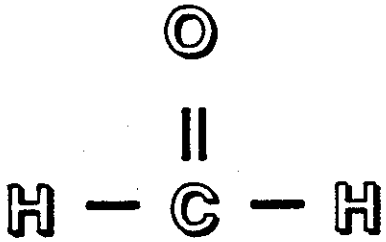
California Environmental Protection Agency

Air Resources Board

TECHNICAL SUPPORT DOCUMENT

Final Report on the Identification of FORMALDEHYDE



as a Toxic Air Contaminant

Part A
Exposure Assessment

STATIONARY SOURCE DIVISION

JULY 1992

ACKNOWLEDGEMENTS

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July, 1992

Formaldehyde was identified as a toxic air contaminant by the Board on March 12, 1992. However, in response to written and oral comments, the Board directed the ARB and the OEHHA staff to work with industry to make clarifications to the report. This is the final report on the formaldehyde identification document which incorporates these clarifications.

INITIAL STATEMENT OF REASONS FOR RULEMAKING

TECHNICAL SUPPORT DOCUMENT

FINAL REPORT ON THE IDENTIFICATION OF FORMALDEHYDE AS A TOXIC AIR CONTAMINANT

PART A

PUBLIC EXPOSURE TO, SOURCES AND EMISSIONS OF,

FORMALDEHYDE IN CALIFORNIA

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July, 1992

PUBLIC EXPOSURE TO, SOURCES AND EMISSIONS OF FORMALDEHYDE IN CALIFORNIA

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I.

INTRODUCTION

According to section 39655 of the California Health and Safety Code, a toxic air contaminant (TAC) is "an air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health." This report, Part A of the Technical Support Document, "Proposed Identification of Formaldehyde as a Toxic Air Contaminant" (prepared by the staff of the Air Resources Board), is an evaluation of the compound's emissions, ambient and indoor concentrations, statewide population exposure, and atmospheric persistence and fate. The Part B report prepared by the staff of the Office of Environmental Health Hazard Assessment (OEHHA) assesses the health effects of formaldehyde. The Air Resources Board (ARB or "the Board") will consider the Part A and Part B reports, the findings of the Scientific Review Panel (SRP), written comments, and public testimony to determine if formaldehyde should be identified as a TAC.

A. SUMMARY OF CALIFORNIA HEALTH AND SAFETY CODE SECTIONS 39660-39662 (IDENTIFICATION OF TOXIC AIR CONTAMINANTS)

Section 39660(f) of the California Health and Safety Code requires the use of the following criteria for prioritizing compounds for evaluation as possible toxic air contaminants: 1) risk of harm to public health, 2) amount or potential amount of emissions, 3) manner of usage, 4) persistence in the atmosphere, and 5) ambient concentrations.

Once a compound is selected to enter the TAC identification process, the ARB requests relevant information from the public and a written evaluation of available health effects information (Part B) from the OEHHA. The OEHHA staff's evaluation is required to contain an estimate of the threshold exposure level above which the compound causes or contributes to adverse health effects. In the case where no threshold of significant

adverse health effects can be determined, the OEHHA is required to state the range of risk to humans resulting from current or anticipated exposure.

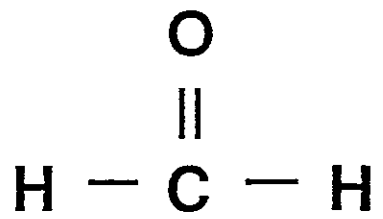
Simultaneous with the preparation of the OEHHA health evaluation, the ARB staff prepares an exposure assessment (Part A) including information on the compound's usage, emissions or potential emissions, environmental persistence, and available ambient and indoor exposure levels.

Following a public comment period, the Staff Report/Executive Summary and Parts A, B, and C are formally reviewed by the SRP at a public meeting. Upon reviewing the data, assessments, and conclusions of the report and ascertaining that appropriate scientific methods were used to gather and analyze the data presented, the SRP submits written findings to the ARB (the Board). At a public hearing, the Board decides whether or not the evidence in the document supports the identification of the compound as a toxic air contaminant and, if so, whether there is evidence of a threshold exposure below which adverse effects are not expected to occur. Once a compound is identified as a toxic air contaminant and listed in section 93000 of Title 17 of the California Code of Regulations, the ARB staff prepares a report on the need and appropriate degree of regulation pursuant to sections 39665-39668 of the Health and Safety Code.

B. FORMALDEHYDE AS A CHEMICAL COMPOUND

Formaldehyde (HCHO) is a colorless gas at normal temperatures with a pungent, irritating odor. It is the simplest member of the family of aldehydes and has a unique structure: the attachment of the carbonyl directly to the two hydrogens. As a result of its unique structure, formaldehyde has a high degree of chemical and photochemical reactivity, good thermal stability in comparison with other carbonyl compounds, and is capable of undergoing a wide variety of chemical reactions, many of which are useful in commercial processes.

Structure of Formaldehyde



Formaldehyde is both directly emitted into the atmosphere as well as formed in the atmosphere as a result of photochemical oxidation of reactive organic gases (ROG) in polluted atmospheres containing ozone and nitrogen oxides. Photochemical oxidation is the largest source (could be as high as 90 percent) of annual average formaldehyde concentrations in the outdoor ambient air. Short-term formaldehyde concentrations by photochemical oxidation can vary significantly depending on the season, location and time of day. The largest sources of directly emitted formaldehyde are from combustion of fossil fuels from automobiles, trucks and buses and process emissions from oil refineries.

Indoor formaldehyde sources are numerous and include such diverse products as building materials, clothing, furniture, draperies, paper products, and fingernail hardeners. A potentially large source of formaldehyde indoors is pressed wood products made with urea-formaldehyde resins. Such products include hardwood plywood, particleboard, and medium-density fiberboard. Formaldehyde is also emitted from combustion sources, including cigarettes.

The overall mean statewide formaldehyde exposure, weighted by population, is estimated to be 4.4 ppbv (parts/10^9)(5.4 ug/m^3). Basin-specific, population-weighted mean concentrations vary from a minimum of 3.2 ppbv (3.9 ug/m^3) in the San Francisco Bay Area Air Basin to a maximum of 5.1 ppbv (6.3 ug/m^3) in the South Coast Air Basin. The overall geographic mean formaldehyde concentration calculated as the average of the six basin averages was 4.0 ppbv (4.9 ug/m^3). This value is approximately 8 percent lower than the population-weighted exposure estimate of 4.4 ppbv

(5.4 ug/m^3), indicating that the highest concentrations of formaldehyde tend to be in the areas of higher population density.

Formaldehyde is removed from the lower troposphere mainly by photolysis and reaction with the OH radical, and by wet deposition (leading to incorporation of formaldehyde into rain, cloud and fog water). The estimated lifetime of formaldehyde due to photolysis and OH radical reaction is ~0.3 days. Rain or fog or both can shorten the atmospheric lifetime of formaldehyde.

The Federal Clean Air Act Amendments of 1990 require the listing of formaldehyde as a hazardous air pollutant in section 112(b) [section 7412, Title 42, United States Code]. Therefore, pursuant to section 39655 of the California Health and Safety Code, formaldehyde is required to be identified as a TAC.

II.

PHYSICAL PROPERTIES OF FORMALDEHYDE

Formaldehyde is a colorless, flammable gas with a pungent irritating odor. Formaldehyde gas is soluble in water, alcohols, and other polar solvents, is stable from 25 to 100° C and decomposes very slowly up to 300° C. It condenses to a liquid at -19° C.

In the presence of air and moisture at room temperature, formaldehyde readily polymerizes to paraformaldehyde, a white solid mixture of linear poly-oxymethylene glycols containing 90 to 99 percent formaldehyde (a convenient storage form of formaldehyde). In aqueous solutions, formaldehyde reacts with water to form methylene glycol. Polymerization takes place slowly below room temperature but is accelerated by the presence of impurities. Warming pure liquid formaldehyde to room temperature in a sealed container causes rapid polymerization and the evolution of heat (63 kJ/mole). Decomposition produces carbon monoxide and hydrogen gas. When catalyzed by certain metals (platinum, copper, or chromia and alumina), formaldehyde decomposition can produce methanol, methyl formate, formic acid, carbon dioxide, and methane.

Pure liquid formaldehyde, however, polymerizes rapidly above -80° C. Polymerization is prevented by mixing 35 to 50% formaldehyde with 10 to 15% methanol and water to form a stable solution known as formalin (SAI, 1983; NRC, 1981).

Because of its unique structure, formaldehyde has a high degree of chemical and photochemical reactivity and good thermal stability in comparison with other carbonyl compounds. This structural uniqueness is due to the attachment of the carbonyl directly to the two hydrogens. Formaldehyde is capable of undergoing a wide variety of chemical reactions,

many of which are useful in commercial processes. The commercial forms of formaldehyde include paraformaldehyde, formalin solutions, polymers, resins, and other derivatives.

Because of its high chemical reactivity and good thermal stability, formaldehyde is used as a reactant in numerous commercial processes to synthesize a wide variety of products. These reactions fall into three categories: 1) oxidation-reduction reactions, 2) addition or condensation reactions with organics and inorganics, and 3) self-polymerization reactions.

Physical properties of pure monomeric formaldehyde are presented in Table II-1.

TABLE II-1

PHYSICAL PROPERTIES OF MONOMERIC FORMALDEHYDE

Synonyms: Methanal, methyl aldehyde, methylene oxide, formic aldehyde, oxymethylene

Chemical Formula	HCHO
CAS Registry Number	50-00-0
Molecular Weight	30.03
Boiling Point (at 101.3 kPa), ^{o}C	-19
Melting Point, ^{o}C	-118
Density at -20^{o}C, g/ml	0.8153
Density at -80^{o}C, g/ml	0.9151
Vapor Density	1.067 (air = 1)
Heat of Vaporization, H_v	
at 19^{o}C, kJ/mol	23.3
at -109 to -22^{o}C, J/mol	$27384 + 14.56T - 0.1207T^2$ (T=K)
Heat of Formation, H_f at 25^{o}C, kJ/mol	-115.9
Gibbs Free Energy, G_f^o at 25^{o}C, kJ/mol	-109.9
Heat Capacity, $^{o}C_p$, J/(mol*K)	35.4
Entropy, S^o, J/(mol*K)	218.8
Heat of Combustion, kJ/mol	561 - 571
Heat of Solution in Water and Lower Aliphatic Alcohols, kJ/mol	63
Critical Constants	
Temperature, ^{o}C	137.2 - 141.2
Pressure, MPa	6.784 - 6.637
Flammability in Air	
Lower/Upper Limits, mol %	7.0/73
Ignition Temperature, ^{o}C	430

a. $\text{Log}_{10} P = A-(B/(C+t))$; Where P = vapor pressure in pascals (Pa) and t = temperature in ^{o}C.

Source: USEPA, 1984.

SECTION II REFERENCES

National Research Council (NRC) (1981), Formaldehyde and Other Aldehyde.

Science Applications, Inc. (SAI) (1983), Formaldehyde: A Survey of Airborne Concentration and Sources (Interim Report). Science Applications, Inc. (SAI) Contracted by ARB in Sacramento, CA.

U.S. Environmental Protection Agency (U.S. EPA) (1984), Locating And Estimating Air Emissions From Sources Of Formaldehyde, EPA-450/4-84-007e, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle, NC (March).

III.

PRODUCTION, USES AND EMISSIONS

A. PRODUCTION

Formaldehyde (HCHO) is both directly emitted into the atmosphere as well as formed in the atmosphere as a result of photochemical oxidation of reactive organic gases (ROG) in polluted atmospheres containing ozone and nitrogen oxides. Photochemical oxidation is the largest source (could be as high as 90 percent) of annual average formaldehyde concentrations in the outdoor ambient air in California.

Aside from photochemical production, the largest source of direct formaldehyde emissions appear to come from the combustion of fossil fuels from automobiles, trucks and buses (Lawson et al. 1990).

Table III-1 lists formaldehyde emissions from major sources and approximate quantities in tons per year of formaldehyde they emit. Figures III-1 and III-2 show the percentage of formaldehyde emissions from the listed sources.

1. Formation and Production

Formaldehyde is produced in the environment by photo-oxidation of unburned reactive organic compounds. Thus, photo-oxidation production of formaldehyde is dependent upon incomplete combustion products [reactive organic gases (ROG)] in the ambient air. In addition to its atmospheric production by photo-oxidation, formaldehyde is also produced commercially by the catalytic oxidation of methanol. Its commercial preparation involves the passage of methanol vapors over a heated catalyst at temperatures of about 300 ^{o}C. The catalyst used may be either silver or a metal oxide.

TABLE III-1

SUMMARY OF ESTIMATES OF ATMOSPHERIC
EMISSIONS OF FORMALDEHYDE IN CALIFORNIA

Source	Inventory Year	Emissions (TPY)	Ref.
PRODUCTION			
As a Photo-oxidation Product	1987	150,000	a
Commercial Production			
Silver Catalyst process	1989	2	b
EMISSIONS			
Mobile Sources			
On-Road Motor Vehicles	1987	11,000	c
Other Mobile Sources	1987	5,300	d
Stationary Sources - Process Emissions			
Oil Refineries (processes)	1988	650-2,700	e
Copper Plating Solutions	1982	50	f
Incineration	1982	Negligible	
Pressed Wood Products	1989	120	b
Non-Vehicular Fuel combustion (excluding wood)			
Industrial sources	1987	740	
Area Sources	1987	350	g
Other Uses			
Domestic Products	1983	160	i
Consumptive Uses	1981	5	h
Sterilizers	1982	1	j
Storage & Handling	1982	Negligible	

a. Midpoint of low and high estimates. Atmospheric formation of HCHO varies widely during period of day, atmospheric conditions and from area to area so estimates could vary by ±50 percent.

b. California Environmental Protection Agency (CalEPA) 1991. SARA, Title III, Section 313, Preliminary Toxic Chemical Release Inventory, Superfund Amendments and Reauthorization Act of 1986. 1989 information reported to CalEPA.

Table III-1 (Con't.)

c. From ARB's Emission Data System (EDS): 1987 Base Year Emission Inventory, Formaldehyde From On-Road Motor Vehicles (Run Date: 7/12/90). Based on the uncertainty involved in calculating emission estimates for all types of sources, there is a potential underestimate of hydrocarbon emissions of 50 to 100 percent.

d. From ARB's Emission Data System (EDS): 1987 Base Year Emission Inventory, Formaldehyde From Other Mobile Sources (Run Date: 8/28/91).

e. The range of estimates are based on the uncertainty in process rate data (See Appendix I-C for detail).

f. This estimate is for the South Coast Air Basin (SoCAB) only. A statewide estimate is not available (SCAQMD, 1983).

g. Area sources include agricultural production, oil and gas extraction, manufacturing, and residential.

h. From SAI-84/1642, Formaldehyde: A Survey of Airborne Concentrations And Sources, Final Report, June, 1984.

i. This emission estimate was extrapolated from the emission estimate for the SoCAB (1983), and was based on the assumption that the population ratio of the SoCAB to California is 0.47. The estimate for the SoCAB was taken from: Emission of Potentially Toxic/Hazardous Air Contaminants in the South Coast Air Basin (SCAQMD, Engineering Division, 1983).

j. This estimate is for the SoCAB only. Statewide estimates are not available (SCAQMD, 1983).

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a. Formation of Formaldehyde by Photo-oxidation

The amount of formaldehyde produced by photo-oxidation is difficult to estimate because of the complexity of the chemical reactions by which formaldehyde is formed. A number of factors affect the formation of formaldehyde such as sunlight and the presence of other atmospheric contaminants such as nitrogen oxides (NOx), ozone, and ROG. Topography, climatic variations and meteorological variables also influence the distribution and concentration of formaldehyde formed by photo-oxidation.

Rogozen and Ziskind (1984) have developed a rough estimation technique which estimates the net generation rate (production minus removal) by multiplying reactive organic gas (ROG) emissions from all sources by a photochemical conversion efficiency factor. A range of efficiency factors have been developed based on limited experimental data and represent the fraction of volatile organic compounds (VOC) that is converted into formaldehyde. Although there is much uncertainty associated with this estimation method, it does offer some idea of the volume of formaldehyde being formed in the atmosphere.

Rogozen and Ziskind (1984) in the Science Applications Incorporated (SAI) report entitled Formaldehyde: A Survey of Airborne Concentrations and Sources assumed a steady-state photochemical conversion efficiency factor of 0.06 to 0.12. These conversion factors are ratios between the net photochemical formation rate of formaldehyde and the average annual day ROG emissions for the South Coast Air Basin. Atmospheric formation of formaldehyde varies widely during time of day, atmospheric conditions and from area to area. To be conservative, the staff assumed that these factors were applicable to all parts of California. By using these factors and the ROG emissions for the entire State in 1987, an estimate of formaldehyde in the ambient air can be made. The 1987 statewide emissions for ROG were approximately 1.7 million tons. Using this ROG estimate and the steady-state conversion factor of 0.06 to 0.12, the staff estimates that formaldehyde production due to photochemical conversion in 1987 ranged from approximately 10.2×10^4 tons to 20.4×10^4 tons, or approximately 88 percent of total formaldehyde emissions in California. The mid-point of this range of emission estimate is approximately 15×10^4 tons (See Appendix I-A). Since this calculation is based on the emission inventory, which may be underestimated by 50 to 100 percent (see p. A-13), the estimate of photochemically produced formaldehyde may be underestimated as well.

b. Commercial Production

Formaldehyde is produced in the United States by using either a silver catalyst or a molybdenum and iron oxide catalyst. About 75 percent of the formaldehyde produced in the U.S. is produced by the silver catalyst method whereby methanol is dehydrogenated and oxidized in the presence of a silver catalyst to produce formaldehyde and hydrogen. The remaining 25 percent of the formaldehyde is produced by the second method where a mixture of methanol and air is passed over a catalyst consisting of molybdenum and iron oxide. Emissions of formaldehyde produced by either method come from the absorber vent, product fractionator vent, start up operations (usually routed through the absorber), storage and handling, and fugitive sources.

Borden Incorporated located in Fremont is the only California facility producing formaldehyde commercially. This facility uses the silver catalyst method and has an annual production capacity of 224 x 10^6 lbs per year (SAI, 1984). However, according to to SARA Title III data, emissions from this plant for the year 1989 is estimated to be 2 tons (Cal-EPA, 1989).

B. USES

Formaldehyde has a wide number of uses in the industrial, governmental, and consumer sectors of the economy. Some of these include use as a chemical sterilant, leather tanner, plater, preservative, embalming fluid, and fumigant. It is also used in the manufacture of commercial products such as resins, wrinkle-proof fabrics, rubber products, dyes, textiles, plastics, paper products and cosmetics (HESIS, 1990). According to the National Research Council's (NRC) publication titled Formaldehyde and Other Aldehydes (1981), about 50 percent of the formaldehyde produced is consumed in the production of urea-formaldehyde and phenol-formaldehyde resins. These resins are used in the production of plywood, particleboard, foam insulation, and a wide variety of molded or extruded plastic items. The same report states that another 20 to 25 percent is used in the production of other resins or high polymers, including polyacetals, melamine resins,

and alkyl resins. The remaining 20 to 25 percent of the State's formaldehyde (or formaldehyde solutions, often referred to as formalin) is probably used in such miscellaneous products as trioxane, pyridine, disinfectants, embalming fluids, and textile-treatment agents.

C. EMISSIONS FROM MOBILE SOURCES

In addition to commercial production (discussed above), emissions of formaldehyde result from fuel combustion from mobile sources, industrial fuel combustion, oil refining processes, and miscellaneous consumptive uses (Table III-1).

1. Mobile Sources

ARB estimates that mobile sources emitted approximately 16,000 tons of formaldehyde into the ambient air in 1987. Formaldehyde emissions from mobile sources are estimated by multiplying total organic gas (TOG) emissions for 1987 by the weight fraction of formaldehyde from the exhaust stream. The weight fractions were taken from the California Air Resources Board's speciation manual entitled: Identification of Volatile Organic Compound Species Profile (ARB, 1991a), while the TOG emission estimates were taken from the 1987 emission inventory in the California Air Resources Board's Emission Data System (See Appendix I-B).

To estimate emissions, different classes of vehicles were studied, including those vehicles that use gasoline and are equipped with catalytic converters, those not equipped with catalytic converters, diesel cars, trucks, buses, and motorcycles.

During the past few years, a number of independent investigators have conducted studies that assert that the total hydrocarbon emission inventory (representing all types of sources) may be underestimated by substantial amounts. Investigations conducted during the last year by the ARB staff have shown that these underestimates are in the neighborhood of 50 to 100

percent. ARB staff believes that a significant portion of this error is in the on-road motor vehicle portion of the inventory; however, studies to date have not been able to establish error bands for specific categories of the inventory. Efforts towards improving both the mobile and stationary source portions of the inventory continue and a major effort is underway to obtain improved emission rates and vehicular activity data for the on-road motor vehicle emission estimates.

a. On-Road Motor Vehicles

ARB estimates that on-road motor vehicles emitted approximately 11,000 tons of formaldehyde into the ambient air in 1987 (ARB, 1991a; and ARB, 1990a). Light-duty passenger cars equipped with catalytic converters emitted approximately 2,200 tons of formaldehyde while those not equipped with catalytic converters emitted approximately 3,400 tons of formaldehyde. For those light-duty passenger cars that burn diesel fuel, the formaldehyde emissions were approximately 160 tons.

Light-and medium-duty trucks equipped with catalytic converters emitted less formaldehyde (approximately 920 tons) when compared to those not equipped with catalytic converters (about 1,200 tons). In the same inventory year, light-and medium-duty diesel trucks emitted approximately 41 tons of formaldehyde.

Formaldehyde emissions from all heavy-duty gasoline (non-catalytic) trucks were significantly higher (approximately 580 tons) than formaldehyde emissions from heavy-duty gasoline trucks equipped with catalytic converters (about 3 tons). However, all heavy-duty diesel trucks and urban buses emitted about 2,700 tons of formaldehyde in 1987. In the same inventory year, motorcycles were responsible for approximately 150 tons of formaldehyde emissions.

b. Other Mobile Sources

Formaldehyde emissions associated with all off-road motor vehicles and other mobile sources were about 5,300 tons for 1987 (ARB, 1991b). Of this

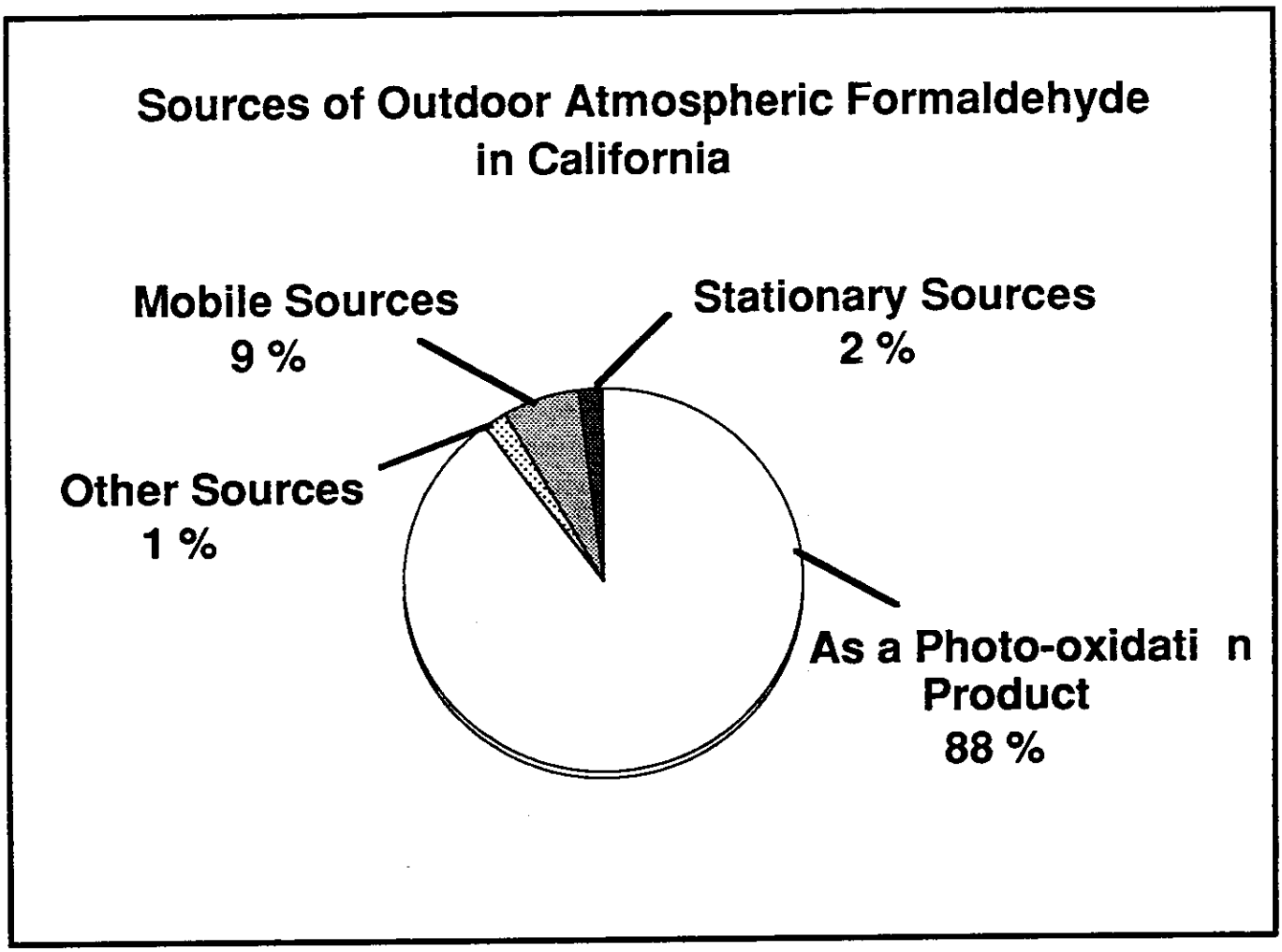

FIGURE III-1

Note:

Mobile sources include light-duty, medium-duty, heavy-duty vehicles, trains, aircrafts, motorcycles, off-road vehicles, and mobile and utility equipment. Stationary sources include refineries and copper plating solutions. Other sources such as domestic products, area sources, and consumptive uses constitute less than 1% of the total accountable formaldehyde emissions in California. The 88% photo-oxidation product is a result of annual secondary formation in the atmosphere, and may be underestimnated due to the underestimate in emissions inventory for total hydrocarbon.

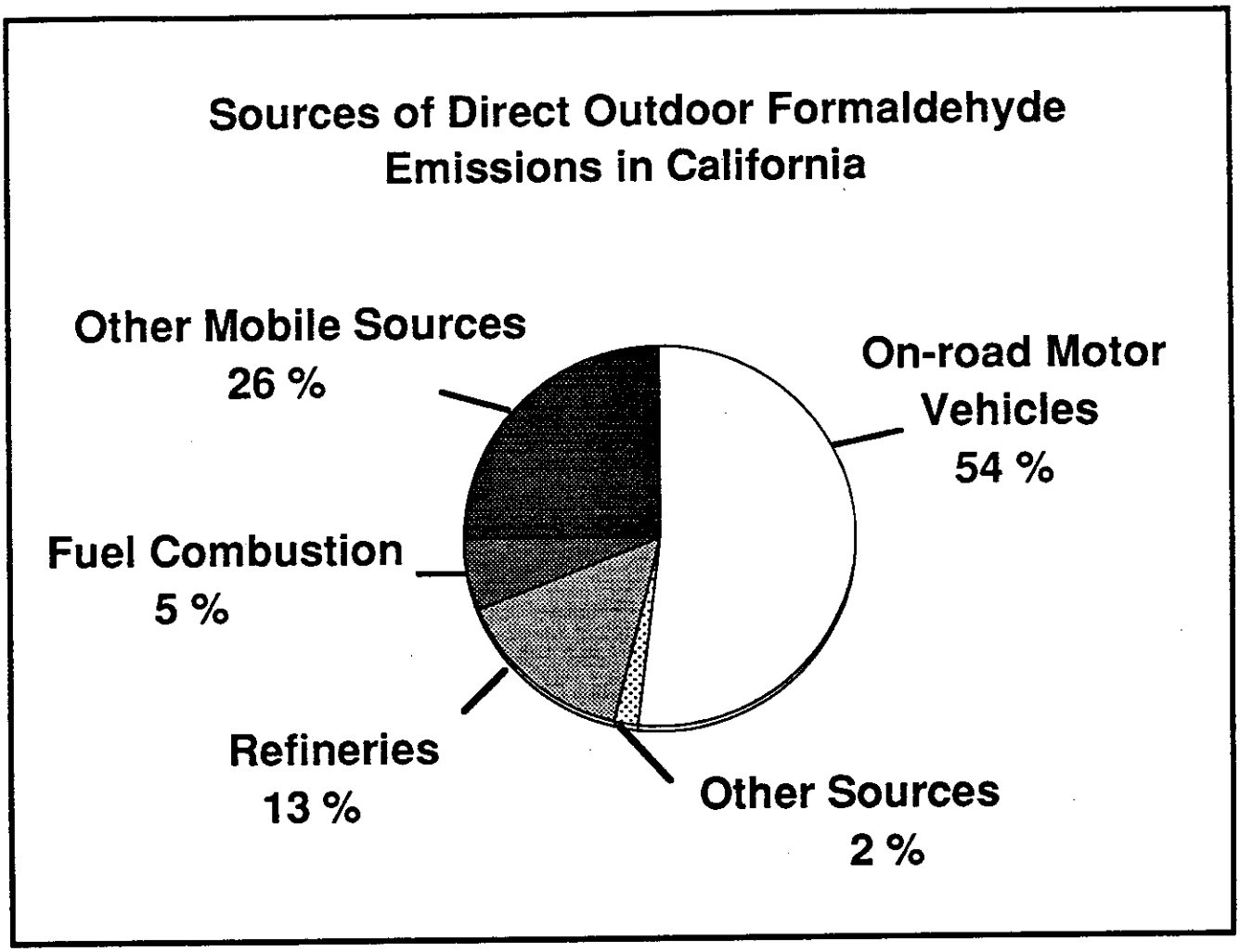

FIGURE III-2

Notes:

1. This Figure represents approximately 12% of the total formaldehyde in the outdoor California ambient air. The other 88% is from the secondary formation of annual average formaldehyde in the atmosphere due to the photo-oxidation of hydrocarbons (see Figure III-1).

2. On-road motor vehicles include light-duty, medium-duty, and heavy-duty vehicles. Emission estimates for on-road motor vehicles may be underestimated as a result of the underestimate in emissions inventory for total hydrocarbon. Other mobile sources include trains, aircrafts, off-road vehicles, and mobile and utility equipment. Other sources include formaldehyde production, consumptive, and domestic uses.

total, trains were 951 tons, ships were 223 tons, and aircraft were 64 tons. Off-road motor vehicles such as recreational vehicles and commercial boats were responsible for approximately 1,300 tons. Mobile and utility equipment such as tractors, refrigeration units, and lawn mowers accounted for approximately 2,780 tons of formaldehyde (See Appendix I-B).

c. Trends

Based on the ARB's motor vehicle inventory, there has been an approximately 11-percent decrease in total organic gas (TOG) emissions from on-road motor vehicular exhaust between 1987 and 1989. During this same period, TOG emissions from other mobile sources increased approximately 12 percent (ARB, 1991c; ARB, 1991a; ARB, 1990a; and ARB, 1990b). Because TOG emissions from on-road vehicles are greater than that from other mobile sources, the combined effect is a net decrease of approximately six percent in exhaust TOG emissions.

Large reductions in emissions from individual motor vehicles have been achieved because of ARBs motor vehicle emission control program. For example, exhaust emission standards of hydrocarbons from 1988 model-year passenger vehicles equipped with oxidative catalysts are 95 percent lower than the uncontrolled levels of 1965 models. As a result, emissions of formaldehyde from these vehicles have been reduced accordingly.

In September 1990, the Board adopted a Low Emission Vehicle & Clean Fuels regulation and a Phase I Reformulated Gasoline regulation. In November 1991, the Board adopted a Phase II Reformulated Gasoline regulation. These regulations will ensure the continued downward trend in emissions from on-road motor vehicles.

D. EMISSIONS FROM STATIONARY SOURCES

Stationary sources contributing to formaldehyde emissions are those producing or using: hydrocarbon-based fuels, urea-formaldehyde and phenol-formaldehyde resins, copper plating solutions, and incinerators. The use of

coal as a fuel contributes little if any formaldehyde emissions in California, since coal is not used extensively in the state (Table III-1). Furthermore, the use of copper plating solutions and incineration processes appear to be small small sources of formaldehyde and will be examined in more detail during the ARB risk management program.

1. Oil Refining

Formaldehyde is a product of incomplete combustion in petroleum refineries. Catalytic cracking, coking operations, and fuel combustion are major sources of formaldehyde from refineries. Other operations such as catalytic reforming, catalytic hydrorefining, and catalytic hydrotreating may also be sources of formaldehyde.

Catalytic cracking refers to operations where catalysts are used to break down heavy oils (high molecular weight compounds) to lighter products. The spent catalysts are then regenerated by combusting the deposited coke. This combustion process emits formaldehyde. Coking operations involve the thermal coking of heavy residual oil to other products and petroleum coke (U.S. EPA, 1984). Incomplete combustion of coke generates formaldehyde. Formaldehyde emissions from fuel combustion in refineries have been estimated in the fuel combustion section. This section only discusses formaldehyde emissions from petroleum processing.

The United States Environmental Protection Agency (U.S. EPA) reported formaldehyde emission factors from three distinct operations at refineries. These emission factors are 4.85 lbs per 1,000 barrels (bbls) of fresh feed from fluidized catalytic cracking (FCC); 2.2 lbs per 1,000 bbls of fresh feed from moving-bed cracking or thermal catalytic cracking (TCC); and 1.19 lbs per 1,000 bbls of fresh feed from coking operations (U.S. EPA, 1990).

Using data on feed rates to catalytic cracking units, to thermal operations, and the appropriate emission factors, the staff estimates that

refineries emitted approximately 650 tons to 2,700 tons of formaldehyde in 1988 (see Appendix I-C).

2. Copper Plating Solutions

In its 1983 report: Emission of Potentially Hazardous Air Contaminants in the South Coast Air Basin, the South Coast Air Quality Management District (SCAQMD) reports that Shirpley Co., Inc. of Irvine is the only producer of formaldehyde based "electroless copper plating solution" in the South Coast Air Basin. The SCAQMD staff estimated this facility emitted approximately 0.5 ton of formaldehyde in 1982 (SCAQMD, 1983).

As much as 90 percent of formaldehyde input may be lost to the atmosphere during the plating out of copper from the copper plating solution; the remaining 10 percent is disposed with the sludge at landfills. Bell Industries, Electronic Systems Division, in Santa Ana and Crown City Plating, in El Monte, are two companies in the SoCAB that are known to use electroless copper plating in their operations. Electroless copper plating tanks are vented in accordance with the Occupational Safety and Health Administration (OSHA) standards. For the 1982 inventory year, the SCAQMD staff estimated these sources emitted 46.7 tons of formaldehyde to the atmosphere (SCAQMD, 1983).

The total formaldehyde emissions from the production and the use of copper plating solution were estimated to be approximately 50 tons in the South Coast Air Basin. Statewide estimates are not available.

3. Incineration

Limited data indicate that incineration is a major source of formaldehyde. In the 1983 SCAQMD report, 0.07 tons per day of total

reactive gas emissions were from municipal incinerators, so the formaldehyde contributions are negligible. According to the Bay Area Air Quality Management District (BAAQMD) (Clayton, 1982), formaldehyde emissions from incineration in the San Francisco Bay Area Air Basin are also presumed to be negligible.

4. Non-Vehicular Fuel Combustion Sources

a. Stationary Industrial Sources

Formaldehyde is formed as a by-product of combustion. Fuel combustion at industrial and utility power generation facilities was responsible for an estimated 740 tons per year of formaldehyde emitted to the ambient air in 1987. This figure does not include formaldehyde emissions from wood combustion sources because reliable estimates of the quantity of wood burned in 1987 are not available. The estimate for fuel combustion is based on the fuel usage data from the California Air Resources Board's EDS for 1987. Emission factors for different fuel-types were obtained from the SAI, 1984 Report, and from EPA, 1988. These factors and the fuel usage data are presented in Appendix I-D.

b. Area Sources

Area sources are defined as sources that individually emit less than 25 tons of total organic gases (TOG), nitrogen oxides (NOx), sulfur oxides (SOx), particulate matters (PM) or less than 250 tons of carbon monoxide (CO) and are not included in the point source inventory. Based on the TOG emissions from area fuel combustion sources and the VOC profiles, ARB estimated area sources emitted approximately 350 tons of formaldehyde in 1987 (ARB, 1989b). These sources are associated with fuel combustion from boilers or stationary internal combustion engines in the oil and gas

extraction industry, the chemical manufacturing industry, agricultural production, and from residential heating units.

5. Pressed Wood Products

According to the 1989 SARA Title III data, which is retained by the California Environmental Protection Agency (CalEPA), five reconstituted wood processing plants emitted formaldehyde levels of 120 tons per year. Therefore, ARB estimates that as of 1989 at least 120 tons are emitted from reconstituted wood processing plants in California.

6. Resin Use

Formaldehyde-based resins are used in a large variety of products. Resins are used in products such as cotton permanent press, grocery bags and waxed paper. Total U.S. consumption of resins in 1980 was estimated at approximately 1,370,000 tons (SAI, 1984), which contained an estimated 650,000 tons of formaldehyde. In the 1984 final report, Formaldehyde: A Survey of Airborne Concentrations and Sources, SAI estimates that the 1981 formaldehyde emissions from formaldehyde-based resin products were approximately 5 tons.

E. OTHER USES

Formaldehyde is used in a wide variety of other industrial and consumer products. Emissions from the use of these products are believed to be minor compared to those estimated for the major sources (Table III-1).

1. Domestic Products

Formaldehyde is added in limited amounts (an average of 40,000 ppbv) to detergents, cosmetics and other domestic chemicals as an antimicrobial agent (Table-III-2). Approximately 35 percent of marketed cosmetic shampoos, 23 percent of bubble-bath formulations, and 20 percent each of hair rinses and hair conditioners contain formaldehyde as an antimicrobial preservative. In most commercial formulations the usual formaldehyde concentration in these products probably does not exceed 0.02 percent.

Another cosmetic use of formaldehyde is as a nail hardener. Finger nails treated with formaldehyde solutions become harder and more resistant to breakage. For this application, the formaldehyde concentration is significantly higher, up to approximately 5 percent (ACS, 1985).

TABLE III-2

PRODUCT FORMULATION DATA FOR COSMETICS CONTAINING FORMALDEHYDE[1]

Product Category	Total Number of Products	Number Containing Formaldehyde	Percent
Shampoos (noncoloring)	909	316	35
Bubble baths	475	109	23
Hair conditioners	478	95	20
Wave sets and hair rinse (noncoloring)	338	69	20
Other Bath preparations	132	24	18
Other hair preparations (noncoloring)	177	13	7
Bath oils, tablets, & salts	237	10	4
Other products in categories listing HCHO	5000	78	2

1. American Chemical Society, 1985. Formaldehyde- Analytical Chemistry and Toxicology.

Domestic chemicals contain low boiling-point solvents which vaporize during use. Organic emissions from this vaporization are estimated at 1.1

tons per 1000 people. Formaldehyde content is placed at 0.6 percent by weight of total organic emissions. Based on 1983 population statistics, the SCAQMD estimated this source emitted approximately 150,000 lbs of formaldehyde in the South Coast Air Basin (SCAQMD, 1983). Assuming a population ratio of 0.47, (SoCAB to California) the total State annual estimate is approximately 310,000 lbs or 160 tons.

2. Sterilizers

Formaldehyde (as formalin) can be used as a sterilizer. Based on its 1983 report: Emission of Potentially Hazardous Air Contaminants in the South Coast Air Basin, the SCAQMD estimated the annual emissions of formaldehyde gas, from sterilizing uses, in the South Coast Air Basin at 2781 pounds or 1.4 tons in 1982 (SCAQMD, 1983). Statewide estimates are not available at this time.

3. Formaldehyde from Storage and Handling

Based on the 1983 SCAQMD report the average uncontrolled storage and handling emissions were estimated to be about 0.04 pounds per ton. Based on industry sources, 10×10^6 pounds of formalin (37 percent solution of formaldehyde) are used annually in the South Coast Air Basin (SoCAB). Formaldehyde emissions were calculated to be 74 pounds per year (0.04 tons/yr). Statewide estimates are not available.

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IV.

EXPOSURE TO FORMALDEHYDE

A. AMBIENT MONITORING IN CALIFORNIA

The toxics sampling network in California for formaldehyde consists of 19 monitoring stations statewide (Figure IV-1). Nine of these monitors are located in Southern California (south of Bakersfield), while the other 10 are located in the northern portion of the state.

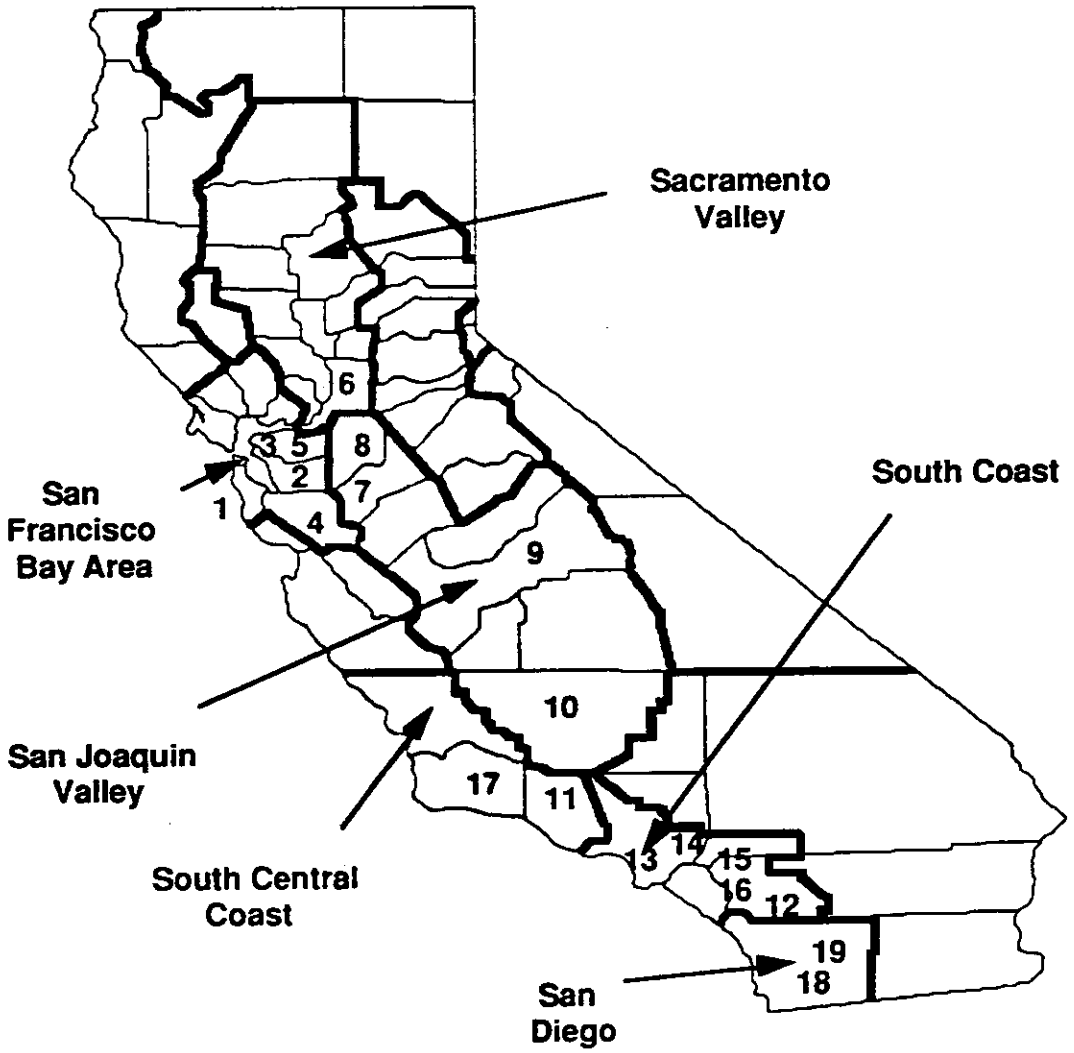
Data used in this exposure analysis were collected during the period of September 1988 through August 1989. The data for this period (hereafter referred to as "the study period") represent the most recent period for which the data are of consistent and verifiable quality. In addition, a monitoring station at Burbank was operated for 3 months (June-August) during the study period but had an insufficient data to be included in the exposure estimate.

Individual samples were collected over a 24-hour period using two 2, 4-dinitrophenyl hydrazine-coated SepPak cartridges in tandem. The aldehydes present in the air react with the 2,4-dinitrophenylhydrazine coating to form hydrazones. The hydrazone derivatives are extracted from the cartridges with acetonitrile, and the extract is analyzed using Reverse-Phase High Performance Liquid Chromatography with a ultraviolet detector.

A summary of data availability for each of the monitoring sites used in the analysis is presented in Table IV-1. The statewide formaldehyde data for the study period represent 19 sites and a small percentage of all possible days during the sampling period.

Figure IV-1

ARB Toxics Network Monitoring Sites



1. San Francisco	6. Citrus Heights	11. Simi Valley	16. Upland
2. Fremont	7. Modesto	12. Riverside	17. Santa Barbara
3. Richmond	8. Stockton	13. Long Beach	18. Chula Vista
4. San Jose	9. Fresno	14. Los Angeles	19. El Cajon
5. Concord	10. Bakersfield	15. El Monte	

Table IV-I

SUMMARY OF FORMALDEHYDE DATA[1]
September 1988 - August 1989

Site Location	S	O	N	D	J	F	M	A	M	J	J	A	Samples
SOUTHERN CALIFORNIA SITES													
South Coast Air Basin													
El Monte	o	o	o	o	o	o	o	o	o	o			45
Long Beach	o	o	o	o	o	o	o	o	o	o	o	o	58
Los Angeles	o	o	o	o	o	o	o	o	o	o	o	o	56
Rubidoux	o	o	o	o	o	o	o	o	o	o	o	o	58
Upland	o	o	o	o	o	o	o	o	o	o	o	o	50
South Central Coast Air Basin													
Santa Barbara	o	o	o	o	o	o	o	o	o	o	o	o	21
Simi Valley	o	o	o	o	o	o	o	o	o		o	o	26
San Diego Air Basin													
Chula Vista	o	o	o	o	o	o	o	o	o	o	o	o	25
El Cajon	o	o	o	o	o	o	o	o	o	o	o	o	23
NORTHERN CALIFORNIA SITES													
San Francisco Bay Area Air Basin													
Concord	o	o	o	o	o	o	o	o	o	o	o	o	25
Fremont	o	o	o	o	o	o	o	o	o	o	o	o	25
Richmond	o	o	o	o	o	o	o	o	o	o	o	o	25
San Francisco		o	o	o	o	o	o	o	o	o	o	o	21
San Jose	o	o	o	o	o	o	o	o	o	o	o	o	24
San Joaquin Valley Air Basin													
Bakersfield	o	o	o	o	o	o	o	o	o	o	o	o	25
Fresno	o	o	o	o	o	o	o	o	o	o	o	o	26
Modesto	o	o	o	o	o	o	o	o	o	o	o	o	25
Stockton	o	o	o	o	o	o	o	o	o	o	o	o	24
Sacramento Valley Air Basin													
Citrus Heights	o	o	o	o	o	o	o	o	o	o	o	o	24

1. A "o" indicates at least one sample was collected during the month. These samples are based upon 24 hour averages.

The number of samples available per site during the study period range from 18 to 26 in northern California, averaging 24 observations per site for the study period; the number of samples available per site in southern California range from 21 to 58, averaging 40 observations per site. Formaldehyde was sampled on an every sixth day schedule in the South Coast Air Basin and on a once every twelfth day in the other air basins. This increase in sampling frequency accounts for the larger dataset for the South Coast in comparison to the other five air basins. There were no concentrations reported below the 0.1 ppbv (0.12 ug/m^3) limit of detection.

B. ESTIMATING AMBIENT CONCENTRATIONS

Results of Analysis

Summary statistics for each site during the study period are summarized in Table IV-2. The minimum, maximum, median, and estimated mean annual concentration, along with the coefficient of variation and standard deviation are reported for each site. Basin results are included for each statistic except the coefficient of variation.

Mean annual formaldehyde concentrations were calculated as the mean of available monthly means. This approach provides equal weighting for each month even when the number of samples per month varies. The mean of monthly means is a more reliable estimator of annual exposure than the arithmetic average of all study period concentrations. Mean annual concentrations ranged from a minimum of 2.5 ppbv (3.1 ug/m^3) at Richmond to a maximum of 6.0 ppbv (7.4 ug/m^3) at El Monte. Basin averages ranged from a minimum of 3.2 ppbv (3.9 ug/m^3) in the San Francisco Bay Area to a maximum of 4.9 ppbv (6.2 ug/m^3) in the South Coast.

Table IV-2

SUMMARY OF SAMPLE STATISTICS COLLECTED
September 1988 - August 1989
(concentrations are in parts per billion volume*)

AIR BASIN Site Location	Minimum Conc.	Maximum Conc.	Median Conc.	Mean[1] Conc.	Std.[2] Dev.	CV[3]
SOUTHERN CALIFORNIA SITES						
South Coast Air Basin						
El Monte	1.1	19.0	5.2	6.0	3.3	64
Long Beach	0.2	19.0	3.2	4.6	3.3	89
Los Angeles	0.3	22.0	4.7	5.4	2.8	76
Rubidoux	0.5	11.0	3.7	3.9	1.7	63
Upland	0.3	12.0	4.2	4.8	1.4	52
Basin Summary	0.2	22.0	4.4	4.9	2.6	
South Central Coast Air Basin						
Santa Barbara	1.2	11.0	2.4	3.4	2.2	74
Simi Valley	0.6	13.0	3.6	4.0	1.4	66
Basin Summary	0.6	13.0	2.9	3.7	1.8	
San Diego Air Basin						
Chula Vista	0.7	11.0	1.9	2.8	1.8	82
El Cajon	1.6	12.0	3.9	5.2	2.4	58
Basin Summary	0.7	12.0	2.4	4.0	2.2	
NORTHERN CALIFORNIA SITES						
San Francisco Bay Area Air Basin						
Concord	0.3	11.0	2.7	3.5	2.2	71
Fremont	0.7	11.0	2.2	3.2	2.2	78
Richmond	1.1	7.3	2.0	2.5	1.2	78
San Francisco	0.7	13.0	2.3	3.5	2.5	93
San Jose	0.5	12.0	2.2	3.0	1.9	78
Basin Summary	0.3	13.0	2.2	3.2	2.0	
San Joaquin Valley Air Basin						
Bakersfield	0.3	7.1	2.8	3.0	2.5	55
Fresno	1.1	9.7	3.1	4.1	1.8	57
Modesto	0.4	16.0	2.8	4.1	2.9	89
Stockton	1.0	9.8	3.7	4.0	1.5	54
Basin Summary	0.3	16.0	3.2	3.8	2.2	
Sacramento Valley Air Basin						
Citrus Heights	0.9	11.0	4.3	4.3	2.1	56

1. Basin Means are the mean of the site means, based on 24 hr. averages.
2. Basin Standard Deviations are pooled values of the standard deviations across sites within a basin.
3. Coefficient of Variation is calculated as the standard deviation of all values divided by the mean of all values expressed as a percentage. Basin results are not given.

* 1 ppbv = 1.23 ug/m^3

A coefficient of variation (CV) statistic provides information about the distribution of data and for formaldehyde is reported for each monitoring site. The CV expresses as a percentage the magnitude of the variation relative to the magnitude of the concentrations being measured. The CV is equal to the standard deviation of all observations divided by the mean of all observations multiplied by 100. The CV for the study period ranges from a low of 52 percent at Upland to a high of 93 percent at San Francisco. There appears to be no significant difference in the range of values for the CV between northern and southern California indicating that the distribution of values is the same.

The median is defined as the 50th percentile and can be used as an alternative measure of central tendency to the mean. At all 19 monitoring sites, the median is less than or equal to the average of all reported concentrations. During the study period, median concentrations ranged from a minimum of 1.9 ppbv (2.3 ug/m^3) at Chula Vista to a maximum of 5.2 ppbv (6.4 ug/m^3) at El Monte. A median concentration significantly different from the mean indicates the data have a non-normal distribution. Differences between the median and mean range from 0.03 ppbv (0.04 ug/m^3) at Citrus Heights to 1.4 ppbv (1.7 ug/m^3) at Long Beach. In the past, the distribution of the ambient toxic air contaminant (TAC) data has generally been assumed to be log-normal. The Shapiro-Wilk test was used to test the distribution of the formaldehyde data against the hypothesis of log-normality (Shapiro-Wilk, 1965). Even though the data from most sites are skewed as though distributed log-normally, the staff was unable to substantiate any assumption of log-normality.

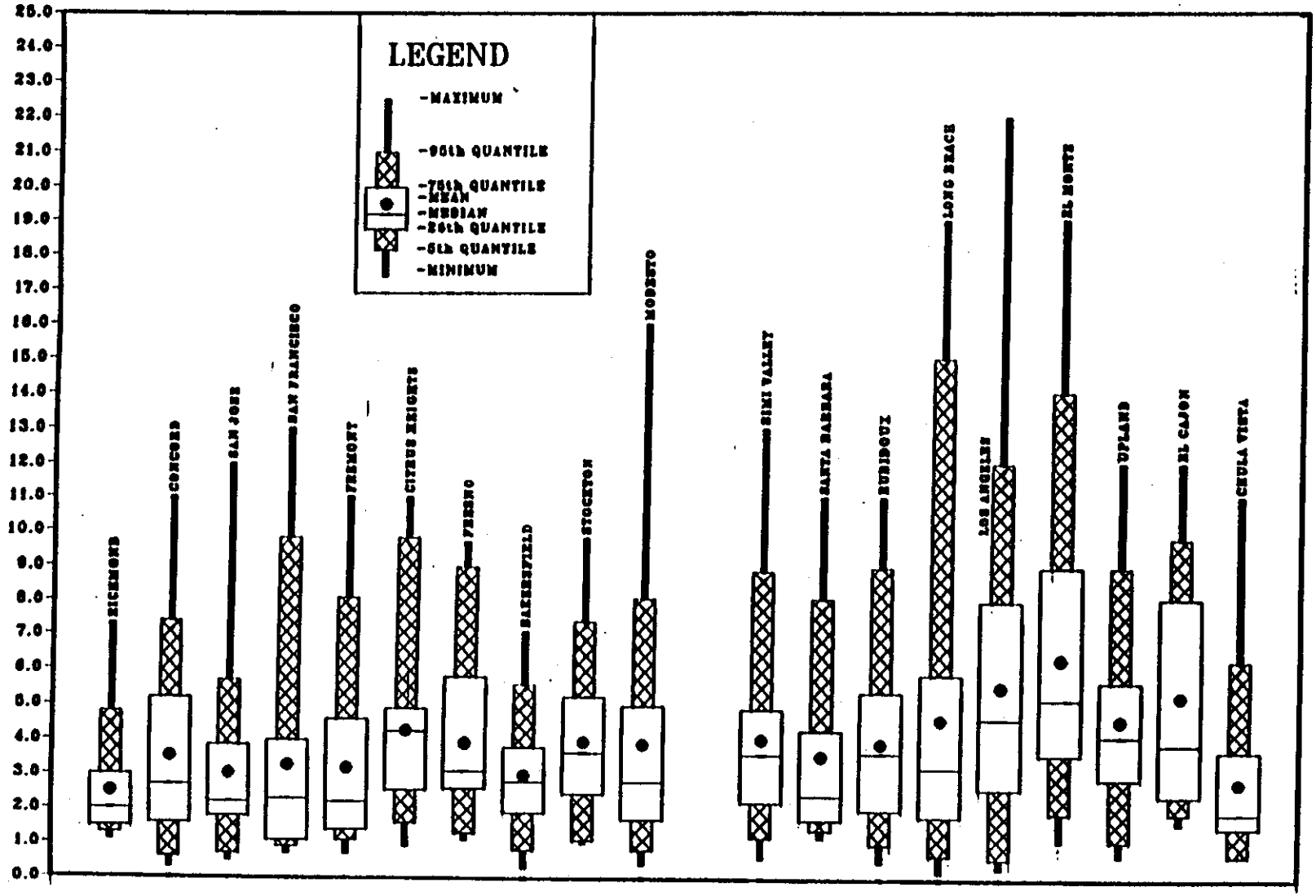
The observed distribution of values from each site is presented graphically in Figure IV-2. In general, the southern California sites appear to have slightly higher concentrations than the northern California sites. Figure IV-3 presents the same data on a month-by-month basis without

FIGURE IV-2

MEAN ANNUAL FORMALDEHYDE CONCENTRATION

PLOTTED USING EXTENDED BOX PLOTS

BASED ON SEPTEMBER 1988 – AUGUST 1989 DATA



Monitoring Sites Throughout California

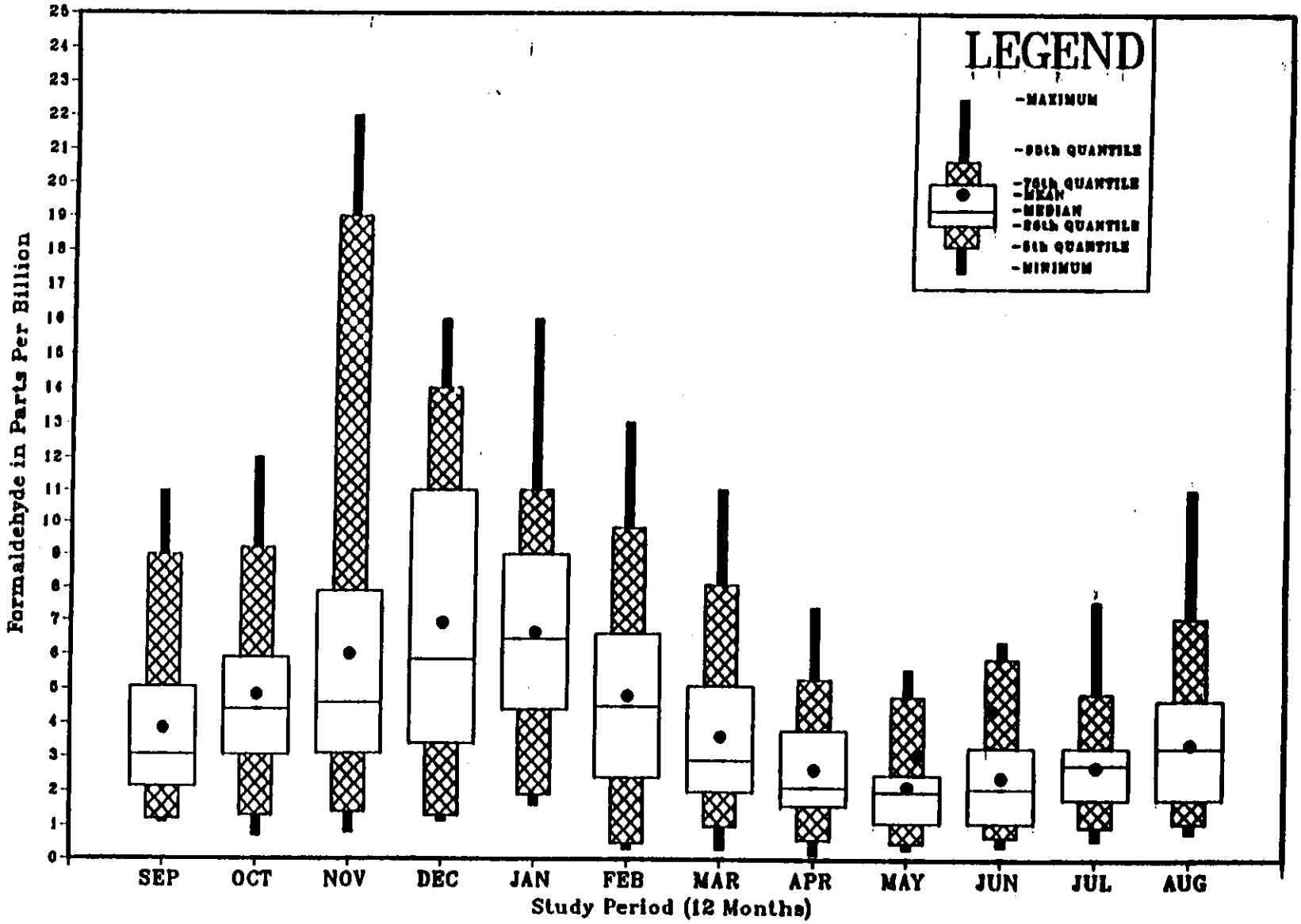
ARB/TSD:October 89

FIGURE IV-3

MONTHLY RANGES IN CONCENTRATIONS (ALL SITES COMBINED)

PLOTTED USING EXTENDED BOX PLOTS

BASED ON SEPTEMBER 1988 – AUGUST 1989 DATA



ARB/TSD:October 89

regard to site. It should be noted from Figure IV-3 that ambient formaldehyde levels appear to be influenced significantly by seasonal changes in meteorological patterns, i.e. concentrations are higher in the winter and lower in the summer based on dose. These two figures represent overall statewide ambient conditions and may not reflect actual concentrations of formaldehyde in places such as the South Coast Air Basin where high concentrations are found both in summer and winter months depending on combustion sources and photochemical oxidation periods. This pattern is similar to the seasonal patterns demonstrated by a relatively inert criteria pollutant with generally widespread emissions, such as carbon monoxide.

One of the factors influencing formaldehyde concentrations is the concentration of formaldehyde with other pollutants in the ambient air. Reported data for the short-term ambient concentrations of formaldehyde in California since 1980 are given in Table IV-3. These particular data were all collected in the South Coast Air Basin, and vary from <1 ppbv (<1.23 ug/m^3) up to 86 ppbv (105 ug/m^3), with recent concentrations measured in the California Air Resources Board-funded intercomparison studies at Glendora in the South Coast Air Basin having a range of 3 to 22 ppbv (4 to 27 ug/m^3) Lawson et al. (1990).

It may be expected that the ambient atmospheric formaldehyde levels encountered in the South Coast Air Basin are among the highest to be expected in California because of the number of combustion sources associated with periods of high photochemical reactivity. The ambient atmospheric formaldehyde mixing ratios in California range from a few tenths of a part per billion (for clean tropospheric air) up to a few tens of ppb, with the actual values depending to a large extent on the organic precursor emissions, the extent of photochemical activity and the meteorological conditions present in the atmosphere. Formaldehyde concentrations in the

Table IV-3

RECENT MEASUREMENTS OF FORMALDEHYDE CONCENTRATIONS
IN AMBIENT AIR IN CALIFORNIA

HCHO Conc. (ppbv)	Sampling Times	Measurement Date and Place	Reference
2-40	1 hr	5-6/1980, Los Angeles	Grosjean (1982)
3-48	1 hr	9-10/1980, Claremont	Grosjean (1982)
10-41	1 hr	7/1980, Riverside	Singh et al. (1982)
18-60	1 hr	7-10/1980, Los Angeles	Grosjean et al. (1983)
65-70	30 min	7-8/1980, Burbank	Grosjean et al. (1983)
53	30 min	7/1980, Pasadena	Grosjean et al. (1983)
5	30 min	8/1980, Pamona	Grosjean et al. (1983)
33	30 min	8/1980, Newhall	Grosjean et al. (1983)
38-47	45 min	9-10/1980, Rosemead	Grosjean et al. (1983)
27	1 hr 30 min	9/1980, Covina	Grosjean et al. (1983)
42	30 min	9/1980, Cucamonga	Grosjean et al. (1983)
59-66	1 hr	10/1980, El Monte	Grosjean et al. (1983)
34	30 min	10/1980, San Dimas	Grosjean et al. (1983)
34	30 min	10/1980, Upland	Grosjean et al. (1983)
0.7-35	2 hr	10/1980, Azuza	Grosjean et al. (1983)
0.5-40	2 hr	10/1980, Lennox	Grosjean et al. (1983)
4-86	45 min	9-11/1981, Los Angeles	Grosjean and Fung (1984)
1.5-11	4 to 6 hrs	9/1985, Claremont	Grosjean (1988)
3-22	1 hr	8/1986, Glendora	Lawson et al. (1990)
3-35	1 hr	6-12/1987, SoCAB sites	Fung (1989)

ambient air also reflect seasonal variations (Lawson et al. 1990).

Further studies indicate that levels of formaldehyde concentrations fluctuate during diurnal and seasonal periods. During the Southern California Air Quality Study (SCAQS), high levels of formaldehyde existed during daytime hours with low levels at night. Peak concentrations occurred at mid-day with highest peaks observed at Anaheim with concentrations of 35.2 ppbv (one hour sample averages). Typical summer inland formaldehyde levels had a range of approximately 16-25 ppbv during the day, and 3-5 ppbv range at nighttime. The average summer concentrations were between 9 and 14 ppbv. Average fall concentrations ranged from approximately 10 to 17 ppbv. In general, concentrations of formaldehyde were higher in the fall than in summer with the exception of coastal cities (Fung, 1987).

Diurnal patterns of ambient formaldehyde concentrations in relation to other primary and secondary pollutants show that direct emissions from motor vehicles is the major source of ambient formaldehyde in the South Coast Air Basin during the early morning. Formaldehyde exhibited a morning and an afternoon peak each day during the Carbonaceous Species Methods Comparison Study (Lawson et al. 1990). The morning peak was shown to be associated with nitrogen oxides (NOx) and particulate black carbon concentrations; the afternoon peak was associated with the observation of peak concentrations of photochemically produced ozone at the site. The results of the study showed that peak formaldehyde concentrations in the morning from directly emitted formaldehyde were comparable to the mid-day peaks which are due to photochemical formation of formaldehyde. These results indicate that directly emitted formaldehyde may be a greater contributor to total atmospheric levels than previously thought (Fujita et al. 1990).

C. POPULATION EXPOSURE

Population Exposure Estimates

Mean population exposure estimates were calculated using the study period formaldehyde data. Exposures for the South Coast Air Basin and San Francisco Bay Area Air Basin were estimated by interpolating station values to census tract centroids. For the other air basins, a basin-wide mean concentration was estimated from the means for all sites in the basin.

It was then assumed that all people in those basins (except the Sacramento Valley Air Basin since it had only one monitoring station) with a sampling site were exposed to this estimated basin-wide mean concentration. Population data used in the exposure analysis represent 1980 census data updated to 1985. The results of the exposure analysis are summarized in Table IV-4.

The overall ambient outside statewide formaldehyde exposure, weighted by population, is best estimated to be 4.4 ppbv (5.4 ug/m^3). A total of 20,178,400 people are estimated to reside in the study areas, representing approximately 80 percent of the State's population. Basin-specific, population-weighted mean concentrations vary from a minimum of 3.2 ppbv (3.9 ug/m^3) in the San Francisco Bay Area Air Basin to a maximum of 5.1 ppbv (6.3 ug/m^3) in the South Coast Air Basin.

Figure IV-4 shows the total number of people exposed to various mean annual formaldehyde concentrations. It shows that within the study area are 3 million people exposed to a mean annual average concentration of 5.2 ppbv (6.4 ug/m^3), 2.5 million people are exposed to 3.8 ppbv (4.7 ug/m^3) and the remaining people are exposed to a mean annual concentrations ranging from 2.4-5.6 ppbv (2.9-6.9 ug/m^3). Figure IV-5 presents the same data as that in Figure IV-4, but now plotted as the cumulative population exposed to an

Table IV-4

SUMMARY OF AVAILABLE OUTDOOR FORMALDEHYDE CONCENTRATIONS AND POPULATION-WEIGHTED EXPOSURE ESTIMATES
(units are in parts per billion volume)

Air Basin Site Location	LOWER BOUND	SITE MEAN	UPPER BOUND	Population
SOUTHERN CALIFORNIA SITES				
South Coast Air Basin				
El Monte	4.2	6.0	7.9	
Long Beach	2.9	4.6	6.5	
Los Angeles	4.0	5.4	7.0	
Rubidoux	3.0	3.9	4.8	
Upland	4.1	4.8	5.5	
POPULATION-WEIGHTED EXPOSURE FOR SoCAB		5.1		10,092,133
South Central Coast Air Basin				
Santa Barbara	2.3	3.4	4.6	
Simi Valley	3.2	4.0	4.8	
EXPOSURE FOR SCCAB		3.7		925,822
San Diego Air Basin				
Chula Vista	2.0	2.8	3.9	
El Cajon	3.9	5.2	6.6	
EXPOSURE FOR SDAB		4.0		2,135,872

* 1 ppbv = 1.23 ug/m^3

See Table IV-4,
Continued next page

Table IV-4 (continued)

SUMMARY OF AVAILABLE OUTDOOR FORMALDEHYDE CONCENTRATIONS
AND POPULATION-WEIGHTED EXPOSURE ESTIMATES
(units are in parts per billion volume)

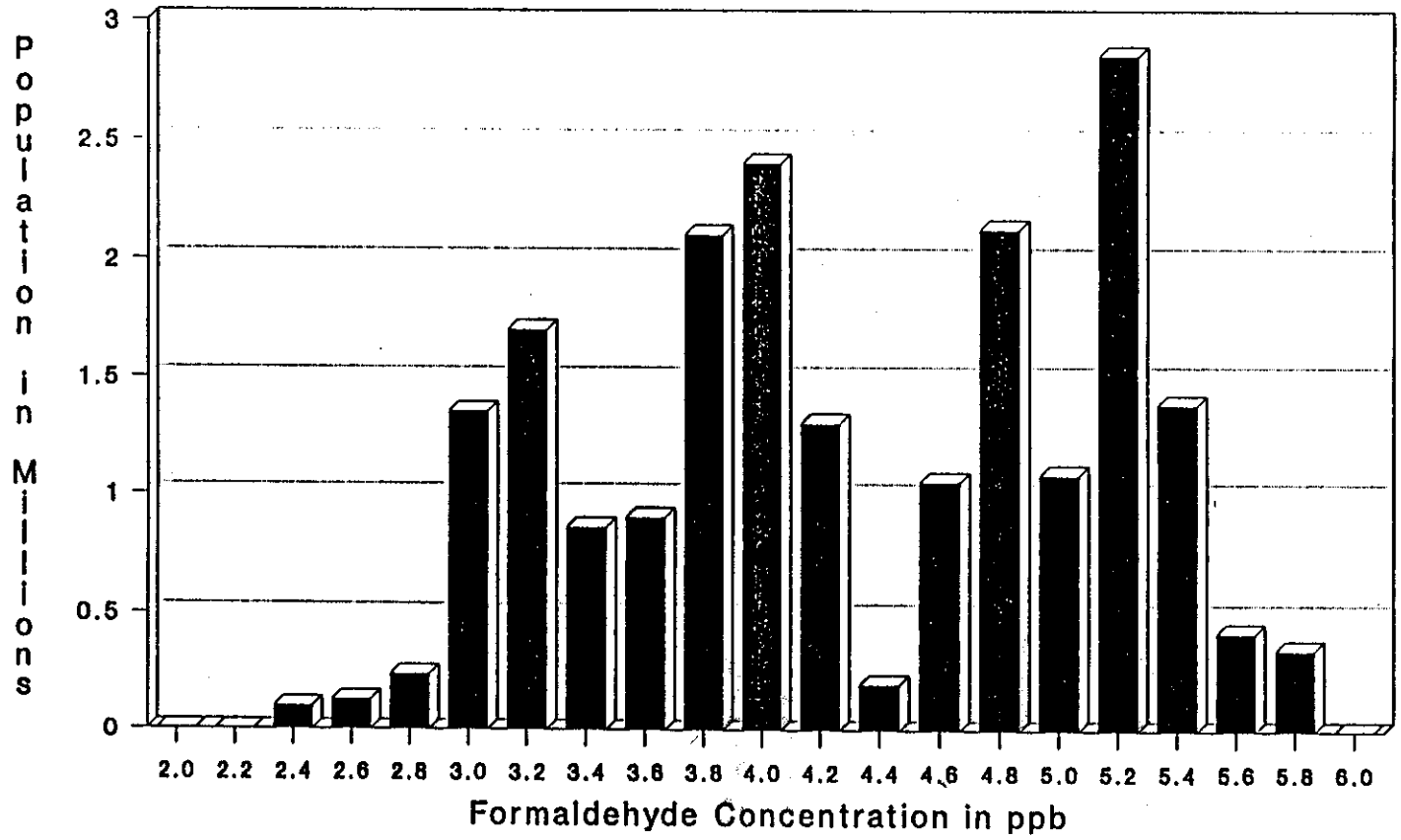
Air Basin Site Location	LOWER BOUND	SITE MEAN	UPPER BOUND	Population
NORTHERN CALIFORNIA SITES				
San Francisco Bay Area Air Basin				
Concord	2.5	3.5	4.7	
Fremont	2.1	3.2	4.3	
Richmond	1.9	2.5	3.1	
San Francisco	2.3	3.5	5.0	
San Jose	2.1	3.0	4.1	
POPULATION-WEIGHTED EXPOSURE FOR SFBAAB		3.2		4,394,374
San Joaquin Valley Air Basin				
Bakersfield	2.7	3.0	3.5	
Fresno	3.2	4.1	5.1	
Modesto	2.7	4.1	5.7	
Stockton	3.3	4.0	4.8	
EXPOSURE FOR SJVAB		3.8		1,740,400
Sacramento Valley Air Basin				
Citrus Heights	3.3	4.3	5.3	
EXPOSURE FOR SVAB[1]		4.3		889,806
OVERALL POPULATION-WEIGHTED EXPOSURE[2]		4.4		20,178,400

1. Exposure estimates are for Sacramento County residents only.

2. Based on 24 hr. sample averages.

FIGURE IV-4

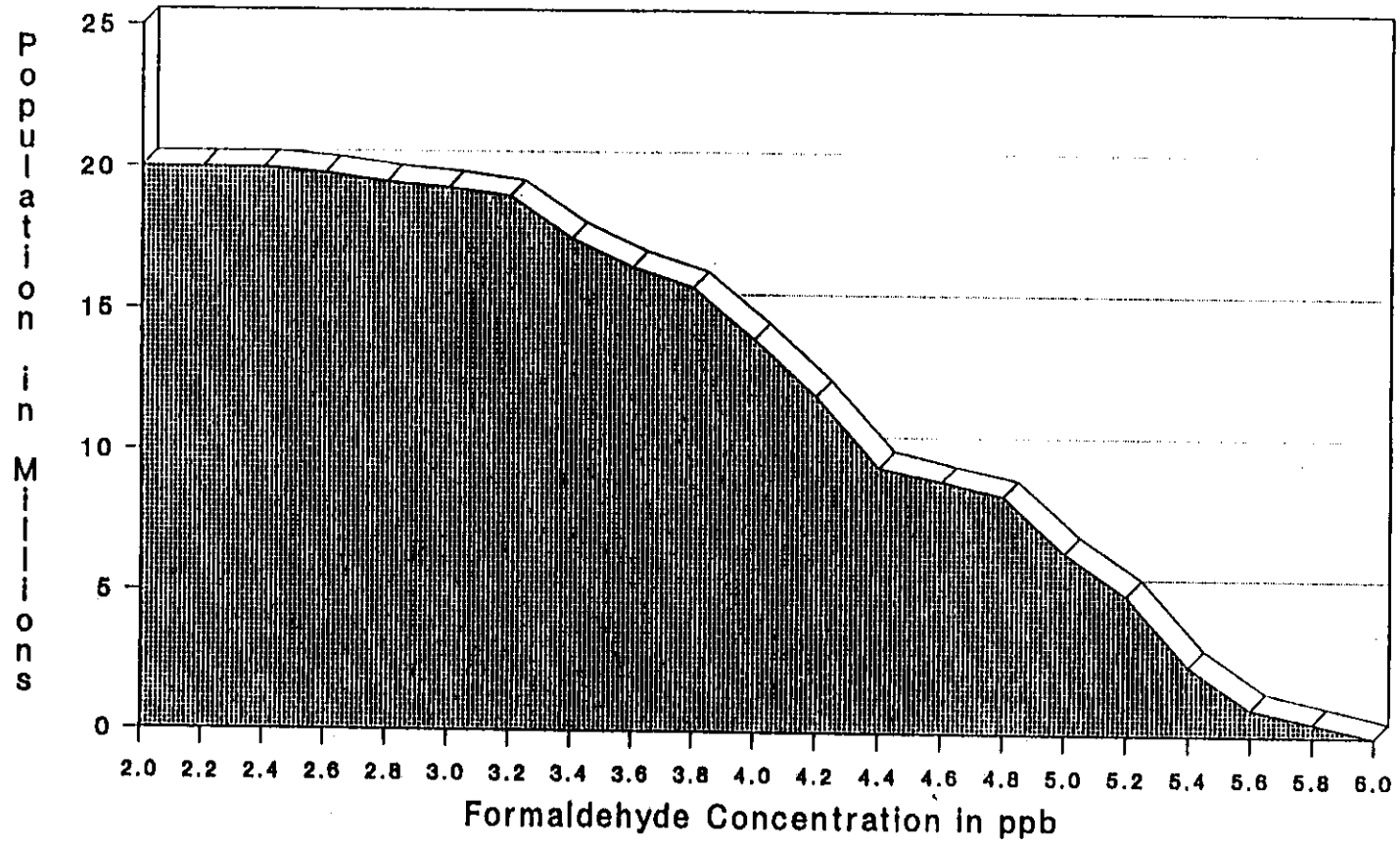
Mean Annual Ambient Outdoor Formaldehyde Exposure



Based on August 1988-September 1989 Data

FIGURE IV-5

Estimated Cumulative Ambient Outdoor Formaldehyde Exposure



Based on August 1988-September 1989 Data

estimated mean annual formaldehyde concentration.

The overall geographic mean formaldehyde concentration calculated as the average of the six basin averages was 4.0 ppbv (4.9 ug/m^3). This value is approximately eight percent lower than the population-weighted exposure best estimate of 4.4 ppbv (5.4 ug/m^3), indicating that the highest concentrations of formaldehyde tended to be in the areas of higher population density.

D. EXPOSURE TO FORMALDEHYDE NEAR EMISSION SOURCES

Sources of formaldehyde exposure that are expected to have above ambient air concentrations are near commercial production sources, facilities producing pressed wood products, congested freeways, and oil refineries. Information from the Air Toxics "Hot Spots" Act (AB 2588) will be used to prioritize and estimate near source exposures in the control phase if the Board identifies formaldehyde as a toxic air contaminant.

In addition, indoor environments consistently exhibit higher concentrations than outdoor environments. Since Californians spend most of their time indoors, indoor inhalation is a significant portion of the total exposure to formaldehyde and may be considered a potential near exposure source.

E. INDOOR EXPOSURE TO FORMALDEHYDE

Formaldehyde concentrations are generally much higher indoors than outdoors due to the abundance of building materials and consumer products in buildings that emit formaldehyde. Combustion sources such as gas stoves and cigarettes can also intermittently contribute to indoor levels of

formaldehyde. Consequently, indoor air exposures are the primary determinant of people's daily inhaled doses of formaldehyde. Formaldehyde sources, concentrations, and estimates of inhaled daily doses of formaldehyde from indoor air are summarized in the sections below and discussed in detail in the technical report, Exposure to Formaldehyde From Indoor Air (ARB, 1990).

1. Sources of Formaldehyde in Indoor Air

Formaldehyde sources are ubiquitous in indoor environments and include such diverse commodities as particle board, clothing, and shampoo. Building materials (especially newly manufactured pressed wood products made with urea-formaldehyde resins), because they emit relatively large amounts of formaldehyde and are present in large quantities, can make significant contributions to indoor formaldehyde concentrations. Formaldehyde emissions from pressed wood products made with formaldehyde-based resins are highest when the products are new. Later, as the products age, formaldehyde is released more slowly and the emission rates eventually become relatively small. This aging process varies with the type of product and, for pressed wood products, can take a number of years. Thus, older pressed wood products, as a result of the off-gassing of formaldehyde over time, are believed to make a smaller contribution to indoor formaldehyde concentrations. Pickrell et al. (1986) (Table IV-5) measured the formaldehyde emission rates of seven categories of newly-purchased consumer products (pressed wood products, urea-formaldehyde foam products, insulation products, paper products, clothing, fabric, and carpets). The investigators found that pressed wood products and urea-formaldehyde foam insulation had much higher formaldehyde release rates than most of the other products tested. However, it should be noted that industry data show that the emissions from many urea-formaldehyde bonded pressed wood products being sold now are significantly lower than the emissions of such products sold in the late 1970s/early 1980s when Pickrell et al. measurements were made (Table IV-5.1). Also, urea-formaldehyde foam insulation is no longer installed in California homes (see section 1.b below). Table IV-6 shows

Table IV-5

EMISSION RATES OF SELECTED INDOOR SOURCES OF FORMALDEHYDE[1,2]
($mg/m^2/day$)

	Range	Mean
Pressed Wood Products		
Particle Board	1.8 - 28.0	16.0
Interior Plywood	13.0 - 15.0	14.1
Exterior Plywood	0.001 - 0.056	0.037
Paneling	1.48 - 36.0	11.0
Insulation Products		
UFFI[3]	0 - 28.0	15.4
Fiberglass ceiling panel	0.39 - 0.54	0.46
Rigid round air duct	0.39 - 0.43	0.41
Rigid round fiberglass duct	0.15 - 0.15	0.15
Fiberglass	0.052 - 0.62	0.09
Blackface insulation sheeting	0.34 - 0.42	0.38
Paper Products		
Paper plates & cups	0.075 - 1.0	0.43
New Clothes		
Men's shirts	0.38 - 0.55	0.47
Ladies dresses	0.38 - 0.75	0.57
Girl's dresses	0.12 - 0.14	0.13
Children's clothes	0.015 - 0.055	0.035
Fabrics		
Drapery fabric	0 - 0.35	0.14
Upholstery fabric	0 - 0.011	0.004
Latex backed fabric	0 - 0.1	0.06
Blend fabric	0.02 - 0.03	0.025
Carpets		
Foam backed	0 - 0.065	0.025
Other	0 - 0.004	0.001

Source: Pickrell, et al., 1983.

Table IV-5.1

EMISSION RATES OF LOW EMITTING[1,2] UF-BONDED PRESSED WOOD PRODUCTS
($mg/m^2/day$)

	Range	Mean
Particle Board	0.42 - 2.32	1.06
Interior Plywood/Paneling	0.21 - 1.86	0.59

Source: Provided in communication from the Hardwood Plywood Manufacturers Association and the National Particleboard Association, 1992 and based on industry data from 2-hour desiccator tests.

Footnotes Table IV-5

1. Industry data show that the emissions from many urea-formaldehyde bonded pressed wood products being sold now are significantly lower than the emissions from such products sold in the late 1970s/early 1980s when the Pickrell et al. measurements were made. See data provided by industry in Table IV-5.1.

2. Formaldehyde emissions from combustion sources are shown on Table IV-6.

3. Emission rates for products described above tend to decrease with product age.

4. UFFI is no longer installed in California homes.

Footnotes Table IV-5.1

1. "Low emitting" means products conforming to standards established by the United States Department of Housing and Urban Development for products used in manufactured housing.

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emission rates from indoor combustion sources, which release formaldehyde intermittently (i.e. while they are in use). In general, newer (before appreciable aging) building materials tend to be the highest emitters, followed by combustion sources, paper products, new clothes, draperies and other fabrics.

a. Pressed Wood Products

Formaldehyde is a component of the resins used in the manufacture of pressed wood products such as plywood, particle board, and medium density fiberboard. Those materials gained widespread use after World War II because of their low cost and durability (Meyer and Hermanns, 1986). They are used extensively in the construction of single family and mobile homes and are found in subfloors; cabinets; hardwood paneling; roof, wall, and floor sheathing; and exterior siding (Emery, 1986).

Table IV-6

FORMALDEHYDE EMISSION RATES OF COMBUSTION SOURCES

Product	Estimated Use	Formaldehyde Emission Rate (mg/h) Measured During Use	Average over 24 hr
Gas burner	1.0 h/day	16 ± 10	0.67 ± 0.41
		4.3 ± 2.6	0.18 ± 0.11
Gas oven	0.7 h/day	23 ± 3.4	0.67 ± 0.10
Kerosene heater			
Convective	8 h/day	1.0 ± 0.66	0.33 ± 0.22
Radiant	8 h/day	4.0 ± 2.0	1.3 ± 0.66
Cigarettes	10 cig/day	0.97 ± 0.06	0.40 ± 0.03
		1.44	0.60

Source: Matthews et al., 1985; based on Traynor et al., 1982 a,b

Regulations limiting emissions from certain building materials were developed as a result of numerous health complaints from people living in mobile homes. In 1984 the U.S. Department of Housing and Urban Development (HUD) imposed limits on formaldehyde emissions for some types of particle board and interior plywood at 300 ppbv and 200 ppbv (test chamber concentrations), respectively, to attain indoor air concentrations of no more than 400 ppbv in manufactured housing (mobile homes)[24 CFR 3280.309 (a)]. These standards are based on stable temperature (75 ± 2 degrees F), air exchange rate (0.5 ACH), and humidity (50%) conditions. Each of these conditions influence the rate and amount of emissions off pressed wood products, with increases in temperature appearing to influence the majority of emissions from indoor sources (Pitts et al. 1989).

HUD did not impose a limit on emissions from medium density fiberboard. However, in 1987, the National Particleboard Association recently approved a voluntary industry standard which limits emissions from medium density fiberboard to 300 ppbv (test chamber concentration, National Particleboard Association, NPA 9-87). The U.S. Consumer Product Safety Commission is currently participating in the development of a voluntary standard to further limit formaldehyde release from pressed wood. This standard will be based on a national consensus standard developed in association with several industrial organizations.

As a result of these standards and the subsequent use of lower-emitting pressed wood products in buildings, concentrations in homes built recently may be lower (to an unknown extent) than in homes built before the early 1980's.

b. Insulation Products

Insulation materials also contain urea-formaldehyde resins which can emit formaldehyde indoors. A major source of formaldehyde from insulation material is urea-formaldehyde foam insulation (UFFI). In the 1970's UFFI was injected into wall cavities of older homes to make them more energy efficient. In 1982 the Consumer Product Safety Commission banned UFFI. The ban was challenged successfully in the U.S. Court of Appeals (1983) by UFFI and formaldehyde manufacturers. However, by that time manufacturers had generally stopped production of UFFI because of consumer complaints and other insulating materials had been substituted. The California Energy Commission adopted insulation standards in 1982 which permit the use of UFFI only if its formaldehyde emissions are less than 0.01 percent by weight in a standard test protocol. Since this limit is practically unachievable, these rules effectively prohibit the use of UFFI in California. Therefore, although UFFI is permitted, it is generally not found in newer homes.

c. Furnishings

Formaldehyde is emitted from furnishings containing formaldehyde resins. Furniture constructed with particle board and wood veneer emits formaldehyde. Formaldehyde polymers are used in the manufacture of floor coverings. Wallpaper, especially prepasted wall papers and those consisting of fibers or layers of paper bonded with formaldehyde resin, can also emit formaldehyde (Gammage and Gupta, 1984).

The textile industry uses formaldehyde-based resins for producing fabrics resistant to flames, creasing, crushing, and shrinking. Such fabrics are used commonly in curtains, bedsheets, and other furnishings.

Cotton fabrics are often treated with formaldehyde-containing cross linking agents (methylolamides, formed by reacting formaldehyde with certain amides, are commonly used) to impart permanent press qualities (Andrews and Reinhardt, 1985). Formaldehyde-containing compounds are also used as binders to improve the adherence of pigments to cloth (Andrews and Reinhardt, 1985; Gammage and Gupta, 1984).

d. Combustion Sources

Formaldehyde can be formed as a combustion by-product. While formaldehyde is emitted continuously from building materials and furnishings as discussed above, it is emitted intermittently from combustion sources (i.e. while they are in use). Gas appliances, kerosene heaters, and cigarettes can emit measurable amounts of formaldehyde (Traynor et al., 1982a; Traynor et al., 1982b; Girman et al., 1982; Girman et al., 1983). However, such combustion sources do not appear to affect the average formaldehyde concentration inside the home significantly (Hawthorne et al., 1988; Traynor et al., 1985; Traynor and Nitschke, 1984). Although combustion sources did not significantly affect formaldehyde concentration levels, temperature strongly influenced the rate of formaldehyde outgassing found in a mobile office/home environment. The results demonstrate that as temperature in the mobile office/home increases very rapidly, outgassing of formaldehyde also increases (Pitts et al. 1989).

Table IV-6 shows typical formaldehyde emission rates and estimated use (Matthews et al., 1985). The values for emissions were calculated, using a

mass balance equation, from concentrations measured in a test chamber (from Traynor et al., 1982a,b). Additional information on formaldehyde emissions from cigarette smoke is provided below.

e. Cigarette Smoke

Cigarette smoke can elevate formaldehyde concentrations in experimental chambers. Lofroth et al. (1989) noted that sidestream smoke from machine-smoked cigarettes raised the formaldehyde concentration in a 13.6 m^3 chamber which was ventilated at a rate of approximately 3.6 air changes per hour. When one cigarette was smoked every 30 minutes, the formaldehyde concentration was elevated from the background level of 14 ug/m^3 (11 ppbv) to 80 and 84 ug/m^3 (approximately 70 ppbv). The formaldehyde concentration reached 170 and 173 ug/m^3 (approximately 140 ppbv) when one cigarette was smoked every 15 minutes. Urch (1985) introduced both mainstream and sidestream smoke from machine-smoked cigarettes into a 15 m^3 chamber with no fresh air exchange. "Moderate" levels of cigarette smoke (as defined by the level of carbon monoxide in the chamber) raised the chamber concentration from 34 ug/m^3 (28 ppbv) to 157 ug/m^3 (128 ppbv). "Heavy" levels raised the concentration to 278 ug/m^3 (226 ppbv).

Information regarding the relative contribution of cigarette smoke to average indoor formaldehyde concentrations is not conclusive, but data suggest that this contribution is not large. Hawthorne et al. (1988) conducted a study of about 300 homes which was designed to measure the effect of combustion sources such as cigarettes, woodstoves, and kerosene heaters on indoor air quality. The investigators concluded that none of those three sources appeared to influence indoor formaldehyde levels greatly. Likewise, Traynor and Nitschke (1984) and Traynor et al. (1985) monitored 30 homes to investigate the indoor air quality impact of

combustion sources such as cigarettes, kerosene heaters, gas ranges, coal- and wood-burning stoves, wood-burning fireplaces, and gas- and oil-fired furnaces. From the data presented, the presence of cigarette smokers did not appear to elevate average indoor formaldehyde concentrations. In contrast, Rogozen et al. (1984) concluded from their survey of 64 California homes that average formaldehyde concentrations were higher in homes where smokers were present. However, it is not clear if cigarette smoke was actually the cause of the higher formaldehyde concentrations because group means for different levels of smoking were not significantly different.

f. Consumer Products

Formaldehyde is also used in consumer products such as clothing, paper products, starch-based glues, room deodorizers, cosmetics, and toiletries. Fabrics treated with formaldehyde-containing compounds are often used in clothing (see above discussion on the use of formaldehyde in textiles) and can emit formaldehyde. Formaldehyde-containing resins are used to treat paper products to impart added strength and resistance to water. Typical paper products treated with urea-formaldehyde resin include grocery bags, waxed paper, facial tissues, napkins, paper towels, and disposable sanitary products (Gammage and Gupta, 1984). Formaldehyde is also used in certain cosmetics and toiletries as an antimicrobial preservative. Typical products that contain formaldehyde include shampoos, bubble baths, and hair conditioners. The usual concentration of formaldehyde in these products is approximately 0.1 percent. Formaldehyde is used in toothpaste as a preservative and in some products as a tooth desensitizing agent. Nail hardeners may contain up to five percent formaldehyde if certain restrictions and labeling requirements are followed (Scheuplein, 1985). It is likely that the contribution to indoor air concentrations of formaldehyde from these sources is small.

2. Indoor Concentrations of Formaldehyde

The results of more recent California surveys of randomly-selected residences indicate that formaldehyde concentrations inside California residences generally range from less than 10 ppbv to almost 500 ppbv. Concentrations inside mobile homes are somewhat higher than in conventional homes, which in turn generally have higher formaldehyde concentrations than public/commercial buildings. Indoor concentrations of formaldehyde are generally much higher than outdoor concentrations. A more detailed review of indoor monitoring data is included in the technical report (ARB, 1990).

a. Mobile Homes

Mobile homes in particular have been found to have higher indoor concentrations of formaldehyde, largely due to the extensive use of pressed wood products in a smaller space. Several investigators have measured formaldehyde in California mobile homes (Table IV-7). In the largest study, the Department of Health Services (DHS) conducted a statewide survey of formaldehyde concentrations in an age-stratified random sample of mobile homes in the summer of 1984 and the winter of 1985. The investigators mailed two passive formaldehyde samplers to each mobile home and instructed the occupants to place one sampler in the kitchen and one in the master bedroom. The samplers were exposed for seven days under normal living conditions and then returned for analysis. The investigators thus obtained integrated one-week measurements for 663 mobile homes in the summer and 523 in the winter (472 of which were monitored during both seasons). The geometric mean formaldehyde concentration measured in the summer was 72 ppbv (arithmetic mean 91 ppbv) and the values ranged from below the detection limit of 10 ppbv up to 464 ppbv. In the winter, the geometric mean

TABLE IV-7

FORMALDEHYDE CONCENTRATIONS IN MOBILE HOMES

LOCATION	AVERAGE CONC. (ppbv)	RANGE (ppbv)	n	REFERENCE
California, statewide	72*	<10-464	663 summer	Sexton, et al., 1986
	78*	17-314	523 winter	
California, statewide	114	68-144	3	Rogozen, et al., 1984
California, southern	160***	50-300	10 park 1	Colome, et al., 1983
	110	30-150	14 park 2	
California;	210	20-680	81	Clayton Environmental Consultants, 1982
Texas;	300	100-770	34	
MI, IN, MN;	350	<20-1,640	87	
GA, FL, NC	410	50-1,800	59	
Texas, four counties	150	<20-780	164	Stock, et al., 1985; Stock, et al., 1984
Wisconsin, statewide	160**	<100-800	65	Hanrahan, et al., 1984
Wisconsin, 3 locations	370*	<100-2,840	137	Hanrahan, et al., 1985

* geometric mean

** median

*** data apparently reported in reverse order in reference, corrected here

was 78 ppbv (arithmetic mean 91 ppbv) and the measured values ranged from 17 ppbv to 314 ppbv (Sexton et al., 1986). Other small surveys conducted in California obtained measurements of indoor formaldehyde concentrations that were within the range measured in the DHS survey (Rogozen et al., 1984; Colome et al., 1983).

b. Conventional Homes

Based on the California data presented in Table IV-8, the average formaldehyde concentration inside conventional (non-manufactured) homes is roughly 50 ppbv and ranges from approximately 20 ppbv to above 150 ppbv (Rogozen et al., 1984; Sexton et al., 1986; Wagner, 1982). The higher concentrations tend to be found in newer homes. Average formaldehyde concentrations measured in California homes are generally comparable with those measured in other parts of the country. The greater range in the values obtained from the rest of the country (from less than 10 ppbv to approximately 380 ppbv) may be due to differences in construction and insulation practices, climate, home selection, home age, sampling protocols, or the number of homes sampled.

Current information on formaldehyde concentrations in homes with UFFI is limited. In the early 1980's, it was estimated that UFFI contributes, on average, about 100 ppb to indoor formaldehyde concentrations (Gammage and Gupta, 1984). Since UFFI is no longer in use and the emission of formaldehyde from that source decreases with time, the contribution to indoor concentrations is less. However, the magnitude of its concentration is not well known. Some evidence suggests that formaldehyde concentrations inside homes with UFFI may now be comparable with those of conventional homes without UFFI (Weintrub, 1989).

TABLE IV-8

FORMALDEHYDE CONCENTRATIONS IN CONVENTIONAL HOMES

LOCATION	AVERAGE CONC. (ppbv)	RANGE (ppbv)	n	REFERENCE
California, 4 urban areas	50 85	18-120 46-153	64 6 new	Rogozen, et al., 1984
California, SF Bay Area	35*	13-85	51	Sexton, et al., 1986
California, Sacto./Davis	109	78-163	12	Wagner, 1982
Pacific northwest WA, MT, OR, ID	83**	20-375	876	Reiland, et al., 1988
Oregon & Washington, Portland & Spokane areas	82* 72*	22-343	29 energy-efficient 23 standard	Turk, et al., 1987b
Texas, Houston area	70	< 8-290	78	Stock and Mendez, 1985

*geometric mean

**median

CONTINUED ON NEXT PAGE

TABLE IV-8 (Cont.)

FORMALDEHYDE CONCENTRATIONS IN CONVENTIONAL HOMES

LOCATION	AVERAGE CONC. (ppbv)	RANGE (ppbv)	n	REFERENCE
Texas, Houston area	70*	30-180	43	Stock, 1987
East Tennessee, Kingston/ Harriman	43* 58*	20-170 10-230	319 winter 299 summer	Hawthorne, et al., 1988
East Tennessee, Oak Ridge/ Knoxville area	62	< 25->200	40	Hawthorne, et al., 1986
New York, northeast & central regions	38	7-151	30	Traynor, et al., 1985; Traynor and Nitschke, 1984
New York	30	< 20-110	50	Syrotynski, 1986

* geometric mean

c. Offices and Public Buildings

Limited data obtained inside offices and public buildings indicate that average formaldehyde concentrations are generally lower than those in homes and range from less than 20 ppbv to approximately 60 ppbv (Rogozen et al., 1984, Turk et al., 1987a, Sheldon et al., 1988 a, b; Hawthorne et al., 1988). Rogozen et al. (1984) monitored 9 California workplaces and reported an average indoor concentration of 34 ppbv. Turk et al. (1987a) monitored 38 buildings in Oregon and Washington and reported an average concentration of 21 ppbv. A weighted average concentration from those two studies is approximately 24 ppbv. The addition of formaldehyde-emitting office furniture may cause at least a temporary elevation of indoor formaldehyde concentrations. These data do not take into account certain occupational or public environments where strong sources of formaldehyde would cause higher levels (fabric stores, biology laboratories, etc.). Limited data suggest that in-vehicle exposures to formaldehyde are about the same as exposures from the ambient air (Shikiya et al., 1989).

3. Factors Influencing Formaldehyde Concentrations in Indoor Air

The interaction of many factors influences formaldehyde concentrations indoors. These factors include the rate of formaldehyde emission from indoor sources, the age of the sources, the ratio of the surface area of the sources to the indoor air volume, the ventilation rate, the temperature, and the humidity. Mobile homes, with a large amount of high-emitting materials in a relatively small air space, and newer homes with large amounts of new (before appreciable aging) building materials, tend to have the highest indoor formaldehyde concentrations. In general, increasing ventilation to a large degree, such as by opening windows, can decrease indoor formaldehyde

concentrations. The decrease in air infiltration found in energy-efficient homes will result in elevated indoor formaldehyde concentrations if that decrease is extreme, but moderate decreases are less likely to affect formaldehyde concentrations markedly. However, an increase in temperature can significantly affect indoor formaldehyde concentrations due to the off-gassing of formaldehyde products. In a given home, the formaldehyde concentrations can vary significantly during the day, during different seasons, and over time as sources age.

4. Contribution to Total Exposure

Section 39660.5(d) of the Health and Safety Code states "the state board shall identify the relative contribution to total exposure to the contaminant from indoor concentrations, taking into account both ambient and indoor air environments." Formaldehyde concentrations are generally much higher indoors than outdoors due to the abundance of building and consumer products in modern buildings that emit formaldehyde. Tables IV-7 and IV-8 show that maximum one-week average indoor formaldehyde concentrations measured in more recent California surveys exceed 150 ppbv in conventional homes and 400 ppbv in mobile homes. In contrast with available indoor data, ARB ambient monitoring data (Table IV-2) show that the highest 24-hour average ambient outdoor formaldehyde concentration measured was 22 ppbv, recorded at the Los Angeles station. Although some of the difference between these indoor and outdoor data may be due to the differences in measurement techniques and other factors, indoor concentrations have been consistently higher in surveys that obtained concurrent indoor and outdoor formaldehyde measurements. Table IV-9 compares indoor and outdoor formaldehyde concentrations measured concurrently in some of those surveys. Although the data presented in that table are derived from limited surveys, they show that indoor concentrations can be about two to twenty times higher than outdoor concentrations.

Table IV-9

COMPARISON OF INDOOR AND OUTDOOR FORMALDEHYDE CONCENTRATIONS

Range of indoor concentrations (ppbv)	Outdoor concentration (ppbv)	Reference
20 - 201	< 10	Fanning, 1979
66 - 214	< 10	Berk et al., 1980
51 - 68	3 - 4	Berk et al., 1981
50 - 100	< 25 - 30	Lipschultz et al., 1981
<5 - 79	< 5	Offerman et al., 1981
21 - 41	5	Turiel et al., 1983
<100 - 800	40	Hanrahan et al., 1984
< 8 - 290	20*	Stock and Mendez, 1985
< 20 - 780	< 20	Stock et al., 1985

* 8 of 13 measurements were below detection limits, number listed is average of detectable measurements

F. ESTIMATES OF THE INHALED DOSE OF FORMALDEHYDE FROM INDOOR AIR

Estimates of the amounts of formaldehyde inhaled through indoor air in residences and offices and public buildings are shown in Table IV-10 and indoor concentrations used to estimate inhaled doses are shown in Table IV-11. The term "inhaled dose" is used to describe the estimates of the amounts inhaled. This term is used because the inhaled dose may not necessarily represent a delivered true dose, since it does not take into account the fraction of the inhaled amount that is absorbed and delivered to target tissue.

Estimates of the inhaled dose of formaldehyde have been developed for the average Californian, who spends about 62 percent of his/her time (about 15 hours a day) indoors at home (Wiley et al., 1990). Estimates are also included for people who spend up to 100 percent of their time in the home since those individuals can represent a significant segment of the population. On a given day, about 7 percent of adult Californians on average spend at least 95 percent of their time at home; Californians aged 65 and older spend, on average, 75 to 79 percent of their time at home (ibid.). Young children would also be expected to spend a greater portion of their time at home.

In California, mobile homes may present a particularly high exposure environment because they have the highest indoor formaldehyde concentrations and are occupied by proportionately more retired people, who may spend more time indoors (Liu et al., 1986b). The estimates of inhaled doses from residential exposures were calculated using indoor concentration estimates relevant to California, an average value for breathing volume, and time-activity information. For mobile homes, the average indoor formaldehyde

Table IV-10

ESTIMATES OF THE INHALED DOSE OF FORMALDEHYDE
FROM INDOOR AIR

	EXPOSURE RANGE (micrograms per day)	AVERAGE EXPOSURE (micrograms per day)
Residential indoor air:		
mobile home		
a. 62% of time at home	<126 - 6,320	885 - 1,010
b. 100% of time at home	<245 - 12,300	1,720 - 1,960
conventional home		
a. 62% of time at home	252 - 1,900	632
b. 100% of time at home	491 - 3,680	1,230
Offices and public buildings:*		
	<157 - 471 (6 hr. exposure)	192

* Based on limited data obtained primarily outside of California. Data do not take into account certain occupational or public environments where strong sources of formaldehyde would cause higher levels (fabric stores, biology laboratories, etc.)

Assumptions:
1. An average person inhales 20 cubic meters of air per day.
2. On a given day, an average Californian spends 62% of their time at home, but many people spend up to 100% of their time at home.
3. An average Californian spends about 6 hours per day indoors away from home, assumed to be in an office or public building.

Table IV-11

INDOOR CONCENTRATIONS USED TO ESTIMATE INHALED DOSES OF FORMALDEHYDE

	CONCENTRATION RANGE	AVERAGE CONCENTRATION
Residential indoor air:		
mobile home		
a. parts per billion	<10 - 500	70 - 80
b. micrograms per cubic meter	<12.3 - 614	85.9 - 98.2
conventional home		
a. parts per billion	20 - 150	50
b. micrograms per cubic meter	24.5 - 184	61.4
Offices and public buildings:*		
a. parts per billion	<20 - 60	24
b. micrograms per cubic meter	<24.5 - 73.6	30

* Based on limited data obtained primarily outside of California. Data do not take into account certain occupational or public environments where strong sources of formaldehyde would cause higher levels (fabric stores, biology laboratories, etc.)

concentration is approximately 70 ppbv to 80 ppbv (85.9 to 98.2 ug/m^3) and ranges from less than 10 ppbv to 500 ppbv (12.3 to 614 ug/m^3). The average adult inhales approximately 20 m^3 of air per day; approximately 3 m^3 is inhaled during 8 hours of sleep, and approximately 1.06 m^3 per hour is inhaled during the rest of the day [(20-3 m^3)/16 hours] (International Commission on Radiological Protection, 1975). A person who spends all day inside a mobile home and inhales 20 m^3 of air per day would inhale between 1,720 and 1,960 ug of formaldehyde per day on average. The amount inhaled could range from less than 245 ug/day to 12,300 ug/day. The average Californian, who spends 62 percent of the time at home inhales approximately 10.3 m^3 of air per day in that environment [3 m^3(8 hrs. sleep) + (6.9 hr. X 1.06 m^3/hr.). The average amount of formaldehyde inhaled by Californians spending 62 percent of their time in their mobile home is estimated to be about 885 to 1,010 ug/day, and would range from less than 126 ug/day to 6,320 ug/day. There are approximately 1 million persons living in mobile homes in California who could be exposed to these concentrations (DOF, 1988).

Estimates of inhaled doses from exposures in conventional homes were calculated from the average indoor formaldehyde concentration of 50 ppbv (61.4 ug/m^3) and range of 20 ppbv to 150 ppbv (24.5 to 184 ug/m^3). People who spent all of their time in a conventional home and inhaled 20 m^3 of air per day would inhale an average of 1,230 ug of formaldehyde per day. The amount of formaldehyde inhaled would range from 491 to 3,680 ug/day. A person spending 62 percent of their time at home would inhale an average of 632 ug/day of formaldehyde, but the amount inhaled could range from 252 to 1,900 ug/day. There are approximately 29 million persons living in conventional homes in California who could be exposed to these concentrations (DOF, 1988).

A population-weighted average indoor concentration from mobile and conventional homes is 62 ug/m^3. For people spending 62% of the time inside the home, the average amount of formaldehyde inhaled per day from that environment is approximately 640 ug.

A rough estimate of the amount of formaldehyde inhaled from the air inside offices and public buildings was calculated using indoor concentration estimates and an estimate of the volume of air inhaled in 6 hours, since the average Californian spends 6 hours per day indoors away from the home (Jenkins et al., 1991). For offices and public buildings, the average indoor concentration is roughly 24 ppbv (30 ug/m^3), and ranges from less than 20 ppbv (24.5 ug/m^3) to approximately 60 ppbv (73.6 ug/m^3). In 6 hours, an average person would inhale approximately 6.4 m^3 of air (6 hours X 1.06 m^3/hr.). Thus, the average inhaled dose of formaldehyde from the air inside offices and public buildings would be 192 ug/day and would range from less than 157 ug/day up to 471 ug/day. It should be noted that this estimate is based on limited indoor concentration data. Also, the data do not take into account certain occupational or public environments such as fabric stores or biology laboratories where strong sources of formaldehyde would cause higher indoor concentrations.

G. EXPOSURE THROUGH OTHER ROUTES

The extent of exposure to formaldehyde from routes other than inhalation is very small under normal circumstances. Levels in California drinking water appear to be very low. Formaldehyde levels in food are higher, but much of the formaldehyde present in food is not absorbed; that which is absorbed through ingestion is converted rapidly to harmless metabolites (Scheuplein, 1985). It should be noted that, with respect to the potential carcinogenicity of formaldehyde, the ingestion route is

probably not significant. There are well-developed means of detoxifying absorbed aldehydes; it is surmised that only in specialized organs and areas such as the nasal cavity that inhalation of appreciable amounts may overcome local defense mechanisms (Casarett et al., 1986). Systemic absorption through the skin appears to be negligible, however, dermal sensitization and irritation due to formaldehyde exposure is clearly documented.

H. CANCER RISK OF EXPOSURE TO AIRBORNE FORMALDEHYDE

The cancer risk from both indoor and outdoor exposures to formaldehyde in California is presented in Table IV-12. These estimates are based on ambient population-weighted exposure, mobile and conventional home exposures, office and public building exposures as well as time spent indoors and outdoors in California. The ARB uses the Office of Environmental Health Hazard Assessments' (OEHHA) best value for unit risk to estimate excess cancer cases. Based on OEHHAs' best value for unit risk of $7 \times 10^{-6} ppbv^{-1}$ [$6 \times 10^{-6} (ug/m^3)^{-1}$), the number of potential excess cancer cases to indoor and outdoor exposure to formaldehyde is estimated to be 7,000 and 150, respectively, for a California population of 30 million.

Because air is constantly exchanged between indoor and outdoor environments, emissions from outdoor sources contribute somewhat to indoor concentrations and emissions from indoor sources contribute to outdoor concentrations. If it is assumed that the 4.4 ppb statewide ambient outdoor concentration contributes fully to the indoor concentration, an upper bound estimate can be made for outdoor source contribution. The outdoor source estimate would be 31 potential lifetime cancers per million; the indooor source contribution would be 204 potential lifetime cancers per million; with a total risk of 235 potential lifetime cancers per million.

Table IV-12

CANCER RISK FROM INDOOR AND OUTDOOR EXPOSURES IN CALIFORNIA TO FORMALDEHYDE[a]

LOCATION	AVERAGE CONCENTRATION (ug/m^3)	PERCENT OF TIME IN LOCATION[e]	AVERAGE AIR VOLUME[f,i] (m^3/day)	DOSE RATE[g] (ug/day)	POTENTIAL EXCESS CANCER CASES[h]
INDOORS					
AT HOME	62[b] (51 ppbv)	62	10.3	640	5,400
AWAY FROM HOME	30[c] (24 ppbv)	25	6.4	190	1,600
TOTAL INDOORS		87	16.7	830	7,000
OUTDOORS	5.4[d] (4.4 ppbv)	13	3.3	18	150

a -Excludes occupational exposure.

b -Population-weighted residential concentration; average indoor concentration of conventional homes is 61 ug/m^3, that for mobile homes is 92 ug/m^3. In California 29 million people reside in conventional homes and 1 million people reside in mobile homes, based on Department of Finance estimates (1988).

c -Estimated from limited measurements inside offices and public buildings in western states (Rogozen et al., 1984; Turk et al., 1987a).

d -ARB outdoor population-weighted exposure.

e -Average values based on ARB study results (contract no. A6-177-33).

f -Average air volume is the amount of air inhaled on average per day by an individual in that location. Assumes a total of 20 m^3 breathed on average per day. Assumes breathing at a resting rate of 3 m^3 per 8 hours spent sleeping/resting per day, and breathing at the non-resting rate of 1.06 m^3 per hour [(20 - 3m^3)/16 hours] for the remainder of the day. Thus, the

average volume of air breathed while indoors at home (14.9 hours) equals the resting rate of 3 m^3 for 8 hours (average night's rest) plus 6.9 hr X 1.06 m^3/hr., or 3 m^3 + 7.3 m^3 = 10.3 m^3. The average volume of air breathed indoors away from home equals 6 hrs (0.25 X 24 hrs) X 1.06 m^3/hr = 6.4 m^3. The average volume of air breathed outdoors equals 3.12 hrs (0.13 X 24 hrs) X 1.06 m^3/hr = 3.3 m^3.

g -Dose rate = average concentration X amount of air inhaled on average per day in that location.

h -Excess cancer cases = dose rate x unit risk [2.8 x 10^{-7} $(ug/day)^{-1}$, which corresponds to the upper confidence limit best value of 7 x 10^{-6} $ppbv^{-1}$ [6 x 10^{-6} $(ug/m^3)^{-1}$)] x California population (30 million persons exposed). Numbers not exact due to rounding.

i -Report of the Task Group on Reference Man, International Commission on Radiological Protection, No. 23, Pergamon Press, New York, 1975, pp. 345-347.

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V.

ATMOSPHERIC CHEMISTRY

A. INTRODUCTION

The concentration of formaldehyde in the atmosphere depends upon direct emissions, secondary formation, chemical and physical removal processes. Direct emissions from mobile and stationary sources are discussed in Chapter III while secondary formation, persistence, and fate of formaldehyde are discussed here.

The following summarizes the key points which are described in more detail in Sections B, C, and D:

- o In polluted atmospheres, secondary formaldehyde formation from the degradation of organic pollutants is expected to dominate direct emissions.
- o Regardless of whether formaldehyde is directly emitted or derived from secondary formation, its atmospheric persistence is approximately 0.3 days which is sufficient time to allow dispersal throughout an air basin.
- o The dominant atmospheric removal mechanism for formaldehyde is by photolysis and oxidation by hydroxyl radicals during daylight hours.
- o Episodic wet deposition events lead to shorter atmospheric lifetimes of formaldehyde.

B. ATMOSPHERIC FORMATION OF FORMALDEHYDE

Formaldehyde formation from the degradation of organic pollutants in urban atmospheres is the major contributor to the total atmospheric formaldehyde. Therefore, secondary formaldehyde formation frequently exceeds direct emissions from combustion sources in urban areas (Grosjean et al., 1983, Lawson et al., 1990).

Formaldehyde is formed in the troposphere from the tropospheric degradation reactions of many organic compounds. In the "clean" troposphere, HCHO is formed as a product of the atmospheric reactions of methane:

$$OH + CH_4 \rightarrow HO_2 + CH_3$$

$$CH_3 \rightarrow\rightarrow CH_3O$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

(Ravishankara, 1988; Atkinson, 1990).

The formation of CH_3O and/or CH_3 radicals during the atmospheric degradation reactions of organic compounds thus leads to the formation of HCHO.

In polluted atmospheres, sources of CH_3 radicals include the important atmospheric reactions of acetaldehyde and the decomposition reactions of the

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO$$

$$OH + CH_3CHO \rightarrow H_2O + CH_3CO \xrightarrow{O_2} CH_3C(O)OO \rightleftharpoons NO_2$$

$$CH_3 + CO_2$$

more complex alkoxy radicals; for example

$$(CH_3)_3CO \rightarrow CH_3COCH_3 + CH_3.$$

Analogous decompositions of alkoxy radicals can also lead directly to HCHO. For example, the β-hydroxyalkoxy radicals formed after OH radical addition to the terminal alkenes (such as the $CH_3CHOHCH_2O$ radical formed from propene) decompose, at least in part, as follows:

$$CH_3CHOHCH_2O \rightarrow CH_3CHOH + HCHO.$$

The simplest α-hydroxy radical, CH_2OH, which is formed from the

decomposition reactions of $R_1R_2C(O)CH_2OH$ β-hydroxyalkoxy radicals, reacts rapidly with O_2 to yield HCHO and the HO_2 radical (Atkinson and Lloyd, 1984; DeMore et al., 1987; Atkinson et al., 1989):

$$CH_2OH + O_2 \rightarrow HCHO + HO_2.$$

In addition, the gas-phase reactions of O_3 with alkenes containing terminal $=CH_2$ groups lead to the formation of HCHO. For example, for the reaction of O_3 with ethene at room temperature and atmospheric pressure of air (Atkinson and Lloyd, 1984; Atkinson and Carter, 1984; Atkinson, 1990)

$$O_3 + CH_2{=}\ CH_2 \rightarrow HCHO + 0.37\ CH_2OO + 0.12\ HO_2 + 0.13\ H_2$$

$$+ 0.19\ CO_2 + 0.44\ CO + 0.44\ H_2O$$

with similar HCHO yields for other 1-alkenes (Atkinson, 1990).

Thus, in polluted airmasses characteristic of urban areas, the atmospheric formation of HCHO from organic precursors occurs. Grosjean et al. (1983) concluded from ambient measurements that in many cases the atmospheric formation of HCHO dominates over direct emission of HCHO from combustion sources. More recent ambient air monitoring data in the South Coast Air Basin (SoCAB) (Lawson et al. 1990) provide clear evidence for directly emitted HCHO as well as HCHO formed in the atmosphere by photochemical reactions or organic precursors. However, Lawson et al. (1990) also conclude that the atmospheric formation of HCHO dominates over direct emissions of HCHO under conditions of high photochemical activity in the SoCAB. Lawson et al. found that high peak ambient concentrations of formaldehyde existed not only during high ozone periods but in the morning as well. This suggests that in urban locations mobile sources contribute more than previously thought to the atmospheric burden of formaldehyde.

C. PERSISTENCE OF ATMOSPHERIC FORMALDEHYDE

The persistence of atmospheric formaldehyde (the length of time formaldehyde remains unaltered in the atmosphere) is determined by its tropospheric lifetime (τ). Tropospheric lifetime is defined as the time required to decrease the concentration of formaldehyde to 1/e (=0.368) of its initial concentration. Photolysis and the reaction with hydroxyl radicals in the atmosphere is primarily responsible for the estimated ~0.3

day tropospheric lifetime of formaldehyde, with episodic wet deposition events leading to shorter lifetimes. All of these processes occur in the troposphere, the region of the atmosphere extending from the earth's surface to an altitude of approximately 15 km (Finlayson-Pitts and Pitts 1986).

1. Chemical Removal of Formaldehyde (HCHO) from the Atmosphere

The chemical removal of atmospheric formaldehyde is the result of the sum of photolysis and several distinct oxidative reactions. Formaldehyde is oxidized in reactions with hydroxyl radicals, ozone, nitrate radicals, and hydroperoxyl radicals. Each of these chemical degradations of formaldehyde is associated with a particular reaction speed determined by the reaction rate constant (k) and the atmospheric concentrations of reactants:

$$HCHO + B \xrightarrow{k} \text{products}$$

where B is the atmospheric oxidant, and

$$\tau = 1/k[B].$$

Table V-1 lists the estimated average atmospheric lifetime of formaldehyde relative to each oxidative removal reaction. Since the shortest lifetime is associated with photolysis, photolysis is the single most important chemical removal mechanism. Photolysis, reaction with the hydroxyl radical (the second most important removal process), and the remaining oxidative reactions are discussed in order of importance in subsections 1.a., 1.b., and 1.c., respectively.

Table V-1

ESTIMATED ATMOSPHERIC LIFETIME RELATIVE
TO EACH OXIDATIVE REMOVAL REACTION

Oxidant	Atmospheric Concentration (mol cm^{-3})	Rate Constant ($cm^3 mol^{-1} sec^{-1}$)	Atmospheric Lifetime	References
Hydroxyl radical	1.5×10^6	9.77×10^{-12}	1.6 days	Atkinson & Pitts 1978 Stief et al. 1980 Prinn et al. 1987
Ozone	7×10^{11}	$<2.1 \times 10^{-24}$	$>2 \times 10^4$ yr.	Braslavsky & Heicklen 1976 Logan 1985
Nitrate radical	2.4×10^8	6×10^{-16}	160 days	Dlugokencky & Howard 1989 Platt et al. 1984 Atkinson et al. 1986
Hydroperoxyl radical	$\sim 10^7$	7.9×10^{-14}	~15 days	Barnes et al. 1985 Veyret et al. 1989 Hard et al. 1984 Zellner & Weibring 1989
Photolysis			0.4 days	Atkinson et al. 1989 Rogers 1990

Note: Temperature is 298°K for all chemical reactions.

a. Photolysis

Photolysis of formaldehyde is the chemical decomposition of atmospheric formaldehyde induced by sunlight. The rate of photolysis depends on three variables which are, in turn, wave-length dependent: absorption cross section (σ)[1], the photolysis quantum yield (ϕ)[2], and the radiation intensity (J)[3].

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

The absorption cross sections and quantum yields for the photolysis of HCHO have most recently been reviewed and evaluated by DeMore et al. (1987) and Atkinson et al. (1989). The most recent IUPAC evaluation (Atkinson et al., 1989) accepts the absorption cross-section data of Moortgat et al. (1983). At the longer wavelengths, these absorption cross-sections of Moortgat et al. (1983) are higher than those measured by Bass et al. (1980), but are substantiated by the recent data of Rogers (1990) and Cantrell et al. (1990). The recommended absorption cross-sections and quantum yields for the photolysis processes

$$HCHO + h\nu \rightarrow H + HCO$$
$$HCHO + h\nu \rightarrow H_2 + CO$$

are those tabulated and presented by Atkinson et al. (1989). These lead to a tropospheric lifetime of formaldehyde of τ= 0.3 days for a zenith angle of 40^o (Rogers, 1990).

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1. Absorption cross-section: absorption spectrum of formaldehyde.
2. Photolysis quantum yield: the number of formaldehyde molecules photolyzed divided by the total number of photons absorbed.
3. Radiation intensity: the total light intensity from direct scattered and reflected light which is incident on a horizontal surface of unit area.

b. Reaction with the Hydroxyl (OH) Radical

After evaluating the available data (Hoare 1962, 1966, Baldwin and Cowe 1962, Blundell et al. 1965, Westenberg and Fristrom 1966, Hoare and Peacock 1966, Morris and Niki 1971a,b, Peeters and Mahnen 1973, Vandooren and Van Tiggelen 1977, Niki et al. 1978, Atkinson and Pitts 1978, Stief et al. 1980, Temps and Wagner 1984, Zabarnick et al. 1988, and Niki et al. 1984) concerning the kinetics and mechanism of the reaction of the hydroxyl radical with formaldehyde, Atkinson (1989) recommended a rate of:

$$k = 9.77 \times 10^{-12} cm^3 \text{ molecule}^{-1} \text{second}^{-1} \pm 30\% \text{ at } 298^{o}K.$$

Prinn et al. (1987) estimated the concentration of hydroxyl radicals in the atmosphere to be 1.5×10^6 molecules cm^{-3} during daylight hours (12-hr average). Combining the rate constant for reaction with the OH radical with this atmospheric OH radical concentration leads to

$$\tau = 1/k[OH] = 1.6 \text{ days.}$$

This OH radical reaction with formaldehyde can proceed by the pathways

$$OH + HCHO \rightarrow HCO + H_2O \quad (2a)$$

$$\rightarrow HCOOH + H \quad (2b)$$

$$\rightarrow H + CO + H_2O \quad (2c)$$

Morrison and Heicklen (1980), Temps and Wagner (1984) and Niki et al. (1984) have shown from product studies that reaction pathway (2b) is negligible, accounting for $\leq 2\%$ of the overall reaction (Niki et al., 1984). Morrison and Heicklen (1980) did not observe any formation (<10%) of HCOOH, and concluded that reaction pathways (2a) and (2c) occur with approximately equal probability. More recently, Temps and Wagner (1984), using a discharge flow technique with LMR detection to monitor both OH and HCO

radicals, have shown that reaction pathway (2a) accounts for 100 ± 5% of the overall reaction. Thus, at room temperature the OH radical reaction with formaldehyde proceeds essentially entirely by the H-atom abstraction process:

$$OH + HCHO \rightarrow H_2O + HCO.$$

The resulting HCO radical reacts rapidly with O_2 to yield the HO_2 radical (DeMore et al., 1987; Atkinson et al., 1989):

$$HCO + O_2 \rightarrow HO_2 + CO.$$

c. Reaction with Ozone (O_3), Nitrate (NO_3) Radicals, and Hydroperoxyl (HO_2) Radicals

The atmospheric lifetime of formaldehyde resulting from oxidation by ozone, nitrate radicals, and hydroperoxyl radicals is estimated as >2 X 10^4 years, 160 days, and ~15 days, respectively. The ozone and hydroperoxyl radical reactions proceed during both day and night hours while the nitrate radical reaction occurs at night and early morning. These lifetimes were determined by the rate constant and concentration of reactants associated with each reaction ($r = k[B]$ where B is the atmospheric oxidant) (Atkinson et al. 1989, Atkinson, 1990).

2. Physical Removal of Formaldehyde (HCHO) from the Atmosphere

Atkinson evaluated the available data on physical removal processes and found that wet deposition is expected to increase the atmospheric removal of formaldehyde above that of formaldehyde photolysis (Atkinson 1988, 1990, Bidleman, 1988).

Dry deposition removes organic gases by absorption or adsorption to snow or moist surfaces. Because dry deposition occurs only at ground

surfaces, it plays a limited role in removing formaldehyde from the atmosphere.

Since formaldehyde dissolves in aqueous solutions, it is reasonable to assume that the compound is subject to wet deposition by incorporation into clouds, rain, and fog. The degree of formaldehyde hydration calculated using Henry's law coefficient ($H^* = 3.0 \pm 0.7 \times 10^3$ mol atm^{-1} at 298^oK) of Betterton and Hoffmann (1988) is significant (2.3×10^3) when compared to that of acetaldehyde (1.4). In addition, gas-phase organic compounds which are very efficiently rained out (and for particles, which are also very efficiently rained out) have a washout ratio (concentration in rain/concentration in air) of 10^5 to 10^6 (Eisenreich et al., 1981; Atkinson, 1988). The value of H* of Betterton and Hoffmann (1988) corresponds to a washout ratio of $W = 7.3 \times 10^4$ at 298^oK. With a washout ratio of this magnitude, wet deposition of HCHO is expected to be significant as a tropospheric loss process for HCHO during rain or fog events.

D. ATMOSPHERIC LIFETIME OF FORMALDEHYDE

As discussed above, the tropospheric lifetime of HCHO is determined from the loss rates of both the chemical and physical loss processes. Reactions with the hydroxyl radical and photolysis are the major tropospheric chemical loss processes. The reaction with the hydroxyl radical and photolysis occur only during daytime hours with photolysis serving as the driving force for the estimated overall lifetime of formaldehyde. Wet deposition will, on average, lead to a shorter tropospheric lifetime, but since wet deposition is episodic in nature, the above lifetime calculated from OH radical reaction and photolysis is best regarded as being the tropospheric lifetime, with faster removal of HCHO from the lower troposphere during rain and/or fog events. Thus, photolysis and reaction with the OH radical are the major tropospheric chemical loss processes, with an overall lifetime of HCHO of ~0.3 days.

E. CONCLUSIONS

Formaldehyde is both directly emitted into the atmosphere as well as being formed in the atmosphere from the photochemical degradation of methane and non-methane organic compounds. HCHO is removed from the lower troposphere mainly by photolysis and reaction with the OH radical, and by wet deposition (leading to incorporation of formaldehyde into rain, cloud and fog water). The estimated lifetime of HCHO due to photolysis and OH radical reaction is ~0.3 days, with episodic wet deposition events leading to shorter lifetimes. Reported ambient atmospheric HCHO concentrations in the Los Angeles air basin (expected to have among the higher levels encountered in California) range up 86 ppbv, with mixing ratios measured during a recent intercomparison study in 1986 ranging up to 25 ppbv.

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APPENDICES

APPENDIX I-A: Formaldehyde Formation from Photo-oxidation

For the purpose of estimating net formaldehyde generation due to photo-oxidation reactions, ARB assumed a steady-state conversion factor of 0.06 to 0.12 as the upper and the lower limit of weight fractions of formaldehyde in the state's total ROG emissions. Multiplying these factors by the statewide ROG emissions resulted in the photo-oxidation estimates presented below.

	MOTOR VEHICLE	INDUSTRIAL	AREA SOURCE	TOTAL
STATEWIDE VALUES: (ROG in TPY)	398,164	29,372	1,269,636	1,697,172

SAMPLE CALCULATIONS

$$EMS = K\ (ROG\text{-}statewide) \qquad (1)$$

Where:

EMS = Formaldehyde emissions rate in tons per year
K = Weight fraction of ROG converted to formaldehyde, (dimensionless)
ROG = Reactive organic gas estimate for the entire state, tons per year

Using equation (1), emission estimates were made as follows:

Minimum EMS = 0.06 (1,697,172) tons per year

= 101,830 tons per year

= 2.03×10^8 lbs per year

Maximum EMS = 0.12 (1,697,172) tons per year

= 203,660 tons per year

= 4.04×10^8 lbs per year

Mid-point = (maximum + minimum)/2

= 152,745 tons per year or approximately 150,000 tons/yr

NOTE: K = 0.06 and 0.12 OR minimum and maximum values, respectively.

APPENDIX I-B: Emission Estimates from Mobile Sources

The emission estimates listed in Appendix I-B were obtained by multiplying TOG emissions by the weight fraction of formaldehyde from the vehicle exhaust streams. The weight fractions and the TOG emission estimates were retrieved from the California Air Resources Board's Emission Data System (1987).

Vehicle Class	Fuel Type	Emission Control System	Weight Fraction	TOG (TPY)	Emissions (TPY)
Light-Duty Passenger	Diesel		.0879	1,814	159
	Gasoline	Non-Catalytic	.0285	120,136	3,424
	Gasoline	With-Catalytic	.0154	140,977	2,171
Light/ Med-Duty Trucks	Diesel		.0879	471	41
	Gasoline	Non-Catalytic	.0285	42,957	1,224
		With-Catalytic	.0154	59,798	920
Heavy-Duty Gas Trucks		Non-Catalytic	.0285	20,250	577
		With-Catalytic	.0154	179	3
Heavy-Duty Diesel Trucks			.0879	29,244	2,571
Urban Bus			.0879	1,241	109
Motorcycles			.0285	5,358	153
TOTAL				422,425	11,352

APPENDIX I-B (Cont.): Emission Estimates from Mobile Sources

Source	Weight Fraction	TOG (TPY)	Emissions (TPY)
Off Road Vehicles	.0299[1]	38,601	1,154
	.0879[2]	1,654	145
Trains	.0879[2]	10,814	951
Ships	.0009[3]	779	0.7
	.0879[2]	2,533	223
Aircraft-Govt.	.0299[1]	247	7
Aircraft-Other	.0299[1]	1,891	57
Mobile Equipment	.0879[2]	17,081	1,501
	.0299[1]	17,717	530
Utility Equipment	.0299[1]	25,124	751
TOTAL		116,441	5,320

1. Weight fraction of formaldehyde in the exhaust of all gasoline-powered vehicles (ARB, 1991).
2. Weight fraction of formaldehyde in the exhaust of all diesel-powered vehicles (ARB, 1991).
3. Weight fraction of formaldehyde in the exhaust of all engines powered by distillate or residual oil (ARB, 1991).

APPENDIX I-C: Oil Refining By Catalytic Cracking, Coking and Other Methods

Based on the "Annual Refining Survey" of the Oil and Gas Journal, California refineries had a rated charge capacity of approximately 2.28 million barrels per calendar day of crude oil in 1988 (OGJ, 1989). According to OGJ, catalytic cracking units had a rated charge capacity of 645,500 bbls per stream day (223,827 thousand bbls per year), and thermal operations (assuming coking operations) had a rated charge capacity of 503,200 bbls per stream day (174,485 thousand bbls per year) in 1988 (OGJ, 1989). There are no data to estimate the exact amount of fresh feed going into either FCC or TCC units. However, EPA estimated that 94% of the fresh feed in 1979 is used in FCC units and that the TCC units are becoming obsolete since 1979 (U.S. EPA, 1987). To be conservative (because the formaldehyde emission factor for FCC units is greater than that for TCC units), the staff assumes that all of the amount of fresh feed going to catalytic cracking is going into the FCC units. The staff estimates formaldehyde emissions for refinery processes as follows:

$$EMS = RC * EF$$

where:

EMS = formaldehyde emissions, tons/year.
RC = rated charge capacity, bbls/yr.
EF = formaldehyde emission factor, lbs/1000 bbls.

Formaldehyde emission factors are different depending on the refining processes; thus, formaldehyde emissions are different from these processes. Table 1 lists formaldehyde emissions from refining processes, along with the charge capacities and the formaldehyde emission factors.

Considering the possibility of additional formaldehyde emissions from other operations such as catalytic reforming, catalytic hydrorefining, and catalytic hydrotreating, the staff includes a range of estimates of formaldehyde emissions from petroleum refining processes. To account for these other operations, the staff adds the process rates of all catalytic units as reported in the OGJ to estimate maximum process rates for catalytic cracking units. This process rate is then used to estimate the high end of the range shown in Table 1 for formaldehyde emissions from catalytic cracking units in refineries.

APPENDIX I-C (CONT.) Formaldehyde Emissions From Oil Refineries in California

Table 1
Formaldehyde Emissions from refinery Processing in California

Source	Charge capacity[1] (1000 bbls/yr)		EF (lbs/1000 bbls)	Formaldehyde Emissions (tons/yr)	
	Low	High		Low	High
Catalytic Cracking	223,827	1,062,945[2]	4.85	543	2,580
Thermal Operations[3]	174,485	174,485	1.19	104	104
Total[4]				650	2,700

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1 OGJ, 1989. Charge capacities are expressed as the volume of crude oil that the facility can process per calendar year. These numbers were estimated based on the rated charge capacities per stream day. The OGJ assumed that the capacity per calendar day equals approximately 95% of capacity per stream day.

2 This number was estimated by adding all process rates for catalytic units as reported in the OGJ. Specifically, 223,827 thousand bbls of oil was processed in catalytic cracking units; 194,700 thousand bbls in catalytic reforming units; 133,499 thousand bbls in catalytic hydrocracking units; 182,044 thousand bbls in catalytic hydrorefining units; 328,875 thousand bbls in catalytic hydrotreating units.

3 Assumed to be coking operations.

4 The totals have been rounded to at most two significant figures.

APPENDIX I-D: Formaldehyde Emissions from Fuel Combustion Sources

Emission estimation methods and emission factor estimates for combustion sources vary widely. To be conservative, the staff used the 1987 CARB EDS data and the EPA applicable emission factors for different fuel types to estimate formaldehyde emissions for the 1987 inventory year. Results are tabulated below. Sample calculations are also presented for natural gas combustion.

FUEL TYPE	ANNUAL CAPACITY/USAGE(RATE)[a]	EMISSION[b] FACTOR	EMISSIONS (TONS/YEAR)
Natural Gas	1.8×10^{12} cubic ft.	0.038 ng/J	81
Wood	N/A.	0.48 lb/ton	N/A
Coal	8,000 tons	170.2 lbs/10^{12} Btu	.017
Residual Oil	1.02×10^{9} gals	405 lbs/10^{12} Btu	31
Distillate Oil	2.1×10^{10}gals	405 lbs/10^{12} Btu	585
Waste Combu.	2.4×10^{7} tons	1.1 g/Mg	27
Diesel-Industrial	6.4×10^{6} gals	13.2 ng/J	13
		TOTAL	737

N/A: Data are not available due to insufficient information.

a. Fuel Combustion-Process Rates And TOG Emissions, Inventory Year: 1987, Air Resources Board, Emission Inventory Branch.

b. EPA-450/2-88-006a, Toxic Air Pollutant Emission Factors- A Compilation For Selected Air Toxic Compounds And Sources.

SAMPLE CALCULATIONS

Formaldehyde Emissions = Process Rate x Emission Factor x Conversion Factor

Natural Gas:

Formaldehyde Emissions = 1.8×10^{12} ft^3 x 0.038 ng/J x 1050 Btu/ft^3 x 1054.2 J/Btu x 2.2×10^{-12} lb/ng x 1 ton/2,000lbs

= 83 tons per year

APPENDIX II Indoor Formaldehyde Measurement Techniques

Formaldehyde concentrations in non-occupational indoor air environments are typically measured using fixed-site sampling devices. Those devices can be grouped into different categories. Continuous devices provide "on-the-spot" formaldehyde measurements; integration devices collect the air sample over a period of time for later analysis in the laboratory. Most of the devices used for residential formaldehyde monitoring fall into the latter category.

Commonly-used formaldehyde sampling devices can be grouped further. Active samplers require a power source to draw the air sample into the collection medium; passive samplers do not require a power source, but rely on the diffusion of formaldehyde into the collection medium. Commonly-used active formaldehyde samplers use a portable pump to draw air through impingers filled with water or a solution of one percent sodium bisulfite. A commonly-used passive formaldehyde sampler consists of a diffusion tube containing a sodium bisulfite sorbent pad at one end (Godish, 1985). Active and passive samplers using 2,4-dinitrophenylhydrazine (2,4-DNPH) as a collection medium are receiving increased usage (EPA, 1989).

Formaldehyde samples collected in impingers or by passive samplers are typically analyzed using colorimetric methods. Two widely-used methods are the chromotropic acid method and the modified parasaniline method. Samples collected on 2,4-DNPH are usually analyzed using high performance liquid chromotography (HPLC) (Hawthorne et al., 1984).

Passive samplers provide for inexpensive and convenient monitoring of a relatively large number of residences. Although passive samplers have some limitations (Godish, 1985; Fortmann et al., 1988), validation studies performed on a commonly-used passive sampler (developed by Lawrence Berkeley Laboratory) show that it can provide a reasonable measure of indoor formaldehyde concentrations over a one week measurement period (Wagner, 1982).

APPENDIX III: GLOSSARY

Absorption: The dissolving of a gaseous pollutant in a liquid solvent.

Additive: The combined effect of two or more pollutants is approximately equal to the sum of effects of individual pollutants.

Adsorption: The removal of a gaseous pollutant from a gas stream by allowing the pollutant molecules in the gas stream to become attached to a solid surface.

Aldehyde: Any of a class of highly reactive organic chemical compounds obtained by oxidation of primary alcohols, characterized by the common group CHO.

Ambient air: Outdoor air; more specifically, the troposphere.

Ambient (air) monitoring: The collection of ambient air samples and the analysis thereof for air pollutant concentrations.

Annual average population-weighted concentration: The annual average population-weighted exposure divided by the total population exposed (e.g. formaldehyde 4.4 ppb).

Annual average population-weighted exposure: The sum of the annual average outdoor concentration (C) estimated for each census tract multiplied by the population (P) exposed in each census tract, e.g. $E = (C_1 \times P_1) + (C_2 \times P_2)$ ....., divided by the population exposed.

Antagonistic: The combined effect of two chemicals is less than the sum of the effect of each chemical alone.

Areawide exposure: The average exposure the general population experiences in a large area surrounding sources of TAC's. This is generally based on ambient air monitoring data for populated areas.

Atmospheric Lifetime: The atmospheric lifetime τ of a chemical is defined as the time to decay to a concentration of 1/e (= 0.368) of the initially present concentration of that chemical.

Atmospheric half-life: The time required for one-half of the quantity of an air pollutant to react and/or breakdown in the atmosphere (formaldehyde = days).

Cancer: A malignant new growth.

Carcinogenic effects: Effects that cause cancer. Able to produce malignant tumor growth.

Catalyst: A substance, usually present in small amounts relative to the reactants, that modifies, especially increases, the rate of chemical reaction without being consumed in the process.

Coefficient of variation (CV): The CV is the precision relative to the mean of the population expressed in percentages. The CV is equal to the standard deviation of all observations divided by the mean of all observations multiplied by 100.

Condensation: The physical process by which a liquid is removed from a vapor or vapor mixture. The state of being condensed or compressed.

Decomposition: Separation into constituents by a chemical reaction. Organic decay.

Deposition (dry): Removal of gases and particles on to ground surfaces (including snow and other moist surfaces).

Deposition (wet): Removal of gases and particles by precipitation.

Dispersion Modeling: Technique for estimating the annual average concentration of a pollutant resulting from emissions from a specific source. We provide emission rate data to modeling staff which combine these data with data on wind speed and other meteorological conditions impacting the source to estimate the annual average concentration attributable to the source's emissions. The concentration predicted from dispersion modeling is assumed to be in addition to background concentrations measured by ambient air monitoring.

Dose: The concentration of the pollutant and the length of time that the subject is exposed to that pollutant.

Emission factor: An estimate of the rate at which a pollutant is released into the atmosphere as a result of some activity (e.g. mg/kg).

Emission rate: The weight of a pollutant emitted per unit of time (e.g. tons/year).

Excess carcinogenic risk: The number of potential excess lifetime cancer cases occurring per million persons continuously exposed for 70 years to a given concentration of a TAC; e.g. the excess carcinogenic risk from formaldehyde exposure = <1 to 40 potential lifetime cancer cases per million

persons continuously exposed to 1 ppb formaldehyde (<1 - 40 potential lifetime cancer cases /10^6 ppb persons). In this case, <1 would be the risk based on the lower bound potency and 40 would be the risk based on the upper bound potency.

Exposure (E): The concentration (C) of the pollutant in the air multiplied by the population (P) exposed to that concentration over a specified time period, e.g. E = C X P (typical units are millions pf ppb-persons averaged over one year).

Fugitive: Difficult to determine, comprehend or retain; elusive. Often used as an estimate of emissions that are not quantified.

Hot spot exposure: Relatively high-level exposure to people living or working near sources of TACs. This is generally based on modeling of emissions data but may also be based on hot spot (near source) ambient air monitoring data.

ISCST Model: Industrial Source Complex Short Term Model, one of many air quality models which provide modelling for multiple point or area sources.

Individual cancer risk: The increased probability, expressed as chances in a million, that a person experiencing 70 years of continuous exposure to a TAC will get cancer.

Irradiation: To expose to radiation. The act of irradiating or the condition of being irradiated.

Lifetime: Covering the lifespan of an organism (generally considered 70 years for humans).

Limit of Detection (LOD): The concentration at or above which a compound can reliably (at the 99.9% confidence level) be detected in the sample. LOD = A + 3S: A is the least squares intercept calculated from the multipoint data; S is the standard deviation of replicate determinations of the lowest standard. At least 3 replicates are required. The lowest standard must be run at 1 to 5 times the estimated detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by: S = RSD X A where RSD is the relative standard deviation of the lowest standard analyzed.

Mean: A number that represents a set of numbers in any of several ways determined by a rule involving all members of the set; average.

Median: The middle value in a distribution, above and below which lie an equal number of values; mid-point.

Method of Detection: The method used by which the laboratory staff estimates the LOD.

Mobile source: Any motorized vehicle, such as cars, trucks, airplanes, and trains.

Monomer: Any molecule that can be chemically bound as a unit of a polymer.

Motor Vehicle: On-road or off-road cars, trucks or motorcycles.

Non-carcinogenic effects: A finite dose, or threshold, below which adverse effects will not occur. Non-cancer effects include birth defects, organ damage, death and many others.

Oxidation: The combination of a substance with oxygen. A reaction in which the atoms in an element lose electrons and its valence is correspondingly increased.

Photochemically formed pollutant: A secondarily formed pollutant due to atmospheric photochemistry (e.g. formaldehyde).

Photolysis: Chemical decomposition induced by light or other radiant energy.

Polymer: Any of numerous natural and synthetic compounds of usually high molecular weight consisting of up to millions of repeated linked units, each a relatively light and simple molecule.

Potency: A comparative expression of chemical or drug activity measured in terms of the relationship between the incidence or intensity of a particular effect and the associated dose of a chemical, to a given or implied standard or reference.

Potentiator: A toxic substance made worse by the presence of a non-toxic substance.

ppbv: Parts per billion volume; the number of parts of a given pollutant in a billion parts of air.

Reactive Organic Gases (ROG): Include all organic gases except methane and a number of organic compounds such as low molecular weight halogenates that have been identified by the Environmental Protection Agency as essentially non-reactive.

Route of Exposure: The means by which toxic agents gain access to an organism (e.g., ingestion, inhalation, dermal exposure).

Standard Deviation: A statistic used as a measure of dispersion in a distribution, the square root of the arithmetic average of the squares of the deviations from the mean.

Synergistic: The combined effect of pollutants is worse than the simple sum of effects of individual pollutants.

Toxic air contaminant (TAC): An air pollutant which may cause or contribute to an increase in serious illness, or which may pose a present or potential hazard to human health. Substances identified by EPA as hazardous air pollutants shall be identified by the Board as toxic air contaminants.

Total Organic Gases (TOG): Organic gases consist of hydrocarbons, aldehydes, ketones, organic acids, alcohols, esters, ethers, and other compounds containing hydrogen and carbon in combination with one or more other elements.

Travel Blank: Used in estimating concentrations of measured substances. A travel blank is a blank system that tells us that our instruments and methods are working properly and that our filled test samples are accurate. It also provides an estimate of the level of contamination due to transport and handling of the cartridges.

Troposphere: 'The lowest region of the atmosphere between the earths' surface and the tropopause, characterized by decreasing temperature with increasing altitude.

Unit cancer risk: A measure of the probability of an individual's developing cancer as a result of exposure to a specific unit ambient concentration (e.g., 1 ug/m). For example, an inhalation unit cancer risk value of $24 \times 10^{-6}/(ug/m^3)$ for formaldehyde implies that if one million people breathe a given concentration of 1 ug/m^3 for 70 years; 24 of the one million will develop cancer as a result of this exposure.

Valence: Atom in outer shell or next to outer shell that can participate in forming chemical bonds with other atoms. Capacity to form bonds with other atoms.

Volatile: Evaporating readily at normal temperatures and pressures. Capable of being readily vaporized.