

FORMALDEHYDE:
A SURVEY OF AIRBORNE
CONCENTRATIONS AND SOURCES

FINAL REPORT

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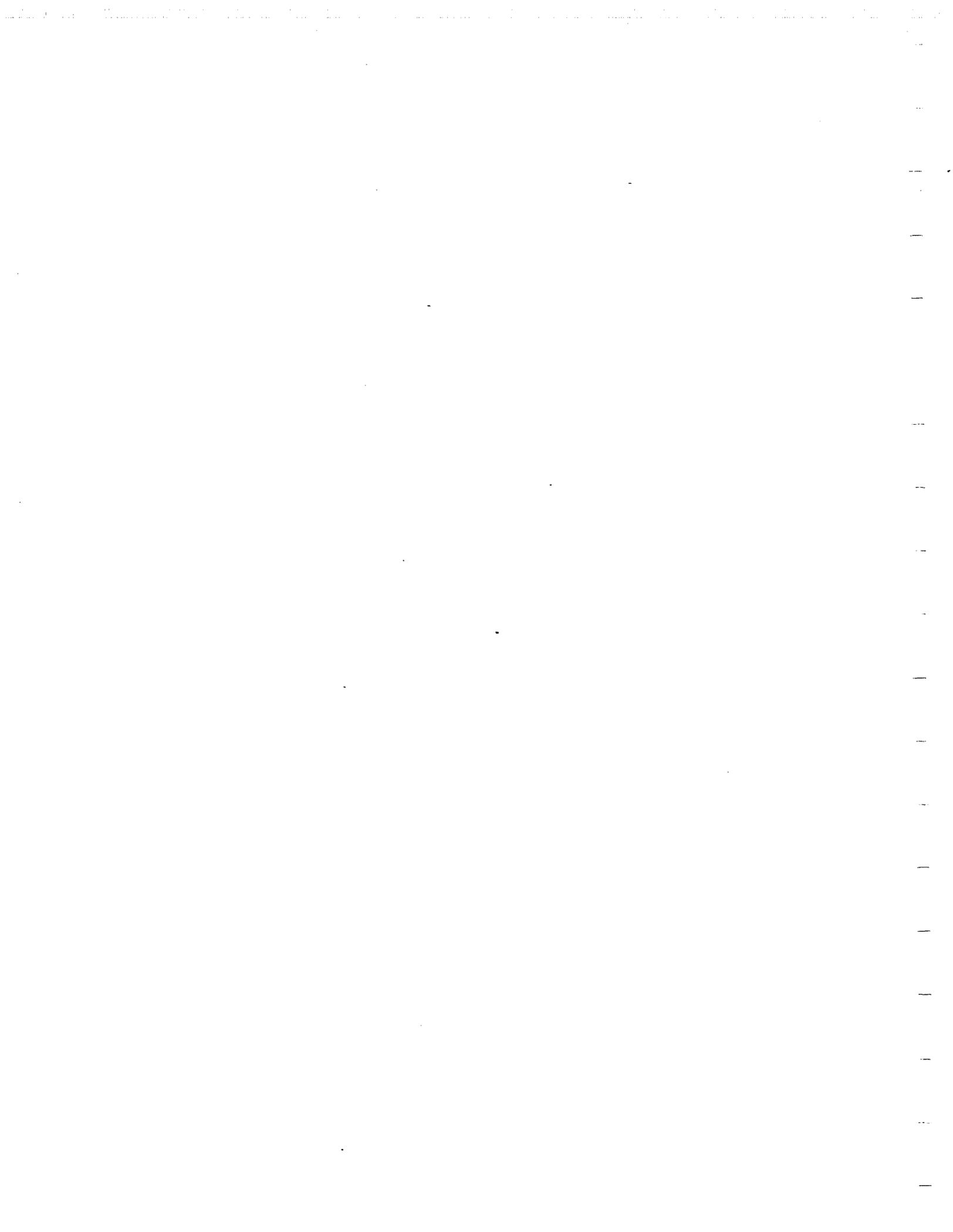
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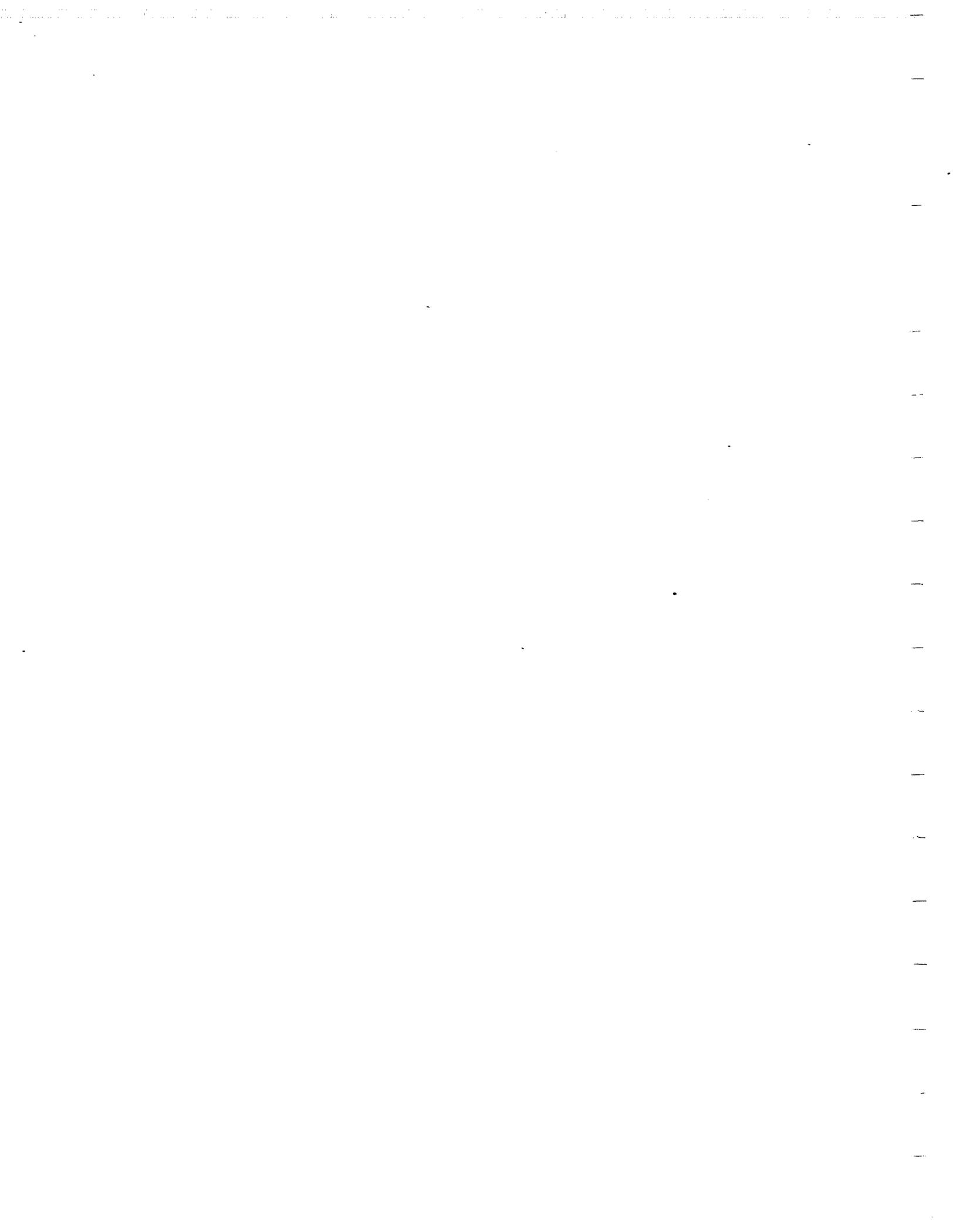
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ABSTRACT

The objectives of this study were to develop a materials balance for formaldehyde in California and to estimate statewide emissions; gather and summarize data on indoor and outdoor concentration levels; review and evaluate formaldehyde sampling and analytical methods; measure concentrations in residences, in ambient air and upwind and downwind from suspected major point sources; and estimate public exposure. These objectives were accomplished through literature surveys, field measurement programs and use of a statistically-based exposure model.

Formaldehyde enters the atmosphere through release of formaldehyde emissions and through photochemical formation from reactive organic precursors. The total addition to the atmospheric burden in 1981 is estimated to have been 118,000 tons, or 107 million kilograms (107,000 kkg). The sole commercial producer of formaldehyde in the state emits about 1.9 tons (1.7 kkg) per year. Photochemical formaldehyde production is responsible for $97,000 \pm 33,000$ tons/year ($88,000 \pm 30,000$ kkg/yr), or the great bulk of formaldehyde loading. The uncertainty in this estimate is at least 50 percent. All other formaldehyde production is the result of fossil fuel combustion. Motor vehicles account for about 64 percent of combustion-related emission. The largest stationary combustion sources are oil refineries. The South Coast and San Francisco Bay Area air basin account for about 49 and 24 percent of the state's production-related emissions. It should be emphasized that all these emission estimates are based upon emission factors having unknown, but probably large, uncertainty ranges.

Questionnaires were mailed to California's seven known producers of formaldehyde resins. From their responses, total formaldehyde use and emissions associated with these facilities are estimated to be 57 million lbs and 5.4 tons (4.8 kkg), respectively. Almost 1,300 plants in California are believed to use formaldehyde or formaldehyde-based resins to produce a wide variety of consumer products. Emissions from these sources are unknown but are believed to be quite small compared with combustion emissions, as are emissions from use of consumer products which contain formaldehyde.

Data on ambient formaldehyde concentrations in California are quite limited. Concentrations in Southern California have ranged from 0 to 150 ppb, and appear to be decreasing from levels observed in the late 1960s. A review of the literature showed that formaldehyde levels in conventional houses range from below detectable limits (15 or 100 ppb, depending on the method) to about 500 ppb. Mean values in surveys of mobile homes range from 270 to 880 ppb. It is generally agreed that outdoor formaldehyde concentrations exert little direct influence on indoor levels. Indoor formaldehyde may be expected to correlate with the presence or absence of urea-formaldehyde foam insulation; plywood and particle board; furniture, carpets and textiles; combustion processes; room deodorizers, paper products and other consumer products; and smoking. Formaldehyde concentrations may also depend heavily upon indoor-outdoor air exchange rates.

Our review of a wide variety of active sampling and analytical techniques concluded that 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by high performance liquid chromatography (HPLC) was best for the short-term ambient and "hot spot" sampling to be conducted under this project. The best approach for long-term passive sampling of indoor exposures was determined to be sodium-bisulfite-based diffusion tubes developed by Lawrence Berkeley Laboratory.

A total of 81 residences were selected at random for passive sampling measurements. Participants deployed the samplers for one week and furnished information on their homes' characteristics and on their activities during the week. The mean formaldehyde concentrations for the non-mobile home residences, mobile homes and a supplementary sample of six new homes were 50, 114 and 85 ppb, respectively. Although the limited size of the data set precluded detecting small differences among sample groups, the mean formaldehyde concentration for the new residences was significantly higher than for the other houses. Homes with gas cooking and cigarette smoking were found to have higher concentrations than homes with electric cooking and no smoking. Some significant geographical variation in indoor concentrations was noted. It is likely, however, that formaldehyde variation among residences depends upon factors for which data were not collected.

Upwind and downwind sampling was conducted at Los Angeles International Airport, an oil refinery, a fossil fuel-burning electric power plant, and a resin plant. The resin plant was the only facility which appeared to contribute formaldehyde to the atmosphere of the surrounding area.

Hourly formaldehyde measurements were made in January 1983 at the South Coast Air Quality Management District's Lennox and Pico-Rivera monitoring stations and in May and June at Pico-Rivera and Azusa. Simultaneous sampling was conducted in a commuter automobile driving between and around the stations. Winter fixed-site concentrations varied from 4.3 to 33.3 ppb; commuter exposures varied from 2.0 to 23.3 ppb and 11.3 to 22.5 ppb, respectively. Values observed at Azusa were significantly higher than those at Pico-Rivera. Commuter exposures were higher than values at both fixed sites in January, but higher in summer only with respect to the Pico-Rivera station. Although analysis of New Jersey data showed a good correlation between formaldehyde and simultaneously measured carbon monoxide and ozone concentrations, only weak correlations were found for previously-reported California data and the results of this study. It was therefore not possible to generalize from our ambient concentration data to other parts of the state.

Average daily exposures of California residents to formaldehyde were estimated by means of a Monte Carlo simulation model. The mean and median exposures predicted were 53 and 46 ppb, respectively; 95 percent of the population would be exposed to 107 ppb or less. Sensitive individuals could experience eye irritation at the median predicted exposure, while upper airway irritation would be experienced by some people at the upper end of the predicted exposure distribution.

Since indoor exposure comprises most of the total exposure of the general public to formaldehyde, a comprehensive field program to determine the causes of high levels should be conducted by the appropriate agency. Improved emission factors for all combustion sources are also needed, particularly for photochemical modeling.

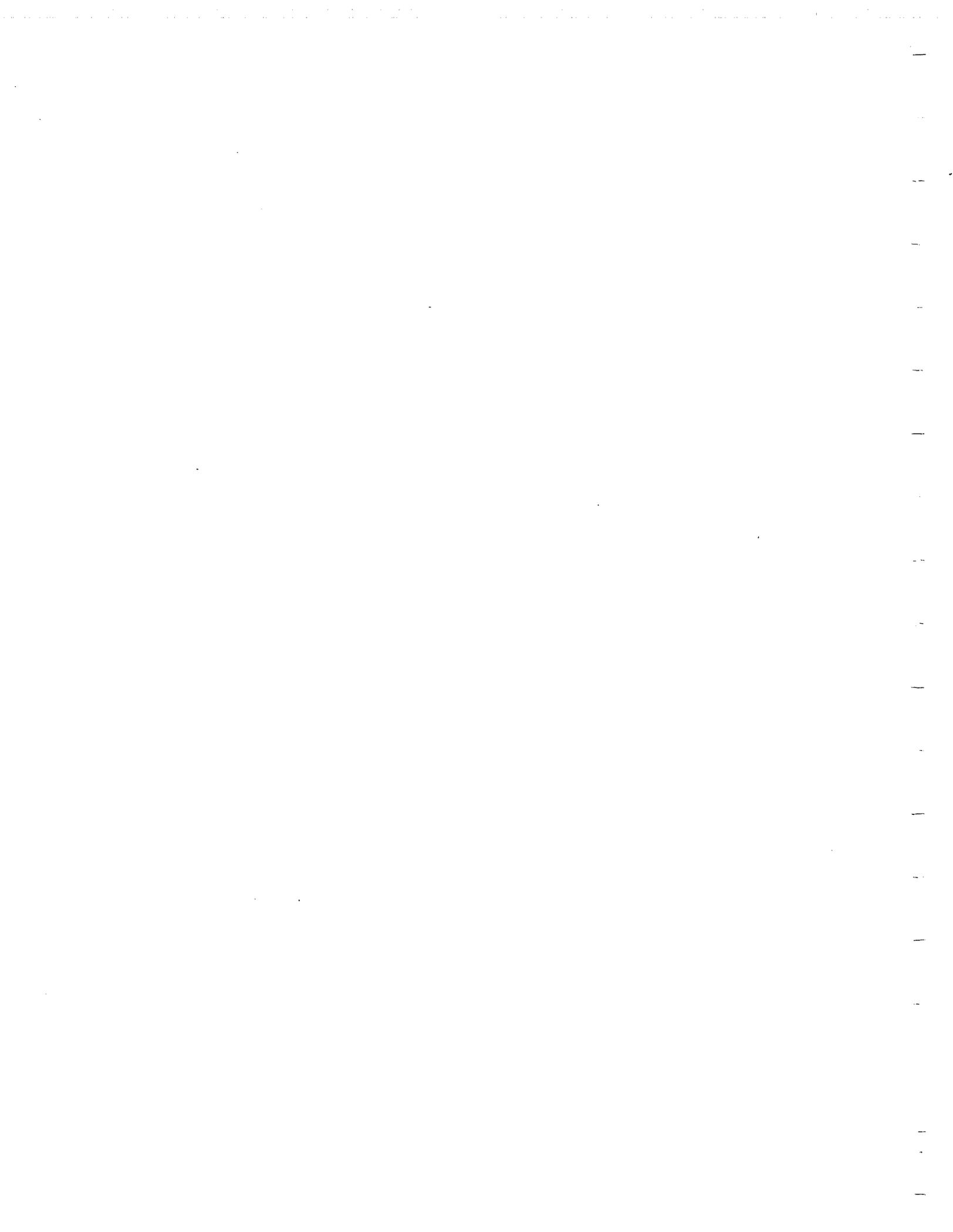


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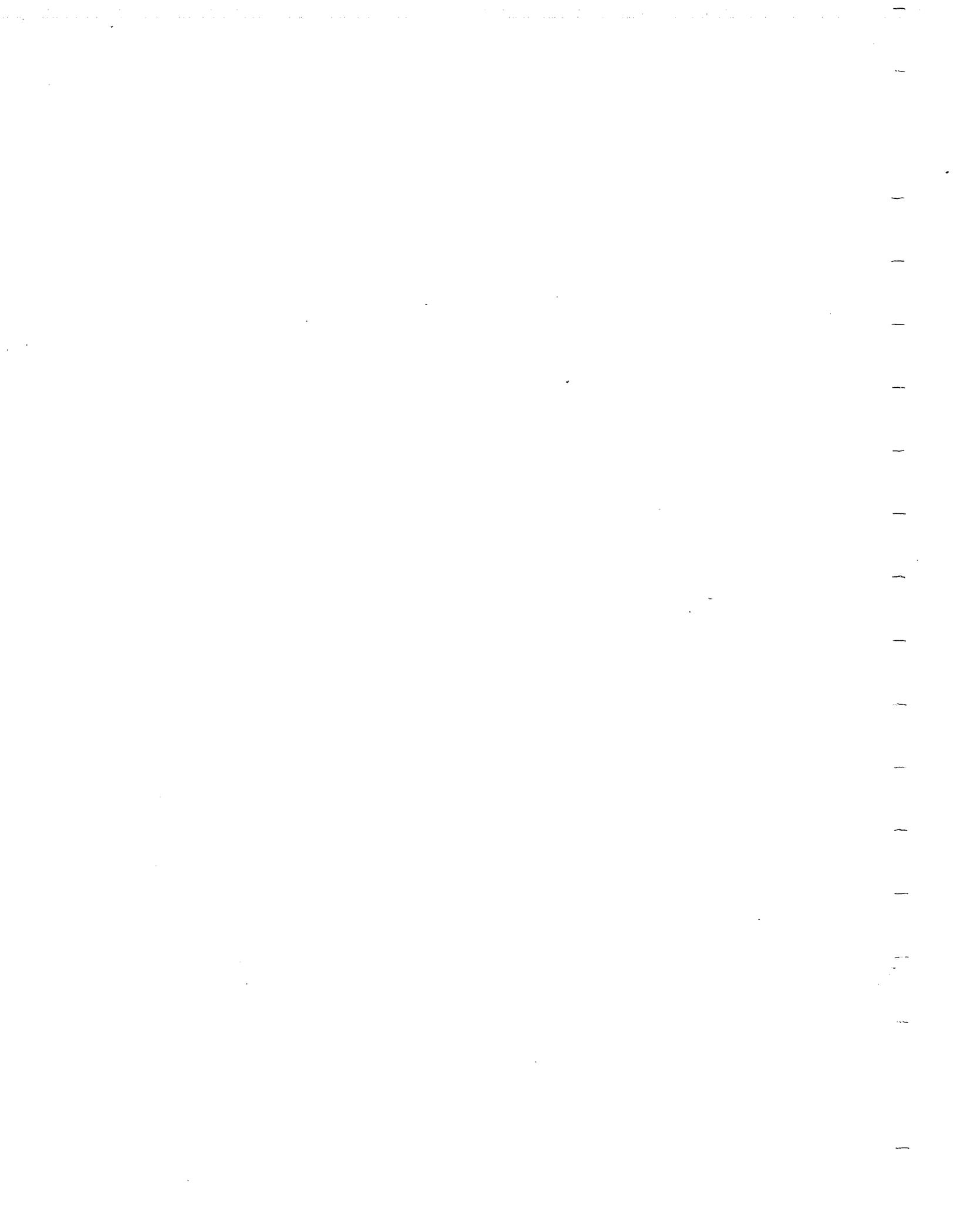
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1.0

INTRODUCTION AND SUMMARY

1.1 PURPOSE AND OBJECTIVES

Formaldehyde is of particular interest as an air pollutant, since it is not only widely used, but is a confirmed animal carcinogen and therefore is also suspected of being a human carcinogen. Formaldehyde-based resins are used in a variety of consumer products, including urea-formaldehyde foam insulation, plywood, particle board, and furniture. Regulation of the substance has been the subject of considerable controversy. For example, a federal appeals court recently overturned the Consumer Product Safety Commission's year-old ban on the use of urea-formaldehyde foam insulation. On the other hand, the U.S Environmental Protection Agency, reversing previous policy, now regards formaldehyde as warranting priority review for possible health hazards. In order to place the formaldehyde issue in perspective, the California Air Resources Board (ARB) needed information on the use of this chemical in the state, and on the potential for public exposure. Science Applications, Inc.'s (SAI's) objectives under this contract were:

- To compile available data related to formaldehyde emissions from outdoor and indoor sources.
- To survey formaldehyde concentration and exposure levels in outdoor and indoor environments.
- To develop a formaldehyde materials balance for the State of California encompassing all significant direct and indirect sources and predicting population exposure profiles.
- To critically evaluate available formaldehyde sampling and analytical methods.
- To construct a data base of formaldehyde concentrations through field monitoring of significant sources and exposure environments.
- To synthesize the above information reporting all procedures, assumptions, quality controls, conclusions and recommendations.

1.2 OUTLINE OF THE RESEARCH

The objectives of the study were accomplished through a combination of literature reviews, field measurement programs, an industrial survey, and modeling. Research under this contract was conducted by SAI between August 1982 and August 1983. The major elements of the study were as follows.

1.2.1 Literature Reviews

Our first task was to review the literature for information necessary to construct a "formaldehyde materials balance" for California. Formaldehyde release rates were estimated for direct production and for several indirect production sources; the latter included mobile sources (automobiles, trucks and buses, motorcycles and aircraft) and a variety of stationary sources (oil refineries, electric power plant, and industrial and residential combustion equipment).

Photochemical production of formaldehyde was also investigated. Consumptive uses of formaldehyde and associated atmospheric releases were then identified and quantified. Information from California formaldehyde-based resin producers was obtained through a mail survey. Emission estimates are presented in Chapter 2.

The next step was to review the literature on ambient and indoor exposure to formaldehyde in California. Using data from a New Jersey study, a method for relating formaldehyde concentrations to those of carbon monoxide and ozone was developed for application later in the study. Factors affecting indoor formaldehyde concentrations were identified. Results of this second literature review are presented in Chapter 3.

Carbonyl sampling and analytical methods were reviewed and evaluated by SAI's subcontractor, Environmental Research and Technology, Inc. (ERT), with the objective of choosing those to be used for SAI's field sampling. Chapter 4 contains the results of ERT's review of both active and passive methods.

On 19 November 1982, SAI submitted to the ARB an interim report containing the results of the three literature reviews. An indoor and outdoor field sampling program was proposed at that time. After ARB approval, field sampling began in January 1983.

1.2.2 Field Sampling

Our review of the literature indicated that indoor formaldehyde concentrations would likely be greatest in the winter, since (1) doors and windows would generally be closed, allowing the buildup of indoor air pollutants; and (2) indoor combustion sources such as portable space heaters and gas cooking stoves would be more heavily used than in other seasons. Our indoor sampling program was therefore conducted in January and February, 1983. A randomly-selected group of residents throughout the state were mailed passive formaldehyde sampling tubes, which were exposed for one week. The samplers were then analyzed for formaldehyde by Lawrence Berkeley Laboratory (LBL). Since the original sample group contained a disproportionately low number of new residences, a supplementary sampling effort was conducted in June 1983. These summer measurements probably did not provide "worst-case" exposure values. Although some workplace sampling was conducted, occupational exposure assessment was outside the scope of this project. The indoor sampling program's methods and results are presented in Chapter 5.

To ascertain the influence of suspected major point sources ("hot spots") of formaldehyde, a combination of source testing and dispersion and/or photochemical modeling would ordinarily be performed. Given the resource limitations of this study, however, a program of upwind and downwind sampling was conducted instead. Measurement sites included Los Angeles International Airport, the Mobil Oil Corporation refinery in Torrance, Southern California Edison's Ormond Beach electric power plant, and the Reichhold Chemicals, Inc. resin plant in South San Francisco. Measurements were also made in a shopping mall to determine whether emissions from permanent press clothing could be detected. In all cases, one-hour samples were collected by SAI in impingers containing 2,4-dinitrophenylhydrazine (DNPH), and were then analyzed by ERT using high-performance liquid

chromatography (HPLC). Field and laboratory methods and results are presented in Chapter 6.

One-hour ambient formaldehyde concentrations were also measured by the DNPH/HPLC method. In order to be able to test associations between formaldehyde, carbon monoxide and ozone concentrations, these measurements were conducted at the South Coast Air Quality Management District's Azusa, Lennox and Pico-Rivera monitoring stations. Samples were collected in January 1983 (Lennox and Pico-Rivera) and May-June 1983 (Azusa and Pico-Rivera). Multiple regression analyses were then used to explore possible relationships among measured formaldehyde, carbon monoxide and ozone concentrations.

In order to obtain an estimate of commuter exposure to formaldehyde, one-hour impinger samples were collected in an automobile which followed a pre-determined route between and around each pair of fixed-site monitoring stations mentioned above. Since this was an exploratory survey, no attempt was made to vary vehicle operating characteristics systematically or to determine the relative contribution of extravehicular and in-vehicle sources to the observed driver exposure. Results of the ambient and commuter sampling program are presented in Chapter 7.

1.2.3 Estimation of Public Exposure to Formaldehyde

Finally, a Monte Carlo simulation model was used to estimate time-weighted average exposures experienced by the general public. Literature values were used to estimate the time spent by the average person in residences, commuting and outdoors. Results from our field sampling program and from the literature were used to construct cumulative probability distributions from which the model chose formaldehyde concentrations at random. The model's assumptions and results are presented in Chapter 8.

1.3 FINDINGS AND CONCLUSIONS

1.3.1 California Emissions Inventory

1.3.1.1 Emissions from Formaldehyde Production

- (1) Table 1.3-1 summarizes SAI's estimates of atmospheric emissions from direct and indirect production sources of formaldehyde in 1981.
- (2) The sole direct formaldehyde producer in the state is the Borden Chemical Company plant in Fremont, whose annual emissions are estimated to be 1.9 tons (1.7 kkg). Most of these emissions are from fugitive sources.
- (3) Photochemical oxidation of hydrocarbons by oxygen, ozone or nitrogen oxides; irradiation of oxygen-containing hydrocarbons; and free radical reactions involving OH are responsible for both the production and degradation of formaldehyde in the atmosphere. Net production was estimated from literature data to be $97,000 \pm 33,000$ tons/yr ($88,000 \pm 30,000$ kkg/yr); thus this source accounts for the great bulk of formaldehyde in the atmosphere. The uncertainty in these estimates is at least 50 percent, however.
- (4) All other formaldehyde production is the result of combustion of fossil fuels. Motor vehicles (including aircraft) account for about 64 percent of combustion-related emissions. The largest stationary combustion emission sources are oil refineries.
- (5) The six counties having the largest mobile source and industrial formaldehyde emissions are Los Angeles (7,700 tons), Contra Costa (1,700 tons), San Diego (1,500 tons), Orange (1,300 tons), Ventura (850 tons) and Santa Clara (850 tons).

Table 1.3-1

SUMMARY OF SAI ESTIMATES OF ATMOSPHERIC
EMISSIONS OF FORMALDEHYDE IN CALIFORNIA

Source	Estimated Annual Emissions	
	kkg	tons
A. <u>Direct Production</u>		
Silver catalyst process	1.7	1.9
B. <u>Indirect Production</u>		
Photooxidation of volatile organic compounds	88,400	97,500 ^a
Automobiles	5,600	6,200
Trucks and buses	3,900	4,300 ^b
Oil refineries	3,700	4,100
Electric power plants	2,500	2,800
Aircraft operations	1,400	1,500
Fuel oil combustion (except power plants)	630	690
Natural gas combustion (except power plants)	590	650
Motorcycles	<u>340</u>	<u>380</u>
Total Indirect Production	106,060	118,120
C. <u>Consumptive Uses</u>^c		
Formaldehyde-based resins	4.8	5.4
Totals	107,000	118,000

^a Midpoint of low and high estimates. Estimate could vary by ± 50 percent.

^b Very rough estimate.

^c Emissions from other sources have not been quantified for California, but are believed to be negligible.

The South Coast and San Francisco Bay Air basins account for 48.5 and 24.1 percent of the state's production-related emissions, respectively.

- (6) It should be emphasized that all these emission estimates are based upon emission factors having unknown, but probably large, uncertainty ranges. Reported values should be considered accurate to at best + 50 percent.

1.3.1.2 Releases Associated With Formaldehyde Consumption

- (1) Formaldehyde is used to produce a variety of polymeric resins which find their way into numerous industrial, commercial and consumer products. The resin may be chemically unstable under certain conditions, resulting in the release of formaldehyde.
- (2) Questionnaire forms were mailed to California's seven known producers of formaldehyde-based resins, to obtain information on nameplate capacity of the three main resin types (phenolic, urea-formaldehyde and melamine-formaldehyde); 1981 production; net formaldehyde use; type and efficiency of volatile organic carbon (VOC) emission control devices, if any; percent of waste streams subject to control; and any emissions measurement data. On the basis of confidential data supplied by the producers, we estimate total formaldehyde use in the state's resin plants in 1981 to be 57 million lbs. Associated with this use were an estimated 5.4 tons (4.8 kkg) of emissions.
- (3) Almost 1,300 plants in California use formaldehyde or formaldehyde-based resins to produce consumer products, including adhesives, plywood, mobile homes, particle board, furniture, wiring insulation and paper products. Emissions from these industrial uses are unknown but are believed to be quite small compared with combustion emissions.

- (4) Other formaldehyde emissions may occur as a result of use of consumer products, such as textiles, cosmetics and deodorants, and disinfectants. Again, total emissions are small compared with those from combustion processes. However, outgassing of formaldehyde from furniture, particleboard, plywood cabinets and other products can be a significant source of indoor formaldehyde exposure, as will be discussed below.

1.3.2 Review of Previous Research

In order to plan the field sampling programs described later, we reviewed the literature on public exposure to formaldehyde. Since occupational exposures were outside the scope of this study, the review was limited to ambient and residential exposure.

1.3.2.1 Ambient Formaldehyde Concentrations

- (1) Data on the concentration of formaldehyde and other aldehydes in ambient air are quite limited; thus this study makes an important contribution to the data base.
- (2) In nine studies conducted in southern California between 1960 and 1980, formaldehyde concentrations of 0 to 150 parts per billion (ppb) were measured. Although the data are too limited to permit firm conclusions, it appears that carbonyl concentrations have been decreasing since the late 1960s and early 1970s.
- (3) Ambient aldehyde concentrations have been observed to vary significantly with time of day, day of week and month of year. Since photochemical processes account for most of the formaldehyde in ambient air, concentrations are affected significantly by such factors as light intensity and temperature.

(4) Since project resources were insufficient to conduct ambient sampling throughout the state, the possibility of relating formaldehyde concentrations to those of pollutants for which an extensive data base exists was explored. Carbon monoxide (CO) was used as a surrogate for direct combustion emissions, while ozone was used as surrogate for formaldehyde formation by photochemical processes. Using New Jersey data, it was demonstrated that an excellent statistical relationship could be derived to explain the formaldehyde concentration at time t with the CO concentration at that time and the ozone concentration three hours later. As will be seen below, however, this model did not fit southern California data very well.

1.3.2.2 Indoor Exposure to Aldehydes

- (1) A review of the literature showed that formaldehyde concentrations in conventional houses (with or without urea-formaldehyde foam insulation) range from below detectable limits (15 or 100 ppb, depending upon the measurement method) to about 500 ppb. (Higher values have been reported but the measurement method upon which they are based is suspect.)
- (2) Concentrations of up to 4,200 ppb have been measured in mobile homes. Reported mean values in several surveys range from 270 to 880 ppb.
- (3) Although the emphasis in the study was upon formaldehyde, other carbonyls have been detected in indoor air pollution surveys. Among these are acetone, benzaldehyde, methyl ethyl ketone (MEK) and acetophenone.
- (4) It is generally agreed that outdoor formaldehyde concentrations exert little if any direct influence on indoor levels.

- (5) According to our literature review, indoor formaldehyde concentrations may be expected to correlate with the presence or absence of urea-formaldehyde foam insulation; plywood, panelling, and other wood construction elements; furniture, carpets and textiles; combustion processes such as gas stoves, ovens and unvented space heaters; room deodorizers, paper products and other formaldehyde-containing consumer products; and smoking. Some of these expectations were tested in our indoor air sampling program, which is discussed below.
- (6) The concentration of formaldehyde and many other indoor air pollutants also depends heavily upon the rate at which indoor and outdoor air are exchanged (the infiltration rate). Decreasing this rate from 1 air change per hour (ach), a common value for California homes, to 0.2 ach, characteristic of a well-insulated house, could in a typical situation double the equilibrium indoor formaldehyde concentration.
- (7) Limited field data suggest that indoor formaldehyde concentrations increase with increasing humidity.

1.3.3 Review of Formaldehyde Sampling and Analytical Methods

Techniques for sampling and analyzing ambient formaldehyde were reviewed in depth by SAI's subcontractor, ERT. In selecting methods to be used for sampling, ERT used the following criteria:

- Sampling efficiency
- Sampling specificity
- Flexibility of sampling operations
- Simplicity of sampling operations
- Logistical simplicity

The following criteria were used to evaluate analytical techniques:

- Analytical specificity
- Analytical sensitivity
- Flexibility of analytical method

- Analytical dynamic range
- Potential for determination of other carbonyls
- Cost-effectiveness
- Comprehensive documentation

1.3.3.1 Active Sampling and Analytical Techniques

- (1) Ten spectrophotometric and six spectrofluorometric methods of analysis for formaldehyde were evaluated. Two classes of chromatography were investigated: those using direct gas chromatographic (GC) analysis of samples after concentration and those depending upon chromatographic analysis of derivatives. Nine types of derivatization techniques were examined. Other active sampling methods evaluated include spectroscopy, ion chromatography, and chemiluminescence.
- (2) Results of two interlaboratory comparisons of formaldehyde measurements were presented. In the first, various carbonyls were collected from a smog chamber and analyzed by infrared spectroscopy, chemiluminescence and 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by high-performance liquid chromatography (HPLC). In the second study, both laboratory-generated and field-sampled mixtures of formaldehyde and acetaldehyde were analyzed by the chromotropic acid, chemiluminescence and DNPH-HPLC methods.
- (3) The DNPH-HPLC method was determined to be the best for use in the ambient and "hot spot" sampling portions of this project. The technique's detection limit for formaldehyde in ambient air has been estimated to be $0.018 \mu\text{g}/\text{m}^3$, or about 0.015 ppb, for a 60-liter sample.

1.3.3.2 Passive Sampling and Analytical Techniques

- (1) The use of passive samplers, although increasingly popular for personal, workplace and residential monitoring, has been limited in the case of formaldehyde.

- (2) Samplers using 3-methyl-2-benzothiazolonehydrazine (MBTH) as the reagent are suitable only for measuring total aliphatic aldehydes and are thus not suitable for this project.
- (3) Passive sampling-analysis combinations evaluated included sodium bisulfite-chromotropic acid (three devices) and molecular sieve-pararosaniline or MBTH.
- (4) The sampler chosen for use in the indoor formaldehyde monitoring was a sodium bisulfite-based tube developed by Lawrence Berkeley Laboratory (LBL). According to tests conducted by LBL, its detection range is 18 to 1000 ppb after 168 hours of exposure. Measurements are not subject to significant interference from substances in residential environments. The sampler's accuracy, based upon field comparisons with a reference method, is +15 percent.

1.3.4 Survey of Formaldehyde in the Indoor Environment

1.3.4.1 Selection of Residences to Sample

- (1) A total of 81 residences and six worksites were selected for indoor air formaldehyde measurements using the LBL passive diffusion tube samplers described above.
- (2) The "sampling frame" for selection of residences was the set of California telephone directories. Prospective participants were chosen at random and interviewed by telephone. Selection continued until the sample distribution in various descriptive categories (e.g. geographical area, age of house, etc.) approximated that for the state as a whole.
- (3) Since the initial set of residences did not contain sufficient "newer" homes (i.e. four years old or less), a "supplementary" sample of six new residences was selected by the same methods.

1.3.4.2 Sampler Deployment and Analysis

- (1) Samplers for the original group of residences were mailed in January and February 1983. Samplers for the supplementary group were sent out in June 1983. Participants were instructed to attach the devices at "nose level" in a room which the family frequently occupies. Kitchens, bathrooms, and locations near open windows were to be excluded.
- (2) Participants filled out forms providing details about residential characteristics and activities of the residents during the sampling week.
- (3) Midway through the one-week exposure, participants were called to verify that the samplers had been deployed properly. After they were returned to SAI, the devices were mailed to LBL for analysis.

1.3.4.3 Measured Concentrations

- (1) The mean formaldehyde concentration for the 64 non-mobile home residences in the original sample was 49.8 ppb, with a standard deviation of 21.0 ppb. Concentrations ranged from 18 to 120 ppb.
- (2) Concentrations in the supplementary sample of the 6 "new" non-mobile home residences ranged from 46 to 153 ppb. The mean and standard deviation were 84.5 and 37.5 ppb, respectively.
- (3) Three mobile homes were sampled. Formaldehyde concentrations ranged from 68 to 144 ppb and had a mean and standard deviation of 114 and 40.4 ppb, respectively.
- (4) Ten participants deployed samplers both in their residences and at their workplaces. Concentrations ranged from below the

lower detection limit of 18 to 57 ppb and had a mean of 33.6 ppb. Because of the small number of workplace samples, no attempt was made to relate these results to possible contributory factors.

- (5) In order to obtain an idea of the distribution of carbonyl species in indoor air, one-hour impinger sampling was conducted at two of the homes in the original passive monitoring group. Formaldehyde constituted 61 and 80 percent by volume of the total carbonyls present in the two houses. In both cases, acetaldehyde was the next most common species. Other species detected in at least one of the homes were acetone, methyl ethyl ketone, benzaldehyde and hexanal.

1.3.4.4 Statistical Evaluation of Results

Before discussing our findings, two limitations on the results must be mentioned. First, project resources were insufficient to permit a sample size large enough to detect small differences among subgroups of the residential sample. In addition, infiltration rates, which can be critical in determining indoor air pollutant concentrations, were not measured.

Passive sampler values and data on residential characteristics and sampling week activities were analyzed by several statistical methods to identify potential factors which could best explain variations in formaldehyde concentrations. The following are the results of these analyses.

- (1) Fisher's Exact Test was used with data for the 10 residences with the highest and 10 residences with the lowest measured formaldehyde levels to test the null hypothesis of no association between formaldehyde concentrations and residence characteristics or activities. Using a p value of 0.05, no evidence for rejecting this hypothesis was found. (The lowest p value, 0.057, was associated with cigarette smoking during the sampling week.)

- (2) Analysis of variance (ANOVA) tests with the entire data set showed significant differences among subgroup means only for geographic location and type of heating fuel. Highest to lowest mean concentrations were found in the San Francisco Bay area, Sacramento Valley, Los Angeles/Long Beach and San Joaquin Valley.
- (3) The observed results for heating fuel are contrary to what one might expect: higher formaldehyde levels were associated with electric heating than for gas heating. The mean for the electric homes may have been skewed by the inclusion of three homes whose concentrations exceeded two standard deviations from the mean for the entire sample set.
- (4) Using a two-sided t test, it was determined that the mean formaldehyde concentration for the new (0 to 4 year-old) residences was significantly higher than that for the houses in all other age groups.
- (5) Group means for different levels of smoking were not significantly different for the entire sample. However, the mean concentration in homes where at least some cigarettes were smoked was significantly higher than in homes where none were smoked. (The differential was about 9 ppb, which is below the sensitivity of the passive samplers.)
- (6) From our literature review, we expected that type of cooking fuel, cigarette smoking and whether windows were opened would be the factors in our data set most likely to affect indoor formaldehyde levels. Homes with gas cooking and cigarette smoking were found to have significantly higher formaldehyde concentrations (by 19 ppb) than homes with electric cooking and no smoking. No significant influence of window opening and closing could be detected with our data.

- (7) Multiple regression analyses were performed using all the variables in our data set. The variables included in the "best" regression equation were home insulation, number of rooms, cigarette smoking, individual room heating, gas heating fuel, gas cooking fuel and fireplace use. The correlation coefficient for this equation is only 0.50.
- (8) It is likely that formaldehyde variation among residences depends to a large extent upon factors for which data were not collected in this study, such as air exchange rates.

1.3.5 "Hot Spot" Exposure Sampling

- (1) Facilities chosen for upwind and downwind sampling included Los Angeles International Airport, Mobil Oil Corporation's Torrance refinery, Southern California Edison's Ormond Beach Generating Station, and the Reichhold Chemicals, Inc. resin plant in South San Francisco. In addition, sampling was conducted at a shopping mall in southern California.
- (2) Concentrations at Los Angeles International Airport ranged from 6.0 to 28.6 ppb. No major effect of airport operations on ambient formaldehyde concentrations can be discerned from our data.
- (3) Formaldehyde concentrations (4.8 to 15.1 ppb) around the Mobil refinery were not significantly above background. Because the wind shifted quite frequently, we are uncertain whether the measured levels were the maximum values resulting from the refinery's contribution.
- (4) The location of sampling sites downwind from the Ormond Beach power plant was optimized by use of a dispersion model. Formaldehyde concentrations varied from 6.3 to 17.8 ppb. Again, due to frequent wind shifts, sampling sites were not at the points of maximum concentration during much of the

sampling. Highway traffic and jet aircraft exhaust from a nearby naval air station probably contributed to the measured concentrations.

- (5) The resin plant was the only facility which appeared to be contributing formaldehyde to the atmosphere of the surrounding area. The maximum differential between downwind and upwind concentrations was 22.9 ppb.
- (6) Ambient formaldehyde concentrations in the shopping mall were 25.5 and 25.0 ppb at 11 a.m. and 12 noon, respectively.
- (7) Carbonyl species distributions were determined for the airport, refinery and power plant samples. Formaldehyde was the largest component in all cases, although it represented less than half of the volumetric concentration at the refinery. Acetone was detected at all three sites. Other carbonyls present in at least one location were acetaldehyde, propanal, methyl ethyl ketone, butanal, and benzaldehyde.

1.3.6 Ambient and Commuter Exposure Sampling

1.3.6.1 Measurement Results

- (1) Hourly average formaldehyde concentrations at the Lennox and Pico-Rivera monitoring stations ranged from 7.3 to 18.2 ppb and 4.3 to 33.3 ppb, respectively, during the January 1983 sampling. Commuter exposures during this time varied from 10.7 to 91.5 ppb.
- (2) In the May-June 1983 sampling, concentrations at Pico-Rivera and Azusa were 2.0 to 17.0 ppb and 5.6 to 23.3 ppb, respectively. Commuter exposures in the summer sampling ranged from 11.3 to 22.5 ppb.

- (3) The only statistically significant difference in mean formaldehyde concentrations was that between the Azusa (13.5 ppb) and Pico-Rivera (7.8 ppb) stations in summer.
- (4) The mean commuter exposure was higher in winter than at either of the monitoring stations, but higher in summer only with respect to the Pico-Rivera station.
- (5) Given the high variance in the data and the small number of samples, no diurnal pattern in concentration could be discerned.

1.3.6.2 Correlation Between Formaldehyde and Indicator Pollutants

- (1) Using 239 combinations of formaldehyde, carbon monoxide and ozone measurements from 4 previous studies, several regression analyses were performed. The best linear regression equation had a correlation coefficient of 0.43, indicating limited usefulness in predicting formaldehyde concentrations.
- (2) Regression equations with higher statistical significance were obtained with data subsets corresponding to limited geographical locations. For example, the one for Azusa had an r value of 0.71.
- (3) Inclusion of our ambient sampling data in the three-pollutant data sets did not improve any of the correlations.
- (4) The results of these analyses suggest that reasonably good predictive equations may be derived for particular geographic areas, but that these results have very limited value for extending predictions to the rest of the state.

1.3.7 Estimation of Public Exposure to Formaldehyde

- (1) Average daily exposures of California residents to formaldehyde were estimated by means of a Monte Carlo simulation model.

- (2) The mean and median formaldehyde exposures for 1,000 runs of the model were 53 and 46 ppb, respectively. The highest predicted time-weighted exposure was 143 ppb, and 95 percent of the population would be exposed to 107 ppb or less.
- (3) Because people spend the vast majority of the time indoors, and because indoor concentrations are generally higher than those outdoors, the frequency distribution for total exposure is quite similar to that for indoor exposure.
- (4) Sensitive individuals could experience eye irritation at the median level of exposures predicted by the model. Upper airway irritation would be experienced by some people at the upper end of the predicted exposure distribution.

1.4 RECOMMENDATIONS

On the basis of our findings in this study, we make the following recommendations.

- (1) Since indoor exposure comprises most of the total exposure of the general public to formaldehyde, and since exposures at the upper end of predicted ranges can produce deleterious health effects, we recommend a comprehensive field measurement program by the appropriate agency to determine the causes of high (e.g. greater than 100 ppb) indoor concentrations. Our preliminary estimates indicate the need to sample a minimum of 500 homes, using a stratified sampling design.
- (2) Improved emission factors are needed for all combustion sources of formaldehyde. Not only does exposure to the measured ambient formaldehyde concentrations pose a significant health risk, but also formaldehyde is a participant in photochemical smog reactions. A better picture of the formaldehyde content of total hydrocarbon emissions from specific sources would be

valuable in photochemical pollution modeling and other analyses.

- (3) Considering the overwhelming contribution of photochemically-generated formaldehyde to total ambient concentrations, a better understanding of formation and depletion rates is necessary.
- (4) Since most California residents spend roughly one third of their time at workplace, a field measurement survey of at least the scope of the residential survey conducted under this contract should be undertaken.

CALIFORNIA MATERIALS BALANCE

The purpose of this chapter is to quantify and specify the locations of sources of airborne releases of formaldehyde in California in 1981-1982. In Section 2.1 we discuss direct and indirect formaldehyde production, the latter being associated with mobile, stationary, and atmospheric sources. Emissions of formaldehyde from the use of industrial and consumer products are discussed in Section 2.2. Finally the distribution of emissions by county is presented in Section 2.3.

2.1 PRODUCTION OF FORMALDEHYDE

Formaldehyde production from direct and indirect sources in 1981 is estimated to be 1.7 kkg (1.9 tons) and 106,060 kkg (118,120 tons), respectively. One facility in California is responsible for all direct production in the state. Most (83 percent) of the indirect production is due to photooxidation of volatile organic compounds in the atmosphere.

2.1.1 Direct Production of Formaldehyde

The formaldehyde industry is characterized by a large number of plants of moderate capacity usually located near sites where their products are used. The sole California formaldehyde producer is Borden in Fremont. This plant uses the silver catalyst process, in which CO and H₂ are reacted under pressure to yield methanol, which is then catalytically oxidized to formaldehyde (NRC, 1981). The final formaldehyde product is separated from reaction gases by means of a water-based product fractionator. The off gases are directed to a boiler which uses byproduct hydrogen and any carbon compounds as a fuel source for steam generation. A schematic diagram of the process is shown in Figure 2.1-1.

Air emissions from formaldehyde production can occur at the product fractionator vent, during handling and storage, from various fugitive sources and from the handling and disposal of liquid waste streams.

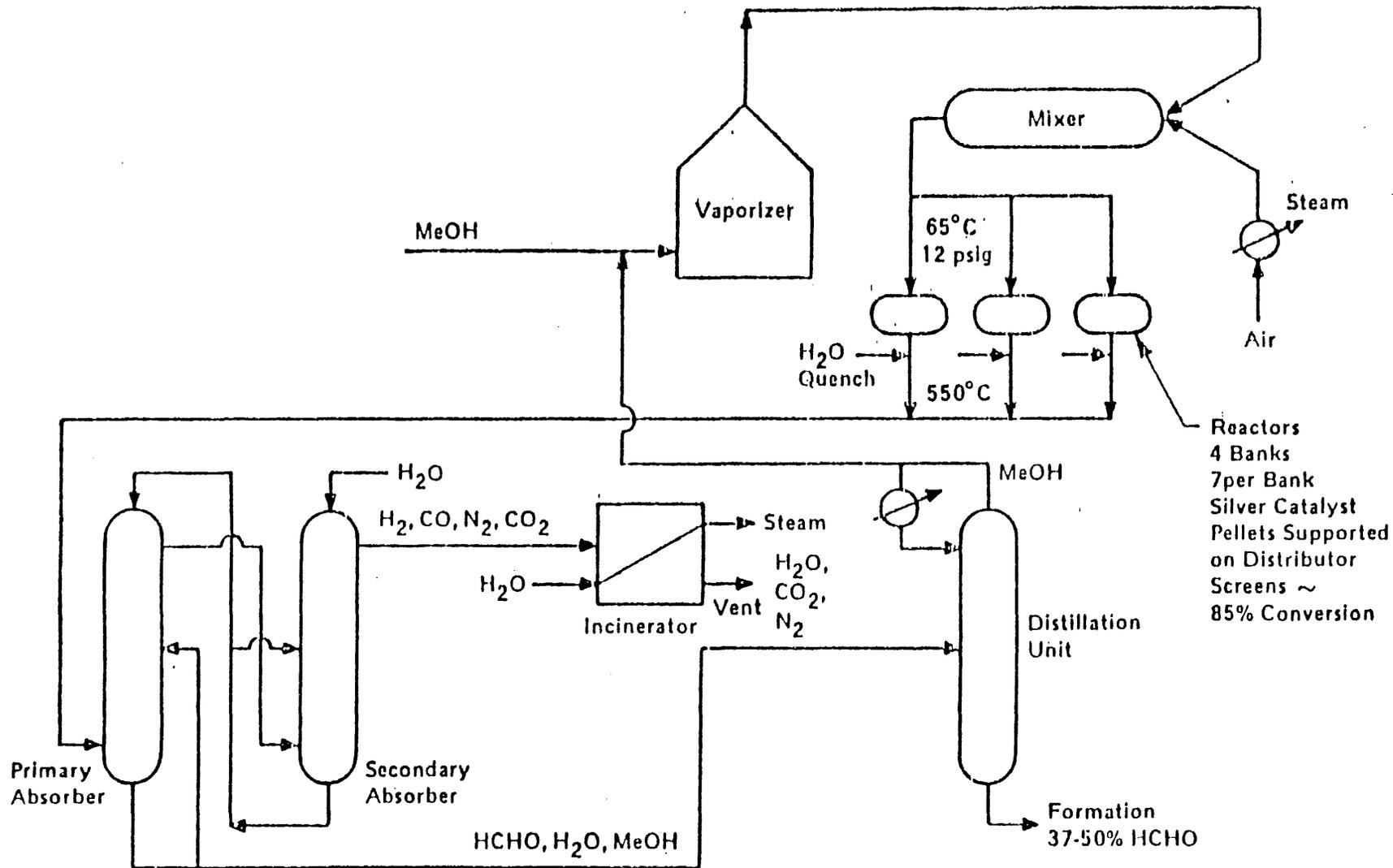


Figure 2.1-1. Silver Catalyst Process Used by Borden for Formaldehyde Production (Kitchens et al., 1976).

The Bay Area Air Quality Management District tested the output from one of the waste boilers in 1981 and reported total non-methane organic carbon (NMOC) at less than 0.1 lbs/hr. at a production rate of 340,000 pounds/day of 50 percent formaldehyde solution (Fend, 1981). This would indicate that process emissions of formaldehyde are negligible. Because some of the off gases pass through an absorber and a scrubber before combustion, it is estimated that a maximum of 10 percent of the <0.1 lb/hr NMOC or <0.01 lb/hr is formaldehyde, resulting in an annual release of 84 pounds.

Systems Applications, Inc. (1979) have estimated fugitive emissions from HCHO production to be 2.06×10^{-5} pounds/pound produced, and storage emissions to be 4.11×10^{-5} pounds/pound produced. For the Borden plant, these factors yield annual emission estimates of 2,550 lb and 1,280 lb for storage and fugitive emissions, respectively. Formaldehyde may also volatilize from process wastes before wastewater treatment. Data in this area were not available, and therefore no estimates were made for this source. The total emissions from the Borden plant are therefore estimated to be 3,759 lb/yr.

2.1.2 Indirect Production of Formaldehyde

Approximately 106,000 kkg/yr (118,000 tons/yr) of formaldehyde are produced by the following inadvertent and natural sources.

2.1.2.1 Mobile Sources

Automobiles

In general, aldehyde emissions increase with increasing mileage but not at a constant rate. A U.S. Environmental Protection Agency study of total aldehyde emissions (Carey, 1981) showed that high mileage cars averaged 18.05 mg/km (range: 7.5 - 28.6 mg/km) while emissions from low mileage cars averaged 12.4 mg/km (range: 6.2 - 18.6 mg/km). The results of formaldehyde monitoring of four catalyst-equipped car models are shown in Figure 2.1-2. It is seen that, at 15,000 miles, HCHO emissions had risen by a factor of 1.1 to 9.5 over their initial values.

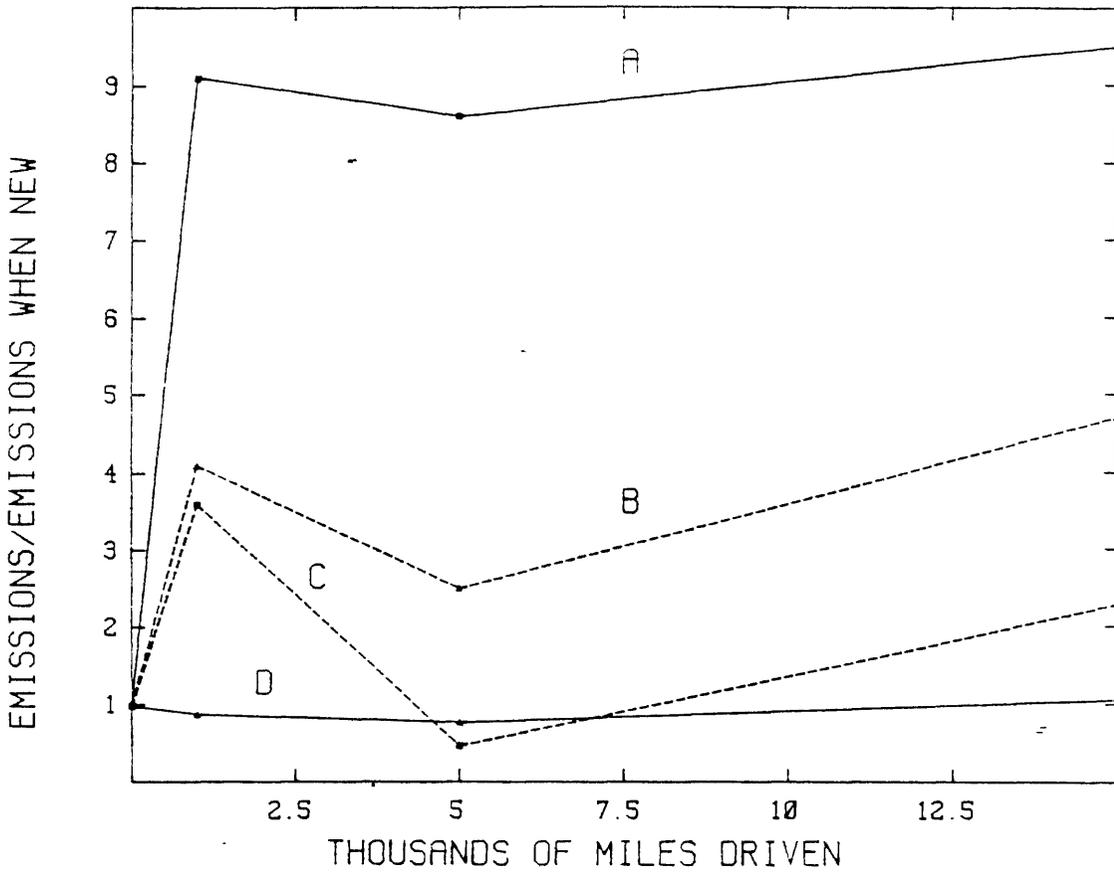


Figure 2.1-2. Ratio Between In-Use Emissions and Initial Emissions For: (A) 1978 Ford Pinto With Oxidation Catalyst, (B) 1978 Pontiac Sunbird With 3-Way Catalyst, (C) 1978 Saab 99 With 3-Way Catalyst, and (D) 1979 Mercury Marquis With Oxidation Catalyst (Original Data From Carey, 1981).

Tests reported by Smith and Carey (1982) showed that high-mileage cars equipped with 3-way and oxidation catalysts had emissions 100 and 250 percent, respectively, of those of low-mileage cars. Their data are shown in Table 2.1-1. Smith and Carey also reported emissions of 9 to 66 mg/km for cars without catalytic converters. Table 2.1-2, which contains data reported by Carey (1981), shows how the use of catalytic converters decreases aldehyde emissions.

Table 2.1-3 shows the results of recent U.S. Environmental Protection Agency measurements of formaldehyde emissions from catalyst-equipped 1975-1981 model cars (Gable and Sigsby, 1983). The Federal Test Procedure (FTP) was used to simulate commuter driving. Although two other test procedures were also used, the FTP is the best known and the most applicable to California. Note that the complex nature of the emissions and controls, together with the small number of test vehicles, resulted in high standard deviations about the mean values. Data on miles traveled by vehicles of different ages in 1980 were obtained from the Federal Highway Administration (Sherrer, 1982) and the U.S. Department of Energy (Egan, 1982). The final piece of information necessary to estimate formaldehyde emissions from automobiles was the number of vehicles in each age class. At the end of 1980 there were 11,921,719 registered autos in California (CDOT, 1982). The age distribution of these vehicles was:

<u>Vehicle Age (Years)</u>	<u>Percent of Registered Autos</u>
0-1	11.6
2-3	17.5
4-5	16.3
6-7	15.6
8-9	12.2
10 or more	22.0

A typical calculation of emissions is, for the case of cars which were three years old in 1980,

$$\begin{aligned}
 \text{No. cars} &= (0.175)(0.5)(11,921,719) = 1.043 \times 10^6 \\
 \text{Vehicle miles travelled} &= (13 \times 10^3 \text{ miles/car})(1.043 \times 10^6 \text{ cars}) \\
 \text{Emissions} &= (1.356 \times 10^{10} \text{ VMT}) (1.609 \text{ km/mi})(33.2 \text{ mg/km}) \times 2.205 \\
 &\quad \times 10^{-6} \text{ lb/mg} = 1.60 \times 10^3 \text{ lb}
 \end{aligned}$$

Table 2.1-1

FORMALDEHYDE EMISSIONS FROM HIGH-MILEAGE CARS

Automobile	Catalyst	Year	Mileage	Emissions (mg/km)
Buick Regal	Oxidation	1978	54,522	8.83
Mercury Marquis	3-way	1979	46,462	ND
Mercury Marquis	3-way	1979	48,766	2.88
Ford Granada	Oxidation	1978	56,933	5.38
Volvo 245 DL	3-way	1978	59,031	1.75
Olds Cutlass	Oxidation	1978	47,278	1.13
Chevrolet Malibu	Oxidation	1978	37,577	6.36
Chevrolet Monte Carlo	Oxidation	1978	67,460	5.31
Ford Fiesta	Oxidation	1978	67,963	1.7
Chrysler New Yorker	Oxidation	1978	66,038	17.01

Source: Smith and Carey, 1982

Table 2.1-2

ALDEHYDE EMISSIONS FROM AUTOMOBILES WITH AND WITHOUT CATALYTIC CONVERTERS
(Emissions in mg/km)

Type of Auto	Year(s)	Total Aldehyde Emissions		Formaldehyde Emissions	
		Non-Catalyst	Catalyst	Non-Catalyst	Catalyst
VW Beetle	1975	45.99	6.84		
VW Dasher	1975	68.37	14.29 ^a		
VWs	1972-1976	45.16 ^a	7.33 ^a		
Unspecified	1977-1979				1.26 ^b
Unspecified	1970			32.31 ^c	

Source: Carey (1981)

^a Average for eight cars.

^b Average for nine cars.

^c Average for four cars.

Table 2.1-3
EMISSION FACTORS FOR CATALYST-EQUIPPED VEHICLES

Vehicle Year	Formaldehyde Emissions, mg/km			
	Mean	95-Pct. Confidence Range		
1975	40.6	0	-	260.4
1976	23.7	0	-	78.1
1977	35.8	0	-	89.6
1978	33.2	0	-	98.9
1979	17.2	0	-	51.7
1980	16.0	0	-	46.0
1981	2.19	1.31	-	3.05
1982	3.67	0.62	-	6.71

Table 2.1-4 shows the results of our calculations. Formaldehyde emissions from automobiles are estimated to be 5.65 million kg (12.5 million lb).

Aircraft

Emission factors for aircraft operations at airports were developed as follows. First, Kitchens et al. (1976), after a review of rather early literature, chose 5 lb formaldehyde/1000 gal aviation fuel as an average estimate for turboprop and piston engines. If we assume densities of 6.6 and 5.9 lb/gal for jet fuel and gasoline, respectively (Pratt and Whitney, 1964), then the emission factors become 1.5 and 1.7 lb/ton fuel.

Although Kitchens et al. present data on formaldehyde in jet exhaust, we preferred to use the results of tests conducted in 1970 by the Los Angeles County Air Pollution Control District (Burlin and Parmelee, 1970; Burlin and Ramlo, 1970). Measured emissions of total aldehydes for each part of the normal airport-associated operating cycle were:

<u>Phase</u>	<u>lb HCHO/ton fuel</u>
Idle	6.0
Takeoff	3.3
Climb	4.3
Approach	3.7

To estimate emissions from aircraft it is first necessary to define a relevant operating cycle. Since public exposure to aircraft emissions occurs almost entirely as a result of airport operations, we define the operating cycle as the combination of idle, takeoff, climb and approach times. Fuel consumption, which is the main determinant of HCHO emissions, varies with the operating mode and the type of aircraft. A general equation for the emissions from aircraft type i during mode j is:

$$E_{ij} = T_{ij} \times F_{ij} \times N_i \times H_{ij}$$

Table 2.1-4

CALCULATION OF FORMALDEHYDE EMISSIONS FROM CALIFORNIA AUTOMOBILES IN 1980

Car Age (year)	Miles Travelled Per Car in 1980 ^b	Emission Factor (mg/km)	Fraction of California Cars	Emissions (1000 kg/yr)	Emissions (1000 lb/yr)
1	10,000	16.0	0.116	356	785
2	12,000	17.2	0.0875	346	764
3	13,000	33.2	0.0875	724	1,597
4	15,000	35.8	0.0815	839	1,851
5	10,000	23.7	0.0815	371	817
6	10,000	40.6	0.078	607	1,339
7 ^a	10,000	32	0.078	479	1,056
8 ^a	10,000	32	0.061	375	826
>9 ^a	9,000	32	0.281	1,552	3,423
Totals				5,649	12,458

^a Non-catalyst equipped

^b Estimates from Egan (1982).

where T_{ij} is the time spent by aircraft type i in mode j , F_{ij} is the corresponding fuel consumption (mass/time) per engine, N_i is the number of engines per aircraft type i , and H_{ij} is the formaldehyde emission rate (mass HCHO/mass fuel). The emissions from aircraft type i for one operating cycle are then:

$$E_i = \sum_{j=1}^4 E_{ij}$$

Finally, the total emissions per year are estimated from:

$$E = \sum_{i=1}^3 O_i E_i$$

where O_i is the number of operations per year for aircraft type i . Emission factor calculations are summarized in Table 2.1-5.

Operations are construed here to mean both takeoffs and landings. The Federal Aviation Administration and the Civil Aeronautics Board jointly publish an annual compilation of flights (departures) by certified carriers by airport and equipment type (FAA, 1981). It was assumed that each departure was preceded by an arrival. No data could be obtained for private aircraft. Total emissions are estimated to be 1.349 million kg (2.974 million lb). Table 2.1-6 lists formaldehyde emissions from flights associated with the various state airports.

Other Motor Vehicles

Motorcycles have apparently not been tested in as much detail as automobiles and a brief literature search did not reveal data on their volatile organic carbon emissions. Cupitt (1982) indicated that a previous EPA "best estimate" of 0.1 g/km was probably still good. The California Department of Transportation reports 687,699 registered motorcycles at the end of 1981 (CDOT, 1982). The Federal Highway Administration (FHA) reports an average of 3,087 miles travelled per vehicle (Svercl, 1982). It is therefore estimated that 750,000 pounds of formaldehyde were released to the air through motorcycle use in 1981.

Table 2.1-5

DERIVATION OF TAKEOFF/LANDING CYCLE FORMALDEHYDE
EMISSION FACTORS FOR AIRCRAFT

Emission Factor Component	Units	Cycle Phase	Engine Type		
			Jet	Turboprop	Piston
Fuel Use	lb/hr	Idle	968	303	20.3
		Takeoff	9242	1136	125
		Climb	7451	1041	102.1
		Approach	2756	548	55.7
Time in Phase	min	Idle	26	26	13
		Takeoff	0.5	0.5	0.6
		Climb	2.5	2.5	0.5
		Approach	4.5	4.5	4.6
Number of engines			3.2	2.5	1.5
Emission factor	lb HCHO/ ton fuel	Idle	6	1.4	0.81
		Takeoff	3.3	0.0045	0.0717
		Climb	4.3	0.0133	0.5055
		Approach	3.7	0.0383	0.317
Emission/Phase	lb/HCHO	Idle	4.03	0.223	0.00267
		Takeoff	0.4	0.000	0.00000
		Climb	2.13	0.000	0.00017
		Approach	1.22	0.000	0.00005
Total Emissions Per Cycle	lb/HCHO		7.79	0.223	0.00289

Table 2.1-6

FORMALDEHYDE EMISSIONS ASSOCIATED WITH CERTIFIED AIRLINE DEPARTURES FROM CALIFORNIA AIRPORTS

Location	Jets ^a	Emissions (1000 lbs)	Turboprops ^a	Emissions (1000 lb)	Piston ^a	Emissions (1000 lb)	Total Emissions (1000 lb)
Bakersfield	0	-	79	0.05	0	-	0.05
Meadowsfield	0	-	3,121	2.2	319	0.05	2.2
Blythe	0	-	3	-	795	0.15	0.15
El Centro	0	-	2,259	0.9	416	0.1	1.0
Eureka/Arcata	1,003	4	-	0	0	-	4.0
Fresno	5,727	27.9	5,367	3.75	134	0.025	26.7
Indio/Palm Springs	2,995	12	494	0.35	0	0	12.4
Lake Tahoe	0	-	3,526	2.45	0	-	2.5
Hollywood/Burbank	14,050	56	870	0.6	0	-	56.6
Long Beach	877	3.5	0	-	0	-	3.5
Los Angeles Int'l	139,283	557	26,529	18.5	13,783	2.75	578.3
Orange County	14,362	57.5	5,592	3.9	794	0.15	61.5
Merced	0	-	897	0.65	0	-	0.7
Modesto	0	-	2,290	1.6	0	-	1.6
Edwards AFB	0	-	142	0.1	0	-	0.1
Ontario Int'l	13,218	52.8	4,105	2.85	3,752	0.75	61.4
Oxnard/Ventura	0	-	2,740	1.9	195	0.04	1.9
Palmdale/Lancaster	0	-	690	0.5	0	-	0.5
Palomar	0	-	0	-	1,225	0.25	0.3
Red Bluff/Redding	2,292	9.2	0	-	0	-	9.2
Sacramento	15,487	61.9	3,560	2.5	314	0.06	64.5
Salinas/Monterey	2,793	11.2	2,699	1.9	343	0.07	13.1
San Diego Int'l	28,888	115.5	4,542	3.2	9,150	1.85	120.6

Table 2.1-6

FORMALDEHYDE EMISSIONS ASSOCIATED WITH CERTIFIED AIRLINE DEPARTURES FROM CALIFORNIA AIRPORTS
(Continued)

Location	Jets ^a	Emissions (1000 lbs)	Turboprops ^a	Emissions (1000 lb)	Piston ^a	Emissions (1000 lb)	Total Emissions (1000 lb)
San Francisco/ Oakland	15,125	60.5	0	6.25	257	0.03	60.5
San Francisco Int'l	99,290	397.1	8,950	6.25	257	0.05	403.4
San Jose	21,782	87.1	3,900	2.75	325	0.06	89.9
San Luis Obispo	0	-	1,589	1.1	504	0.1	1.2
Santa Barbara	1,152	4.6	5,419	3.8	1,399	0.3	8.7
Stockton	709	2.8	2,306	1.6	0	-	4.4
George AFB	2	-	0	-	0	-	
TOTAL	379,040	1,516	91,669	64	33,830	6.8	1,587

^a Number of flights based on data from FAA, 1981.

A little more information was available for the combination of trucks and buses. (Registration data for each vehicle type were unavailable.) The 1980 fraction of U.S. trucks and buses registered in the state was 0.111 (MVMA, 1982) and the distance travelled in California, according to FHA data (Svercl, 1982), was 7.11×10^{10} km.

Carey (1981) has estimated heavy-duty diesel truck emissions of formaldehyde to be an average of 55.5 mg/km. The basis for this estimate is unclear. It is not based upon actual measurements and, when asked by SAI for an explanation, Carey (1982) could not recall her methodology. A search of the literature failed to yield a more justifiable value; therefore, our estimate of 3950 kkg (8.70 million lbs) of formaldehyde in the exhaust from trucks and buses should be considered highly uncertain.

2.1.2.2 Stationary Sources

Stationary sources contributing emissions would be those using or producing hydrocarbon-based fuels, and incinerators. The use of coal as a fuel contributes little if any formaldehyde in California, since coal is used to a small extent in the state. The SCAQMD reports 0.07 tons/day of total reactive gas emissions from municipal incineration, so the HCHO contribution would be negligible. HCHO emissions from incineration in the San Francisco Bay Air Basin are also presumed to be negligible (Clayton, 1982). Total emissions from stationary sources are estimated to be 8,240 tons/year.

Oil Refining

Kitchens et al. (1976) report emission factors of 19 lbs HCHO/1000 bbl for fluid catalytic cracking units and 12 lbs HCHO/1000 bbl for thermoforming units. These factors may be outdated, since the results of a 1960 study were used to estimate formaldehyde emissions and all aldehydes were assumed to be formaldehyde. Application of better emission controls during the past 20 years may have resulted in a reduction of emission factors. In a recent unpublished study (Bryan, 1982), EPA used the data of Kitchens et al but assumed 70 percent of the aldehyde emissions to be formaldehyde.

California's 43 refineries have an aggregate rated capacity of 2,645,100 bbl/day, most of which is for catalytic cracking (OGJ, 1981). Since about 85 percent of the charge capacity of California refineries is in catalytic units, we have used a weighted emission factor of $(0.85)(19) + (0.15)(12) = 18$ lb/1000 bbl for total aldehydes. Assuming that HCHO constitutes 70 percent of the total aldehydes, we arrive at an emission factor of 12.6 lb HCHO/1000 bbl. At the suggestion of the U.S. Department of Energy's Energy Information Office (Frietas, 1982), we assumed that the refineries operated at 67 percent of their capacities in 1981. The calculation results in an estimate of 2.23×10^4 lb/day (8.15 million lb/year) of statewide formaldehyde emissions. Table 2.1-7 lists the emissions on a plant-by-plant basis.

The predicted formaldehyde releases in Table 2.1-7 were compared with total facility organic emissions (either TOG or ROG) as identified in corresponding air pollution control district inventories. In some cases the formaldehyde fraction appears to be plausible, while in others it is unrealistic. This is not surprising given the uncertainty in the emission factors.

Electric Power Generation

Table 2.1-8 lists California's utility-operated electric power plants, along with their oil and gas consumption in 1981. According to Kitchens et al. (1976), an uncontrolled emission factor for natural gas and residual fuel oil combustion in this industry is $1 \text{ lb}/10^6 \text{ ft}^3$. Under standard temperature and pressure, this emission factor is equivalent to 0.024 lb HCHO per 1000 lb natural gas. Goldstein and Waddams (1967), in a work cited by Natusch (1978), report an emission factor of 0.2 lb/1000 lb for power plants. Hangebrauck et al. (1964), meanwhile, reported emissions of 0.0025 to 0.06 lb HCHO per 1000 lb of natural gas combusted in a variety of devices. The geometric mean of these estimates is 0.029 lb HCHO/1000 lb or $1.2 \text{ lb}/10^6 \text{ ft}^3$. Our literature review found no more recent estimates.

Table 2.1-7

ESTIMATED FORMALDEHYDE EMISSIONS FROM CALIFORNIA REFINERIES, 1981

Company	City	County	Capacity ^a (10 ³ bbl/ day)	Emissions (10 ³ lbs/ year)
Atlantic Richfield	Carson	Los Angeles	212	653.2
Beacon Oil	Hanford	Kings	17.9	55.2
Champlin Petroleum	Wilmington	Los Angeles	60	184.9
Chevron, USA	Bakersfield	Kern	26	80.1
	El Segundo	Los Angeles	405	1247.9
	Richmond	Contra Costa	365	1124.7
Coastal Petroleum	Bakersfield	Kern	8.5	26.2
Conoco Oil	Paramount	Los Angeles	46.5	143.3
DeMenno-Kerdoon	Compton	Los Angeles	15	46.2
Douglas Oil	Santa Maria	Santa Barbara	9.5	29.3
Eco Petroleum	Signal Hill	Los Angeles	11	33.9
Edgington Oil	Long Beach	Los Angeles	41.6	128.2
Exxon	Benicia	Solano	103	317.4
Fletcher Oil & Refining	Carson	Los Angeles	29.5	90.9
Getty	Bakersfield	Kern	63	194.1
Gibson Oil & Refining	Bakersfield	Kern	4.6	14.2
Golden Bear Div, Witco Chemical Corp.	Oildale	Kern	11	33.9
Golden Eagle Refining	Carson	Los Angeles	16.5	50.8
Gulf Oil	Santa Fe Springs	Los Angeles	51.5	158.7
Huntway Refining	Wilmington	Los Angeles	5.4	16.6
Kern County Refining	Bakersfield	Kern	21.4	65.9
Lunday-Thagard Oil Co.	South Gate	Los Angeles	10.9	33.6
Macmillan Ring-Free Oil Co.	Signal Hill	Los Angeles	13	40.1
Marlex Oil & Refining	Long Beach	Los Angeles	19	58.5
Mobil Oil	Torrance	Los Angeles	123.5	380.5
Newhall Refining	Newhall	Los Angeles	21	64.7
Oxnard Refining	Oxnard	Ventura	4.7	14.5
Pacific Refining	Hercules	Contra Costa	89 ^b	274.2
Powerine Oil	Santa Fe Springs	Los Angeles	44.1	135.9
Road Oil Sales	Bakersfield	Kern	6	18.5
Sabre Refining	Bakersfield	Kern	12.4	38.2
San Joaquin Refining	Oildale	Kern	27	83.2
Shell Oil	Martinez	Contra Costa	104	320.5
	Wilmington	Los Angeles	108	332.8
Sierra Anchor	McKittrick	Kern	14	43.1
Sunland Refining	Bakersfield	Kern	15	46.2
Texaco	Wilmington	Los Angeles	75	231.1
Tosco Corp.	Bakersfield	Kern	41 ^b	126.3
	Martinez	Contra Costa	126	388.2

Table 2.1-7

ESTIMATED FORMALDEHYDE EMISSIONS FROM CALIFORNIA REFINERIES, 1981
(Continued)

Company	City	County	Capacity ^a (10 ³ bbl/ day)	Emissions (10 ³ lbs/ year)
Union Oil of Calif.	Los Angeles	Los Angeles	108	332.8
	Rodeo	Los Angeles	111	342
USA Petrochem	Ventura	Ventura	27.9	86.0
West Coast Oil	Oildale	Kern	21	64.7
Total				8151.2

^a Barrels per calendar day

^b Estimated: Barrels per calendar day = Barrels per stream day x 1.05

Table 2.1-8

FORMALDEHYDE EMISSIONS ASSOCIATED WITH
GAS AND OIL USE BY ELECTRICITY GENERATING POWER PLANTS

Utility	Plant	Fuel Use		Formaldehyde Emissions (1000 lb/yr)		
		Oil (1000 bbl)	Gas (1000 mcf)	Oil	Gas	Total
Burbank Glendale	Magnolia-Olive	51	5,454.0	5.1	6.5	12
	Glendale		4,417.6		5.3	5
Imperial	El Centro	105	4,160.8	10.6	5.0	16
	Coachella		380.5		0.5	1
	Rockwood		16.9		0.02	0
L.A. Dept. Water/Power	Harbor		1,088		1.3	1
	Haynes	3,745	33,943	377.5	40.7	418
	Scattergood	52	20,368	5.2	24.4	30
	Valley	166	4,979	16.7	6.0	23
Pacific Gas and Electric	Avon	89	3,502.9	8.9	4.2	13
	Contra Costa	--	59,802.7		71.8	72
	Humboldt Bay	73	5,833	7.3	7.0	14
	Hunters Point	526	18,758.7	53.0	22.5	76
	Kern	--	13,045.6		15.7	16
	Martinez	23	3,421.8	2.3	4.1	6
	Morro Bay	2,136	34,163.3	215.3	41.0	256
	Moss Landing	3,225	78,584.1	325.1	94.3	419
	Oleum	153	6,210.2	15.5	7.5	23
	Pittsburg	3,308	57,634.9	333.4	69.2	403
	Potrero	382	12,091.9	38.5	14.5	53
	Oakland	252	--	25.4		25
Pasadena	Broadway	--	4,631.5		5.6	6
	Glenarm	15	419.4	1.5	0.50	2

Table 2.1-8

FORMALDEHYDE EMISSIONS ASSOCIATED WITH
GAS AND OIL USE BY ELECTRICITY GENERATING POWER PLANTS
(Continued)

Utility	Plant	Fuel Use		Formaldehyde Emissions (1000 lb/yr)		
		Oil (1000 bbl)	Gas (1000 mcf)	Oil	Gas	Total
San Diego Gas and Electric	Encina	6,227	15,005	627.7	18.0	646
	Kearny	1	513	0.1	0.6	1
	Miramar	--	198.1		0.2	0
	Naval Station	1	2,478	0.1	3.0	3
	N. Island	10	1,658	1.0	2.0	3
	Silver Gate	--	2,193		2.6	3
	South Bay	1,933	18,650	194.8	22.4	217
	Station B	1	572	0.1	0.7	1
Southern California Edison	Alamitos	6,468	41,504.2	652.0	49.8	702
	Cool Water	65	22,732	6.6	27.3	34
	El Segundo	1,963	29,858	197.9	35.8	234
	Etiwanda	2,853	24,839	287.6	29.8	317
	Highgrove	--	709		0.9	1
	Huntington Beach	2,138	20,825	215.5	25.0	241
	Long Beach	299	13,430	30.1	16.1	46
	Mandalay	2,272	5,667	229.0	6.8	236
	Ormond Beach	7,984	20,810	804.8	25.0	830
	Redondo	327	53,799	33.0	64.6	98
	San Bernardino	35	5,665	3.5	6.8	10
Ellwood	1	33	0.1	0.04	0	
Total		46,879	654,046.1	4,725	785	5,510

Source: Fuel consumption data from Cost and Quality of Fuels for Electric Utility Plants-1981 (USD0E, 1982a).

Emission factor estimates for combustion of residual oil in power plants vary widely. Kitchens et al. (1976) report 0.3 lb HCHO per 1000 lb fuel. Goldstein and Waddams (1967) estimate 0.1 lb emissions per 1000 lb fuel. Chass et al. (1960) report only 0.075 lb/1000 lb for total aldehydes and ketones combined. None of these values is based upon recent measurements. To be conservative, we have used Kitchens et al.'s estimate of 0.3 lb/1000 lb.

Since use of wet scrubbers (chiefly for SO₂ control) would be expected to remove at least some of the carbonyl emissions, we contacted all air pollution control districts having utility power plants within their jurisdictions, to ascertain whether such controls were used in 1981. Only the El Centro and Rockwood power plants in Imperial County used scrubbers (ICAPCD, 1982). Unfortunately, no formaldehyde emission factors were available for this case. However, the uncontrolled formaldehyde emissions from these plants represent less than 0.3 percent of the total for this source category.

Formaldehyde emissions from gas- and oil-fired electric power plants are estimated to be 356 kkg (785,000 lb) and 2,150 kkg (4.73 million lb) per year, respectively. The statewide total is 2506 kkg/yr (5.52 million lb/yr, or 2,758 tons/yr). Emissions from each power plant are shown in Table 2.1-8.

Industrial and Residential Fuel Use

Industrial power and heat generation consumed 15.5×10^6 bbl of distillate fuel and 423.35×10^9 ft³ of natural gas in California in 1980 (USD0E 1982b). Residential use was 529.3×10^9 ft³ of gas and 94,000 bbl of oil. The Department of Energy has not yet published the summary data for 1981. Formaldehyde generation rates for the different fuels and uses are listed in Table 2.1-9.

Note that the cooking emission rates provided by Traynor et al. (1981) are almost an order of magnitude higher than those of Kitchens et al. (1976). Although the Traynor values are high, our experience shows them to be reasonable. We have therefore used $25,000 \mu\text{g}/\text{m}^3$ as an intermediate emission factor.

Table 2.1-9

EMISSION FACTORS FOR INDUSTRIAL AND RESIDENTIAL
FUEL COMBUSTION

Device	Distillate Fuel Oil	Type of Fuel Industrial Gas	Residential Gas	Ref.
<u>Various</u>	0.28 lb/1000 lb	2 lb/10 ⁶ ft ³		1
<u>Heaters</u>				
Space			2,400 $\mu\text{g}/\text{m}^3$	1
Floor Furnace			3,600 $\mu\text{g}/\text{m}^3$	1
Water Heater			9,600 $\mu\text{g}/\text{m}^3$	1
<u>Cooking</u>				
Bake Oven			7,200 $\mu\text{g}/\text{m}^3$	1
Oven Range			13,200 $\mu\text{g}/\text{m}^3$	1
Range			62,480 $\mu\text{g}/\text{m}^3$	2
Gas Oven			100,000 $\mu\text{g}/\text{m}^3$	2

Sources: 1 - Kitchens et al. (1976), 2 - Traynor et al. (1981).

Gas use for the various purposes is not well characterized. The U.S. Department of Energy will be collecting this type of data sometime in the near future and the American Gas Association (AGA) currently surveys utilities for data on single family homes (Pavle, 1982). According to an AGA survey of five utilities, the percentage of natural gas use represented by heating of single-family homes in 1981 varied between 43.6 percent (Long Beach Gas) and 83.5 percent (Pacific Gas and Electric). Southern California Gas Company (57.2 percent heating) served 3.3 million homes and PGE served 2.67 million. Since these utilities serve such a large segment of the population, we estimate that, on the average, 60 percent of total gas used is for heating. (The weighted average of 67 percent was reduced to take into account gas used for cooking in apartments.) Estimates of formaldehyde emissions from residential and industrial sources are shown in Table 2.1-10.

2.1.2.3 Photochemical Production of Formaldehyde

Photochemical oxidation of hydrocarbons by oxygen, ozone or nitrogen oxides, irradiation of oxygen-containing hydrocarbons, and free radical reactions involving OH are some of the reaction pathways by which formaldehyde may be formed in the atmosphere (NRC, 1981; Kitchens et al., 1976). Many of these reactions are also responsible for the subsequent degradation of formaldehyde, making it difficult to estimate the quantity produced. The following discussion is intended to be general and the reader is cautioned as to the large uncertainty inherent in any estimation of photochemically-produced formaldehyde.

A very rough estimate of the net generation rate (i.e. production minus removal) of formaldehyde in the atmosphere can be obtained by multiplying hydrocarbon emissions from all other sources by a photochemical conversion efficiency factor. For example, Kitchens et al. (1976) assumed a conversion factor of 0.1 to 0.2, to be applied only to automobile exhaust hydrocarbons. A steady state, i.e. net, conversion factor of 0.10 to 0.12 has been suggested by Whitten of Systems Applications, Inc. (1982).

Table 2.1-10
 FORMALDEHYDE EMISSIONS FROM
 INDUSTRIAL AND RESIDENTIAL FUEL USE

Fuel Type	Quantity	HCHO Emission Factor	Emissions (1000 lb)
Gas, Industrial	423.35 x 10 ⁹ ft ³	2 ^b lbs/10 ⁶ ft ³	850
Oil, Industrial ^a	15.5 x 10 ⁶ bbl	0.28 lbs/10 ³ lbs	1370
Oil, Residential ^a	94 x 10 ³ bbl	0.28 lbs/10 ³ lbs	8.3
Gas, Residential Heat	317.6 x 10 ⁹ ft ³	0.25 lbs/10 ⁶ ft ³	79
Gas, Residential Other	211.7 x 10 ⁹ ft ³	1.75 lbs/10 ⁶ ft ³	370
Total			2680

^a Distillate oil, 7.5 lbs/gal

^b Emission factor reported to only one significant figure in the literature.

By analyzing simultaneously obtained data on ambient aldehydes and carbon monoxide, Grosjean (1982) estimated formaldehyde/CO and acetaldehyde/CO emission rate ratios of 2.5×10^{-3} and 2.1×10^{-3} respectively; net atmospheric photochemical production rates for the two carbonyls would be as high as 80,000 and 60,000 kg/day. Note that these conversion factors apply to relatively smoggy days. On an average annual day in 1979, reactive organic gas (ROG) emissions in the South Coast Air Basin were 1,533 tons (SCAQMD/SCAG, 1982). The ratio between the net photochemical formation rate of formaldehyde and these average annual day ROG emissions was 0.06. Since Grosjean's estimates are for smoggy days, this ratio likely overstates the actual value.

For the purpose of estimating photochemical production of formaldehyde, we assume a steady-state conversion factor of 0.06 to 0.12. The average annual day emissions of total organic gases in the San Francisco Bay Air Basin were 1,740 tons/day in 1979 (BAAQMD, 1982). If we assume that ROG emissions represented 80 percent of the TOG, then the photochemical production of formaldehyde for the state's two most important basins would be:

$$\begin{aligned} \text{Minimum} &= 0.06 [1533 + (0.8)(1740)] \text{ tons/day} \times 365 \text{ days/yr} \\ &= 6.4 \times 10^4 \text{ tons/yr} = 1.3 \times 10^8 \text{ lb/yr} \\ \text{Maximum} &= 0.12 [1533 + (0.8)(1740)] \text{ tons/day} \times 365 \text{ days/yr} \\ &= 1.3 \times 10^5 \text{ tons/yr} = 2.6 \times 10^8 \text{ lb/yr} \end{aligned}$$

This estimate of 130 to 260 million lb/yr makes photochemical production the largest single source of formaldehyde emissions in the state.

2.2 CONSUMPTION OF FORMALDEHYDE AND ASSOCIATED RELEASES

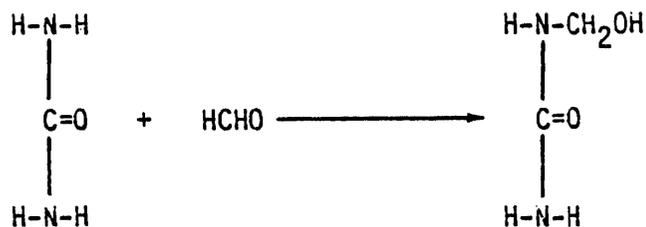
Formaldehyde is used to produce a variety of polymeric resins which find their way into numerous industrial, commercial, and consumer products. Formaldehyde itself can be used in a variety of industrial processes and it is still used in embalming. The resin and other adducts derived from formaldehyde may be chemically unstable under certain conditions, resulting in the reversion to original reactants and thereby causing formaldehyde emissions.

2.2.1 Resin Manufacture

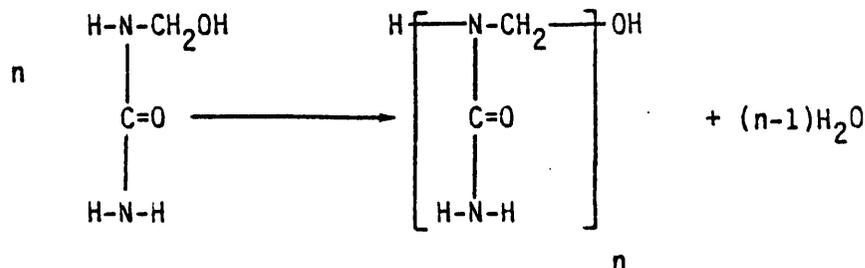
Formaldehyde is used in the formulation of two major classes of synthetic resins. Phenolic resins are formed by the condensation of formaldehyde and phenol, alkyl-substituted phenol, or resorcinol, while urea/melamine resins use urea or melamine as the monomer (Hughes et al., 1978). These resins represent 98 percent of the adhesives produced by the U.S. plastics industry.

Phenolic resins are produced in one or two stages. In the one-stage process, an excess of formaldehyde is added to the phenolic monomer, resulting in a liquid thermosetting resin (Wilkins, 1977). Given the excess of HCHO, VOC emissions from these resins are more likely than for the two-stage resins. The latter are solids at room temperature, and require the addition of HCHO and hexamethylenetetramine ("hexa") and/or heat to become ductile.

Another type of resin is produced by the polymerization of formaldehyde with urea, H_2NCONH_2 , or melamine, $H_2CNCNC(NH_2)NC(NH_2)N$. The reaction proceeds in two steps (NRC, 1981). First, an acid- or base-catalyzed addition of urea (U) and formaldehyde (F) takes place:



The intermediate product formed, which is basically a monomer, undergoes the following condensation reaction to form a thermoplastic resin:



Some additional formaldehyde is necessary to react with unreacted -NH_2 groups and to provide cross-links between polymer chains. As noted by the National Research Council, the amount of HCHO added to the reaction mixture is critical, since:

- An excess of formaldehyde results in faster polymerization, which reduces manufacturing costs;
- Sufficient HCHO is needed to provide adequate cross-linking and to create satisfactory properties in the final product; and
- Unreacted formaldehyde slowly diffuses from the consumer product made from the U-F resin.

Formaldehyde emissions from U-F resin products may also occur when the resin comes into contact with water (or a humid atmosphere); the resulting hydrolysis reaction is essentially the reverse of the reactions shown above (Meyer, 1979).

U-F resin production can be by batch or continuous processes. Often phosphates or triethanolamine are added to neutralize the catalyst after curing. Resins are then modified with various additives to impart desired properties. U-F resins are used commercially as spray-dried solids and as aqueous colloidal dispersions. The dry resins are cheaper to ship and are more stable in storage than the liquid forms, but are more expensive.

The main emission sources in a formaldehyde-based resin plant are the reaction kettles. In some cases, gases are deliberately vented if the pressure becomes too high. Formica (1976) has estimated total hydrocarbon emission from phenol-formaldehyde manufacture to be 7.5 lb/ton of product (uncontrolled) or 0.075 lb/ton (with incineration). In the process described by Formica, 600 lb of HCHO are used to make one ton of resin. The uncontrolled and controlled emission rates are therefore 0.0125 and 0.000125 lb per lb of HCHO input. Hughes et al. (1978) estimate 25 g of uncontrolled VOC emissions from production of 1 kg of urea-formaldehyde resin. From Morrison and Boyd (1973), three moles of HCHO and two moles of urea are required for each mole of UF resin. It can be shown that, for a 100-percent

yield, 1 kg of resin requires about 428 g of HCHO. Hughes et al.'s emission rate is thus equivalent to 0.058 g of HCHO per gram of formaldehyde, or 0.058 lb emissions per lb of HCHO.

Systems Applications, Inc. (1979) surveyed a number of producers of formaldehyde-based chemicals and derived estimates of 0.004, 0.0005, and 0.0005 lb/lb HCHO for process, storage and fugitive emissions, respectively. Total uncontrolled emissions would be 0.005 lb per lb HCHO. The range of literature estimates of uncontrolled formaldehyde emissions is therefore 0.005 to 0.058 lb/lb HCHO, or roughly one order of magnitude.

Capacity and production data for the seven known California producers of formaldehyde-based resins were not listed in the Chemical Economics Handbook (SRI, 1982) or any other source of industry economic information. We therefore conducted a written survey of the plants. Resin producers were asked for information on:

- Nameplate capacity for each type of resin in 1981;
- Production of each type of resin in 1981;
- Net formaldehyde use;
- Type and efficiency of VOC emission control devices, if any;
- Percent of waste streams subject to control, if any; and
- Any emissions measurement data.

Table 2.2-1 shows the results of our survey, to which six of the seven operating plants responded. Except where otherwise noted, emissions are those reported by the companies. In order to preserve confidentiality, we have not included production and capacity data for individual companies. Total formaldehyde use in the state's resin plants in 1981 was 56.96 million pounds. Total emissions are estimated to have been 4.8 kkg (5.4 tons).

2.2.2 Resin Application

Formaldehyde-based resins are used in a large variety of products. Total U.S. consumption of resins for 1980 was 2,735 million pounds (SRI,

Table 2.2-1

CALIFORNIA PRODUCERS OF FORMALDEHYDE-BASED RESINS

Company	Plant Location	County	Resins ^a	Emission Controls	Emission Estimate kkg/yr	Emission Estimate tons/yr
Borden	Fremont	Alameda	U,P	Vent scrubbers	1.5 ^e	1.7 ^e
Cargill	Lynwood	Los Angeles	U,M	NR ^b	NR	NR
Georgia-Pacific	Elk Grove ^c	Sacramento	P	Conservation vents	0.6	0.7
	Richmond ^d	Contra Costa	U,M	-	-	-
	Ukiah	Mendocino	U,P	None	0.8	0.9
United Technologies/Inmont	Anaheim	Orange	P	None	<0.01	<0.01
Monsanto	Santa Clara	Santa Clara	U,P,M	Condensers and packed column liquid contact scrubbers	0.8	0.9
Reichhold	S. San Francisco	San Mateo	U,P,M	Caustic scrubbers	1.1 ^e	1.2 ^e
Totals					4.8	5.4

^a U = urea-formaldehyde, P = phenolic-formaldehyde, M = melamine-formaldehyde.

^b NR = Did not respond to survey.

^c Formerly owned by Union Carbide.

^d Closed in 1982.

^e Estimated by SAI.

1981), which contained an estimated 1,250 million pounds of formaldehyde. Table 2.2-2 lists the 1980 U.S. demands by market segment for various resin-based products, and Table 2.2-3 lists some of the final products containing the various resins. The type and quantity of specific resin use within the state cannot be determined without extensive research. In addition, some reluctance by industry trade groups was encountered in our attempts to ascertain the nature of various processes in which resins were used and the potential for airborne emissions. We have, however, identified the major industries where these resins are used and determined the number of facilities of each type in each California county. (See Tables 2.2-4 and 2.2-5).

2.2.2.1 Wood Products

This is the major use of formaldehyde resins. The adhesive, urea-formaldehyde, is admixed with wood chips and shavings before or during particle board formation. Board products are pressed at 300 to 400 psi at temperatures between 200 and 400°F. Undoubtedly there is some reversion of the resin during use (Zinn, 1982). The production of soft-wood plywood is similar except that the adhesive is primarily phenol-formaldehyde, which, when cured, is not subject to reversion caused by hydrolysis (Erb, 1982). Hardwood-type plywood primarily uses urea-formaldehyde as the adhesive. The majority of U.S. production is used for furniture, and it is estimated that 80 percent of the hardwood plywood used domestically is imported already finished (McDonald, 1982).

2.2.2.2 Cellulosic Products

Resins are used in cotton permanent press fabrics to improve shrink resistance and maintain creases. The mechanism seems to be cross-linking with cellulose. In the paper industry, resins are used to improve wet strength and grease resistance. Grocery bags are one of the products made with formaldehyde resins.

Table 2.2-2

1980 U.S. DEMAND FOR FORMALDEHYDE-BASED RESIN
(Uses in million lb/yr)

Product Group	Type of Resin			Total
	Phenolic	Urea	Melamine	
Molding Compounds	260	52	30	342
Laminates	95		39	134
Abrasives	35			35
Friction Materials	30			30
Insulation	250			250
Foundry	90			90
Plywood	380	80		460
Rubber	40			40
Other Adhesive, non-wood	?			
Coatings	20			20
Adhesive, unspecified wood	100		10	110
Particle Board		700		700
Fiberboard		150		150
*Paper		50	25	75
Textiles		35	12	47
Surfactants		25	50	75
Fiberglass		45		45
Foam		5		5
Other Uses	110	8	9	127
Total	1,410	1,150	175	2,735

Source: SRI, 1982

Table 2.2-3

USES OF FORMALDEHYDE RESINS

Major Product	Melamine	Resin Type Phenolic	Urea
Molding Compounds	Dinnerware Buttons	Housewares Machine parts Wiring insulation Appliances	Closures Electronic equipment Knobs, buttons Toilet seats
Paper Treating	Greaseproof paper Grocery bags Waxed paper		Labels, cartons, Greaseproof paper Grocery bags Sanitary products
Laminates	Counter tops	Furniture	
Adhesive wood	Mobile homes Furniture	Mobile homes Furniture	Mobile homes Furniture

Table 2.2-4
 INDUSTRIES WHERE FORMALDEHYDE AND FORMALDEHYDE-BASED
 RESINS ARE USED

SIC Code	Definition
2261	Finishing plants, cotton
2431	Millwork
2434	Wood kitchen cabinets
2435	Hardwood veneer and plywood
2436	Softwood veneer and plywood
2439	Structural wood members, not elsewhere classified
2451	Mobile homes
2452	Prefabricated wood buildings
2492	Particleboard plants
2499	Wood products manufacturers, NEC
2643	Bag manufacturers, except textile bags
2645	Die-cut paper and board manufacturers
2649	Converted paper and paperboard products manufacturers, NEC
2861	Gum and wood chemical manufacturers
2891	Adhesive and sealants manufacturers

Table 2.2-5

NUMBER OF FACILITIES WHERE FORMALDEHYDE
AND FORMALDEHYDE-BASED RESINS ARE USED,
BY COUNTY AND SIC CODE

County	Standard Industrial Classification Code ^a														
	2261	2431	2434	2435	2436	2439	2451	2452	2492	2499	2643	2645	2649	2861	2891
Alameda		8	16			2				9	3		6		9
Butte		8						1							
Contra Costa										4					1
Del Norte					2				1						
Fresno		9	9			3		2							
Humboldt					2				1						
Kern			8							1					
Lake						1									
Lassen		3													
Los Angeles	6	96	102	8	3	5	11	6		167	26	24	25		48
Madera									1						
Mendocino		2							1	5					
Merced		1	4							2					
Nevada										1					
Orange		33	37			3	4	8		39	5	2	7		10
Placer		6						3		4					
Plumas		2													
Riverside			13			5	18	5		5					
Sacramento		18	24				2	5		6				1	
San Bernardino		4	27	2		8	9			2					
San Diego		15	36			5				14					
San Francisco		15	6							11			2		2
San Joaquin		7					2			3					
San Luis Obispo										3					
San Mateo		3	16												6

Table 2.2-5

NUMBER OF FACILITIES WHERE FORMALDEHYDE
AND FORMALDEHYDE-BASED RESINS ARE USED,
BY COUNTY AND SIC CODE
(Continued)

County	Standard Industrial Classification Code ^a														
	2261	2431	2434	2435	2436	2439	2451	2452	2492	2499	2643	2645	2649	2861	2891
Santa Clara		19	28							9	2		3		
Shasta		7		1	1										
Sierra		4		2											
Siskiyou		4			2										
Sonoma		8			1	2				12					
Stanislaus		8					1								
Sutter		3					2								
Tehama		4			1										
Tulare			7				3				1				
Ventura			3				1				2	1			
Yolo						2	8			1	1				
Yuba		4				1	3								
Totals	6	291	336	13	12	37	64	30	4	298	40	27	43	1	76

Source: County Business Patterns 1979: California (USDOC, 1981).

2.2.2.3 Consumer Products

As was shown in Table 2.2-3, formaldehyde-based resins are used in a variety of products within the consumer sector. As with most of the industrial applications, the resins need to be fairly stable under conditions of use. This is accomplished by cross-linking with other agents to produce a very stable resin. Emissions from these stabilized resins would be expected to be minor. One area of potential consumer exposure is degradation of the resins used in clothing. A preliminary exposure assessment by EPA included reference to exposure in a clothing warehouse (Bryan, 1982), and it may be inferred that consumers might be exposed either in the home or in clothing stores.

2.2.2.4 Other Formaldehyde Uses

As seen in Table 2.2-6, formaldehyde is used in a wide variety of other industrial and consumer products. Emissions from use of these products are believed to be minor compared to those estimated above. Note that formaldehyde has not been used in artificial kidney manufacture in California since 1978 (Gaber, 1983).

2.3 SUMMARY

Table 2.3-1 shows SAI's estimates of statewide atmospheric emissions of formaldehyde. In reviewing these results it should be borne in mind that all estimates are based upon the use of emission factors having significant uncertainty.

Aside from photochemical production, whose quantification is quite problematic, the largest sources of HCHO emissions appear to be automobiles, trucks and buses, oil refineries, electric power plants, and airports.

Table 2.3-2 summarizes the mobile source and industrial emissions of formaldehyde by county and source. Vehicular emissions were apportioned to counties according to the number of autos, motorcycles and trucks registered.

Table 2.2-6

MINOR USES OF FORMALDEHYDE AND FORMALDEHYDE-BASED
FORMULATIONS

Agriculture

1. Treatment of bulbs, seeds and roots to destroy microorganisms.
2. Soil disinfectant.
3. Prevention of rot and infections during crop storage.
4. Treatment of animal feed grains.
5. Chemotherapeutic agent for fish.

Analysis

Small quantities are used in various analytical techniques.

Concrete and Plaster

Formaldehyde is used as an additive agent to concrete to render it impermeable to liquids and grease.

Cosmetics and Deodorants

Formaldehyde is utilized in deodorants, foot antiperspirants and germicidal soaps.

Disinfectants and Fumigants

Formaldehyde is employed to destroy bacteria, fungi, molds and yeasts in houses, barns, chicken coops, hospitals, etc.

Dyes

1. Manufacture of intermediate for production of rosaniline dyes.
2. Preparation of phenyl glycine, an intermediate in the manufacture of indigo dyes.
3. Used to prepare formaldehydesulfoxylates, which are stripping agents.

Embalming

Formaldehyde is used in connection with other embalming agents to preserve and harden animal tissue.

Hydrocarbon Products

1. Prevent bacterial action from destroying drilling fluids or muds.
2. Remove sulfur compounds from hydrocarbons.
3. Stabilize gasoline fuels to prevent gum formation.
4. Modify fuel characteristics of hydrocarbons.

Table 2.2-6

MINOR USES OF FORMALDEHYDE AND FORMALDEHYDE-BASED
FORMULATIONS
(Continued)

Leather

Tanning agent for white washable leathers.

Medicine

1. Treatment of athlete's foot and ring worm.
2. Hexamethylenetetramine is used as a urinary antiseptic.
3. Conversion of toxins to toxoids.
4. Synthesis of Vitamin A.
5. Urea-formaldehyde is used as a mechanical ion exchange resin.

Metals Industries

1. Pickling agent additive to prevent corrosion of metals by H_2S .
2. Preparation of silver mirrors.
3. Hexamethylenetetramine is used to produce nitrilotriacetic acid and formaldehyde to produce ethylenediaminetetracetic acid. These compounds are excellent metal sequestering agents.

Paper

Formaldehyde is used to improve the wet-strength, water shrink, and grease resistance of paper; coated papers and paper products.

Photography

1. Used in film to harden and insolubilize the gelatin and reduce silver salts.
2. Photographic development.

Rubber

1. Prevent putrefaction of latex rubber.
2. Vulcanize and modify natural and synthetic rubber.
3. Hexamethylenetetramine is used as a rubber accelerator.
4. Synthesis of tetraphenylmethylenediamine, a rubber antioxidant.

Solvents and Plasticizers, Surface Active Compound

1. Synthesis of ethylene glycol.
2. Synthesis of formals.
3. Synthesis of methylene derivatives.
4. Synthesis of surface active compounds.

Table 2.2-6

MINOR USES OF FORMALDEHYDE AND FORMALDEHYDE-BASED
FORMULATIONS
(Continued)

Starch

Formaldehyde is used to modify the properties of starch, by formation of acetals and hemiacetals.

Textiles

Modification of natural and synthetic fibers to make them crease, crush and flame resistant and shrink-proof.

Wood

Used as an ingredient in wood preservatives.

Source: Kitchens et al., 1976.

Table 2.3-1

SUMMARY OF SAI ESTIMATES OF ATMOSPHERIC
EMISSIONS OF FORMALDEHYDE IN CALIFORNIA

Source	Estimated Annual Emissions	
	kg	tons
A. <u>Direct Production</u>		
Silver catalyst process	1.7	1.9
B. <u>Indirect Production</u>		
Photooxidation of volatile organic compounds	88,400	97,500 ^a
Automobiles	5,600	6,200 ^b
Trucks and buses	3,900	4,300 ^b
Oil refineries	3,700	4,100
Electric power plants	2,500	2,800
Aircraft operations	1,400	1,500
Fuel oil combustion (except power plants)	630	690
Natural gas combustion (except power plants)	590	650
Motorcycles	340	380
Total Indirect Production	106,060	118,120
C. <u>Consumptive Uses</u>^c		
Formaldehyde-based resins	4.8	5.4
Totals	107,000	118,000

^a Midpoint of low and high estimates. Estimate could vary by \pm 50 percent.

^b Very rough estimate.

^c Emissions from other sources have not been quantified for California, but are believed to be negligible.

Table 2.3-2

MOBILE SOURCE AND INDUSTRIAL FORMALDEHYDE EMISSIONS IN CALIFORNIA BY COUNTY AND SOURCE
(Emissions in tons/yr)

	Vehicular	Aircraft	Oil Refining	Power Generation	Industrial/ Residential Gas/Oil	Chemical and Resin Production	Total
Del Norte	7				1		8
Humboldt	48	4		7	6		65
Mendocino	30				4	1	34
Trinity	4				0		4
Alameda	534	59		13	61	2	667
Contra Costa	346		1,054	259	36		1,695
Marin	124				26		150
Napa	48				5		53
San Francisco	251			65	37		353
San Mateo	348	388			33	1	768
Santa Clara	687	85			73	1	845
Solano	109		159		13		281
Sonoma	148				14		162
Monterey	129	11		210	16		366
San Benito	10				1		11
Santa Cruz	93				11		104
San Luis Obispo	73			128	9		210
Santa Barbara	150	5	15		17		187
Ventura	256		50	533	30		869
Los Angeles	3,498	604	2,353	789	417		7,661
Orange	1,019	57		121	109		1,306
Riverside	305	12			38		355
San Bernardino	397	52		181	51		681
San Diego	883	113		437	106		1,539

Table 2.3-2

MOBILE SOURCE AND INDUSTRIAL FORMALDEHYDE EMISSIONS IN CALIFORNIA BY COUNTY AND SOURCE
 (Emissions in tons/yr)
 (Continued)

	Vehicular	Aircraft	Oil Refining	Power Generation	Industrial/ Residential Gas/Oil	Chemical and Resin Production	Total
Lassen	10				1		11
Modoc	4				0		4
Siskiyou	18				2		20
Butte	67				8		75
Colusa	7				0		7
Glenn	10				1		11
Sacramento	38	61			44	1	143
Shasta	55	9			6		70
Sutter	25				3		28
Tehama	16				2		18
Yolo	51				6		57
Yuba	21				3		24
Fresno	224	23			29		276
Kern	174		417	8	23		623
Kings	27		28		4		59
Madera	26				3		29
Merced	55				7		62
San Joaquin	157	3			19		179
Stanislaus	121				15		136
Tulare	99				14		113
Alpine	0				0		0
Inyo	8				1		9
Mono	4				0		4
Imperial	38			9	5		53

Table 2.3-2

MOBILE SOURCE AND INDUSTRIAL FORMALDEHYDE EMISSIONS IN CALIFORNIA BY COUNTY AND SOURCE
 (Emissions in tons/yr)
 (Continued)

	Vehicular	Aircraft	Oil Refining	Power Generation	Industrial/ Residential Gas/Oil	Chemical and Resin Production	Total
Amador	10				1		11
Calaveras	10				1		11
El Dorado	43				5		48
Mariposa	5				0		5
Nevada	26				3		29
Placer	62				6		68
Plumas	8				1		9
Sierra	1				1		2
Tuolumne	16				2		18
Lake	19				2		21
Totals	10,954	1,487	4,076	2,760	1,340	6	20,609

Aircraft emissions were assigned to counties by airport location; it was assumed that emissions due to takeoffs and landings were generated in the corresponding county. Power plant and oil refinery emissions were assumed to occur in the counties where the facilities were located. County emissions from residential and industrial use of gas and oil were allocated on the basis of population. To a first approximation this value is probably acceptable, although as previously discussed there are some fairly wide differences in residential baseline gas use.

The six counties having the largest mobile source and industrial formaldehyde emissions are Los Angeles (7,661 tons), Contra Costa (1,695 tons), San Diego (1,539 tons), Orange (1,306 tons), Ventura (869 tons) and Santa Clara (845 tons). The South Coast and San Francisco Bay Air Basins account for 48.5 and 24.1 percent of the state's emissions, respectively.

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REVIEW OF PREVIOUS RESEARCH

In order to plan the field sampling programs described later in this report, we reviewed the literature on public exposure to formaldehyde. Since occupational exposures were outside the scope of this study, our review was limited to ambient and indoor exposures.

3.1 AMBIENT FORMALDEHYDE CONCENTRATIONS

3.1.1 Reported Concentrations

Data on the concentration of formaldehyde and other aldehydes in ambient air are quite limited. Total annual aldehyde concentrations in unpolluted air, as summarized by the National Research Council's Committee on Aldehydes (1981a), range from less than 0.2 parts per billion (ppb) to 10 ppb. The upper limit may be an anomaly, since concentrations lower than 10 ppb have been reported for polluted urban air (Cleveland et al., 1977). At the remote locations reported by the NRC, the highest HCHO level was 0.6 ppb (in the Amazon Basin).

According to the NRC review, hourly average total aldehyde concentrations in polluted ambient urban air range from about 10 to 50 ppb during daylight hours. Formaldehyde constitutes 30 to 75 percent of the total. Acetaldehyde and acrolein may be present at about 60 percent and 10 to 15 percent of the formaldehyde concentration, respectively. Concentrations of higher aliphatic aldehydes and aromatic aldehydes are believed to be a small percentage of the total.

Table 3.1-1 summarizes the results of aldehyde measurement programs conducted in Southern California between 1960 and 1982. Although the data are too limited to permit firm conclusions, it appears that carbonyl concentrations have been decreasing since the late 1960s and early 1970s.

3.1.2 Factors Affecting Ambient Aldehyde Concentrations

Ambient aldehyde concentrations have been observed to vary significantly with time of day and day of the week. Figure 3.1-1, for example,

Table 3.1-1

AMBIENT ALDEHYDE CONCENTRATIONS IN SOUTHERN CALIFORNIA, 1960-1982
(All concentrations in ppb)

Location	Dates	Total Aldehydes		Formaldehyde		Acrolein		Ref.
		Range	Average ^a	Range	Average	Range	Average	
Los Angeles	Jul-Nov 1960	10-360	130 + 150	0-130	36 + 27	1-11	8.8 - 10.1	1
Los Angeles	Sep-Nov 1961	5-140	53 + 38	5-150	39 + 25	1-14	10 + 13	2
Huntington Park	Aug-Nov 1968	3-173	44 + 28	4-136	29 + 21	0-8	3.4 + 2.6	3
El Monte	Aug-Nov 1968	12-148	51 + 27	0-90	24 + 18	0-8	1.8 + 2.3	3
Riverside	Jul-Oct 1977			<38				4
Claremont	Oct 1978			<71				5
Claremont	Aug-Sep 1979			4.2-12				7
Claremont	Sep 1979			8.5-38				7
Los Angeles	May-Jun 1980			<40				6
Los Angeles	May-Jun 1980			<71				6
CSULA	Jun 1980			8-53				7
CSULA	Jun 1980			24-59				8
Palos Verdes	Sep 1980			2.3-32				7
Claremont	Sep-Oct 1980			0.3-22.6				7
Claremont	Sep-Oct 1980			<48				6
Los Angeles	Jul-Oct 1980			5-70				6
Azusa	Oct 1980			0.7-35.4				9
Lennox	Oct 1980			0.5-39.6				9
Los Angeles	Nov 1980			2.3-13.4				7

Sources: Reported by National Research Council (1981a) and by Grosjean (1982). References are: 1-Renzetti and Bryant 1961; 2-Altshuller and McPherson, 1963; 3-Scott Research Laboratories, 1969; 4-Tuazon et al., 1980; 5-Tuazon et al., 1981; 6-Grosjean, 1982; 7-Kok, 1983. Additional sources are: 8-Hanst et al., 1982; 9-Grosjean et al., 1983.

^a Mean + standard deviation.

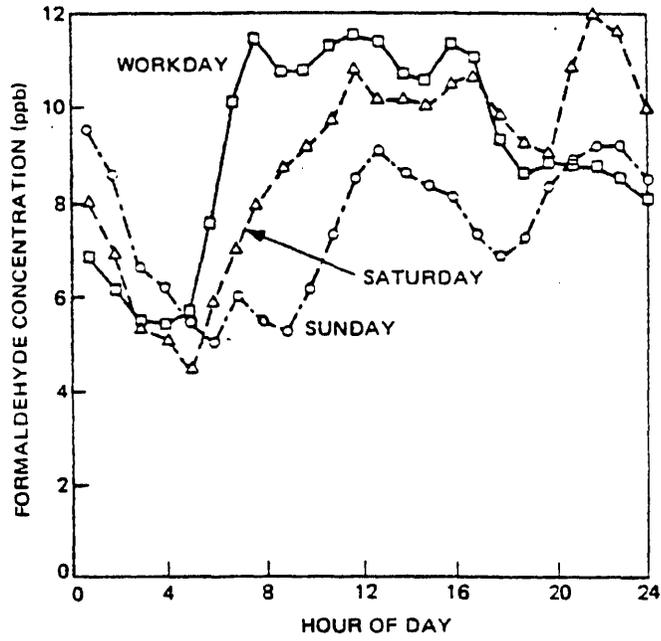


Figure 3,1-1. Average Diurnal Variation of Formaldehyde Concentrations Measured at Newark, NJ for Different Days of the Week, 1972-1974 (Cleveland et al., 1977).

shows the diurnal variation of formaldehyde on workdays, Saturday and Sunday, as averaged for measurements made between 1 June and 31 August in 1972, 1973 and 1974 in Newark, New Jersey. Figure 3.1-2 shows diurnal profiles for ozone (O_3), peroxyacetyl nitrate (PAN) and three carbonyls at Claremont, California in September 1980. In general, ambient formaldehyde concentrations are higher in the daylight hours than at night. Figure 3.1-3 shows average hourly HCHO concentrations over Newark, NJ on days for which the maximum ozone concentration exceeded 100 ppb.

According to the NRC (1981a), atmospheric conditions are responsible at least in part for day-to-day and year-to-year variations in ambient aldehyde levels. Some of the ways by which meteorological factors act are:

- Wind conditions affect dispersion of pollutants;
- Rain, standing water, and moist surfaces serve as sinks for carbonyls;
- The extent of cloud cover and the position of the sun affect light intensity, which alters the rate of photochemical reactions.
- Air temperature affects the rate of chemical processes; and
- Temperature inversions are more frequent in certain seasons.

On the basis of observed temporal variation of concentrations of HCHO and other pollutants, such as that seen in Figures 3.1-2 and 3.1-3, Cleveland et al. (1977) speculate upon a possible relationship among HCHO, carbon monoxide and ozone. Carbon monoxide concentrations can serve as a surrogate for formaldehyde emission patterns, while ozone, which is not emitted to any significant extent by urban sources, can be a surrogate for formaldehyde formation by photochemical processes. According to Cleveland et al., the formaldehyde concentration pattern shown in Figure 3.1-3 appears like a superposition of the O_3 and CO curves. The O_3 peak occurs later than that of formaldehyde, since the ozone is rapidly scavenged by nitric oxide in the morning, while HCHO is unaffected.

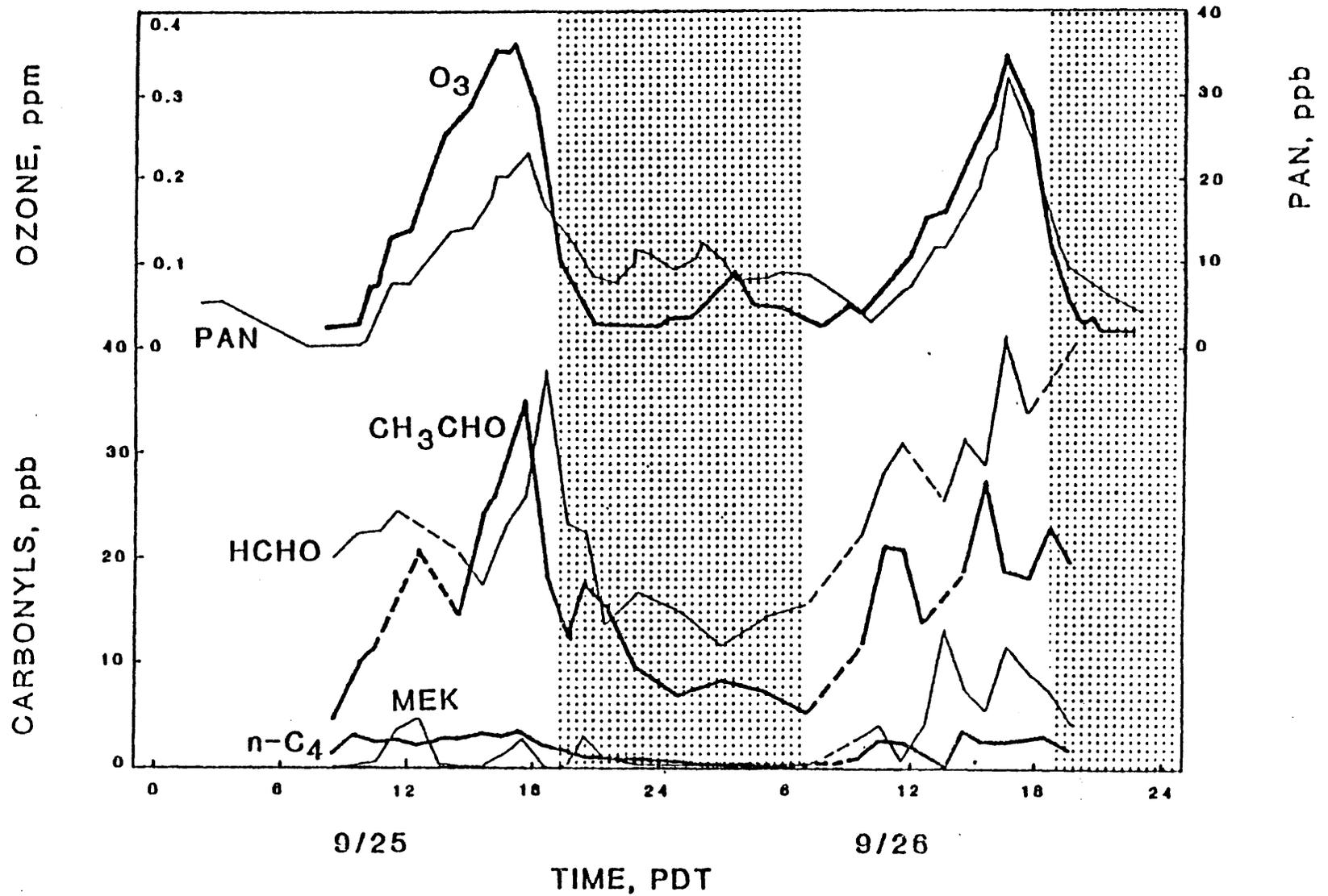


Figure 3.1-2. Diurnal Profiles for Ozone, PAN and Selected Carbonyls, Claremont, CA, 25-26 September 1980 (Grosjean, 1982).

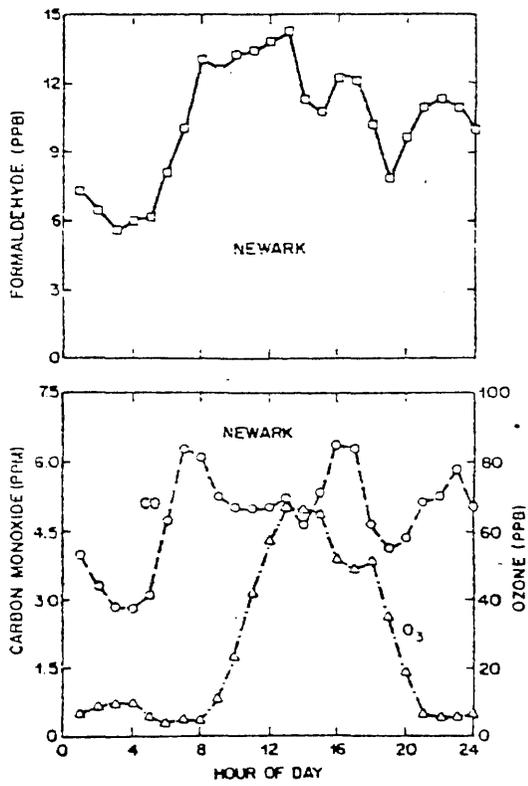


Figure 3.1-3. Average Formaldehyde, Carbon Monoxide (CO) and Ozone (O₃) Concentrations at Newark, NJ on Days for Which Maximum Ozone Exceeded 100 ppb (Cleveland et al., 1977).

In order to test Cleveland et al.,'s informal hypothesis, we conducted a multiple linear regression analysis on their data for Newark, New Jersey. The resulting equation was as follows:

$$\text{HCHO}_t = 2.252 + 1.298 \text{CO}_t + 0.068 \text{Ozone}_{t+3} \quad (3.1-1)$$

where HCHO_t is the formaldehyde concentration (ppb) and CO_t is the carbon monoxide concentration (ppm) at time t and Ozone_{t+3} is the ozone concentration (ppb) three hours after time t . The correlation between dependent and independent variables is fairly high ($r^2 = 0.877$) and the standard error of regression is 1.05 ppb. In Figure 3.1-4 we plot the measured values of HCHO along with concentrations predicted by Equation 3.1-1. The fit is seen to be rather close. The success of this exercise raised the possibility that statistical methods could be used to obtain at least a reasonable approximation of HCHO concentrations from readily obtainable data on hourly CO and O₃ concentrations. The statistical relationship between formaldehyde, ozone and carbon monoxide in California is discussed in Section 7.3.

3.2 INDOOR EXPOSURE TO ALDEHYDES

The objectives of the following review were (1) to obtain a preliminary idea of the extent of public exposure to formaldehyde and other aldehydes in indoor environments, and (2) to help us prescribe limits of detection for the sampling techniques to be used in our field measurement program. In order to compare reported concentrations with the detection limits discussed in Chapter 4, all values will be presented as parts per billion (ppb). Concentrations in $\mu\text{g}/\text{m}^3$ may be obtained by multiplying ppb times 1.227.

3.2.1 Summary of Indoor Exposure Data

Formaldehyde has only recently been measured in non-occupational indoor environments. Table 3.2-1 summarizes the results of research reported during the past four years. Measurements made in northern Europe (chiefly in Denmark) were not included in our table, since the housing construction types and climates to which they apply are quite different from those likely to be found in California.

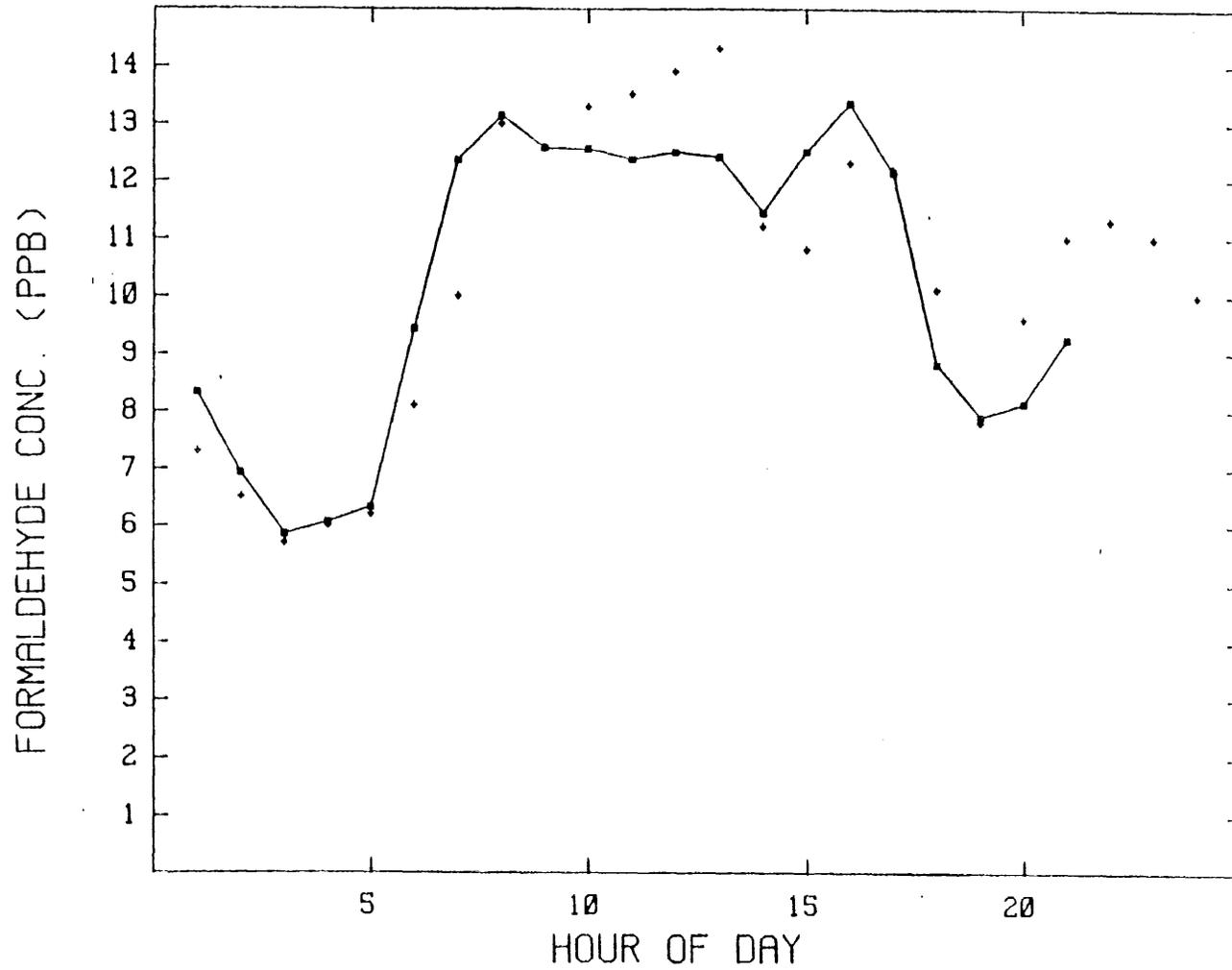


Figure 3.1-4. Measured (+) and Predicted (■) values of Formaldehyde Concentrations Over Newark, NJ. (Measured Values Are From Cleveland et al., 1977.)

Table 3.2-1

SUMMARY OF LITERATURE DATA ON INDOOR FORMALDEHYDE CONCENTRATION
(All concentrations in ppb)

Indoor Environment	Location	No. of Units	HCHO Concentration			Reference ^a
			Range	Mean	Method	
Normal Houses	Pittsburgh, PA	1	? - 500 ^b	150 ^b	MBTH	*Moschandreas et al., 1978
	Various	19	5 - 501	149	MBTH	*Moschandreas et al., 1978
	Wisconsin ^c	27 ^d	1st visit: 2nd visit: 3rd visit:	580 360 300	Chromotropic Acid	Dally et al., 1981
	Indiana	43	30 - 170	60	Chromotropic Acid	Godish, 1981
	Unknown ^e	3	20 - 320		Unknown	Schenker and Weiss, 1981
	Connecticut ^{c,e}	68	400 - 8300		Draeger detector ^g	Sardinas et al., 1979
<u>Energy-Efficient Houses</u>	MD,CA,MN, WI	5	0 - 210	93	Pararosaniline and Chromotropic acid	*Lin et al., 1979
	OR,NJ	3		41	Unknown	Hollowell et al., 1981
	Rochester,NY	10	0 - 64	29	Unknown	Offermann et al., 1981

Table 3.2-1

SUMMARY OF LITERATURE DATA ON INDOOR FORMALDEHYDE CONCENTRATION
(continued)
(All concentrations in ppb)

Indoor Environment	Location	No. of Units	HCHO Concentration		Method	Reference ^a
			Range	Mean		
Mobile Homes	Pittsburgh, PA	2	100 - 800	360	MBTH	*Moschandreas et al., 1978
	Washington ^c	?	0 - 1770	270	Chromotropic acid	*Breyse, 1979
	Minnesota	?	0 - 300	400	Chromotropic acid	*Garry et al., 1980
	Wisconsin	65	20 - 4200	880	Chromotropic acid	NRC, 1981a
	Unknown ^f	?	150 - 200		Unknown	*Fanning, 1979
	Unknown	1	59 - 234		Pararosaniline	*Hollowell et al., 1980
	Wisconsin	137	100 - 2840	460	Chromotropic acid	Hanrahan et al., 1981
	Washington	187		640 ^c	Chromotropic acid	Stone et al., 1981
Public Buildings	Unknown	?	0 - 230 ^b		MBTH	*Lin et al., 1979

- a References marked with an asterisk were cited by NAS, 1981a.
- b Total aliphatic aldehydes.
- c Dwellings whose residents complained of indoor air exposure and/or possible formaldehyde-related symptoms.
- d Includes 10 mobile homes.
- e Homes with urea-formaldehyde foam insulation.
- f Tightly-insulated office trailers.
- g Draeger tube results are accurate to + 30 percent (National Draeger, Inc., 1984). These values were determined by short-term grab sampling and thus do not represent time-weighted exposures.

The concentration ranges shown in Table 3.2-1 are not necessarily representative of those encountered in our survey. Indeed, many of the measurement programs whose results are reported here were conducted in response to complaints about high formaldehyde exposures. Nevertheless, it appears that HCHO concentrations in conventional houses (with or without urea-formaldehyde foam insulation) range from below detectable to about 500 ppb. The finding of Sardinias et al. (1979) of HCHO levels up to 8300 ppb in Connecticut is highly suspect, since the relatively inaccurate Draeger tube method was used. Concentrations in mobile homes range from below detectable to 4,200 ppb; reported mean values are between 270 and 880 ppb. Figure 3.2-1 shows the cumulative distribution of HCHO concentrations in 44 conventional and mobile homes in Wisconsin. The median value was approximately 800 ppb.

Although the emphasis in this section has been on formaldehyde, it should be noted that other carbonyls have been detected in the indoor environment. Although virtually ignored in even recent reviews of indoor pollution (e.g., National Research Council, 1981a, 1981b; and Yocom, 1982), a number of carbonyls appear to be major indoor air pollutants. Samples collected on Chromosorb 102 in 36 Washington and Chicago homes were analyzed by Jarke et al. (1981) using gas chromatography-mass spectrometry. Up to 120 organic contaminants were identified at concentrations ranging from 0.5 to 100 ppb, including the 13 carbonyls listed in Table 3.2-2. Of these, acetone, benzaldehyde, methyl ethyl ketone and acetophenone were among the most abundant pollutants. In a survey of volatile organics in schoolrooms, Johansson (1978) also found acetone to be among the most abundant pollutants, with mean concentrations of about $20 \mu\text{g}/\text{m}^3$. Benzaldehyde was also identified, though at lower levels. These studies, although limited in number and scope, clearly suggest that carbonyls other than formaldehyde should not be ignored when assessing human exposure to indoor pollutants.

3.2.2 Factors Affecting Indoor Formaldehyde Concentrations

It is generally agreed that outdoor formaldehyde concentrations exert little if any direct influence on indoor levels. Indoor concentrations may be expected to correlate with the presence or absence of the following sources:

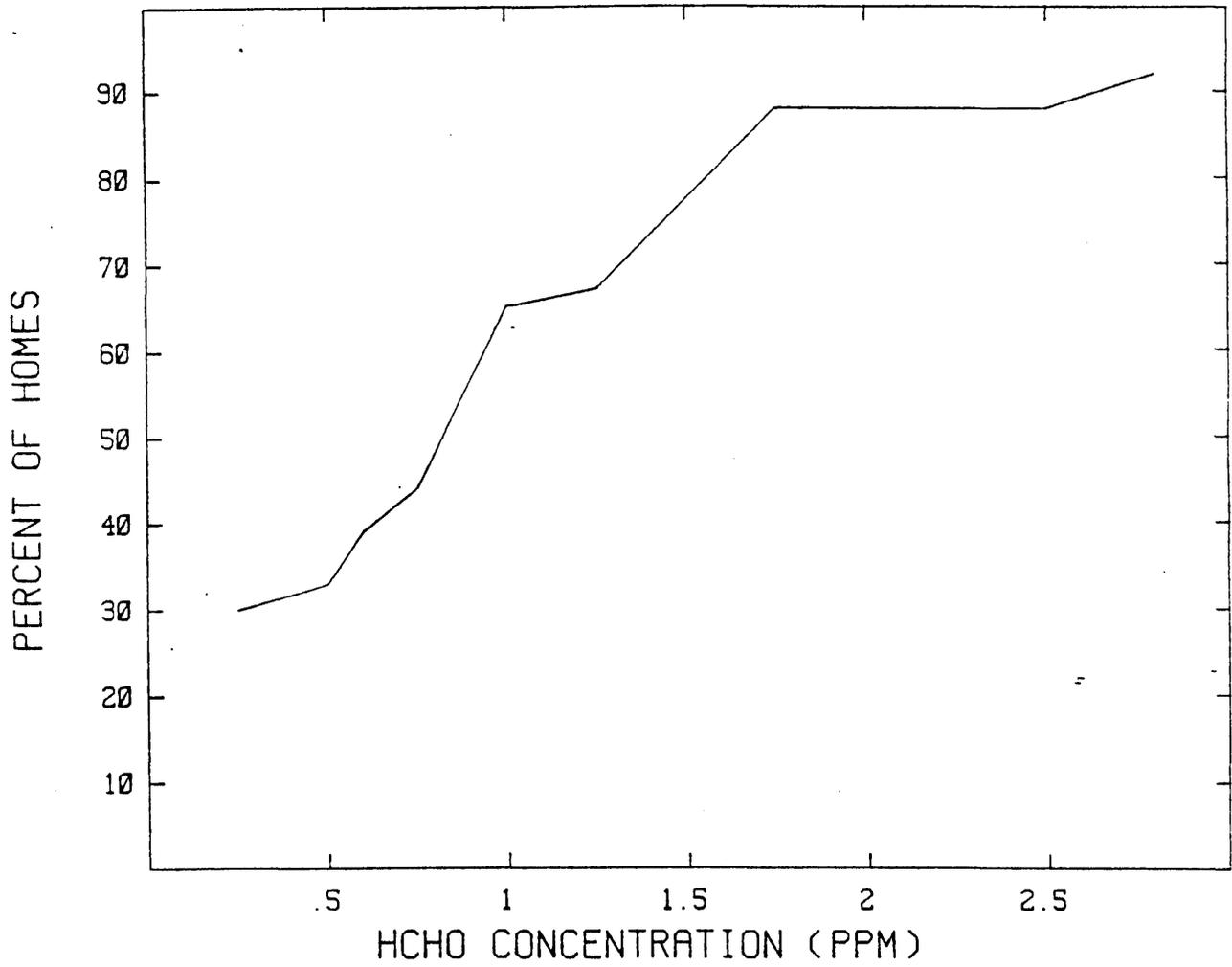


Figure 3.2-1. Cumulative Distribution of Formaldehyde Concentrations in 44 Conventional and Mobile Homes in Wisconsin.

Table 3.2-2

CARBONYL COMPOUNDS^a IDENTIFIED
IN WASHINGTON AND CHICAGO HOMES

Aldehydes	Ketones
Acetaldehyde	Ketone
Propanal	Acetone
Crotonaldehyde	2-Butanone (methyl
Ethyl hexanal	ethyl ketone)
Nonanal	Methyl isobutyl ketone
Decanal	Acetophenone
Benzaldehyde	
Phenyl acetaldehyde	

Source: Jarke et al., 1981

^a Individual concentrations ranged from 0.5 to 100 ppb.

- Urea-formaldehyde foam insulation
- Plywood, panelling and other wood construction elements
- Furniture, carpets and textiles
- Combustion processes such as gas stoves, ovens and unvented space heaters
- Room deodorizers, paper products and other formaldehyde containing consumer products
- Smokers

According to the Consumer Product Safety Commission, homes with urea-formaldehyde foam insulation (UFFI) have an average formaldehyde concentration four times that of homes without UFFI (Gupta et al., 1981). This statement is somewhat simplistic, since the formaldehyde concentration also depends upon several other factors besides the presence of carbonyl generators. One of the most important of these is the age of outgassing sources. It has been established through several measurement programs (e.g. Hadermann and Pendergrass, 1980 and Stone et al., 1981) that the rate of outgassing of formaldehyde from building materials decreases exponentially with time. Another important variable is the infiltration rate, commonly expressed in air changes per hour (ach), which is a measure of the extent to which indoor and outdoor air are exchanged. Most houses in California would be expected to have infiltration rates between about 0.5 and 1.5 ach (NCR, 1981b), although in houses which have been sealed tightly to conserve energy, the rate may be as low as 0.2 ach. The influence of the infiltration rate can be seen in the following equation, which was modified by SAI from versions proposed by Bridge and Corn (1972) and Moschandreas and Stark (1978):

$$C(t) = C_0 e^{-kt} + \frac{C_i Q_i + G}{Q_i + EQ_r + Dv} (1 - e^{-kt}) \quad (3.2-1)$$

where $k = (Q_i + EQ_r + Dv)m/v$
and $C(t) = \text{the concentration in a room } (\mu\text{g}/\text{m}^3) \quad (3.2-2)$
 $C_0 = \text{the initial concentration in the room } (\mu\text{g}/\text{m}^3)$
 $Q_i = \text{the volumetric infiltration rate } (\text{m}^3/\text{min})$

- E = the efficiency of a filtering or absorption device acting on room air
 Q_r = the volume rate of air through the filter (m³/min)
 C_i = the concentration of the pollutant in the outdoor air (μg/m³)
 D = the physical or chemical decay factor for the pollutant (min)⁻¹
 v = the volume of the room (m³)
 t = time (min)
 G = pollutant generation rate (μg/min)
 m = mixing factor (dimensionless)

The decay factor, D, is equal to (ln 2)/t_{1/2}, where t_{1/2} is the half-life of the pollutant. The equation can be simplified by assuming no treatment of room air and complete mixing (i.e., EQ_r = 0 and m = 1).

To see the effect of infiltration rate on equilibrium indoor concentration, we set t equal to infinity in Equation 3.2-1. The equilibrium concentration, C_e, is then:

$$C_e = \frac{C_i Q_i + G}{Q_i + \frac{v \ln 2}{t_{1/2}}} \quad (3.2-3)$$

for the case of complete mixing and no air treatment. In a typical case, C_i = 10 μg/m³, v = 100 m³ and G = 200 μg/min. The half-life of formaldehyde in the atmosphere is about 75 minutes (Calvert et al., 1972), although this value may be different in indoor environments. The remaining variable, Q_i, may be restated as Q_i = Iv, where I is the infiltration rate in air changes per minute. Figure 3.2-2 shows the effect upon equilibrium concentration of varying the infiltration rate. Decreasing the infiltration rate from 1 to 0.2 ach increases the equilibrium HCHO concentration from 95 to 195 ppb. Of course, in a real situation, the infiltration rate (as well as other factors which influence concentration) may vary from hour to hour, so that equilibrium is never actually reached.

Indoor formaldehyde concentrations may depend upon temperature, in that outgassing rates generally increase with increasing temperature. Moschandreas and Rector (1981) found no obvious relationship between HCHO concentration and

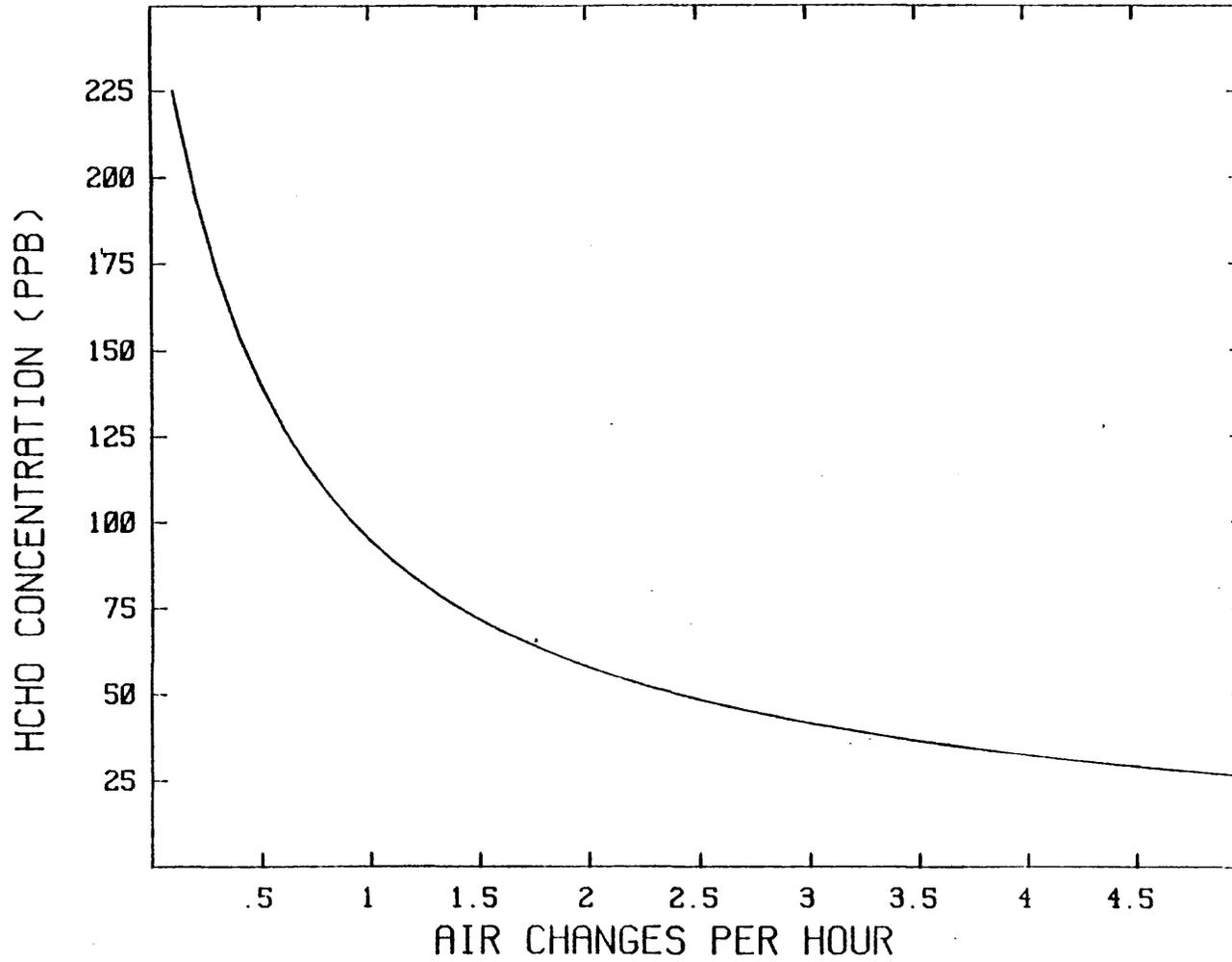


Figure 3.2-2. Effect of Infiltration Rate on Equilibrium Indoor Formaldehyde Concentration, for HCHO Outgassing rate of 0.2 mg/min.

temperature in an energy-efficient house in Maryland. Their results, however, showed that indoor HCHO concentrations increased with relative humidity.

3.2.3 Time Spent in Indoor Environments

In designing a formaldehyde exposure study, it is important to know what percentage of the time people are exposed to different sources of formaldehyde. Table 3.2-3 shows the average number of hours per day spent by employed men, employed women and married housewives in various environments, as determined by a survey of 44 U.S. cities (Szalai, 1982). The category "at one's workplace" could constitute indoor or outdoor time, depending upon the nature of one's occupation. It is clear, however, that the great majority of people's time is spent indoors. The percentage of time spent in the home ranges from 56 for employed men to 87 for married housewives.

Figure 3.2-3 shows the frequency distribution of home-to-work commuting times for employed persons in the U.S. (excluding persons who work at home). The average commuting time is 22 minutes. The "in transit" category in Table 3.2-3 includes this commuting time, plus time spent for other types of travel. Unfortunately, cross-sectional studies such as those for which these data are shown do not show variations with season of the year, age, or geographical location. They do indicate, however, that emphasis upon formaldehyde measurement in homes is justified. In addition, given the very small percentage of time spent outdoors, the contribution of outdoor concentrations to total population formaldehyde exposure may be expected to be negligible, except perhaps in areas near significant point emission sources.

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Table 3.2-3

AVERAGE NUMBER OF HOURS PER DAY SPENT IN VARIOUS
ENVIRONMENTS, 44-CITY STUDY

Location	Employed Men	Employed Women	Housewives
In personal residence	13.4	15.3	20.9
Just outside one's home	0.2	0.0	0.1
At one's workplace	6.7	5.0	0.0
In transit	1.6	1.3	0.9
At other homes	0.5	0.6	0.7
At places of business	0.7	1.1	1.1
In restaurants and bars	0.4	0.2	0.1
In all other locations	0.5	0.3	0.3
<hr/>			
Approximate percentage of times per day spent indoors	97	98	99
<hr/>			
Approximate percentage of time per day spent in residence	56	64	87
<hr/>			

Source: Data from Szalai, 1972.

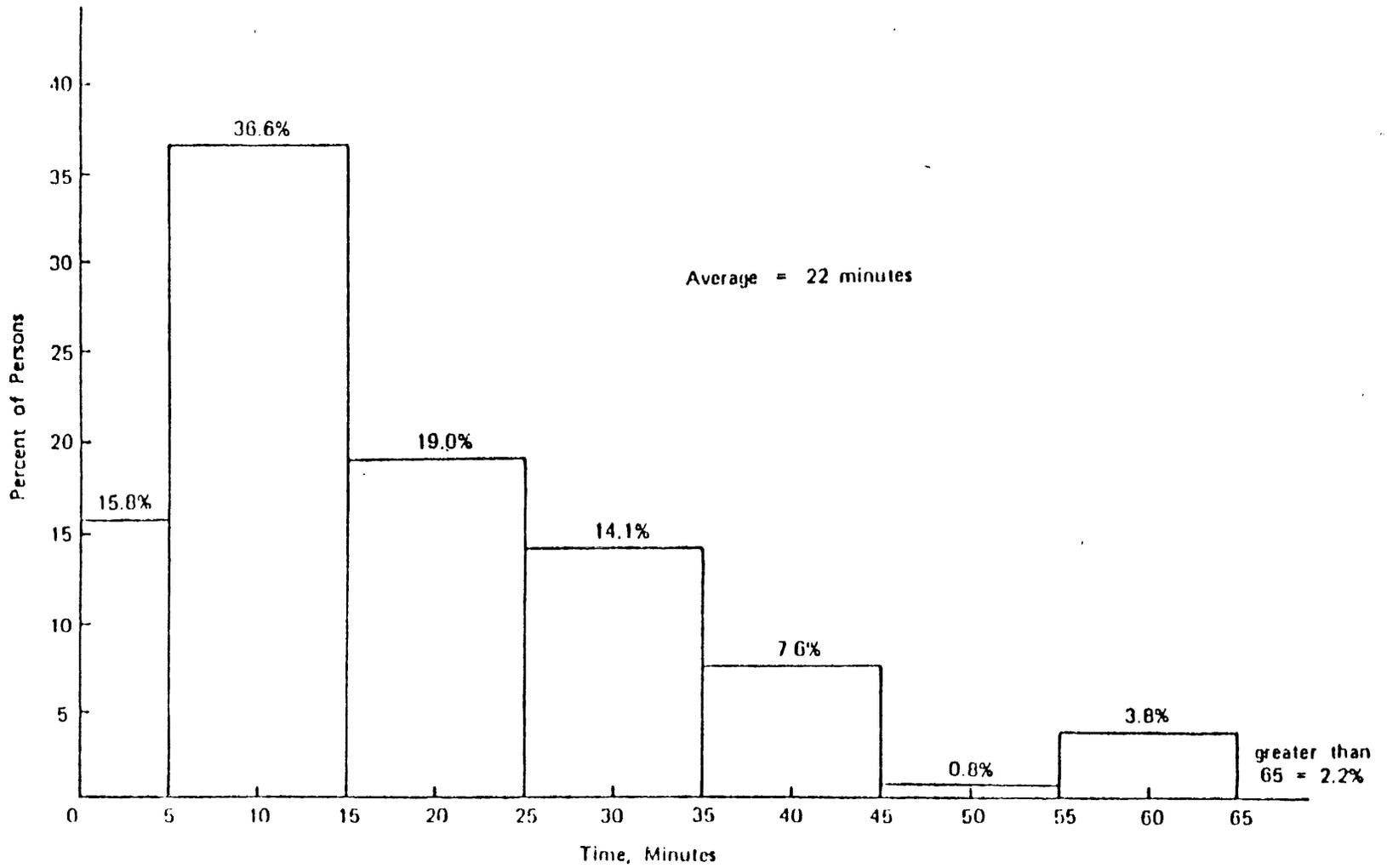


Figure 3.2-3. Frequency Distribution of Home-to-Work Commuting Times for Employed Persons in the United States (NRC, 1981b).

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REVIEW OF FORMALDEHYDE SAMPLING and ANALYTICAL METHODS

4.1 CRITERIA FOR EVALUATING METHODS

Perhaps surprisingly in view of the long-recognized importance of formaldehyde as an atmospheric pollutant, efforts to develop reliable, cost-effective methods for the determination of airborne formaldehyde have been somewhat limited. Methods available up until recently have thus reflected to a large extent the trends in analytical chemistry several decades ago and the corresponding emphasis on colorimetry. The subsequent advent of gas chromatography (GC) as a major analytical tool had little impact on the development of new methods for airborne formaldehyde, since it was soon discovered that formaldehyde is not amenable to direct GC analysis. However, a number of modern methods, including spectroscopy and liquid chromatography, have been successfully applied in the past few years to trace level measurements of formaldehyde and other carbonyls in outdoor air, while a number of passive methods have been proposed for the quantitation of formaldehyde in the indoor environment.

This chapter documents our selection of methods for field sampling. We began by reviewing available sampling and analytical protocols most suited to the project needs in terms of specificity, detection limits, and logistical and budget constraints. The criteria used for method selection included:

Sampling Evaluation Criteria

- Sampling efficiency: the sampling device must retain formaldehyde and be free of breakthrough, evaporation and decomposition problems;
- Sampling specificity: the sampling device must be capable of trapping formaldehyde without interferences from other pollutants such as sulfur dioxide, oxides of nitrogen, etc.;
- Flexibility of sampling operations: temperature and humidity should have no significant effect on sampling efficiency. Flow rate and sampling time should be easily modified for special sampling requirements;

- Simplicity of sampling operations: the sampling protocol should not require lengthy training of the field testing staff and should be easy to implement for all types of applications;
- Logistical simplicity: sampling devices should be small for easy handling, storage, and shipping from and to the analytical laboratory;

Analytical Evaluation Criteria

- Analytical specificity: the method selected must be specific for formaldehyde, i.e., free of interferences from other co-emitted aldehydes and carbonyl compounds;
- Analytical sensitivity: analytical detection limits should be in the nanogram range for quantitation of formaldehyde in ambient air, both indoors and outdoors;
- Flexibility of analytical method: operating conditions should be amenable to rapid modifications in order to address analytical difficulties specific to a given source type (e.g., unknown compound coeluting with formaldehyde, solvent emission interfering with solvent(s) employed for sampling and analysis, etc.);
- Analytical dynamic range: the method should be applicable over several orders of magnitude in formaldehyde concentrations, given the wide range of source strengths expected to be encountered in this program;
- Potential for determination of carbonyls other than formaldehyde: the analytical method should be specific not only for formaldehyde but also for a number of aldehydes and ketones expected to be present in the air matrix to be sampled;
- Cost-effectiveness of sampling and analytical methods: the sampling and analytical approaches should not involve sophisticated, expensive instrumentation whose operation would be prohibitive considering the large number of measurements required for this project; and
- Comprehensive documentation of methods: sampling and analytical protocols, including quality assurance and quality control aspects of the measurement method, should be well documented.

Sections 4.2 and 4.3 describe active and passive methods, respectfully, for sampling and analyzing airborne formaldehyde. Inter-laboratory comparisons of the major methods are discussed in Section 4.4. Alternative methods are then evaluated in Section 4.5 against the criteria presented above. Finally, sampling methods for the field research performed under this contract are provided in Section 4.6.

4.2 ACTIVE SAMPLING AND ANALYTICAL TECHNIQUES

Four categories of active sampling methods are discussed in this section: spectrophotometric (colorimetric) methods, chromatographic methods, spectroscopic methods, and other active sampling methods. Passive sampling methods are covered in Section 4.3. Only the differential ultraviolet absorption method can be considered as a true in-situ method, in which the measurement process does not require any sample handling. A few methods have minimal sampling requirements, such as the long path infrared method, in which only filling of the infrared cell is required, and some of the direct chromatographic methods which only require cryogenic trapping of collected air. However, as discussed later, some of these methods have other severe limitations. All other methods involve "off-line" sampling using impingers, solid and liquid adsorbents, or filters. Finally, only a few spectrophotometric methods have been applied to passive measurements of airborne formaldehyde.

4.2.1 Spectrophotometric Methods

Methods included in this category involve the reaction of formaldehyde with a number of reagents to form colored products (chromophores) and the quantitation of the chromophore on the basis of its known absorbance at specific wavelengths. A list of spectrophotometric methods for formaldehyde is given in Table 4.2-1, along with the corresponding detection limits and major interferences discussed in a recent review by the National Academy of Sciences (1981). Of the methods listed in the table, only the chromotropic acid, pararosaniline and MBTH methods have been investigated in some detail. The chromotropic acid method is recommended by both the National Institute for Occupational Safety and Health (NIOSH) and the Intersociety Committee for Formaldehyde Measurements in Occupational Environments. The method involves sampling with impingers (two in series, each containing 20 ml of water) and subsequent color development ($\lambda_{\max} = 580 \text{ nm}$) with chromotropic acid in the presence of concentrated sulfuric acid.

TABLE 4.2-1

SUMMARY OF SPECTROPHOTOMETRIC METHODS FOR FORMALDEHYDE ANALYSIS IN AMBIENT AIR
(National Academy of Sciences 1981)

Method	Minimal Detectable Concentration		λ_{\max} , nm	Interference
	$\mu\text{g/ml}$	ppm (est.) ^a		
Chromotropic acid	0.25	0.1	580	Nitrogen dioxide, alkenes, acrolein, acetaldehyde, phenol, formaldehyde precursors
	0.1	0.04	580	
Pararosaniline	0.1	0.04	570	Sulfur dioxide, cyanide Virtually specific
	0.1	0.05	560	
Phenylhydrazine	1.1	0.4	520	Color not stable
J-acid (7-amino-4-hydroxy-2-naphthalene-sulfonic acid)	0.3	0.1	468	Formaldehyde precursors
Phenyl-J-acid	0.4	0.13	660	Formaldehyde precursors
p-Phenylenediamine	1.7	0.5	485	Sulfur dioxide, aliphatic aldehydes
Tryptophan	0.15	0.06	575	Virtually specific
MBTH	0.05	0.015	628	Higher aliphatic aldehydes
Purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole)	0.15	0.05	549	Higher aldehydes
Acetylacetone	1.4	0.5	412	Specific (?)

^aBased on sampling at 1 slpm for 1 h into 25 ml of impinger solution and recording a difference of 0.05 absorbance unit between blank and sample.

The pararosaniline method, first developed by Lyles et al. (1965) on the basis of the classical Schiff test for aldehydes, involves sampling in water impingers and color development ($\lambda_{\max} = 560 \text{ nm}$) with a mixture of two reagents, pararosaniline + concentrated hydrochloric acid and tetrachloromercurate - sodium sulfite. One commercially available analyzer (CEA Instruments, Inc. Model 555) employs the pararosaniline method for "continuous" monitoring of formaldehyde in occupational air. Matthews (1982) modified the CEA instrument, obtained an improved detection limit of 10 ppb, and applied the modified instrument to measurements of formaldehyde in indoor air. Miksch et al. (1981) recently proposed a modified version of the pararosaniline method (mercury salt deleted). Ozone (200 ppb) and sulfur dioxide (200 ppb) added to the matrix air did not interfere with the formaldehyde measurements.

Good agreement was found between the chromotropic acid and modified pararosaniline methods in the number of formaldehyde measurements in indoor air. Matthews (1982) also found good agreement between the automated pararosaniline method (modified CEA analyzer) and the modified pararosaniline method of Miksch et al. (1981), assuming in the latter case a water impinger formaldehyde trapping efficiency of 92 percent.

The MBTH method, by far the most commonly employed method for the determination of "total aliphatic" aldehydes in air, is not specific for formaldehyde and will not be discussed further in this review.

Improved detection limits can generally be achieved by using fluorescent derivatives of formaldehyde. Two of the reagents already listed in Table 4.2-1, acetylacetone (Nash method) and J-acid, have been employed for spectrofluorometric measurements, along with 1,3-cyclohexanedione and its 5,5-dimethyl homolog. The corresponding emission and detection wavelengths, detection limits and interferences are listed in Table 4.2-2 (National Academy of Sciences, 1981). More recently, Suzuki and Imai (1982) proposed a fluorometric method for acrolein involving sampling on 13X molecular sieves and o-aminobiphenyl as the fluorescent reagent. Fluorescence intensities were also investigated for four other fluorescent reagents and twelve carbonyls

TABLE 4.2-2

SUMMARY OF SPECTROFLUOROMETRIC METHODS OF ANALYSIS FOR FORMALDEHYDE
(National Academy of Science 1981)

Method	Minimal Detectable Concentration		λ excitation, nm	λ emission, nm	Interferences
	$\mu\text{g/ml}$	ppm^a			
1,3-Cyclohexanedione	0.2	0.07	395	460	Higher aldehydes
Dimedone (5,5-dimethyl-cyclohexanedione-1,3)	0.08	0.03	470	520	Higher aldehydes
J-acid (7-amino-4-hydroxy-2-naphthalene-sulfonic acid)	0.6	0.1	470	520	Aldehyde precursors, acrolein
J-acid	0.05	0.02	470	520	Aldehyde precursors, acrolein
Acetylacetone	1.2	0.4	410	510	Specific (?)
Acetylacetone	0.005	0.002	410	510	Specific (?)

^aBased on sampling at 1 slpm for 1 h into 25 ml of impinger solution and recording a difference of 0.05 absorbance unit between blank and sample.

including formaldehyde. In view of the good collection efficiency obtained by other investigators for formaldehyde on 13X molecular sieves (see later discussion), the method developed by Suzuki and Imai (1982) for acrolein appears applicable to formaldehyde as well.

4.2.2 Chromatographic Methods

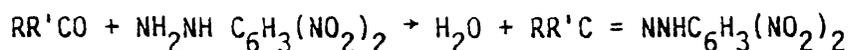
These methods can be divided into two categories: (1) direct chromatography analysis after sample concentration and (2) chromatographic analysis of the derivatives formed upon reaction of formaldehyde with selected reagents during sampling. The few direct chromatography methods all involve gas chromatography (GC), with no liquid chromatography (LC) method reported to date. In contrast, numerous LC methods, as well as GC methods, have been reported for the quantitation of formaldehyde after derivatization.

4.2.2.1 Direct Gas Chromatography Methods

For a number of years, direct GC analysis has been performed for aldehydes and ketones at the high concentrations typical of automobile exhaust (e.g., Hughes and Hurn, 1960; Seizinger and Dimitriades, 1972) and of laboratory studies of hydrocarbon photochemistry (e.g., Kerr and Sheppard, 1981). At the parts per billion (ppb) level required for ambient and indoor measurements, only three studies have reported direct GC analysis of formaldehyde, acetaldehyde and acrolein, respectively. Hoshika (1977) employed cryogenic concentration on tris-(2-cyanoethoxy)propane at liquid oxygen temperature and reported ~1.5-10 ppb of acetaldehyde in Magoya, Japan. Gold et al. (1978) employed 13X molecular sieves for sampling of acrolein in air, and suggested that their method was applicable to other aldehydes as well. Indeed, Yokouchi et al. (1979) also employed 13X molecular sieves for sampling of formaldehyde followed by GC separation on a Porapak T glass column and quantitation using a mass spectrometer as the detector with ion monitoring of the fragments $m/e = 29$ and $m/e = 30$. Using this method, Yokouchi and coworkers reported ~10 ppb of formaldehyde in two hour samples collected in Tsukuba, Japan.

4.2.2.2 Chromatography Methods Involving 2,4-Dinitrophenylhydrazine (DNPH) Derivatization

Of the several derivatives readily obtained by nucleophilic addition on the carbonyl bond of aldehydes and ketones, 2,3-dinitrophenylhydrazones have received much attention for both gas and liquid chromatography assay of trace levels of these compounds including formaldehyde. The coupling reaction involves the reagent 2,4-dinitrophenylhydrazine (DNPH) added to the carbonyl containing compound.



Because DNPH is a weak nucleophile, the coupling reaction is carried out in the presence of acid, which promotes the protonation of the carbonyl. DNPH derivatives have been prepared for a large number of carbonyls including formaldehyde, aliphatic aldehydes and ketones (e.g., acetaldehyde, acetone), unsaturated aliphatic carbonyls (e.g., acrolein), aromatic carbonyls (e.g., benzaldehyde, acetophenone), keto acids (e.g., pyruvic acid), and polyfunctional carbonyls (Shriner et al., 1956; Papa and Turner, 1972a, 1972b; Fung and Grosjean, 1981).

A list of studies involving the quantitation of formaldehyde and other carbonyls as 2,4-dinitrophenylhydrazones is given in Table 4.2-3 according to analytical method, sampling device, and type of environmental application. Although this list is limited to applications relevant to this project. (i.e., ambient air, engine exhaust, smog chamber studies and indoor pollutants), the DNPH method has been applied to a number of other trace level measurements of carbonyls such as carbonyl impurities in alcohols (e.g., Demko, 1979) and hydrocarbons (e.g., Scoggins, 1973), and keto acids in biochemical samples (e.g., Ariga 1972; Katzuki et al., 1971, 1972). Early environmental applications of the DNPH method focused on gas chromatographic analysis of engine exhaust (e.g., Fracchia et al., 1967; Bureau of Mines, 1971) using a flame ionization detector (FID). More recently, lower detection limits have been obtained with electron capture detection (ECD) using packed columns (Andersson et al., 1979; Neietzert and Seiler, 1981), or capillary columns (Johnson et al., 1981).

TABLE 4.2-3

CHROMATOGRAPHY METHODS INVOLVING
2,4-DINITROPHENYLHYDRAZONES

<u>Reference</u>	<u>Sampling Method</u>	<u>Analytical and Detection Methods*</u>	<u>Application</u>
Fracchia et al. (1967)	Impinger	GC-FID	Auto exhaust
Bureau of Mines (1969)	Impinger	GC-FID	Auto exhaust
Smythe and Karasek (1973)	Impinger	GC-FID	Diesel exhaust
Dietzmann (1979)	Impinger	GC-FID	Engine exhaust
Andersson et al. (1979)	XAD-2	GC-ECD	Urban air
Neitzert and Seiler (1981)	Cryogenic	GC-ECD	Troposphere
Johnson et al. (1981)	Impinger	GC-ECD	Urban air, engine exhaust
	Impinger	HPLC-UV (360 nm)	Urban air, engine exhaust
Mansfield et al. (1977)	Impinger	HPLC-UV (254)	Tobacco smoke
Kuwata et al. (1979)	Impinger	HPLC-UV (254)	Exhaust, urban air
Kuntz et al. (1980)	Impinger	HPLC-UV (254, 360)	Ambient air
Beasley et al. (1980)	Silica gel	HPLC-UV (340)	Ambient air
Fung and Grosjean (1981)	Impinger	HPLC-UV (360)	Ambient air, smog chamber
Lowe et al. (1981)	Rotating flask	HPLC-UV (254)	Troposphere
Grosjean and Fung (1982)	Glass beads	HPLC-UV (360)	Ambient air
Grosjean (1982)	Impinger	HPLC-UV (360)	Urban air (gas phase)
	Filter	HPLC-UV (360)	Urban air (part- iculate phase)
Creech et al. (1982)	Impinger	HPLC-UV (340)	Diesel exhaust

*GC = Gas chromatography with flame ionization (FID) or electron capture (ECD) detector; HPLC-UV = high performance liquid chromatography with ultraviolet detection, wavelength indicated in parentheses.

Because of the poor thermal stability of DNPH derivatives under most GC conditions (Papa and Turner, 1971a), more recent work has focused on high performance liquid chromatography (HPLC) with ultraviolet detection (Papa and Turner, 1971b; Kuwata et al., 1979; Fung and Grosjean, 1981). As seen in Table 4.2-4, detection limits of a few nanograms of the DNPH derivatives of interest are now routinely achieved with HPLC methods. Sampling in most cases involves liquid DNPH reagent in small impingers, and the impinger collection efficiency has been investigated in detail over a wide range of sampling conditions (Grosjean and Fung, 1982). Several investigators have also reported good collection efficiencies with DNPH impregnated on solid supports such as glass beads (Fung and Grosjean, 1981; Grosjean and Fung, 1982), silica gel (Beasley et al., 1980) and Amberlite XAD-2 (Andersson et al., 1982).

New developments and applications of the DNPH method have been published recently. Sampling concentration by cryogenic trapping (Neitzert and Seiler, 1981) and by use of liquid DNPH reagent in rotating flasks (Lowe et al., 1981) have been described. Jacobs and Kissinger (1982) applied an electrochemical detector to the quantitation of carbonyl DNPH derivatives separated by liquid chromatography, and reported better sensitivity than that of the conventional ultraviolet detector. No environmental applications were described. Grosjean (1982) applied the DNPH method to ambient particulate matter collected on Teflon filters, and reported on the particulate phase concentration of selected carbonyls in Los Angeles air.

4.2.2.3 Chromatographic Methods Involving Derivatives Other Than DNPH

These methods can be divided in two groups, one involving GC analysis of carbonyl-sodium bisulfite adducts, and the other involving GC and HPLC analysis of derivatives prepared by reaction of carbonyls with nucleophiles such as substituted amines. A list of these methods is given in Table 4.2-5.

The bisulfite method (Levaggi and Felstein, 1970) involves collection with impingers containing one percent aqueous sodium bisulfite solution, and subsequent GC-FID analysis of the C₂-C₅ aliphatic aldehydes.

TABLE 4.2-4

ANALYTICAL DETECTION LIMITS FOR THE DNPH-HPLC METHOD
(Fung and Grosjean 1981)

<u>Carbonyl</u>	<u>Lowest Quantifiable Limit, Nanograms (a)</u>	<u>Equivalent Detection Limit in Ambient Air, $\mu\text{g m}^{-3}$ (b)</u>
Formaldehyde	1.1	$1.8 \cdot 10^{-2}$
Acetaldehyde	2.0	$3.3 \cdot 10^{-2}$
Propanal	2.3	$3.8 \cdot 10^{-2}$
n-Butanal	5.0	$8.3 \cdot 10^{-2}$
3-Methylbutanal	3.2	$5.4 \cdot 10^{-2}$
Benzaldehyde	5.9	$9.8 \cdot 10^{-2}$
2-Butanone	3.3	$5.5 \cdot 10^{-2}$
Cyclohexanone	3.7	$6.2 \cdot 10^{-2}$
5-Hydroxy-2-pentanone	5.7	$9.5 \cdot 10^{-2}$

(a) At an integrator-microprocessor signal/noise ratio of 4.

(b) On the basis of a 60 liter sample (e.g., sample collected for one hour at a flow rate of 1 liter/min).

TABLE 4.2-5

CHROMATOGRAPHIC METHODS INVOLVING DERIVATIVES
OTHER THAN DNPH

<u>Reference</u>	<u>Reagent</u>	<u>Derivative</u>	<u>Sampling Device</u>	<u>Analytical Method</u>	<u>Application</u>
Levaggi and Feldstein (1970)	Sodium bisulfite	Bisulfite adduct	Impinger	GC-FID	Exhaust, ambient air
Bureau of Mines (1970)	Hydroxylamine	Oxime	Impinger	GC-FID	Exhaust
Levine et al. (1981)	Benzyl oxyamine	o-Benzyl oxime	Impinger	GC-MS	Exhaust
Nambara et al. (1975) Koshy et al. (1975)	Pentafluoro- benzyloxyamine	o-Pentafluoro Benzyloxime	--	GC-ECD	--
Kobayashi et al. (1979)	Pentafluoro- phenylhydrazine	Pentafluoro- phenyl hydrazone	--	GC-FID, GC-ECD	--
Kennedy and Hill (1982)	N-Benzyl- ethanolamine	3-Benzyl- oxazolidine	Chromosorb 102	GC-FID	Ambient air
Moree-Testa and Saint-Jalm (1981)	o-Phenylene diamine	Quinoxaline	--	GC-MS, HPLC-UV	--
Johnson et al. (1981)	1-Dimethylamino naphthalene- 5-sulfonyl hydra- zine (dansyl hydrazine)	Dansyl hydrazone	Impinger	HPLC-fluor- escence	Exhaust, ambient air

Formaldehyde is not amenable to analysis using this method, but can be quantitated from the same bisulfite solution using the chromotropic acid method described earlier in this section. Although adopted by the American Public Health Association Intersociety Committee (1972), the bisulfite method has been employed by only a few investigators, including Ellis et al. (1965) for a qualitative study of oxygenates in engine exhaust and the Radian Corporation (1978) for ambient measurements in the Houston area. In the latter study, no data could be obtained due to a poor detection limit (about 15 ppb for each carbonyl).

Hydroxylamine derivatives (oximes) have been employed in engine exhaust studies using gas chromatography (Bureau of Mines 1970; Levine et al., 1981). Quinoxalines are amenable to both GC and HPLC analysis (Moree-Testa and Saint Jalm, 1981), but have not been applied to environmental measurements. Pentafluoro derivatives of both oximes (Nambara et al., 1975; Koshy et al., 1975) and hydrazones (Kobayashi et al., 1979) can be detected at the picogram level using electron capture GC, but again there has been no environmental application of these derivatives. Johnson et al. (1981) employed dansylhydrazine as the sampling reagent, and quantitated the resulting dansylhydrazones by HPLC with fluorescence detection. The results compared favorably with those obtained by HPLC analysis of DNPH derivatives. Kennedy and Hill (1982) sampled formaldehyde in air with N-benzylethanolamine on a solid sorbent, Chromosorb 102, and quantitated the corresponding formaldehyde 3-benzylloxazolidine by GC-FID. The detection limit was 6.6 µg as formaldehyde, suitable for occupational exposure studies but too high for most ambient or indoor air measurements.

4.2.3 Spectroscopic

In principle, most spectroscopic methods are suitable for formaldehyde measurements, but suffer from lack of sensitivity and prohibitive cost for field applications. A fluorescence method based on laser excitation of formaldehyde has been reported (Becker et al., 1975) with a detection limit of 50 ppb. Microwave spectroscopy has been applied for formaldehyde measurements at levels as low as 10 ppb after sample concentration (Hrubesch 1973).

Infrared spectroscopy, using sophisticated optics, long optical path (~1 kilometer), and Fourier-transform spectrometry, has been applied to ambient air measurements of a number of important pollutants (Hanst 1971; Hanst et al., 1973, 1982) including formaldehyde, for which a detection limit of ~6 ppb has been achieved with a 1 kilometer path instrument (Tuazon et al., 1980). Detection limits for other carbonyls are too high for ambient air measurements. Calibration problems may lead to large uncertainties. For example, a factor of about 1.6 was needed (Tuazon et al., 1980) to correct previously published formaldehyde data (Tuazon et al. 1978).

A method involving differential optical absorption in the near ultraviolet has been recently developed by Perner and Platt (1979) for ambient measurements of a number of trace species including formaldehyde. The measurements are conducted in situ, with typical light paths of several kilometers. The stated detection limit for formaldehyde is 0.1 ppb with 5 kilometer light path (Platt and Perner, 1980).

4.2.4 Other Active Sampling Methods

Several electrochemical methods (polarography, amperometry) are briefly described in the National Academy of Sciences (1981) review. Atomic absorption can also be employed to measure reduced silver following oxidation of aldehydes to carboxylic acids using Tollen's reagent (Oles and Siggia 1974). These methods have not been applied to atmospheric measurements.

An ion chromatographic method involving oxidation, by hydrogen peroxide, of formaldehyde and acetaldehyde to formate and acetate, respectively, has been recently described (Kim et al., 1980; Lorrain et al., 1981). The first study involved sampling of formaldehyde on charcoal impregnated with a "proprietary oxidant," ultrasonication of the charcoal with 0.1 percent H_2O_2 , and quantitation of formate by ion chromatography (Dionex, 1979; Kim et al., 1980). The second study (Lorrain et al., 1981) involved sampling with an alkaline H_2O_2 solution in an impinger, and ion chromatography separation of formate and acetate. Field tests were limited to source samples (boiler) with a stated detection limit of 90 ppb for formaldehyde.

Slawinska and Slawinski (1975) have described a flow system in which formaldehyde and gallic acid oxidized with alkaline hydrogen peroxide produce strong chemiluminescence in the spectral range 560-850 nm. The corresponding detection limit for formaldehyde in aqueous samples was about 1 $\mu\text{g/L}$. Kok (1981) extended the method to formaldehyde in air by sampling with water impingers and performed ambient measurement in the Los Angeles atmosphere as part of an interlaboratory comparison study involving the chromotropic acid, chemiluminescence, and DNPH-HPLC methods. Results of this and other interlaboratory studies are discussed later in this section.

4.3 PASSIVE SAMPLING METHODS

4.3.1 Passive Sampling of Formaldehyde

Passive sampling devices have been employed for a number of years for determining personal exposure to hazardous chemicals (Palmer et al., 1976). Thus, passive diffusion and permeation devices are available for monitoring personal exposure to chlorine, sulfur dioxide, vinyl chloride, benzene, ammonia, hydrogen sulfide and hydrogen cyanide (West, 1980). Passive dosimeters may employ solid sorbents as the collection medium (e.g., charcoal, Porapak N, Chromosorb 102), thus allowing for GC analysis of a number of organic vapors such as benzene, toluene, vinyl acetate, etc., from a single passive sample (Orofino and Usmani, 1980).

The use of passive samplers, although increasingly popular for personal, workplace and residential monitoring, has been limited in the specific case of formaldehyde. Nichols (1978) used plastic film impregnated with 3-methyl-2-benzothiazolonehydrazine (MBTH), a reagent widely employed for the determination of "total aliphatic" aldehydes in air. Geisling (1981) and Geisling et al. (1981) described a passive monitor developed at Lawrence Berkeley Laboratory and based on chromotropic acid analysis of formaldehyde collected on a filter placed in a glass tube and impregnated with sodium bisulfite. Laboratory tests indicated good collection efficiency ($100 \pm 5\%$) and a detection limit of 100 ppb for a possible sampling period of 100 hours. Difficulties were noted in the preparation of impregnated filters, and recommendations were made to validate the method in the field and to study potential interferences. Reagents other than sodium bisulfite were

investigated, and good trapping efficiencies were reported for filters impregnated with methoxyamine hydrochloride and p-nitrophenyl hydrazine, but these studies were not pursued.

The LBL passive sampler was further characterized in a recent report by Hodgson et al. (1982). For a passive sampling time of one week (the device has not yet been validated for shorter sampling times), the sampler is suitable to determine formaldehyde in the range 0.018 to 1.0 ppm. Due to rapidly decreasing collection efficiencies above 60 percent humidity, sampling at high ambient humidities is not recommended. Interferences inherent in the chromotropic acid analytical method were studied. No interference was found from acrolein spiked on filters at acrolein:formaldehyde concentration ratios of up to 10. The passive method was compared to the active sampling (impinger-pararosaniline) method also employed at LBL (Miksch et al., 1981). With the bubbler trapping efficiency for formaldehyde assumed to be 95 percent, the results showed a systematic difference: formaldehyde concentrations reported using active sampling were 87 percent of those measured using the passive method. The causes for the observed discrepancy between the two methods results are being investigated.

The commercially available 3M Company passive formaldehyde monitor (Badge #3750) also entails collection of formaldehyde using sodium bisulfite-impinger paper followed by chromotropic acid analysis. The device has been characterized with respect to sampling efficiency, sensitivity, and range of applicability (Rodriguez et al. 1981). Potential interferences tested included ethanol, a major indoor pollutant, and phenol, a known interferent in the chromotropic acid method. The stated lowest quantifiable limit (LQL) of the 3M badge is somewhat below that of the LBL filter, 0.8 ppm-hr vs 1.8 ppm-hr (e.g., 8 ppb vs 18 ppb for a one week sample of 100 hours). The 3M badge has been employed for sampling periods of less than one week and as short as a few hours, with a stated LQL of, for example, 0.2 ppm for a four-hour sample. An interesting aspect of the 3M study (Rodriguez et al. 1981) is the investigation of the sampler collection efficiency as a function of air velocity. A sharp drop was observed at face velocities lower than 20 feet/minute. Since air circulation in dwellings is typically in the range of 10 to 30 feet/minute, passive sampling may lead to a serious underestimate of formaldehyde levels in stagnant indoor air.

The DuPont Type C-60 formaldehyde badge (DuPont 1982) is also a passive sampler using aqueous sodium bisulfite and quantification by the chromotropic acid method. Sampling is controlled by diffusion through a multicavity diffuser. The stated detection limit is 2 ppm-hr, and the device has been tested in the range of 2 to 54 ppm-hr. Validation studies conducted with the device included studies of sampling efficiency as a function of temperature and humidity, stability before and after sampling, and response linearity vs concentration. Good agreement was obtained between the passive badge and two active sampling devices, a bisulfite impinger and a silica gel tube, when sampling test and occupational atmospheres. Interferences from ethanol, butanol, toluene and phenol were minimized by use of a proprietary additive to the bisulfite solution. Attempts were made to develop a badge involving bisulfite impregnated on solid substrates including silica gel, glass fiber filter (e.g., LBL method) and filter paper (e.g., the 3M Company method). A number of difficulties were noted, but not documented, including low collection efficiency and poor stability. For these reasons, the solid support approach was not investigated further and the liquid badge was developed instead.

Hawthorne and Matthews (1981) employed a permeation device consisting of a dimethyl silicone membrane through which formaldehyde permeates at a constant rate. Formaldehyde is then collected either in water or on molecular sieves, and quantitated using either the pararosaniline or MBTH methods. The LQL's were 50 ppb (MBTH) and 100 ppb (pararosaniline) for a ten-hour sample. Although the device has not been fully characterized, problems were noted with both the stability of formaldehyde in water and the decreasing capacity of the molecular sieves to collect formaldehyde due to saturation with ambient water vapor. No interference studies were reported.

4.4 INTERLABORATORY COMPARISON OF FORMALDEHYDE METHODS

To our knowledge, no comprehensive interlaboratory comparison study of formaldehyde measurement methods, either outdoors or indoors, has been reported in the peer-reviewed literature. ERT researchers have recently been involved in two interlaboratory comparison studies. The scope and results of these studies are briefly summarized below.

The first study was conducted at EPA's Research Triangle Park, NC laboratories and involved participants from laboratories associated with EPA, Northrop Services, Harvey Mudd College, and ERT. The methods compared included infrared spectroscopy, chemiluminescence and DNPH-HPLC. A few samples were also collected and analyzed by the chromotropic acid, pararosaniline and MBTH methods. Known amounts of formaldehyde, alone or together with other carbonyls, were introduced in a smog chamber where the infrared measurements were carried out. All other participants collected samples from the chamber through a ten-fold dilution sampling manifold. The study also involved acetaldehyde, benzaldehyde and methyl ethyl ketone (MEK) measurements in carbonyl mixtures, in irradiated hydrocarbon-NO₂ and hydrocarbon-HONO mixtures, and in smog chamber runs involving the dark reaction of ozone with olefins. The smog chamber matrix was either dry (<1 percent relative humidity or humid (50 percent relative humidity). No ambient samples were collected.

Samples analyzed using the DNPH-HPLC method were collected on cartridges packed with DNPH-impregnated glass beads, which exhibit good collection efficiency for formaldehyde in dry air and acetaldehyde in humid air (Grosjean and Fung, 1982). For formaldehyde in dry air either alone (five runs) or in mixtures with acetaldehyde (one run) and with acetaldehyde, benzaldehyde and MEK, results of the infrared (IR) and DNPH-HPLC (ERT) methods obeyed the following linear regression equation:

$$(\text{HCHO})_{\text{ERT}} = 1.22 (\text{HCHO}/10)_{\text{IR}} - 2.67, r = 0.920, n = 7$$

for concentration ranges of 3 to 79 ppb (ERT) and 100 to 670 ppb (IR). The factor of 10 in the above equation takes into account the 1:10 dilution of the IR sample prior to DNPH-HPLC analysis.

For acetaldehyde in humid air (CH₃CHO alone, one HCHO + CH₃CHO + MEK mixture, one HCHO + CH₃CHO + MEK + benzaldehyde mixture, one cis-2-butene-ozone run, one irradiated cis-2-butene-NO₂ run, and one isoprene-ozone run as a control run in which methacrolein and methyl vinyl ketone, but no acetaldehyde, are formed), the linear regression equation obtained was:

$$(\text{CH}_3\text{CHO})_{\text{ERT}} = 1.09 (\text{CH}_3\text{CHO}/10)_{\text{IR}} + 15.0, r = 0.975, n = 6$$

The acetaldehyde concentration ranged from 0 to 560 ppb and from 0 to 4,870 ppb, respectively in the ERT and IR method data sets. The reasonable agreement between the two methods for all systems studied, including complex photochemically reactive mixtures, appears to rule out any major interferences from other pollutants when using the DNPH-HPLC method.

The second study was conducted by ERT and Harvey Mudd College researchers (Grosjean and Kok, 1981) and involved a large number of side-by-side measurements using the chromotropic acid (CA) chemiluminescence (CL) and DNPH-HPLC methods. In the first phase of the study, ppb concentrations of formaldehyde, acetaldehyde and HCHO-CH₃CHO mixtures were generated in both the static mode using Teflon chambers and the dynamic mode using a vacuum dynamic dilution system. The first phase of the study also included a limited number of comparisons with a long path Fourier-transform infrared instrument (FTIR) operated by Dr. Hanst of the EPA (Hanst et al., 1982). In the second phase of the study ambient measurements were conducted at two sites in the Los Angeles area. California State University, Los Angeles (CSLA) and Claremont.

On standard samples of formaldehyde prepared in the static mode (3-m³ Teflon bags), reasonable agreement was obtained between the several methods (units are ppb HCHO):

$$\begin{aligned} \text{HCHO(HPLC)} &= 0.95 \text{ HCHO(FTIR)} - 17.9, r = 0.85, n = 18, \\ \text{HCHO(CL)} &= 1.35 \text{ HCHO(FTIR)} - 25.2, r = 0.97, n = 18, \text{ and} \\ \text{HCHO(CL)} &= 0.98 \text{ HCHO(HPLC)} + 28.4, r = 0.76, n = 22 \end{aligned}$$

In this comparison, significant scatter about the regression line was encountered for HCHO concentrations below about 25 ppb.

Much better agreement was obtained in side-by-side comparisons conducted in the dynamic mode using a vacuum dilution system under more controlled conditions (i.e. with matrix air being pure air, constant humidity

of <1 percent or 50 percent, no sample homogeneity problems, more rigorous carbonyl preparation and sampling protocol). The following linear regression equations were obtained in this case:

$$\text{HCHO (CA)} = 0.90 \text{ HCHO (nominal)} + 38.4, r = 0.90, n = 11$$

$$\text{HCHO (CL)} = 1.27 \text{ HCHO (nominal)} - 89.4, r = 0.91, n = 6$$

$$\text{HCHO (HPLC)} = 0.94 \text{ HCHO (nominal)} + 4.8, r = 0.90, n = 6$$

These relations indicate good agreement between the three methods even though the regressions derived for the CL method exhibit a higher slope and a large negative intercept. In the range of formaldehyde concentrations studied (117 to 323 ppb) there was no indication of interference due to acetaldehyde, and none of the three methods appears to be influenced by humidity in the range <1 percent to 50 percent as expected since all three methods employed aqueous reagent collection devices.

Results of ambient measurement of formaldehyde conducted in June 1980 at California State University at Los Angeles (CSLA), under conditions of light to moderate smog, exhibited more scatter than those obtained for standard samples. Although many CL:HPLC formaldehyde ratios clustered around 1:1, diurnal variations of these ratios were observed with a trend towards much higher values (up to 3:1) in the late afternoon. Even more scatter was observed in the formaldehyde measurements conducted in September-October 1980 in Claremont during severe smog conditions ($\text{O}_3 > 0.4$ ppm). While the chromotropic acid and HPLC methods yielded comparable results, results from the CL method were consistently lower (typically by a factor of three) than those obtained using either HPLC or CA methods. Thus, application of the CL method to ambient measurements in photochemically polluted air appears to be limited due to interference problems, and a recommendation was made that potential interferents in the CL method be studied under laboratory conditions (Grosjean and Kok, 1981).

4.5 EVALUATION AND SELECTION OF FORMALDEHYDE MEASUREMENT METHODS

Using the criteria listed in Section 4.1, we have attempted to evaluate the methods reviewed in the preceding paragraphs in terms of their

potential application to Task IIB. The criteria emphasized include both sampling and analytical considerations as follows:

- Sampling: efficiency, specificity (interference-free), cost-effectiveness, simplicity, flexibility, logistical aspects and documentation; and
- Analysis: specificity (interference-free), sensitivity, dynamic range, cost-effectiveness, flexibility, capability of measuring carbonyls other than formaldehyde, and documentation.

A simplified summary of the method evaluation process according to the above criteria is given in Table 4.5-1. A more detailed evaluation is presented in the following paragraphs according to method category.

4.5.1 Spectrophotometric Methods

Only five of the spectrophotometric and fluorometric methods listed in Table 4.2-1 and 4.2-2 have been sufficiently tested in the field to warrant further discussion. The MBTH and AHMT methods are not specific for formaldehyde (National Academy of Sciences, 1981; Fushimi and Miyaka, 1980). Of the three remaining methods, the acetylacetone method suffers from poor collection efficiency and analytical problems (Zafirou et al. 1980; Klippel and Warneck, 1980). The chromotropic acid and pararosaniline methods are limited to formaldehyde, a disadvantage if cost-effective information concerning outdoor and indoor levels of carbonyls other than formaldehyde is needed. The National Academy of Sciences review (1981) discusses a number of interferences: sulfur dioxide (and sulfite and bisulfite) in the pararosaniline method, and nitrogen dioxide, alkenes, phenols, acrolein and acetaldehyde in the chromotropic acid method. Krug and Hirt (1977) also noted a substantial nitrate interference in the chromotropic acid method. Although improved protocols have been recently developed for both chromotropic (Kok et al., 1981) and pararosaniline methods (Miksch et al., 1981), further interference studies may be needed in view of the large number of pollutants found in both indoor and outdoor environments and their range of concentrations.

TABLE 4.5-1

SUMMARY OF METHODS EVALUATION*

Method	Sampling Protocol				Analytical Protocol				
	Efficiency	Specificity (inter- ferences)	Cost	Flexi- bility	Speci- ficity	Cost	Sensi- tivity	Flexi- bility, Dynamic Range, Others	Other Carbonyls
<u>Spectrophotometric</u>									
Chromotropic acid	●	--	●	●	--	●	--	--	0
Pararosaniline	●	--	●	●	--	●	--	--	0
MBTH	●	0	●	●	0	●	--	--	●
Acetylacetone (Nash)	0	●	●	●	●	●	--	--	0
AIMT	●	0	●	●	0	●	--	--	0
<u>Chromatographic</u>									
GC-MS	●	--	●	●	--	0	●	--	0
DNPH-GC	●	●	●	●	●	●	●	--	●
DNPH-HPLC	●	●	●	●	●	●	●	●	●
Bisulfite-GC	●	--	●	●	0	●	0	--	●
Dansyl-HPLC	●	●	●	●	●	●	●	●	●
Oxazolidine-GC	●	--	●	●	--	●	0	--	0
<u>Spectroscopic</u>									
Infrared	--	--	--	--	●	0	--	--	0
Differential ultraviolet	--	--	--	--	●	0	●	●	0
<u>Other Active Sampling Methods</u>									
Ion chromatography	--	0	●	--	0	●	0	--	**
Chemiluminescence	●	0	●	●	0	●	●	--	0
<u>Passive Methods</u>									
Bisulfite	●	--	●	0	--	●	0	--	0

*● good, 0 poor, --intermediate, or no data, or does not apply.

** Acetaldehyde only.

4.5.2 Chromatographic Methods

The direct method of Yokouchi et al. (1979) involves sampling of formaldehyde on 13X molecular sieves, GC separation on a glass column, and quantitation using a mass spectrometer. Although not extensively tested in the field, the method appears promising and may be cost-effective in analytical laboratories already equipped with a mass spectrometer.

The HPLC methods listed in Table 4.2-3 and involving DNPH derivatives appear to meet all our criteria including sampling specificity, analytical specificity and detection limits. These methods also allow for both sampling and analytical flexibility, and are capable of measuring, from a single sample, a large number of carbonyls in addition to formaldehyde. Sampling efficiencies have been independently tested by a number of investigators over a wide range of conditions for impingers, and, to some extent, for solid adsorbent samplers (Grosjean and Fung, 1982). Since the sampling reagent is specific to carbonyls and the analytical separation and detection protocol are optimized for DNPH derivatives, the potential for interferences from other organic and inorganic pollutants is minimal. Tests conducted in the laboratory (Lowe et al., 1980) and in photochemically-polluted Los Angeles air (Grosjean, 1982) have shown that ozone (up to 200 ppb), sulfur dioxide (up to 90 ppb), nitrogen dioxide (up to 150 ppb), and urban levels of hydrocarbons, nitric acid, free radicals and other ambient pollutants do not interfere with the DNPH method.

The gas chromatographic methods (GC-DNPH) listed in Table 4.2-3 have essentially the same advantages as the corresponding HPLC methods discussed above. For a DNPH derivative, better detection limits are obtained with electron capture detection than with flame ionization detection. The ECD detection limits are comparable to those afforded by the HPLC-DNPH methods (Johnson et al., 1981). A potential problem with the GC method is the poor thermal stability of DNPH derivatives (Papa and Turner, 1972a). Another problem, for unsymmetrical carbonyls, is the resolution of the two DNPH isomers, (syn and anti-) into two peaks (Johnson et al., 1981). This effect complicates the chromatograms and makes it necessary to establish two

calibration curves. For these reasons, under equal sensitivity requirements, preference is given to the HPLC method over its GC counterpart.

Ambient air application of the chromatographic methods involving derivation other than DNPH (Table 4.2-5) have been limited to the sodium bisulfite, oxazolidine and dansylhydrazine methods. The sodium bisulfite method is not applicable to formaldehyde and as mentioned before, the current detection limit of the oxazolidine-GC method is too high for ambient and indoor measurements. The dansylhydrazine-HPLC fluorescence method of Johnson et al. (1981) is potentially the most sensitive method, since the fluorescent detector affords substantially lower detection limits than the ultraviolet detector. The collection efficiency of the sampling reagent, dansylhydrazine, has not been extensively tested.

4.5.3 Spectroscopic Methods

Ambient formaldehyde measurements have been performed using long-path infrared and differential ultraviolet methods. Both methods are limited to one carbonyl, formaldehyde. As mentioned before, the infrared method is not very sensitive (detection limit = 6 ppb at 1 km path) while the ultraviolet method has a reported detection limit of 0.1 ppb (5 km path). Neither method is readily amenable to indoor measurements. Both methods, especially the infrared method, are prohibitively expensive for field sampling (National Academy of Sciences, 1981).

4.5.4 Other Active Sampling Methods

Of the several miscellaneous methods discussed in Section 4.2.4, the ion chromatography and chemiluminescence techniques appear to have good potential for cost-effective ambient measurements. At its present stage of development (Kok, 1981), the chemiluminescent method needs to be further characterized for severe interferences and/or analytical problems when sampling photochemically-polluted air (Grosjean and Kok, 1981). Slawinska and Slawinski (1975) reported substantial positive interferences from several other aldehydes, and suggested other interferents as well. Problems with the ion chromatographic method may include insufficient detection limits for

formate (and acetate), as well as interferences due to oxidation by H_2O_2 of organics (other than formaldehyde) to formate.

4.5.5 Passive Sampling Methods

The passive sampling method under consideration involves collection of formaldehyde with sodium bisulfite and subsequent assay using the chromotropic acid method, whose potential interference problems have been discussed earlier. Collection devices tested to date include the Lawrence Berkeley Laboratory tube containing an impregnated glass filter (Geisling 1981: Geisling et al., 1981), the 3M Company impregnated paper badge (Rodriguez et al., 1981), and the DuPont liquid bisulfite solution badge (DuPont 1982). These devices appear suitable for long-term sampling (e.g., at least one week with the LBL sampler) in the indoor environment. Pending further validation studies, current limitations of the bisulfite/chromotropic acid passive method should be kept in mind. These limitations may include poor formaldehyde collection efficiency at low face velocities (stagnant air) and interferences from a number of indoor pollutants other than those tested to date, i.e., acrolein, ethanol, and phenol.

4.6 RECOMMENDATIONS

The DNPH-HPLC method, of which several slightly different variations have been recently documented in the peer-reviewed literature, is recommended as the optimum method to meet the requirements of the outdoor measurements component of this project. The method is readily applicable to short-term indoor measurements as well. The method is also suitable for measurements of carbonyls other than formaldehyde, both outdoors and indoors. Detailed sampling and analytical protocols for the DNPH-HPLC method are attached as appendices to this sampling plan.

With modest method development focusing on sampling efficiency, the dansylhydrazine-HPLC method could be applied for greater sensitivity. For longer term indoor measurements, passive sampling with sodium bisulfite followed by chromotropic acid assay appears to be the method of choice, providing that some aspects of the method validation be further documented, including potential interference and collection efficiency as a function of air flow face velocity.

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