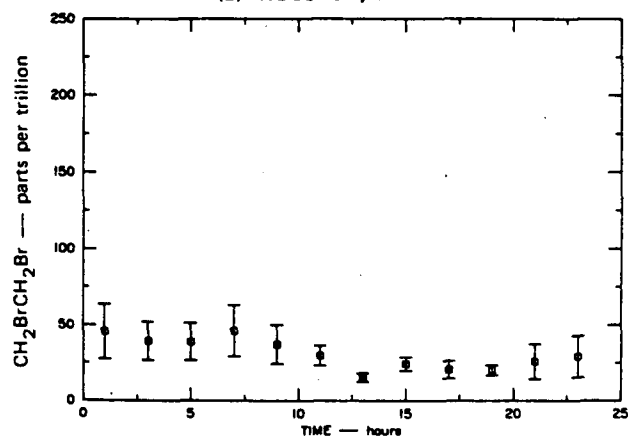
Because of its potential stratospheric significance, a great deal of data on 1,1,1 trichloroethane have been collected in clean environments around the globe. Once again the urban data base has been limited. Simmonds et al. (1974) conducted limited measurements in Los Angeles in 1973 and reported a concentration range of 0.01 ppb to 2.3 ppb with an average of 0.37 ppb. The absolute coulometric technique utilized by these authors is known to underestimate the actual concentrations, especially for relatively inefficient electron absorbers (Lillian and Singh, 1974). As a comparison, our average concentrations are 1 ppb at Los Angeles (Site 1) and 0.7 ppb at Riverside (Site 7). The agreement is quite good if one recognizes that the emissions of 1,1,1



(a) PHOENIX, AZ



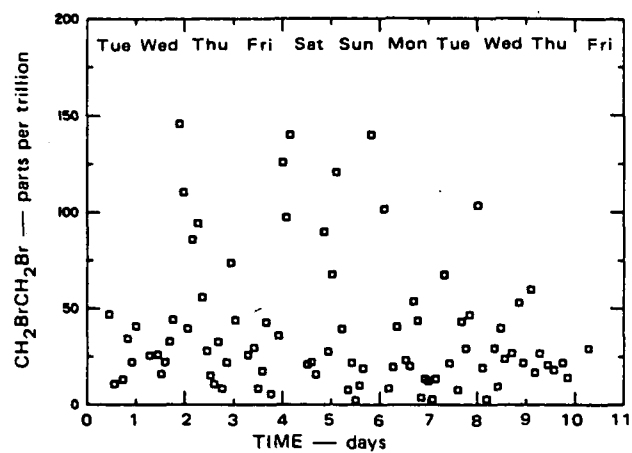
(b) HOUSTON, TX



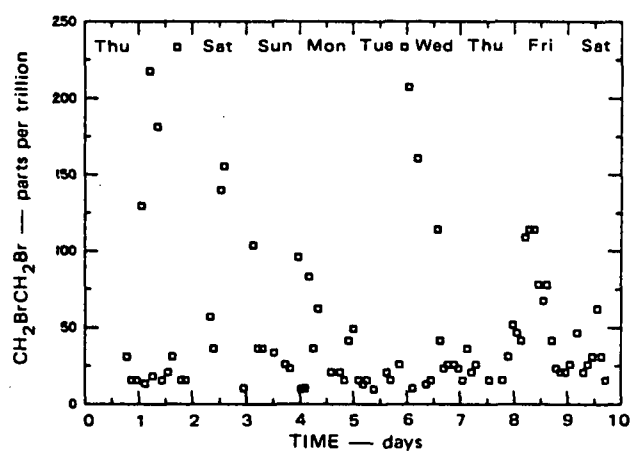
(c) DENVER, CO

Figure 26. Mean diurnal variation of 1,2 dibromoethane.

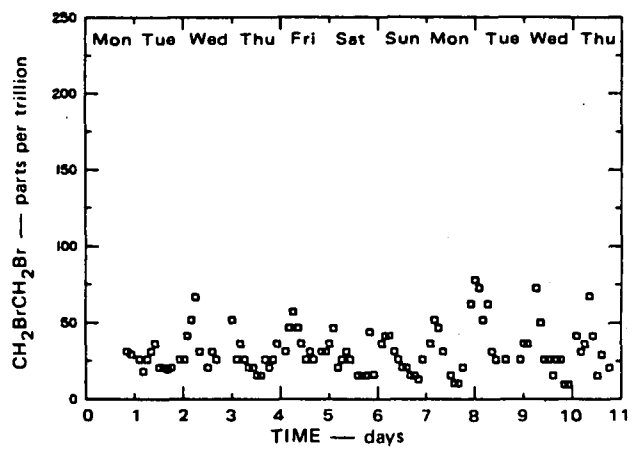




(a) PHOENIX, AZ



(b) HOUSTON, TX



(c) DENVER, CO

Figure 27. Atmospheric concentrations of 1,2 dibromoethane.

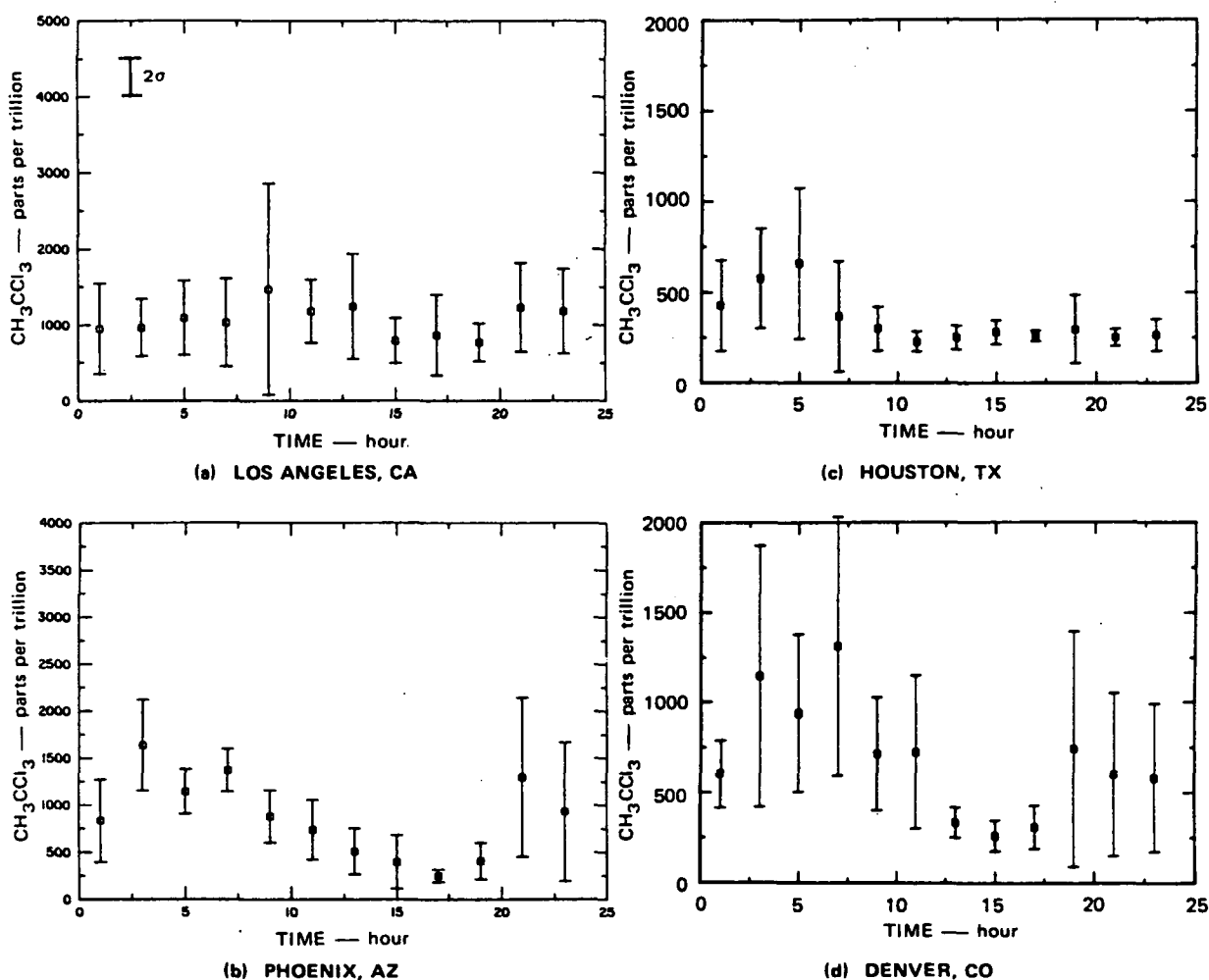


Figure 28. Mean diurnal variation of 1,1,1 trichloroethane.

trichloroethane have nearly doubled in the last six to eight years. A substantial amount of data have also been reported by Pellizzari and Bunch (1979). Once again they report a significant number of measurements that are inconsistent with measured as well as estimated background levels (Table 13).

1,1,2 trichloroethane, a suspected carcinogen, was measured at extremely low concentration levels at all sites. Typical average concentration was around 0.01 ppb, except at Houston (Site 4) and Riverside, where average concentrations of 0.03 ppb and 0.04 ppb, respectively, were measured. A maximum concentration of 0.15 ppb was measured at Houston; at all other sites maximum measured levels were below 0.1 ppb. Bozzelli et al. (1980) report a concentration range in New Jersey that is qualitatively estimated to be between 0-0.01 ppb, although they report one data point as high as 11 ppb in Elizabeth, New Jersey. Pellizzari and Bunch (1979) also report levels of <0.01 ppb to

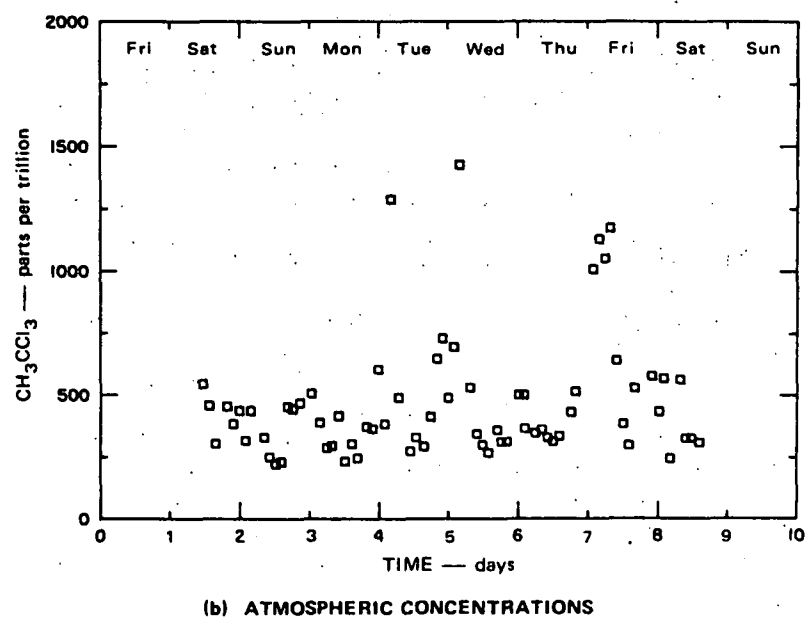
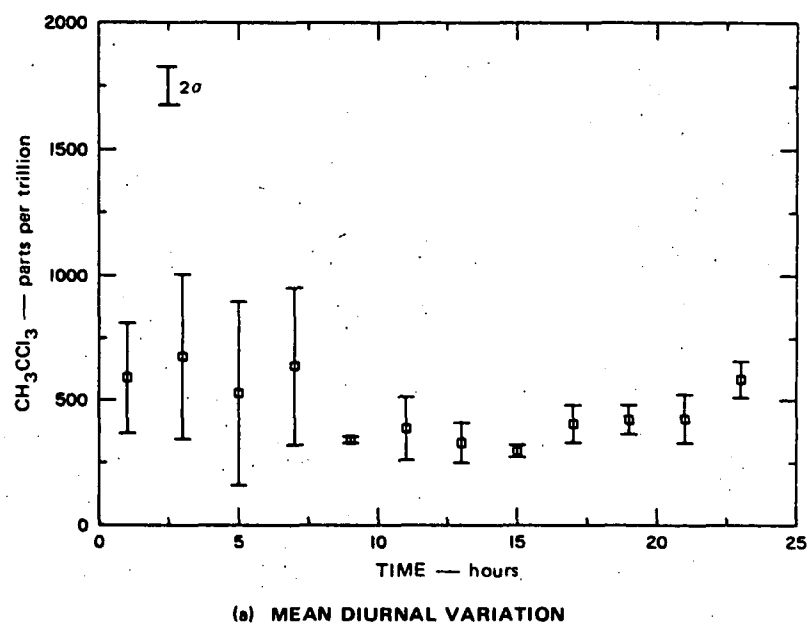


Figure 29. 1,1,1 trichloroethane behavior at Staten Island, NY.

2 ppb at sites in New Jersey, Texas, and Louisiana. Despite its structure similarity to 1,1,1 trichloroethane, the 1,1,2 isomer is 30 times more reactive (Table 8). A daily chemical loss rate of about 3 percent is estimated (Table 8).

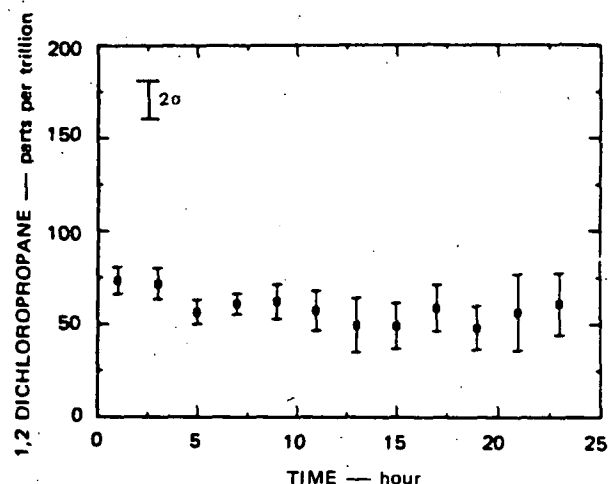
Tetrachloroethanes--Two tetrachloroethane isomers (1,1,1,2 and 1,1,2,2) were measured, both of which were present at extremely low concentrations. The two isomers were present together at an average concentration of less than 0.02 ppb. At no time did the concentration of either one of these chemicals exceed 0.1 ppb. The symmetric isomer (1,1,2,2) is found to be a bacterial mutagen and a suspected carcinogen (Table 1). The asymmetric isomer (1,1,1,2) has been tested for mutagenicity with negative results. Tetrachloroethanes are virtually inert (Table 8) in the atmosphere.

Bozzelli et al. (1980) analyzed nearly 209 Tenax® cartridge samples of air collected from New Jersey for 1,1,2,2 tetrochloroethane and were able to quantify only six. The average concentration in these six samples was 3 ppb. Pellizzari and Bunch (1979) have also reported data for 1,1,2,2 isomer in the 0.01 ppb range although levels as high as 3 ppb were also measured near industrial sites.

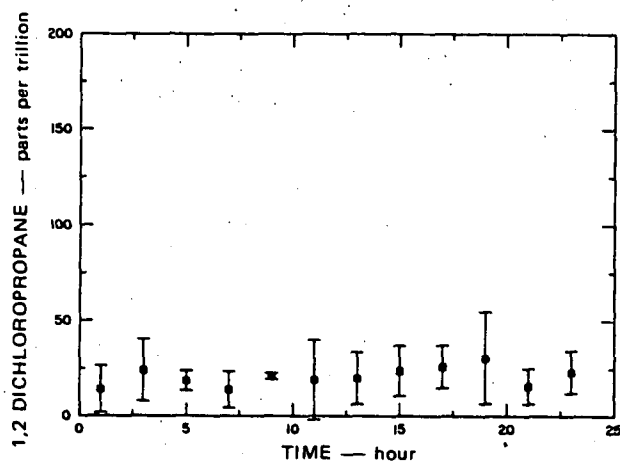
1,2 dichloropropane--1,2 dichloropropane, a bacterial mutagen (Table 1), was the only chlorinated propane measured. Its average measured concentration was in the range of 0.02 ppb to 0.05 ppb at all sites except Houston (Site 4), where an average concentration of 0.08 ppb and a maximum concentration of 0.25 ppb were measured. At no other site did the maximum concentration ever exceed 0.01 ppb. We expect 1,2 dichloropropane to be fairly reactive and estimate a daily loss rate of about 10 percent (Table 8). Figure 30 shows the mean diurnal variations of 1,2 dichloropropane at Riverside and Staten Island. Seven samples from Louisiana (Tenax® trapped) were analyzed by Pellizzari and Bunch (1979). In five out of seven, an average 1,2 dichloropropane concentration of 0.02 ppb was measured. One sample was measured at the 1-ppb level.

#### Chloroalkenes

Six chloroalkenes were sought: vinylidene chloride (1,1 dichloroethylene), (cis) 1,2 dichloroethylene, trichloroethylene, tetrachloroethylene, allyl chloride (3 chloro-1-propene), and hexachloro-1,3 butadiene. Of these, allyl chloride, a suspected carcinogen, was never detected at our measurement sensitivity of 5 ppt (Table 10-12). Similarly, vinylidene chloride (a bacterial mutagen and suspected carcinogen) was never measured at an average concentration exceeding 0.03 ppb. Approximately 30 to 50 percent of the time, vinylidene chloride was below the limit of detection of about 5 ppt. Concentration as high as 0.22 ppb was detected in Denver (Site 5), but maximum concentrations were typically in the order of 0.1 ppb. The low abundance of vinylidene chloride is related to its relatively low emission levels (Table 9) as well as to its high reactivity. A 30 percent daily chemical loss rate (Table 8) could prevent any atmospheric accumulation of vinylidene chloride. Another equally reactive dichloroethylene (cis-1,2) was found to be somewhat more ubiquitous. Average concentrations at all sites varied between 0.02 ppb and 0.08 ppb. A concentration as high as 0.6 ppb was measured in Denver



(a) RIVERSIDE, CA



(b) STATEN ISLAND, NY

Figure 30. Mean diurnal variation of 1,2 dichloropropane.

(Site 6). Unlike vinylidene chloride, the symmetric isomer is not found to be a mutagen. No carcinogenicity data on 1,2 dichloroethylene are currently available.

Vinylidene chloride has also been measured by Pellizzari and Bunch (1979) at several U.S. locations. Trace quantities were detected but quantification at below 0.05 to 0.1 ppb level was generally not possible. Occasionally, however, scattered data between 0.01 ppb and 0.6 ppb have been reported. A nearly identical situation exists for 1,2 dichloroethylene, with extremely limited data reported in the range of 0.01 ppb to 1 ppb. In both cases, it is evident that the measurement sensitivity was inadequate during much of the experimentation of Pellizzari and Bunch (1979).

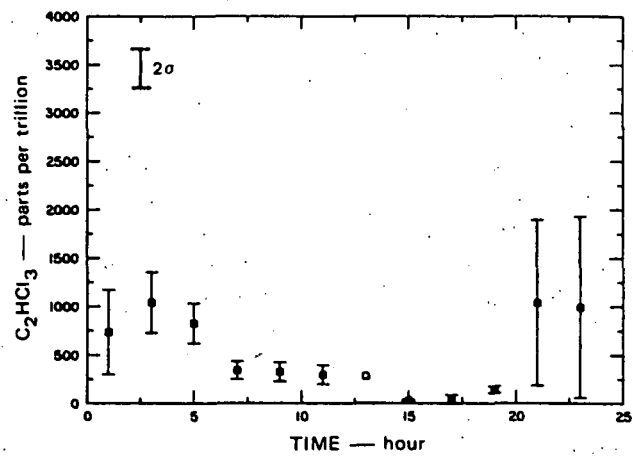
Tri- and Tetra-Chloroethylenes--One of the two dominant chloroethylenes is trichloroethylene. It is a large-volume chemical (annual U.S. emissions = 0.15 million tons) that is also a bacterial mutagen and a suspect carcinogen

(Table 1). As stated earlier, disagreement on the carcinogenicity of trichloroethylene still persists (Albert, 1980; Demopoulos et al., 1980). The highest concentration of 3 ppb was measured in Los Angeles. At most other sites (except Sites 7 and 9) the highest measured concentration was between 1 and 2 ppb. The maximum and minimum concentration levels in Tables 10-12 clearly show a wide variability. Average concentrations at all sites were between 0.1 ppb and 0.6 ppb, compared with a geochemical background of about 0.01 ppb to 0.02 ppb (Table 13) at midlatitudes. Part of the atmospheric variability of trichloroethylene is due to its relatively fast atmospheric removal rate. We estimate a daily chemical loss rate of about 17 percent (Table 8).

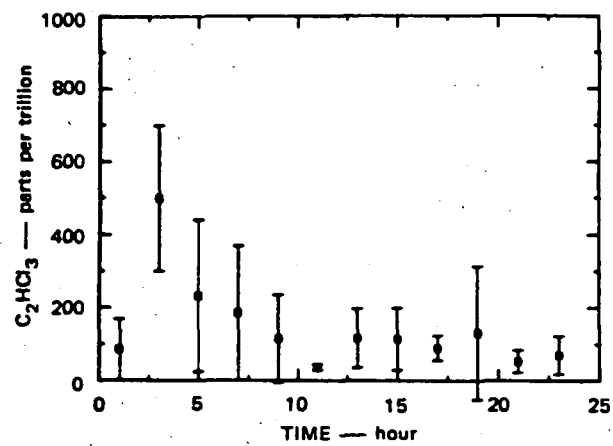
Figure 31 shows the mean diurnal variation of trichloroethylene at Phoenix (Site 2), Houston (Site 4), and Denver (Site 6). In all cases the highest averages are encountered during the stagnant nighttime hours. The afternoon minimum is due to a superimposition of dilution caused by deep vertical mixing and to the compound's substantial reactivity. The high nighttime values are also often associated with increased variability. This is perhaps best illustrated in Figure 32, where both the mean diurnal profile and the raw data are shown for Pittsburgh (Site 9). A look at the raw data clearly shows the high nighttime averages are greatly influenced by the unusually high concentrations measured on a few nights.

Trichloroethylene has been measured by a number of investigators in urban environments (Singh et al., 1977c, 1979a,b; Lillian et al., 1975; Bozzelli et al., 1980; Pellizzari and Bunch, 1979). Lillian et al. (1975) reported average concentrations of 0.1 ppb to 0.9 ppb at several east coast locations. A concentration as high as 18 ppb was reported from Bayonne, New Jersey. Bozzelli et al. (1980) were able to quantify less than 50 percent of the collected samples and report average concentrations of 1 to 2 ppb from six New Jersey sites. Ohta et al. (1976) reported high concentrations (average = 1.2 ppb) of trichloroethylene from Tokyo. Pellizzari and Bunch (1979) show a wide variability with concentrations as high as 17 ppb from industrial sites in Edison, New Jersey.

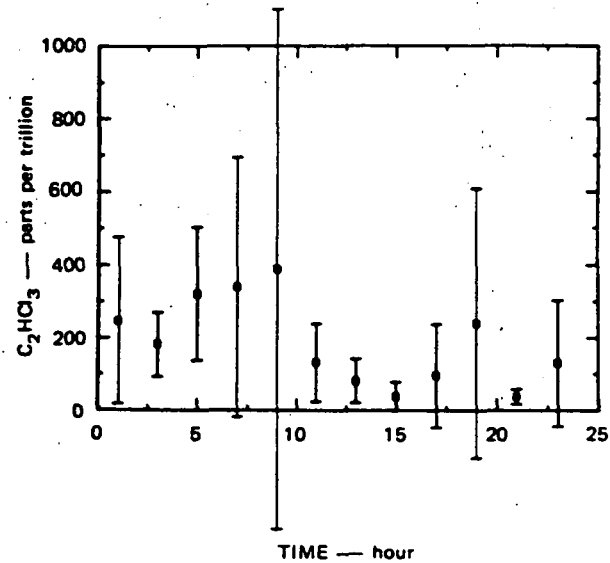
The second large-volume chloroethylene that is also a suspected carcinogen (Albert, 1980; Greenberg and Parker, 1979) is tetrachloroethylene. Approximately 0.3 million tons of this chemical are emitted annually in the United States (Table 9). Unlike trichloroethylene, the reactivity of tetrachloroethylene is modest. We estimate that slightly less than 2 percent is depleted daily (Table 8). Because of its larger emissions and its reduced reactivity, tetrachloroethylene is present at a background concentration of approximately 50 ppt (Table 13). At all sites except Los Angeles (Site 1) and Phoenix (Site 2), the average measured tetrachloroethylene concentration was between 0.3 ppb and 0.6 ppb. At Los Angeles and Phoenix, considerably higher average concentrations (1.5 ppb and 1.0 ppb, respectively) were measured. The highest measured concentration was 7.6 ppb at St. Louis (Site 5); at all other sites maximum tetrachloroethylene levels were typically between 1 ppb and 3 ppb. Average concentration of tetrachloroethylene was higher than



(a) PHOENIX, AZ



(b) HOUSTON, TX



(c) DENVER, CO

Figure 31. Mean diurnal variation of trichloroethylene.

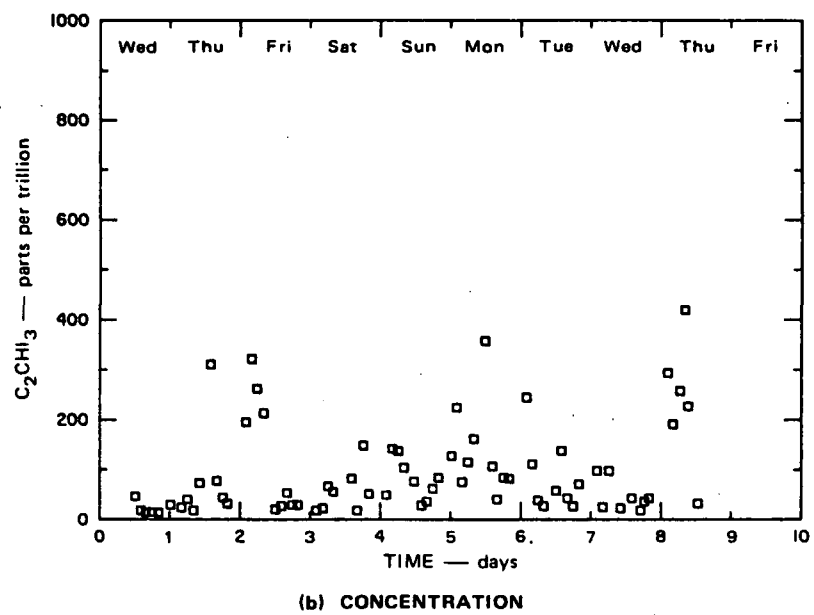
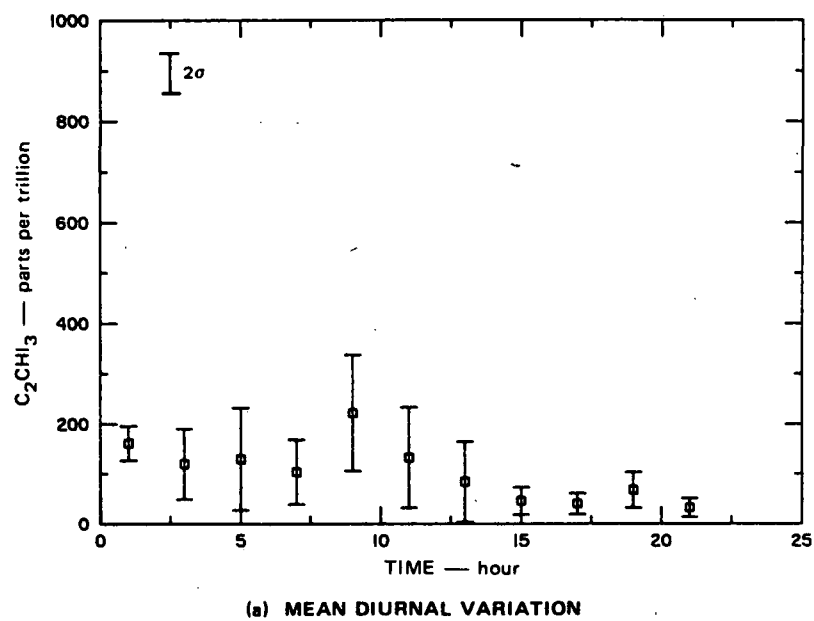


Figure 32. Trichloroethylene behavior at Pittsburgh, PA.



trichloroethylene at all sites. Typically this ratio was between two and four. At remote sites, a similar ratio is also encountered (Table 13; Singh et al., 1981c).

The diurnal behavior of tetrachloroethylene was very similar to that of trichloroethylene. Figure 33 shows the mean diurnal behavior of tetrachloroethylene at Phoenix (Site 2) and Denver (Site 6). Once again high nighttime values are encountered. The mean diurnal variation of tetrachloroethylene at Pittsburgh, with the raw data, are shown in Figure 34. Once again the reasons for the higher standard deviations observed at nighttime are clear.

A number of studies dealing with the atmospheric abundance of tetrachloroethylene were recently reviewed by Greenberg and Parker (1979). Additional data have also been provided by Singh et al. (1980). Lillian

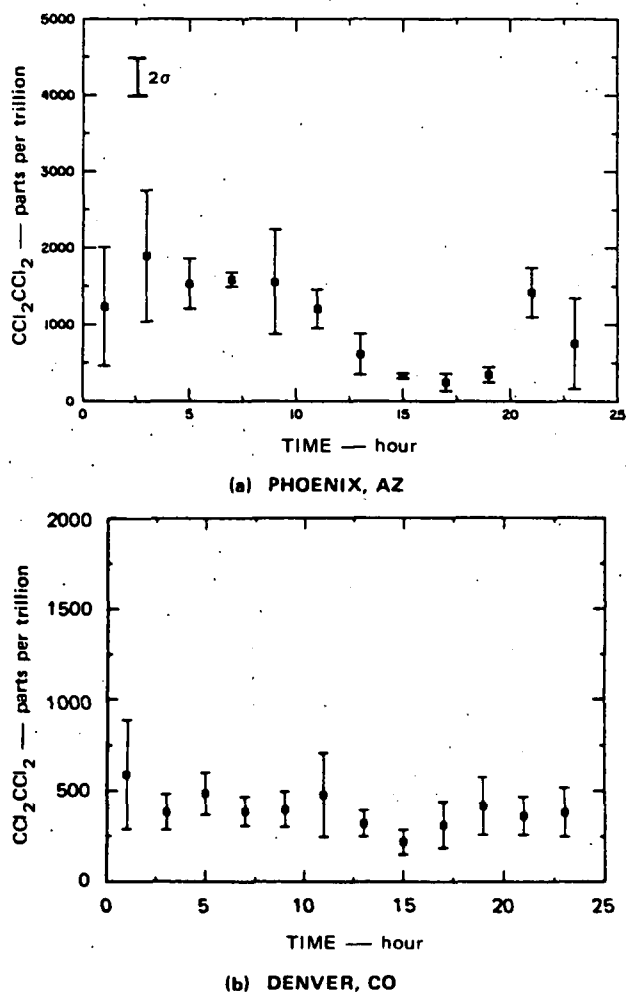


Figure 33. Mean diurnal variation of tetrachloroethylene.

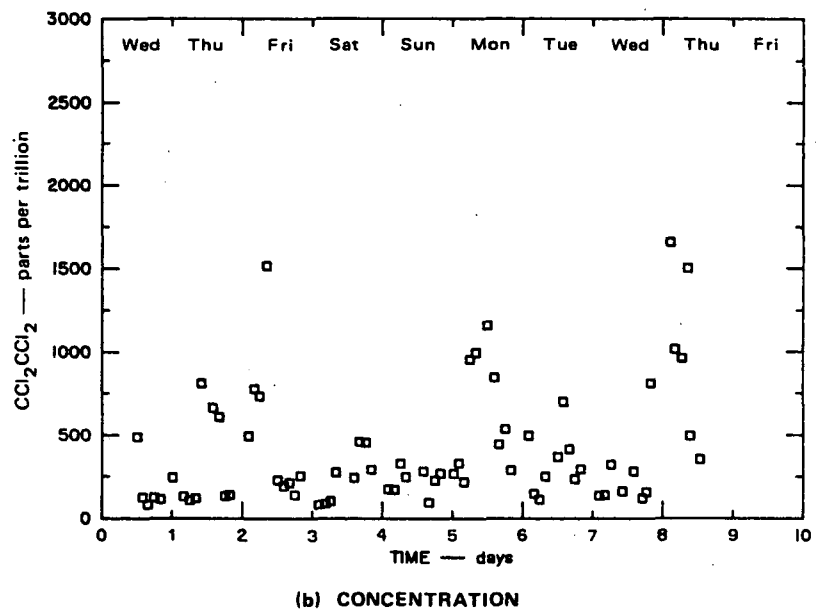
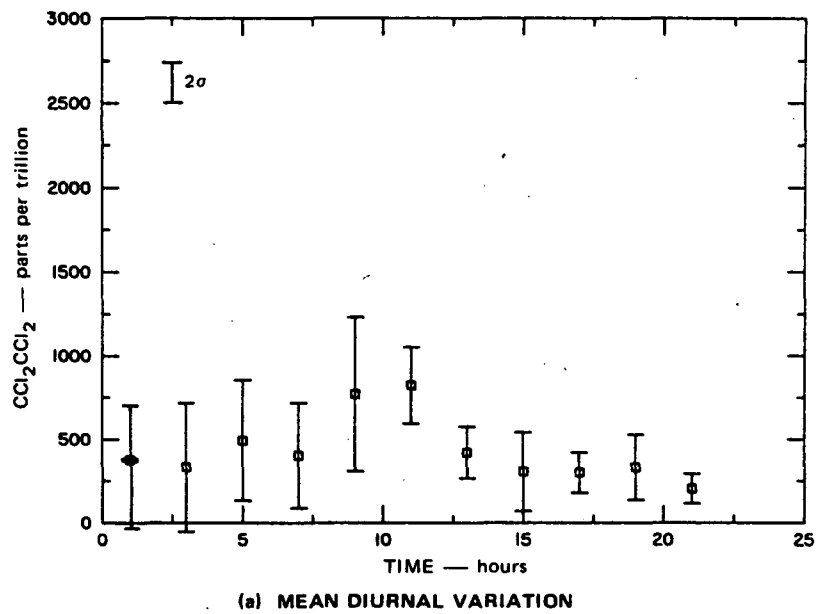


Figure 34. Tetrachloroethylene behavior at Pittsburgh, PA.

et al. (1975) reported average concentrations of 0.1 ppb to 4.5 ppb, with a maximum value of 8.2 ppb reported from Bayonne, New Jersey. They reported the highest average concentration, 4.5 ppb, from New York City.

Bozzelli et al. (1980) were able to quantify only a small fraction of the samples collected. An average concentration range of 0.3 ppb to 4 ppb was found at six New Jersey sites. Contrary to our findings, their average tetrachloroethylene levels are higher than the trichloroethylene levels in only three of the six sites. Although Pellizzari and Bunch (1979) have detected tetrachloroethylene in the ambient air, much of the data could not be quantified. Ohta et al. (1976) also reported an average tetrachloroethylene concentration of 1.2 ppb from Tokyo.

Hexachloro-1,3 butadiene--From the best information we could obtain from private sources, hexachloro-1,3 butadiene (a bacterial mutagen) is no longer manufactured in the United States, but it has been identified in the effluents of sewage treatment plants; thus secondary sources may exist. It may also be formed as a byproduct during the combustion of plastics. It was measured at an average concentration of 1 to 11 ppt; at no time did its concentration exceed 0.15 ppb. No information is available on the reactivity of this chemical, but its structure would suggest that it is likely to be highly reactive. Pellizzari and Bunch (1979) have also reported measuring hexachloro-1,3 butadiene at Niagara Falls (New York) between 4 and 100 ppt. At selected sites in Louisiana and Texas, they reported concentration of <1 ppt to 50 ppt. A single measurement showing a concentration as high as 0.3 ppb was also made in Deer Park, Texas.

#### Chloroaromatics

Six chloroaromatics were sought: monochlorobenzene, *o*-chlorotoluene, *o*-*m*-*p* dichlorobenzenes, and 1,2,4 trichlorobenzene. No data on *p*-dichlorobenzene could be collected because of unknown interferences. Because of an apparently malfunctioning detector, all chloroaromatic data from Sites 8-10 had to be discarded. The production, estimated emissions, and use patterns of the dominant chlorobenzenes were shown in Table 9. It is obvious from the table that modest amounts of these materials are released into the environment. [Of the six chlorobenzenes sought, *o*-chlorotoluene (also known as benzyl chloride) is the only species that is a clear bacterial mutagen and a suspected carcinogen (Table 1). Bacterial tests other than the salmonella-typhimurium ("Ames Assay") have indicated positive bacterial mutagenicity for dichlorobenzenes.] Once in the atmosphere, chlorobenzenes are moderately reactive. A chemical loss rate of approximately 7 percent per day for monochlorobenzene and less than 3 percent per day for di- and tri-chlorobenzenes is estimated. *o*-chlorotoluene is somewhat more reactive, and approximately 23 percent of its atmospheric burden could be chemically depleted in one day (Table 8).

Monochlorobenzene was found to be the most abundant of the chlorobenzenes. Its average concentration at all of the sites monitored was between 0.1 ppb to 0.3 ppb, although concentrations as high as 2.8 ppb were encountered. These levels are not inconsistent with its relatively large source

(yearly U.S. emissions of about 0.08 million tons) and a moderate removal rate (7 percent/day). Figure 35 shows the mean diurnal variation of monochlorobenzene at Denver, which is typical of all chlorobenzenes at this site.

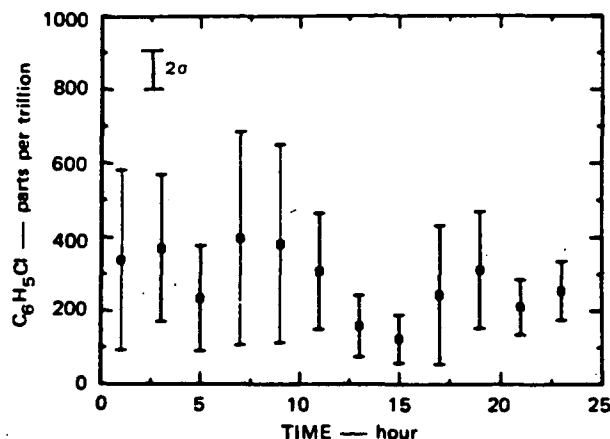


Figure 35. Mean diurnal variation of monochlorobenzene at Denver, CO.

Data on chlorobenzenes was generally only sparsely available in literature. Monochlorobenzene was measured by Bozzelli et al. (1980): Data from the six sites in New Jersey indicated average levels that were between 0.5 and 1.0 ppb. Pellizzari and Bunch (1979), who use very similar sampling techniques, report a large body of data below their limit of detectability of approximately 0.05 ppb. Occasionally, however, they report concentrations as high as 1 ppb.

$\alpha$ -chlorotoluene was frequently below our limit of detection of 5 ppt, and its concentration never exceeded 0.11 ppb. We can only attribute this behavior to relatively fast removal rate (23 percent per day) and low emissions. The absence of  $\alpha$ -chlorotoluene is not inconsistent with its estimated yearly U.S. emissions of only about 45 tons. No data that were representative of open ambient atmospheres could be found. Pellizzari and Bunch (1979) measured this chemical near a Stauffer plant site in Edison, New Jersey, at between 1-ppb and 2-ppb concentration levels.

Both of the dichlorobenzenes (o- and m-) together were present at an average concentration of between 10 ppt and 40 ppt at all of the sites monitored. Ortho-dichlorobenzene was measured at the highest concentration of 0.24 ppb in Phoenix (Site 2) and a very comparable maximum concentration of 0.23 ppb at Denver (Site 6). At all other sites the maximum concentration of o-dichlorobenzene was well below 0.1 ppb. The meta-isomer was frequently less abundant, and its maximum concentration never exceed 0.06 ppb. Given the order of magnitude lower emissions of o-dichlorobenzene when compared to monochlorobenzene (Table 9), these levels do not appear unreasonable. Figures 36 and 37 show the mean diurnal variations off o- and m-dichlorobenzene at selected sites.

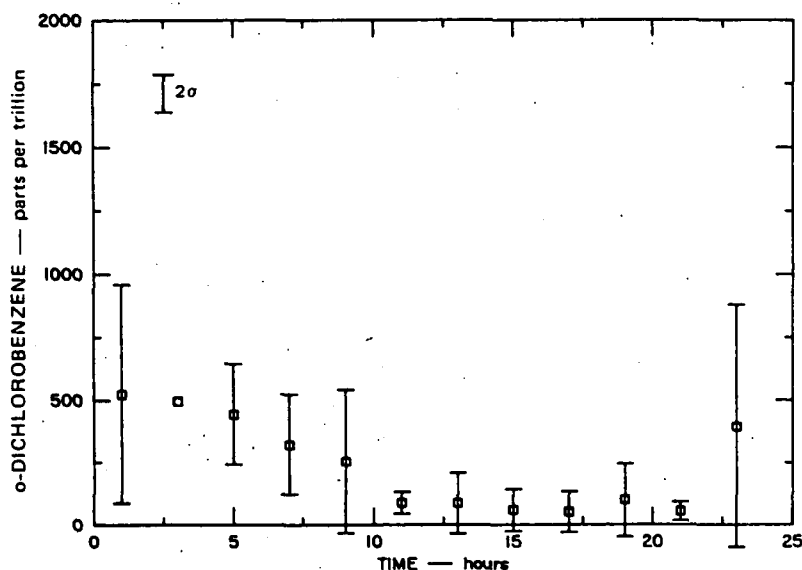


Figure 36. Mean diurnal variation of o-dichlorobenzene at Phoenix, AZ.

In ambient surveys conducted by Pellizzari and Bunch (1979), a bulk of the data base reports trace quantities or nondetectable levels of these dichlorobenzenes. Part of the reason for this is inadequate measurement sensitivity. The measurement sensitivity as reported by these authors varies from sample to sample but for o- m-dichlorobenzenes was typically in the 0.01 to 0.05 ppb range. Much of the data reported in this study would also be unquantifiable at these sensitivity levels. Pellizzari and Bunch (1979) do occasionally report concentrations in the range of 0.005 ppb to 3 ppb for these chemicals. Their data, however, are obtained in the vicinity of industrial sources.

1,2,4 trichlorobenzene was ubiquitously present, but its ambient concentration never exceeded 40 ppt. Typical average concentrations were in the 1 to 10 ppt range. Figure 38 shows the mean diurnal behavior of 1,2,4 trichlorobenzene at Riverside. This diurnal pattern was typical of other pollutants at this site. As discussed earlier, trichlorobenzenes are highly unreactive and a daily loss rate of less than one percent is computed (Table 8).

#### Aromatic Hydrocarbons

Eight important aromatic hydrocarbons were sought. Benzene is a suspected human carcinogen (Table 1). Carcinogenicity as well as mutagenicity information on toluene is disputed (Albert, 1980), although the compound has been classified as a potential mutagen (U.S. SG, 1980). In most other cases, toxicity data are currently highly uncertain. Although aromatic hydrocarbons are manufactured in large quantities, direct releases constitute a minor part of the atmospheric emissions. Both from the ambient measurements as well as the emissions data (NAS, 1976; Mayrsohn et al., 1976) it is clear that the

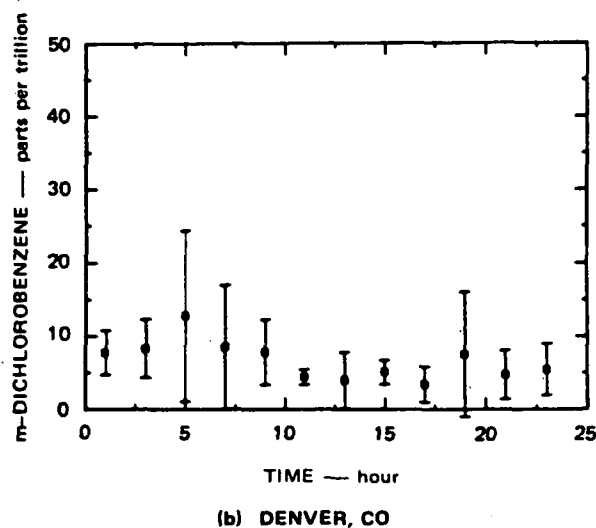
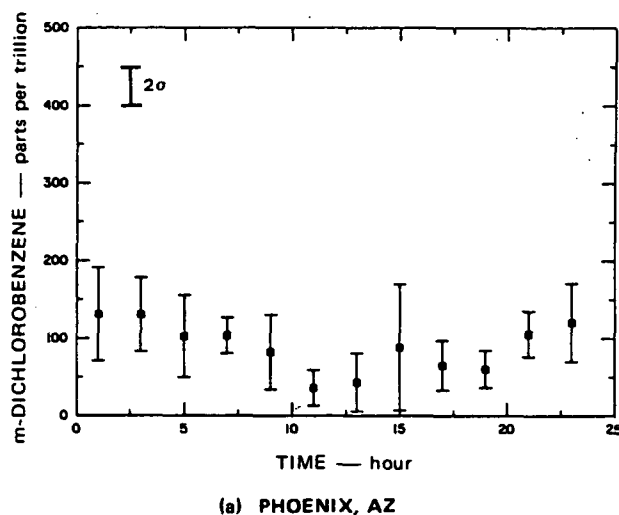


Figure 37. Mean diurnal variation of m-dichlorobenzene.

dominant ambient source is automobile exhaust. Although a considerable body of data on aromatic hydrocarbons is available (e.g. Mayrsohn et al., 1976), nearly all of those data were collected during daytime.

The two dominant aromatic hydrocarbons are benzene and toluene. The average benzene concentration at all sites ranged between 1.5 and 6 ppb, although concentrations as high as 65 ppb were measured. The average toluene levels were in the 1.5-ppb to 12-ppb range, and concentrations as high as 67 ppb were measured. At all sites except Pittsburgh (Site 9), toluene average concentration was higher than benzene. The average toluene/benzene concentration ratio at all ten sites was 1.6, with a range of 0.8 to 2.1. In the only place where average benzene levels were higher than toluene (Pittsburgh) considerable stationary sources of benzene (coke ovens) are known to exist (Mara and Lee, 1977). Both benzene and toluene are photochemically reactive, and daily loss rates of 11 percent and 41 percent respectively can be computed

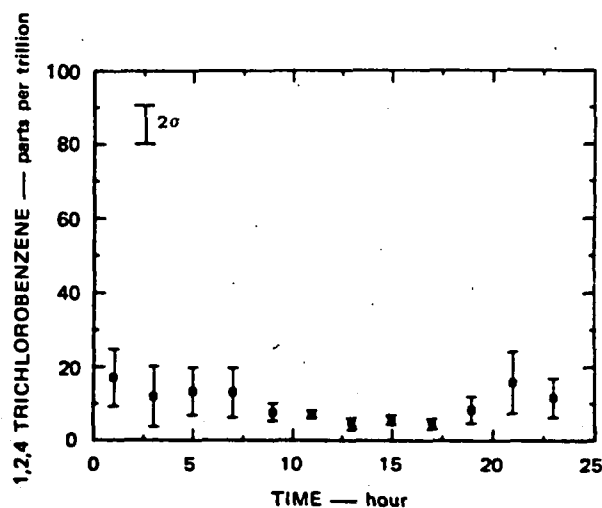


Figure 38. Mean diurnal variation of 1,2,4 trichlorobenzene at Riverside, CA.

(Table 8). This greater reactivity of toluene cause toluene/benzene ratio to decline as the air masses age. This is partly the reason for a below average ratio of 1.1 at St. Louis (Site 5), where relatively clean atmospheric conditions were encountered. The mean diurnal behavior for all aromatic hydrocarbons measured at a given site was virtually identical, which is suggestive of a common source. Figures 39 and 40 show the mean diurnal profile for benzene and toluene at selected sites. It is clear from these two figures that distinct diurnal patterns exist. Although exceptions can be found, a fairly common feature is the high nighttime and low afternoon concentrations. Figure 41 shows the same observation for m/p xylenes. The ambient levels of xylenes (o,m/p) and other aromatic hydrocarbons are shown in Tables 10-12. The xylene isomers collectively can approach or exceed the concentration levels of benzene, despite the xylenes' extremely high reactivity (Table 8). As a group aromatic hydrocarbons are important because of their high abundance, potential toxicity, and high reactivity. Many of the products of oxidation of aromatic hydrocarbons (e.g. cresols, aromatic aldehydes, phenols) may have toxic effects that exceed those associated with the parent molecule (Helm et al., 1980).

As is typical with virtually all our diurnal-variation findings, we were unable to find any data taken over the last decade to verify the patterns observed here. Much of the hydrocarbon data collected to date was obtained primarily to study photochemical air pollution, which is driven by sunlight and therefore essentially ceases at night. Comparisons of average concentrations are still possible, however. Mayrsohn et al. (1976) report data from several locations in the California South Coast Air Basin. Both the measured levels of aromatics as well as the ratios (e.g. toluene/benzene ratio varies from 1 to 3, with an average of about 2) are consistent with our results from Los Angeles (Site 1). Similarly, early morning (6:00 am - 9:00 am) data collected by Westberg et al. (1978) from a site in Houston are compatible with our Houston (Site 4) data. The average toluene/benzene ratio of 1.8 measured

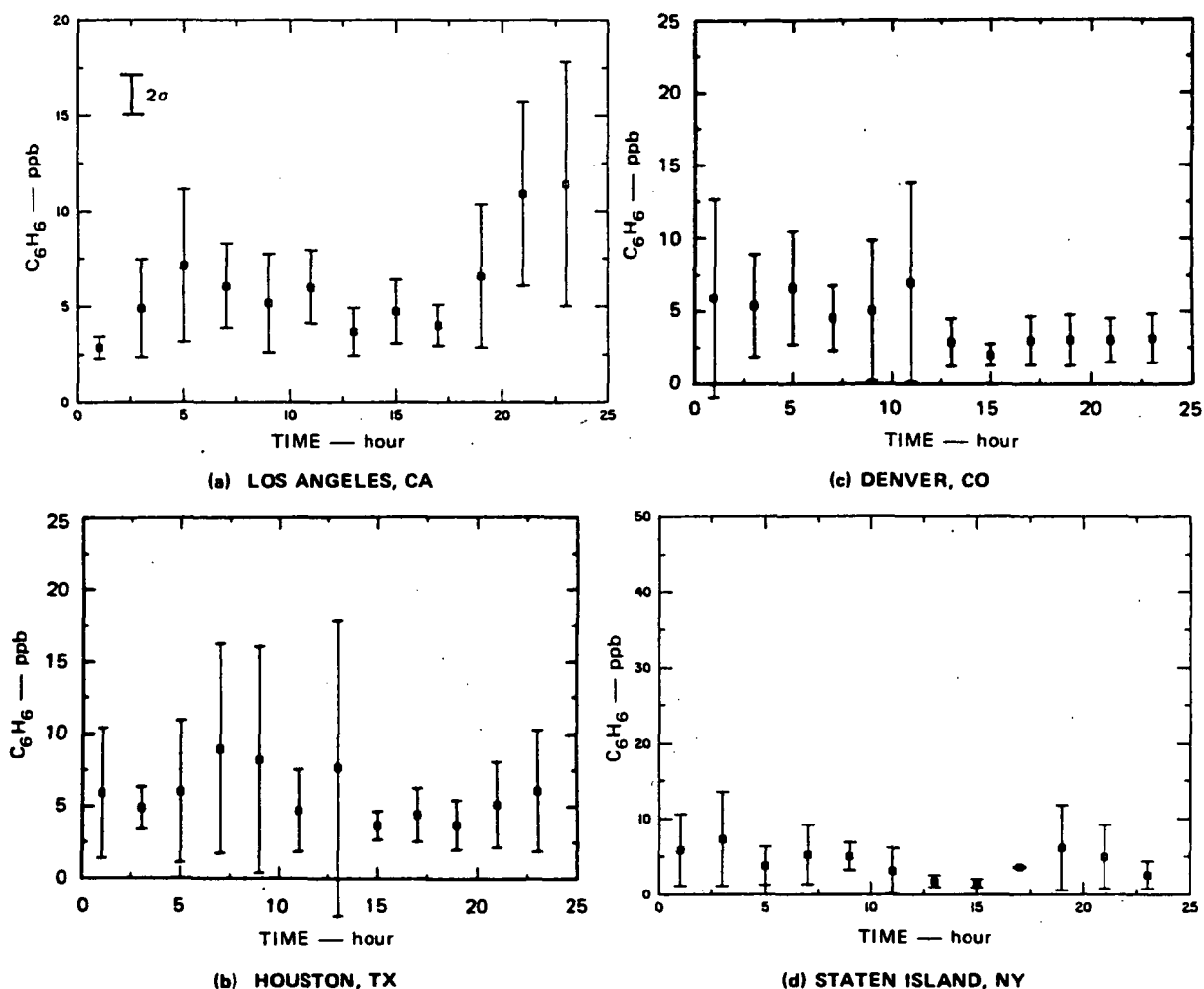


Figure 39. Mean diurnal variation of benzene.

by Westberg et al. (1978) is identical to ours. Our average benzene and toluene levels (5.8 ppb and 10.3 ppb, respectively, can be compared with Westberg's 5.5 ppb and 10.1 ppb.

Other aromatic hydrocarbons also show relatively good agreement. Denver was the only city from which nighttime data on aromatic hydrocarbons were also available. Although these data (Ferman et al., 1977) have not been fully processed, a qualitative look appeared to support a diurnal profile similar to that shown in Figures 39 and 40. Figure 42, showing the ambient measurements at Pittsburgh, clearly points to the commonality of the sources during periods of high concentrations.

#### Oxygenated Species

Five oxygenated species were sought: formaldehyde, acetaldehyde, phosgene, peroxyacetyl nitrate (PAN), and peroxypropionyl nitrate (PPN). Acetaldehyde analysis was possible only in the third year, after the DNPH-HPLC method was implemented.



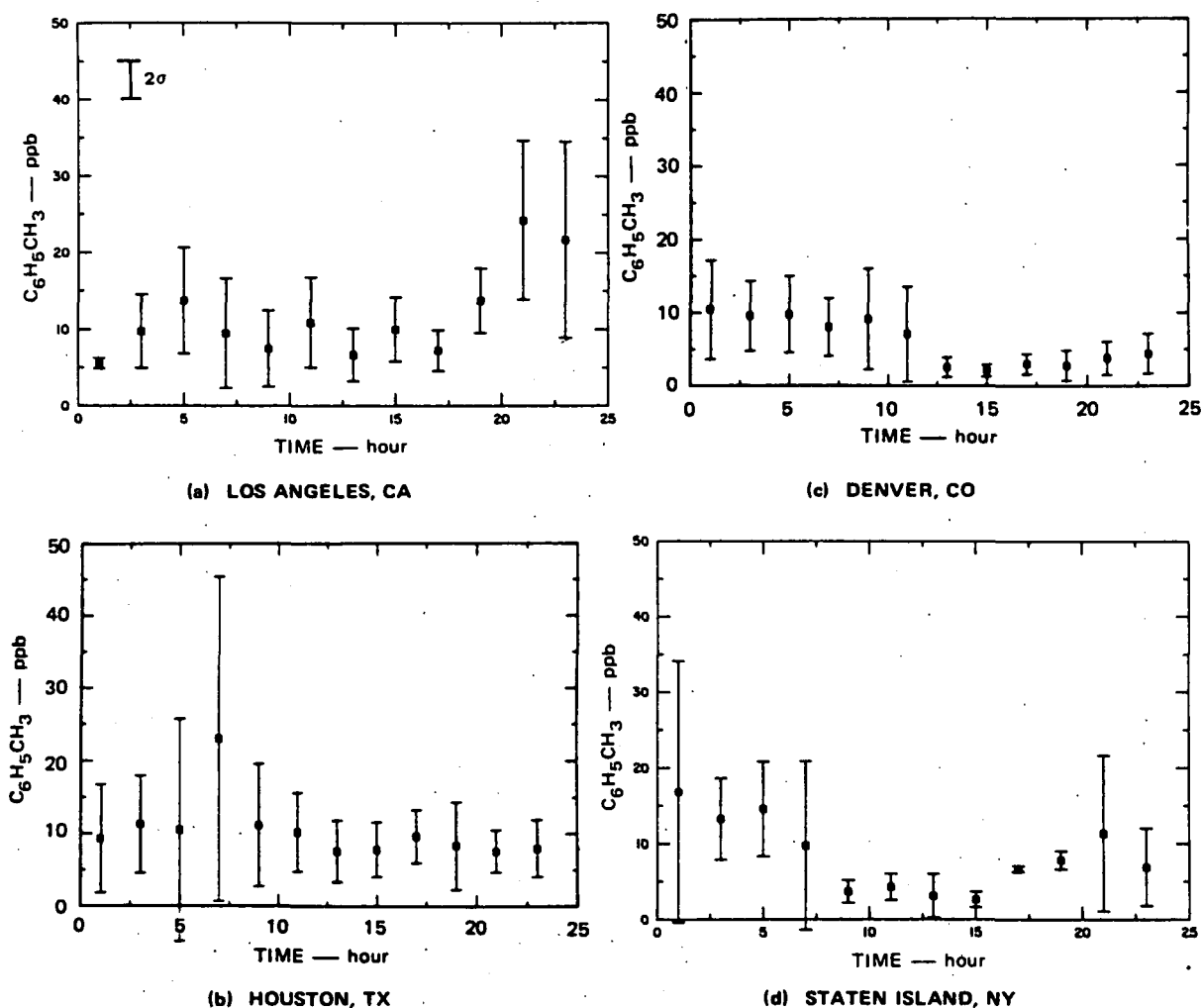


Figure 40. Mean diurnal variation of toluene.

Formaldehyde, a suspected carcinogen and a bacterial mutagen (Table 1) was measured at relatively high concentrations that varied between 6 ppb to 46 ppb. Considerable ambient data on formaldehyde have been collected over the last two decades by using the chromotropic-acid procedure. Table 14 summarizes similar data collected by SRI at several cities during short-term field studies. Typically, we encountered formaldehyde concentrations averaging 10 to 20 ppb. Table 15 shows formaldehyde concentrations at sites in Pittsburgh and Chicago, where concurrent measurements with the chromotropic-acid and the more specific DNPH-HPLC procedures were made. A comparison between formaldehyde data collected by these two methods at Pittsburgh and Chicago is shown in Figure 43. The three data points shown with asterisks in Table 15 are excluded because sampling problems were encountered during the DNPH-HPLC collection process. The corresponding chromotropic-acid data are, however, valid. A linear regression analysis (Figure 43) of formaldehyde-concentration data (ppb) by the DNPH-HPLC method (Y) and the chromotropic-acid method (X) is best represented by the fit  $Y = 0.95X - 0.04$  with a regression coefficient of

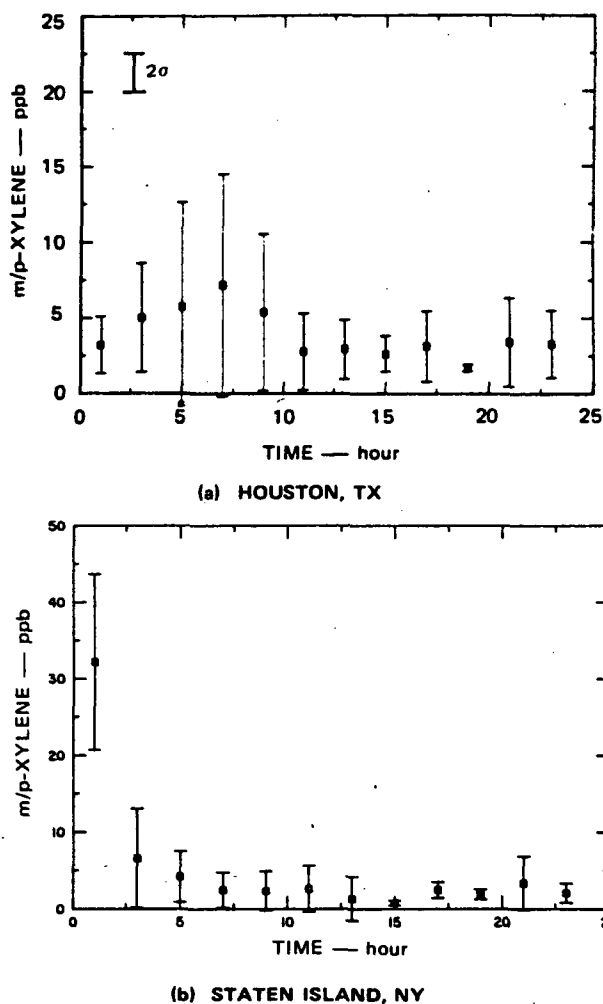


Figure 41. Mean diurnal variation of m/p-xylene.

0.71. The intercept is not significantly different from zero. The error on the slope is 30 percent. Averages computed from the Pittsburgh and the Chicago data individually are very nearly identical (Table 15). The variability in the fractional differences  $[Y - 0.95X/(Y + X)0.5]$  is computed to be less than  $\pm 30$  percent. This disagreement is not considered unreasonable since the overall accuracy of either of these methods, in their present state of development, is expected to be comparable to these differences. A substantial part of the uncertainty associated with the DNPH-HPLC method is caused by impurities in solvent solutions and can be eliminated or further reduced in the future. Although additional studies under atmospheric conditions should be made, it does appear that past formaldehyde data, collected by and large by the chromotropic-acid procedure, represents a valid data base.

Altshuller and McPherson (1963) measured an average of 40 ppb formaldehyde compared to 19 ppb measured in this study at Riverside (Table 15). Cleveland et al. (1977) have reported extensive measurements from New Jersey with average concentration of about 10 ppb. The peak concentrations, as

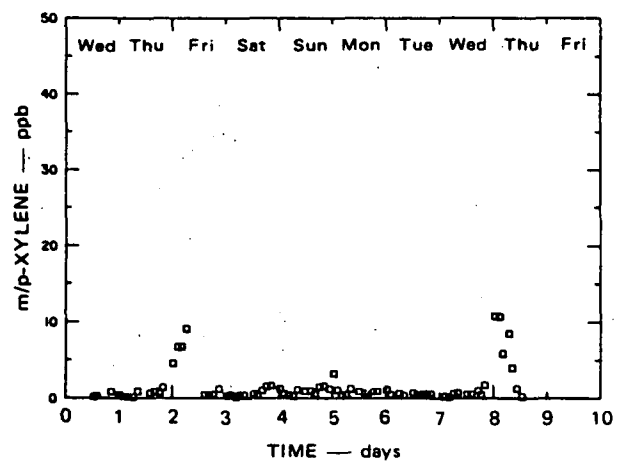
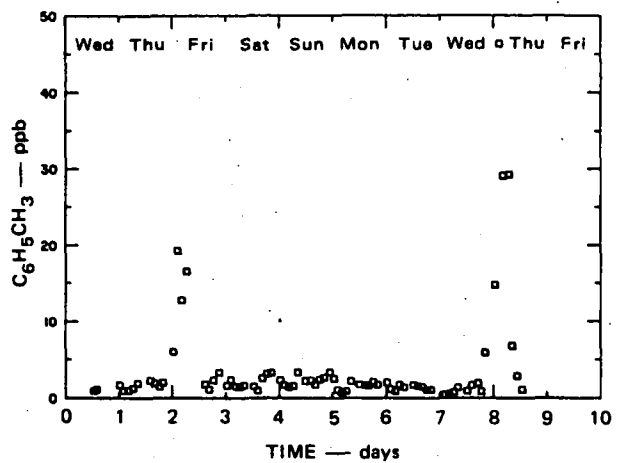
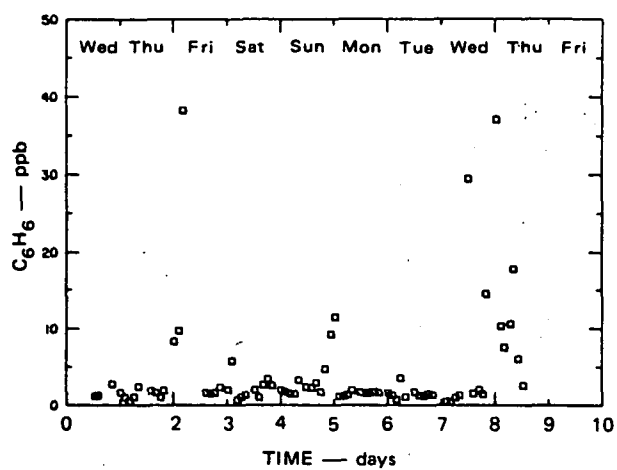


Figure 42. Aromatic hydrocarbons at Pittsburgh, PA.

TABLE 14. AMBIENT FORMALDEHYDE LEVELS IN SELECTED LOCATIONS  
AS MEASURED WITH THE CHROMOTROPIC-ACID PROCEDURE

Field Site			Experiment Period	Number of Data Points*	Concentration* (ppb)	
City	Latitude (°N)	Longitude (°W)			Max	Average $\pm \sigma$
St. Louis, MA	38°46'	90°17'	5-7 June 80	11	18.7	11.3 $\pm$ 4.5
Denver, CO	39°45'	104°59'	23-24 June 80	18	28.7	12.3 $\pm$ 5.9
Riverside, CA	33°59'	117°18'	8-10 July 80	18	41.0	19.0 $\pm$ 7.6
Staten Island, NY	40°35'	74°12'	3-4 April 81	17	45.9	14.3 $\pm$ 9.1
Pittsburgh, PA	40°26'	79°56'	15-16 April 81	21	35.1	20.6 $\pm$ 5.2
Chicago, IL	41°45'	87°42'	27-28 April 81	8	17.2	12.8 $\pm$ 3.3

\*Each data point represents approximately a 2-hour average concentration.

TABLE 15. COMPARISON OF FORMALDEHYDE AND ACETALDEHYDE DATA

Sampling Site and Date	Sampling Period (hours)	Formaldehyde Concentration (ppb)		Acetaldehyde Concentration (ppb)
		DNPH-HPLC Method	Chromotropic-Acid Method	DNPH-HPLC Method
Pittsburg				
15 April 1981	1655-1830	28.5		0.2
	1645-1845		22.8	
	1830-2000	16.4		1.0
	1950-2050		15.3	
	2000-2130	10.3		1.1
	1950-2150		16.4	
	2140-2310	19.7		2.1
	2150-2250		16.0	
	2310-0030	25.7		1.0
	2250-0100		21.2	
16 April 1981	0040-0200	12.4		1.3
	0100-0200		19.1	
	0200-0340	22.9		2.6
	0200-0400		25.0	
	0340-0510	12.8*		0.8*
	0319-0500		28.5	
	0510-0700	12.4		2.1
	0500-0700		19.5	
	0910-1050	10.1*		1.8*
	0920-1020		27.2	
Average (all data)		17.2 ± 6.7	21.1 ± 4.7	1.4 ± 0.7
Average (excluding asterisked data)†		18.5 ± 6.7	19.4 ± 3.5	1.4 ± 0.8
Chicago				
27 April 1981	1830-2000	13.1		2.4
	1800-2000		13.0	
	2030-2200	5.6		2.2
	2030-2200		9.1	
	2200-2400	15.6		3.4
	2200-2400		9.9	
28 April 1981	0003-0200	9.9		1.7
	0002-0200		10.5	
	0200-0400	12.1		0.9
	0200-0400		17.2	
	0400-0600	6.6*		0.3*
	0400-0600		17.2	
Average (all data)		10.5 ± 3.9	12.8 ± 3.6	1.8 ± 1.1
Average (excluding asterisked data)†		11.3 ± 3.8	11.9 ± 3.3	2.1 ± 0.9

\*Sampling problems encountered--outlier data.

†Although the corresponding chromotropic-acid data are reliable, they are excluded for consistent comparisons.

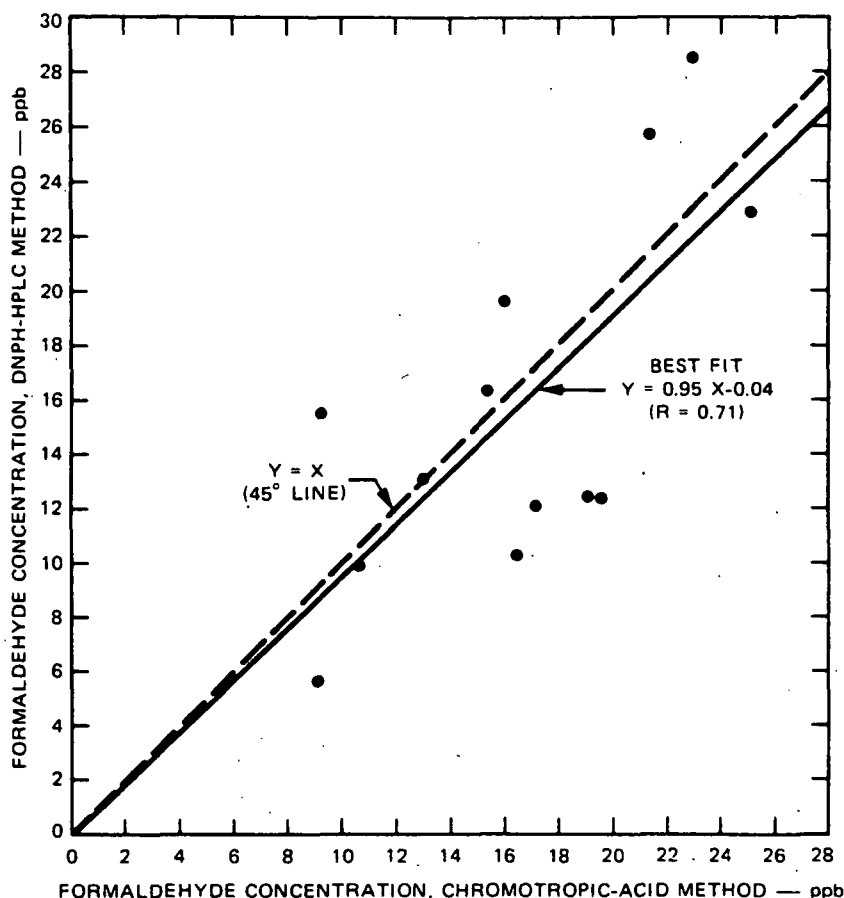


Figure 43. Comparison of formaldehyde concentrations as measured by the chromotropic acid and the DNPH-HPLC procedure.

measured by the upper decile, were in the 14- to 20-ppb range. These are similar to our average Staten Island levels of 14 ppb. Similarly, Joshi (1977) reported average concentrations of about 10 ppb from Houston, although maximum concentrations as high as 27 ppb were measured. Kok (1980), using a chemiluminescent technique, reports formaldehyde levels of 8 ppb to 38 ppb (average 19 ppb) during a pollution episode (September 13-14, 1979) in Los Angeles. Kuwata et al. (1979) used the DNPH-HPLC procedure to report average concentrations of 27 ppb from limited measurements in Osaka, Japan. In clean background locations formaldehyde levels of about 0.4 ppb have been measured and computed from mechanisms involving methane oxidation (Table 13; Ehhalt and Tonnissen, 1980).

Acetaldehyde data are significantly more sparse than formaldehyde data. Hoshika (1977) and Kuwata et al. (1979) provide a limited number of measurements. From these data, acetaldehyde levels of 1 to 10 ppb in the ambient air have been reported. Kuwata et al. (1979), who measured both formaldehyde and acetaldehyde, report average acetaldehyde concentrations of about 4.8 ppb. (On the average, formaldehyde is about six times more abundant than acetaldehyde in Osaka.) Table 15 shows the concentrations of formaldehyde and

acetaldehyde as measured by the DNPH-HPLC procedure during our study. The average acetaldehyde concentrations at Pittsburgh and Chicago are in the 1- to 2-ppb range, and therefore are significantly lower than corresponding formaldehyde levels. The average formaldehyde/acetaldehyde ratio of 12 and 6 at Sites 9 and 10 respectively is comparable to a ratio of 6 reported from Osaka by Kuwata et al. (1979).

The reactivity of acetaldehyde (due to photolysis and reaction with OH radicals) is comparable to that of formaldehyde, and a daily loss rate of about 80 to 95 percent respectively can be computed (Table 8). When one considers automobile exhaust as a major emission source, 65 to 75 percent (by volume) of all aldehydes is formaldehyde, while 7 to 10 percent is acetaldehyde (NAS, 1976). If we assume equal reactivity, a formaldehyde/acetaldehyde ratio of 6 to 11 is entirely consistent with an automobile source.

Singh and Hanst (1981) estimate that approximately 40 ppt of acetaldehyde is present in the lower troposphere as an intermediate photochemical product of nonmethane hydrocarbons. No information on the carcinogenicity of acetaldehyde could be found.

It appears that the DNPH-HPLC method may provide a technique for the ambient analysis of a wide variety of carbonyl compounds. A comparison of emission levels (NAS, 1976) and acetaldehyde field data would suggest that higher aldehydes ( $C_3 - D_7$ ) are likely to be present at even lower concentrations (sub-ppb). In our sampling protocol, a measurement sensitivity of 0.05 ppb is feasible. Both the measurement sensitivity and the accuracy of data collected by the DNPH-HPLC method could be further improved by reducing or eliminating solvent impurities. While this study was limited to formaldehyde and acetaldehyde, the presence of other carbonyls was evident. There is some evidence that acetaldehyde may not be mutagenic (U.S. SG, 1980; Sasaki and Endo, 1978).

Phosgene was not detected at most sites, largely because the coulometer was also used for analysis of PAN and PPN. Extensive column conditioning is also required for phosgene analysis, which could only be done with great difficulty in the field. Average phosgene levels as high as 50 ppt (but often below 20 ppt) were encountered. Phosgene is expected to be a photochemical product of the oxidation of chlorinated ethylenes (Singh, 1976; Gay et al., 1976).

As is clear from Tables 10-12, PAN and PPN average levels were quite low. Highest PAN and PPN concentrations of 16.8 ppb and 2.7 ppb respectively were measured in Los Angeles (Site 1). The maximum PAN levels of 16.8 ppb at Los Angeles (Site 1) can be compared with a maximum of 4.4 ppb in Houston (Site 4), 5.8 ppb in Riverside (Site 7) and 3.9 ppb in Staten Island (Site 8). Daily average PAN levels were in the 0.3 ppb to 5 ppb range, with significantly reduced values at night. The PAN/PPN average ratio varied from 4 to 10. PPN was nondetectable a significant fraction of the time (30 to 60 percent). Figure 44 shows the mean diurnal variation of PAN and PPN at Phoenix (Site 2). This diurnal behavior of PAN is fairly typical of all urban sites

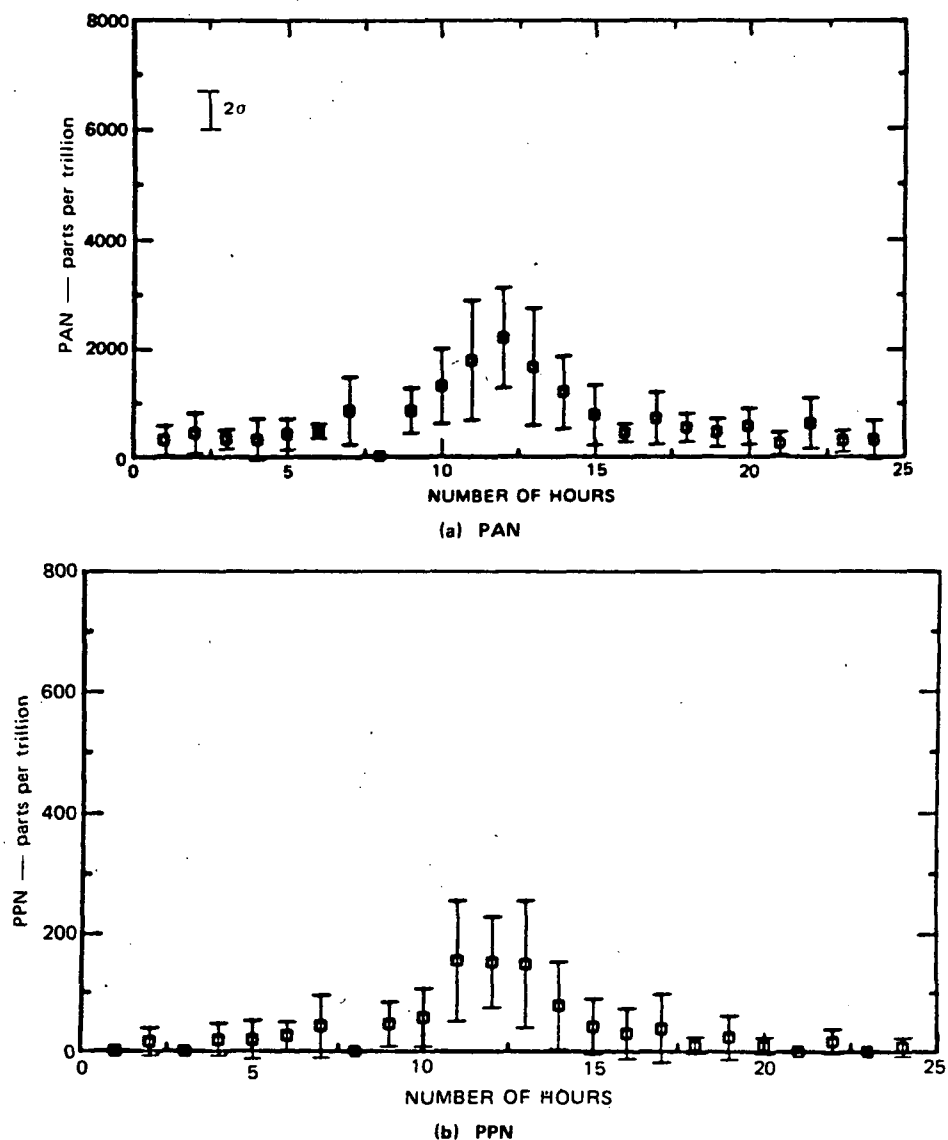


Figure 44. Average diurnal variation of PAN and PPN at Phoenix — Site 2.

(e.g. Nieboer and Von Ham, 1976). It is pertinent to repeat here that the absolute coulometric analysis was used for PAN and PPN measurements; a method that has yet to be rigorously tested.

PAN has been measured by a number of investigators (EPA, 1978). From Los Angeles, Hoboken (New Jersey), and St. Louis, average daytime PAN levels of 18 ppb (0 to >70 ppb), 4 ppb (0 to 10 ppb), and 6 ppb (0 to >12 ppb) respectively have been measured. Measurements from the Houston area, as reported by Ludwig and Martinez (1979), indicate significantly lower PAN levels between 0 and 16 ppb, with about 70 percent of the data reported as 0 (less than 0.2 ppb). Little data from clean background locations are available, but measurements



from rural sites suggest PAN levels in the 0.1- to 0.5-ppb range (Singh et al., 1979a; Lonneman et al., 1978). Singh and Hanst (1981) estimate that at midlatitudes the lower troposphere contains about 10 to 30 ppt of PAN.

Both PAN and PPN are rapidly removed from the atmosphere, and a daily loss rate of 99 percent is computed (Table 8). Because this loss rate is highly temperature dependent, PAN is nearly infinitely stable at upper levels of the troposphere (Singh and Hanst, 1981). PAN has not been tested for mutagenicity or carcinogenicity, but it is a well-known eye irritant and is known to cause visible damage to agricultural crops (EPA, 1978).

## SECTION 7

### SUMMARY AND CONCLUSIONS

This three-year research effort comprised a program of analytical methods development, field-data collection, data processing, and data interpretation for a group of 44 organic chemicals, of which 29 are bacterial mutagens and more than a dozen are suspected carcinogens. All field measurements were conducted on-site with the help of an instrumented mobile environmental laboratory. The chemical categories targeted for field measurements included chlorofluoromethanes, halomethanes (nonfluorinated), haloethanes, chloroethylenes, chloroaromatics, aromatic hydrocarbons, and oxygenated species. The ambient analysis of these species was possible with the help of electron capture gas chromatography for the halogenated and nitrogenated species, flame ionization gas chromatography for hydrocarbons, and high-performance liquid chromatography for aldehydes. After the analytical methods development was completed, a total of ten field studies were conducted at a selected site within the following cities:

- Los Angeles, California
- Phoenix, Arizona
- Oakland, California
- Houston, Texas
- St. Louis, Missouri
- Denver, Colorado
- Riverside, California
- Staten Island, New York
- Pittsburgh, Pennsylvania
- Chicago, Illinois.

Although these studies were of short term-duration, our practice of round-the-clock operation allowed for extensive data collection. The degree of temporal and spatial variability in the atmospheric abundance of toxic chemicals is clear from data presented. Typical concentrations of most chemicals measured were in the sub-ppb range, with the exception of aromatic hydrocarbons and formaldehyde (where average concentrations in the 5 to 20 ppb range were frequently encountered). For most predominantly man-made chemicals, average concentrations in urban atmospheres were one to two orders of magnitude higher than in clean remote atmospheres.

Distinct mean diurnal variations in the concentrations of these atmospheric chemicals exist. For most chemicals, the mean diurnal variations are determined by source strength and prevailing meteorology, with chemistry playing only a nominal role. Chemical loss rates for a majority of species were shown to be <10 percent/day. For several primary pollutants, afternoon mixing leads to sufficient dilution to cause an afternoon minimum in concentrations; secondary photochemical pollutants, however, show a clear afternoon maxima (e.g. PAN, PPN). Thus for many of the toxic chemicals the highest concentrations in the ambient air are encountered at nighttime or early morning hours. There is abundant evidence that most of the chemicals measured here (except methyl halides and aldehydes) have nearly exclusive man-made origin. The significant elevation in concentration above background in urban areas points to large sources associated with man-made activities: Methyl iodide was the only chemical that appears to have an exclusive natural source.

The chemicals measured in this study are important not only for their potential toxicity but also for their role as indicators of urban photochemistry. The many chemicals with a range of removal rates (lifetimes) provide an ideal opportunity for studying the chemistry of the urban atmosphere. Such analysis, however, must wait until accurate emissions information becomes available.

Some man-made chemicals are sufficiently stable and are released in large enough quantities to have become a part of the global environment. Carbon tetrachloride is one such chemical, which is nearly uniformly distributed over the globe as a result of slow accumulation and a lack of rapid removal mechanisms (Singh et al., 1976; 1979a,b). Methylene chloride, 1,2 dichloroethane, and tetrachloroethylene, however, are emitted in such large quantities (global release rates of 0.4 to 0.6 million tons per year for each) that even a relatively fast atmospheric removal rate (atmospheric lifetime of two to eight months) does not prevent their spread and accumulation.

An investigation of the mutagenicity of chemicals clearly showed that methyl chloride, methyl bromide, methyl iodide, and formaldehyde are mutagens. These chemicals are known to be a ubiquitous part of our natural atmosphere (and oceans, in the case of methyl halides).

The total exposure to mutagens and carcinogens from the urban ambient air is of course much higher than measured here because of nongaseous species (e.g. polyaromatic hydrocarbons) as well as other gaseous species for which either toxicity studies are inconclusive or measurement methods are inadequate (e.g. oxygenated chemicals). Most synthetic chemicals in this study came into major use after 1950. Since then, their production and release have continued to grow exponentially, with a doubling time of about six years (Bauer, 1978). Because of the long time lag (10 to 50 years) associated with the onset of cancer (LaFond, 1978), a significant risk may not be identified until a future date. It is also possible that continuous exposure to low levels of such chemicals may erode any human threshold that may exist or enhance the frequency of cancer occurring from other primary causes, such as cigarette smoking (Albert and Burns, 1977).

On the whole, we conclude that typical urban atmospheres contain chemicals that are known to be toxic at much higher concentrations. The risks associated with exposure to ambient levels of these species are highly uncertain. The task of characterizing the atmosphere, with which this study is most concerned, is itself at best highly incomplete. Much more atmospheric and toxicity data will be needed to determine the risks associated with long-term exposures to low levels of toxic species.

## SECTION 8

### RECOMMENDATIONS FOR FUTURE RESEARCH

One of the primary functions of this study was to develop techniques for the atmospheric measurement of important organic chemicals and to apply these under field conditions. Both of these objectives were partially achieved, but the analytical methods for chloroaromatics and (especially) for oxygenated species must be further improved.

The DNPH-HPLC technique was applied to the measurement of formaldehyde and acetaldehyde, but the presence of other aldehyde was evident. In addition, only ten sites could be studied each for a period of about 9 to 11 days each. The data base must be expanded to include other sites and other chemicals, and researchers must conduct studies during several seasons. Because of the complexity of the mix of ambient chemicals, it is possible that significant spatial and temporal variations exist. The interpretation of data collected to date is incomplete, at least in part due to lack of emissions inventories of these chemicals. In many cases complex secondary sources are evident.

Interlaboratory comparisons of field data should be rigorously pursued. Preliminary comparisons with other data, the bulk of which are collected by using solid sorbents (mostly Tenax®) followed by GC-MS analysis, suggest some inconsistencies that could be resolved with additional research and interlaboratory comparisons.

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