# ASSESSMENT OF INDOOR CONCENTRATIONS, INDOOR SOURCES AND SOURCE EMISSIONS OF SELECTED VOLATILE ORGANIC COMPOUNDS

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Prepared for:

Research Division
California Air Resources Board
1102 Q Street
P.O. Box 2815
Sacramento, CA 95812

Submitted by:

Indoor Environmental Program
Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Prepared by:

Alfred T. Hodgson and John D. Wooley

Approved by:

Joan M. Daisey
Principal Investigator

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# Abstract

The California Air Resources Board (CARB) is required to consider indoor exposures in assessing the risks to public health posed by compounds being reviewed for classification as toxic air contaminants. This literature review was performed to evaluate the existing data on the potential indoor uses and sources, the indoor concentrations and exposures, and the source emissions of candidate compounds not yet in the formal review process. The study was primarily restricted to organic compounds in Groups IIB and III of the "Toxic Air Contaminant Identification List, February, 1990." Data for 47 individual compounds were reviewed. The body of this report contains a section for each compound or group of closely related compounds in which the data from the literature are summarized and evaluated.

Data on indoor concentrations and personal exposures which adequately fulfill the CARB's needs were found only for styrene, xylenes, p-dichlorobenzene and methyl chloroform. These compounds were included in field studies conducted in California by the U.S. EPA. Indoor concentrations for a number of other compounds are being obtained from ongoing field studies sponsored by the CARB.

The candidate compounds can generally be classified into three groups according to broad similarities among their likely indoor sources. A number of the compounds may be present in building materials, interior-finish materials, furnishings and various consumer products as minor constituents, such as unreacted monomers and chemical intermediates, additives and contaminants. Emissions from these products and materials may occur under certain circumstances. Some of the compounds are major constituents of expendable consumer products that are available in retail outlets. Exposures to these compounds occur when the products are used indoors. Combustion processes, including sidestream cigarette smoke and wood burning, are indoor sources of other compounds.

The data on source emissions of the candidate compounds are very limited. Of all the compounds, p-dichlorobenzene was the only one for which adequate measurements have been made of emission rates from the dominant indoor sources. These sources are moth repellents and room deodorizers in solid form.

Recommendations were developed for a multi-component laboratory study to provide data on source emission rates for selected compounds. Three different studies, which parallel the similarities in the sources of the compounds, were defined. Priorities were assigned to these studies and to the individual compounds in each study based on several criteria. In general, compounds in CARB Group II received the highest priority for further investigation.

The laboratory study with the highest priority would investigate the potential emissions of volatile candidate compounds that are minor constituents of products and materials. It is suggested the emphasis be placed on measurements of 1,3-butadiene, 1,4-dioxane, ethyl acrylate, propylene oxide, acrylonitrile, the N-nitroso compounds and toluene diisocyanates. The approach would be to screen possible sources for emissions and to measure emission rates for any significant sources using environmental chambers. The study with the next highest priority would investigate emissions of volatile candidate compounds resulting from the use of expendable consumer products. The approach would be to measure emissions while the products are actively being used in a room-size environmental chamber. Products containing 1,4-dioxane should be emphasized. The third study would investigate emissions of compounds in environmental tobacco smoke. Compounds with high priority for this study are 1,3-butadiene, acetaldehyde, hydrazine and the N-nitrosamines.

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# Disclaimer

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# CHAPTER 1

# Summary and Conclusions

## Background

The California Air Resources Board (CARB) is required to consider indoor exposures in assessing risks to public health posed by compounds being reviewed for classification as toxic air contaminants. Consequently, the goal of the Indoor Air Quality/Personal Exposure Assessment Program (Indoor Program) of the CARB is to obtain health effects information and data that are applicable to California on the indoor concentrations and personal exposures for the candidate compounds. If significant risks are identified, the goal is to reduce exposures. To achieve these goals, the Indoor Program sponsors a number of interrelated research activities, the objectives of which are to: 1) obtain data regarding health effects; 2) develop monitoring methods if suitable methods are unavailable; 3) obtain indoor concentration and exposure pattern data; 4) identify indoor sources and obtain source emissions data; 5) determine activity patterns for Californians; and 6) develop and validate a total exposure model which can be used to perform risk assessments.

For some compounds under review, the existing indoor concentration and personal exposure data may be adequate with respect to the CARB's goals. However, for many, the sources of indoor exposure have not been fully identified, and no, or only limited, indoor concentration and personal exposure data are available. To directly obtain more information, the CARB is currently sponsoring field surveys to measure indoor concentrations and exposures for a variety of compounds. Because of the expense and difficulty of measuring concentrations and exposures over all pertinent indoor conditions using field surveys, the CARB has initiated a research effort to identify indoor sources and measure source emission rates of selected candidate compounds. This literature review represents the first phase of that effort. Ultimately, source emissions data will be used in a total exposure model to estimate exposures for the selected compounds under a variety of indoor conditions.

## Study Objectives

This literature study was performed to evaluate the existing data on selected candidate toxic air contaminants not yet in the formal CARB review process. The specific objectives were to: 1) compile and review the existing data on the potential indoor uses and sources, the indoor concentrations and exposures, and the source emissions of the candidate organic compounds; 2) evaluate the adequacy of these data with respect to the goals of the CARB; and 3) identify those compounds for which laboratory studies of source emissions would be a suitable way to obtain input data for a model of total exposure.

## Reviewed Compounds

This study was primarily restricted to volatile and semivolatile organic compounds in Groups IIB and III of the "Toxic Air Contaminant Identification List, February, 1990." Several broad categories of compounds in these groups were specifically excluded from review by agreement with the CARB. These categories were polycyclic aromatic hydrocarbons, polychlorinated biphenyls, environmental tobacco smoke, coke-oven emissions, radionuclides, and metals. Two Group IIA compounds, acetaldehyde and 1,3-butadiene, and epichlorohydrin, which is not on the identification list, were included at the request of the Project Manager.

A total of 47 compounds were reviewed. The majority of these are volatile organic compounds (VOC). For the purposes of this study, VOC are simply defined as organic compounds with atmospheric-pressure boiling points of 250° C, or less.

## Methods

The first steps in this study were to identify and assemble the available literature for the candidate compounds. Literature citations were obtained from a manual search of the investigators' reprint files, from several specialized data sources, and from computerized searches of the Chemical Abstract Service (CAS) and the National Technical Information Services (NTIS) databases.

The CAS database contains bibliographic citations for approximately 8.4 million references published world wide. The NTIS database contains citations for U.S. government reports. The searches of these databases were conducted using the CAS numbers of the compounds and subject categories which encompassed a wide range of indoor uses and sources of the compounds. Retrieved records were down loaded and entered into a bibliographic database on an IBM-compatible personal computer using "Biblio-Links" and "Pro-Cite" software. References obtained from other sources were manually keyed into the database. The created database contains approximately 225 records, many of which have searchable abstracts, key words and index terms. A complete listing of the citations in this database is presented in the Appendix.

Additional information for the candidate compounds was extracted from five other major data sources: 1) the Clinical Toxicology of Commercial Products database, 2) the Hazardous Substances Data Bank, 3) the NASA/McDonnell Douglas Materials Testing Data Base, 4) the National Volatile Organic Compound database, and 5) the California Total Exposure Assessment Methodology (TEAM) studies.

## Organization

The methods used in conducting the literature reviews and descriptions of the major data sources are presented in Chapter 3, "Introduction."

The data for the 47 compounds under review are summarized and evaluated in Chapter 4, "Compound Reviews," which comprises the body of this report. The compounds have been grouped into five chemical classes: hydrocarbons, oxygen-containing compounds, halogen-containing compounds, nitrogen-containing compounds, and sulfur-containing compounds. Within each group, compounds are arranged alphabetically.

The section for each compound or group of related compounds is divided into five subsections. Under "Uses and Sources," the general uses of the compound are described, and the possible indoor sources are identified. Any quantitative data on indoor concentrations are summarized under "Concentration Data." When available, data which show the frequency distributions of the concentrations in indoor air are presented. Emphasis is placed on data obtained in California and the U.S. Any quantitative measurements of emissions are summarized in the "Emissions Data" subsection. In the "Summary" subsection, the adequacy of the data for estimating indoor concentrations and exposures in California is discussed. If additional data are needed, methods for acquiring these data are recommended. The concluding "Reference" subsection gives the literature citations used in the review.

In Chapter 2, "Recommendations," a plan is presented for a multi-component laboratory study which can be developed to provide additional data on source emission rates for selected candidate compounds. This plan is based on the findings of the literature reviews of the individual compounds.

In Chapter 5, "Methods for Measuring Emissions of VOC," various techniques which have been used to estimate and measure emissions of VOC from sources are reviewed.

The Appendix is a listing of all of the reference citations contained in the bibliographic database that was created as part of this study.

## Results and Conclusions

Indoor concentrations and personal exposures for a number of the candidate compounds have either previously been measured or are currently being measured by field studies conducted in California. These field studies are summarized in Table 1.1.

Six of the compounds, styrene, the xylenes, 1,4-dioxane, chlorobenzene, p-dichlorobenzene and methyl chloroform, were included in the California TEAM studies conducted by the U.S. EPA in 1984 and 1987 in and around Los Angeles (two seasons each year) and in 1984 in Contra Costa County (one season). Measurements of the compounds in fixed-site indoor and outdoor air, personal air, breath and drinking water samples were made for stratified random samples of residents in both areas. The sample sizes were relatively large. The results were weighted to represent the entire populations of the study areas, which were approximately 350,000 for the Los Angeles study and 90,000 for the Contra Costa County study.

The xylenes, p-dichlorobenzene and methyl chloroform occurred ubiquitously in indoor, outdoor and personal air. Styrene was often present in indoor air at concentrations above the limit of detection, and 1,4-dioxane and chlorobenzene were occasionally found. With the exception of chlorobenzene, which only occurred in a small percentage of the samples, there were sufficient data to construct frequency distributions of indoor concentrations and personal exposures for both study areas.

In general, the existing data on the indoor concentrations and personal exposures for the other compounds under review were found to be very limited in quantity and usefulness. Only a few studies relevant to California have been conducted. Most often, these studies did not utilize statistically valid sampling strategies or sufficient numbers of samples.

Table 1.1. Completed and ongoing California field studies of candidate compounds.

| | Field Study | | |
|---|---|---|---|
| Compound | California TEAM | Woodland, California | California PTEAM |
| 1,3-Butadiene | — | √ | — |
| Styrene | √ | √ | — |
| Xylenes | √ | √ | — |
| Acetaldehyde | — | — | — |
| Acrolein | — | √ | — |
| Cresols | — | — | — |
| Di(2-ethylhexyl)phthalate | — | √ | √ |
| 1,4-Dioxane | √ | √ | — |
| Ethyl acrylate | — | — | — |
| Glycol ethers and acetates | — | — | — |
| Maleic Anhydride | — | — | — |
| Phenol | — | — | — |
| Propylene oxide | — | √ | — |
| Allyl chloride | — | √ | — |
| Benzyl chloride | — | √ | — |
| Chlorobenzene | √ | √ | — |
| Chloroprene | — | √* | — |
| p-Dichlorobenzene | √ | √ | — |
| Epichlorohydrin | — | — | — |
| Hexachlorobenzene | — | √ | — |
| Methyl bromide | — | √ | — |
| Methyl chloroform | √ | √ | — |
| Pentachlorophenol | — | √ | — |
| Tri-/Tetrachlorophenols | — | √ | — |
| Vinylidene chloride | — | √ | — |
| Acrylamide | — | — | — |
| Acrylonitrile | — | √ | — |
| 1,1-Dimethylhydrazine | — | — | — |
| Hydrazine | — | — | — |
| 4,4'-Methylenedianiline | — | — | — |
| Nitrobenzene | — | √ | — |
| N-Nitroso compounds | — | — | — |
| Toluene diisocyanates | — | — | — |
| Dimethyl sulfate | — | — | — |

*Qualitative analysis only.

The CARB has taken the lead in sponsoring the necessary field studies. One of these is measuring concentrations and personal exposures for 32 very volatile, volatile and semivolatile organic compounds in a probability-based sample of approximately 130 homes in Woodland, CA. A pilot phase was conducted in a small number of homes to evaluate methods for sampling and analysis. The main study will be conducted over a 24-hour period in one season. A second phase is planned which would involve similar monitoring during a different season in Woodland or in a different region of the State. In addition to all of the California TEAM study compounds discussed above, the Woodland study is monitoring a number of other candidate compounds for which there are few or no previous data (Table 1.1). These are 1,3-butadiene, acrolein, di(2-ethylhexyl)phthalate, propylene oxide, allyl chloride, benzyl chloride, chloroprene (qualitative data only), hexachlorobenzene, methyl bromide, pentachlorophenol, 2,3,4,6-tetrachlorophenol, 2,4,6-trichlorophenol, vinylidene chloride, acrylonitrile and nitrobenzene.

The second phase of the Particulate Total Exposure Methodology (PTEAM) study, which is jointly sponsored by the U.S. EPA and the CARB, is being conducted in a representative sample of 175 homes in Riverside, CA. This study is measuring indoor and outdoor concentrations of polycyclic aromatic hydrocarbons and phthalate esters. Included in these measurements are combined vapor- and particle-phase concentrations of di(2-ethylhexyl)phthalate. The field work for this study was conducted during Fall, 1990, with final results expected in early 1992.

One of the findings of this literature review is that the candidate compounds can generally be classified into three groups according to the broad similarities among their likely indoor sources. This classification suggests that there may be certain similarities among the patterns of personal exposures to the compounds within the population. The source categories for the compounds are shown in Table 1.2. Compounds with a variety of sources often fall into more than one category.

A number of the compounds may be present in building materials, interior-finish materials, furnishings and various consumer products as minor constituents, such as unreacted monomers and chemical intermediates, additives and contaminants. These are indicated in Table 1.2 under the heading, "Monomer/Minor Constituent." Traces of monomers and intermediates may persist in some of these materials after production and may subsequently be released in the indoor environment. For example, studies suggest that the release of the unreacted styrene monomer from materials, such as polystyrene insulation, is an important indoor source of this compound. The compounds which can be classified as monomers and intermediates are 1,3-butadiene, styrene, ethyl acrylate, maleic anhydride, phenol, allyl chloride, chloroprene, epichlorohydrin, vinylidene chloride, acrylamide, acrylonitrile, 4,4'-methylenedianiline, nitrobenzene and toluene diisocyanates. The toluene diisocyanates are notable because they are used in the manufacture of a number of large-volume products that are found in residences, including polyurethane carpet pads, foam furniture cushions, varnishes and caulks. The other compounds which may be present in materials and products as minor constituents are acetaldehyde, di(2-ethylhexyl)phthalate, 1,4-dioxane, propylene oxide, benzyl chloride, chlorobenzene, hexachlorobenzene, dimethylhydrazine, the N-nitroso compounds and dimethyl sulfate.

Some of the candidate compounds are major constituents of expendable consumer products that are available in retail outlets. Exposures to these compounds occur when the products are used in indoor environments. In many cases, the highest exposures occur during the active use of products, such as the brushing, rolling or spraying of architectural coatings. The compounds in this category are indicated under

Table 1.2. Source categories of candidate compounds.

| | Source Category | | |
|---|---|---|---|
| Compound | Monomer/ Minor Constituent | Consumer Product Source | Combustion or ETS Source |
| 1,3-Butadiene | √ | — | √ |
| Styrene | √ | — | √ |
| Xylenes | — | √ | √ |
| | | | |
| Acetaldehyde | √ | — | √ |
| Acrolein | — | — | √ |
| Cresols | — | √ | √ |
| Di(2-ethylhexyl)phthalate | √ | — | — |
| 1,4-Dioxane | √ | √ | — |
| Ethyl acrylate | √ | — | — |
| Glycol ethers and acetates | — | √ | — |
| Maleic Anhydride | √ | — | — |
| Phenol | √ | √ | √ |
| Propylene oxide | √ | — | — |
| | | | |
| Allyl chloride | √ | — | — |
| Benzyl chloride | √ | — | — |
| Chlorobenzene | √ | √ | — |
| Chloroprene | √ | — | — |
| p-Dichlorobenzene | — | √ | — |
| Epichlorohydrin | √ | √ | — |
| Hexachlorobenzene | √ | — | — |
| Methyl bromide | — | √ | — |
| Methyl chloroform | — | √ | — |
| Pentachlorophenol | — | √ | — |
| Tri-/Tetrachlorophenols | — | √ | — |
| Vinylidene chloride | √ | — | — |
| | | | |
| Acrylamide | √ | — | — |
| Acrylonitrile | √ | — | — |
| 1,1-Dimethylhydrazine | √ | — | — |
| Hydrazine | — | — | √ |
| 4,4'-Methylenedianiline | √ | — | — |
| Nitrobenzene | √ | — | — |
| N-Nitroso compounds | √ | — | √ |
| Toluene diisocyanates | √ | — | — |
| | | | |
| Dimethyl sulfate | √ | — | — |

the heading, "Consumer Product Source." The xylenes are widely used as solvents in a large number of common household products, such as cleaners, paints, spray paints, varnishes, primers, paint removers, adhesives, lubricants, pesticides and herbicides. Cresols are used in some degreasers, paintbrush cleaners and disinfectants. Phenol is also used in some disinfectants, as well as medicinal preparations. Consumer sources of exposure to 1,4-dioxane include architectural coatings, paint/varnish removers, polishes, adhesives, cleaners, detergents, fumigants and cosmetics. The glycol ethers and their acetate derivatives are used as solvents in a variety of architectural coatings and common household products, such as cleaners, adhesives and cosmetics. Epichlorohydrin is also used as a solvent in some architectural coatings. Chlorobenzene is used in paints, adhesives, polishes, waxes and pharmaceuticals. The dominant sources of p-dichlorobenzene are moth repellents and room deodorizers in solid form. Methyl chloroform is another widely used solvent. It is found in a variety of household cleaners, spot removers, paint/varnish removers, primers, wood finishes, polishes and lubricants. Methyl bromide is used as an insecticide, herbicide and fungicide. All indoor use of pentachlorophenol is now banned; however, historically it has been extensively used as a biocide in wood preservatives. Because of its low volatility, elevated concentrations can persist for years after product application. The tri- and tetrachlorophenols are used as preservatives in some products and as disinfectants.

Combustion processes including environmental tobacco smoke (ETS) are indoor sources of some of the compounds. These are indicated under the heading, "Combustion or ETS Source." The compounds which are components of ETS are 1,3-butadiene, styrene, xylenes, acetaldehyde, acrolein, cresols, phenol, hydrazine and the N-nitrosamines. Cigarette smoke was the only identified indoor source of hydrazine. Data on the emissions of these compounds in the sidestream smoke of cigarettes are summarized in this report. Several studies detected emissions of acetaldehyde, acrolein, cresols and phenol as by-products of incomplete combustion during the burning of wood. Consequently, wood-burning appliances, particularly fireplaces with poor draught and leaky wood stoves, are potential indoor sources of these compounds. However, the emissions data are insufficient to determine the significance of wood burning as a source relative to ETS.

This literature review found that quantitative data on source emissions which can be used in a model for total exposure are rare. The measurement of emissions of volatile compounds from indoor sources is only now becoming a topic of interest among researchers. Some studies of building materials have produced quantitative data on the emission rates of a few candidate compounds from a very limited number of sources. Emissions of some of the candidate compounds in the sidestream smoke of cigarettes have been quantified, but much of these data are of limited use because of inconsistent methodologies and the small number of measurements that were made.

Of all of the compounds that were reviewed, p-dichlorobenzene is the only one for which emission rates from the dominant indoor sources have been adequately measured. The dominant sources are limited to moth repellents and room deodorizers which, because of their similar form, are expected to have similar emissions. The U.S. EPA has measured emissions from moth crystal cakes in chamber studies and has successfully used the data in a mass-balance model to predict indoor concentrations in a test house.

The data for only a few compounds were judged to be adequate with respect to the CARB's goal to consider indoor concentrations and personal exposures during their review of candidate toxic air contaminants. In making this judgement, no consideration was given to the fact that a compound is included in an ongoing field study sponsored by the CARB since the results of the field measurements are not available at this time.

As previously noted, there are considerable data on indoor concentrations and exposures for some of the compounds which were included in the California TEAM studies. The xylenes, p-dichlorobenzene and methyl chloroform were found to occur ubiquitously in indoor air, and styrene was often detected. Since frequency distributions for indoor concentrations and personal exposures were obtained for relatively large populations, the data for these compounds are probably adequate for use in the CARB's review process. The data for 1,4-dioxane were judged to be marginally adequate because this compound has been found above typical limits of detection in only a relatively small percentage of the homes sampled. Therefore, 1,4-dioxane was considered as a candidate for future study.

The potential indoor sources of styrene, xylenes and methyl chloroform are numerous. If the exposure and health effects data for any of these compounds demonstrate that there is a high risk of adverse health effects, then it would be important to know the relative contributions of the various sources in order to develop effective mitigation strategies. This could be determined in laboratory studies but would be relatively expensive due to the large numbers of sources.

This literature review identified many data gaps with respect to the CARB's goals. Some of the data needs will be filled by the ongoing field studies. However, as noted above, field studies can not cover all pertinent indoor conditions. Therefore, there is a need for data on source emission rates that can be input into a model of total exposure. After reviewing the existing data, recommendations were developed for a multi-component laboratory study of selected compounds on source emission rates. In addition, field studies to obtain data on indoor concentrations and exposures are recommended for some compounds. The CARB groups were considered to be a guide to the relative importance of health effects and, therefore, were used to establish priorities among the components of the laboratory study and also among investigations of individual compounds within a component. Investigations of Group II compounds were always given higher priority than investigations of Group III compounds because, by definition, the health effects information for Group III compounds is limited or not yet sufficient to support review of the compounds. Additional considerations in establishing priorities were preliminary assessments of the relative importance of potential indoor sources and the availability of existing data which might be used to make at least first-order estimates of indoor exposures.

The recommended laboratory study of source emissions is broken down into three categories which parallel the similarities in the sources of the compounds shown in Table 1.2. These categories are: 1) emissions of minor constituents from products and materials; 2) consumer product emissions; and 3) ETS emissions. The study of emissions of minor constituents from products and materials was given a higher priority than the study of consumer product emissions because it would provide data for more compounds in CARB Group II. The study of emissions from ETS was given the lowest priority because some data already exist for this source. Field studies are recommended as an efficient means to generate additional data predominantly for semivolatile compounds. The field studies were not assigned a priority relative to the laboratory studies. The recommended laboratory and field studies are summarized in Table 1.3. The suggested priority rankings for the study of compounds within a category are indicated in the table.

Highest priority should be given to a laboratory study that would investigate the potential emissions of volatile candidate compounds that are minor constituents of products and materials, such as unreacted monomers and chemical intermediates, additives and contaminants. It is suggested that emphasis be placed on measurements of 1,3-butadiene, 1,4-dioxane, ethyl acrylate, propylene oxide, acrylonitrile, the

Table 1.3. Summary of recommendations for further studies of candidate compounds showing priority rankings for compounds within each study.

| | | Recommended Study | | | |
|---|---|---|---|---|---|
| Compound | CARB Group | Emissions of Minor Constituents | Chamber Study of Consumer Products | ETS Emissions | Field Studies |
| 1,3-Butadiene | IIA | 1[a] | — | 1 | — |
| Styrene | IIB | ------------Adequate Data------------ | | | |
| Xylenes | III | ------------Adequate Data------------ | | | |
| | | | | | |
| Acetaldehyde | IIA | — | — | 1 | 1 |
| Acrolein | III | — | — | 2 | — |
| Cresols | III | — | 2 | 2 | — |
| Di(2-ethylhexyl)phthalate[b] | IIB | — | — | — | 1[c] |
| 1,4-Dioxane | IIB | 1 | 1 | — | — |
| Ethyl acrylate | IIB | 1 | — | — | — |
| Glycol ethers and acetates | III | — | 2 | — | — |
| Maleic Anhydride | III | 3 | — | — | — |
| Phenol | III | 2 | 2 | 2 | — |
| Propylene oxide | IIB | 1 | — | — | — |
| | | | | | |
| Allyl chloride | III | 2 | — | — | — |
| Benzyl chloride | III | 2 | — | — | — |
| Chlorobenzene | III | 2 | 2 | — | — |
| Chloroprene | III | 2 | — | — | — |
| p-Dichlorobenzene | IIB | ------------Adequate Data------------ | | | |
| Epichlorohydrin | — | 3 | 3 | — | — |
| Hexachlorobenzene[b] | IIB | — | — | — | 1[c] |
| Methyl bromide | III | — | 2 | — | — |
| Methyl chloroform | III | ------------Adequate Data------------ | | | |
| Pentachlorophenol[b] | III | — | — | — | 2[c] |
| Tri-/Tetrachlorophenols[b] | IIB,III | — | — | — | 1,2[c] |
| Vinylidene chloride | III | 2 | — | — | — |
| | | | | | |
| Acrylamide[b] | IIB | — | — | — | 2 |
| Acrylonitrile | IIB | 1 | — | — | — |
| 1,1-Dimethylhydrazine | IIB | 2 | — | — | — |
| Hydrazine | IIB | — | — | 1 | — |
| 4,4'-Methylenedianiline[b] | IIB | — | — | — | 2 |
| Nitrobenzene | III | 2 | — | — | — |
| N-Nitroso compounds | IIB | 1 | — | 1 | — |
| Toluene diisocyanates[b] | IIB | 1 | — | — | 1 |
| | | | | | |
| Dimethyl sulfate | IIB | 2 | — | — | — |

[a] 1 indicates highest priority for further study, 3 indicates lowest priority.

[b] Semivolatile compound, *i.e.*, boiling point greater than 250° C.

[c] Included in ongoing field study.

N-nitroso compounds and toluene diisocyanates since few or no data are currently available on indoor concentrations or source emissions of these CARB Group II compounds.

The general approach for the study would be to identify possible sources of the compounds, which would then be semiquantitatively screened for emissions in small-scale laboratory experiments. If potentially significant sources are found in this screening process, it is recommended that quantitative measurements of emissions from these sources be made under standardized conditions using small- and/or large-scale environmental chambers. Considerations in conducting chamber experiments and in analyzing emission rate data are presented in Chapter 5, "Methods for Measuring Emissions of VOC."

The study with the next highest priority would investigate emissions of volatile candidate compounds resulting from the application of expendable consumer products, using an environmental chamber. Within this category, 1,4-dioxane was given the highest priority ranking because it is in CARB Group II. Possible consumer sources of indoor exposure to 1,4-dioxane which could be studied include, architectural coatings, paint/varnish removers, polishes, cleaners and adhesives. It is recommended that the experiments be conducted in a room-size environmental chamber so that consumer usage patterns and application techniques can be realistically simulated by an individual using the products.

The third laboratory study is an investigation of emissions of volatile candidate compounds in ETS. Of the volatile candidate compounds which are associated with ETS, 1,3-butadiene, acetaldehyde, hydrazine and the N-nitrosamines should be given the highest priority for study because they belong to CARB Group II. The experiments should be performed using a smoking machine in a large-scale environmental chamber, rather than with a sidestream sampler, in order to simulate an environment in which chemical reactions and sorption losses can occur.

This literature review also identified a number of candidate compounds for which field studies are the best way to obtain additional data on indoor concentrations and personal exposures. All of the semivolatile compounds and one volatile compound fall into this category (Table 1.3).

The semivolatile compounds, di(2-ethylhexyl)phthalate, hexachlorobenzene, 2,4,6-trichlorophenol and toluene diisocyanates, were given the highest priority ranking for investigation because they are CARB Group II compounds with known or suspected indoor sources. Although acrylamide and 4,4'-methylenedianiline are in Group II, they were given reduced priority because their indoor sources are expected to be limited and not widespread. With the exception of toluene diisocyanates, indoor concentrations of these compounds are currently being measured in ongoing field studies.

Acetaldehyde, which was also given the highest priority ranking, is the only volatile compound to be included among the compounds for which field studies are recommended. This compound is used as a specific ingredient in very few products. However, it is expected to be present in most indoor environments since it is emitted by numerous non-combustion and combustion sources. Due to the large number of poorly defined sources of acetaldehyde, laboratory studies of emissions would not be an efficient way to obtain additional data on indoor exposures.

# CHAPTER 2

# Recommendations

## Introduction

Recommendations for further study of the candidate toxic air contaminants were made based on the results of the literature review. The recommendations are presented here in the form of a plan for a multi-component laboratory study which can be developed by the CARB to provide data for the candidate compounds on source emission rates. In addition, field studies to obtain data on indoor concentrations and exposures are recommended for some compounds.

In making these recommendations, it was necessary to establish priorities among the components of the laboratory study and also among investigations of individual compounds within a component. The toxicities of the compounds were considered only in a limited manner. The CARB groups were taken as a general guide to relative toxicity and were used as the primary basis in setting priorities. Investigations of Group II compounds were always given higher priority than investigations of Group III compounds because, by definition, the health effects information for Group III compounds is limited or not yet sufficient to support review of the compounds. It is expected that the priorities suggested here may be altered when toxicity is considered more specifically. Additional considerations in establishing priorities were preliminary assessments of the relative importance of potential indoor sources and the availability of existing data which might be used to make at least first-order estimates of indoor exposures.

The first step in making these recommendations was to decide if the existing data for any of the compounds were sufficient to give them a reduced priority for further study. Data on indoor concentrations and exposures and on source emissions were assessed. The fact that a compound is included in an ongoing field study sponsored by the CARB was not considered since the results of the field measurements are not available at this time.

There are considerable data on indoor concentrations and exposures for many of the compounds included in the California Total Exposure Assessment Methodology (TEAM) studies. The studies were conducted by the U.S. EPA in 1984 and 1987 in and around Los Angeles (two seasons each year) and in 1984 in Contra Costa County (one season). Measurements of the compounds in fixed-site indoor and outdoor air, personal air, breath and drinking water were made for stratified random samples of residents in both areas. The sample sizes were relatively large. The results were weighted to represent the entire populations of the study areas which were approximately 350,000 for the Los Angeles Study and 90,000 for the Contra Costa Study. Xylenes, p-dichlorobenzene and methyl chloroform were found to occur ubiquitously in indoor air, and styrene was often detected in indoor air. Frequency distributions for indoor concentrations and personal exposures were obtained for all of these compounds. Consequently, the data for styrene, xylenes, p-dichlorobenzene and methyl chloroform are probably adequate with respect to the CARB's mandate to consider indoor concentrations and exposures in their decision making process. Frequency distributions were also obtained for 1,4-dioxane, but this compound has been found above typical limits of detection in only a relatively small percentage of the homes sampled. These data are considered to be only marginally adequate, and further study of 1,4-dioxane seems warranted.

The indoor sources of the commonly occurring TEAM study compounds are generally well known. A large number of products contain and emit xylenes and methyl chloroform. There are also a variety of combustion and non-combustion sources of styrene. If the exposure and health effects data for any of these compounds demonstrate that there is a high risk of adverse health effects, then it would be important to know the relative contributions of the various sources in order to develop effective mitigation strategies. This would be relatively expensive to determine in laboratory studies due to the large numbers of sources. Consequently, such studies should not be initiated until a need is established.

The dominant sources of p-dichlorobenzene in indoor air are moth repellents and room deodorizers in solid form. These are expected to have similar emissions characteristics. The U.S. EPA measured emissions from moth crystal cakes in chamber studies and used the data in a mass-balance model to predict indoor concentrations in a test house. Although there are remaining questions about "sink" effects due to sorption of p-dichlorobenzene onto surfaces, further study of emissions of p-dichlorobenzene is probably not warranted at this time. This compound might be a good candidate for demonstrating and validating a comprehensive exposure model which uses source emission rates as one of the input parameters.

The following recommendations incorporate investigations of all the candidate compounds except styrene, the xylenes, p-dichlorobenzene and methyl chloroform, as discussed above. The recommended laboratory study of source emissions is broken down into three categories which parallel the similarities in the sources of the compounds which are discussed in Chapter 1. These categories are: 1) emissions of minor constituents from products and materials; 2) consumer product emissions; and 3) environmental tobacco smoke (ETS) emissions. Some of the compounds have multiple sources and can be studied in more than one category. The study plans for the three categories are presented below in order of their suggested priority. The study of emissions of minor constituents from products and materials was given a higher priority than the study of consumer product emissions because it would provide data for more compounds in CARB Group II. The study of emissions from ETS was given the lowest priority because some data already exist for this source. Field studies are recommended as an efficient means to generate additional data predominantly for semivolatile compounds. The field studies are presented last but were not assigned a priority relative to the laboratory studies.

## Laboratory Study of Emissions of Minor Constituents from Products and Materials

This study would investigate the potential emissions of volatile candidate compounds that are minor constituents of products and materials, such as unreacted monomers and chemical intermediates, additives and contaminants.

The compounds recommended for this study are shown in Table 2.1. A number of the compounds are used as monomers or chemical intermediates in the manufacture of various polymeric materials that are incorporated into building materials, interior-finish materials, furnishings and various other consumer products. Traces of monomers and intermediates may persist in some of these materials after production and may subsequently be released in the indoor environment. For example, studies suggest that the release of the unreacted styrene monomer from materials, such as polystyrene insulation, is an important indoor source of this compound. Other compounds are present as plasticizers, other additives or contaminants in products that are used indoors. The volatile monomers and intermediates are 1,3-butadiene, ethyl acrylate, maleic anhydride, phenol, allyl chloride, chloroprene, epichlorohydrin, vinylidene chloride, acrylonitrile and nitrobenzene. Although toluene diisocyanates are considered to be semivolatile by the definition used in this report, they are included in the study because it is likely that useful information about their potential indoor sources can be obtained. The toluene diisocyanates are monomers used in the manufacture of polyurethane products. The other minor constituents included in the proposed study are 1,4-dioxane, propylene oxide, benzyl chloride, chlorobenzene, 1,1-dimethylhydrazine, the N-nitroso compounds and dimethyl sulfate. Acetaldehyde, which is also a minor constituent, was excluded from consideration for this study because it is apparently emitted by a large number of poorly defined non-combustion sources. A field study is a preferable way to obtain additional data for this commonly occurring compound as discussed later.

Table 2.1. Recommendations for a laboratory study of emissions of candidate compounds as minor constituents of products and materials.

| Compound | Potential for Indoor Exposure | CARB Group | Priority Ranking |
|---|---|---|---|
| 1,3-Butadiene | √ | IIA | 1 |
| 1,4-Dioxane | √ | IIB | 1 |
| Ethyl acrylate | √ | IIB | 1 |
| Maleic anhydride | ? | III | 3 |
| Phenol | √ | III | 2 |
| Propylene oxide | √ | IIB | 1 |
| Allyl chloride | √ | III | 2 |
| Benzyl chloride | √ | III | 2 |
| Chlorobenzene | √ | III | 2 |
| Chloroprene | √ | III | 2 |
| Epichlorohydrin | √ | – | 3 |
| Vinylidene chloride | √ | III | 2 |
| Acrylonitrile | √ | IIB | 1 |
| 1,1-Dimethylhydrazine | ? | IIB | 2 |
| Nitrobenzene | √ | III | 2 |
| N-Nitroso compounds | √ | IIB | 1 |
| Toluene diisocyanates | √ | IIB | 1 |
| Dimethyl sulfate | ? | IIB | 2 |

The general approach for the study is to identify possible sources of the compounds, which would then be semiquantitatively screened for emissions in small-scale laboratory experiments. If potentially significant sources are identified in the screening stage, it is recommended that quantitative measurements of emissions from these sources be made under standardized conditions using environmental chambers.

The compounds in Table 2.1 have been assigned a priority ranking for additional study based on their CARB categorization and an assessment of whether there is a potential for indoor exposure. By these criteria, studies of 1,3-butadiene, 1,4-dioxane, ethyl acrylate, propylene oxide, acrylonitrile, the N-nitroso compounds and toluene diisocyanates were given the highest priority for study. All of these compounds are considered to be either possible or probable human carcinogens based on International Agency for Research on Cancer (IARC) criteria or U.S. EPA guidelines. Toluene diisocyanates are notable in that they are potent respiratory irritants and sensitizers even at low airborne concentrations.

Since it is probably not feasible to study all of these compounds, the list of compounds for study may need to be further reduced. For various reasons discussed here, 1,4-dioxane, acrylonitrile and the N-nitroso compounds might be given lower priority relative to the other highest ranked compounds. There are a number of possible consumer sources of 1,4-dioxane including laundry presoaks, glass cleaners, adhesives and architectural coatings. Use of these products is expected to be a more important source of indoor exposure to 1,4-dioxane than passive emissions from products and materials in which it is a minor constituent. Therefore, source emissions of 1,4-dioxane would be most appropriately investigated in the environmental chamber study of consumer products discussed in the following section. The primary use of acrylonitrile is in the manufacture of acrylic fibers for fabric and carpeting. Emissions of the monomer from these highly processed materials may be relatively low. This was tentatively confirmed by one study which was unable to detect emissions of acrylonitrile from samples of fabric and carpet. If the lack of significant indoor sources is confirmed by the results of the ongoing CARB sponsored field study in Woodland, CA, then acrylonitrile could be given lower priority for study. The N-nitroso compounds might be given lower priority because some data for indoor sources are available, including measurements of sidestream emissions of N-nitrosamines from cigarettes and several measurements of emissions of N-nitrosodimethylamine from cooking bacon.

Once the compounds of interest have been selected, the next step is to identify the materials and products that are possible sources of emissions. The information summarized in this report serves as a useful starting point. For some compounds, there are a relatively large number of possible sources. To keep the study to a manageable size, it is recommended that a maximum of about five source categories be selected for each compound. The basis for this selection should be an assessment of whether the potential sources are widely distributed in residences. As examples, source categories for the study of 1,3-butadiene are expected to include products containing styrene-butadiene polymers such as residential nylon carpeting, adhesives and plastic architectural moldings. For the study of ethyl acrylate, likely source categories are products containing acrylic polymers such as latex paints and various waxes, polishes and sealants. Expected source categories for propylene oxide are architectural coatings, adhesives, lubricants and possibly shoe polish. Polyurethane carpet pads, foam furniture cushions, varnishes and caulks are suggested source categories for the study of toluene diisocyanates. The final selection of source categories should be made in consultation with the CARB. A number of products and brands within each source category should be investigated to assess the variability among products and manufacturers.

The next step is to collect representative and uncontaminated samples of the products to be evaluated. An attempt should be made to only obtain samples with known histories since product age and storage conditions may have major effects on emissions. This means that it may be necessary to get samples directly from manufacturers.

The adequacy of sampling and analytical methods for the compounds in this study was not indicated in Table 2.1. In general, potential analytical problems were considered to be less severe for this screening study than for environmental chamber or field studies because the performance requirements are less rigorous. In addition, the overall method can be adapted within certain limits to suit the available analytical methods. Nevertheless, analyses of some compounds are expected to be difficult. For example, it will be necessary to validate methods for highly reactive compounds, such as ethyl acrylate and toluene diisocyanates, prior to conducting the experiments. For the other compounds, samples can probably be trapped and concentrated either cryogenically or with sorbent materials. Most analyses can be performed by gas chromatography (GC) with various detector systems such as flame-ionization detectors (GC/FID), mass spectrometers (GC/MS) and thermal energy analyzers (GC/TEA). The emphasis of screening is on detection of the compounds of interest rather than on quantitation of emissions. Therefore, acceptable limits of detection should be specified as part of the protocols that are developed.

If the screening experiments identify significant sources of the compounds, then quantitative measurements of emission rates from these sources can be made using environmental chambers. It is impossible at this time to know how many sources might be identified. However, if large numbers are found, criteria for selecting sources for this phase of the study will have to be developed. Such criteria should allow for the inclusion of sources in which the CARB may have a special interest and take into account the expected prevalence of use of the sources indoors, the anticipated relative emission rates of the sources and the feasibility of making the measurements.

General recommendations for conducting the chamber experiments are given here. Further discussion of considerations in conducting chamber experiments and in analyzing emission rate data are presented in Chapter 5, "Methods for Measuring Emissions of VOC." Large-scale, room-size, environmental chambers have important advantages over small-scale chambers. They can be used to measure emissions from large sources such as complete pieces of furniture and assemblages of building materials. In addition, their use circumvents some of the problems of trying to properly scale environmental parameters to buildings. The major disadvantage of large-scale chambers is that their operating costs are relatively high. Depending upon the sources that are identified in the screening experiments, the measurements of emission rates may most appropriately be made using large- or small-scale chambers. Regardless of their size, the chambers should be constructed of inert, non-contaminating materials. They should be operated at constant temperature typical of indoor conditions. The ventilation rate should also be constant, and in large-scale chambers, typical of indoor conditions. Operating parameters for small chambers should be adjusted so that factors affecting mass transfer scale appropriately to buildings. This may mean that experiments should be run at ventilation rates that are higher than those typically encountered in buildings. Changes in emission rates over time periods of up to one week should be documented. If adequate resources are available, the effects of environmental parameters and product aging on emission rates can be examined. Replicate experiments should be conducted for some products so that experimental variability can be assessed. In addition, the accuracy and precision of the measurements should be determined.

## Environmental Chamber Study of Emissions from Consumer Products

This study would investigate emissions of volatile candidate compounds resulting from the use of expendable consumer products that are readily available in retail outlets, using an environmental chamber. The compounds for which this is an appropriate method of obtaining additional data are cresols, 1,4-dioxane, glycol ethers and their acetate derivatives, phenol, chlorobenzene, epichlorohydrin and methyl bromide (Table 2.2). All of these are volatile compounds which occur as major ingredients in some consumer products. As a result, exposures are likely to be directly associated with the active use of the products.

Cresols are used in degreasers and paintbrush cleaners and as disinfectants in some household sanitizers. Possible consumer sources of indoor exposure to 1,4-dioxane include architectural coatings, paint/varnish removers, polishes, adhesives, cleaners (*e.g.*, glass cleaners), detergents (*e.g.*, laundry presoaks), fumigants and cosmetics. The glycol ethers and their acetate derivatives are widely used in the manufacture of architectural coatings, paint/varnish removers, inks, adhesives, cleaners and cosmetics. Phenol is used in products as a general disinfectant and biocide. Chlorobenzene is used in paints, polishes, waxes, adhesives and pharmaceuticals. Epichlorohydrin is used as a solvent in architectural coatings. Methyl bromide is widely used as a biocide and has a number of indoor applications as an insecticide, herbicide and fungicide. The suggested ranking for studies of emissions of these compounds is shown in Table 2.2. Dioxane was given the highest priority ranking because it is in CARB Group II. Epichlorohydrin was given the lowest priority ranking because it is not classified as a candidate compound. The other compounds were given an intermediate priority ranking because they are in Group III.

Table 2.2. Recommendations for an environmental chamber study of emissions of candidate compounds from consumer products.

| Compound | Potential for Indoor Exposure | CARB Group | Adequate Sampling and Analysis Method | Priority Ranking |
|---|---|---|---|---|
| Cresols | √ | III | √ | 2 |
| 1,4-Dioxane | √ | IIB | √ | 1 |
| Glycol ethers and acetates | √ | III | √ | 2 |
| Phenol | √ | III | √ | 2 |
| Chlorobenzene | √ | III | √ | 2 |
| Epichlorohydrin | √ | – | ? | 3 |
| Methyl bromide | √ | III | √ | 2 |

The general approach for the study is to: 1) identify and select products which are most likely to result in significant indoor exposures to the compounds; 2) conduct experiments in a room-size environmental chamber using protocols which simulate typical consumer use of the products; and 3) measure emissions and exposures so that these data may be input into appropriate models for total exposure and risk.

The data summarized in this report can be used to identify categories of consumer products which are likely to contain the compounds of interest. Information on the content of specific products is more difficult to obtain. The chemical contents of some products are described on their labels. For other products, the information can be obtained by requesting Material Safety Data Sheets from the manufacturers; however, these are often too generic to be useful for this purpose. Another source of information is the Clinical Toxicology of Commercial Products database which contains information on the composition of many consumer products that can accidentally be ingested. If these data sources are found to be inadequate, then a limited screening study will have to be conducted to at least semi-quantitatively measure the content of the compounds of interest in samples of products which are possible sources.

If a compound is found in a number of products, then priorities must be established for the selection of products to be studied. This will necessitate making a judgement about the relative importance of the products with respect to potential indoor exposure. A variety of information, including product compositions, consumer usage patterns and market data, should be considered. Since at least part of the required information may be difficult or impossible to obtain, some subjective judgement will be required. The final selection should be made in consultation with the CARB.

Emissions of volatile organic compounds from many consumer products tend to be highest when the products are actively being used. A good example of active use is the application of an architectural coating. Consequently, it is recommended that this study be conducted in a room-size environmental chamber so that consumer usage patterns and application techniques can be realistically simulated by an individual using the products. Primary emphasis should be placed on typical product-use scenarios. The dependence of source emissions on various product and environmental parameters can be determined within the limits of the budget. As examples, the effects of variations in application techniques, ventilation rate and temperature could be measured. For some products and conditions, the person using the product can receive an exposure considerably different than would be predicted from an area sample taken in the same room. Therefore, a decision must be made regarding measurements of area concentrations versus personal exposure concentrations, or both. If resources are sufficient, it is recommended that both types of measurements be made.

The next step is to collect representative samples of the products to be evaluated. The samples will then need to be chemically characterized to determine the compositions of the compounds of interest. This information can be used to provide a material balance for the chamber experiments.

A detailed experimental protocol, or plan, needs to be written prior to beginning experiments with each product type. This protocol should describe the operation of the environmental chamber, the product application techniques, the sampling and analytical methods and the quality assurance procedures. It is recommended that sufficient resources be allowed for trial experiments during which the application technique can be evaluated and standardized. Replicate experiments should be conducted for some products as an internal quality assurance check.

The method of data analysis for a consumer product source depends upon the emissions characteristics of the source and on the sampling strategy that is used to make the concentration measurements (see Chapter 5, "Methods for Measuring Emissions of VOC"). If personal exposure and chamber concentrations are continuously measured, exposures can be simply estimated by integrating the areas under the concentration versus time curves. Data analysis can include an evaluation of differences in exposures estimated from personal exposure and chamber concentrations. If experiments are conducted using a range of application procedures and environmental parameters, then variations due to these factors can be explored.

If emissions of all six CARB Group II and III compounds in Table 2.2 were to be studied, then only a few product sources could be investigated per compound due to the relatively high expense of conducting this type of experiment. As a result, it might be difficult to adequately assess the relative significance of the various sources of a given compound. A better strategy would be to focus on only one (*e.g.*, 1,4-dioxane) or a few compounds and conduct experiments using a broader range of sources and experimental conditions.

### Laboratory Study of Environmental Tobacco Smoke Emissions

The final recommended laboratory study is an investigation of emissions of volatile candidate compounds in ETS. The volatile candidate compounds which are associated with ETS are 1,3-butadiene, acetaldehyde, acrolein, cresols, phenol, hydrazine and the N-nitrosamines (Table 2.3). Of these, 1,3-butadiene, acetaldehyde, hydrazine and the N-nitrosamines should be given the highest priority for study because they belong to CARB Group II.

Table 2.3. Recommendations for a laboratory study of emissions of candidate compounds in environmental tobacco smoke.

| Compound | Potential for Indoor Exposure | CARB Group | Adequate Sampling and Analysis Method | Priority Ranking |
|---|---|---|---|---|
| 1,3-Butadiene | √ | IIA | √ | 1 |
| Acetaldehyde | √ | IIA | √ | 1 |
| Acrolein | √ | III | √ | 2 |
| Cresols | √ | III | ? | 2 |
| Phenol | √ | III | √ | 2 |
| Hydrazine | √ | IIB | ? | 1 |
| N-Nitrosamines | √ | IIB | ? | 1 |

Only a few measurements of emissions of candidate compounds in ETS have been reported in the literature. These data can be used to make preliminary estimates of population exposures attributable to this source. However, a laboratory study using consistent methodology would contribute significantly to the available database and to the reliability of the estimates. The general approach for the study is to measure diluted sidestream emission rates of the compounds for a representative sample of American blend cigarettes using a smoking machine and a large-scale environmental chamber.

The experiments should be performed in a large-scale environmental chamber rather than with a sidestream sampler, in order to simulate an environment in which chemical reactions and sorption losses can occur. The chamber should be operated at constant ventilation rate and temperature. Cigarettes should be smoked by machine inside the chamber using a standardized smoking regime with mainstream smoke vented outside the chamber. Machine smoking is preferred over human smoking because it is more reproducible and it eliminates the need for paid human subjects. Samples should be collected on appropriate media after multiple cigarettes have been smoked. Emission rates, expressed as mass of compound emitted per cigarette, can be calculated with a single-equation mass-balance model using the smoking frequency, the chamber volume, the air exchange rate and the sampling time as inputs. Emissions from different brands representative of normal and low-tar cigarettes should be measured. In addition, replicate experiments should be conducted so that confidence intervals can be established for the emission rates.

Accurate and precise analyses of the compounds of interest in chamber air will be difficult because tobacco smoke is a complex chemical mixture which can interfere with the analysis of compounds at low concentration. Acetaldehyde and acrolein can be measured simultaneously by collection on 2,4-dinitrophenylhydrazine coated cartridges with analysis by high performance liquid chromatography (HPLC). Phenol can be collected on sorbent samplers and analyzed by thermal desorption with GC/FID or GC/MS. Butadiene can be collected in evacuated canisters, cryogenically concentrated and analyzed by GC/FID or GC/MS. Procedures for the other compounds are less well defined, and validation studies for sampling and analysis will need to be performed. Cresols and hydrazine in tobacco smoke have been derivatized and analyzed by GC/FID or GC/MS. The nitrosamines have been concentrated in buffered aqueous solution and analyzed by GC/TEA. Improved methods for sampling the N-nitrosamines in both the vapor and particle phases in air are currently being developed at Lawrence Berkeley Laboratory.

Indoor concentrations due to cigarette smoking can be estimated from the experimental data using a time-dependent mass-balance equation. The required inputs are the emission rates per cigarette, the number of smoking occupants, the smoking rate, and the building volume and ventilation rate.

## Field Studies

This literature review identified a number of candidate compounds for which field studies are the best way to obtain additional data on indoor concentrations and personal exposures. All of the semivolatile compounds and one volatile compound fall into this category (Table 2.4). Semivolatile compounds are difficult to study in chamber experiments because they are readily lost to surfaces such as chamber walls and sampling lines due to their low equilibrium vapor pressures. In addition, it is difficult to experimentally simulate inhalation exposure conditions since the compounds may partition between vapor and particle phases in air.

Acetaldehyde is the only volatile compound to be included among the compounds for which field studies are recommended. This compound is used as a specific ingredient in very few products. However, it is expected to be present in most indoor environments since it is emitted by numerous non-combustion and combustion sources. Due to the large number of poorly defined sources of acetaldehyde, laboratory studies of emissions are not an efficient way to obtain additional data on indoor exposures.

Acetaldehyde, di(2-ethylhexyl)phthalate, hexachlorobenzene, 2,4,6-trichlorophenol and toluene diisocyanates were given the highest priority ranking for investigation because they are CARB Group II compounds with known or suspected indoor sources (Table 2.4). Two other Group II compounds, acrylamide and 4,4'-methylenedianiline, have few probable indoor sources and were given a lower priority ranking. Pentachlorophenol and the other chlorophenols were given a lower priority ranking because they are in Group III.

Table 2.4. Recommendations for field studies of indoor concentrations and exposures for candidate compounds.

| Compound | Potential for Indoor Exposure | CARB Group | Adequate Sampling and Analysis Method | Priority Ranking |
|---|---|---|---|---|
| Acetaldehyde | √ | IIA | √ | 1 |
| Di(2-ethylhexyl)phthalate | √ | IIB | √ | 1* |
| Hexachlorobenzene | √ | IIB | √ | 1* |
| Pentachlorophenol | √ | III | √ | 2* |
| Tri- and tetrachlorophenols | √ | IIB, III | √ | 1, 2* |
| Acrylamide | ? | IIB | ? | 2 |
| 4,4'-Methylenedianiline | ? | IIB | √ | 2 |
| Toluene diisocyanates | √ | IIB | ? | 1 |

*Included in ongoing field study.

Indoor concentrations of a number of these compounds are currently being measured in field studies. The study in Woodland, CA, sponsored by the CARB is measuring combined vapor- and particle-phase concentrations of di(2-ethylhexyl)phthalate, hexachlorobenzene, pentachlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol in a probability-based sample of approximately 130 homes. This study includes a pilot-study phase in which sampling and analytical methods were evaluated. Concentrations of di(2-ethylhexyl)phthalate are also being measured using the same methodology in a probability-based sample of homes in Southern California by the Particulate Total Exposure Assessment Methodology (PTEAM) study. This study is jointly sponsored by the U.S. EPA and the CARB. The success of these measurements will to a large extent determine the need for additional field studies for these compounds.

The compounds with the highest priority ranking that are not already being measured in field studies are acetaldehyde and toluene diisocyanates. Any field studies of these compounds should be conducted using probability-based samples of homes. If possible, both indoor concentrations and personal exposures should be measured. It is suggested that acetaldehyde be sampled using cartridges coated with 2,4-dinitrophenylhydrazine with analysis by HPLC. This method would allow for the concurrent measurement of acrolein. Toluene diisocyanates are difficult to analyze because they are highly reactive. Therefore, methods for sampling and analysis of toluene diisocyanates in indoor air must be developed and validated before a field study of these compounds can be undertaken. It is anticipated that the selected method will involve derivatization of the compounds in the sample-collection stage.

## Summary

Based on the results of this literature review, it is recommended that a three-component laboratory study be developed to obtain data on the source emission rates of selected candidate toxic air contaminants. The three study components are listed below in order of their suggested priority.

1. Highest priority should be given to a study that would investigate the potential emissions of volatile candidate compounds that are minor constituents of products and materials, such as unreacted monomers and chemical intermediates, additives and contaminants. It is suggested that emphasis be placed on measurements of 1,3-butadiene, ethyl acrylate, propylene oxide and toluene diisocyanates. Little or no data are currently available on indoor concentrations or source emissions of these CARB Group II compounds.

2. The study with the next highest priority would investigate emissions of volatile candidate compounds resulting from the use of expendable consumer products that are readily available in retail outlets, using an environmental chamber. It is recommended that emphasis be placed on measuring emissions from consumer products containing relatively high concentrations of 1,4-dioxane. Other compounds which are suitable for this type of study are cresols, glycol ethers and their acetate derivatives, phenol, chlorobenzene and methyl bromide.

3. The third laboratory study would measure emissions of volatile candidate compounds in ETS. It is suggested that emphasis be placed on measuring diluted sidestream emission rates of 1,3-butadiene, acetaldehyde, hydrazine and the N-nitrosamines. Study of this source is given lower priority than the other laboratory studies because some limited data on emissions of the compounds from cigarettes are available.

This literature review also identified a number of candidate compounds for which field studies would be the best way to obtain additional data on indoor concentrations and personal exposures. All of the semivolatile compounds fall into this category. Of these, toluene diisocyanates should be given the highest priority for study. Acetaldehyde is the only volatile compound for which field studies are recommended.

# CHAPTER 3

# Introduction

## Background

The California Air Resources Board (CARB) is implementing a program to identify and control toxic air contaminants. The status of this program is indicated in an annually updated list of substances of concern in California. The "Toxic Air Contaminant Identification List, February, 1990," groups these substances into four categories (Table 3.1). The substances in Group I have already been identified as toxic air contaminants by the CARB. Groups IIA and IIB contain those substances that have been nominated for review, but are not yet classified as toxic air contaminants. The substances in Group IIA are already in the formal review process, while those in Group IIB have not yet been scheduled for review. Group III contains compounds for which more health effects data are needed before review can begin.

California Health and Safety Code 39660.5 requires the CARB to consider indoor exposures in assessing the risks to public health posed by candidate toxic air contaminants. Consequently, there is a need for information that is applicable to California on the indoor concentrations and personal exposures for the candidate compounds. The quality and quantity of the existing data vary considerably among the compounds. For some compounds, the existing indoor concentration data may adequately fulfill the CARB's mandate. However, for many, the sources of indoor exposure have not been fully identified, and no, or only limited, indoor concentration data are available. To directly obtain more information, the CARB is currently sponsoring several field studies. One study is being conducted in Woodland, CA (Sheldon, 1990a). For the second phase of the study, indoor concentrations and personal exposures for a number of candidate compounds will be measured for a probability-based sample of approximately 130 homes. Another study is being conducted in Riverside, CA, as a collaborative effort with the U.S. EPA's Particulate Total Exposure Methodology (PTEAM) study (Sheldon, 1990b). In this study, concentration data will be obtained for selected semivolatile and particulate-phase compounds in a sample of approximately 175 homes. Because of the expense and difficulty of measuring concentrations and exposures over all pertinent indoor conditions using field surveys, the CARB has initiated a research effort to identify indoor sources and measure source emission rates of selected candidate compounds. This literature review represents the first phase of that effort. Ultimately, source emissions data will be used in a total exposure model to estimate exposures for the selected compounds under a variety of indoor conditions. Data on lifestyles, activity patterns, product usages and housing-stock characteristics will also be utilized as inputs to the model (Jenkins *et al.*, 1990).

## Study Objectives

This literature study was performed to evaluate the existing data on selected candidate toxic air contaminants not yet in the formal CARB review process. The specific objectives were to: 1) compile and review the existing data on the potential indoor uses and sources, the indoor concentrations and exposures, and the source emissions of candidate organic compounds; 2) evaluate the adequacy of these data with respect to the goals of the CARB; and 3) identify those compounds for which laboratory studies of source emissions would be a suitable way to obtain data inputs for a model of total exposure.

## Reviewed Compounds

This study was primarily restricted to volatile and semivolatile organic compounds in Groups IIB and III of the "Toxic Air Contaminant Identification List, February, 1990." Several broad categories of compounds in these groups were specifically excluded from review by agreement with the CARB. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls were excluded because they are mixtures of predominantly particle-phase compounds with generally different routes of exposure than vapor-phase compounds. The PAH are being investigated in current field studies (*e.g.*, Sheldon, 1990b). Environmental tobacco smoke (ETS) was excluded because it is an aerosol containing a complex mixture of hundreds of compounds which warrants separate study. Coke-oven emissions were excluded because they typically do not have a direct impact on indoor environments. Radionuclides were excluded because radon is the most important radionuclide with respect to indoor exposures and is under separate study by the CARB. Finally, the metals, beryllium, lead, manganese and mercury, were excluded. These pollutants, which are generally from controlled outdoor sources, are predominantly particle-phase compounds with different routes of exposure than vapor-phase compounds. In addition, some data on indoor concentrations of the metals, which are expected to be low, are being obtained from the PTEAM study (Sheldon, 1990b). At the request of the CARB Project Manager, acetaldehyde and 1,3-butadiene, two Group IIA compounds already in the review process, were included. Epichlorohydrin, which is not on the identification list, was also included at the request of the Project Manager.

All of the compounds included in the study are listed in Table 3.2. There are a total of 47 individual compounds. The majority of these are volatile organic compounds (VOC). For the purposes of this study, VOC are simply defined as organic compounds with atmospheric-pressure boiling points of 250° C, or less. They exist predominantly in the vapor phase, and inhalation is often the primary route of exposure. The reviewed compounds have been divided into five chemical classes: hydrocarbons, oxygen-containing compounds, halogen-containing compounds, nitrogen-containing compounds, and sulfur-containing compounds. Within each class, the compounds are arranged alphabetically. This is the order in which the compounds are presented in Chapter 4, "Compound Reviews." Table 3.2 also lists the Chemical Abstract Service (CAS) registry number, the chemical formula, the molecular weight, the boiling point, and common synonyms for each compound. The CARB categorization of the reviewed compounds is shown in Table 3.3, which lists the compounds in the order in which they appear on the February, 1990, identification list (Table 3.1). In some cases, only structural isomers (*e.g.*, xylenes) or groups of related compounds (*e.g.*, glycol ethers) are listed. As a cross reference, the page numbers of the compound reviews are included in Table 3.3.

Table 3.1.

## TOXIC AIR CONTAMINANT IDENTIFICATION LIST
## FEBRUARY 1990

I. Substances identified as toxic air contaminants by the Air Resources Board, pursuant to the provisions of AB 1807.

asbestos, benzene, cadmium, carbon tetrachloride, chlorinated dioxins and dibenzofurans (15 species), chromium (VI), ethylene dibromide, ethylene dichloride, ethylene oxide, methylene chloride

II. Substances currently under review for identification as toxic air contaminants, scheduled for review, or nominated for review but not yet scheduled. It will be necessary to develop information on exposure in California to some substances in this category before pursuing review.

A. (Substances already in the review process.) acetaldehyde, benzo(a)pyrene, 1,3-butadiene, chloroform, diesel exhaust, formaldehyde, inorganic arsenic, nickel, perchloroethylene, trichloroethylene, vinyl chloride

B. (Substances not yet under review.) acrylamide, acrylonitrile, beryllium, coke-oven emissions, dialkylnitrosamines, p-dichlorobenzene, 1,1-dimethylhydrazine, di(2-ethylhexyl)phthalate, 1,4-dioxane, dimethyl sulfate, environmental tobacco smoke, ethyl acrylate, hexachlorobenzene, hydrazine, inorganic lead, mercury, 4,4'-methylenedianiline, N-nitrosomorpholine, PAHs, PCBs, propylene oxide, radionuclides, styrene, toluene diisocyanates, 2,4,6-trichlorophenol

III. Compounds for which health effects information is limited or not yet sufficient to support review. Substances in this category are produced and emitted to the air in quantities which might make them of concern at such time as health effects information is strong enough to support review.

acrolein, allyl chloride, benzyl chloride, chlorobenzene, chlorophenols, chloroprene, cresols, glycol ethers, maleic anhydride, manganese, methyl bromide, methyl chloroform, nitrobenzene, phenol, vinylidene chloride, xylenes

## Methods

The first steps in this study were to identify and assemble the available literature on the indoor uses and sources, the indoor concentrations and exposures, and the source emissions of the selected compounds. Literature citations were obtained from a manual search of the investigators' reprint files and from computerized searches of the CAS and National Technical Information Services (NTIS) databases. Hard copies or microfiche of the relevant journal articles, conference proceedings and reports not already on hand were obtained through the University of California library system, from NTIS, and directly from the authors and sponsor organizations. Additional references were extracted from the literature citations in these articles, proceedings and reports. Information was also obtained from several specialized data sources as discussed below.

The CAS database contains bibliographic citations for approximately 8.4 million references published world wide in the last two decades. The search of this database was restricted in that patents and non-English language references were excluded. The searches were conducted using the CAS numbers of the compounds. References for the compounds were searched by categories which encompass a wide range of indoor uses and sources of VOC. These categories included biocides (*e.g.*, pesticides, insecticides, wood preservatives, antiseptics and disinfectants), architectural materials (*e.g.*, general building materials, adhesives, glues, sealants, caulks and insulation), solvents (*e.g.*, paints, stains, inks and copier fluids), lubricants, interior furnishings (*e.g.*, carpets, upholstery and drapery), personal-care and household products (*e.g.*, soaps, cosmetics, shampoos, deodorizers, cleaners, stain removers, fabric softeners, and waterproofing and mothproofing agents), and combustion gases. The NTIS database, which contains bibliographic citations for U.S. government reports, was searched using similar categories.

The CAS database was accessed using the STN International information network (Cincinnati, OH), which allows retrieval of abstracts, key words, and compound and subject index terms for each citation. Retrieved records were down loaded to diskette from the on-line system. These records were reformatted and entered into a bibliographic database on an IBM-compatible personal computer using "Biblio-Links" and "Pro-Cite" software (Personal Bibliographic Software, Inc., Ann Arbor, MI). Records obtained from the NTIS database were handled in a similar fashion. References found through other sources were added manually to the Pro-Cite database. The created database consists of approximately 225 bibliographic records, many of which have abstracts, key words, and compound and subject index terms. The database can be searched and sorted using any or all selected fields.

Additional information on the uses, sources, indoor concentrations and source emissions of the compounds was extracted from five other major data sources: 1) the Clinical Toxicology of Commercial Products (CTCP) database, 2) the Hazardous Substances Data Bank (HSDB), 3) the NASA/McDonnell Douglas Materials Testing Data Base, 4) the National Volatile Organic Compound (NVOC) database, and 5) the California Total Exposure Assessment Methodology (TEAM) studies.

The CTCP database (CTCP, 1990), which is based on the book of the same name, is part of the Chemical Information System (CIS) network (Baltimore, MD). It contains information on the composition of more than 15,000 non-food consumer products that could accidently be ingested. Ingredient lists are provided and edited by the companies that manufacture or market the products. In some cases, quantitative compositional information is also given. The database can be searched using product trade names, manufacturers names, specific compounds, or product-use categories. Toxicity data are also available.

Table 3.2. Data for candidate compounds reviewed by this study.

| Compound | CAS No. | Formula | Molecular Weight | Boiling Point °C | Synonym |
|---|---|---|---|---|---|
| Hydrocarbons | | | | | |
| 1,3-Butadiene | 106-99-0 | $C_4H_6$ | 54 | -4 | bivinyl |
| Styrene | 100-42-5 | $C_8H_8$ | 104 | 145 | ethenylbenzene |
| Xylene isomers | 1330-20-7 | | | | |
| o-Xylene | 95-47-6 | $C_8H_{10}$ | 106 | 144 | 1,2-dimethylbenzene |
| m-Xylene | 108-38-3 | $C_8H_{10}$ | 106 | 139 | 1,3-dimethylbenzene |
| p-Xylene | 106-42-3 | $C_8H_{10}$ | 106 | 138 | 1,4-dimethylbenzene |
| Oxygenated Compounds | | | | | |
| Acetaldehyde | 75-07-7 | $C_2H_4O$ | 44 | 21 | |
| Acrolein | 107-02-8 | $C_3H_4O$ | 56 | 53 | propenal |
| Cresol isomers | 1319-77-3 | | | | |
| o-Cresol | 95-48-7 | $C_7H_8O$ | 108 | 191 | 2-hydroxytoluene |
| m-Cresol | 108-39-4 | $C_7H_8O$ | 108 | 202 | 3-hydroxytoluene |
| p-Cresol | 106-44-5 | $C_7H_8O$ | 108 | 202 | 4-hydroxytoluene |
| Di(2-ethylhexyl)phthalate | 117-81-7 | $C_{24}H_{38}O_4$ | 390 | 384 | di-sec-octyl phthalate |
| 1,4-Dioxane | 123-91-1 | $C_4H_8O_2$ | 88 | 101 | diethylenedioxide |
| Ethyl acrylate | 140-88-5 | $C_5H_8O_2$ | 100 | 100 | 2-propenoic acid ethyl ester |
| Glycol ethers and acetates | | | | | |
| 2-Butoxyethanol | 111-76-2 | $C_6H_{14}O_2$ | 118 | 171 | butyl Cellosolve |
| 2-Ethoxyethanol | 110-80-5 | $C_4H_{10}O_2$ | 90 | 135 | Cellosolve |
| 2-Ethoxyethyl acetate | 111-15-9 | $C_6H_{12}O_3$ | 132 | 156 | Cellosolve acetate |
| 2-Methoxyethanol | 109-86-4 | $C_3H_8O_2$ | 76 | 125 | methyl Cellosolve |
| 2-Methoxyethyl acetate | 110-49-6 | $C_5H_{10}O_3$ | 118 | 145 | methyl Cellosolve acetate |
| Maleic anhydride | 108-31-6 | $C_4H_2O_3$ | 98 | 198 | 2,5-furandione |
| Phenol | 108-95-2 | $C_6H_6O$ | 94 | 182 | |
| Propylene oxide | 75-56-9 | $C_3H_6O$ | 58 | 34 | 1,2-epoxypropane |
| Halogenated Compounds | | | | | |
| Allyl chloride | 107-5-1 | $C_3H_5Cl$ | 76 | 45 | 3-chloro-1-propene |
| Benzyl chloride | 100-44-7 | $C_7H_7Cl$ | 126 | 179 | chloromethyl benzene |
| Chlorobenzene | 108-90-7 | $C_6H_5Cl$ | 112 | 132 | phenyl chloride |
| Chloroprene | 126-99-8 | $C_4H_5Cl$ | 88 | 59 | 2-chloro-1,3-butadiene |
| p-Dichlorobenzene | 106-46-7 | $C_6H_4Cl_2$ | 146 | 174 | 1,4-dichlorobenzene |
| Epichlorohydrin | 106-89-8 | $C_3H_5ClO$ | 92 | 118 | chloromethyloxirane |
| Hexachlorobenzene | 118-74-1 | $C_6Cl_6$ | 282 | 322 | |
| Methyl bromide | 74-83-9 | $CH_3Br$ | 94 | 4 | bromomethane |
| Methyl chloroform | 71-55-6 | $C_2H_3Cl_3$ | 132 | 74 | 1,1,1-trichloroethane |
| Pentachlorophenol | 87-86-5 | $C_6HCl_5O$ | 264 | 310 | |
| Tri- and tetrachlorophenols | | | | | |
| Tetrachlorophenols | 25167-83-3 | $C_6H_2Cl_4O$ | 230 | sublimes | |
| 2,4,5-Trichlorophenol | 95-95-4 | $C_6H_3Cl_3O$ | 196 | sublimes | |
| 2,4,6-Trichlorophenol | 88-06-2 | $C_6H_3Cl_3O$ | 196 | 246 | |
| Vinylidene chloride | 75-35-4 | $C_2H_2Cl_2$ | 96 | 37 | 1,1-dichloroethene |

Table 3.2. Continued. Data for candidate compounds reviewed by this study.

| Compound | CAS No. | Formula | Molecular Weight | Boiling Point °C | Synonym |
|---|---|---|---|---|---|
| Nitrogenated Compounds | | | | | |
| Acrylamide | 79-06-1 | $C_3H_5NO$ | 71 | 125[a] | propenamide |
| Acrylonitrile | 107-13-1 | $C_3H_3N$ | 53 | 78 | 2-propenenitrile |
| Dimethylhydrazine | 57-14-7 | $C_2H_8N_2$ | 60 | 64 | |
| Hydrazine | 302-01-2 | $H_4N_2$ | 32 | 114 | |
| 4,4'-Methylenedianiline | 101-77-9 | $C_{13}H_{14}N_2$ | 198 | 398 | |
| Nitrobenzene | 98-95-3 | $C_6H_5NO_2$ | 123 | 211 | |
| N-Nitroso compounds | | | | | |
| N-Nitrosodiethylamine | 55-18-5 | $C_4H_{10}N_2O$ | 102 | 177 | |
| N-Nitrosodimethylamine | 62-75-9 | $C_2H_6N_2O$ | 74 | 154 | |
| N-Nitrosomorpholine | 59-89-2 | $C_4H_8N_2O_2$ | 116 | NA[b] | |
| Toluene diisocyanates | | | | | |
| Toluene-2,4-diisocyanate | 584-84-9 | $C_9H_6N_2O_2$ | 174 | 251 | |
| Toluene-2,6-diisocyanate | 91-09-7 | $C_9H_6N_2O_2$ | 174 | 131[c] | |
| Sulfur Containing Compounds | | | | | |
| Dimethyl sulfate | 77-78-1 | $C_2H_6O_4S$ | 126 | 189 | sulfuric acid dimethyl ester |

[a] At 25 mm Hg pressure.
[b] Not available
[c] At 18 mm Hg pressure.

The CTCP database was searched using the CAS numbers of the compounds. For each compound, the database gave either a negative response or a list of products that had the compound as an ingredient. These products were grouped into generic categories and counted, as shown in the tables in Chapter 4. The assignment of a given product to a particular generic category was based on the usage information provided by the database. In some cases, particularly for insecticides and herbicides, it was not clear whether the product would be available to the general public. If it was obvious from the database record that the product was intended for industrial or municipal use, it was not counted. In some instances, a given product was listed more than once, sometimes because a change in formulation had occurred. In these cases, the product was counted only once. Because much of the interpretation of the search results was subjective, the quantitative aspects of these summaries are only approximate. The database does, however, provide useful qualitative information on the general sources of these compounds in indoor air.

The HSDB (HSDB, 1990) is a factual, non-bibliographic database that focuses primarily on the toxicology of more than 4,100 potentially hazardous chemicals. The data are derived from a core set of standard reference texts (*e.g.*, Patty's Industrial Hygiene, The Merck Index, Hawley's, Kirk-Othmer) and monographs (*e.g.*, International Agency for Research on Cancer {IARC} publications) supplemented with information from government sources, technical reports and the primary literature. It also contains information on emergency handling procedures, human exposures, analytical methods and environmental fates. The HSDB is peer reviewed by a panel of experts from its major subject fields. It is accessible through the U.S. National Library of Medicine's Toxicology Data Network (Bethesda, MD). For this

Table 3.3. CARB categorization of candidate compounds.

| Compound | Page |
|---|---|
| Group IIA | |
| 1,3-Butadiene | 44 |
| Acetaldehyde | 63 |
| *Not Reviewed* -- benzo(a)pyrene, chloroform, diesel exhaust, formaldehyde, inorganic arsenic, nickel, perchloroethylene, trichloroethylene | |
| Group IIB | |
| Acrylamide | 134 |
| Acrylonitrile | 135 |
| Dialkylnitrosamines | 141 |
| p-Dichlorobenzene | 107 |
| 1,1-Dimethylhydrazine | 137 |
| Di(2-ethylhexyl)phthalate | 77 |
| 1,4-Dioxane | 80 |
| Dimethyl sulfate | 150 |
| Ethyl acrylate | 84 |
| Hexachlorobenzene | 116 |
| Hydrazine | 138 |
| 4,4'-Methylenedianiline | 139 |
| N-Nitrosomorpholine | 141 |
| Propylene oxide | 94 |
| Styrene | 47 |
| Toluene diisocyanates | 148 |
| 2,4,6-Trichlorophenol | 131 |
| *Not reviewed* -- beryllium, coke-oven emissions, environmental tobacco smoke, inorganic lead, mercury, PAHs, PCBs, radionuclides | |
| Group III | |
| Acrolein | 70 |
| Allyl chloride | 97 |
| Benzyl chloride | 99 |
| Chlorobenzene | 101 |
| Chlorophenols | 128 |
| Chloroprene | 106 |
| Cresols | 75 |
| Glycol ethers | 85 |
| Maleic anhydride | 89 |
| Methyl bromide | 118 |
| Methyl chloroform | 120 |
| Nitrobenzene | 140 |
| Phenol | 90 |
| Vinylidene chloride | 132 |
| Xylenes | 54 |
| *Not reviewed* -- manganese | |

study, printouts of the database's manufacturing and use files were obtained for each compound through an on-line search using CAS numbers. The pertinent information from those files was summarized.

The NASA/McDonnell Douglas Materials Testing Data Base contains the results of a study of emissions of VOC from over 5,000 materials, either considered for use in the construction of space-shuttle cabins or likely to be used by crew members of the space shuttles (McDonnell Douglas Corp., 1986). The purpose of this study was to identify and eliminate those materials which might have high emissions and, therefore, pollute the cabin atmosphere. Many of the evaluated materials were specialized assemblies, but a large number were common construction or household items, such as paints, adhesives, pens, and cosmetics.

Emissions in the NASA study were measured in closed containers with a minimum volume of two liters. Specimens were placed in the containers at an initial pressure of 12 psia (620 torr). The net sample loading was typically five grams per liter of container volume. The containers were then heated to 49° C for 72 hours, after which samples of headspace gas were collected and analyzed by gas chromatography/mass spectrometry (GC/MS). The results were reported as $\mu$g of compound emitted per gram of material. This method served its purpose as a relatively simple screening tool for identifying high emitting materials among a large number of materials. However, since it employed closed containers, the concentrations of VOC entering the gas phase were probably limited in many cases by equilibrium effects (see Chapter 5). Therefore, the measured concentrations of VOC may not directly correspond to the chemical compositions of the materials or to the emissions of VOC from these materials under actual conditions in buildings. For example, Baechler *et al.* (1989) only had limited success in comparing the NASA data for paints with two other studies of emissions of VOC from paints. Another limitation of the NASA study with respect to the possible use of the data in models for indoor air quality is that the method did not allow for the measurement of actual emission rates.

The NASA/McDonnell Douglas database is available for use on IBM-compatible personal computers and can be searched by compound. The database contains records for 17 of the candidate compounds under review. Firstly, listings were obtained of all of the materials which emitted these compounds. These materials were placed into generic categories based on the descriptions provided in the database. Specialized assemblies (*e.g.*, electronic equipment, computers, cameras) and other obviously industrial materials were omitted from consideration. The number of commercially available materials in each category were then summed. In a number of cases, particularly for biocides, the decision as to the commercial availability of a material was highly subjective because of the limited information contained in the descriptions. The data are summarized in tabular form in the compound reviews in Chapter 4. Where applicable, the range and median values of the measured concentrations are reported along with the numbers of materials in each category.

The National Volatile Organic Compound (NVOC) database was first prepared for the U.S. EPA in 1983 (Brodzinsky and Singh, 1983) and later updated (Shah and Heyerdahl, 1988). This effort to summarize the available data on the distributions of VOC concentrations in outdoor and indoor air is discussed by Shah and Singh (1988). All available outdoor data and indoor data for residential and commercial buildings and personal exposures were gathered. Then, every effort was made to achieve internal consistency by eliminating data inconsistencies, duplications, unsupported methodologies, and numerical errors. Quality codes were assigned to each reference based on the authors' subjective evaluations of the reliability of the data. The authors point out the inherent limitations of data which come from a wide variety of studies with different objectives and methodologies and caution that the database is best used as a screening tool.

The most recent NVOC database includes a total of 66 VOC measured in indoor environments. For a number of these compounds, the primary data source was the U.S. EPA TEAM studies conducted prior to 1987. The results of the TEAM studies have been presented in a number of publications and are summarized by Wallace (1987). The studies, which used a consistent methodology, were designed to measure human exposures to toxic VOC in air and drinking water. Random samples of residents were selected for participation in the studies which were conducted in several different communities. In some cases, return visits were made to these communities in different seasons. For each participant, samples of outdoor air and personal air were collected for day and night periods and analyzed for a selected number of toxic VOC. Breath samples and drinking water samples were also collected and analyzed for the same compounds. The overnight personal exposure samples were collected with the sampling pumps located at the participants' bedsides during the time they slept but also included any periods away from home. For most participants, the overnight samples provide reasonable measures of VOC concentrations in indoor air . In total, the pre-1987 TEAM studies produced almost 2,000 samples of personal (day-time) and indoor (night-time personal) air.

The entire NVOC database is available from NTIS on diskettes for use on IBM-compatible personal computers. However, the printed project report (Shah and Heyerdahl, 1988) was used as the source for this study. This report lists the number of data points and the mean, median, and lower and upper quartile concentrations for each compound. In this form, the data provide information on the expected distributions of the concentrations and on the form of these distributions. For some compounds which occur ubiquitously in indoor and outdoor air, the concentrations may have nearly log-normal distributions. For other compounds which have unique sources that are not widely found in residences, the distributions of concentrations may be highly skewed.

The California TEAM studies were conducted in 1984 and 1987 in and around Los Angeles and in 1984 in Contra Costa County (Pellizarri *et al.*, 1987; Wallace *et al.*, 1989). The same compounds were measured and the same methodologies were used in these studies as in the TEAM studies conducted in other communities.

## Organization

The data on the potential indoor uses and sources, the indoor concentrations, and the source emissions of the 47 compounds under review are summarized and evaluated in Chapter 4, "Compound Reviews." This chapter is divided into sections for the individual compounds. Structural isomers, and some groups of related compounds are reviewed together in a section. Each section is divided into five subsections: "Uses and Sources," "Concentration Data," "Emissions Data," "Summary," and "References."

Under "Uses and Sources," the general uses of the compound are described, and the possible indoor sources are identified. The primary information sources for this subsection were the CTCP database and the HSDB. In addition, any qualitative emissions data reported in the literature are presented here. Data on indoor concentrations are summarized under "Concentration Data." When available, data which show the frequency distributions of the concentrations in indoor air in California are presented. Data originally reported as mass of compound per volume of air were converted to molar volume ratios expressed typically as parts-per-billion by volume (ppbv). Standard conditions for indoor air (*i.e*, 25° C, 1 atm) were assumed in making these conversions. Conversion factors for each compound are presented in Table 3.4. For a number of the compounds, no data on indoor concentrations were found. Reported measurements of emissions are summarized in the "Emissions Data" subsection. These data range from simple emissions reported as mass of compound emitted per unit measure of source to, in a few cases, actual emission rates reported as mass emitted per unit source per unit time. For many of the compounds, no quantitative data on emissions were found. In the "Summary" subsection, the adequacy of the data for estimating indoor concentrations and exposures in California is discussed. If additional data are needed, methods for efficiently acquiring these data are recommended. Each section concludes with a "References" subsection which gives the literature citations used in the preparation of the review.

In Chapter 5, "Methods for Measuring Emissions of VOC," the various methods which have been used to estimate and measure emissions of VOC from sources are reviewed. The appropriate uses and the limitations of these methods are assessed. The chapter concludes with discussions of specific aspects of emissions experiments conducted in environmental chambers. The information presented in this chapter can be used as a general guide for evaluating and selecting methods for measuring emissions of VOC from materials and products that are used indoors.

In Chapter 2, "Recommendations," a plan is presented for a multi-component study which can be developed to provide additional data for selected candidate compounds either on source emission rates or on indoor concentrations and exposures. This plan is based on the reviews of the literature on the individual compounds and on methods for measuring emission rates. Both laboratory and field studies are recommended. The laboratory studies are organized into three categories which parallel the sources of the compounds to be investigated. Research priorities are established among the laboratory studies and among compounds within each of these studies.

The Appendix is a listing of all of the reference citations contained in the bibliographic database that was created as part of this study. This database contains the citations that were found on the indoor sources, indoor concentrations, and source emissions of the 47 compounds under review and on methods used to measure emissions of VOC. The database was created using an IBM-compatible personal computer and the "Pro-Cite" bibliographic software package. Most of the records contain abstracts, key words, and compound and subject index terms. The database can be searched and sorted by a number of fields for each record.

Table 3.4. Conversion factors for concentration units at standard conditions (25° C, 1 atm).

| Compound | 1 µg/m$^3$ = x ppbv where x = | 1 ppbv = x µg/m$^3$ where x = |
|---|---|---|
| Hydrocarbons | | |
| 1,3-Butadiene | 0.453 | 2.21 |
| Styrene | 0.235 | 4.26 |
| Xylene isomers. | 0.231 | 4.33 |
| Oxygenated Compounds | | |
| Acetaldehyde | 0.556 | 1.80 |
| Acrolein | 0.437 | 2.29 |
| Cresol isomers | 0.226 | 4.42 |
| Di(2-ethylhexyl)phthalate | 0.063 | 16.00 |
| 1,4-Dioxane | 0.278 | 3.60 |
| Ethyl acrylate | 0.245 | 4.09 |
| Glycol ethers and acetates | | |
| 2-Butoxyethanol | 0.207 | 4.83 |
| 2-Ethoxyethanol | 0.272 | 3.68 |
| 2-Ethoxyethyl acetate | 0.185 | 5.40 |
| 2-Methoxyethanol | 0.322 | 3.11 |
| 2-Methoxyethyl acetate | 0.207 | 4.83 |
| Maleic anhydride | 0.249 | 4.01 |
| Phenol | 0.260 | 3.84 |
| Propylene oxide | 0.422 | 2.37 |
| Halogenated Compounds | | |
| Allyl chloride | 0.322 | 3.11 |
| Benzyl chloride | 0.194 | 5.15 |
| Chlorobenzene | 0.218 | 4.58 |
| Chloroprene | 0.278 | 3.60 |
| p-Dichlorobenzene | 0.167 | 5.97 |
| Epichlorohydrin | 0.266 | 3.76 |
| Hexachlorobenzene | 0.087 | 11.50 |
| Methyl bromide | 0.257 | 3.89 |
| Methyl chloroform | 0.185 | 5.41 |
| Pentachlorophenol | 0.093 | 10.80 |
| Tetrachlorophenol isomers | 0.106 | 9.41 |
| Trichlorophenol isomers | 0.125 | 8.02 |
| Vinylidene chloride | 0.255 | 3.93 |
| Nitrogen Containing Compounds | | |
| Acrylamide | 0.344 | 2.90 |
| Acrylonitrile | 0.461 | 2.17 |
| 1,1-Dimethylhydrazine | 0.408 | 2.45 |
| Hydrazine | 0.764 | 1.31 |
| 4,4'-Methylenedianiline | 0.123 | 8.10 |
| Nitrobenzene | 0.199 | 5.03 |
| N-Nitrosodiethylamine | 0.240 | 4.17 |
| N-Nitrosodimethylamine | 0.330 | 3.03 |
| N-Nitrosomorpholine | 0.211 | 4.74 |
| Toluene diisocyanate isomers | 0.141 | 7.12 |
| Sulfur Containing Compounds | | |
| Dimethyl sulfate | 0.194 | 5.15 |

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# CHAPTER 4

# Compound Reviews

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# 1,3-Butadiene

## Uses and Sources

The compound 1,3-butadiene (butadiene) is used primarily as a comonomer in various types of synthetic rubbers and resins, such as styrene-butadiene and nitrile rubbers (HSDB, 1990). A major source of butadiene in indoor air is environmental tobacco smoke (ETS).

## Concentration Data

Data on indoor concentrations of butadiene are very limited. Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for air toxics. Samples for very volatile organic compounds were collected in four houses using 6-liter SUMMA-polished canisters and were analyzed by GC/MS. Three of the houses had concentrations in excess of the 0.12 $\mu g/m^3$ (0.054 ppbv) detection limit. The mean concentration for all four houses was 0.64 $\mu g/m^3$ (0.29 ppbv). Outdoor concentrations were higher.

All other measurements have been made in rooms contaminated with tobacco smoke. Löfroth *et al.* (1989) made two measurements in a tavern in North Carolina. Samples were collected in evacuated canisters and analyzed by GC. The room was approximately 180 $m^3$ in size and was occupied over the course of the sampling period by 5 to 25 persons, many of whom were smoking. Brunnemann *et al.* (1989) measured concentrations of butadiene from ETS in a laboratory and a smoke-filled bar. In the laboratory experiments, 5 to 10 cigarettes were concurrently smoked by a smoking machine over the course of the one-hour sampling period. Samples were taken with ventilation ducts both open and closed. The air exchange rate in the former case was 12 $h^{-1}$. Samples were collected in methanol using midget impingers. A similar method was used in a smoke-filled bar to collect a three-hour sample. The significant parameters and results for both studies are summarized in Table 4.1.

Table 4.1. Airborne concentrations of 1,3-butadiene due to cigarette smoke (from Löfroth *et al.*, 1989; Brunnemann *et al.* 1989).

| Study | Type of building | Occupancy | Ventilation | Concentration (ppbv) |
|---|---|---|---|---|
| Löfroth *et al.* | Tavern (180 $m^3$) | 5-25 | ? | 8.6[a] |
| | Tavern (180 $m^3$) | 5-25 | ? | 5.0[a] |
| Brunnemann *et al.* | Laboratory (16 $m^3$) | --[b] | low | 4.3 |
| | Laboratory (16 $m^3$) | --[c] | 12 $h^{-1}$ | 0.34 |
| | Bar | 5-15 smokers[d] | ? | 1.8 |

[a] Converted from mass/volume units.

[b] 5 cigarettes smoked concurrently (average of 4 runs), lab vents closed.

[c] 5 cigarettes smoked concurrently (average of 2 runs), lab vents open.

[d] 3-hour samples on 2 different days.

## Emissions Data

Sidestream cigarette smoke is a major source of butadiene in indoor air. Löfroth *et al.* (1989) calculated the average emission of butadiene to be 400 µg per cigarette based on measurements made in a 13.6 $m^3$ Plexiglass environmental chamber with controlled air exchange and smoking rates. The cigarettes were machine smoked, and the mainstream smoke was vented outside the chamber.

Brunnemann *et al.* (1989) analyzed sidestream and mainstream smoke from six different types of cigarettes, five of which were purchased on the open market. The cigarettes were smoked by machine in a glass chamber. Sidestream smoke was trapped in methanol using midget impingers and analyzed by GC/MS. The results are shown in Table 4.2. The range for sidestream smoke is 205-361 µg per cigarette which is similar to the chamber results obtained by Löfroth *et al.* (1989).

Table 4.2. Content of 1,3-Butadiene in sidestream and mainstream cigarette smoke (from Brunnemann *et al.*, 1989).

| | Butadiene emission (µg/cig.) | |
|---|---|---|
| Cigarette Type | Sidestream | Mainstream |
| Ky1R4F | 361 | 66 |
| Non-filter | 250 | 60 |
| Filter A | 207 | 54 |
| Charcoal filter | 247 | 54 |
| Low tar | 205 | 16 |
| Low side-stream smoke | 223 | - |

Vehicle exhaust and evaporative emissions of fuel from vehicles may enter the living space of houses with attached garages. Cohen *et al.* (1988) found a strong correlation between indoor concentrations of six chemicals associated with gasoline and the presence of an attached garage. As part of a study on automobile emissions, Sigsby *et al.* (1987) made a detailed analysis of the fuels used in their experiments. They could not separate butadiene from *n*-butane using their analytical procedure. The pair comprised 7.8 percent of the total hydrocarbons present in a regular no-lead gasoline and 3.5 percent of a premium gasoline.

## Summary

Indoor concentration data for butadiene are very limited, partly because investigators typically do not sample or analyze for this compound.

Butadiene is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

It is not known if butadiene is released as a residual monomer from synthetic materials such as styrene-butadiene rubber which is used extensively in building interiors. Butadiene is emitted by cigarettes and will be present in environments contaminated with ETS.

It is recommended that butadiene be included in a laboratory study of emissions of minor constituents from products and materials. Styrene-butadiene rubber is a possible source of this compound. A common product which contains styrene-butadiene rubber is residential nylon carpeting. In addition, emissions of butadiene in the sidestream smoke of cigarettes could be investigated in a laboratory study of ETS. Since some data are available for cigarette emissions, this study should be given lower priority than the study of emissions of the monomer from products and materials. In general, butadiene should be given high priority for laboratory studies because it is in CARB Group II.

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# Styrene

## Uses and Sources

Styrene is used in the manufacture of plastics, resins, synthetic rubber, fiber-glass and paint. It is also used as an artificial flavoring agent (HSDB, 1990). The CTCP (1990) database does not contain any listings for consumer products containing styrene.

In qualitative analyses, emissions of styrene have been detected from plywood, particle board and carpeting (Monteith *et al.*, 1984; Miksch *et al.*, 1982), an Italian liquid wax (Knöppel and Schauenberg, 1989) and a solvent-based adhesive (Girman *et al.*, 1986).

## Concentration Data

The major data sources for indoor concentrations of styrene are the National VOC (NVOC) database, Krause *et al.* (1987) and the U.S. EPA's Total Exposure Assessment Methodology (TEAM) studies (Table 4.3).

Table 4.3. Summary statistics for concentrations of styrene in ppbv (from Shah and Heyerdahl, 1988; Krause *et al.*, 1987; Pellizzari *et al.*, 1987; Wallace *et al.*, 1989).

| Study | N | Average | Percentiles 25 | 50 | 75 | 90 | 95 | Range |
|---|---|---|---|---|---|---|---|---|
| NVOC | 2125 | 1.41 | 0.00 | 0.31 | 0.66 | --[b] | – | – |
| Krause *et al.* (1987)[a] | 230 | 0.59 | – | 0.28 | – | 0.99 | – | <0.24-9.6 |
| TEAM[a] | | | | | | | | |
| *L.A.-Winter '84* | | | | | | | | |
| Overnight Personal | 112 | 0.80 | 0.45 | 0.66 | 1.1 | 1.6 | 2.0 | 0.007-2.2 |
| *L.A.-Summer '84* | | | | | | | | |
| Overnight Personal | 51 | 0.27 | 0.089 | 0.20 | 0.38 | 0.66 | 0.75 | 0.005-1.2 |
| *C.C Summer '84* | | | | | | | | |
| Overnight Personal | 69 | 0.21 | 0.078 | 0.17 | 0.31 | 0.47 | 0.56 | 0.0047-0.96 |
| *L.A.-Winter '87* | | | | | | | | |
| Overnight Kitchen | 42 | 0.74 | 0.35 | 0.63 | 0.87 | 1.5 | 2.0 | 0.10-3.3 |
| Daytime Kitchen | 47 | 0.61 | 0.24 | 0.39 | 0.63 | 1.2 | 1.7 | 0.009-5.4 |
| Daytime Living Area | 45 | 0.84 | 0.28 | 0.49 | 0.93 | 1.6 | 2.1 | 0.009-9.8 |
| *L.A.-Summer '87* | | | | | | | | |
| Overnight Personal | 38 | 0.56 | 0.12 | 0.23 | 0.40 | 0.72 | 1.5 | 0.009-10.5 |
| Overnight Kitchen | 35 | 0.81 | 0.12 | 0.22 | 0.35 | 0.83 | 4.8 | 0.007-19.0 |
| Daytime Kitchen | 36 | 0.31 | 0.089 | 0.16 | 0.30 | 0.89 | 1.2 | 0.045-1.7 |
| Daytime Living area | 40 | 0.48 | 0.11 | 0.17 | 0.39 | 0.95 | 1.5 | 0.045-7.0 |

[a] Values converted from mass/volume units.

[b] Statistic not presented in reference.

There are over 2,000 data points for styrene in the NVOC database. The average concentrations is 1.4 ppbv, and the median concentration is 0.31 ppbv.

Krause *et al.* (1987) made measurements of VOC in 230 West German homes, selected at random. Passive charcoal samplers were exposed for two-week periods between June 1985 and April 1986. The adsorbed compounds were solvent extracted. Styrene was analyzed by GC/FID. The concentrations of styrene in the study are similar to the U.S. concentrations in the NVOC database. The average concentration is 2.5 $\mu g/m^3$ (0.59 ppbv), and the median is 1.2 μg/m3 (0.28 ppbv).

The California TEAM studies were conducted in 1984 and 1987 in and around Los Angeles (two seasons each year) and in 1984 in Contra Costa County (one season). Measurements of selected VOC in fixed-site indoor and outdoor air, personal air, breath and drinking water samples were made for stratified random samples of residents in both areas. The results were weighted to represent the entire populations of the study areas. Samples were collected on Tenax sorbent tubes for approximately 12 hours. The sorbent tubes were thermally desorbed and analyzed by GC/MS. The fixed-site sampling devices were located in the major living area of the houses during the day and in the kitchen both during the day and at night. The over-night personal air samples were collected at the subjects' bedsides during sleeping hours, and, therefore, provide reasonable measures of VOC concentrations in indoor air. The population size for the Los Angeles study was approximately 350,000. The population size for the Contra Costa County study was approximately 90,000.

There is generally good agreement between the results for the two locations. The distributions of styrene were similar for Los Angeles and Contra Costa County in the summer of 1984, with the average and median concentrations in both locations near 1 $\mu g/m^3$ (0.24 ppbv). In Los Angeles, concentrations of styrene were consistently higher in winter than in the summer, with median concentrations over 2 $\mu g/m^3$ (0.47 ppbv). This may have been due to decreased ventilation rates in the winter when windows and doors are more likely to be closed.

## Emissions Data

### *NASA Database*

The results of a search of the NASA database (McDonnell Douglas Corp., 1986) for materials emitting styrene are summarized in Table 4.4. The emissions data from the NASA study can only be considered to be qualitative since the measurements were made at an elevated temperature using closed containers. Fifty-four materials were found to emit styrene. Of these, the coatings category had the highest median emissions. Median emissions from materials in the other categories were relatively low.

### *Building Materials*

Carpets and adhesives used for carpet installation are sources of VOC emissions. Seifert et al. (1989) measured VOC levels in West German rooms with newly installed carpets. Three days after installation, the concentration of styrene in the air of six rooms averaged 23 $\mu g/m^3$ (5.4 ppbv). The range was 16-30 $\mu g/m^3$ (3.7-7.0 ppbv). Four weeks after carpet installation, a different group of 3 rooms averaged 8 $\mu g/m^3$ (1.9 ppbv). The range was 5-13 $\mu g/m^3$ (1.2-3.0 ppbv). The concentration in three control rooms averaged 3 $\mu g/m^3$ (0.70 ppbv).

Table 4.4. Summary of emissions of styrene from materials in NASA database.[a]

| Category | Minimum | Maximum | Median | N[b] |
|---|---|---|---|---|
| Adhesives | 0.04 | 0.3 | – | 2 |
| Coatings | 0.11 | 42 | 25 | 11 |
| Compounds[c] | 0.07 | 47 | 0.6 | 9 |
| Cosmetics | 0.01 | 1.9 | 0.3 | 10 |
| Fabrics | – | 0.1 | – | 1 |
| Foam/Plastic | 0.02 | 3 | 0.2 | 15 |
| Lubricants | – | – | – | 0 |
| Pens/Inks | – | 0.3 | – | 1 |
| Rubber | 0.05 | 1 | 0.32 | 5 |

[a] All measurements reported as µg styrene per gram product.

[b] N=number of materials in category that emitted styrene.

[c] Caulks, resins, epoxies and misc. products.

Sheldon *et al.* (1988) measured emission rates of VOC from 32 materials used in the construction of a new office building in Fairfax, VA. The materials were initially screened for emissions using a dynamic headspace technique. Some of the materials were selected for further testing in a small (12-liter) environmental chamber under controlled conditions (Table 4.5). Most, if not all, of these materials are likely to be used in residential construction.

In both the headspace and chamber experiments, the material with the highest emission rate of styrene was polystyrene foam insulation. The emission rates in chamber and headspace experiments were 6 and 5 µg/m$^2$-h, respectively. Other polymeric materials, such as latex paint, linoleum tile, telephone cable and moldings also had measurable emission rates of styrene.

Sheldon *et al.* (1988) also estimated net specific source strengths for the building using a simple mass-balance model and measurements of ventilation rate and indoor and outdoor concentrations of styrene. Immediately after construction, the mean specific source strength of styrene was 1.2 µg/m$^3$-h with a maximum of 2.3 µg/m$^3$-h. The building was sampled again three months after construction when it was fully occupied. At that time, the mean specific source strength was 0.6 µg/m$^3$-h with a maximum of 1.3 µg/m$^3$-h.

Wallace *et al.* (1987) measured the emission rates of styrene from painted sheetrock (twenty-two 1.98 × 1.22 m surfaces), wallpaper glued to sheetrock (twenty-two 1.98 × 1.22 m surfaces) and carpet glued to wood panels (twelve 1.98 × 1.22 m surfaces). All materials were aged for one week before emissions were measured in a 34-m$^3$ environmental chamber. The carpet was the only one of these materials that emitted styrene. The emission rate was 5.9 µg/m$^2$-h.

Van der Wal *et al.* (1990) measured emission rates of VOC from some building materials commonly used in the Netherlands. The experiments were conducted in a 15-m$^3$ environmental chamber with controlled ventilation rate, temperature and humidity. The two polystyrene foams tested emitted styrene. Measurements were made 1-2 h after the products were unwrapped and 24 h after unwrapping. The initial emission rates from foams A and B were 740 and 500 µg/m$^2$-h, respectively. The emission rates after 24 h were 180 and 5 µg/m$^2$-h, respectively.

Table 4.5. Emission rates of styrene from building materials in $\mu g/m^2$-h (from Sheldon *et al.*, 1988).

| Sample | Headspace | Chamber |
|---|---|---|
| Particle board | 0.13 | 0.18 |
| Carpet adhesive | --[a] | – |
| Black rubber molding | 0.33 | 0.43 |
| Latex paint | – | 1.9 |
| Linoleum tile | 1.1 | 0.63 |
| Polystyrene foam insulation | 4.9[b] | 6.2 |
| Vinyl cove molding | 0.55 | 0.14 |
| Cove adhesive | NM[c] | – |
| Carpet | 0.10 | – |
| Vinyl edge molding | 0.52 | |
| Small diameter telephone cable | 0.67 | |
| Large diameter telephone cable | 0.63 | |
| Urethane sealant | – | |
| Latex paint | – | |
| Tar paper | 0.04 | |
| Primer/adhesive | – | |
| Latex caulk | – | |
| PVC pipe | – | |
| Water repellant mineral board | 0.03 | |
| Cement block | 0.05 | |
| Treated metal roofing | 0.04 | |
| Fiberglass insulation | – | |
| Duct insulation | – | |
| Exterior mineral board | – | |
| Interior mineral board | – | |
| Ceiling tile | – | |
| Red clay brick | – | |
| Plastic laminate | – | |
| Plastic outlet cover | – | |
| Joint compound | – | |
| Linoleum tile cement | – | |

[a] No detectable emissions.

[b] Minimum value. Compound saturated detector during analysis.

[c] Not measured, sampler overloaded.

The experiments described above demonstrated that unreacted styrene monomer can be emitted from polystyrene and other styrene-based polymers. The emission rate of the monomer is dependent on both its diffusion through the material and its evaporation from the material surface. The former process tends to be the rate limiting step. Peev *et al.* (1987) measured the release of styrene from a polystyrene sheet at 40, 60 and 80 °C under various ventilation rates to obtain effective molecular diffusion coefficients for the system. It is possible that these results could be used to estimate emissions of styrene from this material under typical indoor conditions.

*Combustion Sources*

Styrene has been detected in environmental cigarette smoke (Jermini *et al.*, 1976; as quoted in Daisey *et al.*, 1990). The reported emissions were 105±9 µg/cigarette.

Vehicle exhaust and evaporative emissions of fuel from vehicles may enter the living space of houses with attached garages. Cohen *et al.* (1988) found a strong correlation between indoor concentrations of six chemicals associated with gasoline and the presence of an attached garage. Hampton *et al.* (1983) detected styrene in vehicle exhaust.

## Summary

Data for indoor concentrations of styrene that are specific to California are available. These data have been used to construct frequency distributions for indoor concentrations and personal exposures for two communities with populations of approximately 90,000 and 350,000 individuals. Median indoor concentrations were estimated to range between 0.16 and 0.66 ppbv. Additional data for another California community are being obtained by the Woodland field study being conducted by the CARB (Sheldon, 1990).

Styrene is used in the manufacture of a variety of polymeric materials that are used indoors. Quantitative data on emission rates were obtained in several studies for a few building and interior finish materials. These data identified carpets, polystyrene foam insulation, latex paint, linoleum tiles, telephone cable and various moldings as relatively important sources of unreacted styrene monomer. Styrene is also emitted in environmental tobacco smoke; but, the quantitative data for this source are minimal.

Because of the considerable indoor concentration and personal exposure data that exist, laboratory studies of styrene emissions are probably not needed at this time. However, if a significant risk is identified and it becomes important to reduce indoor exposures, laboratory studies could be conducted to better define the relative importance of the various sources of styrene.

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# Xylenes

## Uses and Sources

All three isomers of xylene (o-, m-, p-xylene) are used in the manufacture of chemicals, resins, insect repellants, pharmaceuticals and perfumes. They are found as solvents in a large number of products, including paints and other architectural coatings, adhesives, rubber and herbicides (HSDB, 1990). Xylenes are also back-blended into gasoline. Due to similarities in their boiling points (144.4, 139.1 and 138.4 °C for o-, m-, p-xylene, respectively), all three isomers are often used as a mixed distillate fraction. Because of its somewhat higher boiling point, o-xylene is much easier to purify and is sometimes used in relatively pure form.

The CTCP (1990) database lists over 230 products containing xylenes (all isomers). Over half of these products are insecticides. The results of a search of the CTCP database for xylenes are summarized in Table 4.6.

Table 4.6. Summary of emissions of xylenes from materials in CTCP database.

| Product Category | Number Products | Product Category | Number Products |
|---|---|---|---|
| Cleaning compounds[a] | 6 | Medical/Personal hygiene | 3 |
| Spot/Stain removers | 1 | Deodorants/disinfectants | – |
| Window/glass cleaners | – | Adhesives | – |
| Rug/upholstery cleaners | – | Liquid paper | – |
| Coatings/Inks[b] | 48 | Miscellaneous products | 4 |
| Coating thinners/strippers | 11 | Lubricants/Penetrants | 3 |
| Caulks and grouts | 3 | Engine degreasers | 1 |
| Polishes and Waxes[c] | 1 | Carburetor and choke cleaners | 10 |
| Insect sprays[d,e] | 122 | Car waxes and polishes | – |
| Moth control products | – | Miscellaneous automotive[f] | 10 |
| Herbicides and Fungicides[d] | 10 | Wood preservatives | 2 |

[a] Includes general purpose cleaners as well as drain, oven, tile and bathroom cleaners and degreasers.

[b] Includes paints, varnishes, sealants and other coatings. Inks include marking-pens.

[c] Includes wood, metal and shoe care products.

[d] Not all the items in this category may be available to consumers. Products that were obviously industrial in nature were not included.

[e] Twenty-four of these items were listed specifically as house and garden products.

[f] Includes fuel and oil additives, cleaners products, tire repair products and gasket removers.

In qualitative headspace analyses, emissions of xylenes have been detected from acoustical tile, tileboard cement, vinyl self-stick linoleum, water repellants (over 40 of which emitted xylenes), specialized cleaners, paint removers, spray paints, primers, varnishes, lubricants and adhesives (Miksch *et al.* 1982; Sack and Steele, 1989; Seifert *et al.*, 1989).

Wallace *et al.* (1989b) conducted a study of the influence of personal activities on exposures to VOC. Seven study subjects were asked to perform specific activities suspected of increasing exposures to 17 target compounds. Each subject was monitored for nine sequential time periods over three days using a personal pump and Tenax sorbent tubes. The investigators associated increased exposure to xylenes with painting, stripping paint, using pesticides, cigar smoking and being exposed to automobile and lawn mower exhaust.

Table 4.7. Summary statistics for concentrations of xylenes in ppbv (from Shah and Heyerdahl, 1988; Krause *et al.*, 1987; Pellizzari *et al.*, 1987; Wallace *et al.*, 1989a).

| | | | | Percentiles | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Study | Isomer | N | Average | 25 | 50 | 75 | 90 | 95 | Range |
| NVOC | m-, p- | 2305 | 8.67 | 1.48 | 3.11 | 5.76 | –[a] | – | – |
| | o- | 2216 | 2.84 | 0.46 | 1.11 | 2.14 | – | – | – |
| Krause *et al.* (1987)[b] | m-, p- | 230 | 5.31 | – | 3.70 | – | 9.47 | – | 0.76-70.2 |
| | o- | 230 | 1.62 | – | 1.13 | – | 3.00 | – | 0.28-10.4 |
| TEAM[b] | | | | | | | | | |
| *L.A.-Winter '84* | | | | | | | | | |
| Overnight Personal | m-, p- | 112 | 5.41 | 3.70 | 5.08 | 7.16 | 9.24 | 9.70 | 0.95-13.4 |
| | o- | 112 | 2.47 | 1.62 | 2.24 | 3.23 | 4.39 | 4.74 | 0.28-7.85 |
| *L.A.-Summer '84* | | | | | | | | | |
| Overnight Personal | m-, p- | 51 | 4.57 | 1.34 | 2.01 | 4.16 | 17.3 | 21.3 | 0.14-21.7 |
| | o- | 49 | 1.48 | 0.37 | 0.59 | 1.22 | 5.78 | 6.93 | 0.007-7.85 |
| *C.C.-Summer '84* | | | | | | | | | |
| Overnight Personal | m-, p- | 69 | 2.16 | 0.95 | 1.41 | 2.54 | 4.16 | 6.01 | 0.23-15.7 |
| | o- | 69 | 0.86 | 0.35 | 0.51 | 0.91 | 1.64 | 2.54 | 0.067-8.09 |
| *L.A.-Winter '87* | | | | | | | | | |
| Overnight Kitchen | m-, p- | 42 | 7.76 | 4.07 | 6.95 | 9.33 | 13.8 | 24.7 | 1.22-28.4 |
| | o- | 42 | 2.98 | 1.35 | 2.30 | 3.56 | 5.52 | 10.3 | 0.45-13.0 |
| Daytime Kitchen | m-, p- | 47 | 6.16 | 2.26 | 4.14 | 6.91 | 10.8 | 21.7 | 0.89-40.2 |
| | o- | 47 | 2.36 | 0.85 | 1.53 | 2.54 | 4.39 | 9.45 | 0.30-15.7 |
| Daytime Living Area | m-, p- | 45 | 6.09 | 2.27 | 4.95 | 7.19 | 13.6 | 21.3 | 0.92-31.6 |
| | o- | 45 | 2.36 | 0.86 | 1.85 | 2.66 | 5.54 | 9.59 | 0.50-12.9 |
| *L.A.-Summer '87* | | | | | | | | | |
| Overnight Personal | m-, p- | 40 | 2.82 | 1.61 | 2.20 | 3.53 | 4.99 | 8.04 | 0.34-14.0 |
| | o- | 40 | 0.97 | 0.54 | 0.76 | 1.29 | 1.90 | 2.18 | 0.10-4.18 |
| Overnight Kitchen | m-, p- | 37 | 3.00 | 1.37 | 2.30 | 3.51 | 6.79 | 9.73 | 0.14-4.18 |
| | o- | 36 | 1.13 | 0.51 | 0.83 | 1.36 | 2.59 | 3.56 | 0.04-14.6 |
| Daytime Kitchen | m-, p- | 36 | 2.38 | 1.24 | 2.04 | 2.91 | 4.41 | 6.93 | 0.62-9.45 |
| | o- | 36 | 0.86 | 0.48 | 0.81 | 1.12 | 1.38 | 2.25 | 0.24-3.49 |
| Daytime Living area | m-, p- | 40 | 2.84 | 1.38 | 2.06 | 3.42 | 5.29 | 10.1 | 0.64-14.6 |
| | o- | 40 | 1.00 | 0.46 | 0.77 | 1.04 | 2.02 | 3.74 | 0.01-5.24 |

[a] Statistic not presented in reference.

[b] Converted from mass/volume units.

## Concentration Data

The major sources of indoor concentration data for xylenes are the National VOC (NVOC) database, Krause *et al.* (1987) and the U.S. EPA's Total Exposure Assessment Methodology (TEAM) studies. The results of all three studies are summarized in Table 4.7.

There are over 2,000 data points for both m-, p-xylene and o-xylene in the NVOC database. The average concentrations are 8.7 and 2.8 ppbv, respectively. Median concentrations are 3.1 and 1.1 ppbv, respectively.

Krause *et al.* (1987) measured concentrations of VOC in 230 West German homes, selected at random. Passive charcoal samplers were exposed for two-week periods between June, 1985 and April, 1986. The adsorbed VOC were eluted with carbon disulfide. Xylenes were analyzed by GC/FID. The concentrations of xylenes in the study are similar to the U.S. concentrations in the NVOC database. Median concentrations of m-, p-xylene and o-xylene are 3.7 and 1.1 ppbv, respectively.

The California TEAM studies were conducted in 1984 and 1987 in and around Los Angeles (two seasons each year) and in 1984 in Contra Costa County (one season). Measurements of selected VOC in fixed-site indoor and outdoor air, personal air, breath and drinking water samples were made for stratified random samples of residents in both areas. The results were weighted to represent the entire populations of the study areas. Samples were collected on Tenax sorbent tubes for approximately 12 hours. The sorbent tubes were thermally desorbed and analyzed by GC/MS. The fixed-site sampling devices were located in the major living area of the houses during the day and in the kitchen both during the day and at night. The over-night personal air samples were collected at the subjects' bedsides during sleeping hours, and, therefore, provide reasonable measures of VOC concentrations in indoor air. The population size for the Los Angeles study was approximately 350,000. The population size for the Contra Costa County study was approximately 90,000.

Concentrations of both m-, p-xylene and o-xylene were higher in Los Angeles than in Contra Costa County during the summer of 1984. In both Los Angeles and Contra Costa County, winter-time concentrations of xylenes were higher that summer-time concentrations. This may have been due to decreased ventilation rates in the winter when windows and doors are more likely to be closed. Median concentrations of m-, p-xylene for both communities ranged from 1.4 to 7.0 ppbv. Median concentrations of o-xylene ranged from 0.51 to 2.3 ppbv.

## Emissions Data

### *NASA Database*

The NASA database (McDonnell Douglas Corp., 1986) reports emissions of xylenes from over 1,300 materials and products. These data can only be considered to be qualitative since the measurements were made at an elevated temperature using closed containers. Emissions data for those materials and products releasing more than 1 μg of xylenes per gram of material are summarized in Table 4.8. The categories with the highest median emissions are pens/inks and coatings. These two categories also have the highest percentages of total items with emissions over 1 μg/g (64 and 70 percent, respectively).

*Building Materials*

Krzymien (1989) investigated emissions of VOC from sprayed in place polyurethane foam insulation. One freshly sprayed and three cured foams were tested. Using 4-6 gram samples, dynamic headspace measurements were made at 80° C with both dry and humidified air and at 40° C with humidified air. The author states that the results of this study are only semi-quantitative, primarily because the breakthrough volumes of the analytes on the Tenax samplers were not determined. The average combined concentration of m-, p-xylene for the four samples at 80° C in the dry air samples was 1.1±0.6 mg/m$^3$ (0.25±0.14 ppmv). The range was 0.7-2 mg/m$^3$ (0.16-0.46 ppmv). At 80° C and 90 percent relative humidity, the emission of m-, p-xylene was greater with an average combined concentration of 6.8±2.1 mg/m$^3$ (1.6±0.5 ppbv) and a range of 4-9 mg/m$^3$ (0.92-2.1 ppbv) for the four samples. Emissions of xylenes were not detected at 40° C.

Table 4.8. Summary of emissions of xylenes from materials in NASA database.[a]

| Category | Minimum | Maximum | Median | N[b] |
|---|---|---|---|---|
| Adhesives | 1.1 | 270 | 6 | 25/64 |
| Coatings | 1 | 1600 | 19 | 95/136 |
| Compounds[c] | 1.1 | 24 | 4.6 | 8/29 |
| Cosmetics | 1.2 | 3.7 | – | 2/16 |
| Fabrics | 1.2 | 68 | 3 | 12/72 |
| Foam/Plastic | 1 | 60 | 4.7 | 19/49 |
| Lubricants | – | 10 | – | 1/6 |
| Pens/Inks | 2.7 | 1600 | 21 | 23/36 |
| Rubber | 2 | 11.2 | 6 | 4/28 |

[a] All measurements reported as µg xylenes per gram product.

[b] Number of materials with emissions greater than 1 µg/g divided by total number of materials that emitted xylenes.

[c] Caulks, resins, epoxies and misc. products.

Hartwell (1986) also measured emissions of VOC from polyurethane foam insulation. Two board stock and three spray insulation samples were tested using a dynamic-headspace technique at 80° C with dry nitrogen as the carrier gas. Analysis was by GC/MS. The results for two of the spray samples and both of the board stock samples were only semi-quantitative. The amount of compound present was estimated by comparing its total-ion-current area to the total-ion-current areas for chlorobenzene or n-decane standards. The estimated emission rate of xylenes for the foam samples was 0.003 µg/m$^2$-h. Xylene emissions were not detected from the board stock samples. More accurate data were generated for the third foam sample by determining the percent collection and desorption efficiencies for seven selected compounds, including xylene isomers. For this case, the emission rate of xylenes was lower, 0.00026 µg/m$^2$-h. The collection/desorption efficiency was 91 percent.

Engström (1990) measured emissions of xylenes from 277 building materials used in Sweden. The experiments were conducted at 40° C. All materials were aged at least three months prior to testing. Loading factors of 1.5 m$^2$ of wall material and 0.5 m$^2$ of floor material per m$^3$ of chamber volume were used. Ninety-five percent of the exposed surfaces of insulation and other "hidden" materials were covered with aluminum sheets. Xylenes were emitted by 14 of the samples. The median emission rate was 0.22 μg/h., and the range of emission rates was 0.033-5.61 μg/h.

Mølhave (1982) investigated emissions of VOC from 42 building materials used in Denmark with a 1-$m^3$ chamber. A loading factor of 0.25 $m^2$ of material per $m^3$ of chamber volume was used for all samples. It is not possible to associate the emissions with specific materials from the data provided. Nineteen percent of the samples emitted p-xylene, 38 percent emitted m-xylene and 33 percent emitted o-xylene. The average concentrations of xylenes in chamber air were reported as 3.8, 23 and 7.3 μg/$m^3$ (0.88, 5.3 and 1.7 ppbv) for o-, m-, p-xylene, respectively.

Carpets and the adhesives used with them, are sources of emissions of VOC. Seifert *et al.* (1989) measured concentrations of VOC in West German rooms with newly laid carpets. Samples were collected with passive samplers. Three days after carpet installation, the concentration of m-, p-xylene in the air of six rooms averaged 21 μg/$m^3$ (4.8 ppbv) with a range of 18-29 μg/$m^3$ (4.2-6.7 ppbv). Four weeks after installation, the average concentration in a different group of three rooms averaged 17 μg/$m^3$ (3.9 ppbv) with a range of 10-27 μg/$m^3$ (2.3-6.2 ppbv). The concentration in three control rooms averaged 6 μg/$m^3$ (1.4 ppbv). The adhesive, rather than the carpet, was the major source of xylenes in these experiments.

Sheldon *et al.* (1988) measured emission rates of VOC from materials used in the construction of a new office building in Fairfax, VA. Thirty-two materials were initially screened for emissions using a dynamic headspace technique. Some of the materials were selected for further testing in a small (12-liter) environmental chamber under controlled conditions. Most, if not all, of these materials are likely to be used in residential construction. The results are summarized in Table 4.9.

Net specific source strengths were also estimated for the building using a simple mass-balance model and measurements of ventilation rate and indoor and outdoor concentrations of xylenes. Immediately after construction, the mean specific source strengths of m-, p-xylene and o-xylene were 23 and 10 μg/$m^3$-h, respectively. The building was sampled again four months after construction when it was fully occupied. By that time, the source strengths of all the isomers had decreased, appreciably in the case of o-xylene. The mean specific source strengths were 3.8 μg/$m^3$-h for m-, p-xylene and 0.81 μg/$m^3$-h for o-xylene.

Wallace *et al.* (1987) measured the emission rates of xylenes from painted sheetrock (twenty-two 1.98 × 1.22 m surfaces), wallpaper glued to sheetrock (twenty-two 1.98 × 1.22 m surfaces) and carpet glued to wood panels (twelve 1.98 × 1.22 m surfaces). All materials were aged for one week before emissions were measured in a 34-$m^3$ environmental chamber. The emission rates of m-, p-xylene and o-xylene from the wallpaper/sheetrock assembly were 1.6 and 0.4 μg/$m^2$-h, respectively. The emission rates of these compounds from the carpet/wood assembly were 9.0 and 5.9 μg/$m^2$-h, respectively. The painted sheetrock did not emit xylenes.

*Combustion Sources*

Xylenes have been detected in environmental cigarette smoke (Jermini *et al.*, 1976; as quoted in Daisey *et al.*, 1990). The measurements were made in a 30-$m^3$, unventilated room in which 30 American-blend cigarettes were smoked simultaneously by machine and in a 272-liter Plexiglass chamber in which one cigarette was smoked. The reported emissions were 200±30 μg/cigarette for m-xylene and 478±0 μg/cigarette for o-xylene.

Table 4.9. Emission rates of xylenes from building materials in $\mu g/m^2$-h (from Sheldon *et al.*, 1988).

| | Headspace | | Chamber | |
|---|---|---|---|---|
| Sample | m- , p-xylene | o-xylene | m- , p-xylene | o-xylene |
| Particle board | --[a] | – | 0.20 | 0.08 |
| Carpet adhesive | 23 | 18 | 717 | 301 |
| Black rubber molding | 6.2 | 7.6 | 6.9 | 3.9 |
| Latex paint | 6.4 | 3.0 | 50 | 28 |
| Linoleum tile | 2.6 | 3.3 | 0.92 | 0.89 |
| Polystyrene foam insul. | 1.5 | 0.38 | 1.7 | 0.39 |
| Vinyl cove molding | 4.7 | 2.1 | 5.9 | 1.9 |
| Cove adhesive | NM[b] | NM | 1185 | 202 |
| Carpet | 0.41 | 0.37 | – | 0.83 |
| Vinyl edge molding | 3.7 | 1.6 | | |
| Small dia.phone cable | 5.0 | 3.9 | | |
| Large dia. phone cable | 5.0 | 3.5 | | |
| Urethane sealant | 0.21 | 0.13 | | |
| Latex paint | – | – | | |
| Tar paper | 0.31 | 0.24 | | |
| Primer/adhesive | 0.32 | 0.14 | | |
| Latex caulk | 47 | 74 | | |
| PVC pipe | 0.38 | 0.09 | | |
| Water rep. mineral board | – | – | | |
| Cement block | 0.15 | 0.07 | | |
| Treated metal roofing | 0.09 | – | | |
| Fiberglass insulation | 0.02 | – | | |
| Duct insulation | – | – | | |
| Exterior mineral board | – | – | | |
| Interior mineral board | – | – | | |
| Ceiling tile | – | – | | |
| Red clay brick | – | – | | |
| Plastic laminate | – | – | | |
| Plastic outlet cover | – | – | | |
| Joint compound | – | – | | |
| Linoleum tile cement | – | – | | |

[a] No detectable emissions.

[b] Not measured, sampler overloaded.

Vehicle exhaust and evaporative emissions of fuel from vehicles may enter the living space of houses with attached garages. Cohen *et al.* (1988) found a strong correlation between indoor concentrations of six chemicals associated with gasoline and the presence of an attached garage. Sigsby *et al.* (1987) quantified hydrocarbon emissions from a collection of 46 "in use" (*i.e.*, not new or tuned to manufacturers specifications) passenger vehicles for three different driving regimes. All measurements were made in the laboratory using a dynamometer. They reported that m-, p-xylene was 2.7 percent of the total hydrocarbon emissions, averaged for all three driving regimes. Ortho-xylene was not separated from an unidentified $C_9$ compound. The combined pair comprised an average of 1.7 percent of total hydrocarbons. Halder *et al.* (1986) found that xylenes constituted 0.6-0.7 percent by weight of the total vapor exposure of gasoline handlers. Xylenes are assumed to comprise a similar percentage of evaporative emissions of gasoline in a garage.

Xylenes were detected in air collected in an inverted funnel above the top burners of three gas cooking ranges tested by Moschandreas *et al.* (1983). The average concentration of m-, p-xylene was 9.7±6.0 $\mu g/m^3$ (2.2±1.4 ppbv) for six measurements. Concentrations of o-xylene were lower, averaging 3.2±1.7 $\mu g/m^3$ (0.74±0.4 ppbv) for six measurements.

### *Other Sources*

Volatile organic compounds can enter the substructures of houses built on contaminated soil or near leaking underground fuel tanks. However, it can be difficult to establish relationships between soil-gas pollutants and indoor pollutants. Kliest *et al.* (1989) measured VOC concentrations in 97 houses in the Netherlands, 77 of which were constructed on contaminated soil. The remaining 20 houses served as references. Of the 77, only nine percent had crawl spaces that were clearly contaminated. The concentration data are assumed to be reported as $\mu g/m^3$. Concentrations of m-, p-xylene and o-xylene in the living rooms of the contaminated houses averaged 46 $\mu g/m^3$ (11 ppbv) and 22 $\mu g/m^3$ (5.1 ppbv), respectively. Concentrations of m-, p-xylene and o-xylene in the crawl spaces averaged 760 $\mu g/m^3$ (176 ppbv) and 340 $\mu g/m^3$ (79 ppbv), respectively. The average concentrations of m-, p-xylene and o-xylene in the living rooms of the reference houses were 5.3 $\mu g/m^3$ (1.2 ppbv) and 1.9 $\mu g/m^3$ (0.44 ppbv), respectively. In the crawl spaces of these houses, the concentrations were comparable to outdoor concentrations.

Kullman and Hill (1990) identified three abandoned leaking storage tanks buried beneath a building as the source of gasoline vapors in an adjacent office building. Xylene concentrations in the office building ranged from 260 to 1,700 ppbv.

## Summary

Extensive data for indoor concentrations of xylenes that are specific to California are available. These data have been used to construct frequency distributions for indoor concentrations and personal exposures for two communities with populations of approximately 90,000 and 350,000 individuals. Median concentrations were in the range of 1.4-7.0 ppbv for m-, p-xylene and 0.5-2.3 ppbv for o-xylene. Additional data for another California community are being obtained by the Woodland field study being conducted by the CARB (Sheldon, 1990).

Xylenes are widely used as solvents and are present in numerous consumer products. In general, liquid and aerosol consumer products contain the highest levels of the compounds. Use of these products indoors can result in high-level exposure that is typically of relatively short duration. Long term, relatively low-level exposure may result from emissions of xylenes from building and interior finish materials. Quantitative data on emission rates of xylenes have been obtained for a few building materials. These data identified carpet adhesives and vinyl cove adhesives as sources of xylenes. Other sources were latex caulk, latex paint and various moldings. Environmental tobacco smoke is also a common indoor source of xylenes.

Because of the considerable indoor concentration and personal exposure data that exist for the xylene isomers, laboratory studies of emissions of these compounds from consumer products and building materials are probably not needed at this time. However, if a significant risk is identified and it becomes important to reduce indoor exposures, laboratory studies could be conducted to better define the relative importance of the various sources of xylenes.

## References

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# Acetaldehyde

## Uses and Sources

Acetaldehyde is used for the manufacture of a wide range of organic chemicals, synthetic rubber, plastics, pesticides, photographic formulations, perfumes and fragrances. It is produced during the combustion of wood, tobacco, gasoline and gasohol. Specific consumer product uses according to the HSDB (1990) and CTCP (1990) database are limited to artificial flavorings and room deodorants. Lesh and Mead (1985; as quoted in Rogozen et al., 1987) state that acetaldehyde may be present as a contaminant of nail-polish remover.

Acetaldehyde was detected in dynamic headspace analysis of a detergent and a liquid wax, both from Italy (Knöppel and Schauenberg, 1989).

Acetaldehyde was also one of the most frequently detected compounds in emissions of VOC from carpets (Bayer and Papanicolopoulos, 1990).

## Concentration Data

Data on indoor concentrations of acetaldehyde for homes are limited. The Boise Integrated Air Cancer Project (IACP) conducted by the U.S. EPA made measurements in 20 purposefully selected homes during the winter of 1986-87 (Zweidinger *et al.*, 1988). Air samples were collected in ten pairs of proximally located homes. Each pair had a home with and without a wood-burning stove. Samples were collected concurrently in each pair of homes. Carbonyl compounds were sampled during four different periods using 2,4-dinitrophenyl hydrazine (DNPH) coated cartridges and were analyzed by HPLC. None of the homes contained smokers. The results for acetaldehyde, which are summarized in Table 4.10, were calculated from the reported data using the average percentages of acetaldehyde in the total measured carbonyl concentrations. Indoor concentrations were four to five times higher than outdoor concentrations. Homes without woodstoves had slightly higher concentrations of acetaldehyde than homes with stoves, indicating a source(s) other than use of a woodstove.

Table 4.10 Concentrations of acetaldehyde in ppbv in homes with and without woodstoves from the Boise IACP project. Average concentrations for ten homes (after Zweidinger *et al.*, 1988).

| Sampling Period | Indoors with stove | Indoors without stove | Outdoors |
|---|---|---|---|
| Weekday-Daytime | 9.57 | 11.8 | 2.19 |
| Weekday-Nighttime | 9.30 | 10.3 | 2.57 |
| Weekend-Daytime | 10.4 | 10.7 | 2.09 |
| Weekend-Nighttime | 9.63 | 10.8 | 2.40 |

Another portion of the IACP study measured concentrations of acetaldehyde in three homes with woodstoves in Raleigh, NC (Highsmith *et al.*, 1988). Twelve-hour nighttime samples were collected on two consecutive nights. The DNPH samplers were located in the same room as the operating woodstove. Concentrations of acetaldehyde ranged from 4.5 to 7.9 ppbv. Outdoor concentrations were significantly lower.

De Bortoli *et al.* (1986) measured concentrations of acetaldehyde in 15 homes in Northern Italy. The mean concentration was 17 $\mu g/m^3$ (9.4 ppbv), presumably for fifteen samples, with a range of 1-48 $\mu g/m^3$ (0.56-27 ppbv). Samples were collected on DNPH-coated cartridges.

De Bortoli *et al.* (1990) measured concentrations of acetaldehyde in ten office buildings in Italy, at least one of which was a building in which workers had complained of poor air quality. Samples were collected from 83 offices using DNPH-coated cartridges. The median concentration of acetaldehyde was 9 $\mu g/m^3$ (5 ppbv); the 90th percentile concentration was 24 $\mu g/m^3$ (13 ppbv); and the maximum concentration was 57 $\mu g/m^3$ (32 ppbv).

Grosjean *et al.* (1990) and Druzik *et al.* (1990) measured indoor and outdoor concentrations of acetaldehyde at public sites in Brazil and in the U.S. Samples were collected with DNPH-coated cartridges. The indoor data are summarized in Table 4.11. In Brazil, outdoor concentrations were only somewhat lower than indoor concentrations (4.1-19 ppbv versus 9.2-35 ppbv). In Los Angeles, outdoor concentrations were considerably lower than indoor concentrations (1.7-9.9 ppbv versus 3.6-35 ppbv). The elevated levels in outdoor air in Brazil relative to Los Angeles were probably due the widespread use of ethanol containing fuels (see below).

Table 4.11. Concentrations of acetaldehyde in ppbv measured in public buildings in the U.S. and Brazil (from Grosjean *et al.*, 1990; Druzik *et al.* , 1990).

| Location | Date | Concentration |
|---|---|---|
| Museum A (Eastern U.S.) | 2/18/87 | 3.6 |
| Museum B (Los Angeles) | 7/29/88 | 10, 31 |
| Museum C (Los Angeles)[a] | 8/12/88 | 4.2 |
| | 8/15/88 | 4.5 |
| Museum D (Los Angeles) | 8/30/88 | 13 |
| Museum E (Los Angeles) | 9/16/88 | 24 |
| Museum F (Los Angeles) | 10/4/88 | 23, 35 |
| | 10/5/88 | 14 |
| Library (Los Angeles) | 9/15/88 | 13 |
| Museum G (Salvador, Brazil) | 9/22/88 | 34, 34, 27 |
| Museum H (Salvador, Brazil) | 9/16/88 | 24, 11 |
| Cathedral (Salvador, Brazil) | 9/15/88 | 35, 9.2, 22 |

[a] Measurements taken shortly before the museum opened for the day.

Wang (1975) quantified bioeffluents produced in a college auditorium. Samples of the influent and effluent air were collected from ventilation ducts that only handled air flow to and from the auditorium. Samples were collected on Chromosorb and analyzed by GC. The average concentrations of acetaldehyde in the effluent air were 4.2±2.1 ppbv (389 people, 85 percent male), 1.0±0.2 ppbv (368 people, 86 percent female) and 3.1±1.8 ppbv (225 people, 80 percent female). The first two measurements were made during lectures and the third during an exam. The concentration of acetaldehyde in the unoccupied auditorium was 0.1±0.1 ppbv. This value was similar to that found in the influent air.

Elevated concentrations of acetaldehyde have been measured in spaces contaminated with environmental tobacco smoke (ETS). Löfroth *et al.* (1989) measured concentrations of acetaldehyde in a Raleigh, NC, tavern on two separate nights. The numbers of cigarettes smoked during the sampling periods were not reported. Acetaldehyde was collected on DNPH-coated cartridges and analyzed by HPLC. The concentrations were 183 and 204 μg/m$^3$ (102 and 113 ppbv).

## Emissions Data

### *NASA Database*

The NASA database (McDonnell Douglas Corp., 1986) contains records for over 1,600 materials and products that emitted acetaldehyde. These emissions data can only be considered to be qualitative since the measurements were made at an elevated temperature using closed containers. Data for those products that emitted one or more micrograms of acetaldehyde per gram of material are summarized in Table 4.12. Lubricants and pens/inks had the highest median emission values. These categories also had the highest percentages (43 and 58 percent, respectively) of total items with emissions of 1 μg/g or more. The large number of materials and products that were found to emit acetaldehyde is notable since acetaldehyde is apparently used deliberately in the formulation of only a few types of products.

Table 4.12. Summary of emissions of acetaldehyde from materials in NASA database.[a]

| Category | Minimum | Maximum | Median | N[b] |
|---|---|---|---|---|
| Adhesives | 1 | 200 | 3.7 | 42/106 |
| Coatings | 1 | 230 | 4 | 59/149 |
| Compounds[c] | 1 | 24 | 6.5 | 6/34 |
| Cosmetics | 1 | 67 | 2.8 | 9/32 |
| Fabrics | 1.1 | 13.6 | 5.5 | 8/101 |
| Foam/Plastic | 1 | 6 | 2 | 8/86 |
| Lubricants | 4.5 | 67 | 15 | 9/21 |
| Pens/Inks | 1 | 460 | 22 | 43/74 |
| Rubber | 1 | 5 | 2.1 | 5/63 |

[a] All measurements reported as μg acetaldehyde per gram product.

[b] Number of materials with emissions greater than 1μg/g divided by total number of materials that emitted acetaldehyde.

[c] Caulks, resins, epoxies and misc. products.

### *Building Materials*

Krzymien (1989) investigated VOC emissions from sprayed in place polyurethane foam insulation. One freshly sprayed and three cured foams were tested. Using 4-6 gram samples, dynamic-headspace measurements were made at 80° C with both dry and humidified air and at 40° C with humidified air. The author states that the results are only semi-quantitative, primarily because the breakthrough volumes of the analytes on the Tenax samplers were not determined. The average headspace concentration of acetaldehyde for six samples at 80° C was 169± 112 mg/m$^3$ (93± 62 ppmv). The range was 51-367 mg/m$^3$ (28-204 ppmv). At 40° C, the amount of acetaldehyde released was much lower, ranging from 1-56

$mg/m^3$ (0.56-31 ppmv) for four samples. For each set of conditions, the freshly sprayed material released the most acetaldehyde.

Colombo *et al.* (1990) investigated emissions of VOC from particle board covered with carpet, plywood coated with polyurethane lacquer and gypsum board covered with wall paper. All materials were probably of European origin. The experiments were conducted in 450-liter glass chambers with internal mixing fans. The humidity, temperature and air flow rate through the chambers were controlled. Each group of materials was allowed to equilibrate for two to seven days before measurements were made. Duplicate samples were collected for each group. The emission rate of acetaldehyde from the particle board with carpet was 51 $\mu g/m^2$-h. The emission rate from the plywood with lacquer was 11 $\mu g/m^2$-h. Acetaldehyde was not emitted by the gypsum board with wallpaper.

Bayer (1990) investigated the effect of elevated temperatures on the emissions of VOC from particle board. Experiments were conducted in a 28.5-$m^3$ environmental chamber at ventilations rates of 0.5 and 1.0 $h^{-1}$. One set of boards maintained at 32° C for 11 days emitted acetaldehyde. The emission rate ranged from 1.3 to 4.5 $\mu g/m^2$-h over the experimental period.

### *Combustion Sources*

Schlitt and Knöppel (1989) measured the amount of acetaldehyde released per cigarette using a small chamber and a smoking machine. Acetaldehyde was collected in impingers containing a solution of DNPH in acetonitrile which was analyzed by HPLC. Emissions in the sidestream smoke ranged between 4,700 and 6,100 µg acetaldehyde per cigarette. Wadden and Scheff (1983) summarized the results of earlier studies in which the emission of acetaldehyde in sidestream smoke ranged between 40 and 3,100 µg per cigarette.

Löfroth *et al.* (1989) calculated that the emission of acetaldehyde was 2,400 µg/cigarette based on measurements made in an 13.6-$m^3$ environmental chamber with defined air-exchange and smoking rates. Aldehydes were collected on DNPH-coated cartridges and analyzed by HPLC.

Wood-burning stoves and fireplaces emit acetaldehyde as a product of incomplete combustion. DeAngelis *et al.* (1980) measured emissions from different types of wood. Samples of flue gas were collected using sodium bisulfite in midget impingers. Green oak and pine emitted 0.1 and 0.2 g of acetaldehyde per kilogram of wood, respectively. Seasoned pine emitted 0.03 g/kg.

Lipari *et al.* (1984) also measured emissions of acetaldehyde from different types of wood and log sizes. Samples of flue gas were collected from a fireplace installed in their laboratory using a solution of DNPH in acetonitrile which was analyzed by HPLC. Emissions ranged from 0.083 to 0.200 g of acetaldehyde released per kilogram of wood burned. The average was 0.117 g/kg. The maximum resulted from burning split cedar.

Aldehydes are also produced as a by-product of the combustion of natural gas. Moschandreas *et al.* (1983) measured emissions of selected compounds detected in the exhaust of range-top burners. Acetaldehyde was produced at a rate of 12-19 mg per $10^6$ BTU of gas.

Vehicle exhaust may enter the living space of houses with attached garages. Cohen *et al.* (1988) found a strong correlation between indoor concentrations of six chemicals associated with gasoline and the presence of an attached garage. Sigsby *et al.* (1987) quantified hydrocarbon emissions from a collection of 46 "in use" (*i.e.*, not new or tuned to manufacturers specifications) passenger vehicles for three different driving regimes. All measurements were made in the laboratory using a dynamometer. They reported that acetaldehyde was 24-28 percent of the total aldehyde emissions, which were in turn 1-2 percent of the total non-methane hydrocarbon emissions. Emissions from stationary vehicles may be different. In a smaller study, Lipari and Swarin (1982) found that the concentrations of acetaldehyde in the exhaust of two diesel- and two gasoline-fueled vehicles were 80 to 670 ppbv. The exhaust from an experimental ethanol-fueled vehicle contained up to 20,000 ppbv of acetaldehyde.

*Other Sources*

The rate of production of acetaldehyde by humans was calculated in the study of bioeffluents in a college auditorium discussed above (Wang, 1975). Using a mass-balance model, the average emission rates were estimated to be: 6.2±4.5 mg/person-day (389 people, 85 percent male), 1.9±0.3 mg/person-day (368 people, 86 percent female) and 8.6±4.6 mg/person-day (225 people, 80 percent female).

## Summary

Only a limited number of measurements of acetaldehyde in indoor environments have been reported, often in relation to emissions from combustion sources. There are no data for any probability-based sample of residences in California or the U.S. This lack of data is, at least, partially due to the requirement for a specialized sampling and analysis technique.

Acetaldehyde is likely to be present in most indoor environments at concentrations that exceed outdoor concentrations due to the large number of potential sources of this compound which include building materials, consumer products and combustion processes. The large number of materials and products in the NASA database that emitted acetaldehyde is particularly notable. Indoor sources for which there are at least some emissions data include plywood, an assembly of particle board and carpet, cigarette smoke, wood smoke and gas-stove exhaust. However, the data are generally insufficient to determine the relative importance of these sources.

It is recommended that acetaldehyde be included in a laboratory study of emissions due to ETS. There are some data for this source. However, an additional study would contribute to the available database and to the reliability of the estimates of emission rates of acetaldehyde in the sidestream smoke of cigarettes.

Due to the large number of poorly defined non-combustion sources of acetaldehyde, laboratory studies of emissions from materials and products would not be an efficient way to obtain additional information on indoor exposures for this compound. Instead, it is recommended that acetaldehyde be included in a field study utilizing a probability-based sample of homes. It is suggested that acetaldehyde be sampled using DNPH-coated cartridges with analysis by HPLC. This method would allow for the concurrent measurement of acrolein. Acetaldehyde should be given high priority for a field study because it is in CARB Group II.

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# Acrolein

## Uses and Sources

Acrolein is used in the manufacture of plastics and perfumes, as an aquatic herbicide, biocide and slimicide and as a leak-warning agent in methyl chloride refrigerant (HSDB, 1990). The major sources of acrolein in indoor environments are cigarettes and wood smoke. In a wood-burning community, outdoor air impacted by wood smoke is likely to be a source of acrolein for homes without combustion sources.

## Concentration Data

Measurements of indoor concentrations of acrolein have been made almost exclusively in environments with an active combustion source. An exception was the Boise Integrated Air Cancer Project (IACP) conducted by the U.S. EPA during the winter of 1986-87 in which measurements were also made in control homes (Zweidinger *et al.*, 1988). Air samples were collected in ten pairs of purposefully selected, proximally located homes. Each pair had a home with and without a wood-burning stove. Samples were collected concurrently in each pair of homes. Carbonyl compounds were sampled during four different periods using 2,4-dinitrophenyl hydrazine (DNPH) coated cartridges and were analyzed by HPLC. None of the homes contained smokers. The results for acrolein, summarized in Table 4.13, were calculated from the reported data using the average percentages of acrolein in the total measured carbonyl concentration. Differences in concentrations between homes with and without stoves were minor. Indoor concentrations were about three times higher than outdoor concentrations.

Table 4.13. Concentrations of acrolein in ppbv in homes with and without woodstoves (after Zweidinger *et al.*, 1988).

| Sampling Period | Indoors with stove | Indoors without stove | Outdoors |
|---|---|---|---|
| Weekday-Daytime | 0.63 | 0.63 | 0.18 |
| Weekday-Nighttime | 0.61 | 0.55 | 0.21 |
| Weekend-Daytime | 0.69 | 0.57 | 0.17 |
| Weekend-Nighttime | 0.63 | 0.58 | 0.20 |

Another portion of the IACP study measured concentrations of acrolein in three homes with woodstoves in Raleigh, NC (Highsmith *et al.*, 1988). Twelve-hour samples were collected on two consecutive nights. The DNPH samplers were located in the same room as the operating woodstove. Acrolein concentrations ranged from 0.36 to 2 ppbv. Outdoor concentrations were significantly lower.

Elevated concentrations of acrolein have been measured in environments where people were smoking. Data from several studies of acrolein concentrations in spaces contaminated with environmental tobacco smoke (ETS) are summarized in Table 4.14. Concentrations ranged from 6 ppbv in a large cafeteria with an unspecified number of smokers to 130 ppbv in a closed car with two smokers inside.

Table 4.14. Concentrations of acrolein resulting from cigarette smoke (from Sterling *et al.*, 1982; Löfroth *et al.*, 1989).

| Study | Type of building | Occupancy | Ventilation | Concentration (ppbv) Mean | Concentration (ppbv) Range |
|---|---|---|---|---|---|
| Badre *et al.*, 1978[a,b] | 5 Cafes | Varied | Not given | | 13-44[a] |
| | Room | 18 smokers | Not given | 81 | |
| | Hospital lobby | 12-30 smokers | Not given | 8.7 | |
| | 2 train compartments | 2-3 smokers | Not given | | 8.7-52 |
| | Automobile | 3 smokers | Natural, open | 13 | |
| | Automobile | 2 smokers | Natural, closed | 130 | |
| Fischer *et al.*, 1978[b] | Restaurant (470 $m^3$) | 50-80 | Mechanical | 7 | |
| Weber *et al.*, 1979[b] | Restaurant (440 $m^3$) | 60-100 | Natural | 8 | |
| | Bar (50 $m^3$) | 30-40 | Natural, open | 10 | |
| | Cafeteria (574 $m^3$) | 80-150 | 11 ACH | 6 | |
| Löfroth *et al.*, 1989 | Tavern (180 $m^3$) | 5-25 | ? | 10 | |
| | Tavern (180 $m^3$) | 5-25 | ? | 9 | |

[a] Data converted from mass/volume units.
[b] As summarized by Sterling *et al.*, 1982.

## Emissions Data

### *NASA Database*

The NASA database (McDonnell Douglas Corp., 1986) contains records for over 70 materials and products that emit acrolein (Table 4.15). These emissions data can only be considered to be qualitative since the measurements were made at an elevated temperature using closed containers. The categories with the highest numbers of materials emitting acrolein were foams and plastics, coatings and adhesives. Two lubricants and an adhesive had the highest emissions of acrolein.

### *Combustion Sources*

Cigarette smoke is a major source of acrolein in indoor air. Schlitt and Knöppel (1989) measured the amount of acrolein released per cigarette using a small chamber and a smoking machine. They found 820 and 880 μg of acrolein in the sidestream smoke of a "light" filter and a "strong" unfiltered cigarette, respectively. Löfroth *et al.* (1989) calculated that the average emission of acrolein was 560 μg/cigarette based on measurements made in a 13.6-$m^3$ environmental chamber with defined air exchange and smoking rates.

Wood-burning stoves and fireplaces emit acrolein as a by-product of combustion. Lipari *et al.* (1984) measured emissions of aldehydes from different types of wood and log sizes. Samples were collected from the flue gas of a fireplace installed in their laboratory. Emissions of acrolein ranged from

0.021 to 0.132 g per kilogram of wood burned. The average was 0.049 g/kg. The maximum resulted from burning large pieces of unseasoned ash.

Table 4.15. Summary of emissions of acrolein from materials in NASA database.[a]

| Category | Minimum | Maximum | Median | N[b] |
|---|---|---|---|---|
| Adhesives | 0.01 | 150 | 0.95 | 10 |
| Coatings | 0.02 | 19 | 1 | 20 |
| Compounds[c] | 0.06 | 5 | 0.4 | 6 |
| Cosmetics | 0.1 | 6 | 0.7 | 5 |
| Fabrics | – | 0.2 | – | 2 |
| Foam/Plastic | 0.02 | 1 | 0.2 | 24 |
| Lubricants | 38 | 67 | – | 2 |
| Pens/Inks | – | 0.06 | – | 1 |
| Rubber | 0.04 | 0.2 | 0.1 | 4 |

[a] All measurements reported as µg acrolein per gram product.
[b] N=number of materials in category that emitted acrolein.
[c] Caulks, resins, epoxies and misc. products.

Vehicle exhaust may enter the living spaces of houses with attached garages. Cohen *et al.* (1988) found a strong correlation between indoor concentrations of six chemicals associated with gasoline and the presence of an attached garage. Sigsby *et al.* (1987) quantified hydrocarbon emissions from a collection of 46 "in use" (*i.e.*, not new or tuned to manufacturers specifications) passenger vehicles for three different driving regimes. All measurements were made in the laboratory using a dynamometer. They reported that acrolein was 5.6-8.9 percent of the total aldehyde emissions, which were 1-2 percent of the total non-methane hydrocarbon emissions. Emissions from stationary vehicles may be different. In a smaller study, Lipari and Swarin (1982) found that the concentrations of acrolein in the exhaust of two diesel and two gasoline fueled vehicles were 20 to 270 ppbv.

## Summary

Only a limited number of measurements of acrolein in indoor environments have been reported, often in relation to emissions from combustion sources.

Acrolein is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

Some products and materials have been found to emit acrolein. However, the primary indoor sources are probably combustion processes. Acrolein is emitted by cigarettes and will be present in environments contaminated with ETS. Fireplaces, particularly those with a bad draught, and leaky wood-burning stoves can also be sources of residential exposure to acrolein. The current emissions data are insufficient to determine the relative importance of these source categories.

It is recommended that acrolein be included in a laboratory study of emissions due to ETS since there are only limited data for this source. An additional study would contribute significantly to the available database and to the reliability of the estimates of emission rates of acrolein in the sidestream smoke of cigarettes. Acrolein should be given secondary priority for study because it is in CARB Group III.

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# Cresols

## Uses and Sources

Cresols (o-, m-, p-cresol) are used in degreasing agents and paintbrush cleaners and as additives to lubricating oils. They are also used as disinfectants in household sanitizers and as fumigants. Meta-cresol has been used as an insecticide and miticide for dogs and as a bacteriocide/bacteriostat for treatment of tree diseases. All three isomers are used as chemical intermediates for other compounds and in the manufacture of phenolic resins and pesticides (HSDB, 1990).

External carburetor and engine cleaners contain up to 25 percent cresols or cresylic acids. Over fifty percent of some paint removers are cresols (Rogozen *et al.*, 1987).

Cresols have been measured in mainstream cigarette smoke (Nanni *et al.*, 1990). They are, therefore, expected to be emitted in sidestream smoke, possibly at higher rates than in mainstream smoke.

## Concentration Data

No data on indoor concentrations of cresols were found.

## Emissions Data

Cresols are formed during incomplete combustion of wood and can be emitted by wood-burning stoves and fireplaces. DeAngelis *et al.* (1980) measured stack emissions from different types of wood burned in a fireplace and in two air-tight wood-burning stoves. Volatile organic compounds where collected from the flue gas using a Source Assessment Sampling System (SASS) and a Particulate Organic Matter (POM) sampling train and analyzed by GC/FID. The investigators stated that their combustion variables (*e.g.*, air supply and wood size) were representative of a significant portion of the source population. Fireplace emissions of cresols for seasoned oak were 0.041 g per kilogram of wood burned. Green pine emitted twice this amount (0.085 g/kg). In the wood-burning stoves, seasoned oak emitted 0.18 g/kg; seasoned pine emitted 0.14 g/kg; and green pine emitted 0.23 g/kg. Some of these values are the averages of the results for both sample types (SASS and POM) while other values are for a single sample type.

## Summary

Cresols are emitted by combustion processes and may be present in some consumer products. The lack of data for indoor concentrations suggests either that investigators have not specifically attempted to identify and quantify these compounds or that concentrations are below limits of detection for the commonly employed sampling and analytical methods. The emissions of cresols from burning wood are relatively high; therefore, fireplaces, particularly those with bad draught, and leaky woodstoves can be sources of residential exposure to these compounds. Sidestream cigarette smoke is another probable source. No data on emissions of cresols from consumer products were found.

It is recommended that cresols be included in an environmental chamber study of emissions from consumer products. This study should be conducted in a large-scale chamber using protocols that simulate typical consumer use of products which contain cresols as a major ingredient. Product categories that could be studied include degreasers, paintbrush cleaners and disinfectants.

It is further recommended that cresols be included in a laboratory study of emissions due to environmental tobacco smoke since there are no data for cresols from this likely source. Methods for sampling and analysis of cresols in air contaminated with tobacco smoke may have to be evaluated as part of this study. Cresols should be given secondary priority for study because they are in CARB Group III.

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# Di(2-ethylhexyl)phthalate

## Uses and Sources

Di(2-ethylhexyl)phthalate (DEHP) is used primarily as a plasticizing agent in a variety of polymers such as polyvinyl chloride (PVC). It is also found in insect repellants, cosmetics, rubbing alcohol, adhesives and liquid soaps and detergents and is used as a solvent for lacquers and erasable inks (HSDB, 1990). The only commercially important use of DEHP, other than as a plasticizer, is in dielectric fluids (Life Systems, Inc., 1989).

McLaughlin and Aigner (1990) found that the DEHP content of a PVC-backed carpet was eight percent by weight. A study conducted for the Consumer Product Safety Commission, reported in Life Systems, Inc. (1989), measured emissions of DEHP from eight consumer products: a window curtain, shower curtain, nursery pad, tablecloth, vinyl flooring material and two types of wall paper. The vaporization rates of DEHP from all of these products were stated to be very low; however, no quantitative data were given.

## Concentration Data

The only data for concentrations of DEHP in homes come from a pilot study conducted by Sheldon (1990b). Concentrations of semi-volatile and particulate-phase compounds were measured in nine homes in the Los Angeles, CA, metropolitan area. The study was done to evaluate sampling and analytical methods for a larger investigation. The sampling sites were purposefully selected and the results, thus, cannot be extrapolated to a larger population. Vapor- and particulate-phase phthalate esters were collected over 12-hour periods on quartz fiber filters backed with sorbent beds of XAD-2 resin. For each sample, the filter and sorbent were combined and Soxhlet extracted with dichloromethane. The extracts were analyzed by GC/ECD. Summary statistics for DEHP in indoor and outdoor air are presented in Table 4.16. Mean and median indoor concentrations were 0.005 ppbv.

Di(2-ethylhexyl)phthalate was also measured in a pilot field study conducted in 12 homes in Woodland, CA (Sheldon, 1990a). Several of the samples had concentrations above the estimated method quantitation limit of 75 ng/m$^3$ (0.005 ppbv).

Table 4.16. Concentrations of di(2-ethylhexyl)phthalate in indoor and outdoor air (from Sheldon, 1990b).[a]

| | N | % Detected | Average | Percentiles (ppbv)[a] | | | | | Range |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 5 | 25 | 50 | 75 | 95 | |
| Indoors | 17 | 89.0 | 0.0051 | Trace[c] | 0.0039 | 0.0048 | 0.0075 | 0.0082 | ND[b]-0.011 |
| Outdoors | 17 | 47.3 | 0.0015 | ND | ND | Trace | 0.0022 | 0.0050 | ND-0.0055 |

[a] Converted from mass/volume units.

[b] Not detected.

[c] Below quantitation limit (0.0016 ppbv) but above ldetection limit (0.00053 ppbv).

Weschler (1984) characterized organic compounds associated with indoor aerosol particles in two telephone equipment buildings: one in Wichita, KA and one in Lubbock, TX. Dichotomous samplers were used to collect particles on Teflon filters. The filters were subsequently thermally desorbed and analyzed by GC/MS. The results are for particulate-phase concentrations. The average DEHP concentration in Wichita was 55 ng/m$^3$ (0.0034 ppbv; n=6) and the average concentration in Lubbock was 20 ng/m$^3$ (0.0013 ppbv; n=6). The average outdoor concentration at the two sites was 2.1 ng/m$^3$ (0.00013 ppbv).

Vedel and Nielsen (1984) conducted a limited study of DEHP concentrations in the air of three offices in Denmark, two of which had PVC wall coverings. Air samples were collected on Florisil/anhydrous ammonium sulfate tubes which were extracted with petroleum ether and diethyl ether. The sample eluent was analyzed by GC/MS. In one office, the combined vapor- and particulate-phase concentration of DEHP ranged from 6.9 to 14 ppbv, while in the other two offices, the concentration was below the 3.8 ppbv detection limit.

## Emissions Data

No quantitative data on emissions of DEHP from possible indoor sources were found.

## Summary

Phthalate esters are ubiquitously present in indoor and outdoor air because of their widespread use as plasticizers. Since DEHP is a semivolatile compound with a relatively low vapor pressure, indoor vapor-phase concentrations are expected to be low. However, concentrations can be elevated in indoor environments with high loadings of PVC materials. Although not in the scope of this review, the literature suggests that exposure to DEHP from contaminated food and water may outweigh that from air.

There are no quantitative emissions data for building materials, furnishings, or consumer products. Because of its low volatility and typically high background levels, DEHP is poorly suited for laboratory studies of emissions. Field studies are the most appropriate way to obtain additional data. Di(2-ethylhexyl)phthalate is one of the compounds included both in the Woodland, CA, field study being conducted by the CARB and in the Particulate Total Exposure Assessment Methodology (PTEAM) study being conducted by the U.S. EPA and the CARB (Sheldon, 1990a and 1990b). These studies are measuring indoor concentrations and personal exposure for probability-based samples of relatively large numbers of homes. This study design will allow the results to be applied to the general populations of the study areas. These studies may provide adequate data for assessing indoor exposure to airborne DEHP.

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# 1,4-Dioxane

## Uses and Sources

The compound 1,4-dioxane (dioxane) is used as a degreasing agent and as a solvent for fats, oils, waxes and natural and synthetic resins. It is also used as a stabilizer in chlorinated solvents (*e.g.*, in 1,1,1-trichloroethane at concentrations of 1-3 percent by weight). Possible consumer sources of indoor exposure to dioxane include cleaning and detergent preparations (*e.g.*, laundry presoaks and glass cleaners), adhesives, cosmetics, deodorants, bath preparations, fumigants, polishing compounds, lacquers, paints, varnishes and paint/varnish removers (CTCP, 1990; HSDB, 1990; Rogozen *et al.*, 1987; Sack and Steele, 1989).

Sack and Steele (1989) re-analyzed the data from a U.S. EPA sponsored survey of 1,153 brand-name consumer products (Westat, Inc. and Midwest Research Institute, 1987). Originally, the products were analyzed for six chlorinated solvents using a purge and trap technique with GC/MS detection. The stored GC/MS chromatograms were searched for additional compounds. Dioxane was found to be present in only three products: two lubricants (1-3 percent) and a laundry wash spray (reported as 150 percent).

Knöppel and Schauenberg (1989) detected dioxane in the dynamic headspace analysis of a European detergent.

Bayer and Papanicolopoulos (1990) measured emissions of VOC from textile products using environmental chambers of various sizes. They reported that dioxane was frequently emitted by carpets and draperies.

## Concentration Data

The major data sources for indoor concentrations of dioxane are the National VOC (NVOC) database and the U.S. EPA's Total Exposure Assessment Methodology (TEAM) studies.

There are almost 600 data points in the NVOC database (Table 1). The average concentration of dioxane is 1.0 ppbv. However, the data are highly skewed since the median concentration is zero.

The California TEAM studies were conducted in 1984 in and around Los Angeles (two seasons) and in Contra Costa County (one season). Measurements of selected VOC in fixed-site outdoor and indoor air, personal air, breath and drinking water samples were made for stratified random samples of residents in both areas. The results were weighted to represent the entire populations of the study areas. The samples were collected on Tenax sorbent tubes for approximately 12 hours. The sorbent tubes were thermally desorbed and analyzed by GC/MS. The data presented in Table 4.17 summarize the measurements of dioxane in over-night personal air. These samples were collected with the sampling devices located at the subjects' bedsides during sleeping hours, and, therefore, provide a reasonable measure of indoor VOC concentrations. For each location and season, dioxane was detected in only 12-55 percent of the samples analyzed. It was, nevertheless, possible to construct frequency distributions for the two communities. The population size for the Los Angeles study was approximately 350,000 and the population size for the Contra Costa County study was approximately 90,000. The median concentrations for these populations were 0.24 $\mu g/m^3$ (0.067 ppbv) or less.

Table 4.17. Summary statistics for concentrations of 1,4-dioxane in ppbv (from Shah and Heyerdahl, 1988; Pellizzari *et al*, 1987).

| Study | N | Average | Percentiles 25 | 50 | 75 | 90 | 95 | Range |
|---|---|---|---|---|---|---|---|---|
| NVOC | 585 | 1.03 | 0.00 | 0.00 | 0.092 | --[a] | -- | – |
| TEAM[b] | | | | | | | | |
| L.A.-Winter '84 | 112 | 0.15 | 0.014 | 0.067 | 0.16 | 0.39 | 0.64 | 0.006-1.2 |
| L.A.-Summer '84 | 51 | 0.044 | 0.006 | 0.008 | 0.008 | 0.092 | 0.19 | 0.006-1.2 |
| C.C Summer '84 | 69 | 0.042 | 0.006 | 0.008 | 0.036 | 0.10 | 0.15 | 0.006-0.81 |

[a] Statistic not presented in reference.

[b] Converted from mass/volume units.

A follow-up TEAM study was conducted in Los Angeles in 1987. The investigators returned to the same houses that were previously studied. At this time, dioxane was detected in fewer than 15 percent of the samples analyzed and further statistical analysis of the data for dioxane was not undertaken (Wallace *et al.*, 1989).

Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for air toxics. A total of 12 homes and 8 people were monitored during this study. The homes were purposefully, not randomly, selected. Samples for dioxane were collected on Tenax sorbent tubes over 24-hour periods at a low flow rate and analyzed by GC/MS. Dioxane was detected in 67 percent of the indoor samples. The mean concentration for 12 homes was 0.32±0.24 ug/$m^3$ (0.089±0.067 ppbv). Personal exposures were similar and outdoor concentrations were lower.

## Emissions Data

### *NASA Database*

The results of a search of the NASA database (McDonnell Douglas Corp., 1986) for materials emitting dioxane are summarized in Table 4.18. The emissions data from this study can only be considered to be qualitative since the measurements were made at an elevated temperature using closed containers. Only 16 materials were found to emit dioxane. These are primarily adhesives and coatings. The emissions from the materials were relatively low. The adhesives had the highest emissions of dioxane with a median value of 4.3 µg per gram of material.

### *Building Materials*

Krzymien (1989) investigated emissions of VOC from sprayed in place polyurethane foam insulation. One freshly sprayed and three cured foams were tested. Using 4-6 gram samples, dynamic headspace measurements were made at 80° C with both dry and humidified air and at 40° C with humidified air. The author states that the results are only semi-quantitative, primarily because the breakthrough volumes of the analytes on the Tenax samplers were not determined. The average dioxane concentration for the eight samples at 80° C was 8.5±5.5 mg/$m^3$ (2.4±1.5 ppmv) with a range of 3-16 mg/$m^3$ (0.83-4.4 ppmv). No dioxane was detected at 40° C.

Bayer and Papanicolopoulos (1990) measured emission rates of VOC from an unspecified drapery material and an unspecified drapery lining. The experiments were conducted in an environmental chamber. Samples were collected on multisorbent tubes and analyzed by GC/MS. The emission rate of dioxane from the drapery material was 1.3 ug/m$^2$-h; the emission rate from the drapery lining was 0.08 ug/m$^2$-h.

Table 4.18. Summary of emissions of 1,4-dioxane from materials in NASA database.[a]

| Category | Minimum | Maximum | Median | N[b] |
|---|---|---|---|---|
| Adhesives | 1.0 | 21.0 | 4.3 | 5 |
| Coatings | 0.1 | 0.66 | 0.3 | 7 |
| Compounds[c] | – | – | – | 0 |
| Cosmetics | – | – | – | 0 |
| Fabrics | 0.01 | 0.3 | – | 2 |
| Foam/Plastic | – | – | – | 0 |
| Lubricants | – | – | – | 0 |
| Pens/Inks | – | – | – | 0 |
| Rubber | 0.05 | 1.3 | – | 2 |

[a] All measurements reported as µg 1,4-dioxane per gram product.
[b] N=number of materials in category that emitted 1,4-dioxane.
[c] Caulks, resins, epoxies and misc. products.

## Summary

Data for indoor concentrations of dioxane that are specific to California are available. These data have been used to construct frequency distributions for indoor concentrations and personal exposures for two communities with populations of approximately 90,000 and 350,000 individuals. Concentrations were estimated to be low, with median values of 0.07 ppbv or less. Also, the percentages of homes with detectable concentrations of dioxane were relatively low. Additional data for another California community are being obtained by the Woodland field study being conducted by the CARB (Sheldon, 1990).

The data in the NVOC database suggest that the distribution of indoor concentrations of dioxane is highly skewed. This distribution pattern may be due to the limited use or occurrence of only a few major sources of dioxane. For example, a shelf survey of over 1,000 consumer products only detected dioxane in three products. Since there may be only a few important sources, laboratory studies are expected to be an efficient means to obtain additional data for this compound. Therefore, it is recommended that dioxane be included in both a laboratory study of emissions of minor constituents from products and materials and in an environmental chamber study of emissions from expendable consumer products. Dioxane should be given a relatively high priority in these studies because it is in CARB Group II. Products in which dioxane is used as a stabilizer and anti-oxidant should be screened for emissions in the study of minor constituents. Consumer use of products in which dioxane is a major ingredient is likely to result in the highest exposure to this compound. Such exposure could be investigated using a room-size chamber in which representative consumer products are actively applied. Product types that should be investigated include architectural coatings, adhesives and cleaning and detergent preparations such as glass cleaners and laundry presoaks.

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# Ethyl acrylate

## Uses and Sources

Ethyl acrylate is a chemical intermediate for the production of polymers used in latex paints; textile and paper coatings; floor finishes, polishes and sealants; leather finishes; shoe polishes; pigment binders; and dirt-release agents. The monomer is used in fragrances and synthetic flavorings (HSDB, 1990).

## Concentration Data

No data on indoor concentrations of ethyl acrylate were found.

## Emissions Data

No data on emissions of ethyl acrylate from possible indoor sources were found.

## Summary

There are no data on indoor concentrations or source emissions of ethyl acrylate, and no field studies of this compound are in progress in California.

It is recommended that ethyl acrylate be included in a laboratory study of emissions of minor constituents from products and materials. Because it is in CARB Group II, it should be given high priority for study. Ethyl acrylate is a monomer used in the production of acrylic polymers. A number of materials and products containing these polymers should be screened for potential emissions. Possible types of products to be investigated include latex paints and various waxes, polishes and sealants. It may be necessary to validate a method for sampling and analysis of ethyl acrylate as part of this screening study. If significant sources are identified, emission rates for these sources could be measured under standardized conditions using environmental chambers.

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HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.