TECHNICAL SUPPORT DOCUMENT

REPORT TO THE AIR RESOURCES BOARD
ON CARBON TETRACHLORIDE

PART A - PUBLIC EXPOSURE TO, ENVIRONMENTAL FATE OF, AND SOURCES OF, ATMOSPHERIC CARBON TETRACHLORIDE IN CALIFORNIA

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FINAL DRAFT
REPORT TO THE AIR RESOURCES BOARD ON CARBON TETRACHLORIDE

Part A - Public Exposure to, Environmental Fate of, and Sources of, Atmospheric Carbon Tetrachloride

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I. EXPOSURE TO CARBON TETRACHLORIDE

A. EXPOSURE ABOVE GLOBAL BACKGROUND CONCENTRATIONS

Many Californians are exposed to carbon tetrachloride concentrations greater than the global background concentration; particularly people who reside or work near carbon tetrachloride emission sources. Major emission sources exist in several areas around the state. The San Francisco Bay Area has two large sources of carbon tetrachloride located near each other: the Dow Chemical Plant in Pittsburg (a carbon tetrachloride producer) and the E. I. du Pont Plant in Antioch (a fluorocarbon producer). Together, these two facilities emitted an estimated 31 tons of carbon tetrachloride in 1984. The South Coast Air Basin (SoCAB) also has two sources that emit carbon tetrachloride. They are Allied Chemical in El Segundo (a fluorocarbon producer) and Neville Chemicals in Santa Fe Springs (a chlorinated wax producer). Together, these sources emitted approximately 3 tons of carbon tetrachloride in 1984.

Carbon tetrachloride is used in pesticidal applications mainly as a grain fumigant. In 1984, approximately 20 tons of carbon tetrachloride were emitted into the atmosphere from grain fumigant usages. This was the second largest source of carbon tetrachloride emissions in California. Most of the grain fumigants were used in Yolo and San Joaquin counties.

Other potential sources of carbon tetrachloride emissions are oil companies, scientific laboratories, organic chemical manufacturing companies, pesticide manufacturing companies, publicly owned treatment works, and small sources that use carbon tetrachloride as a miscellaneous solvent or as a feedstock in a manufacturing process. The ARB staff attempted to estimate the emissions from these other sources, but the staff was unable to obtain the information to do so. These sources are primarily located in the San Francisco Bay Area and the South Coast Air Basin. However, the ARB staff believes that these are not significant emission sources.

In order to determine the impact of emission sources on nearby population, the ARB staff modeled the emissions from the Dow and du Pont facilities in the San Francisco Bay Area and Neville Chemical facility in the South Coast Air Basin. The modeling and exposure assessments indicate that some people in the San Francisco Bay Area are exposed to annual average peak concentrations as high as 0.49 parts per billion (ppb)(3.1 microgram per cubic meter (ug/m^3)) of carbon tetrachloride above the background concentration of 0.13 ppb (0.82 ug/m^3), while some people in the South Coast Air Basin are exposed to an annual concentration as high as 0.19 ppb (1.2 ug/m^3) above the background concentration. The maximum annual average concentration that people in the Bay Area and South Coast modeling regions can be exposed to is the sum of the highest annual average concentration above background and the background concentration. Thus, the maximum annual average concentration for the modeled regions are 0.62 ppb (3.9 ug/m^3) and 0.32 ppb (2.0 ug/m^3) respectively. In general, peak hourly average concentrations can be 100 to 1,000 times the maximum annual average concentration. Under worst case meteorological conditions, the peak hourly average concentration from the Dow facility could be as high as 170 ppb (1070 ug/m^3). Cumulative and non-cumulative population exposures from the modeling assessments of the two sources in the Bay Area and the single source in the South Coast Air Basin are summarized in Tables I-1 and I-2 and Figure I-1 and I-2.

Table I-1

Estimated Annual Average Carbon Tetrachloride Exposure Levels Above Background Near Dow Chemical and E.I. du Pont

Carbon Tetrachloride Concentration* (ppb)	(ug/m^3)	Population	Cumulative* Population
<0.001	<0.006	25,000	210,000
0.001 - 0.05	0.006-0.31	174,000	185,000
0.051 - 0.10	0.31-0.63	4,800	11,000
0.101 - 0.15	0.63-0.94	3,000	6,400
0.151 - 0.20	0.94-1.26	1,000	3,400
0.201 - 0.25	1.26-1.57	0	2,400
0.251 - 0.30	1.57-1.88	1,500	2,400
0.301 - 0.35	1.88-2.20	390	930
0.351 - 0.40	2.20-2.51	0	550
0.401 - 0.45	2.51-2.83	0	550
0.451 - 0.50	2.83-3.15	550	550
>0.50	>3.14	0	0

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* Estimates have been rounded. Concentrations do not include background contribution.

Figure I-1

Estimated Annual Average Carbon Tetrachloride Exposure Levels Above Background Near Dow Chemical and E.I. du Pont

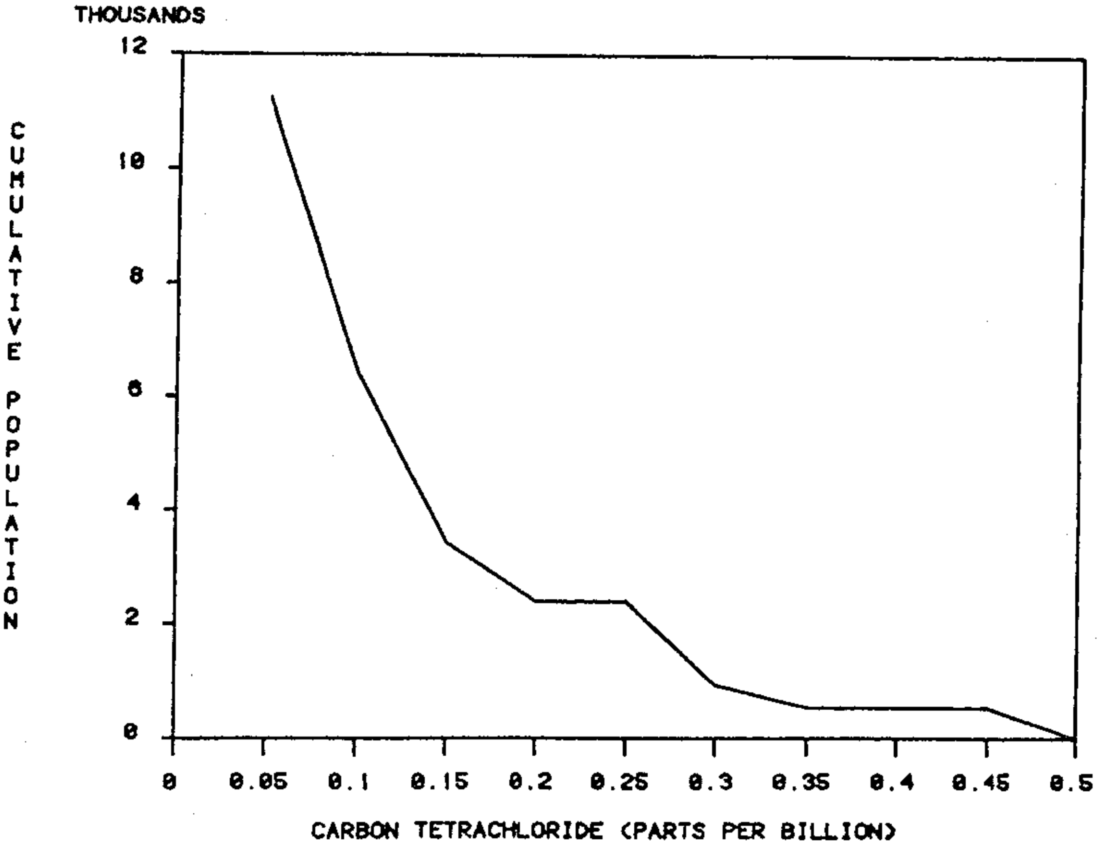

Table I-2

Estimated Annual Average Carbon Tetrachloride Exposure Levels Above Background Near Neville Chemical Company

Carbon Tetrachloride Concentration* (ppb)	(ug/m^3)	Population	Cumulative* Population
<0.001	<0.006	1,350,000	2,270,000
0.001 - 0.05	0.006-0.31	920,000	924,000
0.051 - 0.10	0.31-0.63	2,700	4,200
0.101 - 0.15	0.63-0.94	0	1,500
0.151 - 0.20	0.94-1.26	1,500	1,500
>0.200	>1.26	0	0

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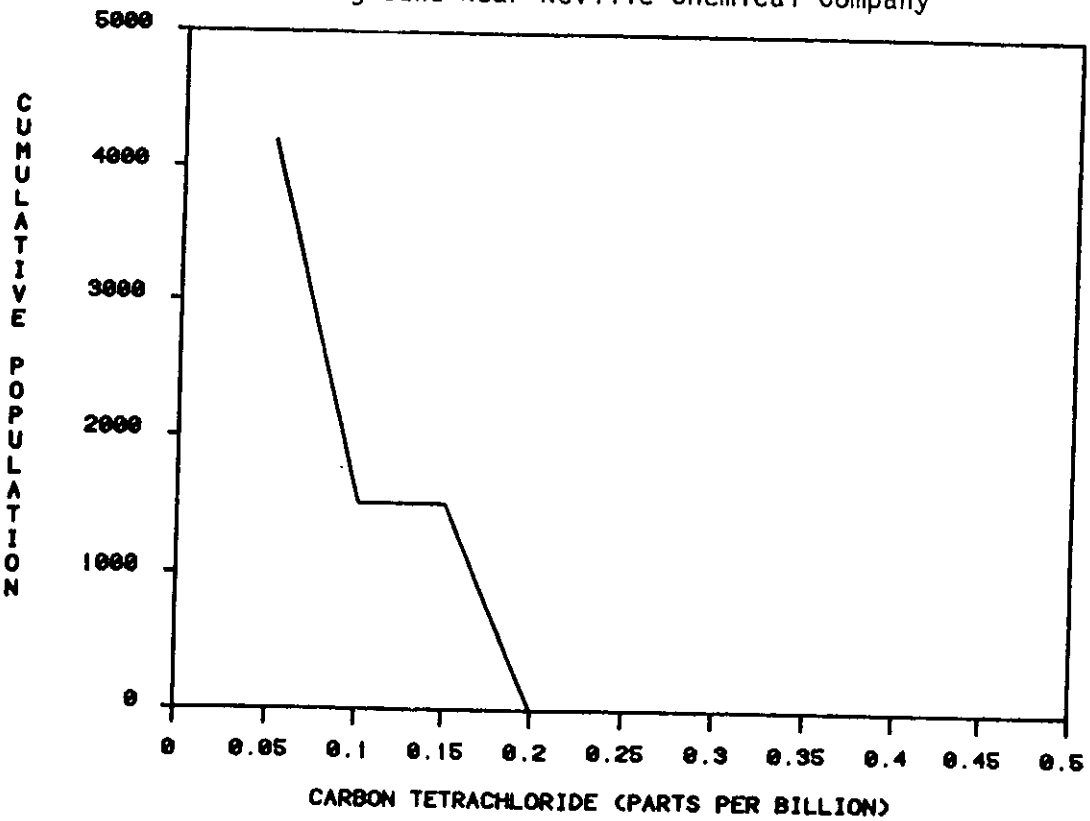
* Estimates have been rounded. Concentrations do not include background contribution.

Figure I-2

Estimated Annual Average Carbon Tetrachloride Exposure Levels Above Background Near Neville Chemical Company



The ARB staff used the Industrial Source Complex Short Term (ISCST) Gaussian dispersion model to estimate the concentration of carbon tetrachloride at gridded receptors around the source (Neville Chemical) or sources (Dow Chemical and du Pont). Meteorological data, as required by the ISCST model, were obtained from Travis Air Force Base for the Bay Area analysis and the Long Beach Airport for the South Coast Air Basin analysis. Population data were derived from the 1980 census, the emission estimates for the facilities were obtained from the Bay Area Air Quality Management District or the South Coast Air Quality Management District.

The concentration for each square kilometer receptor in the 31 X 31 kilometer receptor array was multiplied by the population in the grid cell surrounding the receptor. The exposure value for each receptor was summed to obtain the total exposure contributed by this facility. The concentration and population exposure represent levels that do not include ambient background contributions; possible additive or cumulative exposure is not addressed in this analysis.

Figure I-3 illustrates the annual carbon tetrachloride concentrations interpolated to a 31 X 31 kilometer gridded area surrounding Dow Chemical and du Pont. The two emission points from Dow Chemical are at the center of the grid and the small single peak at the right represents du Pont. Estimates of annual average above background carbon tetrachloride concentrations range from less than 0.001 ppb (0.0006 ug/m^3) at the edges of the gridded area to 0.49 ppb (3.1 ug/m^3) near the center of the source. Therefore, a person near the center of the source can be exposed to concentrations almost 4 times higher than background concentrations. The maximum annual average concentration of 0.62 ppb (3.9 ug/m^3) was estimated for this source by adding the highest concentration of 0.49 ppb

Figure I-3

Annual Average Carbon Tetrachloride Concentrations

Above Ambient (ppb) Near Dow Chemical and E.I. du Pont

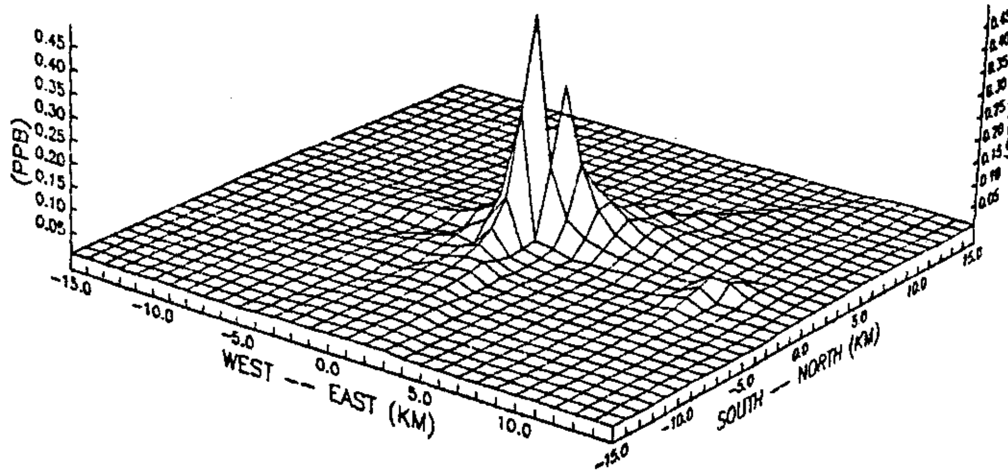
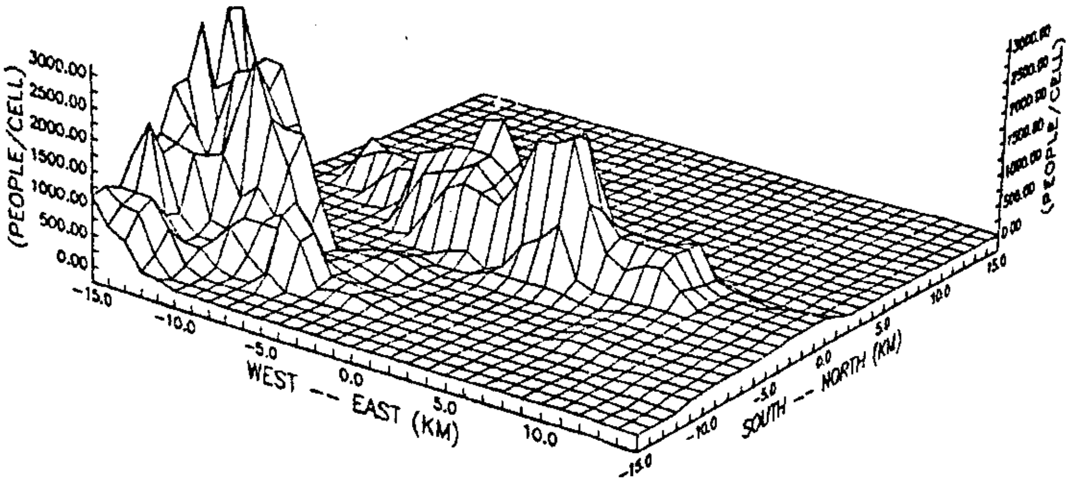


Figure I-4

Population Density Near Dow Chemical and E.I. du Pont



(3.1 ug/m^3) from the emission source and the background concentration of 0.13 ppb (0.82 ug/m^3). A plot of population density within the study area is shown in Figure I-4. The cities of Pittsburg and Antioch are in the center while Concord is at the lower left.

Figure I-5 illustrates the annual carbon tetrachloride concentrations interpolated to a 31 X 31 kilometer gridded area surrounding Neville Chemical Company. Annual average above background concentrations are estimated to range from less than 0.0001 ppb (0.0006 ug/m^3) at the edges of the gridded area to 0.19 ppb (1.2 ug/m^3) near the center of the source. People near the source can be exposed to concentrations 1 1/2 times that of the background concentrations. The maximum annual average concentration of 0.32 ppb (2.0 ug/m^3) for this source is estimated by adding the highest modeled concentration of 0.19 ppb (1.2 ug/m^3) and the background concentration of 0.13 ppb (0.82 ug/m^3). A plot of population density within the Neville Chemical gridded area is shown in Figure I-6.

In addition to estimating the range of annual average concentrations for each area that was modeled, the ARB staff also estimated the annual average population-weighted concentrations. This concentration is defined as the annual concentration that the "average" person in the modeled area is exposed to. For the Bay Area modeling analysis of Dow/duPont, it was estimated that 210,000 people are exposed to an annual average population-weighted concentration of 0.014 ppb (0.09 ug/m^3) above background. In the South Coast Air Basin, the Neville Chemical Company modeling analysis indicated that 2,270,000 people are exposed to an estimated annual average population-weighted concentration of 0.0016 ppb (0.01 ug/m^3) above background.

Figure I-5

Annual Average Carbon Tetrachloride Concentrations Above Ambient Levels Near Neville Chemical Company

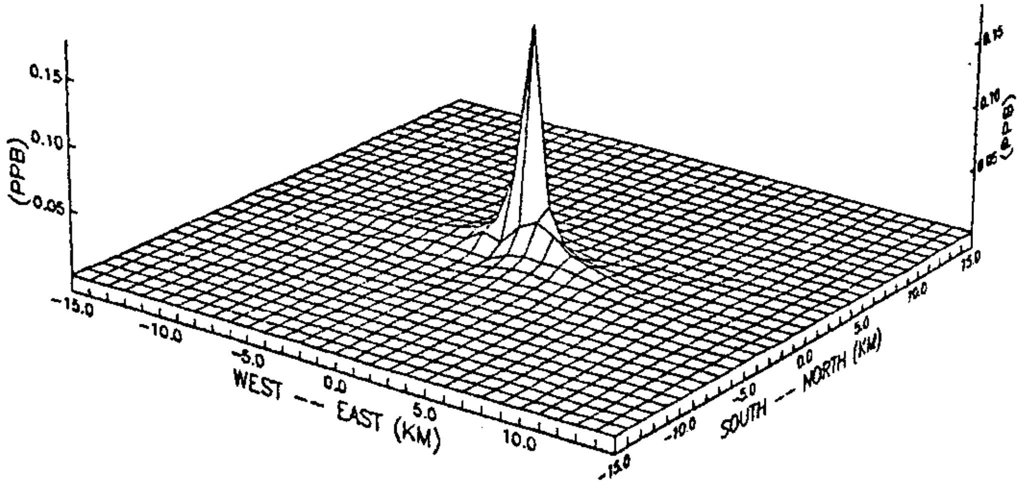
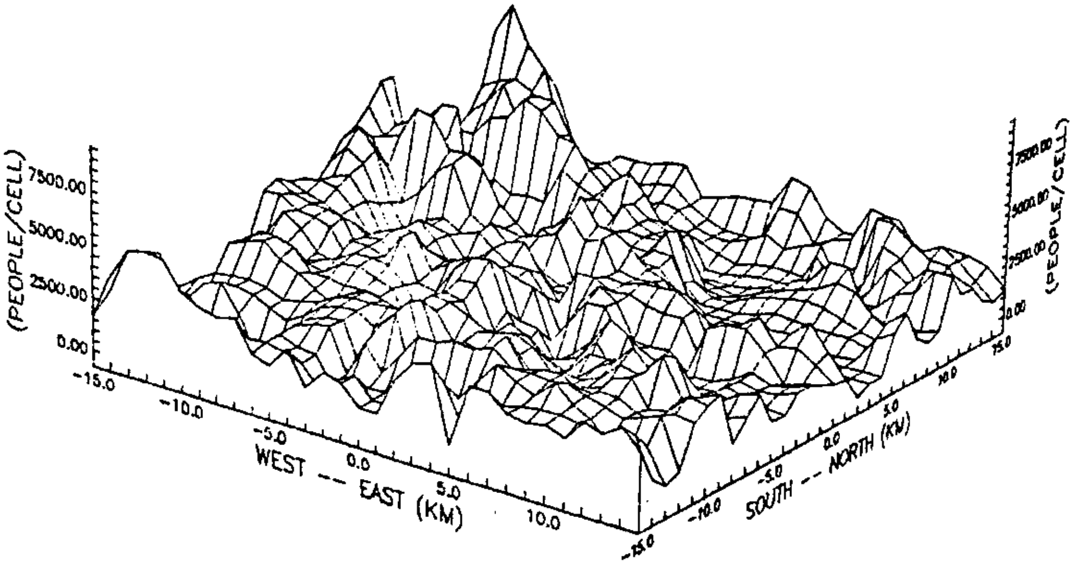


Figure I-6

Population Density Near Neville Chemical Company



To determine the annual average population-weighted concentration, the carbon tetrachloride concentrations in each gridded receptor area within the modeling region are estimated from dispersion modeling analysis. The concentration in each grid is multiplied by the population within the grid and divided by the total population in the modeling region. These values are then summed to give an estimate of the annual average population-weighted concentration for the modeling area. Since the risk is linear to the exposure, the population-weighted annual average concentration along with the DHS upper-limit risk estimate can be used to calculate the excess cancer cases from the release of emissions from the modeled emission sources.

B. EXPOSURE TO GLOBAL BACKGROUND CONCENTRATIONS

Carbon tetrachloride in the atmosphere is emitted mainly by anthropogenic sources. It has been suggested that carbon tetrachloride may be formed in the troposphere from the photolysis of perchloroethylene (Singh, et al., 1976). However, under normal atmospheric conditions, this formation process appears to have an insignificant impact on carbon tetrachloride concentrations in California.

Once in the atmosphere, carbon tetrachloride is very persistent with an atmospheric lifetime estimated to be approximately 50 years. Researchers estimate that the tropospheric carbon tetrachloride concentration is increasing at a rate of approximately 2 percent per year and that presently, a global background concentration between 0.11 and 0.15 ppb (0.69 and 0.94 ug/m^3) exists in the troposphere (Environmental Studies Board, 1978, Prinn, et al., 1983). Based on the ARB's monitoring network, the geographic annual average concentration in California is estimated to be 0.13 ppb (0.82 ug/m^3). Thus, Californians are exposed to at least this concentration of carbon tetrachloride.

Diffusion of carbon tetrachloride from the troposphere to the stratosphere where ultraviolet photolysis can occur is the major identified removal mechanism of carbon tetrachloride. Other possible removal mechanisms for carbon tetrachloride include reactions with hydroxyl radicals and ground state oxygen atoms, absorption into the ocean, adsorption onto particulate matter, and wet deposition. However, all of these mechanisms do not occur rapidly enough to significantly remove carbon tetrachloride from the atmosphere. Therefore, the emission rate is greater than the removal rate for carbon tetrachloride which causes it to accumulate to form the global background level. Chapter III discusses these tropospheric removal mechanisms for carbon tetrachloride in greater detail.

In order to validate the theory that there are no rapid removal mechanisms for carbon tetrachloride, several researchers have estimated global background concentrations based on global emissions and known atmospheric removal mechanisms for carbon tetrachloride and compared the calculated values with measured concentrations. Table I-3 presents the range of carbon tetrachloride concentrations calculated and/or measured by these researchers.

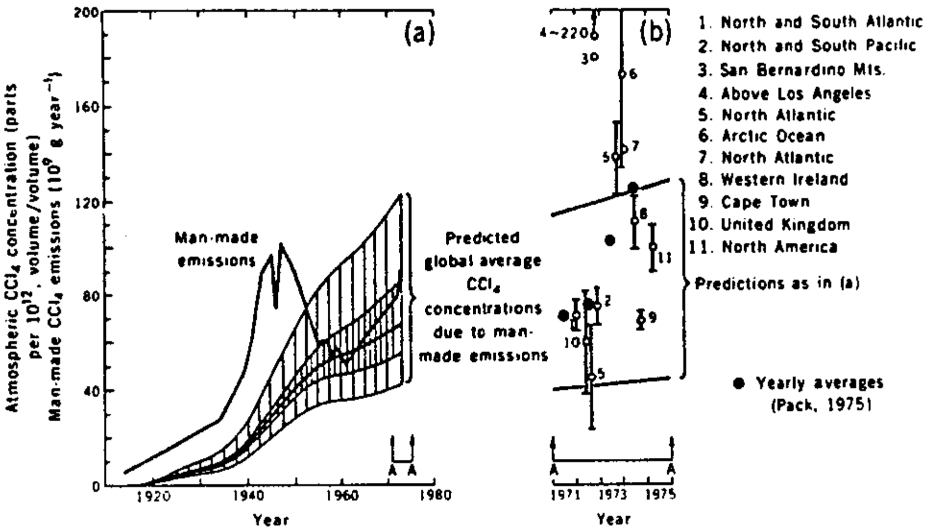
Comparison of the calculated and measured carbon tetrachloride concentrations indicate that the calculated concentrations based on global emissions and known removal mechanisms are in good agreement with the measured concentrations. This implies that all major removal mechanisms were accounted for in the calculated values. The values in Table I-3 are 1976 estimates and should be increased by about 20 percent to account for releases into the atmosphere since 1976 (see Section II). This would give an estimated

Table I-3
Tropospheric Carbon Tetrachloride Concentrations (ppb)*

	Concentration	References
Calculated Tropospheric Concentrations	0.070-0.095	Singh et al., 1976
	0.050-0.130	Galbally, 1976
	0.060-0.088	Altshuller, 1976
	0.120-0.162	NRC, 1976a
Measured Tropospheric Concentrations	0.130	Rasmussen, et al., 1986
	0.103-0.144	Kirschmer, et al., 1983
	0.110-0.150	Borchers, et al., 1983
	0.112-0.132	Prinn, et al., 1983
	0.120-0.140	Rasmussen, 1976
	0.110-0.130	Su & Goldberg, 1977
	0.130-0.170	Lovelock, 1976
	0.061-0.069	Penkett, 1976
	0.130-0.170	Pearman, 1976
	0.060	Goldman, 1976
	0.059-0.065	Sandalls, 1976

*Based on information from a search of computer databases available through May 1987.

Figure I-7
Global Emissions and Resultant Global Concentrations



(a) Predicted global average concentration of carbon tetrachloride due to man-made emissions. The inner hatched area indicates the uncertainty due to loss mechanisms. The shaded area indicates the uncertainty due to loss mechanisms and a ± 30 percent variation in the emission rates. (b) Observed carbon tetrachloride concentrations and predicted global average concentrations from (a).

range of approximately 0.06 to 0.20 ppb (0.38 to 1.26 ug/m^3) for 1986. Figure I-7 shows a direct comparison estimate of global emissions and the resultant estimates of global concentration from the time carbon tetrachloride was first produced (Galbally, 1976).

The most complete and comprehensive study reviewed by ARB staff was the Atmospheric Lifetime Experiment or ALE (Prinn, et al., 1983). Although the purpose of the ALE study was to estimate the atmospheric lifetime of carbon tetrachloride and other halogenated compounds, a number of other useful conclusions came out of the study. It demonstrated that there is a fairly uniform background concentration for carbon tetrachloride which varies only by a few parts per billion around the world and that this concentration is increasing steadily at a rate of approximately 2 percent per year. The ALE study also provided a well documented estimate of the atmospheric lifetime for carbon tetrachloride, 52 ± 15 years. Because the conclusions of the ALE study are fundamental to the conclusions given here, the study has been summarized in Appendix A.

C. AMBIENT CARBON TETRACHLORIDE CONCENTRATIONS IN CALIFORNIA

In 1985, the ARB established a 20 station monitoring network throughout California to measure potentially toxic compounds, including carbon tetrachloride. These monitoring sites were selected so that measured concentrations would be representative of the concentrations that the local population is exposed to. The preliminary 1985 monitoring data indicates that Californians are exposed to an estimated statewide annual average concentration of 0.13 ppb (0.82 ug/m^3). This concentration is consistent with the global background concentrations which have been measured or estimated by various researchers (see Chapter 1, Section B). The ARB staff

Table I-4

1985 ARB Carbon Tetrachloride Monitoring Data
Range of Estimated Mean Concentrations

Air Basin Site Location	Lower Bound (ppb)	Lower Bound (ug/m^3)	Mean Concentration (ppb)	Mean Concentration (ug/m^3)	Upper Bound (ppb)	Upper Bound (ug/m^3)
Sacramento Valley						
Citrus Heights	0.12	0.75	0.13	0.82	0.14	0.88
San Diego						
Chula Vista	0.10	0.63	0.11	0.69	0.12	0.75
El Cajon	0.11	0.69	0.12	0.75	0.13	0.82
San Francisco Bay Area						
Concord	0.12	0.75	0.14	0.88	0.17	1.06
Fremont	0.13	0.82	0.16	1.0	0.19	1.19
Richmond	0.12	0.75	0.14	0.88	0.15	0.94
San Francisco	0.12	0.75	0.13	0.82	0.15	0.94
San Jose	0.13	0.82	0.15	0.94	0.18	1.13
San Joaquin Valley						
Bakersfield	0.14	0.88	0.16	1.0	0.17	1.06
Fresno	0.13	0.82	0.15	0.94	0.16	1.0
Merced	0.12	0.75	0.14	0.88	0.15	0.94
Modesto	0.12	0.75	0.14	0.88	0.15	0.94
Stockton	0.14	0.88	0.16	1.0	0.19	1.19
South Central Coast						
Santa Barbara	0.11	0.69	0.12	0.75	0.13	0.82
Simi Valley	0.11	0.69	0.12	0.75	0.13	0.82
South Coast						
El Monte	0.11	0.69	0.12	0.75	0.13	0.82
Los Angeles	0.12	0.75	0.13	0.82	0.14	0.88
North Long Beach	0.12	0.75	0.13	0.82	0.14	0.88
Riverside	0.11	0.69	0.12	0.75	0.13	0.82
Upland	0.12	0.75	0.14	0.88	0.16	1.0
Statewide			0.13	0.82		

believes that almost all of the ARB monitoring stations are measuring carbon tetrachloride concentrations that represent global background levels. Table I-4 summarizes the annual mean carbon tetrachloride concentrations along with the upper and lower bounds for each of the monitoring stations. The upper and lower bounds give a range of the annual average concentration for each station by taking into account the variability of the sampling data and the small number of samples taken at each station.

Out of 20 monitoring stations, three stations are believed to have slightly elevated annual mean concentrations. These stations are Bakersfield, Fremont, and Stockton. Several factors could cause elevated or high annual mean carbon tetrachloride concentrations in an area. These factors are: (1) the contribution from major point sources of carbon tetrachloride emission sources; (2) minor sources in conjunction with certain meteorological conditions such as temperature inversions; and (3) the photodissociation process of chloroethylenes (perchloroethylene) to form carbon tetrachloride in the troposphere. These factors were reviewed by the ARB staff to determine if any or all of these factors could have caused elevated mean carbon tetrachloride concentrations at any of the monitoring sites.

The ARB staff believes that the most important factor which can influence the elevated mean carbon tetrachloride concentrations are effects caused by local emission sources in the area. Based on known or identified carbon tetrachloride emission sources in California, the Stockton site may be expected to have an elevated mean concentration. This is because of the use of carbon tetrachloride containing pesticides in the area. The Fremont station, on the other hand, may be influenced by smaller sources which are unaccounted for in the inventory along with poor dispersion conditions. At this time, there is not sufficient information to identify these minor sources. The ARB staff could not account for the elevated mean concentration at the Bakersfield station. However, the small number of samples taken and the uncertainties in the analytical and sampling procedures are believed to cause the elevated mean concentration at this station.

In order to determine if small unidentified sources were impacting the measured annual mean concentrations, the ARB staff compared measured carbon tetrachloride concentrations to periods of stagnant atmospheric conditions. Because carbon monoxide (CO) is emitted uniformly throughout the year, high CO concentrations are an indication of poor meteorological dispersion. Therefore, if stagnant conditions were contributing to high carbon tetrachloride concentrations, there should be a correlation between high CO concentrations and high carbon tetrachloride concentrations. The results of the CO and carbon tetrachloride correlation comparison showed no relationship between high carbon tetrachloride levels and conditions of poor dispersion (high CO levels) with the exception of the Fremont station with a correlation coefficient of 0.52. This implies that poor dispersion may be a factor which contributed to elevated carbon tetrachloride at the Fremont station. There was no close correlation for any of the other sites. Table I-5 summarizes the CO versus carbon tetrachloride correlation analysis. The plots of CO versus carbon tetrachloride are shown in Appendix B.

The absence of a strong CO versus carbon tetrachloride correlation at most of the stations indicates that if small emission sources are

Table I-5

Results of the Carbon Monoxide to Carbon Tetrachloride Correlation Analysis

Air Basin Site Location	Number of Observations	Correlation Coefficient
Sacramento Valley		
Citrus Heights	29	0.02
San Diego Air Basin		
Chula Vista	20	0.06
El Cajon	18	0.04
San Francisco Bay Area Air Basin		
Concord	18	0.17
Fremont	17	0.52
Richmond	16	0.03
San Francisco	15	0.04
San Jose	17	0.00
San Joaquin Valley Air Basin		
Bakersfield	25	0.14
Fresno	23	0.02
Merced	-	-
Modesto	23	0.03
Stockton	19	0.20
South Central Coast Air Basin		
Santa Barbara	19	0.05
Simi Valley	11	0.00
South Coast Air Basin		
El Monte	-	-
Los Angeles	20	0.25
North Long Beach	22	0.13
Riverside	20	0.04
Upland	20	0.00

causing elevated concentrations, they are probably intermittent releases of carbon tetrachloride. Currently, two samples a month are taken at each site. The ARB staff feels that two samples a month is not sufficient to reliably estimate the effects of intermittent sources on annual average concentrations. If carbon tetrachloride is identified as a toxic air contaminant, the ARB staff will identify any small sources which may be causing elevated exposures.

Based on a laboratory study under controlled experimental conditions, it has been suggested that carbon tetrachloride can be formed from the photodissociation of perchloroethylene (perc). If the formation process is important in the atmosphere, one would expect a correlation between perc concentrations and carbon tetrachloride concentrations. Since intensity of sunlight is important in this formation process, the ARB staff analyzed the perc and carbon tetrachloride monitoring data for the months of May through September to determine if there is a correlation between the perc and carbon tetrachloride concentrations. Based on our analysis, little correlation was found. Although carbon tetrachloride may be formed by this process, it does not appear to be an important factor in the measured carbon tetrachloride levels in California. The ARB staff feels that there is insufficient information to determine the impact of this formation process under actual tropospheric conditions at this time. A more detailed discussion of the perc photolysis process is contained in Chapter III.

Based on the above analysis, the ARB staff believes that the statewide annual mean carbon tetrachloride concentrations estimated from the ARB monitoring data is essentially the global background concentration and thus, the annual average exposure level for Californians. Elevated concentrations above the global background are occurring in some areas from major point sources, pesticidal usages, and unidentified small users of carbon tetrachloride. However, the information currently available is not sufficient to establish the magnitude of any impacts from either unidentified small sources or atmospheric formation on carbon tetrachloride levels in California. Although annual mean concentrations measured at both the Fremont and Stockton monitoring sites could have been influenced by local sources, the measured mean concentrations are very close to the statewide average and may be an artifact of the small number of samples taken at each site. Therefore, because all of the annual mean concentrations are within ± 0.03 ppb (± 0.19 ug/m^3) of the statewide average, the only exposure estimates above the global background concentration that have been made are for those with major identified point sources in California.

D. EXPOSURE TO CARBON TETRACHLORIDE THROUGH OTHER MEDIA

Although the primary focus of this report is exposure to carbon tetrachloride from the ambient air, exposure can also occur from elevated concentrations in the indoor air, as well as, ingestion of carbon tetrachloride found in drinking water and food products. Table I-6 summarizes the range of intake of carbon tetrachloride from different exposure routes for an adult during the year while Figure I-8

TABLE I-6

Yearly Intake of Carbon Tetrachloride
Through Different Exposure Routes

Exposure Route	Yearly Intake (ug/year)*	
Inhalation		
Ambient and Indoor Air		6,000 - 30,000
Ingestion		
Food	<3,000	
Drinking Water	<400 - 20,000	
Total from Ingestion**		<3,000 - 24,000
Total**		< 9,000 - 54,000

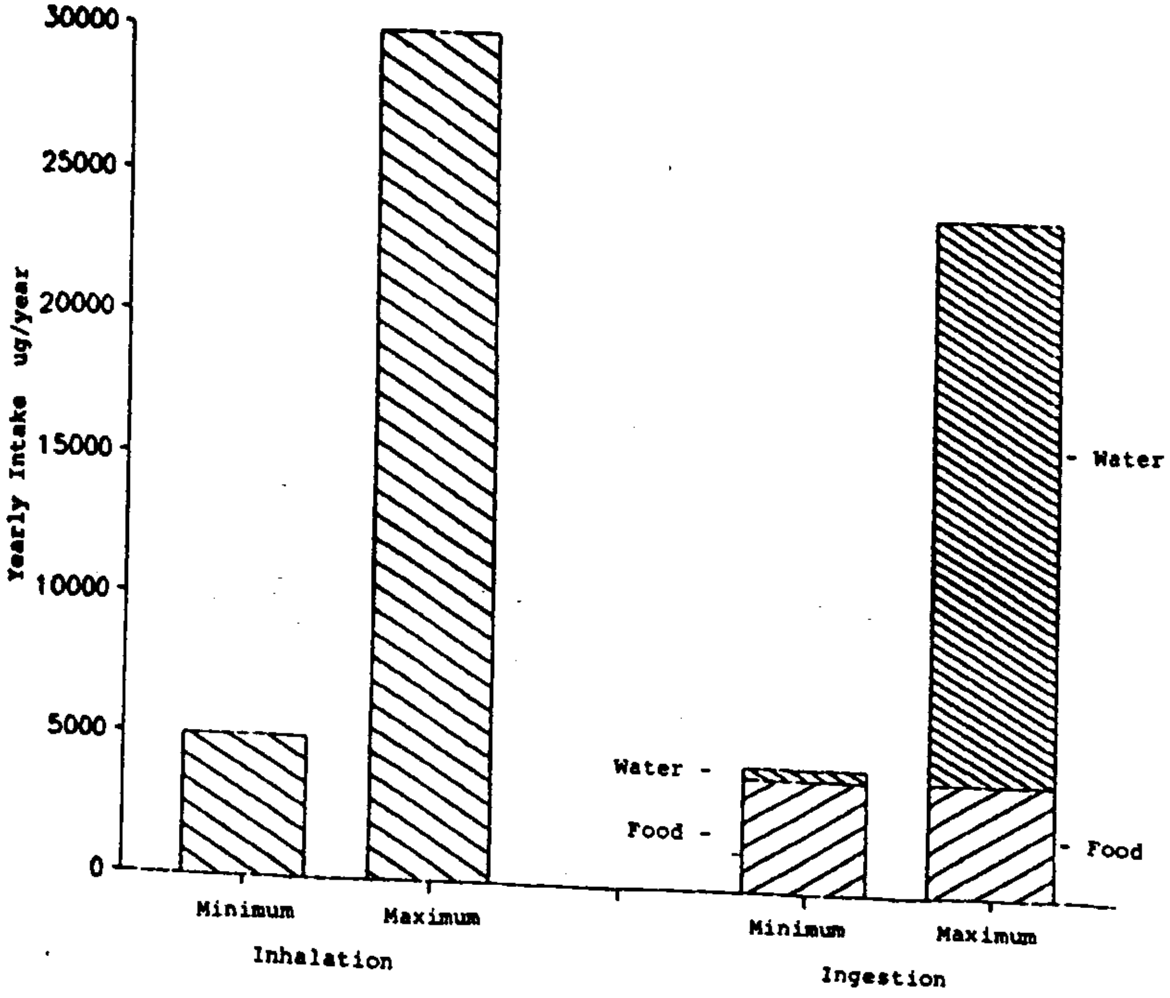
* The upper ranges of the yearly intakes are based on the maximum concentrations found in the different exposure media while the lower range values represent more typical concentrations found in these media. Therefore, the ARB staff believe that the lower ranges of the yearly intakes represent more realistic exposure estimates for most of California's population. Estimates for the yearly intake for each media have been rounded off to one significant figure.

** Total has been rounded.

NOTE: The estimates presented in Table I-6 are based on limited data and should not be considered absolute. This data was tabulated to illustrate the relative intake of carbon tetrachloride over an annual period. Refer to Appendix C for the assumptions used by the ARB staff in determining these estimates.

Figure I-8

Range of the Yearly Intake of Carbon Tetrachloride
Through Different Exposure Routes



presents this information in graphical form. These estimates are based on the maximum concentrations found in each exposure route (see Appendix C for assumptions and sample calculations).

1. Indoor Exposure to Carbon Tetrachloride

Based on the review of available draft reports and conference papers, the ARB staff could not establish with any degree of certainty the relationship between indoor and outdoor concentrations. This is because of uncertainties that were found in the studies that were reviewed. The uncertainties are discussed briefly in this section and in greater detail in Appendix D.

The ARB staff believes that for carbon tetrachloride the ambient outdoor concentration sets the baseline or lower limit for indoor concentrations. This is due to normal air exchanges between the indoor and outdoor air, the small contribution from indoor sources, and the absence of indoor removal processes for carbon tetrachloride. Air exchanges between the indoor and outdoor environments are caused by wind and temperature induced pressure differences which cause air movement from one environment to the other.

This exchange of air typically occurs in residences at a rate of 0.2 to 2.5 exchanges per hour (Diamond and Grimsrud, 1983). The exchange rate can be higher if it is influenced by the operation of air conditioners or the opening of windows. Thus, the air exchange is always rapid relative to the atmospheric persistence of carbon tetrachloride.

If present, indoor removal processes would be expected to lower the indoor concentration below the outdoor concentration, but for carbon tetrachloride, there are no known (or suspected) removal processes unique to the indoor environment. Thus, indoor concentrations lower than outdoor concentrations are not expected.

If present, indoor sources would cause the indoor concentration to be higher than the outdoor baseline concentration. However, there are few indoor sources of carbon tetrachloride. Since 1972, carbon tetrachloride has been banned from consumer products by the Consumer Products Safety Commission (CPSC). However, some households may still have and use these consumer products. It is also possible that carbon tetrachloride is a component in present day consumer products as an "inert" ingredient. Carbon tetrachloride was found in a commercial cleaning product which may have contributed to elevated concentrations measured by Wallace (Wallace, 1986). However, conversation with the CPSC staff indicated that because of the CPSC ban, these types of products are not in widespread use. Other potential sources of indoor carbon tetrachloride include the use of water containing carbon tetrachloride. Some uses such as taking showers or washing dishes may contribute to the indoor carbon tetrachloride concentration. At this time, the contribution of these indoor sources to elevated indoor concentrations have not been correlated or determined.

Indoor and outdoor carbon tetrachloride concentrations have only recently been measured (US EPA, 1984; Wallace, et al., 1984, 1986; Hartwell, et al., 1984; DeBartoli, 1985; Pliel, 1985; Pellizzari, et. al., 1984). These studies include conference papers and draft reports which have not been peer reviewed. Based on a review of these

Table I-7

Summary of Indoor/Outdoor Carbon Tetrachloride
Monitoring Studies

Study Location	# of Samples	Median Concentration[1] (ppb)	Median Concentration[1] (ug/m^3)	%of Samples Above LOQ[2]	Median Duplicate % RSD[3]
Hartwell, et al., 1985					
Greensboro					
Indoor	20	0.03	0.17	55	N.R.[4]
Outdoor	20	0.008[6]	0.04[5]	45	N.R.
Baton Rogue					
Indoor	27	0.01[5]	0.075[5]	48	N.R.
Outdoor	27	0.02	0.15	52	N.R.
Houston					
Indoor	10	0.20	1.3	100	N.R.
Outdoor	10	0.29	1.85	100	N.R.
Wallace, et al., 1984					
New Jersey Feb 81					
Indoor	346-348[6]	0.23[5]	1.5[5]	31	27[7]
Outdoor	81-86[6]	0.13	0.81	53	24[7]
Wallace, et al., 1986					
Los Angeles Feb 84					
Indoor	117	0.10	0.65	97	15
Outdoor	24-25	0.10	0.65	97	28
Los Angeles May 84					
Indoor	52	0.10	0.65	99	42
Outdoor	23	0.11	0.64	100	51
Antioch-Pittsburg Jun 84					
Indoor	71	0.14	0.71	94	12
Outdoor	10	0.05	0.33	95	43[8]
Pliel, 1985					
North Carolina					
Summer					
Indoor	15	0.14[1]	0.88[1]	100	<5
Winter					
Indoor	16	0.14[1]	0.88[1]	100	<5
Outdoor	12	0.15[1]	0.94[1]	100	<5
DeBartoli, 1985					
Northern Italy					
Indoor	16	0.9	6	94	N.R.
Outdoor	16	0.8	5	88	N.R.

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1 Median concentrations, except for the Pliel study where mean concentrations are reported.

2 LOQ - limit of quantitation

3 % RSD - relative standard deviation of duplicate field samples.

$$\frac{\text{standard deviation}}{\text{mean}} \text{ X } 100\%$$

4 N.R. - not reported

5 Estimated median concentration as reported by the author. Less than 50% of samples were measurable. Quantitation limits vary between indoor and outdoor environments and with time.

6 Number of samples reported varied with compound of interest.

7 Mean percent RSD.

8 Value for one pair of field duplicate sample.

monitoring studies, the ARB staff could not establish with certainty if indoor and outdoor carbon tetrachloride concentrations were significantly different. This uncertainty is due to several factors. Some studies showed equal concentrations indoors and out, while others did not. In some studies, a large percentage of the samples were below the limit of detection. Other studies did not report quality assurance results and therefore, the uncertainty in the data could not be assessed. For some studies that reported quality assurance results, uncertainties were large relative to differences between reported indoor and outdoor concentrations. Therefore, the ARB staff was unable to determine if the measured differences were real. However, in the absence of better data, the ARB staff believes that most indoor concentrations are equal to outdoor concentrations. This conclusion is supported by the rapid air exchanges that occurs between the indoor and outdoor environments and the absence of either indoor removal mechanisms or sufficient indoor sources to cause major differences between indoor and outdoor concentrations. The ARB staff believes that conclusions regarding the difference between indoor and outdoor carbon tetrachloride concentrations would require additional research and better monitoring data from future studies. Table I-7 summarizes the findings of these studies. Appendix D discusses each of the indoor/outdoor carbon tetrachloride studies in greater detail.

2. Exposure to Carbon Tetrachloride from Food Products

The maximum intake of food products containing carbon tetrachloride is estimated to be less than 4,000 ug/year. In terms of intake, this estimate may be as significant as the lower limit estimate of intake from the inhalation of ambient air containing carbon tetrachloride. The intake from food products containing carbon tetrachloride is based on very limited information and is an upper limit estimate. EPA is also proposing to ban the use of grain fumigants containing carbon tetrachloride in the United States (Zarow, 1986). This is expected to have a significant impact on reducing the concentration found in food products (Langley, 1986). Because of the above reasons, the ARB staff believes that the maximum intake estimate does not represent the intake level that would normally occur from the ingestion of food products containing carbon tetrachloride. Due to the limited data that is available, the ARB staff could not determine a more accurate intake estimate at this time.

Limited available data indicate that carbon tetrachloride residues in ready-to-eat food products have an average concentration of 2 ug/kg (Pesticide & Toxic Chemical News, 1985). Though the average carbon tetrachloride concentration in food products is low, significantly higher concentrations have been detected in grains treated with fumigants containing carbon tetrachloride. It appears that the amount of carbon tetrachloride remaining as a residue in food grains is dependent upon the fumigation dosage, storage conditions, length of aeration, and extent of processing (U.S. EPA, 1985b) Carbon tetrachloride has been detected in fumigated wheat at concentrations ranging from 76,000 ug/kg (one week after aeration) to 23,000 ug/kg (seven weeks after aeration). Bread prepared from treated wheat aerated for three days contained carbon tetrachloride at concentrations up to 40 ug/kg (Berck, 1974). This is in agreement with Jagielski who reported that the carbon tetrachloride concentration in white bread prepared from treated grain is expected to be below 50 ug/kg provided that the concentration prior to processing is below 50 ug/kg (Jagielski, et al., 1978). The EPA staff also agrees that this concentration is a reasonable upper limit estimate of carbon tetrachloride concentration in processed grain products (McKinney, 1987). Because of EPA's ban on grain fumigants containing carbon tetrachloride and the limited available data, the ARB staff believes that the carbon tetrachloride concentration is likely to be below this upper limit estimate. Therefore, the yearly intake of carbon tetrachloride from this exposure route is also likely to be below the maximum intake level estimated by the ARB staff.

3. Exposure To Carbon Tetrachloride from Drinking Water

The lower range of intake of carbon tetrachloride from drinking water is estimated to be less than the intake from inhalation or ingestion of food products containing carbon tetrachloride. The estimated annual intake ranges from less than 400 ug to 20,000 ug per year (see Table I-6 and Figure I-8). The maximum intake was based on the highest carbon tetrachloride concentration measured by the California Department of Health Services (DHS) during a 1985 groundwater sampling study. Over ninety-eight percent of the samples that were analyzed were below the limit of detection of the analytical equipment which is 0.5 ug/liter (Rogers, 1986a). Rogers also stated that the sources of drinking water in California are surface waters for 60 percent of the population and underground water systems for the remaining 40 percent of the population. Since carbon tetrachloride is relatively volatile, it is rarely detected in surface drinking water and is found more commonly in ground water systems (Rogers, 1986b). The ARB staff believes that most Californians are ingesting less than 400 ug/year of carbon tetrachloride from drinking water.

Of the 2947 wells DHS sampled, which represent 819 large public groundwater systems, less than 2 percent or 38 wells were above 0.5 ug/liter. The concentrations of the carbon tetrachloride that was detected range from 0.6 ug/liter to 29 ug/liter with a median of 2.2 ug/liter. Seventy-five percent of the samples with carbon tetrachloride concentrations above the limit of detection were located in the South Coast Air Basin (DHS, 1986). DHS has indicated that several wells with elevated carbon tetrachloride levels have since been closed. These preliminary results are consistent with EPA findings where EPA estimated that over 86 percent of the population in the United States is exposed to levels below 0.5 ug/liter and that 12.5 percent of the population are exposed to between 0.5 and 5 ug/liter. The remaining 1.5 percent of the population is exposed to levels between 5 and 30 ug/liter (U.S. EPA, 1984).

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II. SOURCES OF ATMOSPHERIC CARBON TETRACHLORIDE

A. PRODUCTION

Carbon tetrachloride (also known as methane tetrachloride, benziform, perchloromethane, and tetrachloromethane) was first produced on a large scale in the United States in 1907, primarily as a dry cleaning agent and for use in fire extinguishers (Grayson, 1980). This compound is currently produced in the United States by nine facilities. Only one company, Dow Chemical, has a carbon tetrachloride production facility in California, which is located in Pittsburg. The facility has a production capacity of about 40,000 tons per year (EPA, 1985a), which is about 11 percent of the carbon tetrachloride produced in the United States (U.S. International Trade Commission, 1984).

Figure II-1 shows United States production, imports, exports, and uses of carbon tetrachloride for the years 1978 to 1983. Production of carbon tetrachloride in the United States increased from approximately 286,000 tons in 1983 to about 356,000 tons in 1984, while production capacity stands at approximately 444,000 tons (*Chemical and Engineering News*, 1985). Producers expected a 5 percent increase in carbon tetrachloride production in 1985 in response to the increased demand for chlorofluorocarbons (*Chemical Marketing Reporter*, 1985). The increased demand for chlorofluorocarbons was attributed to the higher demand for refrigerants in the automobile industry and for foaming agents in the housing construction industry (*Chemical Marketing Reporter*, 1984).

B. USAGE

In 1983, the national use estimates for carbon tetrachloride were: 94 percent for fluorocarbon 11 (trichlorofluoromethane) and fluorocarbon

Figure II-1

U.S. Production, Imports, Exports, and Uses of

Carbon Tetrachloride

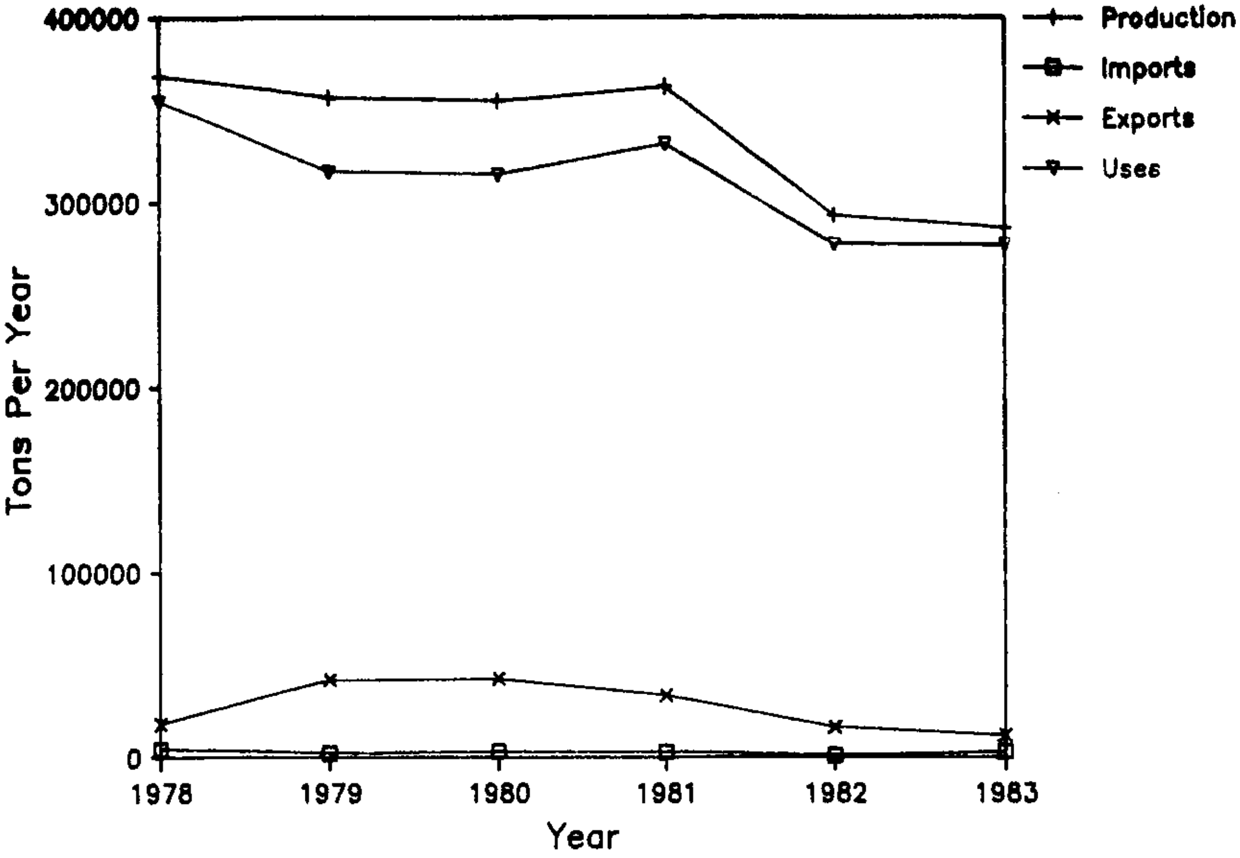
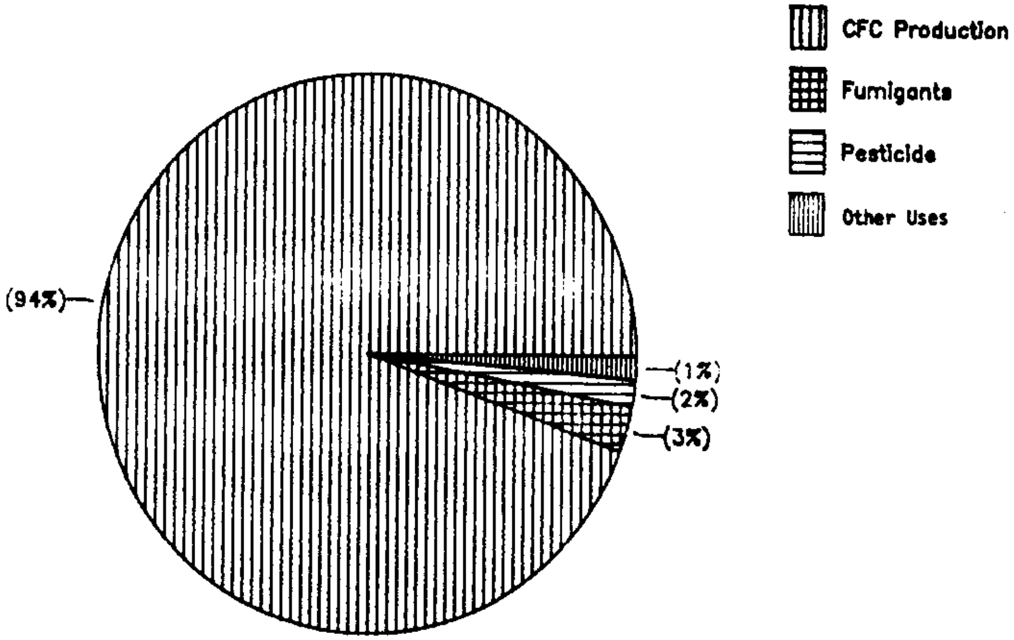


Figure II-2

National Use of Carbon Tetrachloride in 1983



12 (dichlorodifluoromethane) production, 3 percent as a grain fumigant, 2 percent for pesticide production, and 1 percent for other uses. Other uses of carbon tetrachloride include the production of chlorine and carbon tetrabromide (tetrabromomethane), use as a solvent in pharmaceutical manufacturing, and use in household and industrial products (EPA, 1983a). Figure II-2 summarizes the national carbon tetrachloride usages in 1983. In California the use of carbon tetrachloride in the production of fluorocarbon 11 and 12 represents about 89 percent of the carbon tetrachloride produced in the state. Other uses of carbon tetrachloride in California include grain fumigant usage, chlorinated paraffin wax production and miscellaneous solvent use.

Fluorocarbons 11 and 12 were used as aerosol propellants before their use as propellants was restricted by the United States Environmental Protection Agency (EPA) in 1978 (Chemical Purchasing, 1981). Currently, fluorocarbon 11 is used as a blowing agent in the manufacturing of plastic foams and fluorocarbon 12 is used as a refrigerant.

The use of carbon tetrachloride as an industrial solvent and as a dry cleaning agent has decreased in recent years due to concern about its toxicity and the availability of chemical alternatives (Environmental Studies Board, 1978). Its use as a pesticide is also expected to decrease due to EPA's federal regulation which restricts the use of carbon tetrachloride as a grain fumigant (51 FR 15372). Carbon tetrachloride has been banned as a fire extinguishing agent because of its tendency to decompose and form phosgene when sprayed into flames (McKetta, 1979).

C. CURRENT STATIONARY SOURCE EMISSIONS

Carbon tetrachloride is directly emitted from: 1) the production of carbon tetrachloride, chlorofluorocarbons, chlorine, and carbon tetrabromide; 2) the use of pesticides containing carbon tetrachloride; 3) the formulation of liquid pesticides containing carbon tetrachloride; 4) the use of carbon tetrachloride as a solvent in pharmaceutical manufacturing; and 5) the use of carbon tetrachloride as an industrial solvent. Carbon tetrachloride is also emitted when it is formed as a by-product during the production of ethylene dichloride (1,2-dichloroethane), perchloroethylene (tetrachloroethylene), and trichloroethylene (trichloroethene). Based on available information, there are no facilities in California that produce carbon tetrabromide, ethylene dichloride, or trichloroethylene. The Bay Area Air Quality Management District estimated carbon tetrachloride emissions from perchloroethylene production from Dow Chemical to be insignificant when compared to carbon tetrachloride storage tank emissions. Information from Dow Chemical and a solvent distributor, Van Waters and Rogers, indicated that carbon tetrachloride is shipped into and out of California by many distributors to small sources. At the present time, the ARB staff has insufficient information to determine the quantity and uses of carbon tetrachloride distributed to all small sources in California. Table II-1 summarizes carbon tetrachloride emissions and sources in California.

1. Emissions from the Production of Carbon Tetrachloride and Its Uses in Other Products

Dow Chemical's Pittsburg facility is currently the only company in California producing carbon tetrachloride. To produce carbon

TABLE II-1

Estimated Carbon Tetrachloride Emissions in California

Source	Location*	Source Type	Emissions (Tons/Year)	Inventory Year	Reference
Carbon Tetrachloride Production	BAAQMD	Point	30	1984	2
Pesticide/Fumigant Usage	SJV & Yolo-Solano	Area	20	1984	10
Chlorinated Paraffin Wax Production	SCAQMD	Point	3	1984	28
Fluorocarbon Mfg.	BAAQMD & SCAQMD	Point	2	1984	2,28
Misc. Use**	BAAQMD	Point	1	1984	2
Chemical Mfg.		Point	Not available		
Industrial Solvent		Point	Not available		
Oil Companies		Point	Not available		
Perchloroethylene Production		Point	Not available		
Pharmaceutical Mfg.		Point	Not available		
Publicly Owned Treatment Works		Point	Not available		
Scientific Laboratories		Point	Not available		
Total***			60 tons/year		

* BAAQMD: Bay Area Air Quality Management District
SCAQMD: South Coast Air Quality Management District
SJV: San Joaquin Valley
Yolo-Solano: Yolo-Solano Counties

** Emissions as reported by the BAAQMD. Information on carbon tetrachloride usage by the 3 sources are not available.

*** Total of available emission estimates as rounded.

tetrachloride, a hydrocarbon chlorinolysis process is used. A typical flow diagram of this process with possible emission sources is shown in Fig. II-3. Emission sources from this process are storage tanks, valves, flanges, pumps, and compressors. Fresh chlorine along with recycled chlorine and hydrogen are introduced into a vaporizer. The mixed gases are then fed to a refractory-lined reactor which typically operates at temperatures between 500°C and 700°C. Effluent from the reactor consists mainly of carbon tetrachloride, perchloroethylene, hydrogen chloride (HCl), and excess chlorine (Cl_2) with some unreacted hydrocarbons. The hot effluent gas is quenched, followed by the removal of HCl and Cl_2. The liquid stream which results from the process of quenching is separated into carbon tetrachloride and perchloroethylene by distillation (EPA, 1985a). Because the entire process occurs in a closed system, process loss emissions from carbon tetrachloride production are attributed primarily to equipment leaks. The design of the basic operations and the level of control may vary from plant to plant.

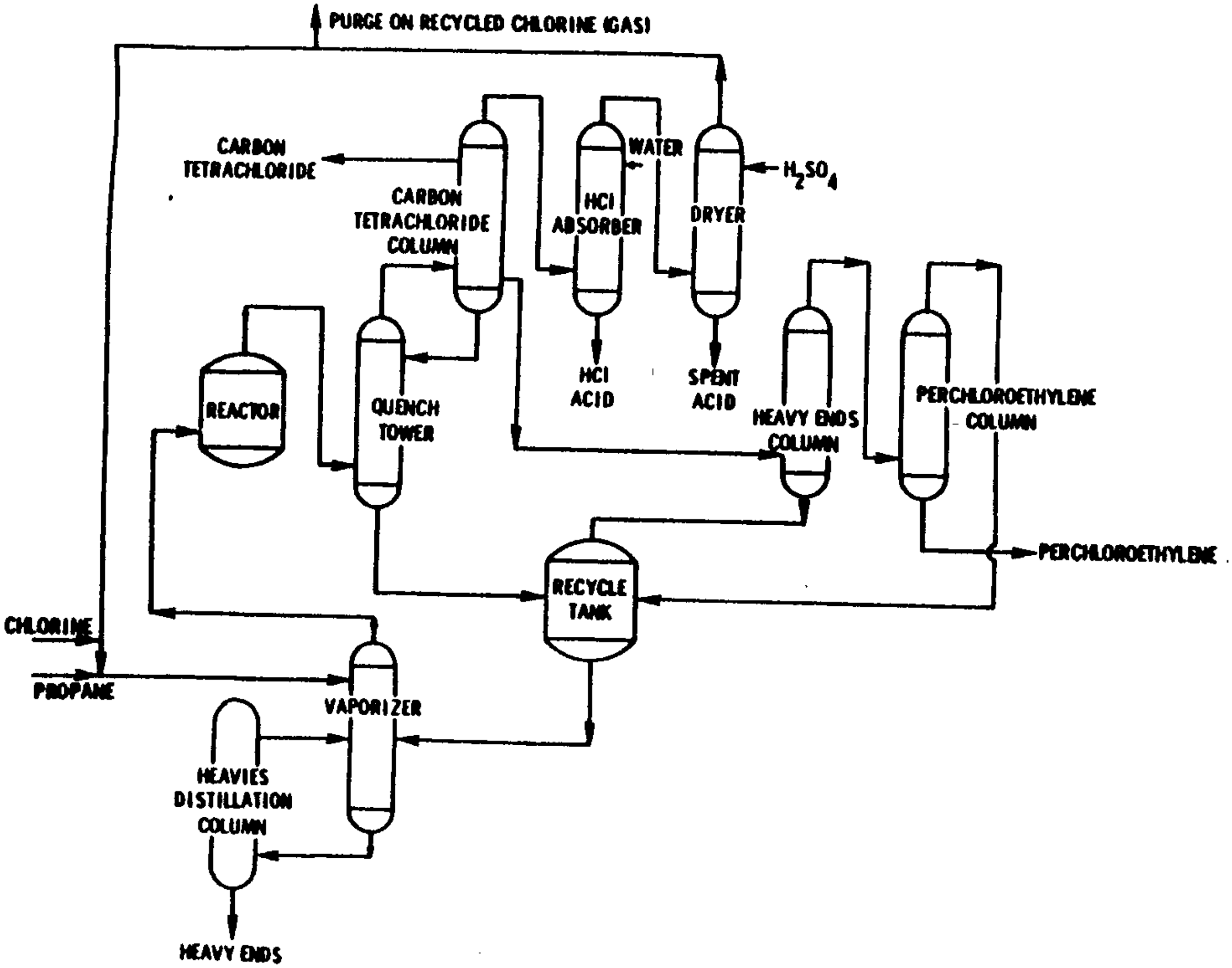
At Dow's Pittsburg facility, carbon tetrachloride is also emitted from the production of perchloroethylene. In addition, this facility uses carbon tetrachloride to formulate liquid pesticides. Based on information provided by Dow, emissions from the processes producing carbon tetrachloride, perchloroethylene, and liquid pesticide formulations are insignificant compared to the emissions from the carbon tetrachloride storage tank working and breathing losses (EPA, 1985a; BAAQMD, 1986).

In 1984, Dow reported carbon tetrachloride emissions to be approximately 30 tons. These emissions are from four fixed-roof storage

Figure II-3

Diagram for a Typical Hydrocarbon Chlorinolysis Process

Used in Producing Carbon Tetrachloride



tanks: two of the storage tanks have capacities of 17,000 gallons each and the other two have capacities of 700,000 gallons each (BAAQMD, 1986). Currently, these tanks are not controlled. Equipment leaks at Dow Chemical are regulated by the Bay Area Air Quality Management District (BAAQMD). The regulations require repair of volatile organic compound leaks greater than 10,000 ppm within 15 days for accessible, nonessential valves and flanges. For essential valves and flanges, leaks must be minimized within 15 days and repaired within six months. Loading and handling of carbon tetrachloride are minor emission sources at Dow and are currently not subject to controls or regulations.

The major use for carbon tetrachloride is as a feedstock in the production of fluorocarbon 11 and fluorocarbon 12. Only two facilities, Allied Chemical in El Segundo, and E. I. du Pont in Antioch, produce fluorocarbon 11 and fluorocarbon 12 in California. E. I. du Pont reported carbon tetrachloride emissions to be 1.5 tons in 1984 (BAAQMD, 1986). These emissions are from storage tanks which are currently uncontrolled. In 1983, Allied Chemical reported its carbon tetrachloride emissions to be 3 tons/year. During that year, Allied installed a vapor recovery system on its carbon tetrachloride storage tank which reduced the 1984 emissions to less than 0.03 tons. This facility is regulated by the South Coast Air Quality Management District (SCAQMD) which requires the plant to perform visual inspections for leaks in valves and flanges annually and visual inspection of pumps and compressors daily.

Fluorocarbons 11 and 12 are produced simultaneously from carbon tetrachloride by a process which substitutes fluorine atoms for chlorine atoms. The chlorofluorocarbons are then separated by distillation (du

Pont, 1986). It is estimated that approximately 3 percent of the carbon tetrachloride is lost in this process (Alexander Grant and Company, 1982), and up to 1 ppm may be separated with fluorocarbon 11 as a contaminant (du Pont, 1986).

Carbon tetrachloride is used as a solvent in the production of chlorinated wax (SCAQMD, 1983b). Currently, Neville Chemical Company in Santa Fe Springs, is the only producer of this wax in California. The 1984 emissions from this source were reported to be 3 tons (SCAQMD, 1984).

2. Emissions From The Use of Carbon Tetrachloride - Containing Products

Carbon tetrachloride is used in pesticides as a component of grain fumigant mixtures. These fumigants are applied to stored grain to control insect infestation (Holtorf and Ludvik, 1981; EPA, 1980). It is assumed most of the carbon tetrachloride used in grain fumigant mixtures evaporates due to its high vapor pressure (Leung et al., 1980; Woodrow, 1983). In 1984, carbon tetrachloride emissions from pesticide use were estimated to be 20 tons (California Department of Food and Agriculture, 1985). Future pesticidal uses will be reduced significantly due to recent restrictions by EPA which cancel the registration of pesticides containing carbon tetrachloride, thus, prohibiting the sale, distribution, and uses of these products in the United States (EPA, 1986). Other reported sources of carbon tetrachloride emissions are listed in Table II-1. Most of these sources are located in the San Francisco Bay Area and their emissions were estimated to be 1.2 tons per year.

3. Other Potential Emission Sources

Carbon tetrachloride is used as a solvent in the manufacturing of certain pharmaceutical products. Based on an EPA survey of authorized drug manufacturers in 1978, the estimated final distribution of carbon tetrachloride usage was: 11 percent air emissions, 7 percent sewer disposal and 82 percent incineration (EPA, 1978). Carbon tetrachloride is also used as a solvent in the manufacture of specialty and small volume chemicals such as chlorosulfonated polyethylene (Hypalon), tetrachloropyridene, and 4-amino-3,5,7-trichloropicolinic acid (EPA, 1984). The ARB staff has not identified any of these types of sources in California.

Information from a carbon tetrachloride producer (Dow Chemical) and a solvent distributor (Van Waters and Rogers) indicated that carbon tetrachloride is shipped into and out of California. In general, the sources are small and have purchased carbon tetrachloride in small quantities at one time. Carbon tetrachloride is used by these sources in manufacturing processes as a feedstock or as an industrial solvent. Localized emission releases to the atmosphere in an area may account for the elevated carbon tetrachloride concentrations measured at some of the ARB monitoring stations, such as the Fremont station. The ARB staff is continuing with its investigation of these minor sources and is contacting solvent distributors and sources to assess potential emissions that are emitted from these sources in California.

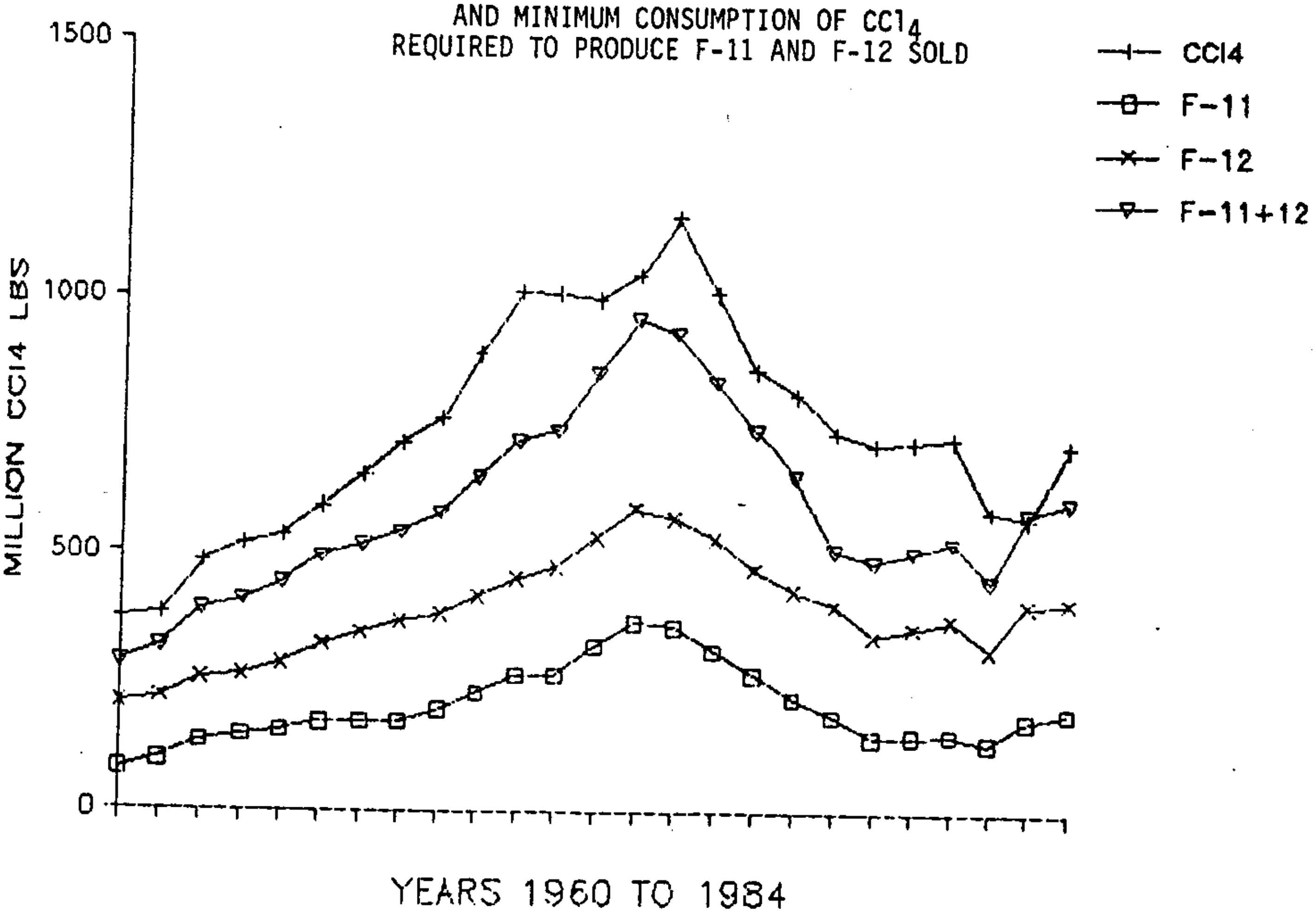
Independent studies by EPA and ARB have shown that carbon tetrachloride may also be emitted from publicly owned treatment works (CARB, 1985; EPA, 1982; Pellizzari, 1982). Source tests for volatile organic compounds by the ARB were conducted at two sewage treatment plants, one in Sacramento and one in Los Angeles. Concentrations up to 2 ppb were measured from the activated sludge process tanks (CARB, 1985). The source of carbon tetrachloride in the sewage is unknown. In addition to the source tests, the ARB is currently sponsoring a study to assess potential toxic compound emissions, including carbon tetrachloride, from publicly owned treatment works. The results are not available at this time, but this emission source will be evaluated if carbon tetrachloride is identified as a toxic air contaminant.

D. IMPACT OF TRENDS IN PRODUCTION, USAGE, AND EMISSIONS

Since 90 to 95 percent of the carbon tetrachloride produced is used in the production of fluorocarbons 11 and 12 (Chemical Marketing Reporter, 1986, 1983, 1981, 1978, 1975, 1972, 1969, 1966, 1964), production of carbon tetrachloride is tied closely to the sales of fluorocarbons 11 and 12 (see Figure II-4). It is estimated that a 1 to 2 percent growth in carbon tetrachloride demand is expected through 1990 (Chemical Marketing Reporter, 1986). However, if EPA does decide to regulate fluorocarbon production, as is expected, carbon tetrachloride demand after 1990 could be reduced significantly.

Emissions of carbon tetrachloride from California and the rest of the United States contribute to the global concentration of carbon tetrachloride. At the current rate of emissions, the global concentration will reach a steady state of approximately double its present value in about 100 years. If the emission rate continues to increase, the global concentration will increase more rapidly and will never reach a steady state.

FIG. II—4, U.S. PRODUCTION OF CCl4



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III. PERSISTENCE IN THE ATMOSPHERE

Once in the atmosphere, carbon tetrachloride is a very stable gaseous compound. Due to the lack of rapid atmospheric removal mechanisms, carbon tetrachloride accumulates in the lower atmosphere, the troposphere, and has a long tropospheric lifetime estimated to be approximately 50 years. Its persistence in the troposphere has led to a global background carbon tetrachloride concentration, which is representative of mean concentrations that are measured in California by the ARB monitoring stations.

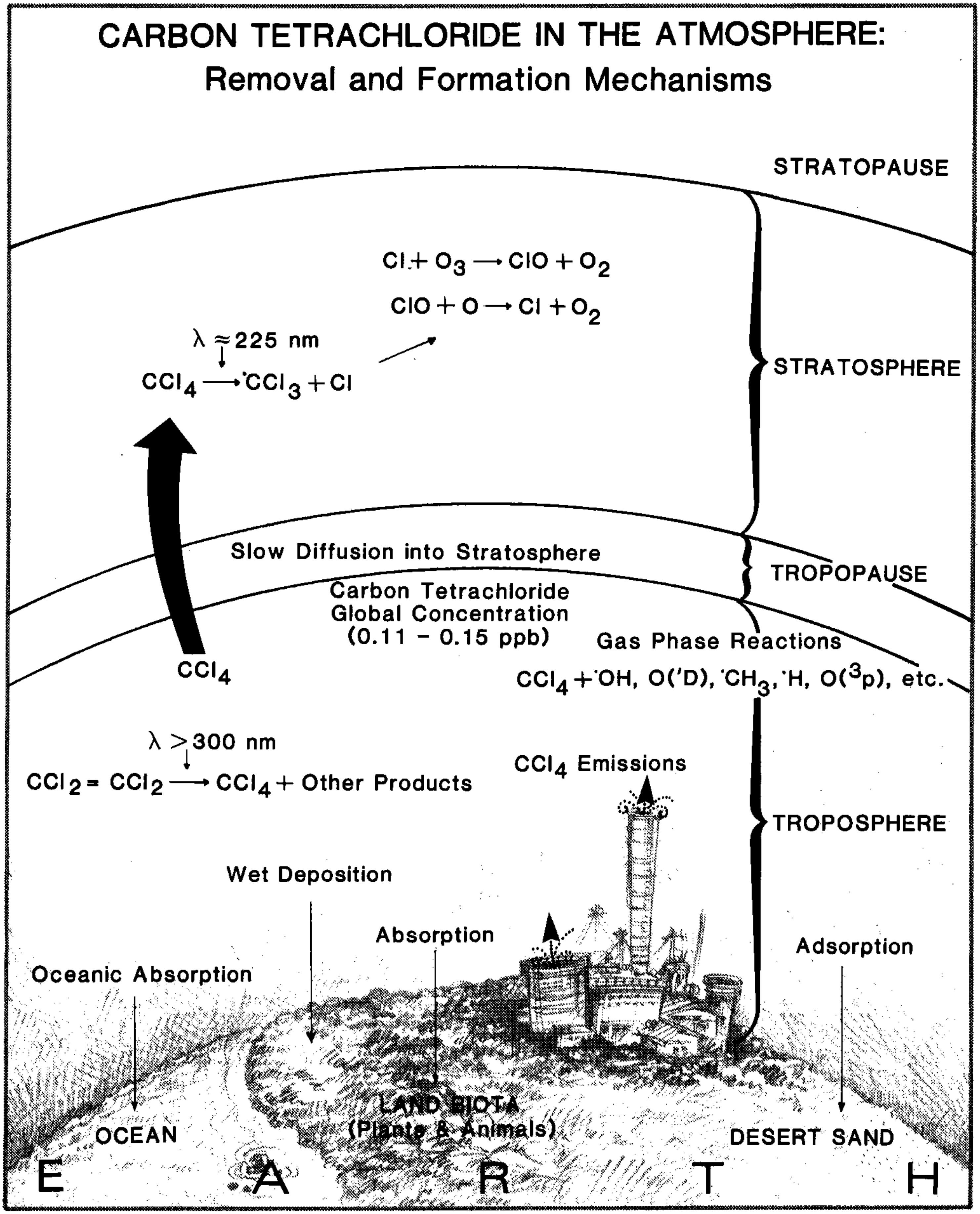
Carbon tetrachloride is emitted mainly from anthropogenic sources. It has also been suggested that carbon tetrachloride can be formed in the troposphere from the photolysis of perchloroethylene (perc). However, this formation process was based on perc photolysis experiments conducted under controlled laboratory conditions. Its impact under normal tropospheric conditions has yet to be determined or quantified.

Of the identified removal mechanisms, the diffusion of carbon tetrachloride from the troposphere to the stratosphere with ultraviolet photolysis then occurring is the major pathway for the removal of carbon tetrachloride. One of the photolysis products, chlorine atoms, is of concern because they can react with ozone to deplete the ozone layer in the stratosphere. This can result in increases in human skin cancer. Figure III-1 presents emission releases to the troposphere, potential tropospheric formation, and removal mechanisms for carbon tetrachloride.

A. PHYSICAL AND CHEMICAL PROPERTIES

The chemical formula of carbon tetrachloride (also known as methane tetrachloride, benziform, perchloromethane, and tetrachloromethane) is

FIGURE III-I



CARBON TETRACHLORIDE IN THE ATMOSPHERE:
Removal and Formation Mechanisms

CCl_4. Carbon tetrachloride is a colorless, non-flammable liquid with a density of 13.22 lbs/gal at 25°C (Zwiacher, et al., 1983) and a characteristic odor. It is miscible with most organic solvents such as benzene, chloroform, and ether, but is essentially insoluble in water. With a vapor pressure of 100 mm Hg at 23°C, carbon tetrachloride is relatively volatile. The density of carbon tetrachloride vapors is over five times that of air, thus, in cases where concentrated gaseous emissions occur, the plume will tend to settle to the ground before dispersing into the air (National Research Council, 1978). Carbon tetrachloride can decompose in direct flames to form phosgene. Reaction of carbon tetrachloride with steam results in the formation of chloromethanes, hexachloroethane, and perchloroethylene (U.S. EPA, 1984). Carbon tetrachloride's physical properties are shown in Table III-1.

B. ATMOSPHERIC FATE OF CARBON TETRACHLORIDE

1. Atmospheric Regions of Importance for Carbon Tetrachloride

The atmosphere can be divided into a number of different regions according to their temperature variations with altitude. These temperature regions are described in Table III-2 and in Figure III-2. For carbon tetrachloride, the important regions in terms of its persistence and removal from the atmosphere are the troposphere, the tropopause, and the stratosphere. The troposphere is the region where carbon tetrachloride is emitted. The tropopause acts as a barrier which inhibits the movement of air masses containing carbon tetrachloride from the troposphere to the stratosphere. Once carbon tetrachloride diffuses into the stratosphere, it undergoes photolysis which is the major removal mechanism for carbon tetrachloride.

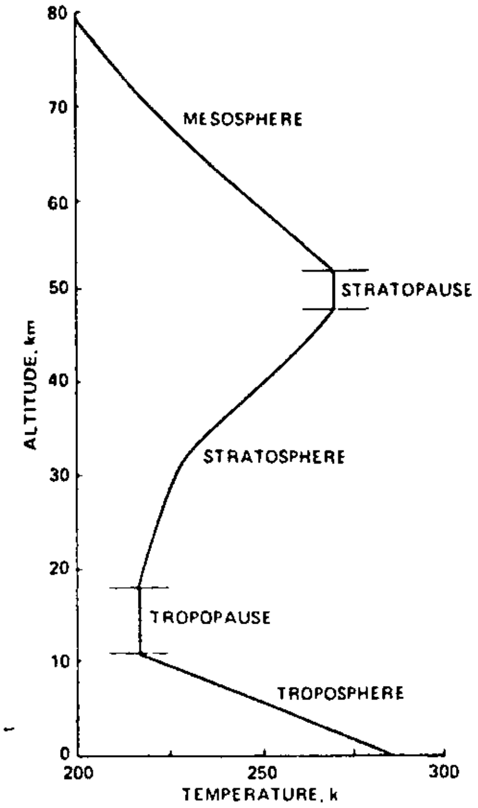
TABLE III-1

The Physical Properties of Carbon Tetrachloride

Properties	Value	Reference
Boiling Point, 760 mm Hg	76.72°C	Kirk-Othmer, 1979
Molecular Weight	153.82	Kirk-Othmer, 1979
Vapor Pressure, 23°C	100 mm Hg	Kirk-Othmer, 1979
Melting Point, 760 mm Hg	-22.92°C	Kirk-Othmer, 1979
Flash Point	None	Kirk-Othmer, 1979
Sol. in H_2O, 25°C, g/199g H_2O	0.08	Kirk-Othmer, 1979
Sol. H_2O in CCl_4, 25°C g/199g CCl_4	0.013	Kirk-Othmer, 1979
Octanol Coeff.	2.64	U.S. EPA, 1984
Vapor Density, Air=1	5.32	Kirk-Othmer, 1979
Density of Solid, g/cm, -80°C	1.81	Kirk-Othmer, 1979
Specific Gravity 0/4°C	1.63	Kirk-Othmer, 1979
Solidification	-23°C	Merck Index, 1983
Heat of Form. KCal/mole		
Liquid	-33.94	Kirk-Othmer, 1979
Vapor	-25.81	Kirk-Othmer, 1979
Latent Heat Fusion, KCal/Mole	0.61	Kirk-Othmer, 1979
Latent Heat Vaporization KCal/Ka	46.53	Kirk-Othmer, 1979

Figure III-2

Major Regions of the Atmosphere



The scale of temperature is in °K. To convert to °C, use the equation °C = °K - 273.

Table III-2

Major Regions of the Atmosphere and Their Characteristics

Region	Temperature Range (°C)	Altitude Range (km)[1]
Troposphere	15 to -56	0 to (10-16)[2]
Stratosphere	-56 to -2	(10-16) to 50
Mesosphere	-2 to -92	50 to 85
Thermosphere	-92 to 1200	85 to 500

---

1. These figures give the boundary of each region.

2. The boundary between the troposphere and stratosphere varies from 10 - 16 km.

The troposphere contains approximately 80 percent of the total mass of the atmosphere. This is the region where almost all the "weather" such as rain, clouds, and snow occurs. The troposphere is characterized by a decrease in temperature (15^{o} to $-56^{o}C$) with increasing altitude. Its composition is fairly homogeneous due to the mixing caused by the constantly circulating air masses. For persistent compounds like carbon tetrachloride, the ambient concentration can steadily increase because these compounds are effectively trapped in the troposphere by a thermal barrier, the tropopause.

The tropopause is the boundary region that separates the troposphere and the stratosphere. This region is characterized by a stable air mass of similar temperature which acts as a barrier to vertical lifting and mixing of cooler air masses from the troposphere to the stratosphere. Because this barrier prevents convective mixing, escape through the tropopause is limited to the relatively slow diffusion process. Diffusion of carbon tetrachloride from the troposphere into the stratosphere followed by photodissociation is the primary removal mechanism for carbon tetrachloride.

The stratosphere is characterized by increasing temperature with increasing altitude due to the presence of ozone which absorbs energy in the form of ultraviolet light. The ozone may reach a concentration as high as 10 parts per million (ppm) in the mid-region of the stratosphere. The ozone acts as a filter, stopping high energy, cancer-causing, ultraviolet radiation from reaching the earth's surface. Depletion of ozone in the stratosphere will allow ultraviolet radiation to penetrate to the earth's surface which can cause increases in human skin cancer. Ultraviolet radiation below 290 nanometers is the same high energy radiation that causes carbon tetrachloride to photodissociate in the stratosphere.

2. Releases and Formation of Carbon Tetrachloride in the Atmosphere

In 1984, the ARB staff estimated that at least 60 tons of carbon tetrachloride was emitted in California from stationary sources and from pesticide/grain fumigant usage. No naturally occurring sources of carbon tetrachloride are known. It has been suggested that carbon tetrachloride can be formed in the troposphere by the photochemical reactions of tetrachloroethylene (perchloroethylene). The ARB staff believes that under normal tropospheric conditions, the amount that can be formed does not contribute significantly to ambient levels.

Under controlled laboratory conditions, Singh prepared synthetic mixtures of perchloroethylene in pure (ultrazero) air. These mixtures were irradiated for several days by simulated tropospheric sunlight in Tedlar bags or flasks. Singh estimated that 5.5 to 8.9 percent of the perchloroethylene was converted to carbon tetrachloride (Singh, et al., 1975). The authors stated that a chlorine sensitized photooxidation reaction is involved. However, in the atmosphere, the ARB and Statewide Air Pollution Research Center (SAPRC) staffs believe that chlorine scavengers would prevent chlorine sensitized photooxidation from occurring to any appreciable extent (SAPRC, 1986). The Singh experiments are not directly comparable to what would occur under normal ambient conditions because of the continuous irradiation that was employed (continuously for 5 to 7 days), as opposed to only about one-half day under ambient conditions. The ARB staff decided, however, to review the 1985 ambient carbon tetrachloride and perchloroethylene monitoring data from the ARB toxic monitoring network to determine if any correlation could be found between the two concentrations. Data for the months of May through September was used because these months have the longest insolation periods of the year.

Based on the ARB staff analysis of the monitoring data, no correlation between carbon tetrachloride and perchloroethylene concentrations was found. Where a correlation factor of 1 indicates a perfect match between perchloroethylene and carbon tetrachloride concentrations, the ARB staff estimated correlation factors of 0.0001 and 0.0008 for Northern and Southern California which indicate no correlation. Figure III-3 and III-4 summarizes the scatter plots that were derived from the analysis of the data for those two areas.

3. Removal Mechanisms for Carbon Tetrachloride in the Atmosphere

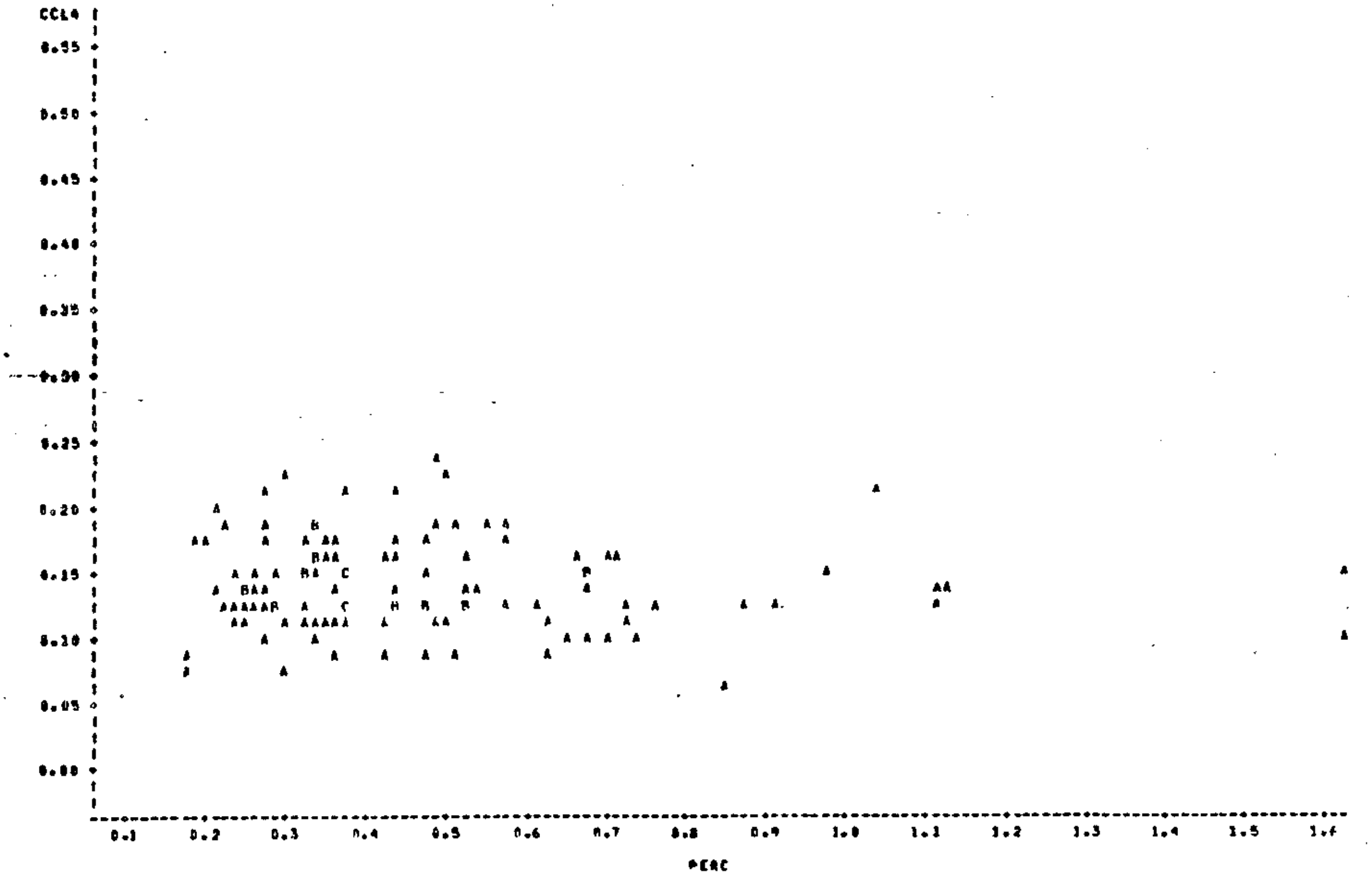
In general, gas phase reactions with radicals, primarily hydroxyl radicals, are the most important tropospheric removal mechanisms for many organic compounds once they are emitted in the troposphere. Other removal mechanisms which may be important for organic compounds are photolysis, absorption into the oceans, adsorption onto particulate matter, wet deposition, and absorption and decomposition in biological systems. However, these removal mechanisms are very slow when it comes to removing carbon tetrachloride from the troposphere. Because of its slow removal rate from the troposphere, carbon tetrachloride accumulates in this region

Figure III-3

Results of Carbon Tetrachloride to Perchloroethylene

Correlation Analysis - Northern California

Correlation Factor = 0.0001

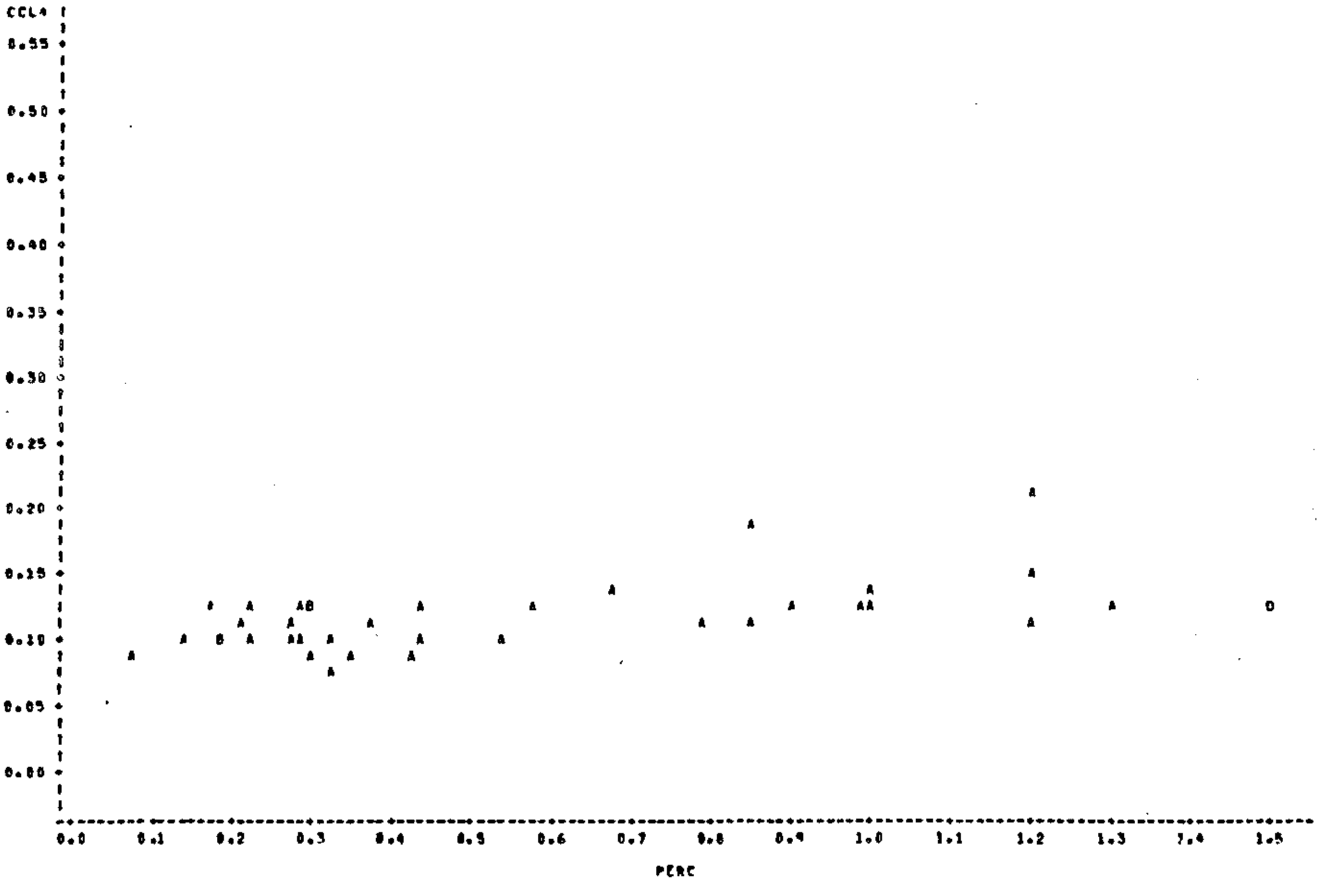


Legand: A = 1 observation, B = 2 observation, etc.

Figure III-4

Results of Carbon Tetrachloride to Perchloroethylene Correlation Analysis - Southern California

Correlation Factor = 0.0008



Legand: A = 1 observation, B = 2 observation, etc.

of the atmosphere. Estimates of the atmospheric lifetime for carbon tetrachloride have ranged from 18 to over 100 years (Galbally, 1976; Singh, et al., 1976; Cox, et al., 1976; Borchers, et al., 1983; EPA, 1987). However, the ARB staff believes that the best estimate, based on the extensive Atmospheric Lifetime Experiment, is approximately 50 years (Simmonds, et al., 1983). This is in agreement with a recent estimate where the atmospheric lifetime of carbon tetrachloride was calculated to be 48 years (Golombek and Prinn, 1986). Table III-3 summarizes the various atmospheric removal mechanisms which are discussed in terms of first order removal rates and estimated removal times. The estimated atmospheric lifetimes, the removal rates, and removal times were summarized from available information obtained as of May 1987.

Of the identified removal mechanisms, diffusion from the troposphere to the stratosphere is the major pathway by which carbon tetrachloride is removed from the troposphere. Once in the stratosphere, carbon tetrachloride becomes reactive in the presence of the short wavelengths of ultraviolet light (Simmonds, et al., 1983; Atkinson, et al., 1976; Lillian, et al., 1975; Galbally, 1976). The initial process in the stratospheric photolysis of carbon tetrachloride at a wavelength of about 225 nanometers involves the detachment of one chlorine atom yielding a trichloromethyl radical and a chlorine atom (National Research Council, 1978; Rebbert and Ausloos, 1976).

$$CCl_4 + h\nu \longrightarrow .CCl_3 + Cl$$

The chlorine atoms can then react with ozone in the stratosphere, thus, contributing to the depletion of ozone.

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

TABLE III-3

Atmospheric Removal Mechanisms and Their Estimated Removal Times

Removal Process	Removal Time[1] τ (years)	Removal Rate $1/\tau$ ($year^{-1}$)	Reference
Stratospheric Photolysis	50	2.0×10^{-2}	Simmonds, et al., 1983
	59	1.7×10^{-2}	NAS, 1976
	40-111	$0.9 - 2.5 \times 10^{-2}$	Galbally, 1976
	30-50	$2 - 3.3 \times 10^{-2}$	Molina and Rowland, 1974
Gas Phase Reactions			
Reactions with $O(^1D)$	667-2000	$0.6 - 1.8 \times 10^{-3}$	Galbally, 1976
Reactions with OH	>330	3×10^{-3}	Cox, et al.,1976
	>8	$<1.3 \times 10^{-1}$	Howard and Evenson, 1976
Absorption into oceans	95-286	$3.5 - 10.5 \times 10^{-3}$	Galbally, 1976
Biological Removal	333-1000	$1.0 - 3.0 \times 10^{-3}$	Galbally, 1976
Adsorption on Silicates	NR[2]	NR	Ausloos,et al.,1977
Wet Deposition	NR	NR	Ohta, et al.,1976

---

[1] The removal time is an estimate of the time required for a given amount of compound to decrease 1/e (0.368) of its original value at time zero.

[2] NR means not reported.

Ozone is very important because it absorbs harmful, high-energy, cancer-causing ultraviolet radiation below 290 nanometers from reaching the earth's surface. Depletion of ozone will allow the ultraviolet radiation to reach the earth's surface which can lead to increased skin cancers in humans.

In support of the stratosphere as a sink, atmospheric measurements of the stratospheric profile of carbon tetrachloride show that its concentration decreases rapidly with altitude (Seiler, et al., 1978; Pierotti, et al., 1980; Borchers, et al., 1983). Simmonds reports that Golombek estimated the stratospheric lifetime of carbon tetrachloride to be 7 1/2 years with an overall atmospheric lifetime of approximately 50 years (Simmonds, et al., 1983).

Absorption into the oceans is believed to be the second most important atmospheric removal mechanism for carbon tetrachloride (Simmonds, et al., 1983; Galbally, 1976). The ocean as a removal mechanism is supported by Liss and Slater who have estimated that from the troposphere, 16 tons per year of carbon tetrachloride is removed to the ocean (Liss and Slater, 1974). In deriving that estimate, Liss and Slater applied Fick's first law of diffusion and Henry's law to the atmospheric/oceanic interface. They also had to estimate gas and liquid phase resistances and utilized Henry's Law constants given by Lovelock, as well as atmospheric and oceanic carbon tetrachloride concentrations estimated by Lovelock (Liss and Slater, 1974). Galbally has estimated that tropospheric removal times by the oceans range from 95 to 286 years (Galbally, 1976). Since carbon tetrachloride is highly resistant to hydrolysis with a half-life of 70,000 years, other oceanic removal processes are probably occurring. Although these removal processes have not been identified, it is speculated that carbon tetrachloride bioaccumulates in marine organisms with subsequent incorporation into sediments (Singh, 1976; NAS, 1976).

In the troposphere, no other removal mechanisms have been shown to be more rapid for carbon tetrachloride than the two mechanisms discussed above. Photolysis is not a significant removal mechanism for carbon tetrachloride in the troposphere because the short wavelengths of ultraviolet light (around 225 nanometers) required for photolysis are absorbed by ozone in the stratosphere and therefore, do not reach the troposphere (Rebbert and Ausloos, 1976; Atkinson, 1986). In addition, gas phase reactions with methyl radicals, hydrogen atoms, and ground state oxygen atoms are not important tropospheric removal mechanisms for carbon tetrachloride (Winer, 1986; Galbally, 1976). These species are not energetic enough to degrade carbon tetrachloride at a significant rate (Winer, 1986).

The most important identified tropospheric gas phase reaction for carbon tetrachloride involves hydroxyl radicals. The uppper-limit rate constants for the reaction of carbon tetrachloride with hydroxyl radicals have been estimated at 4×10^{-15} cm^3/molecule-sec (absolute rate constant) and 1×10^{-16} cm^3/molecules-sec (relative rate constant) (Howard and Evenson, 1976; Cox, et al., 1976). Assuming an average tropospheric hydroxyl radical concentration of 1×10^6 molecules/cm^3, the lower limit atmospheric lifetime for carbon tetrachloride was estimated to be between 8 and 330 years, respectively. However, the upper limit rate constant which gave the lower limit lifetime estimate of 8 years for carbon tetrachloride is questionable because there was an initial drop in the hydroxyl radical concentration, possibly due to a wall effect (Howard and Evenson, 1976). Thus, the actual lower lifetime estimate for carbon tetrachloride due to reaction with hydroxyl radicals is expected to be longer than 8 years.

The reaction of carbon tetrachloride with excited oxygen atoms ($O(^1D)$) is not expected to be an important atmospheric removal mechanism (Galbally, 1976; Atkinson, et al., 1976; Atkinson, 1986). Galbally estimated the atmospheric removal time of carbon tetrachloride due to reaction with $O(^1D)$ at over 650 years (Galbally, 1976). Although $O(^1D)$ is an extremely reactive species, its tropospheric concentration is too low for it to be an important removal mechanism (NAS, 1976). In the stratosphere, where the concentration of $O(^1D)$ is significantly higher than in the troposphere, the degradation of carbon tetrachloride resulting from its reaction with $O(^1D)$ is minor compared to stratospheric photolysis. Atkinson determined an upper limit relative rate constant of 4.2×10^{-10} cm^3/molecules-sec for the reaction of carbon tetrachloride with $O(^1D)$ (Atkinson, et al., 1976). Using this rate constant and a stratospheric $O(^1D)$ concentration of one molecule $O(^1D)/cm^3$, the upper limit stratospheric lifetime of carbon tetrachloride due to reaction with $O(^1D)$ is 75 years. However, the determination of the rate constant reported by Atkinson was complicated by the photolysis of carbon tetrachloride at a rate approximately the same as carbon tetrachloride's reaction with $O(^1D)$. Thus, the rate constant results reported by Atkinson could contain uncertainties (Atkinson, et al., 1976).

A potential removal mechanism which has not been quantified is adsorption onto particulate matter. It has been demonstrated in the laboratory that carbon tetrachloride adsorbed on silica sand or fused quartz decomposes when irradiated with wavelengths above 310 nm (Ausloos, et al., 1977). These wavelengths do reach the troposphere. Limited ambient monitoring in the Saharan troposphere also indicated lower concentrations of carbon tetrachloride in dust cloud samples relative to non-dusty samples (Pierotti, et al., 1978). Although this data suggests that a tropospheric removal mechanism may be acting, it has yet to be conclusively verified and therefore, could not be accounted for in this discussion.

Wet deposition is not expected to be a major tropospheric removal mechanism for carbon tetrachloride. For three compounds including carbon tetrachloride, Ohta demonstrated that wet deposition increased with the compounds' solubility in water (Ohta, et al., 1977). Since carbon tetrachloride is only slightly soluble in water, wet deposition is probably not as important as it is for compounds with greater water solubilities. If carbon tetrachloride is removed by wet deposition, it would be expected to volatilize and re-enter the troposphere.

Another minor tropospheric removal mechanism that has been proposed involves absorption and microbial action in soil and vegetation (NAS, 1976). Galbally estimated the tropospheric removal time of carbon tetrachloride by land biota to be in excess of 333 years (Galbally, 1976).

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APPENDIX A

Atmospheric Lifetime Experiment (ALE)

A. Atmospheric Lifetime Experiment

In 1978 Cunnold, Alyea, and Prinn discussed two different methods for determining the atmospheric lifetimes of chlorofluorocarbons. One method, the "inventory technique", requires knowledge of the atmospheric content and emission history to determine the lifetime. The other method, the "trend technique", requires knowledge of the atmospheric accumulation rate and emission history to determine the lifetime. The "trend technique" is deemed to be the more reliable due to the relative unimportance of absolute measurement accuracy and systematic errors in emissions data; however, the "trend technique" required 3 to 5 years of data with observations made at least daily. Cunnold (et al., 1978) proposed that a remote-station, data-gathering network be implemented.

Based on the above study, Prinn (et al., 1983) began an experiment entitled the "Atmospheric Lifetime Experiment" (ALE), which utilizes the following five globally distributed coastal measurement stations: (1) Adrigole, Ireland, 52°N, 10°W; (2) Cape Meares, Oregon, 45°N, 124°W; (3) Ragged Point, Barbados, 13°N, 59°W; (4) Point Matatula, American Samoa, 14°S, 171°W; and (5) Cape Grim, Tasmania, 41°S, 145°E. Because most of the industrial emissions of chlorofluorocarbons occur in the northern hemisphere at midlatitudes, it was considered highly desirable that two stations operate at these latitudes to avoid the biases that could result from reliance on any one station alone. Each of the ALE stations is intended to be representative of one of the four equal mass subdivisions of the global atmosphere; 0° to 30°N, 30° to 90°N, 0° to 30°S, and 30° to 90°S.

All five ALE stations are equipped with the same microprocessor-controlled Hewlett Packard 5840A dual-channel electron-capture gas chromatograph (Prinn, et al., 1983). Outside air is drawn into each of the instruments by means of a noncontaminating metal bellows pump along a stainless steel line that is securely attached to a large pole so that the air intake is at least 2.0 m above the roof of the instrument building. Separate analysis of a calibration standard as close in concentration to ambient as possible, and under the same conditions, is performed routinely within one hour of the ambient air analysis. Measurement runs along with their accompanying calibration runs are done three to four times daily on the average. At most sites a local caretaker or trained technician makes a daily visit to the station to verify routine performance of the instruments, and each station is visited at least quarterly by the station scientist for detailed servicing of the instrument and for replacement of the calibration gas tank. Considerable care is taken to maintain 1% precision of analysis at ambient levels.

The field calibration standards are prepared at the Cape Meares station by cryogenically liquefying clean ambient air into 35-liter, aircraft-surplus, breathing-oxygen tanks of type-304 stainless steel, passivated by an electropolish (Rasmussen and Lovelock, 1983). The determination of concentrations in the tanks relative to the primary standard is carried out both before and after the use of the tank at a particular site, with each determination consisting of at least six separate analyses. Decline of carbon tetrachloride concentrations in the tanks from heterogeneous surface reaction has been estimated to be 0.15 ±

0.20% per year. Absolute calibration of standards for carbon tetrachloride concentration has been determined by coulometry; the method of exponential dilution for absolute calibration proved to be unreliable for carbon tetrachloride, due to adsorption of the compound onto the glass ampoule by which the compound was introduced to the dilution chamber. The accuracy of absolute calibration for carbon tetrachloride determined by coulometry alone is estimated to be 4%, but 11% is believed to be the more reasonable estimate according to Simmonds (et al., 1983).

Simmonds (et al., 1983) presented ALE results for carbon tetrachloride based on 3 years of data taken from July 1978 to June 1981. The average concentration of carbon tetrachloride in the lower troposphere was 118 pptv (121 pptv in the northern hemisphere), with the average of monthly standard deviations being less than 2 pptv, and was increasing by 2.1 pptv per year. Using a two-dimensional atmospheric transport model consisting of eight tropospheric boxes and one stratospheric box (Cunnold, et. al., 1983), the atmospheric lifetime (1/e-life) of carbon tetrachloride was calculated by the "inventory technique" to be 57 years. Using an optimal estimation technique, incorporating the two-dimensional model, the atmospheric lifetime was calculated by the "trend technique" to be 50 years. The maximum likelihood combination of these two lifetime estimates is 52 years (Simmonds, et al., 1983) and is estimated to be accurate within 30 percent (Prinn, 1986). The inaccuracy of lifetime estimates for carbon tetrachloride is due primarily to incomplete knowledge of emissions history.

Table A-1

Summary of the ALE Monitoring Results

Month	Adrigole, Ireland			Cape Meares, Oregon			Ragged Point, Barbados			Point Matatula, American Samoa			Cape Grim Tasmania		
	χ	σ	N	χ	σ	N	χ	σ	N	χ	σ	N	χ	σ	N
July 1978	-	-	-				114.6	2.7	144	110.7	1.8	61	113.8	2.3	54
Aug. 1978	-	-	-				116.0	2.3	200	111.1	2.0	125	113.1	1.8	124
Sept. 1978	-	-	-				115.3	3.0	165	111.4	1.6	126	113.7	1.6	72
Oct. 1978	-	-	-				114.3	3.5	111	111.2	1.7	106	113.9	1.4	44
Nov. 1978	-	-	-				113.2	3.6	134	113.0	2.3	97	114.3	1.1	70
Dec. 1978	-	-	-				116.6	3.5	131	114.0	1.5	60	113.8	0.8	47
Jan. 1979	-	-	-				118.3	2.8	121	114.9	1.1	18	113.1	1.1	58
Feb. 1979	-	-	-				118.1	2.8	118	113.8	1.5	95	112.6	1.0	92
March 1979	-	-	-				115.9	2.8	94	113.6	1.2	117	112.9	1.3	111
April 1979	-	-	-				-	-	-	114.3	1.5	110	113.2	0.8	115
May 1979	-	-	-				117.9	1.5	80	114.2	1.0	121	113.2	1.1	110
June 1979	-	-	-				118.3	1.5	40	114.2	0.8	115	113.0	1.0	112
July 1979	-	-	-				118.1	1.7	104	114.9	0.9	118	113.0	1.0	94
Aug. 1979	-	-	-				117.9	1.5	123	114.9	0.9	111	112.8	0.9	118
Sept. 1979	-	-	-				117.2	1.6	136	114.8	1.3	99	112.8	0.8	106
Oct. 1979	-	-	-				117.6	1.4	134	115.6	1.1	115	114.1	1.0	94
Nov. 1979	-	-	-				118.5	1.5	96	112.6	1.2	115	114.4	1.1	110
Dec. 1979	126.1	1.7	53	123.4	1.7	55	119.2	1.3	129	115.0	1.5	102	114.5	0.9	85
Jan. 1980	128.2	2.3	61	124.1	1.5	74	119.9	1.5	132	116.5	1.5	99	114.5	1.0	94
Feb. 1980	126.4	2.5	108	123.0	2.2	31	119.6	1.4	105	115.9	1.5	122	114.8	0.9	72
March 1980	124.8	1.7	89	123.5	1.8	10	120.8	1.4	128	115.5	1.4	105	115.3	0.9	117
April 1980	126.3	3.2	104	122.1	0.9	87	120.4	1.5	124	115.7	1.5	115	116.2	1.2	79
May 1980	126.0	2.1	61	122.1	0.8	98	120.5	1.3	137	116.0	1.0	116	116.8	0.9	88
June 1980	125.8	1.8	114	122.0	0.8	114	120.9	1.1	147	116.0	0.8	94	116.6	0.8	85
July 1980	125.9	1.6	110	121.7	1.1	91	120.9	1.4	129	116.2	0.7	117	115.3	1.1	105
Aug. 1980	125.7	1.5	119	121.3	0.9	82	121.2	1.9	47	116.4	0.8	117	115.2	0.7	102
Sept. 1980	125.2	1.9	109	122.6	1.1	112	120.2	1.4	125	116.3	1.2	100	116.1	1.1	74
Oct. 1980	125.2	2.0	79	123.7	1.1	126	120.6	1.7	126	116.1	0.7	17	114.9	1.2	81
Nov. 1980	127.2	1.6	79	124.2	1.2	123	121.2	1.9	118	116.8	0.9	63	116.5	1.5	101
Dec. 1980	127.3	2.5	66	123.9	1.3	119	121.7	1.9	117	117.3	1.1	98	116.4	0.5	96
Jan. 1981	128.3	1.9	120	125.0	1.9	132	121.7	1.4	138	117.6	1.3	42	116.6	0.6	54
Feb. 1981	129.4	2.3	66	123.8	1.2	111	121.8	1.3	119	118.3	1.1	4	115.1	0.6	46
March 1981	132.1	2.4	101	124.1	0.7	128	121.7	1.5	99	117.8	1.9	54	115.7	0.6	88
April 1981	131.5	2.0	53	124.4	0.8	113	122.6	1.6	110	118.0	1.0	136	115.8	0.6	80
May 1981	132.3	2.3	62	125.0	0.9	123	122.7	1.5	123	117.4	1.2	123	116.3	0.6	99
June 1981	127.8	2.0	78	125.0	0.9	115	122.9	1.4	110	117.7	0.9	111	116.9	0.7	62

Legend:

χ = carbon tetrachloride concentration in parts per trillion (ppt)

σ = standard deviation (ppt)

N = number of samples

The atmospheric lifetime of carbon tetrachloride, as determined by the Atmospheric Lifetime Experiment, is in close agreement with the value of 50 years obtained by Golombek (1986) based on stratospheric photodissociation using a three-dimensional model. This agreement implies that stratospheric photodissociation, as was previously suspected, is the major atmospheric removal process for carbon tetrachloride.

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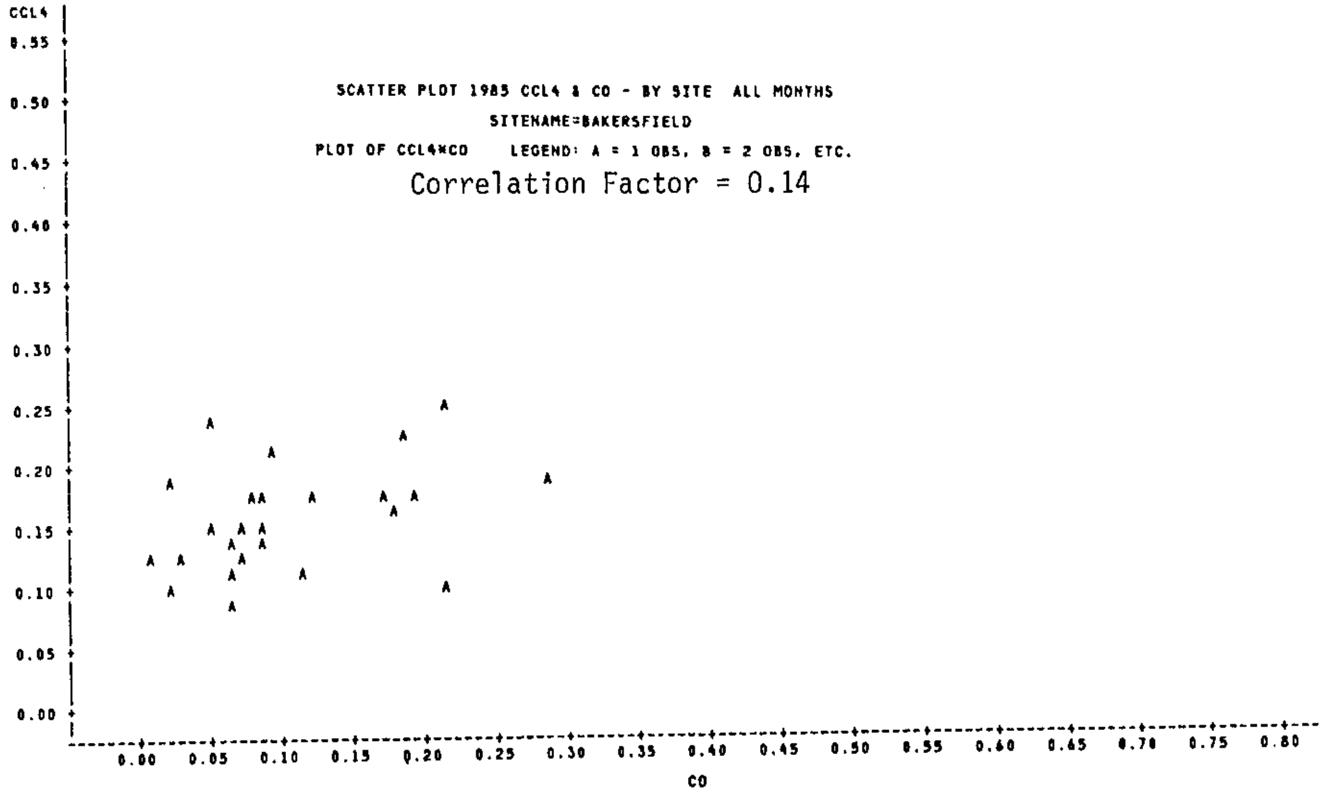
APPENDIX B

Plots From the Carbon Monoxide Versus Carbon Tetrachloride Correlation Analysis

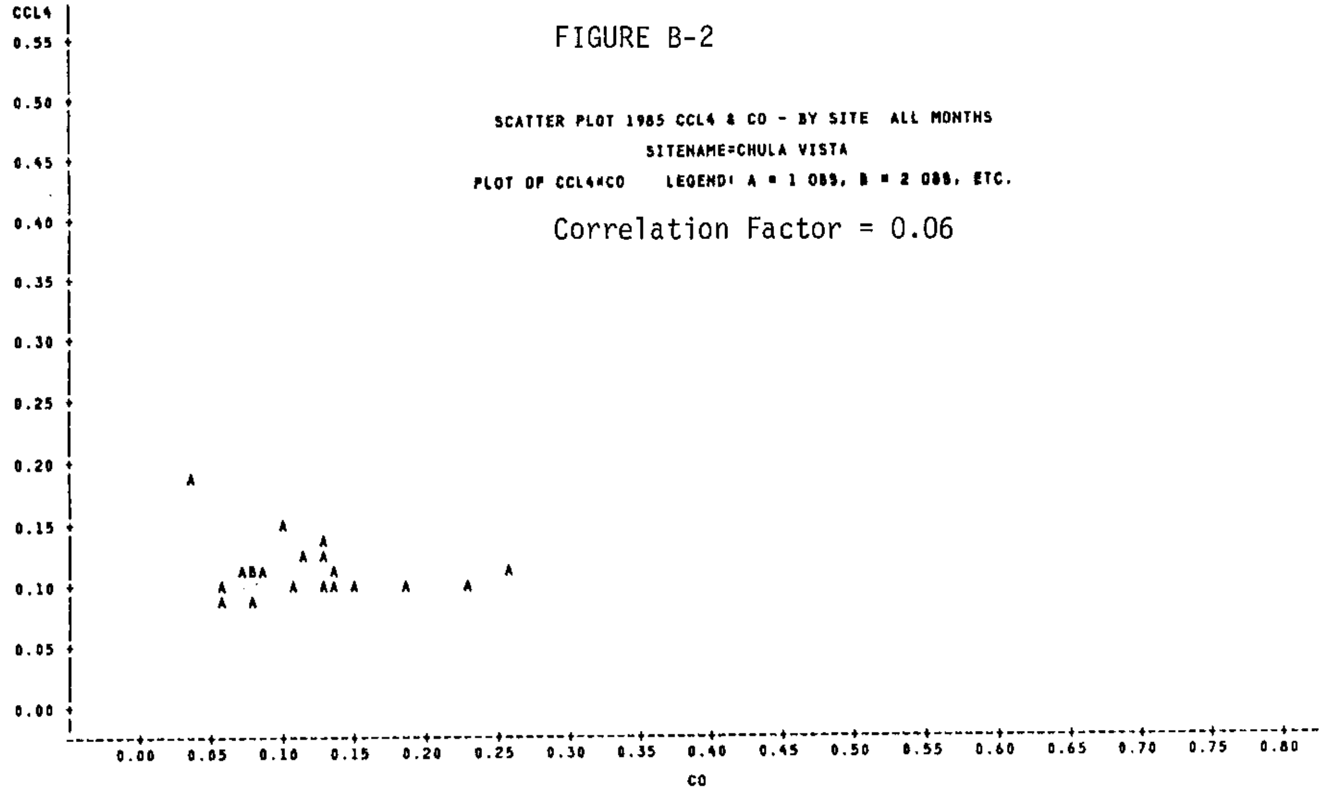
FIGURE B-1



SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=BAKERSFIELD
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.
Correlation Factor = 0.14

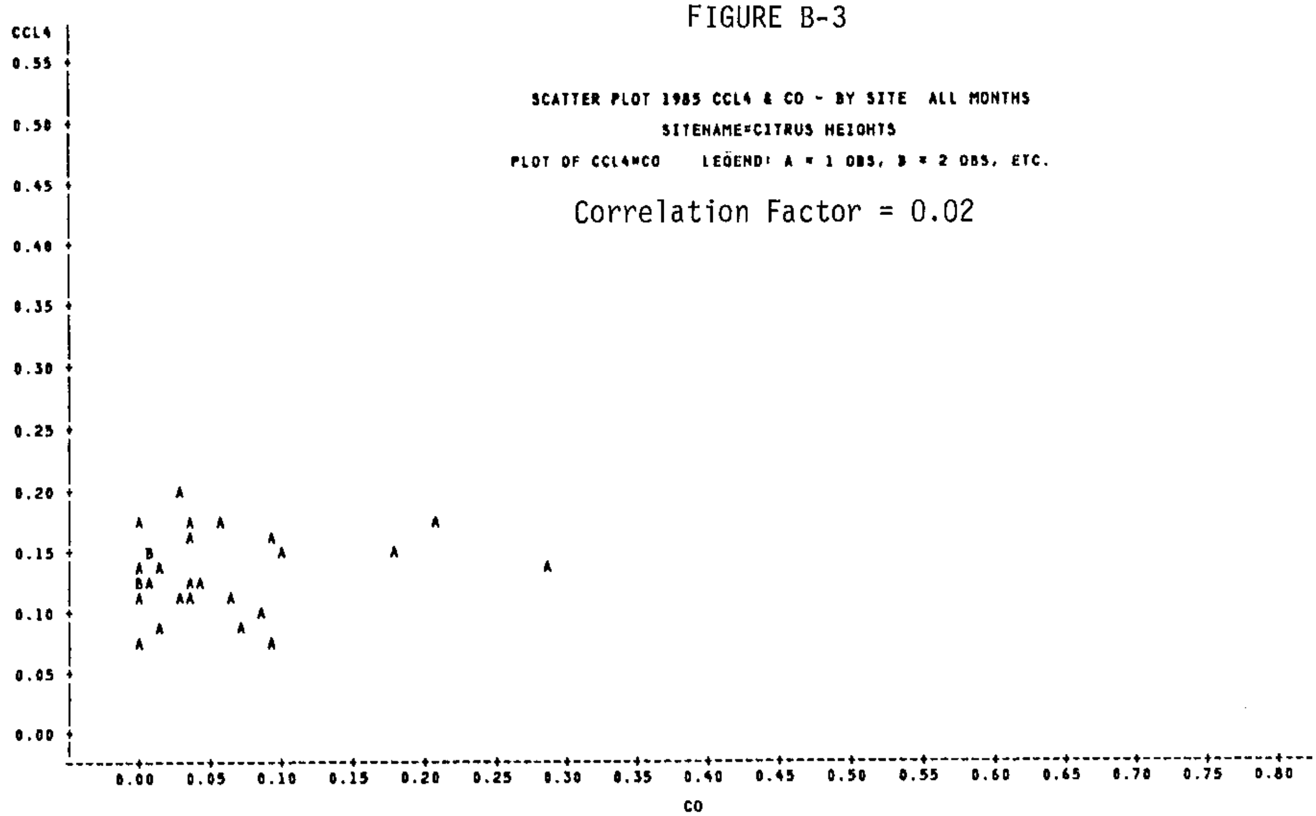
NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

FIGURE B-2



SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=CHULA VISTA
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.
Correlation Factor = 0.06

FIGURE B-3



SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS

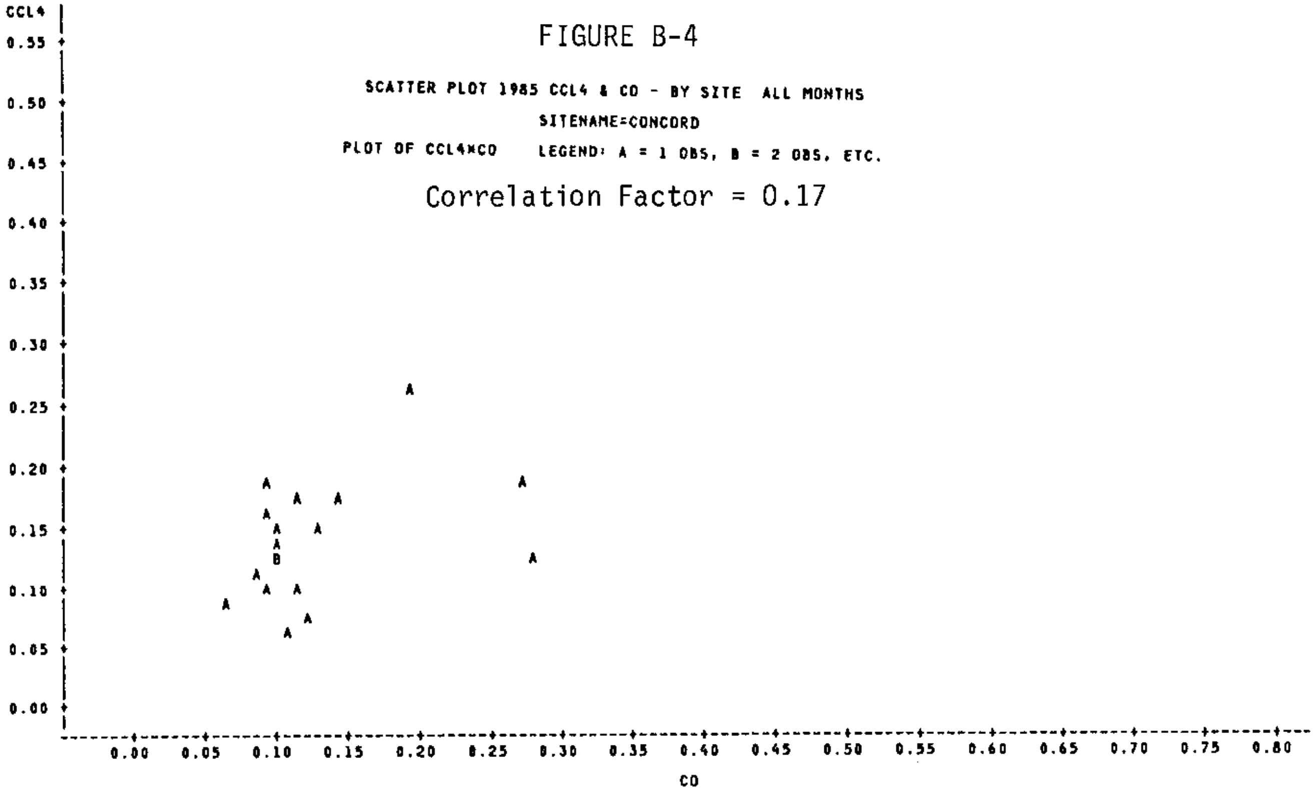
SITENAME=CITRUS HEIGHTS

PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.02

NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

FIGURE B-4



SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS

SITENAME=CONCORD

PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.17

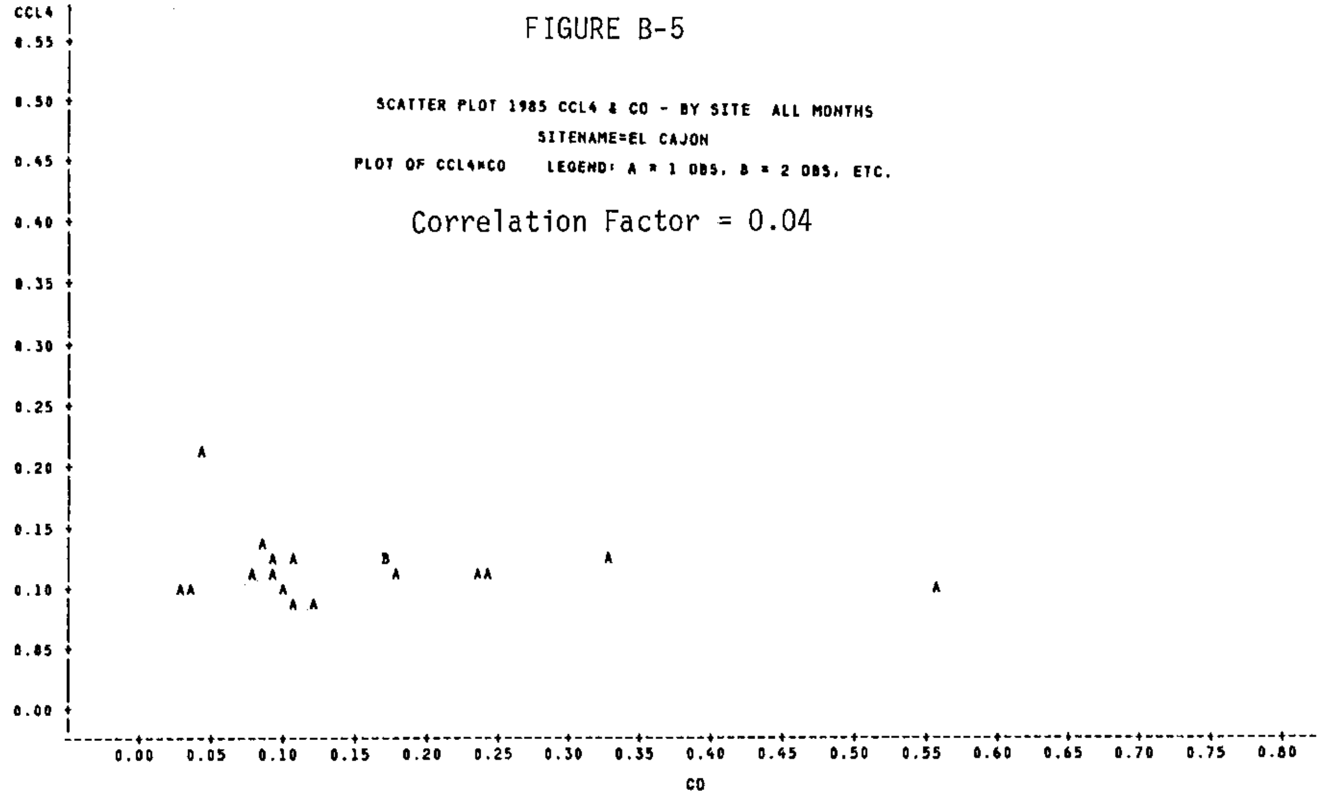


FIGURE B-5

SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS

SITENAME=EL CAJON

PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.04

NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

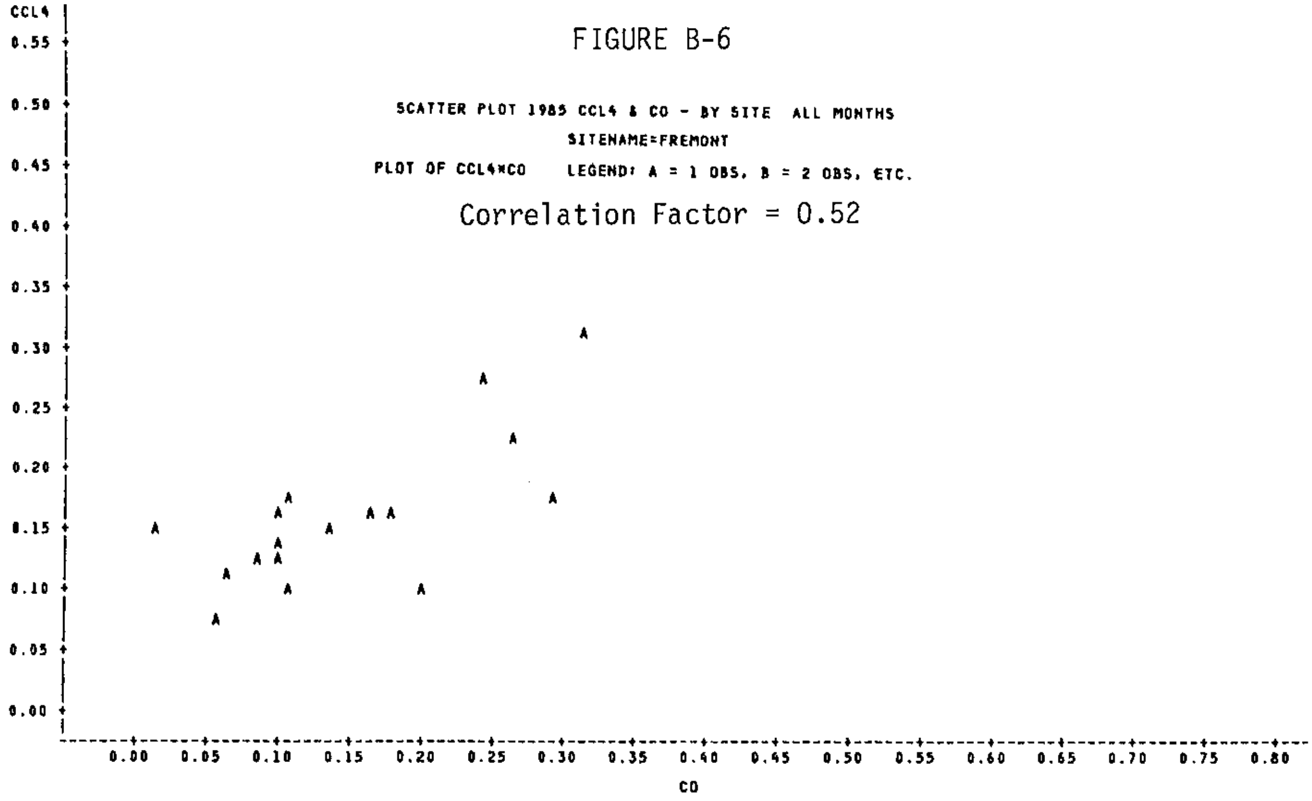


FIGURE B-6

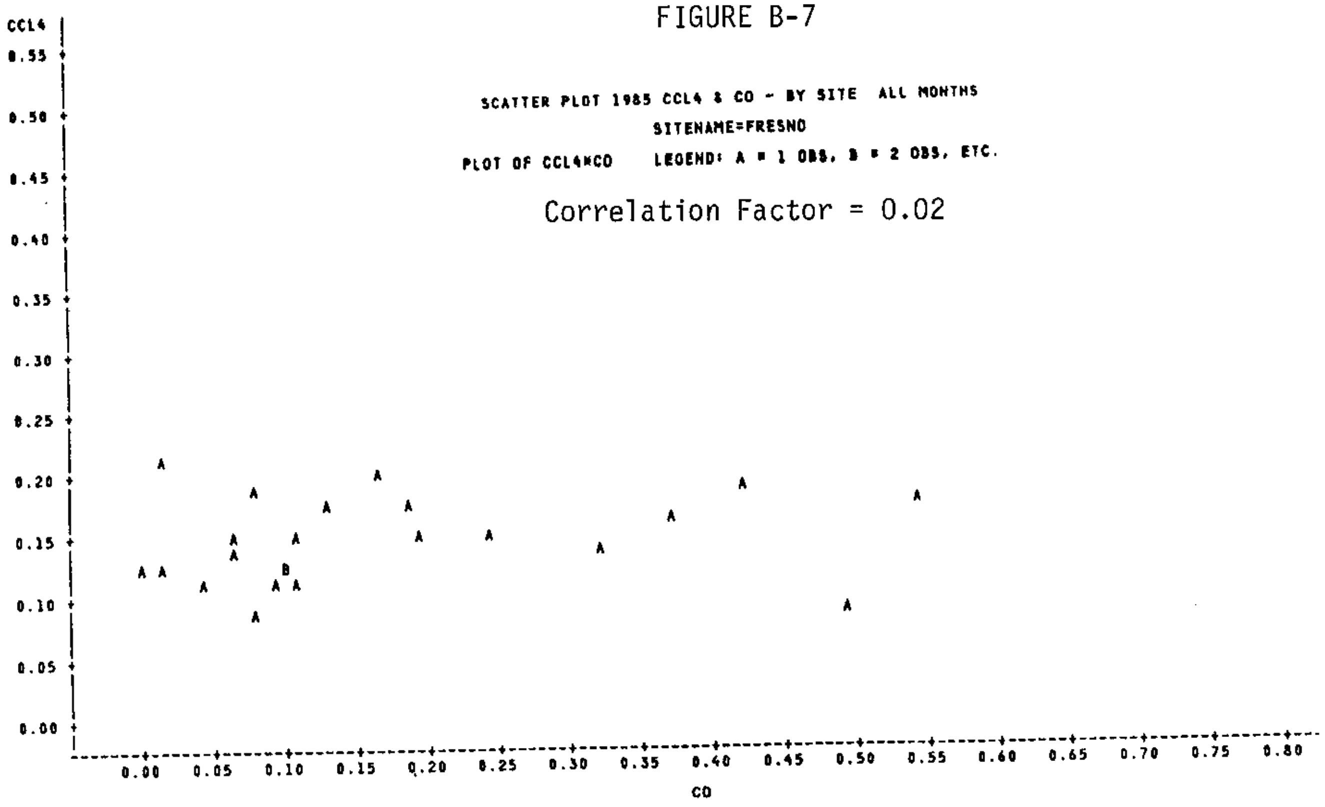
SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS

SITENAME=FREMONT

PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.52

FIGURE B-7

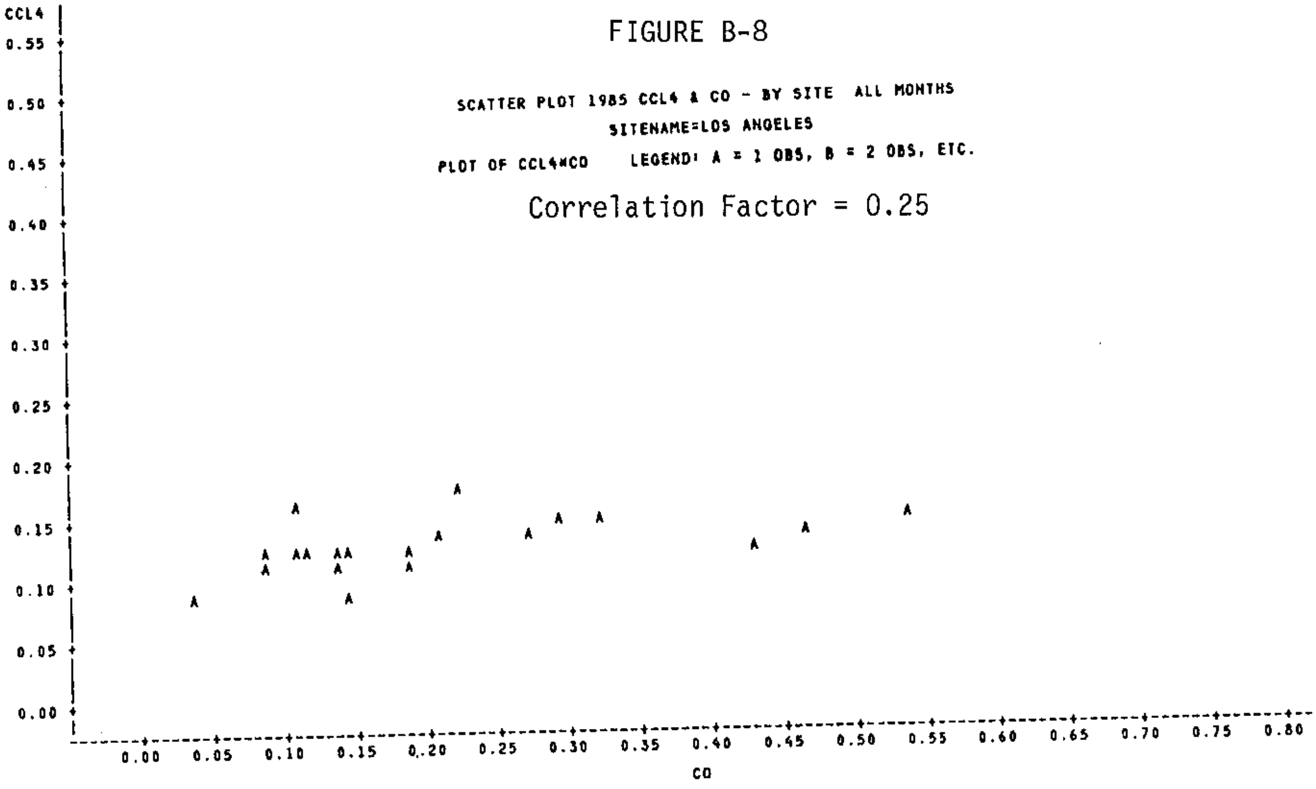


SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=FRESNO
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.02

NOTE: 2 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

FIGURE B-8

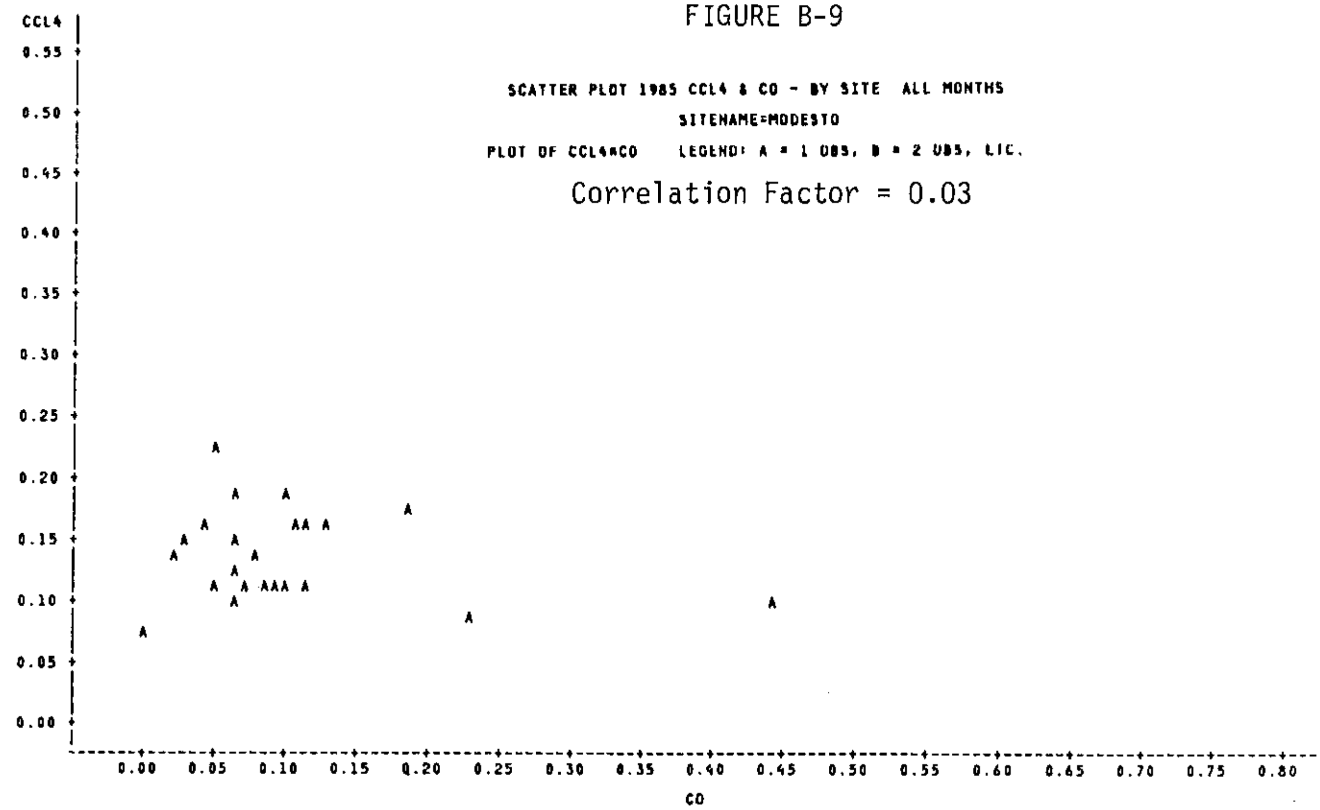


SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=LOS ANGELES
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.25

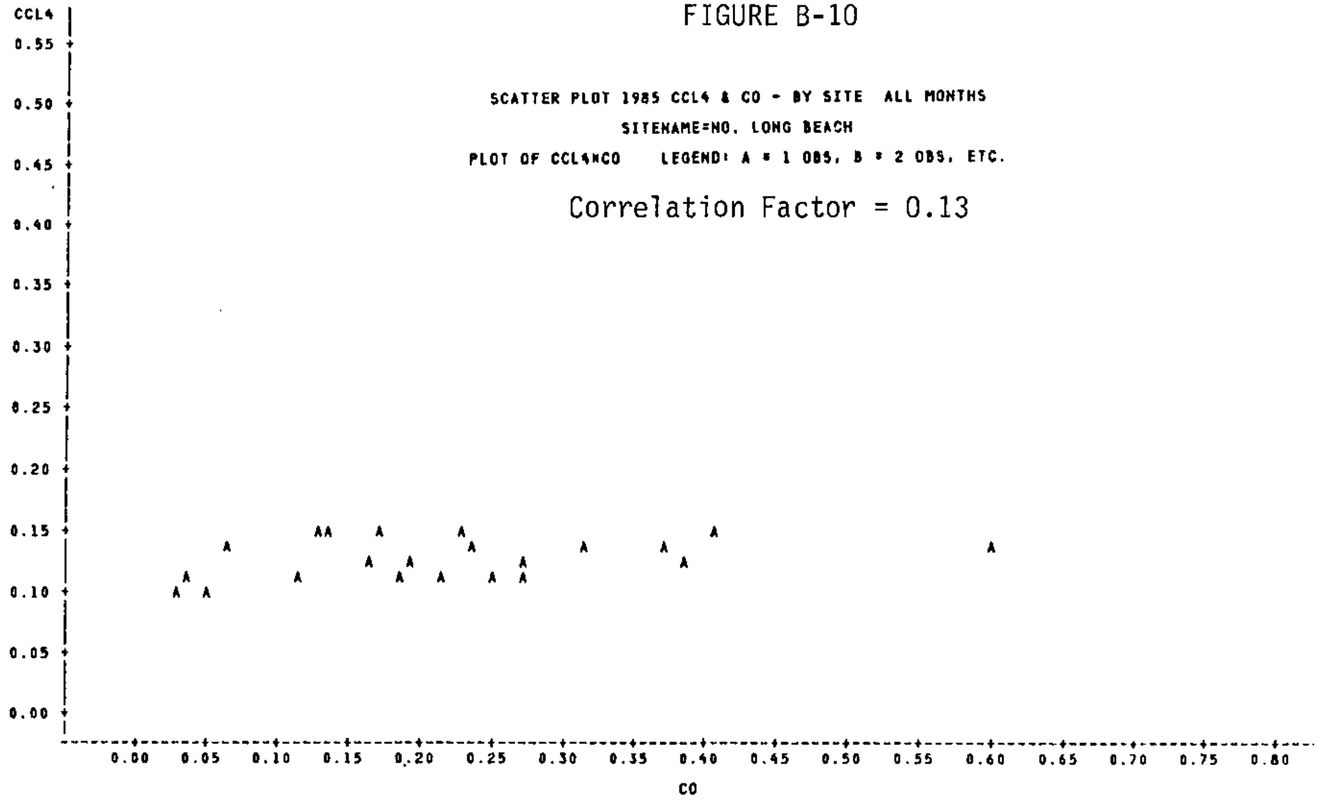
NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

FIGURE B-9



NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

FIGURE B-10



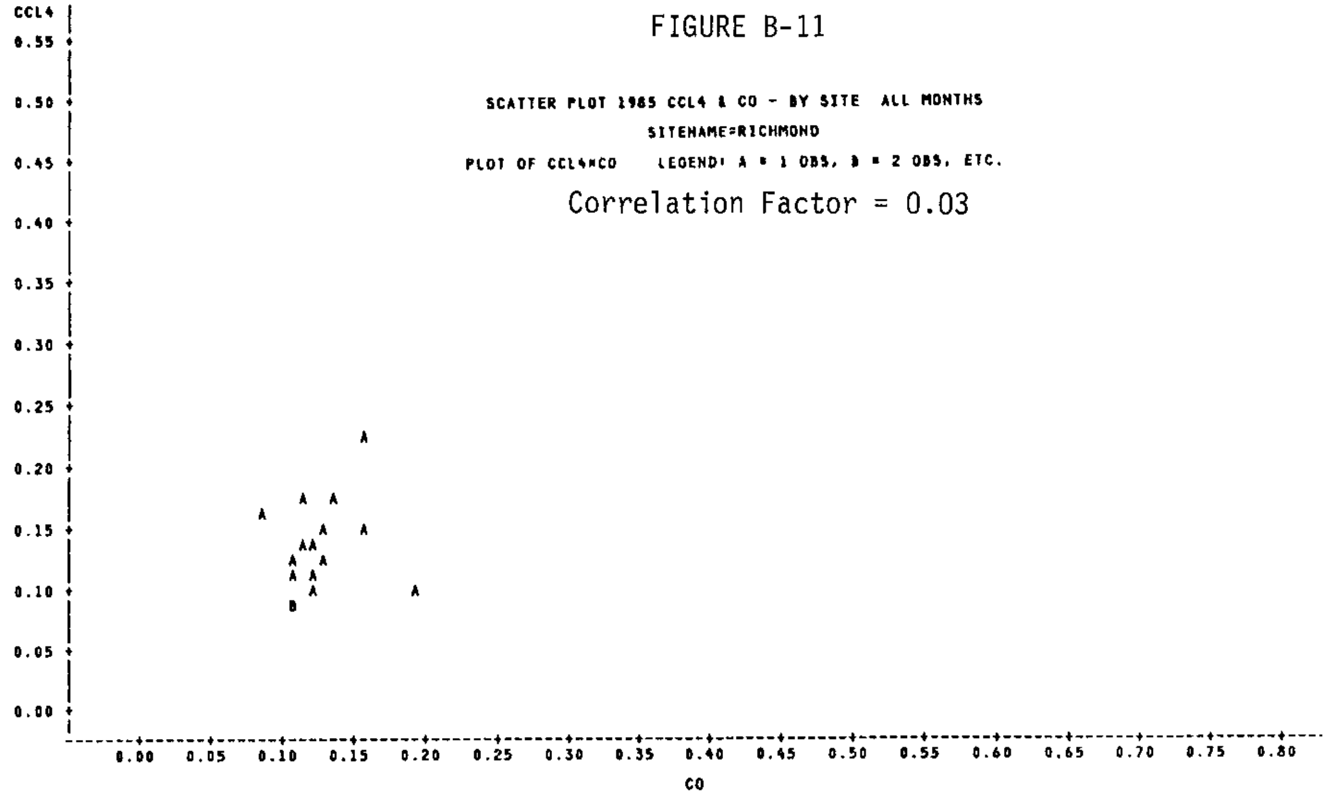


FIGURE B-11

SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=RICHMOND
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.03

NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

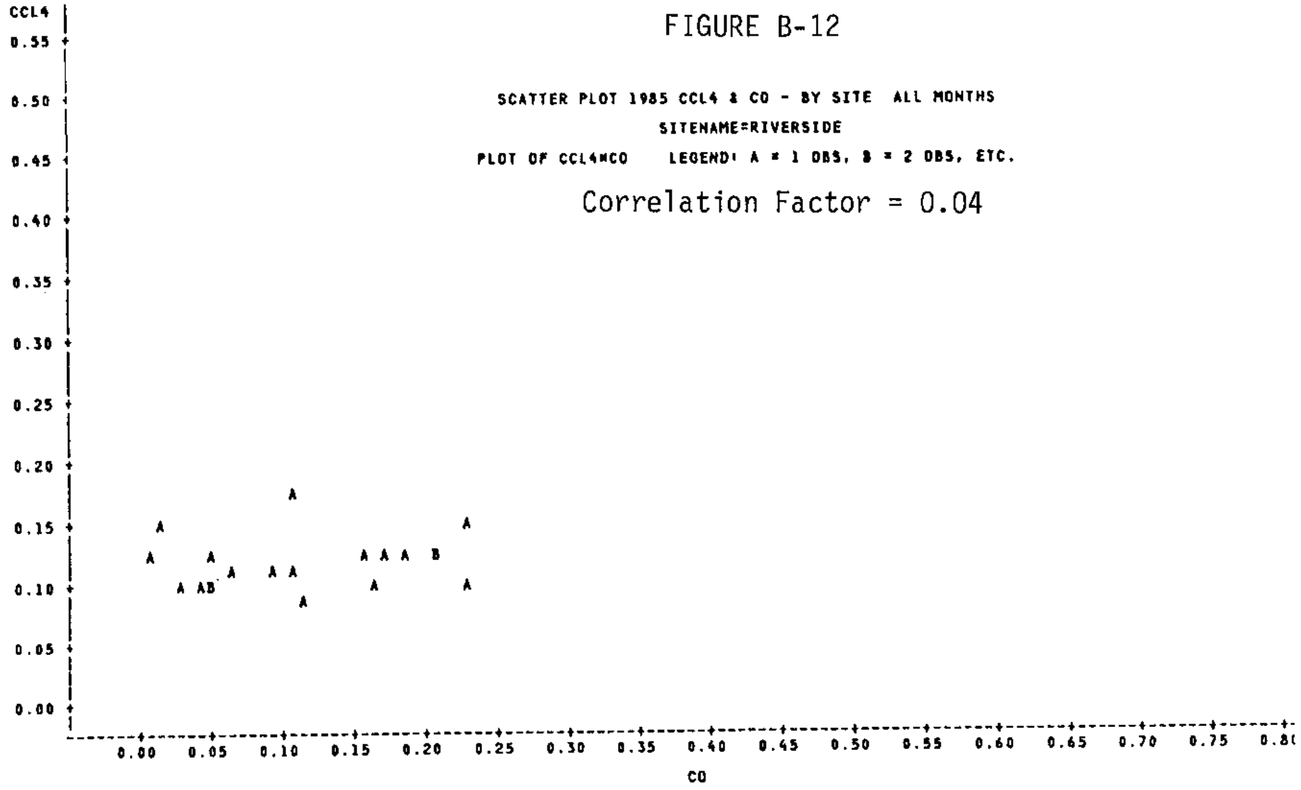


FIGURE B-12

SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=RIVERSIDE
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.04

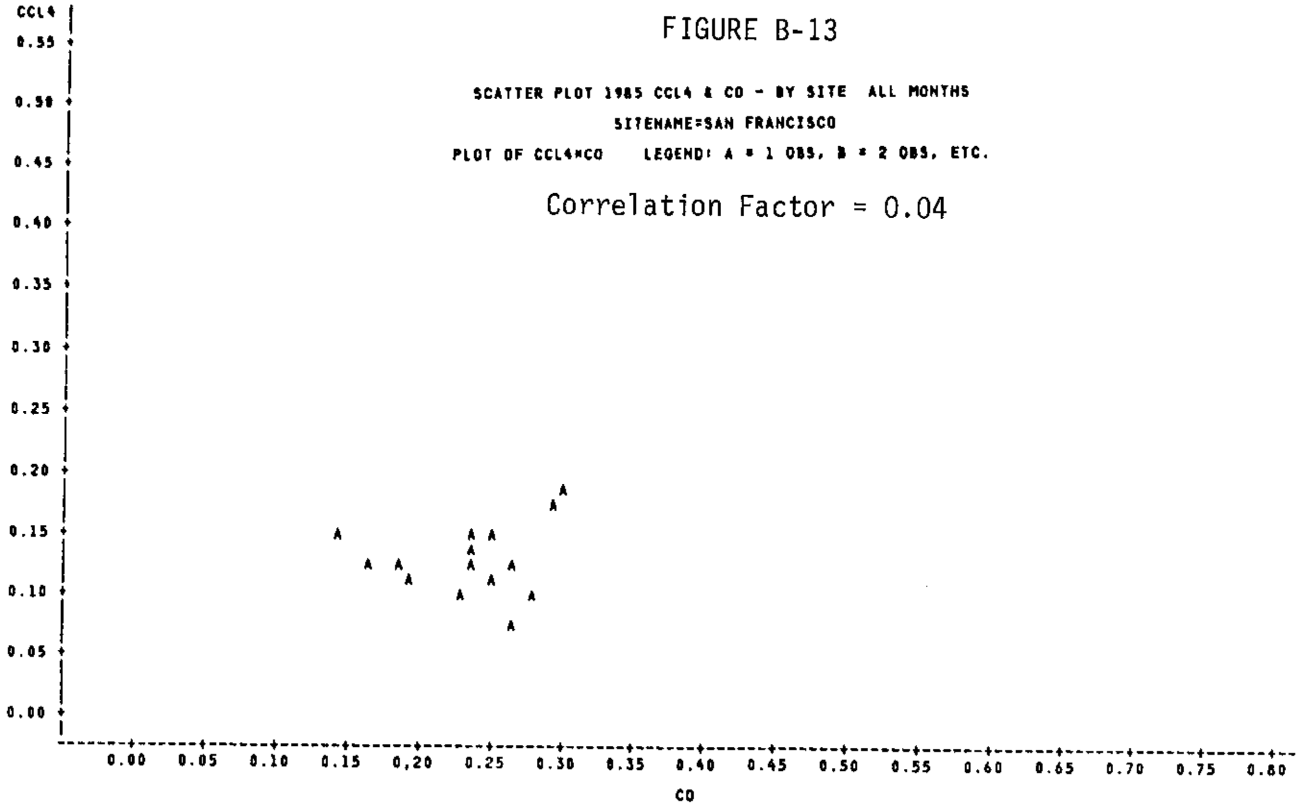


FIGURE B-13

SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=SAN FRANCISCO
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.04

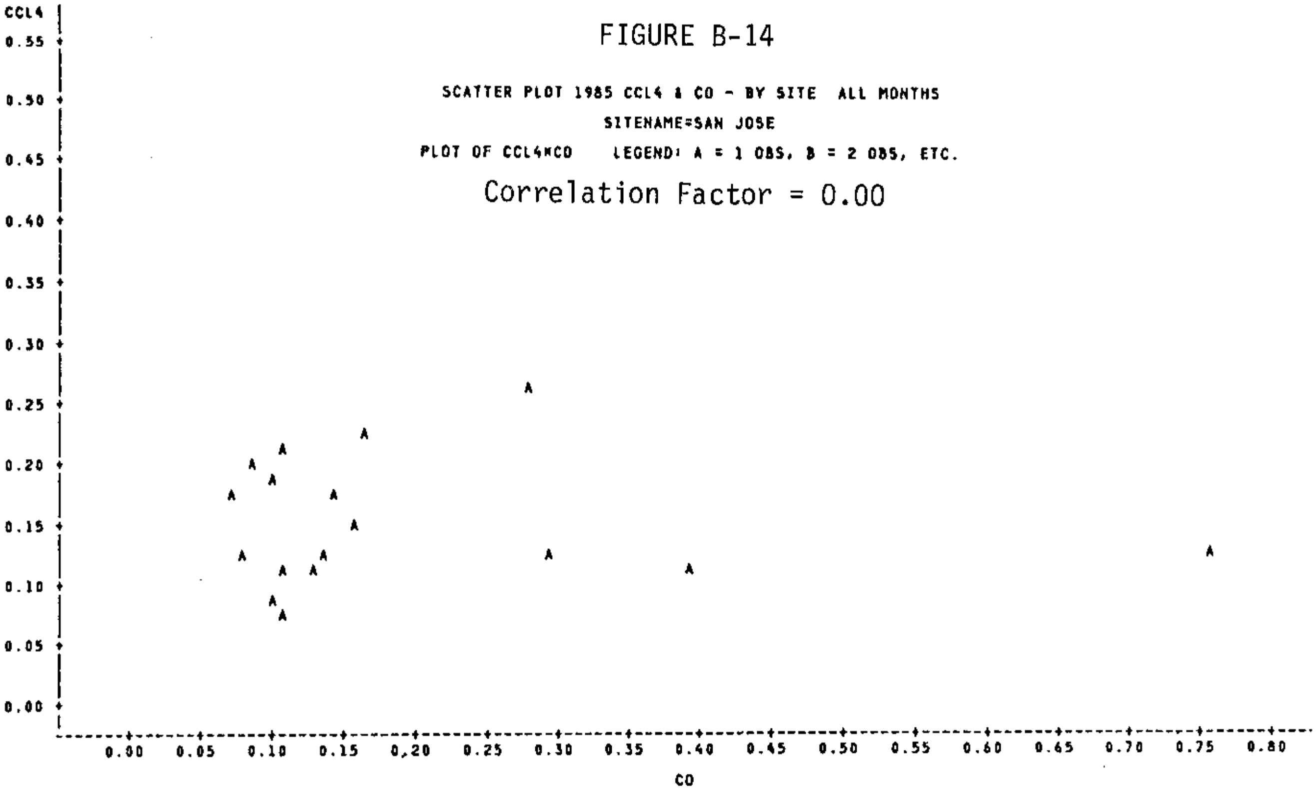


FIGURE B-14

SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=SAN JOSE
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.00

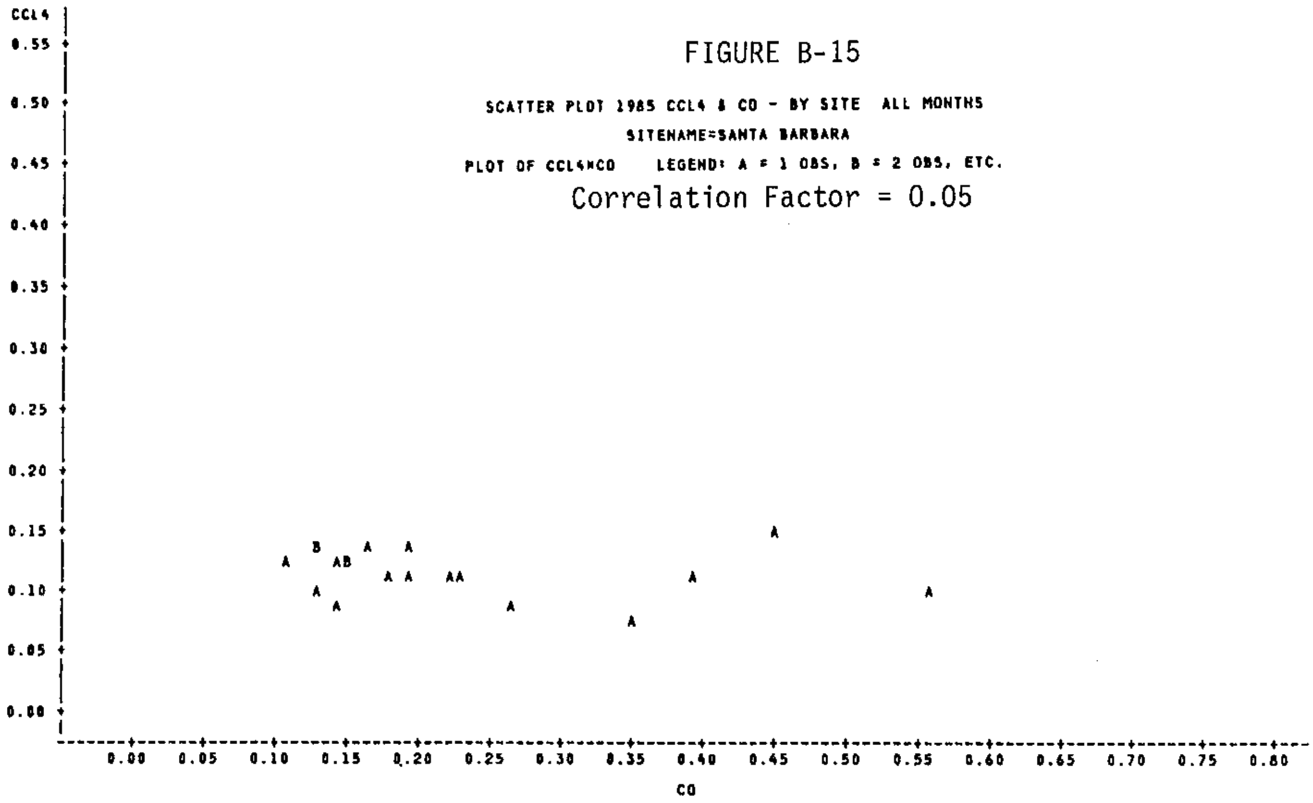


FIGURE B-15

SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=SANTA BARBARA
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.05

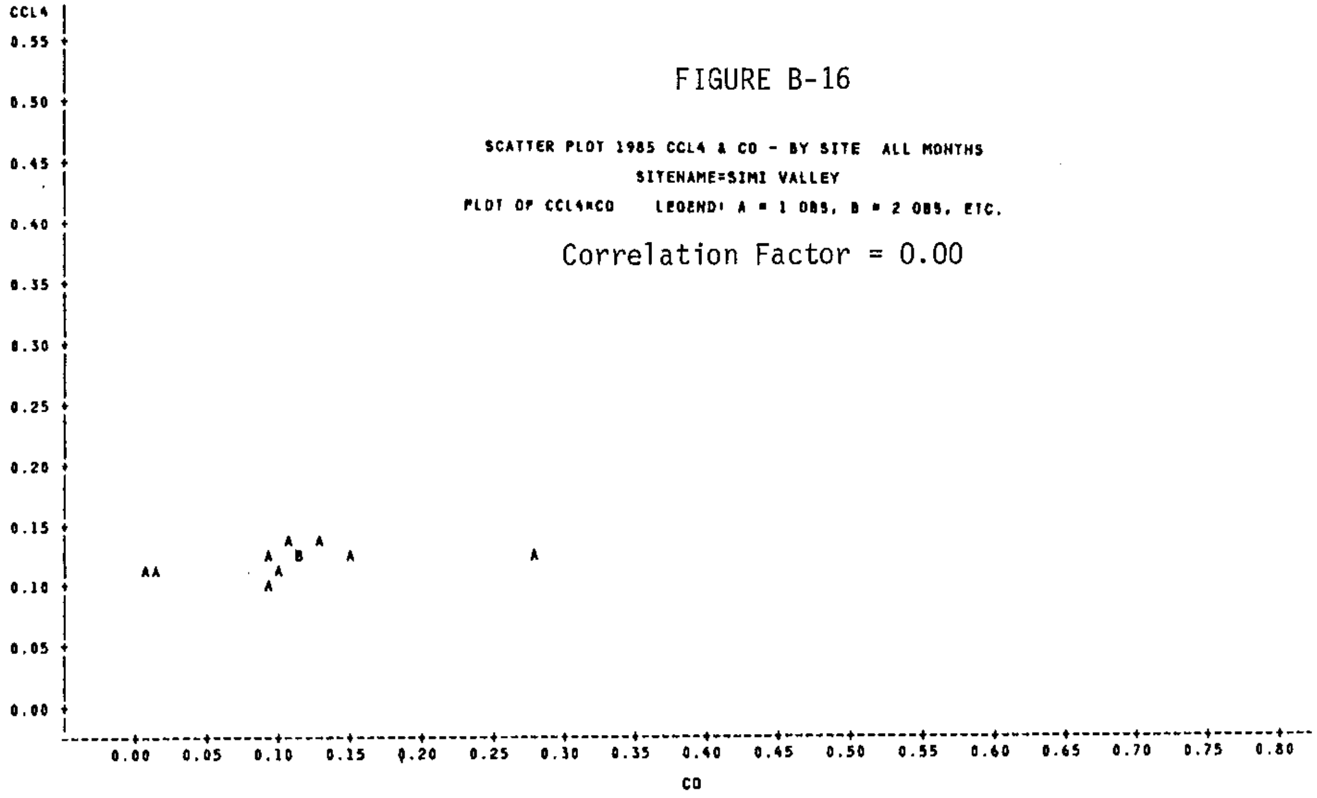


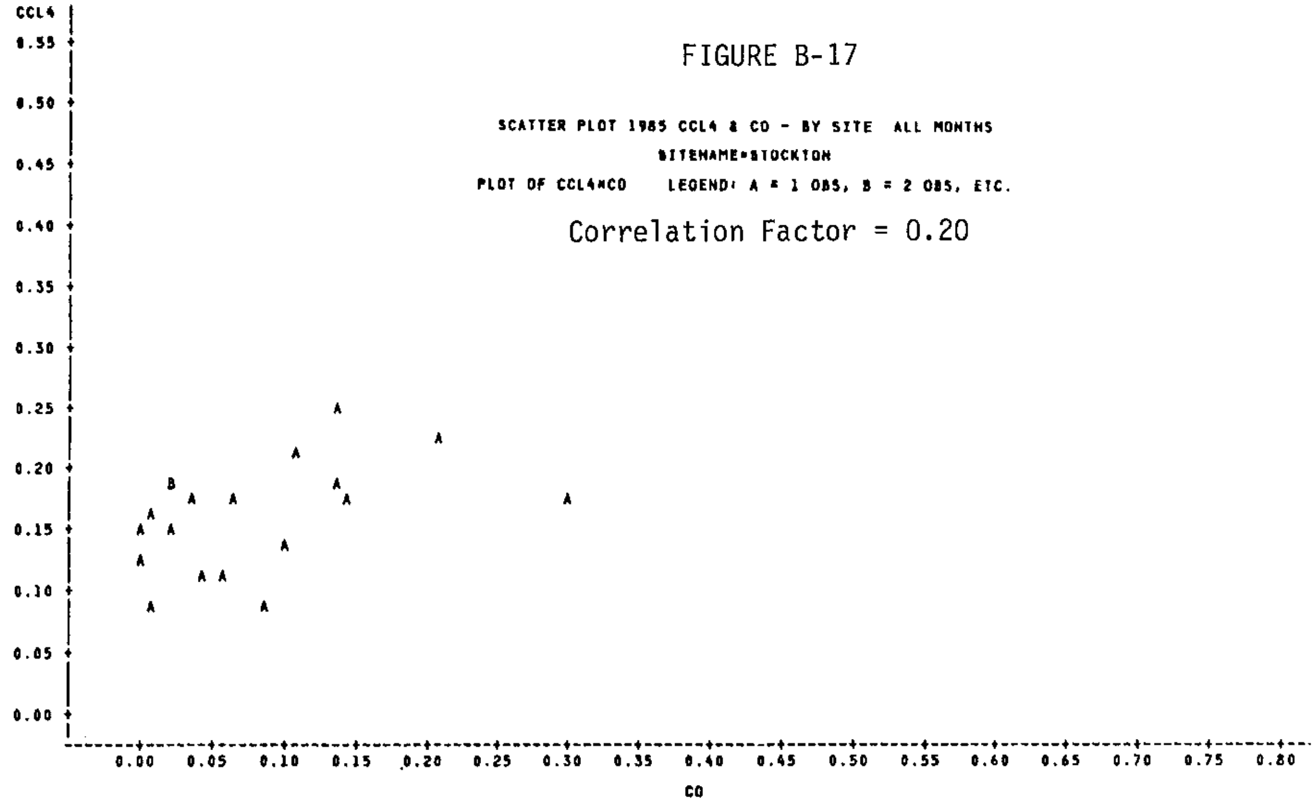
FIGURE B-16

SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS
SITENAME=SIMI VALLEY
PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.00

NOTE: 9 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

FIGURE B-17



SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS

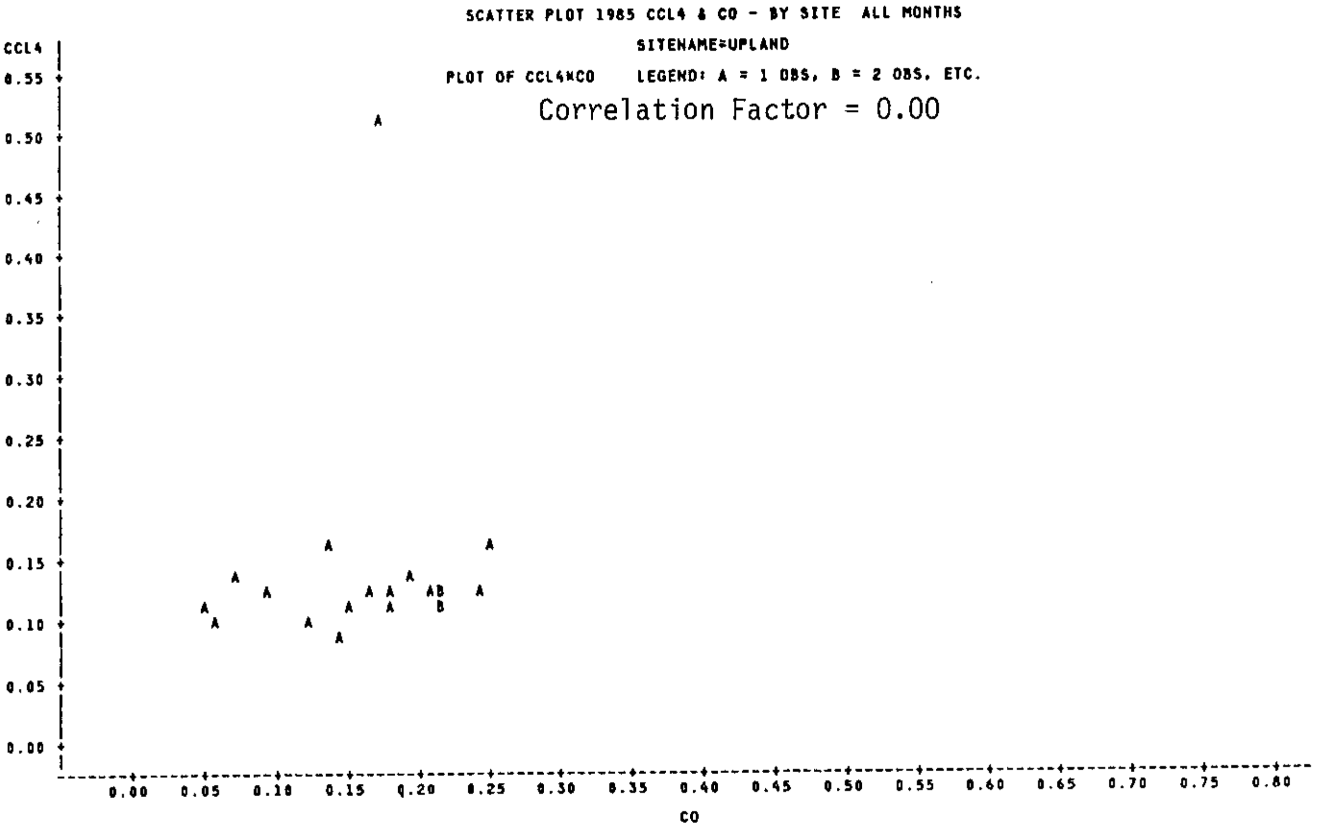
SITENAME=STOCKTON

PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.20

NOTE: 3 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

FIGURE B-18



SCATTER PLOT 1985 CCL4 & CO - BY SITE ALL MONTHS

SITENAME=UPLAND

PLOT OF CCL4*CO LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Factor = 0.00

APPENDIX C

Calculations and Assumptions of Annual Intakes of Carbon Tetrachloride

APPENDIX C

Sample Calculations of the Amount of Carbon Tetrachloride Inhaled or Ingested Annually.*

I. INHALATION OF CARBON TETRACHLORIDE

A. AMBIENT EXPOSURE

Assumptions of exposure for an adult

1. Ambient and indoor carbon tetrachloride concentrations are equivalent.

2. Average carbon tetrachloride concentrations in California range from 0.13 ppb to 0.60 ppb (0.82 ug/m^3 to 3.8 ug/m^3). The 0.13 ppb is the annual average concentration in California as determined from the ARB monitoring data. The 0.60 ppb (3.8 ug/m^3) is the maximum annual average concentration that is estimated from dispersion modeling analysis for people living near Dow Chemical and the du Pont modeling area.

3. Breathing rate of air is 23 m^3/day

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* All estimated annual intakes are rounded off to one significant figure.

Yearly intake of

carbon tetrachloride = $(3.8\ ug/m^3) \times (23\ m^3/day) \times (365\ day/year)$

= 31,901 ug/year

or

30,000 ug/year

II. INGESTION OF CARBON TETRACHLORIDE

A. EXPOSURE FROM FOOD PRODUCTS

Assumptions of exposure from food for an adult

1. The average concentration of carbon tetrachloride in ready to eat food products is 2 ug/kg.

2. Excluding grain products, ready to eat food products represent 50 percent of the diet. The remaining 50 percent of non-grain foods have no carbon tetrachloride residues.

3. The maximum concentration of carbon tetrachloride in grain products is estimated to be 40 ug/kg.

4. An adult consumes 2 kg of food per day. Of this, grain products represents 0.18 kg.

Yearly intake of

carbon tetrachloride = 0.5 (2 ug/kg X 1.82 kg/day X 365 days/year)

+ (40 ug/kg X 0.18 kg/day X 365 days/year)

= 664 ug/year + 2,628 ug/year

= 3,292 ug/year

or 3,000 ug/year

B. EXPOSURE FROM DRINKING WATER

Assumptions of exposure from drinking water for adult

1. The concentration of carbon tetrachloride in California's drinking water ranges from below 0.5 ug/1 to a maximum of 29 ug/1.

2. An average adult consumes 2 liters of water per day.

Sample calculations

Yearly intake of

carbon tetrachloride = (29 ug/1 X 2 1/day X 365 days/year)

= 21,170 ug/year

or 20,000 ug/year

III. DISCUSSION OF ASSUMPTIONS

In estimating exposure to carbon tetrachloride from different exposure routes, several assumptions were made. The inhalation rate of 23 m^3/day and water consumption rate of 2 l/day were based on EPA estimates (U. S. EPA, 1984). The amount of cereal consumed by an adult per day in North America was also based on an EPA estimate (U. S. EPA, 1985). Total food consumption by an adult was based on a World Health Organization estimate (U. S. EPA, 1975).

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APPENDIX D

SUMMARY OF INDOOR/OUTDOOR CARBON TETRACHLORIDE MONITORING STUDIES

Introduction and Conclusion

This appendix summarizes the available information comparing indoor (mostly in homes) and outdoor ambient carbon tetrachloride concentrations. Based on a steady state mass balance model, the indoor concentration is expected to equal or exceed the outdoor concentration if indoor sources are present. Some of the monitoring results support this conclusion; however, other results did not. The ARB staff reviewed each of the studies in an attempt to determine which of the results are the most reliable. After the review, the ARB staff could not establish with certainty if the indoor and outdoor carbon tetrachloride concentrations were significantly different due to uncertainties within each of the studies. However, the ARB staff believes that in California the monitored indoor and outdoor concentrations should be equal or similar.

Expected Concentrations

Carbon tetrachloride can enter the indoor environment in two ways. It can be released by indoor sources or it can infiltrate into the indoors as a contaminant of outdoor air. Similarly, it can be removed when contaminated indoor air is exchanged by exfiltration or ventilated to the outdoors. Carbon tetrachloride could also be removed from the indoor air by removal processes unique to the indoor environment if such processes were present.

The steady-state mass balance model of time averaged indoor concentration for a non-reactive gas is:

$$Ci = Co + (S - R)/Va$$

where:

Ci = indoor concentration (mass/volume)

Co = outdoor concentration (mass/volume)

S = indoor source strength (mass/time)

R = indoor removal rate (mass/time)

V = building volume (volume)

a = effective fractional air exchange rate (/time)

For carbon tetrachloride, there are no known indoor removal processes, so the indoor removal rate (R) is assumed to be zero. Also, because of a Consumer Products Safety Commission (CPSC) ban, consumer products containing carbon tetrachloride are not in widespread use, so the indoor source strength or S is also zero in many cases. Therefore, the indoor concentration will often equal the outdoor concentration (Ci = Co). In cases where there are elevated indoor concentrations, indoor sources can cause or influence these concentrations. Some indoor sources of carbon tetrachloride include drinking water, consumer products, and commercial products that contain carbon tetrachloride. At this time, there is not sufficient information to determine the contribution of these sources to the elevated indoor concentrations.

The above model assumes steady state equilibrium between sources and removal processes of carbon tetrachloride. Therefore, monitored indoor concentrations can only be expected to follow the steady state model where the outdoor concentration, indoor source strength, indoor removal rates, and air exchange rate are constant. The results for samples with averaging times greater than a few hours should also follow this model, since typical air exchange rates are 0.2 to 2.5 air changes per hour due to infiltration alone.

For carbon tetrachloride, there are no known physical reasons to explain average indoor concentrations lower than outdoor concentrations. In a few instances, lower averaged indoor concentrations were reported in some of the studies. For short sample averaging times, such an anomaly could be explained if the homes were near emission sources since outdoor concentrations could be influenced by meteorological factors such as inversions and changes in wind direction. These effects would be felt more slowly in the indoor environment and thus, indoor concentrations could be either higher or lower. With sampling times longer than a few hours, or in areas remote from sources, indoor concentrations lower than outdoor concentrations would be explained only by removal processes unique to the indoor environment or by experimental error.

Available Monitoring Data

Carbon tetrachloride and other compounds have only been recently measured in the indoor (mostly homes) and outdoor environments. The ARB staff reviewed the available studies in an attempt to determine the relationship between indoor and outdoor carbon tetrachloride concentrations. Due to uncertainties and differences in each of the studies, the ARB staff could not establish with any degree of certainty, the relationship between indoor and outdoor carbon tetrachloride concentrations. Some of the uncertainties and differences include: 1) limited number of samples taken in some studies; 2) large percentage of the samples below the limit of quantitation (LOQ); 3) no quality assurance results reported in some studies; 4) for studies that did report quality assurance results, uncertainties were sometimes large relative to differences between reported indoor and outdoor concentrations; and 5) there were major differences in the purpose and design of the studies.

Generally, compounds in the ambient concentration range of carbon tetrachloride (in the low ppb range) are difficult to measure. Accurate determination of a small difference between two concentrations requires precise measurements. While high precision of measurements is necessary, biases of measurement in the same direction, whether high or low, is less critical in assessing the differences in measurements. Therefore, interlaboratory differences in accuracy, for instance due to different calibration standards, are not as important provided the precision of measurements is acceptable. An accurate comparison of monitored results also requires that measurements be made under the same conditions. This would include similar indoor and outdoor sampling methods and analytical procedures which is not always the case in the studies. Therefore, differences between the monitored results are expected.

An analysis of the monitoring studies reviewed by the ARB staff is presented below and the monitoring results are summarized in Table D-1.

U.S. EPA, 1985a - Northrop Services, Inc.

Near Research Triangle Park in North Carolina, a study of indoor and outdoor concentrations of various compounds was conducted for the Environmental Protection Agency (EPA) by Northrop Services, Inc. (U.S. EPA, 1985a). It was reported that the mean indoor and outdoor carbon tetrachloride concentrations for homes in the study were similar. The ARB

Table D-1
Summary of Indoor/Outdoor Monitoring Studies

Site Media	Source	Percent of Samples Measurable	Percent RSD of Duplicate Samples[a,b]		Number of Samples	Concentration[b] (ppb)				Ninetieth Percentile
			Median	Maximum		Minimum	Median	Mean	Maximum	
North Carolina	EPA									
summer indoor	Final	100.	2[d]	5[d]	15	.09		0.14	0.23	
winter indoor	Report	100.	2	5	16	.11		0.14	0.16	
outdoor	1985	100.	2	5	12	.13		0.15	0.16	
New Jersey (TEAM)	EPA									
overnight personal	Interim	31.	24[e]	97[e]	346					0.9
overnight outdoor	Report	53.	15[e]	50[e]	81					0.3
	1984									
LA. Feb. 1984 (TEAM)	EPA Updated									
overnight personnel	Draft	95.	15	63	117		0.10	0.12		0.17
overnight outdoor	Report	97.	28	71	24		0.10	0.11		0.19
LA. May, 1984 (TEAM)	"									
overnight personal		99.	9	42	52		0.10	0.10		0.14
overnight outdoor		100	17	51	23		0.10	0.10		0.15
Contra Costa June 1984 (TEAM)	"									
overnight personal		94	12	54	71		0.11	0.16		0.59
overnight outdoor		95	43	43	10		0.05	0.08		0.07
Greensboro, NC (TEAM)	"									
overnight personal		6	--	--	24					
overnight outdoor		NR[f]	--	--	6					
Devils Lake, ND (TEAM)	"									
overnight personal		14	19	27	20					
overnight outdoor		NR[f]	7	13	5					
Greensboro, NC	Hartwell									
overnight personal	Conference	55			20		0.03		2	
overnight outdoor	Paper	45			20				.3	
	1984									
Baton Rouge, LA										
overnight personal	*	48			27				3	
overnight outdoor		52			27		0.02		4	
Houston, TX										
overnight personal	*	100			10		0.2		0.6	
overnight outdoor		100			10		0.3		0.5	
No. Italy, Nonurban	DeBartoli									
indoor	Final	94			16	.16	0.9	1.0	1.9	2
outdoor	Report	88			16	.16	0.8	1.1	4.5	3
	1985									

a Percent Relative Standard Deviation of duplicate sample pairs = $\frac{\text{Standard deviation}}{\text{Mean}} \times 100\%$

b Blank entries were generally not reported by authors. In some cases median and mean values are omitted where percent measurable was low. Maximum values are reported where upper percentiles were not available, but should be used with caution.

c Concentration greater than 90 percent of measured concentrations (or estimated population exposures in case of TEAM study).

d Analytical precision for repeat runs on the same sample based on references 9 and 10.

e From draft report.

f Not reported by author due to small sample size.

staff believes that these mean concentrations could also be similar to the global background concentrations of 0.11 to 0.15 ppb (0.69 to 0.94 ug/m^3) which have been estimated by other researchers.

In this study, short duration samples (less than 2 minutes) were collected inside and outside the homes, using evacuated Summa polished stainless steel canisters. Whole air samples were analyzed using cryogenic preconcentration and subsequent capillary chromatography with simultaneous flame ionization and electron capture detection. The authors have previously demonstrated high precision (2 percent relative standard deviation) with these methods for carbon tetrachloride (Pliel, et al., 1985). The ARB staff believes that this may be one of the more precise studies reviewed.

Twenty-six homes were sampled, with five homes overlapping the summer and winter seasons. The results of the study are as follows:

Table D-2

Summary of Northrop Services Inc. Study

Season	# of Samples Taken	Mean Carbon Tetrachloride Concentration (ppb)	Mean Carbon Tetrachloride Concentration (ug/m^3)	Range of Concentrations (ppb)	Range of Concentrations (ug/m^3)
Summer-indoor	15	0.14	0.90	0.09-0.23	0.58-1.5
Winter-indoor	16	0.14	0.90	0.11-0.16	0.70-1.0
Outdoor-combined seasons	12	0.15	0.96	0.13-0.16	0.83-1.0

Both the summer indoor maximum concentration of 0.23 ppb (1.5 ug/m^3) and indoor minimum concentration of 0.09 ppb (0.58 ug/m^3) are outside the range of outdoor measurements. It is not known whether outdoor samples were collected at the same time and location as these indoor samples. The higher maximum indoor concentration does show the possibility of elevated indoor concentrations, but sampling times were very short; therefore, comparison of the results must be made with caution.

TEAM Studies - Research Triangle Institute

Under contract with EPA, Research Triangle Institute conducted a series of Total Exposure Assessment Methodology (TEAM) studies. The studies were conducted to estimate the frequency distributions of 20 organic compound concentrations (including carbon tetrachloride) in personal and outdoor air in different cities around the United States. Earlier results were compiled during pilot studies and methods development work in Beaumont, Texas and Chapel Hill, North Carolina. More detailed monitoring studies were later conducted in New Jersey and California. The results have been compiled in a final interim report for the first season of monitoring in New Jersey (U.S. EPA, 1984a). The monitoring data from a later New Jersey study and a comparison study in Greensboro, North Carolina and Devils Lake, North Dakota, and the California study are contained in two final draft reports (U.S. EPAa, Undated; U.S. EPAb, Undated). Additional information were also obtained from conference papers and a journal preprint (Pellizzari, et al., 1984; Hartwell, et al., 1984a; Hartwell, et al., 1984b; Wallace, 1986).

Since the TEAM study measured personal exposure rather than indoor concentrations, a description of the study design and sampling procedures may be helpful. Participants were probabilistically selected to represent the target population. In order to better define the upper percentiles of personal exposure, individuals with suspected high occupational exposure were over-selected for monitoring. Results were then statistically weighted to adjust for that over-selection.

Each study participant wore a personal sampler for twenty-four hours. Two twelve hour samples were collected daily on tenax tubes from approximately 7 p.m. to 7 a.m. and 7 a.m. to 7 p.m. When sleeping, the participant placed the sampler on top of a night stand or dresser in the bedroom. Although instructed to continue normal activities, some participants may have postponed certain activities outside the home until after the monitoring study due to the physical constraints of the personal samplers.

The 12 hour overnight personal exposure monitoring results provide a surrogate for indoor monitoring since participants are more likely to be home during this period. Simultaneous outdoor (backyard) samples were also collected using the same method for some of the participants. The fraction of participants with simultaneous outdoor sampling was about 0.25, 0.2, 0.5 and 0.14 in New Jersey, Los Angeles first and second seasons, and Contra Costa respectively. Therefore, the overnight personal samples and the outdoor samples provided the basis for comparison of indoor and outdoor concentrations.

1. New Jersey TEAM Study

The New Jersey TEAM study was a large study in which many indoor and outdoor samples were taken (U.S. EPA, 1984a). A summary of the New Jersey TEAM study is presented below:

Table D-3

Summary of the New Jersey TEAM Study

Environment	# of Samples Taken	Ninetieth Percentile Concentration (ppb)	(ug/m^3)	% of Samples Below LOQ
Indoor	346	0.90	5.75	69
Outdoor	81	0.32	2.06	47

A large percentage of the indoor and outdoor samples were below the limit of quantitation (LOQ). Because of this, an analysis estimated median of indoor and outdoor concentrations would not give a useful or reliable comparison. The ARB staff believes that a more useful comparison can be made by reviewing estimated concentrations at the ninetieth and ninety-fifth percentiles.

For the ninetieth and ninety-fifth percentiles, overnight personal air concentration exceeded overnight outdoor concentration by 0.58 ppb and 1.27 ppb (3.7 and 8.1 ug/m^3) respectively. This may be attributable to the presence of unspecified indoor sources of carbon tetrachloride, the result of sampling and analytical uncertainties, the result of the limited number of outdoor samples taken compared to the larger number of personal (indoor) samples collected. The ARB staff feels that indoor sources of carbon tetrachloride are unlikely because of the CPSC ban on consumer products containing carbon tetrachloride, but possible presence of such sources could not be ruled out. The other two factors could also have caused discrepencies in the monitoring data, but the ARB staff could not estimate to what extent. Thus, the ARB staff was not able to compare with any degree of certainty of indoor and outdoor measurements from this TEAM study.

2. Los Angeles TEAM Study

Compared to the New Jersey TEAM study, the Los Angeles TEAM study had a much lower LOQ which resulted in over 95% of samples above the LOQ (U.S. EPAa, Undated). Elevated median overnight indoor (personal air) carbon tetrachloride concentrations similar to the New Jersey study were not measured in the Los Angeles TEAM study. At the ninetieth and ninety-fifth percentiles, the Los Angeles indoor and outdoor concentrations were similar.

The results of the Los Angeles TEAM study are summarized as follows:

Table D-4

Summary of the Los Angeles TEAM Study

Study Period	# of Samples	Median (ppb)	Concentration (ug/m^3)	% of Samples Above LOQ	Median Duplicate % RSD
Feb. 1984					
Indoor	117	0.11	0.65	95	15
Outdoor	24	0.11	0.65	97	28
May 1984					
Indoor	52	0.10	0.65	99	42
Outdoor	23	0.11	0.64	100	51

The Los Angeles TEAM data appeared to indicate that homes in the study had a median indoor carbon tetrachloride concentration similar to the median outdoor concentration. However, the maximum relative standard deviation (RSD) of duplicate field samples was high. The maximum RSD was 63 and 71% in the February study and 42 and 51% in the May study for indoor and outdoor field samples respectively. This causes some doubt as to the precision and accuracy of the reported monitoring results. The ARB staff feels that even though these results show similar indoor and outdoor median concentrations for this area, this conclusion could not be supported on the basis of this study alone.

3. Contra Costa TEAM Study

In the Antioch-Pittsburg area, a TEAM study was conducted during June 1984 (U.S. EPAa, Undated). As with the Los Angeles TEAM study, the low LOQ resulted in a majority of the measured samples being above the LOQ. The results of this TEAM study are presented below:

Table D-5

Summary of Contra Costa TEAM Study

Environment	# of Samples Taken	Median Concentration (ppb)	(ug/m^3)	% of Samples Above LOQ	Median Duplicate % RSD
Indoor	71	0.14	0.11	94	12
Outdoor	10	0.05	0.33	95	43

The median overnight personal air concentration was similar to that found in the Los Angeles TEAM study. The median outdoor concentration, estimated from 10 samples, was much lower than the median outdoor concentration measured in the Los Angeles TEAM study (0.05 ppb versus 0.11 ppb). The percent relative standard deviation (RSD) for the one pair of duplicate outdoor field samples taken for this study was 43 percent. It is difficult to assess the precision of the monitored results since the absolute standard deviation is unknown; however, outdoor median concentration lower than the estimated global background level makes the results suspect. For these reasons, comparisons between the outdoor and personal air concentrations in Antioch-Pittsburg area are not conclusive.

4. Other TEAM Studies

As stated earlier, some monitoring data were also collected in TEAM studies in Devils Lake, North Dakota and Greensboro, North Carolina (U.S. EPAb, Undated). The ARB staff believes that the small number of outdoor samples and the low percentage of indoor and outdoor samples that were measurable make comparison of indoor and outdoor measurements unreliable.

Hartwell used the TEAM study methodology to survey halogenated hydrocarbon exposures in the cities of Greensboro, North Carolina, Baton Rouge, Louisiana, and Houston, Texas. The results were presented in a brief conference paper which included median and maximum values and the percent of samples measurable for both indoor and outdoor sites (Hartwell, et al., 1984a). As with some of the earlier TEAM studies for carbon tetrachloride, low percentage of measurable samples resulted due to the high LOQ (except in Houston) and maximum values higher than later TEAM studies were reported. The ARB staff believes that the Los Angeles-Contra Costa TEAM study monitoring results may be the most reliable because of the improvements made since the earlier TEAM studies. Therefore, the Hartwell study results are not sufficient for determining the relationship between indoor and outdoor concentrations.

5. De Bartoli, 1985

In Northern Italy, De Bartoli conducted a study in which paired samples were collected inside and outside of 14 residences and 1 office, in 9 towns, villages, and rural areas. The table below summarizes this study:

Table D-6

Summary of the De Bartoli Study

Environment	# of Samples	Median Concentration (ppb)	Median Concentration (ug/m^3)	Range of Conc. (ppb)	Range of Conc. (ug/m^3)	% of Samples Above LOQ
Indoor	16	0.9	6	<0.16-1.9	<1-12	94
Outdoor	16	0.8	5	<0.16-4.5	<1-29	88

The reported median indoor and outdoor concentrations appear to be similar (0.9 ppb versus 0.8 ppb). However, these median concentrations and the concentrations of other compounds reported in the study are generally an order of magnitude higher than those which have been reported elsewhere. This would suggest that indoor and outdoor emission sources are contributing to the reported median concentrations or that the experimental uncertainties are biasing the results to the high side. As stated earlier, the precision of measurements is more critical in assessing the differences between indoor and outdoor concentrations than the accuracy of the measurements. If the median concentrations and the measurements have the acceptable precision, then the median indoor and outdoor concentrations could be assumed to be similar.

The De Bartoli monitoring data was further reviewed by the ARB staff. Individual pairs of indoor and outdoor measurements for an area in many cases were not similar and for some pairs, higher outdoor concentrations than indoor concentrations were noted by the ARB staff. However, when the results were averaged, the mean concentrations were coincidentally similar. This type of analysis was not possible for the other studies because the only information that was available for comparison was summary results such as mean values, median values, and like percentiles. The ARB staff concluded that from the review of this study, it cannot be determined if there are actual similarities between indoor and outdoor concentrations.

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