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

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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.

Acknowledgements

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Disclaimer

Table of Contents

Page

Page

List of Tables

Page

Page

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.

Compound	Field Study 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	—	—	—

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[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 μg 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 $\mu g/m^3$ = x ppbv where x =	1 ppbv = x $\mu g/m^3$ 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

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).

			Percentiles					
Study	N	Average	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 μg/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 μg/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 μg/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 μg/m^3 (5.4 ppbv). The range was 16-30 μg/m^3 (3.7-7.0 ppbv).. Four weeks after carpet installation, a different group of 3 rooms averaged 8 μg/m^3 (1.9 ppbv). The range was 5-13 μg/m^3 (1.2-3.0 ppbv). The concentration in three control rooms averaged 3 μg/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
<u>TEAM</u>[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 μg/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.

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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 μg/m^3 (9.4 ppbv), presumably for fifteen samples, with a range of 1-48 μg/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 μg/m^3 (5 ppbv); the 90th percentile concentration was 24 μg/m^3 (13 ppbv); and the maximum concentration was 57 μg/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	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]

				Percentiles (ppbv)[a]					
	N	% Detected	Average	5	25	50	75	95	Range
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).

			Percentiles					
Study	N	Average	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.

References

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Glycol ethers and acetates

Uses and Sources

The compounds in this classification that were reviewed are 2-methoxy ethanol (methyl cellosolve), 2-methoxyethyl acetate (methyl cellosolve acetate), 2-ethoxy ethanol (cellosolve), 2-ethoxy ethyl acetate (cellosolve acetate) and 2-butoxy ethanol (butyl cellosolve).

These glycol ethers and their acetate derivatives are widely used as solvents in the manufacture of paints, lacquers, enamels, varnishes, stains, metal coatings and epoxy resin coatings. More than half of their production is consumed by these applications. They are also used as solvents for printing inks, leather finishes, textile dyes and pigments (Piacitelli *et al.*, 1990). The HSDB (1990) reports their use in adhesives, nail polishes, perfumes, liquid soaps, cosmetics, dry cleaning compounds, varnish removers and liquid household products.

Table 4.19. Consumer product categories in CTCP database that emitted glycol ethers and acetates.

	Number of Products				
Product Category	2-Butoxy ethanol	2-Ethoxy ethanol	2-Ethoxy ethyl acetate	2-Methoxy ethanol	2-Methoxy ethyl acetate
Cleaning compounds[a]	35	4	–	–	–
Spot/Stain removers	4	1	–	–	–
Dry cleaning fluids	–	–	–	–	–
Window/glass cleaners	3	2	–	–	–
Rug/upholstery cleaners	6	3	–	–	–
Coatings/Inks[b]	2	10	4	1	–
Coating thinners/strippers	8	6	1	2	–
Caulks and grouts	–	–	–	–	–
Polishes and Waxes[c]	–	–	–	–	–
Insect sprays[d]	7	–	–	–	–
Moth control products	–	–	–	–	–
Herbicides and Fungicides[d]	–	1	–	–	–
Wood preservatives	–	–	–	–	–
Medical/Personal hygiene	2	1	–	–	–
Room deodorants/disinfectants	–	–	–	–	–
Lubricants/Penetrants	–	–	–	–	–
Adhesives	1	–	–	–	–
Liquid paper	–	–	–	–	–
Miscellaneous products	5	–	5	–	–
Engine degreasers	3	–	–	–	–
Carburetor and choke cleaners	3	–	–	–	–
Car waxes and polishes	–	–	–	–	–
Miscellaneous automotive[e]	5	–	–	–	–

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

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

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

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

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

The results of a search of the CTCP (1990) database for these compounds are summarized in Table 4.19. The database lists over 80 products containing 2-butoxy ethanol, the majority of which are cleaning compounds. Ethoxy ethanol is listed as an ingredient in 28 products, over half of which are coatings and inks or stripping agents. Ethoxyethyl acetate and methoxy ethanol are listed as ingredients in only ten and three products, respectively. Methoxy ethyl acetate was not present in any products in the database.

In qualitative headspace analyses, emissions of 2-butoxy ethanol have been detected from liquid wax (Knöppel and Schauenburg, 1989) and silicone caulk (Tichenor and Mason, 1988).

Concentration Data

Data on indoor concentrations of glycol ethers and acetates are very limited. The National VOC (NVOC) database (Shah and Heyerdahl, 1988) contains 14 data points for 2-butoxy ethanol. These data points were obtained with a passive sampler over a four-week period in an office and laboratory complex (C. J. Weschler, Bell Communications Research, Red Bank, NJ, personal communication). The average concentration is 0.214 ppbv; the median is 0.075 ppbv; and the lower and upper quartiles are 0.03 and 0.36 ppbv, respectively.

Sheldon *et al.* (1988) measured concentrations of VOC in three newly constructed and three older public buildings in the U.S. Ethoxyethyl acetate was present in four of these buildings at concentrations ranging from 1.31 to 9.58 μg/m^3 (0.24-1.8 ppbv).

Emissions Data

NASA Database

The results of a search of the NASA database (McDonnell Douglas Corp., 1986) for glycol ethers and acetates are summarized in Table 4.20. These data can only be considered to be qualitative since they were obtained at an elevated temperature using closed containers. Eleven materials emitted 2-butoxy ethanol, 24 emitted 2-ethoxy ethanol, 81 emitted 2-ethoxy ethyl acetate and 13 emitted 2-methoxy ethanol. Adhesives, coatings and pens/inks were the highest emitting categories for all of these compounds. No materials were found to emit 2-methoxyethyl acetate.

Building Materials

Schriever and Marutzky (1990) measured concentrations of 2-methoxy ethanol in a West German schoolroom after refinishing of a parqueted floor with a two-component polyurethane coating. The surface area of the floor was 70 m^2, and the room volume was 200 m^3. The air exchange rate was 0.65 h^{-1}. Ten days after refinishing, the concentration was 0.22 mg/m^3 (71 ppbv). After 90 days, the concentration was 0.026 mg/m^3 (8.4 ppbv).

Mølhave (1982) detected emissions of ethoxyethyl acetate from one of 42 building materials tested in an environmental chamber. A loading factor of 0.25 m^2 of material per m^3 of chamber volume was used in a 1 m^3 stainless-steel chamber. The average chamber concentration for this unspecified material was 5.9 μg/m^3 (1.1 ppbv).

Table 4.20. Summary of emissions of glycol ethers and acetates from materials in NASA database.[a]

	2-Butoxy ethanol				2-Ethoxy ethanol			
Category	Minimum	Maximum	Median	N[b]	Minimum	Maximum	Median	N[b]
Adhesives	–	12.0	–	1	0.1	200	30	3
Coatings	28.3	53.0	–	2	0.09	450	2	14
Compounds[c]	–	–	–	0	–	–	–	0
Cosmetics	–	–	–	0	–	–	–	0
Fabrics	–	–	–	0	–	0.23	–	1
Foam/Plastic	–	–	–	0	–	–	–	0
Lubricants	–	–	–	0	–	–	–	0
Pens/Inks	0.80	130.0	37	7	0.1	2800	390	6
Rubber	–	0.2	–	1	–	–	–	0

	2-Ethoxyethyl acetate				2-Methoxy ethanol			
Category	Minimum	Maximum	Median	N[b]	Minimum	Maximum	Median	N[b]
Adhesives	0.1	900	1.1	5	1.2	30	2.1	5
Coatings	0.05	1578	4.2	66	–	–	–	0
Compounds[c]	–	–	–	0	–	–	–	0
Cosmetics	–	–	–	0	–	–	–	0
Fabrics	0.07	0.7	0.37	3	–	0.33	–	1
Foam/Plastic	0.095	0.7	–	2	–	–	–	0
Lubricants	–	–	–	0	–	–	–	0
Pens/Inks	0.49	4.3	2.4	5	1.6	960	38	7
Rubber	–	–	–	0	–	–	–	0

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

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

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

Two studies have measured emissions of 2-butoxy ethanol from paints. Clausen *et al.* (1990) investigated emissions of VOC from five water-based paints in environmental chambers under controlled conditions over a one-year period. Two of the paints emitted 2-butoxy ethanol. For one paint, the chamber concentration was near 200 mg/m^3 (41 ppmv) immediately after application. The concentration decreased to a low and stable value after two days. Plehn (1990) investigated the emissions of VOC from low-emitting paints and varnishes from West Germany. Six of these products contained up to six percent by weight of 2-butoxy ethanol. Measurements made in a 17-m^3 test chamber showed that concentrations of 2-butoxy ethanol decreased to less than 10 mg/m^3 (2.1 ppmv) within 24 hours of application.

Summary

Data on indoor concentrations of glycol ethers and their acetate derivatives are very limited. Only a few measurements of 2-butoxy ethanol and 2-ethoxyethyl acetate in the U.S. have been reported, and these are for non-residential buildings.

A number of products commonly used by consumers contain glycol ethers and their acetate derivatives as solvents. The emissions data for these sources are primarily qualitative with only a few quantitative measurements of emissions from predominantly European products.

It is recommended that the glycol ethers and their acetate derivatives be included in a laboratory study of emissions and exposures resulting from the active use of expendable consumer products. Some product types that contain relatively large percent compositions of these compounds and are, therefore, suitable for investigation include architectural coatings, paint/varnish removers, inks, adhesives, household cleaners and cosmetics. The experiments should be conducted in a room-size environmental chamber using protocols that simulate typical consumer use of the products. The compounds should be given a secondary priority for study because they are in CARB Group III.

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Maleic anhydride

Uses and Sources

Maleic anhydride is used as a preservative for oils and fats. It is also used as a chemical intermediate in the production of polyester resins (HSDB, 1990). Rogozen *et al.* (1987) state that there are no known consumer product uses for maleic anhydride.

Concentration Data

No data on indoor concentrations of maleic anhydride were found.

Emissions Data

No data on emissions of maleic anhydride from potential indoor sources were found.

Summary

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

Indoor concentrations of maleic anhydride are likely to be nonexistent or very low. However, this compound is used as a chemical intermediate for polyester resins and could be released from some finished products. This possibility could be determined in a laboratory study of emissions of minor constituents from products and materials. Maleic anhydride should be given a relatively low priority for study because it is in CARB Group III and there are few probable sources.

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Phenol

Uses and Sources

Phenol is used as a general disinfectant and as a biocide in germicidal paints and slimicides. Its main use is as a chemical intermediate in the manufacture of a large number of other chemicals, particularly phenolic resins which are widely used in building materials (HSDB, 1990). It is also used in medicinal preparations such as throat lozenges, mouth washes and gargles, toothache drops and medicated shave creams (Syracuse Research Corp., 1989).

Krzymien (1989) investigated emissions of VOC from sprayed in place polyurethane foam insulation. One freshly sprayed and three cured foams were tested at elevated temperatures. Phenol was detected but not quantified in the off-gases of two of the foams.

Rittfeldt *et al.* (1984) detected phenol in the headspace vapors from vinyl floor tiles used in Sweden.

Phenol is a combustion byproduct that has been measured in mainstream cigarette smoke (Nanni *et al.*, 1990). It is, therefore, expected to be emitted in sidestream smoke possibly at higher rates than in mainstream smoke. Phenol is also emitted by wood-burning appliances and internal-combustion engines.

Concentration Data

Very few measurements of indoor concentrations of phenol have been made. 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 phenol in the effluent air were 4.6±1.9 ppbv (389 people, 85 percent male) and 4.0±0.5 ppbv (225 people, 80 percent female). The first measurement was made during a lecture, the second during an exam. The concentration of phenol in the unoccupied auditorium was 1.0±0.3 ppbv. This value was similar to that found in the influent air.

Investigators in Yugoslavia measured concentrations of phenol simultaneously inside and outside of six office buildings and, subsequently, in 18 school buildings (Kalinic *et al.*, 1987). Samples were collected over 24-hour periods in wash bottles containing 0.1 M NaOH. Phenol was then colorimetrically determined with a diazotized *p*-nitroaniline solution. For the office buildings, the average indoor concentration of 7.0±5.9 $\mu g/m^3$ (1.8±1.5 ppbv) was less than the average outdoor concentration of 51±43 $\mu g/m^3$ (13±11 ppbv). Concentrations in the air conditioned buildings were not correlated with outdoor concentrations. In the naturally ventilated buildings, indoor and outdoor concentrations were correlated, suggesting that a considerable portion of the indoor contamination may have been due to outside sources. In the school buildings, the median summer concentration of phenol was about 5 $\mu g/m^3$ (1.3 ppbv). The range was 3.4 to 77.3 $\mu g/m^3$ (0.88 to 20 ppbv). The median winter concentration was similar; the range was 2.2 to 17 $\mu g/m^3$ (0.57 to 4.4 ppbv).

Emissions Data

NASA Database

Only one material in the NASA database (McDonnell Douglas Corp., 1986), a fabric, was found to emit phenol.

Building Materials

Engström (1990) investigated emissions of VOC from 277 European building materials, including 43 floor coverings, 59 wall and ceiling coverings, 55 insulation materials, 45 textiles, 19 paints and eight other furnishings. The remaining materials were insulation products bonded with adhesive to metal plates. Emissions were measured in a 60-liter environmental chamber at a temperature of 40° C and an air exchange rate of 2 h^{-1}. The materials were at least three months old. Phenol was the second most encountered compound after formaldehyde. Only summary statistics are presented; no data are given for individual materials. Phenol was emitted by 48 of the insulations, textiles and floor and wall coverings. The median emission was 0.086 µg/h with a range of 0.034 to 2.71 µg/h.

Combustion Sources

Phenol is formed during incomplete combustion of wood and can be emitted by wood-burning stoves and fireplaces. DeAngelis *et al.* (1980) measured emissions from different types of wood burned in a fireplace and in two air-tight wood-burning stoves. Volatile organic compounds where collected in 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 phenol for seasoned oak were 0.015 g per kilogram of wood burned. Green pine released over twice this amount (0.035 g/kg). In the wood-burning stoves, seasoned oak emitted 0.085 g/kg; seasoned pine emitted 0.093 g/kg; and green pine emitted 0.19 g/kg. Some of these values are the averages of the results from both sample types (SASS and POM) while other values are from a single sample type.

Vehicle exhaust and evaporative emissions of fuel from vehicles may enter the living space of homes 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. Phenol has been shown to be a component of vehicle exhaust (Hampton *et al.*, 1983).

Other Sources

The rate of production of phenol by humans was calculated in the study of bioeffluents in a college auditorium discussed above (Wang, 1975). Using a mass-balance model, the average phenol emission values were estimated to be 9.5±1.5 mg/person-day (389 people, 85 percent male); 3.8±1.8 mg/person-day (410 people, 80 percent female); and 8.7±5.3 mg/person-day (225 people, 80 percent female).

Summary

No concentration data for phenol have been reported for U.S. residences, and no field studies of this compound are in progress in California. This lack of data suggests either that investigators have not attempted to identify phenol or that concentrations are below limits of detection for commonly employed sampling and analytical methods.

The emissions data for building materials are unusable for source modeling because they are entirely for European products and have been presented in summary form only. Emissions from other consumer product sources and environmental tobacco smoke (ETS) have not been investigated. This lack of data makes phenol a good candidate for laboratory studies of source emissions. It should be given a secondary priority ranking in these studies because it is in CARB Group III.

Emissions of phenol from building and interior finish materials could be determined in the laboratory by screening possible sources, such as products containing phenolic resins, for emissions in small-scale experiments. If potentially significant sources are identified, quantitative measurements of emission rates from these sources could be made under standardized conditions using environmental chambers.

It is recommended that phenol also be included in an environmental chamber study of emissions from expendable consumer products. These experiments should be conducted in a room-size chamber using protocols that simulate typical consumer use of products which contain phenol as a major ingredient. The predominant consumer product category which should be investigated is disinfectants.

It is further recommended that phenol be included in a laboratory study of emissions due to ETS since there are no data for phenol from this probable source.

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Propylene oxide

Uses and Sources

Propylene oxide is used as a fumigant for sterilization of packaged foods and fruit products and as an herbicide, insecticide, fungicide and soil sterilizer. It is added to dichloromethane as a stabilizer and is a component of brake fluids (HSDB, 1990). It is also used as a stabilizer in coatings (Rogozen *et al.*, 1987).

Sack and Steele (1989) re-analyzed the data from a U.S. EPA sponsored survey of 1,153 brand-name 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 chromatograms were later searched for additional compounds. The categories in which one or more products contained propylene oxide are shown in Table 4.21 with the number of products tested and the percentage that contained the compound. Table 4.22 lists the product categories which did not contain propylene oxide.

Table 4.21. Consumer product categories that contained propylene oxide (from Sack and Steele, 1989).

Product Category	No. Products	No. Pos./Total[a] %
Spray shoe polish	13	15
Water repellent	41	2
Paint remover	124	12
Spray paint	169	9
Primer and special primer	54	4
Wood finishes	64	16
Silicone lubricant	25	4
Adhesive	62	15
Miscellaneous non-automotive	16	6
Gasket cleaners/Removers	11	27
Belt lubricants/Dressings	11	9
Tire cleaner/Tire paint	13	38

[a] Percent of products in category that contained propylene oxide.

Concentration Data

The only known study of indoor concentrations of propylene oxide produced negative results. 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. None of these houses had concentrations of propylene oxide in excess of the 0.13 ppbv detection limit.

Table 4.22. Consumer product categories that did not contain propylene oxide (from Sack and Steele, 1989).

Product Category	No. Products	Product Category	No. Products
Suede protector	8	Spray cleaner/degreaser	9
Fabric finisher	6	Electric shaver cleaner	11
Spot remover	19	Correction fluid	10
Stain remover	2	Record cleaner	18
Furniture polish	16	Record player cleaner	5
Floor Wax	12	Tape recorder cleaner	10
Wax stripper	1	VCR cleaner	8
Wood Cleaner	16	TV/computer screen cleaner	4
Deodorizer/disinfectant	7	Adhesive removers	8
Oven cleaner	8	Carburetor and choke cleaner	30
Laundry presoak	6	Engine cleaner	18
Anti-static spray	2	Automotive undercoat	6
Spray starch	4	Battery cleaners/protectors	10
Rug cleaner	11	Brake quieters/Cleaners	13
Window cleaner	5	Tire puncture sealers	1
Bathroom cleaner	5	Starting fluid spray	1
Dip metal cleaner	6	Windshield de-icer	2
Specialized cleaner	11	Door spray lubricant	3
Paint thinner	12	Chrome protector/wax	1
Lubricant	51	Vinyl top spray	1
Rust remover	6	Water pump lubricant	1
All purpose liquid cleaner	12	Transmission cleaner	9
Wallpaper removers/adhesive	2	Automotive sealant	5
Caulking	7	Liquid exterior car cleaner	3
Upholstery cleaner	3	Miscellaneous auto products	9

Emissions Data

Only six consumer products in the NASA database (McDonnell Douglas Corp., 1986) were found to emit propylene oxide. Four were adhesives and two were lubricants. The emissions from the adhesives ranged from 0.5 to 19 μg propylene oxide per gram of material. The lubricants emitted 13.3 and 28.9 μg/g. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Summary

The current data on indoor concentrations of propylene oxide are minimal. Propylene oxide 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.

There are no quantitative emissions data for proplyene oxide. Propylene oxide is present in some consumer products that are used indoors. The percent composition of propylene oxide in these products is probably low since the compound is an additive used as a biocide or stabilizer. Therefore, it is recommended that propylene oxide 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. The types of products that could be investigated include architectural coatings, adhesives, lubricants and shoe polish. If significant sources are identified by preliminary screening, source emission rates could be measured under standardized conditions using environmental chambers.

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Allyl chloride

Uses and Sources

Allyl chloride is used in thermosetting resins for varnishes and in plastics and adhesives. It is used in the manufacture of insecticides, pharmaceuticals and resins (HSDB, 1990).

Concentration Data

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 eight people were monitored during this study. The homes were purposefully, not randomly, selected. Samples for allyl chloride were collected on Tenax sorbent tubes over 24-hour periods and analyzed by GC/MS. Allyl chloride was detected in 13 percent of the indoor samples. The mean concentration for 12 homes was 0.28 ± 0.10 $\mu g/m^3$ (0.090 ± 0.032 ppbv).

Emissions Data

No data on emissions of allyl chloride from potential indoor sources were found.

Summary

The current data on indoor concentrations of allyl chloride are minimal. Allyl chloride 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.

Allyl chloride is used as a chemical intermediate and may be emitted by some products that are used indoors. This could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Product types which are possible sources of allyl chloride include some varnishes, adhesives and insecticides. Allyl chloride should be given secondary priority for study because it is in CARB Group III.

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Benzyl chloride

Uses and Sources

Benzyl chloride is used in the manufacture of bactericides, fungicides, flavors, odorants, insecticides, lubricants, plastics, plasticizers and gasoline gum inhibitors (HSDB, 1990). Benzyl chloride is present as a contaminant in butyl benzyl phthalate, a plasticizer used in the manufacture of vinyl floor tiles. Rittfeldt *et al.* (1984) found benzyl chloride in different brands of butyl benzyl phthalate at concentrations ranging from 0.01 to 0.05 percent.

Concentration Data

Data for indoor concentrations of benzyl chloride are very limited. 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 eight people were monitored during this study. The homes were purposefully, not randomly, selected. Samples for benzyl chloride were collected on Tenax sorbent tubes over 24-hour periods at a low flow rate and analyzed by GC/MS. Concentrations of benzyl chloride were below the unspecified limit of detection in all of the houses. Pleil *et al.* (1985) used SUMMA-polished canisters to collect air samples in the homes of co-workers. The samples were analyzed using an automated GC/FID-GC/ECD system equipped with a cyrogenic pre-concentrator. The investigators found benzyl chloride in three of the 31 samples analyzed. The average concentration in the positive samples was 6.2 ppbv with a range of 4.9 to 7.2 ppbv.

Emissions Data

Rittfeldt *et al.* (1984) investigated emissions of benzyl chloride from a new vinyl floor tile. The tile (360 cm^2) was placed on the wall of a one-liter cylindrical chamber which was ventilated with charcoal-filtered air. The ventilation rate was varied between 0.1 and 0.7 l/min. Increasing the ventilation rate caused an increase in the emission rate (Table 4.23).

Table 4.23. Emission of benzyl chloride from vinyl floor tile (from Rittfeldt *et al.*, 1984).

Ventilation (l/min)	Concentration ($\mu g/m^3$)	Emission Rate ($\mu g/m^2$-h)
0.10	5	0.8
0.40	3	2
0.70	1	2

Summary

The limited data that are available suggest that indoor concentrations of benzyl chloride are typically very low. However, concentrations may be elevated in houses with sources that contain butyl benzyl phthalate as a plasticizer, such as vinyl floor tiles.

Benzyl chloride 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.

Emissions data for benzyl chloride are limited to a single study of vinyl floor tiles. Additional data could be obtained by including benzyl chloride in a laboratory study of emissions of minor constituents from products and materials. Products containing butyl benzyl phthalate as a plasticizer should be screened for emissions since benzyl chloride is a contaminant in this compound. Other possible sources of benzyl chloride include various biocides, lubricants and plastics. If significant sources are identified, emission rates could be measured under standardized conditions using environmental chambers. Benzyl chloride should be given secondary priority for study because it is in CARB Group III.

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Chlorobenzene

Uses and Sources

Chlorobenzene is used as a solvent in the manufacture of adhesives, paints, polishes, waxes, pharmaceuticals and natural rubber. It is also used as a tar and grease remover in degreasing operations and is occasionally used as a dry-cleaning solvent (HSDB, 1990). The CTCP (1990) database lists chlorobenzene as an ingredient in only two products: one a coating and the other an herbicide.

Sack and Steele (1989) re-analyzed the data from a U.S. EPA sponsored survey of 1,153 brand-name 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 chromatograms were later searched for additional compounds. Chlorobenzene was not found in any of these products.

Concentration Data

There are over 2,000 data points for chlorobenzene in the National VOC (NVOC) database (Shah and Heyerdahl, 1988). The average concentration is 0.041 ppbv. The median concentration is zero, indicating that the distribution is highly skewed.

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.

Chlorobenzene was only occasionally detected in these studies above the quantifiable limit of 0.4 $\mu g/m^3$ (0.09 ppbv). The range of percent measurable concentrations in air and breath samples was 0-13 percent in Los Angeles in 1984, 0-18 percent for Contra Costa County in 1984, and 0-10 percent in Los Angeles in 1987. Further statistical analysis of the data for chlorobenzene was not undertaken.

Data for indoor concentrations of chlorobenzene in the U.S. are available from two other studies. 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 chlorobenzene were collected on Tenax sorbent tubes over 24-hour periods at a low flow rate and analyzed by GC/MS. Concentrations of chlorobenzene were below the limit of detection (LOD) of 0.3 $\mu g/m^3$ (0.065 ppbv) in all of the homes. Cohen *et al.* (1988) conducted a survey of 35 homes in the Kanawha Valley, WV. The homes were selected based on their proximity to heavy industry. Therefore, the sample population was not representative of the entire population in the area. Passive samplers were placed both inside and outside the homes for a three-week period. Sixty-three percent of the houses had indoor concentrations of chlorobenzene above the LOD of 4.3 $\mu g/m^3$ (0.94 ppbv). None of the outdoor samples were above the LOD. The mean indoor concentration was 16.5±21.9 $\mu g/m^3$ (3.60±4.77 ppbv). The median was 5.62 $\mu g/m^3$ (1.23 ppbv) and the maximum was 72.2 $\mu g/m^3$ (15.7 ppbv). These concentrations are substantially higher than the concentrations in the NVOC database and those in the California studies. It is possible that the difference was due to the proximity of industry to the homes in West Virginia. However, outdoor concentrations were low, suggesting the presence of indoor sources.

Lebret *et al.* (1986) measured VOC concentrations in a survey of over 300 Dutch homes grouped into three age categories. Measurements were taken in 134 post World War II homes in Ede and in 89 prewar homes in Rotterdam during the winter of 1981-82. The following winter, 96 homes in Ede, less than six-years old, were sampled. The homes were selected at random from the housing registers of each city. Samples were collected on charcoal tubes over a period of 5 to 7 days. The samples were desorbed with carbon disulfide and analyzed by GC/FID. For all three groups, the median concentration of chlorobenzene was less than 0.4 $\mu g/m^3$ (0.087 ppbv). The maximum concentration of 27 $\mu g/m^3$ (5.9 ppbv) occurred among the group of less than 6-year old homes in Ede.

Emissions Data

NASA Database

The NASA database (McDonnell Douglas Corp., 1986) contains records for 16 materials or products that emit chlorobenzene, 14 of which are foams and plastics. The median emission of chlorobenzene for the foams and plastics was 2.2 $\mu g/g$. One coating material emitted 1450 $\mu g/g$ and one rubber product emitted 2 $\mu g/g$. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Building Materials

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. In the headspace experiments, the emission of chlorobenzene was only detected from polystyrene foam insulation The emission rate was 0.46 $\mu g/m^2$-h. The other materials did not emit detectable levels of chlorobenzene. However, when tested in the environmental chamber, two of these materials were also found to emit chlorobenzene. A vinyl cove molding had an emission rate of 1.8 $\mu g/m^2$-h and a black rubber molding had an emission rate of 0.31 $\mu g/m^2$-h. The emission rate of chlorobenzene from the polystyrene foam insulation during the chamber studies was 0.38 $\mu g/m^2$-h which is in good agreement with the headspace measurement.

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 headspace concentration of chlorobenzene for the four samples at 80° C in dry air was 27±7 mg/m^3 (5.9±1.5 ppmv). At 80° C and 90 percent relative humidity, the emission of chlorobenzene was greater with an average concentration of 84±23 µg/m^3 (18±5.0 ppmv) for the four samples. The emission was significantly lower at 40° C with the concentration ranging from 0.1-2 mg/m^3 (0.022-0.44 ppmv) for the four samples.

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 are only semi-quantitative. The emission rate of chlorobenzene from the foam samples was 0.02 and 0.01 µg/cm^2-h, respectively. Chlorobenzene emissions from the board stock samples were 0.02 and 0.03, µg/cm^2-h, respectively. More accurate data were generated for the third foam sample by determining the percent collection and desorption efficiencies for seven selected compounds, including chlorobenzene. For this case, the emission rate was lower, 0.0018 µg/cm^2-h. The collection/desorption efficiency was 90 percent.

Combustion Sources

Small amounts of chlorobenzene were detected in air collected through an inverted funnel above the top burners of two of the three gas cooking ranges tested by Moschandreas *et al.* (1983). The concentrations of chlorobenzene in the exhaust air were less than 0.22 ppbv.

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 µg/m^3. Chlorobenzene concentrations in the contaminated houses averaged 16.4 µg/m^3 (3.58 ppbv) in the crawl spaces and 0.2 µg/m^3 (0.044 ppbv) in the living rooms. The mean concentration in both the crawl spaces and the living rooms of the reference houses was less than 0.1 µg/m^3 (0.022 ppbv).

Summary

Data for indoor concentrations of chlorobenzene are available from field studies in the U.S. and California which used probability-based samples of homes. In general, chlorobenzene was only occasionally detected, and concentrations were very low with an average value of less than 0.05 ppbv from the NVOC database.

Chlorobenzene is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). 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.

The data in the NVOC database suggest that the distribution of indoor concentrations of chlorobenzene is highly skewed, perhaps because there are only a few important indoor sources of this compound. For example, chlorobenzene was not detected in over 1,000 consumer products that were surveyed for chlorinated solvents.

There are some data available on emission rates of chlorobenzene from building materials. However, the studies were too limited in scope to be of much use in models for estimating indoor concentrations. Additional data for chlorobenzene could be obtained by including it in both a laboratory study of emissions of minor constituents from products and materials and in an environmental chamber study of emissions resulting from the use of expendable consumer products. Chlorobenzene should be given secondary priority for these studies because it is in CARB Group III. Building materials including plastic moldings and polystyrene and polyurethane insulation could be screened for emissions of chlorobenzene. Emission rates for any significant sources that are identified by screening could be measured under standardized conditions using environmental chambers. If chlorobenzene is found to be a major ingredient of some consumer products, such as paints, waxes, adhesives and pharmaceuticals, then use of these products indoors is likely to result in relatively high exposure to this compound. Such exposure could be investigated by the application of representative products in a room-size environmental chamber.

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Chloroprene

Uses and Sources

The chloroprene monomer is primarily used (both alone and with comonomers) in the manufacture of neoprene rubber. Neoprene rubber is a component of a number of domestic products. The extent to which any unreacted monomer would be released from finished products is unknown. Chloroprene is also used as a component of adhesives that are used in food packaging (HSDB, 1990).

Concentration Data

No data on indoor concentrations of chloroprene were found.

Emissions Data

No data on emissions of chloroprene from potential indoor sources were found.

Summary

Chloroprene 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. Only qualitative data will be obtained for chloroprene.

Unreacted chloroprene may be released from household products containing neoprene rubber. The potential for this release could be determined in a laboratory study of emissions of minor constituents from products and materials. Chloroprene should be given secondary priority for study because it is in CARB Group III.

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p-Dichlorobenzene

Uses and Sources

Para-dichlorobenzene (DCB) is primarily used as a room deodorizer and for moth control. It is also used in pesticides, other agricultural chemicals, abrasives, floor waxes and floor finishes and for dye synthesis (HSDB, 1990; Life Systems, Inc., 1989). The CTCP (1990) database lists over 100 products containing DCB that are marketed as deodorants, moth repellants, or both. Most of them contain 97-100 percent DCB by weight. A few animal repellants, bacteriocides, mildewcides and fumigants are additionally listed. These also contain up to 100 percent DCB by weight.

In qualitative dynamic headspace analyses, emissions of DCB have been detected from hardwood plywood and carpeting (Montieth, *et al.* 1984).

The NASA database (McDonnell Douglas Corp., 1986) does not differentiate between isomers of DCB. Low-level emissions of unspecified DCB were detected from a few fabric products and one adhesive. No room deodorizers appear to have been tested.

Concentration Data

The major sources of data for indoor concentrations of DCB are the National VOC (NVOC) database, Krause *et al.* (1987) and the U.S. EPA's Total Exposure Assessment Methodology (TEAM) studies. All three studies are summarized in Table 4.24.

There are over 2,000 data points for DCB in the NVOC database (Shah and Heyerdahl, 1988). The average concentration is 4 ppbv, and the median concentration is 0.3 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 compounds were desorbed with carbon disulfide and analyzed by GC/FID and GC/ECD. The average concentration of DCB was 22 $\mu g/m^3$ (3.7 ppbv), and the median concentration was 4.7 $\mu g/m^3$ (0.8 ppbv). These concentrations generally agree with the data from the NVOC database and the California TEAM studies.

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.

The concentrations of DCB were similar in both locations in the summer of 1984 with median concentrations near 0.1 ppbv. In Los Angeles, concentrations were higher in the winter than in the summer for both years. This difference was particularly noticeable in the 95th percentile concentrations, which ranged up to 47 ppbv in the winter of 1987. Generally higher concentrations in the winter could have resulted from decreased ventilation rates and greater use of room deodorizers or moth crystals.

Table 4.24. Summary statistics for concentrations of p-dichlorobenzene in ppbv (from Shah and Heyerdahl, 1988; Krause *et al.*, 1987; Pellizzari *et al.*, 1987; Wallace *et al.*, 1989a).[a]

			Percentiles					
Study	N	Average	25	50	75	90	95	Range
NVOC	2121	4.0	0.05	0.28	0.93	–	–	–
Krause *et al.* (1987)	230	3.7	–[b]	0.78	–	2.8	–	<0.17-212
TEAM[b,c]								
L.A.-Winter '84								
Overnight Personal	112	3.4	0.21	0.43	1.22	9.02	16.7	0.005-71.8
L.A.-Summer '84								
Overnight Personal	51	2.30	0.07	0.14	0.45	3.84	18.4	0.01-41.8
C.C.-Summer '84								
Overnight Personal	69	1.21	0.04	0.09	0.50	1.39	6.68	0.01-25.2
L.A.-Winter '87								
Overnight Kitchen	42	6.05	0.23	0.39	3.09	26.6	47.1	0.05-53.4
Daytime Kitchen	46	3.92	0.11	0.23	1.02	11.4	39.2	0.01-55.3
Daytime Living Area	45	4.44	0.17	0.27	1.55	15.3	38.7	0.05-45.6
L.A.-Summer '87								
Overnight Personal	39	2.82	0.07	0.24	1.20	3.82	34.7	0.01-45.4
Overnight Kitchen	34	0.67	0.05	0.12	0.56	2.37	3.74	0.01-5.71
Daytime Kitchen	36	1.08	0.05	0.10	0.62	1.31	5.56	0.01-26.2
Daytime Living area	39	1.20	0.07	0.16	0.59	1.75	7.98	0.01-25.6

[a] Statistic not presented in reference.

[b] Converted from mass/volume units.

[c] m- and p- isomers reported together.

Emissions Data

Consumer Products

Wallace *et al.* (1989b) conducted a study of the influence of personal activities on exposure to VOC. Seven study subjects were asked to perform specific activities suspected of increasing exposure to 17 target VOC. Each subject was monitored for nine sequential time periods over three days using a personal sampling pump and Tenax sorbent tubes. The investigators associated increased exposure to DCB with the use of solid and liquid room deodorizers. Use of a toilet-bowl deodorizer resulted in a large increase in the air concentrations and personal exposures for DCB as shown in Table 4.25.

Table 4.25. Effect of a toilet-bowl deodorizer on indoor air concentrations of, and personal exposures to, p-dichlorobenzene (from Wallace *et al.*, 1989b).[a]

			Personal Exposure	
Time Period	Averaging Time (h)	Air Concentration (ppbv)	Person 1 (ppbv)	Person 2 (ppbv)
1	3.7	0.17	0.17	0.17
2	8.2	0.33	0.33	0.50
3[b]	11.6	11	1.3	7.2
4	4.0	42	40	42
5	12.0	20	50	55
6	8.6	32	37	--[c]
7	3.5	72	71	57
8	11.5	75	78	68
9	8.5	105	75	84

[a] Data converted from mass/volume units.

[b] Deodorant placed in toilet bowl during this period.

[c] Sample lost.

Table 4.26 presents emissions measurements made by Tichenor *et al.* (1990) for moth repellant cakes. The tests were conducted in a 166-liter stainless-steel chamber. The emission rates of DCB increased with increasing chamber ventilation rate and temperature. After two of the tests, the chamber walls were carefully washed with methanol. The volume of solvent was measured and an aliquot analyzed by GC/ECD. About 160 mg of DCB were recovered after test 8 and about 23 mg were recovered after test 9. The final concentrations in the chamber for these tests were 5,300 and 1,170 mg/m^3 (885 and 195 ppmv), respectively. These results demonstrated that there were significant wall losses of DCB that were related to concentrations in the chamber.

Table 4.26. Emissions of p-dichlorobenzene from moth crystal cakes (from Tichenor *et al.*, 1990).

Test Number	Temperature (°C)	Relative Humidity (%)	Air Exchange Rate (h^{-1})	Emission Rate (mg/cm^2-hr)
1	23	20	0.25	1.1
2	23	20	0.50	1.4
3	23	20	1.0	1.6
4	23	50	0.25	1.2
5	23	50	1.0	1.5
6	23	50	2.0	1.8
7	35	20	0.25	4.2
8	35	50	0.25	4.0
9	35	20	1.0	5.0
10	35	50	2.0	5.9
11	35	50	0.5	4.3

Tichenor *et al.* (1990) developed an indoor air quality model to estimate the effects of a number of parameters on the concentrations of pollutants in indoor air. Model predictions of concentrations of DCB resulting from use of moth repellent cakes were in close agreement with actual concentrations measured in a test house when appropriate values for source emission rates, air exchange rate, in-house air movement and losses to sinks were provided. Table 4.27 shows predicted and measured concentrations of DCB in the various rooms of the test house.

Table 4.27. Comparison of measured concentrations of p-dichlorobenzene with model predictions (from Tichenor *et al.*, 1990).

Room	Measured Concentration (ppbv)[a]	Predicted Concentration (ppbv)[a]
Closet	12	12
Corner bedroom	0.85	0.95
Master bedroom	0.65	0.67
Den	0.62	0.67

[a] Data converted from mass/volume units.

Building Materials

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. Most, if not all, of these materials are likely to be used in residential construction. The results are summarized in Table 4.28. Emissions of DCB from these materials were relatively low. No emission rate exceeded 1 $\mu g/m^3$-h.

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 DCB (Sheldon *et al.*, 1988). Immediately after construction, the mean specific source strength of DCB was 0.076 $\mu g/m^3$-h with a maximum of 0.15 $\mu g/m^3$-h. The building was sampled again four months after construction when it was fully occupied. At that time, the mean specific source strength was 0.8 $\mu g/m^3$-h, with a maximum of 1.4 $\mu g/m^3$-h. The increase indicated that sources were imported with the building's occupants.

Wallace *et al.* (1987) measured emission rates of DCB 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/wood assembly was the only material that emitted DCB. The emission rate was 2.5 $\mu g/m^2$-h. The emission rate for the combined use of cleaning agents and an insecticide on a wood panel was 26 $\mu g/m^2$-h.

Hartwell (1986) 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 were only semi-quantitative. The amount of compound present was estimated by comparing its total-ion-current area to the total-ion-current areas of chlorobenzene or n-decane standards. The emission rate of unspecified dichlorobenzene isomers for one of the foam samples was 0.003 μg/m^2-h. No DCB was detected from the second sample. The emission rate of DCB from one of the board stock samples was 0.004 μg/m^2-h. Again, no DCB was detected from the second sample.

Table 4.28. Emission rates of p-dichlorobenzene from building materials in μg/m^2-h (from Sheldon *et al.*, 1988).

Sample	Headspace	Chamber
Particle board	0.14	0.18
Carpet adhesive	–[a]	–
Black rubber molding	0.51	0.97
Latex paint	–	–
Linoleum tile	0.08	–
Polystyrene foam insulation	0.71	0.47
Vinyl cove molding	0.18	–
Cove adhesive	NM[b]	–
Carpet	–	–
Vinyl edge molding	0.18	
Small diameter telephone cable	0.58	
Large diameter telephone cable	0.24	
Urethane sealant	–	
Latex paint	–	
Tar paper	–	
Primer/adhesive	–	
Latex caulk	–	
PVC pipe	–	
Water repellant mineral board	–	
Cement block	–	
Treated metal roofing	–	
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] Not measured, sample overloaded.

Combustion Sources

Small amounts of unspecified DCB were detected in air collected through an inverted funnel above the top burners of one of the three cooking ranges tested by Moschandreas *et al.* (1983). The fuel was municipal gas. The concentrations of DCB in the exhaust air were less than 0.17 ppbv.

Summary

Data for indoor concentrations of DCB in 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 estimated to range between 0.1 and 0.4 ppbv. Additional data for another California community are being obtained by the Woodland field study being conducted by the CARB (Sheldon, 1990).

The most significant indoor source of DCB is cakes, crystals, or pellets of nearly pure compound used as a deodorant or moth repellant. Emissions from moth crystal cakes have been well characterized in chamber studies. The measured emission rates have been used in an indoor air quality model which takes into account losses to surfaces. The ability of the model to predict concentrations of DCB was validated in a test house. If the important parameters are known, this model can be used to predict concentrations of DCB in other environments.

Because both indoor concentration and source emission data exist for DCB, further investigation of this compound should probably be given low priority.

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Epichlorohydrin

Uses and Sources

Epichlorohydrin is used as a solvent for paints, varnishes, lacquers, nail enamels and natural and synthetic resins. It is also used as an insect fumigant and sporicide (HSDB, 1990). Epichlorohydrin is manufactured primarily for use as a chemical intermediate in the production of epoxy resins and elastomers. The elastomers are used to make automotive parts, adhesives and rubber coating for fabrics. These products may contain epichlorohydrin as a trace contaminant (Rogozen *et al.*, 1987).

Concentration Data

No data on indoor concentrations of epichlorohydrin were found.

Emissions Data

The NASA database (McDonnell Douglas Corp., 1986) provides the only data on emissions of epichlorohydrin. The emissions of epichlorohydrin from three adhesives ranged from 0.6 to 13 ng per gram of material. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Summary

There are no data on indoor concentrations of epichlorohydrin, and no field studies of this compound are in progress in California.

Data on emissions of epichlorohydrin could be obtained by including it 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. It should be given a relatively low priority for these studies because it has not yet been classified as a candidate toxic air contaminant by the CARB. Product types which could be screened for possible low-level release of epichlorohydrin include adhesives and rubberized fabric coatings. Epichlorohydrin is a solvent in some architectural coatings. Use of these products indoors could result in relatively high exposure to this compound. Such exposure could be investigated by the application of representative products in a room-size environmental chamber.

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Hexachlorobenzene

Uses and Sources

Hexachlorobenzene is used in the production of synthetic rubber and as a plasticizer for polyvinyl chloride (PVC). The extent to which hexachlorobenzene is released from finished products is unknown. It is also used as a fungicide for commercial crops (HSDB, 1990).

Concentration Data

The Nonoccupational Pesticide Exposure Study (NOPES) was conducted by the U.S. EPA in the Summer of 1986 in Jacksonville, FL, and in the Spring of 1987 and the Winter of 1988 in Jacksonville and Springfield, MA (Immerman and Schaum, 1990). Measurements of selected pesticides in fixed-site indoor and outdoor air, personal air, 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 population size for the Jacksonville study area was approximately 290,000. The population size for the Springfield study area was approximately 135,000. Samples were collected on polyurethane foam plugs using small sampling pumps. The compounds were Soxhlet extracted and concentrated. Quantitative analysis was performed by GC/ECD, and GC/MS was used for confirmation. Only six to 45 percent of the samples had detectable concentrations of hexachlorobenzene. Weighted mean concentrations for all three seasons are shown in Table 4.29. Median concentrations were reported as zero for both study areas in all seasons.

Table 4.29. Weighted mean concentrations of hexachlorobenzene in indoor and personal air (from Immerman and Schaum, 1990). All concentrations are in parts per trillion by volume and have been converted from mass/volume units. Numbers of samples are shown in parentheses.

Study Area	Summer	Spring	Winter
Jacksonville, FL			
Indoor Air	0.11 (62)	0.03 (72)	0.03 (71)
Personal Air	0.08 (63)	0.03 (71)	0.03 (71)
Springfield, MA			
Indoor Air	--[a]	0.00 (49)	0.01 (51)
Personal Air	–	0.00 (48)	0.00 (52)

[a] Measurement not made during this season.

Emissions Data

No data on emissions of hexachlorobenzene from potential indoor sources were found.

Summary

The data for two U.S. communities demonstrate that indoor concentrations and personal exposure for hexachlorobenzene are very low (considerably less than a part per trillion).

Hexachlorobenzene 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, combined vapor- and particle-phase concentrations will be measured in 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.

Hexachlorobenzene partitions between vapor and particle phases in air due to its low vapor pressure at room temperature. In general, it is difficult to measure emissions of semivolatile compounds in chamber experiments because losses to chamber surfaces and sampling lines are substantial. If additional data are needed for hexachlorobenzene, they would best be obtained by a field study.

References

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

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Methyl bromide

Uses and Sources

Methyl bromide, or bromomethane, is widely used as a biocide. It has a number of indoor applications as an insecticide, herbicide and fungicide. In the food industry, methyl bromide is used for pest control on fruits, vegetables, dairy products, nuts and grains (HSDB, 1990).

Concentration Data

Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA to measure indoor concentrations and personal exposures for toxic air contaminants. Samples of very volatile organic compounds were collected in four houses using 6-liter SUMMA-polished cannisters and were analyzed by GC/MS. None of these houses had concentrations of methyl bromide in excess of the detection limit of 0.26 $\mu g/m^3$ (0.067 ppbv)

Emissions Data

No data on emissions of methyl bromide from potential indoor sources were found.

Summary

Methyl bromide 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 possible that a field study will not produce data that are adequate for assessing indoor exposure to methyl bromide since this exposure is expected to be directly related to the episodic use of certain biocides. Therefore, it is recommended that methyl bromide be included in an environmental chamber study of emissions from consumer products. Exposure resulting from the use of biocides could be directly determined by applying the products in a typical manner in a room-size chamber. Methyl bromide should be given a secondary priority for study because it is in CARB Group III.

References

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Methyl chloroform

Uses and Sources

Methyl chloroform, or 1,1,1-trichloroethane (TCE), is widely used as a solvent for natural and synthetic resins, oils, waxes, adhesives, coatings and inks. It is used as a dry cleaning solvent and in many general purpose cleaners. It is also found in aerosol sprays, in which it acts as a vapor-pressure depressant and as a solvent/carrier for the active ingredient (HSDB, 1990).

Table 4.30. Percent weight composition of 1,1,1-trichloroethane in consumer product categories (from Westat, Inc. and Midwest Research Institute, 1987).

Product Category	Brands Tested	Positive/Total[a] %	Composition Range % (w/w)
Non-automotive Products			
Drain cleaners	1	100	97.8
Specialized aerosol cleaners	12	50	0.2-83.8
Spot removers	18	50	10.5-110.8
General purpose spray cleaners	9	44	0.1-71.4
General purpose liquid cleaners	12	33	72.7-126.7
Wood cleaners	13	15	12.3-20.4
Oven cleaners	8	13	97
VCR cleaners	7	14	97.8
Tape recorder cleaners	15	33	0.2-101.5
Electric shaver cleaners	12	17	2.5-20.3
Adhesive removers	9	22	0.1-95.0
Paint removers/strippers	109	6	0.1-25.7
Primers/special Primers	61	3	1.2-61.8
Wood stains/varnishes/finishes	63	9	0.1-21.4
Suede protectors	8	88	4.8-118.5
Water repellents	32	50	0.2-116.2
Spray shoe polishes	11	45	11.4-62.3
Fabric finishes	5	40	77.9-85.1
Silicone lubricants	28	54	0.2-91.1
Lubricants	53	32	0.1-104.5
Adhesives	66	26	0.2-121.1
Typewriter correction fluids	9	89	16.0-110.1
Miscellaneous products	17	24	12.5-67.5
Automotive Products			
Brake quieters/cleaners	12	75	0.4-75.6
Belt lubricants/dressings	10	60	11.4-72.0
Door spray lubricants	2	50	95.6
Ignition wire driers	7	43	24.3-43.6
Tire cleaners/paints	14	42	0.1-90.3
Transmission cleaners/lubricants	7	14	113.0
Battery terminal protectors/cleaners	10	10	37.1

[a] Percent of products in category that contained 1,1,1-trichloroethane.

A U.S. EPA sponsored survey of 1,153 brand-name products for the presence of six chlorocarbon solvents provides extensive data on the TCE composition of consumer products (Westat, Inc. and Midwest Research Institute, 1987). Each material was analyzed by a purge and trap GC/MS method and the results reported as percent TCE by weight. Table 4.30 lists all the product categories with products that contained <u>more</u> than one percent TCE by weight. Table 4.31 lists the categories with products that contained <u>less</u> than one percent TCE by weight. The survey did not include all possible consumer sources of TCE. Insecticides and health and beauty aids, for example, were not tested.

Table 4.31. Consumer-product categories that contained less than one percent 1,1,1-trichloroethane by weight (from Westat, Inc. and Midwest Research Institute, 1987).

Product Category	Brands Tested
Non-automotive Products	
Aerosol furniture polish/wax/cleaner	10
Aerosol spray paints	155
Air deodorizers/disinfectants	7
Anti-static sprays	1
Bathroom/kitchen cleaners	6
Caulking products	7
Dip dye metal cleaners	6
Floor wax	11
Laundry presoaks/pre-cleaners	6
Non-aerosol furn polish/wax/cleaner	5
Paint thinners	11
Record cleaners	19
Rug/upholstery cleaners	12
Spray starches	4
Stain removers	2
Stereo/record player cleaners	6
TV/computer screen cleaners	5
Video disk cleaners	3
Wallpaper removers/adhesives	2
Wax stripper	1
Window/glass cleaners	6
Automotive Products	
Automotive sealants	5
Automotive undercoats	6
Bumper/chrome waxes	1
Carburetor cleaners	29
Engine degreasers	20
Gasket removers/adhesives	12
Liquid exterior car cleaners	3
Rust removers	7
Starting fluid sprays	1
Tire puncture sealers	1
Upholstery cleaner sprays	3
Vinyl top sprays	1
Water pump lubricants	1
Windshield de-icers	2
Miscellaneous automotive	8

Wallace *et al.* (1989b) conducted a study of the influence of personal activities on exposure to VOC. Seven study subjects were asked to perform specific activities suspected of increasing exposure to 17 target VOC. Each subject was monitored for nine sequential time periods over three days using a personal sampling pump and Tenax sorbent tubes. One subject visited a dry-cleaning establishment for ten minutes; the resultant personal exposure to TCE, averaged over an 11-hour period, was 1,000 µg/m^3 (183 ppbv). Contact with dry-cleaned clothes may also have resulted in increased exposure of another subject to TCE.

Concentration Data

The major sources of indoor concentration data for TCE are the National VOC (NVOC) database, Krause *et al.* (1987) and the EPA's Total Exposure Assessment Methodology (TEAM) studies (Table 4.32).

Table 4.32. Summary statistics for concentrations of 1,1,1-trichloroethane in ppbv (from Shah and Heyerdahl, 1988; Krause *et al.*, 1987; Pellizzari *et al.*, 1987; Wallace *et al.*, 1989a).

			Percentiles					
Study	N	Average	25	50	75	90	95	Range
NVOC	2120	48.9	0.55	1.84	5.51	--[b]	–	–
Krause *et al.* (1987)[a]	230	1.46	–	0.80	–	2.41	–	<0.19-48.8
TEAM[a]								
L.A.-Winter '84								
Overnight Personal	112	7.49	3.52	4.81	9.25	15.5	24.1	0.01-44.4
L.A.-Summer '84								
Overnight Personal	51	2.50	1.13	1.33	2.04	3.15	4.44	0.35-66.6
C.C Summer '84								
Overnight Personal	69	1.17	0.43	0.80	1.63	2.22	2.96	0.06-7.40
L.A.-Winter '87								
Overnight Kitchen	42	4.48	1.50	3.55	6.51	9.32	12.5	0.24-16.7
Daytime Kitchen	47	2.59	1.21	1.77	3.44	5.64	8.08	0.42-10.5
Daytime Living Area	45	2.76	1.14	2.33	3.18	6.09	8.44	0.67-11.1
L.A.-Summer '87								
Overnight Personal	40	1.91	0.96	1.44	2.20	3.79	6.14	0.34-9.77
Overnight Kitchen	37	2.42	1.02	1.68	2.68	4.42	11.7	0.06-12.7
Daytime Kitchen	38	3.42	0.89	1.96	2.35	4.48	10.8	0.28-55.7
Daytime Living area	40	2.72	0.96	1.67	2.78	5.00	13.0	0.32-22.0

[a] Converted from mass/volume units.
[b] Statistic not presented in reference.

There are over 2,000 data points for TCE in the NVOC database (Shah and Heyerdahl, 1988). The average concentration is 49 ppbv while the median concentration is only 1.8 ppbv. This indicates that the data are highly skewed.

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 compounds were desorbed with carbon disulfide and analyzed by GC/FID and GC/ECD. The average concentration is 7.9 μg/m^3 (1.5 ppbv), and the median is 4.3 μg/m^3 (0.80 ppbv). These concentrations are somewhat lower than concentrations measured in the U.S.

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.

The results for the two locations in the summer of 1984 are similar with somewhat higher concentrations of TCE for the Los Angeles population. In Los Angeles, relatively high concentrations occurred during the winter of 1984, perhaps due to decreased ventilation rates. Differences between the two seasons were less pronounced in 1987.

Emissions Data

NASA Database

The NASA database (McDonnell Douglas Corp., 1986) contains records for 73 materials or products that emitted TCE (Table 4.33). The median emissions were relatively low. Adhesives had the highest emissions with a median of 1.2 μg TCE released per gram of material and a maximum value of 1500 μg/g. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Table 4.33. Summary of emissions of 1,1,1-trichloroethane from materials in NASA database.[a]

Category	Minimum	Maximum	Median	N[b]
Adhesives	0.01	1500	1.2	14
Coatings	0.1	11.7	0.36	9
Compounds	–	0.07	–	1
Cosmetics	0.005	0.2	–	2
Fabrics	0.002	0.5	0.03	13
Foam/Plastic	0.01	92.9	0.15	14
Lubricants	0.8	1	1	3
Pens/Inks	0.04	0.2	0.1	5
Rubber	0.02	10.7	0.2	12

[a] All measurements reported as μg TCE per gram product.
[b] N=number of materials in category that emitted TCE.

Consumer Products

Many aerosol spray products contain TCE as a solvent. Otson *et al.* (1984) investigated the effects of two aerosol fabric protectors (FP1, FP2) on indoor levels of TCE and petroleum distillates. Approximately 450 grams of each product were applied to two square meters of fabric in a house in separate experiments. Both integrated and grab samples were collected using passive and active samplers at various times during the eight hours after the products were applied. Both products were tested with all exterior doors and windows closed (unventilated). Product FP1 was also tested with two exterior doors and a second-floor window open (ventilated). Air exchange rates were not measured. Exposure concentrations for the person who applied the products are shown in Table 4.34. The subject remained in the house for eight hours after product application.

Table 4.34. Personal exposures to 1,1,1-trichloroethane in ppmv from use of fabric protectors (after Otson *et al.*, 1984).[a]

Test Conditions	Averaging Time (min)	Passive Sampler	Active Sampler
FP1-Unventilated	0-15[a]	660	--[b]
	15-30	642	–
	0-480	61[c]	73
FP2-Unventilated	0-15	816	–
	15-30	889	–
	0-480	65[c]	64
FP1-Ventilated	0-15	400	–
	15-30	430	–
	0-480	15[c]	15

[a] Converted from mass/volume units.

[b] Measurement not made for this time period.

[c] Duplicate measurement, precision <±10%.

Otson *et al.* (1984) also conducted experiments in a closed 28-m^3 test chamber. Application of 225 g of fabric protector resulted in a maximum concentration of TCE of 10,300 mg/m^3 (1,910 ppbv). The initial concentrations were highest near the floor, where small children might be at risk. When the room was opened, concentrations dropped rapidly.

Building Materials

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. Most, if not all, of these materials are likely to be used in residential construction. The results are summarized in Table 4.35. The material with the highest emission rate is a latex caulk.

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 TCE (Sheldon *et al.*, 1988). Immediately after construction, the mean specific source strength of TCE was 7.6 μg/m^3-h with a

Table 4.35. Emission rates of 1,1,1-trichloroethane from building materials in μg/m^2-h (from Sheldon *et al.*, 1988).

Sample	Headspace	Chamber
Particle board	--[a]	–
Carpet adhesive	–	–
Black rubber molding	0.12	0.11
Latex paint	–	–
Linoleum tile	0.06	–
Polystyrene foam insul.	–	–
Vinyl cove molding	0.17	0.30
Cove adhesive	NM[b]	–
Carpet	–	–
Vinyl edge molding	0.20	
Small dia. phone cable	–	
Large dia. phone cable	0.21	
Urethane sealant	–	
Latex paint	–	
Tar paper	–	
Primer/adhesive	–	
Latex caulk	4.9[c]	
PVC pipe	–	
Water rep. mineral board	–	
Cement block	–	
Treated metal roofing	–	
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] Not measured, sampler overloaded.

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

maximum of 48 μg/m^3-h. The building was sampled again four months after construction when it was fully occupied. At that time, the mean specific source strength was 12 μg/m^3-h with a maximum of 40 μg/m^3-h. The lack of decrease in source strength with time suggests that occupant activities may have contributed to emissions of TCE.

Wallace *et al.* (1987) measured the emission rates of TCE 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. In addition, cleaning agents were applied to the surfaces of a wood panel placed in the chamber. An insecticide was sprayed onto a portion of the same panel after the cleaning was completed. The emission rates of TCE for the painted sheetrock, wallpaper/sheetrock assembly and carpet/wood assembly were 1.9, 5.0 and 16 μg/m^3-h, respectively. The emission rate from the combined use of cleaners and insecticide was 2,200 μg/m^3-h.

Combustion Sources

Small amounts of TCE were detected in the air collected through an inverted funnel above the top burners of three gas cooking ranges tested by Moschandreas *et al.* (1983). The concentrations of TCE in the exhaust air were 4.3 ± 5.5 μg/m^3 (0.8 ± 1.0 ppbv).

Summary

Extensive data for indoor concentrations of TCE that are specific to California are available. These data have been used to construct frequency distributions for indoor concentrations and personal exposure for two communities with populations of approximately 90,000 and 350,000 individuals. Median concentrations were estimated to range between 0.8 and 4.8 ppbv. Additional data for another California community are being obtained by the Woodland field study being conducted by the CARB (Sheldon, 1990).

A large number of consumer products contain TCE as a solvent. For example, of the 1,153 brand-name products tested in a shelf survey, 16 percent were found to contain TCE. In addition, some building materials emit TCE. As a result, indoor concentrations of TCE are expected to be almost always elevated with respect to outdoor concentrations.

Because adequate indoor concentration data exist for TCE, further investigation of this compound should probably be given low priority.

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Pentachlorophenol

Uses and Sources

Pentachlorophenol (PCP) is an effective, general purpose biocide that is primarily used as a wood preservative. All non-wood applications of PCP were banned by the U.S. EPA in 1987 (EPA, 1987) and indoor use has now been banned by the U.S. EPA (EPA Region IX, personal communication). Products containing PCP are now only available to licensed applicators. Indoor sources should, therefore, be limited to historically treated building materials, with the possible exception of imported products such as rope and wicker baskets.

Concentration Data

Levin and Hahn (1986) measured concentrations of PCP in an office building in Southern California. The building's structural beams, which were exposed in the interior, had been pressure treated with PCP. Measurements were made before and after the beams were sealed to reduce the vaporization of PCP. Concentrations of PCP in pre-remedial air samples averaged 30.7 $\mu g/m^3$ (2.8 ppbv, 6 samples) with no ventilation and 27.2 $\mu g/m^3$ (2.5 ppbv, 7 samples) with low ventilation. After the beams were sealed and ventilation system defects were corrected, concentrations of PCP ranged from 0.9 to 9.9 $\mu g/m^3$ (0.08-0.9 ppbv) at various ventilation rates.

Saur *et al.* (1982) measured concentrations of PCP in 11 different buildings in the U.S. that had been designed for widely varying uses. The results are summarized in Table 4.36. The concentrations are for single measurements. The highest concentration, 3.5 ppbv, occurred in an unventilated basement. Most of the concentrations of PCP were considerably less than 1 ppbv.

Krause *et al.* (1989) measured concentrations of PCP in 104 homes in West Germany. Indoor air concentrations ranged from 2 to 25 $\mu g/m^3$ (0.19-2.3 ppbv). The median was 5 $\mu g/m^3$ (0.46 ppbv). An average of 40 liters of wood preservative, containing approximately 2 kg of PCP, had been used on about 130 m^2 of wood in each of the homes within the nine years prior to the measurements. Dust samples were collected from a subset of 65 of the homes. The median concentration of PCP in these samples was 13.3 µg per gram of dust (ppm). Control dust samples were collected from 41 homes that had not been treated with PCP. The median concentration of PCP in these samples was only 0.008 µg/g (ppm).

Barbieri *et al.* (1990) measured concentrations of PCP in house-dust samples collected in homes in Northern Italy. Five of these homes did not have any prior use of PCP and five had wood surfaces that had been previously treated with PCP. The range of concentrations of PCP in dust from the treated homes was 20-166 ppm. The range of concentrations in dust from the control houses was 2-11 ppm. The study additionally found a significant correlation between PCP concentrations in dust and urine which suggests that PCP exposure may be attributable to house dust.

Table 4.36. Air concentrations of pentachlorophenol in eleven buildings (from Saur *et al.*, 1982).

Building Type	Building Age	Vent. Rate	PCP carrier[a]	Wood Loading ($m^2/100m^3$)[b]	Temperature (°C)	PCP Conc. (ppbv)[c]
Office/Lab-basement	4	Low	A	72.1	21	3.5
Office/Lab-main floor	4	Medium	A	0.0	21	0.8
Warehouse	6	Medium	A	8.8	11	0.3
Research barn	–	Medium	A	6.2	16	0.05
Pole barn (enclosed)	5	High	A	16.8	17-27	0.004
Pole barn (enclosed)	5	Medium	A	56.3	17	0.08
House-basement	1	Low	B	0.3	21-27	0.09
House	3	Low	C	22.6	23	0.03
Natatorium-pool room	2	Medium	D	12.8	28	0.03
Natatorium-mech. room	2	Medium	D	10.5	28	0.01
Log home	1	Medium	C	36.0	18-29	0.01
Warehouse	9	High	A	24.6	15-24	0.009
Greenhouse	11	High	A	15.7	18-28	0.008
Log home	1	Medium	C	40.3	18-28	0.04

[a] A = P9 Type A; B =Woodtreat TC gel; C = Mineral spirits; D = Dichloromethane.

[b] Surface area of treated wood to volume of building airspace.

[c] Data converted from mass/volume units.

Emissions

Building Materials

Ingram *et al.* (1983) used a small chamber to measure emissions from wood specimens treated with PCP. One set of samples consisted of southern yellow pine boards (28 × 7.6 × 1.9 cm) that were dip treated in a commercial wood preservative formulation containing about five percent PCP in mineral spirits. A second set of samples was made up of similar-sized wood blocks cut from logs that had been commercially dip treated in the same formulation. Chamber concentrations from the first set of samples averaged 140 $\mu g/m^3$ (13 ppbv) at 31° C. Emissions from the log sections were much lower, with chamber concentrations averaging 20.4 $\mu g/m^3$ (1.9 ppbv). Wood blocks were also pressure treated with PCP in dichloromethane. Emissions from these samples were relatively high, with chamber concentrations averaging 175 $\mu g/m^3$ (16 ppbv). Samples treated with PCP in an oil-based carrier had even higher emissions. A variety of sealant coatings were applied to all of the treated samples, most of which reduced emissions of PCP by 80-90 percent.

Combustion Sources

Traynor *et al.* (1990) detected PCP in the emissions of unvented kerosene space heaters. An average of 5.4 ng of PCP were released per kilojoule of fuel consumed during tests of five properly tuned radiant heaters. Two mal-tuned convective heaters emitted 130 ng/kJ. The kerosene fuel was tested for chlorinated compounds, but the concentrations were below the detection limits of 10 ppm. The PCP may have been formed via free-radical chemistry. Dichloromethane used outside of the test chamber before and after the experiments was a possible source of the chlorine, as was airborne sea salt.

Summary

Data on indoor concentrations of PCP in U.S. residences are minimal. Because PCP has a relatively low vapor pressure, it partitions between vapor- and particle-phases in air. European field studies suggest that exposure to PCP may be primarily due to contact with dust, either dermally or through inhalation. The low vapor pressure of PCP also results in persistent vapor-phase concentrations that are measurable for years after products containing PCP have been used.

Since the indoor use of PCP has been banned by the U.S. EPA, population exposure to this compound is primarily limited to occupants of historically treated homes and is expected to decrease slowly with time.

Pentachlorophenol 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, combined vapor- and particle-phase concentrations will be measured in 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.

Pentachlorophenol is not well-suited for a laboratory study of emissions because losses to chamber surfaces and sampling lines are expected to be substantial due to its low vapor pressure. If additional data are needed for PCP, they would best be obtained by a field study.

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Tri– and tetrachlorophenols

Uses and Sources

The trichlorophenol isomer, 2,4,5-trichlorophenol, is used as a preservative for adhesives, synthetic textiles, rubber, wood and paints. It is also used around swimming pools and in bathrooms and hospital rooms as a bactericide and fungicide. Other tri- and tetrachlorophenols are used as intermediates in the manufacture of phenolic resins and dyes. Some are used directly as flea repellants, mold inhibitors, antiseptics, disinfectants and anti-gumming agents in gasoline (HSDB, 1990).

All tri- and tetrachlorophenols are found as contaminants in commercial grade solutions of pentachlorophenol (Crosby, 1981).

Concentration Data

No data on indoor concentrations of tri- and tetrachlorophenols were found.

Emissions Data

No data on emissions of tri- and tetrachlorophenols from potential indoor sources were found.

Summary

Like pentachlorophenol, these compounds have low vapor pressures and will partition between vapor- and particle-phases in air. Contact with dust, either dermally or through inhalation, may be the most important route of exposure.

Both 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol are included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, combined vapor- and particle-phase concentrations will be measured in 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.

These compounds are not well-suited for a laboratory study of emissions because losses to chamber surfaces and sampling lines are expected to be substantial due to their relatively low vapor pressures at room temperature. If additional data are needed, they would best be obtained by a field study.

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Vinylidene chloride

Uses and Sources

Vinylidene chloride is primarily used as a monomeric intermediate in the production of plastics, particularly Saran-type polymers. It is also used in adhesives (HSDB, 1990). The extent to which any monomer is released from finished products is unknown.

Concentration Data

The major sources of data for indoor concentrations of vinylidene chloride are the National VOC (NVOC) database (Shah and Heyerdahl, 1988) and some of the U.S. EPA's Total Exposure Assessment Methodology (TEAM) studies which are incorporated into the NVOC database. There are no data for vinylidene chloride from the California TEAM studies.

There are 2,120 data points for vinylidene chloride in the NVOC database. The mean indoor concentration is 19.7 ppbv. However, the data are highly skewed since the 25th, 50th and 75th percentile concentrations are all zero. The limit of detection for the TEAM studies was 2.6 ppbv. The compound was detected in only a few samples as indicated by the low percent measurable values.

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 cannisters and were analyzed by GC/MS. None of these houses had concentrations of vinylidene chloride in excess of the detection limit of 0.79 $\mu g/m^3$ (0.2 ppbv).

Emissions Data

Finkel *et al.* (1979) attempted to measure the release of vinylidene chloride monomer from six polymeric materials, three carpets and three fibers. Both dynamic-headspace experiments, conducted at 50° C and 50 percent humidity and direct insertion mass spectral analysis failed to detect the monomer in any of the samples. The limit of detection of vinylidene chloride was approximately 0.04 ppm in a 10-g sample of the material.

Summary

Data for indoor concentrations of vinylidene chloride are not available for California. However, the data for other parts of the U.S. are extensive. These data indicate that the distribution of indoor concentrations is highly skewed and that concentrations rarely exceed typical limits of detection of several parts per billion.

Vinylidene chloride 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.

Vinylidene chloride is primarily used as a monomer in the manufacture of Saran-type plastics. The potential release of unreacted monomer from finished products could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Vinylidene chloride should be given a secondary priority for study because it is in CARB Group III.

References

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

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Acrylamide

Uses and Sources

Acrylamide is used in adhesives, permanent-press fabrics, paper and textile sizes and soil conditioners (HSDB, 1990). Its primary use is in the production of polyacrylamides used as flocculants for water treatment (Suta, 1979).

Concentration Data

No data on indoor concentrations of acrylamide were found.

Emissions Data

No data on emissions of acrylamide from potential indoor sources were found.

Summary

Acrylamide is a semivolatile compound which will partition between vapor and particle phases in air. Indoor concentrations of this compound have not been measured but are expected to be quite low because there are few probable indoor sources. Acrylamide is not included in an ongoing California field study.

In general, it is difficult to measure emission rates of semivolatile compounds using environmental chambers because losses to chamber surfaces and sampling lines are substantial. Data for this compound would best be obtained by including it in a field study that measured both vapor- and particle-phase concentrations. Acrylamide is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

References

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

Suta, B. E. (1979) *Assessment of human exposure to acrylonitrile.* EPA Contract No. 68-02-2835. U.S. EPA, Washington, D.C.

Acrylonitrile

Uses and Sources

Acrylonitrile is used as a comonomer in the production of many types of elastomers, resins and polymers, including acrylic fibers. It is often used in varying proportions with styrene and butadiene to produce ABS plastics which have a wide variety of applications. It is also used as fumigant and in insecticides (HSDB, 1990). More than 60 percent of the acrylic fibers produced are used for the manufacture of apparel. Carpeting is the second largest use. Acrylic fibers are also incorporated into numerous home furnishings (Suta, 1979). The extent to which unreacted acrylonitrile monomer would be released from finished products is unknown.

Concentration Data

Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for toxic air contaminants. Samples for very volatile organic compounds were collected in four houses using 6-liter SUMMA-polished canisters and were analyzed by GC/MS. One house had concentrations in excess of the 0.89 $\mu g/m^3$ (0.41 ppbv) detection limit. The mean concentration for the four houses was 0.61 $\mu g/m^3$ (0.28 ppbv).

Emissions Data

Finkel *et al.* (1979) attempted to measure the release of acrylonitrile monomer from six polymeric materials, three carpets and three fibers. Both dynamic-headspace experiments, conducted at 50° C and 50 percent humidity and direct insertion mass spectral analysis failed to detect the monomer in any of the samples. The limit of detection of acrylonitrile was approximately 0.02 ppm in a 10-g sample of material.

Summary

Acrylonitrile 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.

The primary use of acrylonitrile is in the manufacture of acrylic fibers for fabric and carpeting. One study showed that the release of the monomer from these highly processed materials is low. This result could be corroborated by a laboratory screening study of emissions of minor constituents from products and materials. Acrylonitrile should be given a high priority for study because it is in CARB

Group II. However, since the emission rates are expected to be low, the study of other Group II compounds could take precedence.

References

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

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Suta, B. E. (1979) *Assessment of human exposure to acrylonitrile.* EPA Contract No. 68-02-2835. U.S. EPA, Washington, D.C.

1,1-Dimethylhydrazine

Uses and Sources

Dimethylhydrazine has varied uses as a chemical intermediate, a component of jet and rocket fuel, a stabilizer for organic peroxide fuel additives and a control agent for plant growth. It is also used in photography (HSDB, 1990).

Concentration Data

No data on indoor concentrations of dimethylhydrazine were found.

Emissions Data

No data on emissions of dimethylhydrazine from potential indoor sources were found.

Summary

There are no data on indoor concentrations or source emissions of dimethylhydrazine, and this compound is not included in an ongoing California field study.

Indoor concentrations of dimethylhydrazine are expected to be quite low because there are few probable indoor sources. It is possible, however, that dimethylhydrazine could be released from some finished products. This could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Dimethylhydrazine is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

References

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

Hydrazine

Uses and Sources

Hydrazine is used as a rocket fuel and as a corrosion inhibitor in the boiler water at power plants and in the heating water of district water systems. It is also used as a chemical intermediate in the production of pesticides and pharmaceuticals (Kauppinen *et al.*, 1989). Hydrazine is found as a contaminant in maleic anhydride, a widely used growth inhibitor for tobacco suckers. Tobacco smoke is probably the predominant indoor source of hydrazine (Liu *et al.*, 1974).

Concentration Data

No data on indoor, non-occupational, concentrations of hydrazine were found.

Emissions Data

Liu *et al.* (1974) trapped hydrazine emitted from cigarettes by reaction with pentafluorobenzaldehyde to form decafluorobenzaldehyde azine (DFBA) which prevents loss by reaction with other smoke constituents. The DFBA was then enriched by chromatography and analyzed by GC/FID and GC/ECD. The average emission of hydrazine in the sidestream smoke of commercial cigarettes was 94 ng per cigarette.

Summary

There are no data on indoor concentrations of hydrazine, and this compound is not included in an ongoing California field study.

Environmental tobacco smoke (ETS) is expected to be the major source of hydrazine in indoor air. Since the data on emissions of hydrazine from this source are minimal, it is recommended that the compound be included in a laboratory study of ETS emissions. Methods for analysis of hydrazine in air contaminated with ETS may have to be evaluated as part of this study. Hydrazine should be given a high priority for study because it is in CARB Group II.

References

Kauppinen, T. P., Alho, J. M. and Lindroos, L. O. (1989) Exposure to hydrazine and its control in power plants. *Appl. Ind. Hyg.* 4, 245-250.

Liu, Y. Y., Schmeltz, I. and Hoffmann, D. (1974) Chemical studies on tobacco smoke: Quantitative analysis of hydrazine in tobacco and cigarette smoke. *Anal. Chem.* 46, 885-889.

4,4'-Methylenedianiline

Uses and Sources

The compound 4,4'-methylenedianiline (MDA) is used as a curing agent for polyurethane elastomers and polyurethane epoxy resins and as a chemical intermediate in the production of polyamide and polyimide resins and fibers. It is also used as a corrosion inhibitor (HSDB, 1990). The extent to which unreacted MDA would be released from finished products is unknown.

Concentration Data

No data on indoor concentrations of MDA were found.

Emissions Data

No data on emissions of MDA from potential indoor sources were found.

Summary

Methylenedianiline is a semivolatile compound which will partition between vapor and particle phases in air. Indoor concentrations of this compound have not been measured but are expected to be quite low because there are few probable indoor sources. Methylenedianiline is not included in an ongoing California field study.

In general, it is difficult to measure emission rates of semivolatile compounds using environmental chambers because losses to chamber surfaces and sampling lines are substantial. Data for this compound would best be obtained by including it in a field study that measured both vapor- and particle-phase concentrations in indoor air. Methylenedianiline is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

References

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

Nitrobenzene

Uses and Sources

Nitrobenzene is used in soaps; in shoe, metal and floor polishes; as a preservative in spray paints; and as a substitute for almond essence. It is used as a chemical intermediate in the manufacture of pesticides, rubber chemicals, pharmaceuticals and isocyanates (HSDB, 1990). Small amounts of unreacted nitrobenzene may be present as a contaminant in this second group of products.

Concentration Data

Nitrobenzene was measured in the pilot phase of the Woodland, CA, field study (Sheldon, 1990). Ten of the 25 indoor, outdoor and personal air samples had concentrations in excess of the 0.04 $\mu g/m^3$ (0.007 ppbv) detection limit. The range of measurable concentrations of nitrobenzene in samples from unspecified locations was 0.04-0.21 $\mu g/m^3$ (0.009-0.042 ppbv).

Emissions Data

No data on emissions of nitrobenzene from potential indoor sources were found.

Summary

Nitrobenzene 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 recommended that nitrobenzene be included in a laboratory study of emissions of minor constituents from products and materials. Possible product types for investigation include various polishes, soaps and pesticides. If significant sources are identified by preliminary screening, source emission rates could be measured under standardized conditions using environmental chambers. Nitrobenzene should be given a secondary priority for study because it is in CARB Group III.

References

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

Sheldon, L. S. (1990) *Indoor pollutant concentrations and exposures, Revised interim report.* Contract No. A833-156. California Air Resources Board, Sacramento, CA.

N–Nitroso compounds

Uses and Sources

N-Nitrosodimethylamine (NDMA) is used as an industrial solvent, antioxidant, plasticizer, rubber accelerator and lubricant additive. N-Nitrosodiethylamine (NDEA) is used as an antioxidant, stabilizer and gasoline and lubricant additive. N-Nitrosomorpholine (NMOR) has no commercial uses in the U.S. (HSDB, 1990).

The primary source of the nitrosamines in indoor air is environmental tobacco smoke (ETS). Other possible sources include rubber products, leather upholstery, cosmetics, beer and scotch, and cooking bacon. For most sources, the nitrosamines are formed either as a by-product of manufacture or during product use (*i.e.*, cooking bacon).

Concentration Data

The results of analyses of nitrosamines must be interpreted cautiously. Artifactual formation of the compounds can occur rapidly if conditions are right. For example, Angeles *et al.* (1978) found that formation of nitrosamines occurred readily in nonaqueous solutions like dichloromethane if solid nitrites and secondary amines were present.

Cigarette smoke is the predominate source of the nitrosamines in indoor air. Brunnemann and Hoffmann (1978) made measurements in environments where smoking was occurring. These results are summarized in Table 4.37. Details as to the sizes of the spaces, the numbers of smokers and the ventilation rates were not reported. Samples were collected with midget impingers containing ascorbic acid buffered at pH 4.5 as the trapping solution. Analysis was by GC/TEA. Control measurements were made in the homes of non-smokers, where the concentrations of NDMA were less than 1.7 ppbv. Concentrations in smoking environments ranged up to 79 ppbv.

Table 4.37. Concentrations of N-nitrosodimethylamine in indoor air (from Brunnemann and Hoffmann 1978)[a].

Environment	Occupancy	Ventilation	Concentration (ppbv)
Train bar car	Primarily smokers	Air conditioned	43
Train bar car	Primarily smokers	Natural	36
Bar	Primarily smokers	Not given	79
Sports Hall	Not given	Not given	30
Betting parlour	Not given	Not given	17
Discotheque	Not given	Not given	30
Bank	Not given	Not given	3.3
House[b]	Not given	Not given	<1.7
House[b]	Not given	Not given	<1.0

[a] All data converted from mass/volume units.

[b] Controls. No smokers present.

A similar investigation was conducted by Stehlik *et al.* (1982) for a variety of environments contaminated with ETS. These results are summarized in Table 4.38. For one set of measurements, subjects were asked to smoke as much as possible during sampling. Ventilation in the rooms was low or absent. Another set of measurements were conducted in environments where smoking occurred, but the occupants were unaware that measurements were being made. In the unnaturally high smoking environments, the levels of contamination were elevated and all subjects agreed that they would have left the rooms or opened the windows under normal circumstances. Concentrations of NDMA ranged up to 50 ppbv. Under natural smoking conditions, concentrations of NDMA were generally lower, ranging from less than 3 to 23 ppbv. The cause of the discrepency between these results and the generally higher concentrations obtained by Brunnemann and Hoffmann (1978) is not known.

Table 4.38. Concentrations of N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) in indoor air (after Stehlik *et al.* 1982).

Environment	Size (m^3)	Occupancy	Tobacco products consumed	Sample time (hr)	Ventilation[b]	NDMA (ppbv)[c]	NDEA (ppbv)[c]
Unnatural conditions[a]							
Conference room	43	11	64 cigarettes	2	None	23	< 2.4
Office	22	3	35 cigarettes	2	None	43	< 2.4
Office	22	3	38 cigarettes	2	None	50	< 2.4
Office	22	3	28 cigarettes	2	Low	26	< 2.4
Office	22	2	12 cigarettes	2	Low	6.6	2.4
Office	46	7	18 cig., 2 pipes	2	Low	26	< 2.4
Conference room	43	10	40 cigarettes	2	Low	7.3	< 2.4
Natural conditions							
Work room	207	7	Continuous smoking	2	Low	7.6	< 2.4
Conference room	301	15	26 cig., 1 pipe, 6 cigarillos	2	Low	10	< 2.4
Office	70	6	27 cigarettes	2	Low	9.9	7.2
Conference room	50	12	37 cig., 4 pipes, 3 cigars	2	None	6.6	4.8
Suburban restaurant	120	20	20-30 cig., 2 pipes	2	?	< 3.3	< 2.4
Restaurant in Vienna	160	23	20 cigarettes	1	?	3.3	< 2.4
Restaurant in Vienna	180	25	25-30 cigarettes	1	?	13	< 2.4
Restaurant in Vienna	160	23	15-20 cigarettes	1	?	17	< 2.4
Dance club	320	30-70	Not determined	4	?	23	48

[a] In unnatural conditions, occupants were asked to smoke as much a possible during the sampling period. In natural conditions, nothing was done to influence the occupants smoking behavior.

[b] In unventilated rooms, the windows and door remained closed over the course of the measurement. In low ventilation rooms, the windows remained closed but the door was opened and closed several times.

[c] All data converted from mass/volume units.

Another source of exposure to N-nitroso compounds is the materials used in automobile interiors. Rounbehler *et al.* (1980) measured concentrations of N-nitroso compounds in a group of 38 automobiles. All but one were new and tested at dealerships. NDMA was present in all but one of the vehicles at concentrations up to 0.83 $\mu g/m^3$ (0.27 ppbv). The mean concentration was 0.29 $\mu g/m^3$ (0.096 ppbv). NMOR was present in 16 vehicles at concentrations up to 2.5 $\mu g/m^3$ (0.53 ppbv) with a mean concentration of 0.65 $\mu g/m^3$ (0.14 ppbv). NDEA was found at lower concentrations in 17 vehicles. Leather interiors produced the highest levels of NDMA, followed by cloth, then vinyl interiors. Samples collected in the rear seats were consistently higher than samples collected in the front seats of the same vehicle. In at least one vehicle, the spare tire was identified as the primary source of N-nitroso compounds. The concentration of NMOR in the spare-tire well of this vehicle was almost 70 times greater than that measured in the rear seat.

Emissions Data

Combustion Sources

Adams *et al.* (1987), Brunnemann *et al.* (1977) and Brunnemann *et al.* (1980) conducted experiments on emissions of nitrosamines in sidestream and mainstream cigarette smoke. The experimental protocols were similar in all three studies. Weight-selected cigarettes were smoked sequentially by machine and the sidestream smoke was directed through two gas washing bottles containing ascorbic acid buffered at pH 4.5. The trapping solution was extracted with dichloromethane and the organic fraction was analyzed by GC/TEA. Table 4.39 summarizes the results of these studies.

Table 4.39. Sidestream emissions of N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) from cigarettes (from Adams *et al.*, 1987; Brunnemann *et al.*, 1977; Brunnemann *et al.*, 1980).

Study	Cigarette Type	Number Brands Tested	NDMA (ng/cigarette)	NDEA (ng/cigarette)
Adams *et al.*	U.S. commercial nonfilter	1	735	
(1987)	U.S. commercial filter	2	597, 611	
	U.S. commercial perforated filter	1	685	
Brunnemann *et al.*	U.S. and foreign commercial nonfilter	3	40±26	2.7±1.6[a]
(1977)	U.S. and foreign commercial filter	1	5.7	1.3
	Little cigar with filter	1	43	1.1
Brunnemann *et al.*	Swiss commercial nonfilter	1	359	
(1980)	Swiss commercial filter	11	262±78	
	German commercial filter	6	249±85	
	German commercial nonfilter	4	280±101	

[a] Only two of the three brands tested.

Brunnemann *et al.* (1977) found that the air velocity around the burning cone of a cigarette between puffs affects the yield of volatile nitrosamines. This is evident from their data for a U.S. brand which showed that increasing the flow rate through the sampling device from 250 ml/min to 500, 1,000 and 1,500 ml/minute increased the emission of NDMA in the sidestream smoke from 90 to 250, 530 and 680 ng per cigarette, respectively. This result is expected, considering the way nitrosamines are formed in cigarette smoke (Neurath, 1972).

Brunnemann and Hoffmann (1978) also detected NDMA in the smoke of burning sticks of incense from Hong Kong, Taiwan and the Peoples Republic of China.

Consumer Products

Spiegelhalder and Preussmann (1984) measured concentrations of N-nitroso compounds in 145 samples of cosmetics and toiletries obtained in retail shops in West Germany. Care was taken to include widely-used products. The N-nitroso compounds were separated from the product matrices by vacuum distillation and were analyzed by GC/TEA. The results for NDMA and NMOR are presented in Table 4.40. A single product was found to contain 15 µg/kg (ppb) NDEA.

Table 4.40. Concentrations of N-nitrosodimethylamine (NDMA) and N-nitrosomorpoline (NMOR) in µg/kg (ppb) for cosmetics and toiletries (from Spiegelhalder and Preussmann, 1984).

		NDMA			NMOR		
			Concentration			Concentration	
Product type	N	# pos.[a]	Max.	Ave.	# pos.[a]	Max.	Ave.
Shampoos	45	23	24	6.3	13	640	133
Color toners	7	1	10	–	–	–	–
Hair conditioners	16	5	5	3.3	–	–	–
Foam baths	7	–	–	–	–	–	–
Shower gels	9	3	10	4.3	4	380	145
Cream and oil baths	8	1	20	–	2	440	–
Cosmetic bath additives	5	–	–	–	–	–	–
Children's shampoos	5	4	20	6.4	1	230	–
Children's bath/care prod.	8	3	10	–	6	360	80
Body lotions and rubs	6	–	–	–	–	–	–
Face tonics, cleaners and masks	29	12	3	1.5	–	–	–

[a] Number of products in a category found to contain NDMA or NMOR.

Nitrosamines are present in rubber products due to the use of amine-based accelerators during their manufacture. Preussmann and Eisenbrand (1984) summarized some of their results for rubber products. They found up to 200 µg NDMA per kilogram of product (0.2 ppm) and up to 100 µg NDEA per kilogram. (0.1 ppm) They also found nitrosatable compounds in concentrations up to 16 ppm in products made from natural rubber.

Many pesticides and herbicides which contain amine compounds are contaminated with relatively high levels of N-nitroso compounds. Bontoyan *et al.* (1979) analyzed a number of these products by GC/TEA or HPLC/TEA. They found the highest levels of N-nitrosamines in substituted amine, dinitroaniline and amine salt formulations. Similar results were obtained by Zweig *et al.* (1980). They found that most dinitroaniline based pesticides contained levels of nitrosamines ranging from less than 1 to 430 mg/kg (ppm). Analysis of over 60 dimethylamine salt pesticides (*e.g.*, the dimethylamine salt of 2,4-D) showed NDMA contamination at concentrations ranging from 2 to 85 mg/kg (ppm). Four of 28 quaternary salt compounds tested contained morpholine. These were possibly contaminated with NMOR at concentrations up to 15.8 mg/kg (ppm) but the identification of NMOR was not confirmed.

Mixed-bed resin ion-exchange water softeners with anion resins containing amine functional groups can form NDMA if the water being treated contains traces of nitrite (Gough *et al.*, 1977). The extent to which the NDMA would vaporize during water use is unknown.

Other Sources

Beer and scotch whiskey contain trace levels of N-nitroso compounds. Spiegelhalder *et al.* (1979) analyzed 158 samples of commercially available beer in West Germany. Of these, 111 were found to contain NDMA. The mean concentration of NDMA was 2.7 µg/kg (ppb), with a maximum value of 68 µg/kg (ppb). Two samples contained NDEA at concentrations of 0.5 and 3.0 µg/kg (ppb). Goff and Fine (1979) conducted similar measurements on 18 brands of U.S. domestic and imported beers and on seven brands of scotch whiskey. All eighteen beers contained NDMA at levels ranging from 0.4 to 7.0 µg/liter. Six of the whiskeys also contained NDMA at levels ranging from 0.3 to 2.0 µg/liter. It is not known how much of these contaminants would volatilize into room air.

Cooking bacon may also release NDMA to the air. Lee *et al.* (1978) measured 46 µg of NDMA in the condensible vapor formed during the frying of one kilogram of bacon. Ten micrograms remained in the cooked meat and the fat. In a similar study, Gough and Walters (1976) found that 90 to 100 percent by weight of the NDMA in bacon components after frying was present in the condensable vapor.

Summary

Concentrations of N-nitroso compounds have not been measured in any statistically-selected sample of residences in California or the U.S. They are also not included in an ongoing California field study. These compounds, however, are expected to be widely present, probably at very low concentrations. The predominate indoor source of nitrosamines is ETS. Emissions of N-nitroso compounds are also expected from interior furnishings, rubber products and cosmetics. Other potential sources include cooking bacon, beer and whiskey, pesticides and domestic water treated with ion-exchange resins.

Data for N-nitroso compounds could be obtained by laboratory studies. It is recommended that they be included both in a study of ETS emissions and in a screening study of emissions of minor constituents from products and materials. The N-nitroso compounds should be given a relatively high priority for these studies because they are in CARB Group II. Since some data are already available for cigarette emissions, the study of ETS should be given lower priority than the study of emissions from products and materials. Possible sources which could be examined in a screening study include plastic and leather upholstery, rubber products, cosmetics, biocides and food products. If significant sources are identified, emission rates can be measured under standardized conditions using environmental chambers.

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Toluene diisocyanates

Uses and Sources

The two isomers of toluene diisocyanate, toluene 2,4-diisocyanate and toluene 2,6-diisocyanate, are generally used as a mixture in the manufacture of polyurethane products. Toluene diisocyanates are, therefore, used in a large number of products with architectural applications. They are a component of polyurethane coatings, paints, varnishes, cement sealers, mastic sealants and adhesives. They are also used in the manufacture of flexible polyurethane foams and of polyurethane elastomers. The former are widely incorporated into furnishings and the latter are used to coat fabrics. Toluene diisocyanates have an additional use as a cross-linking agent for nylon (HSDB, 1990). Polyurethane mastic sealants used in building construction may contain up to 7.6 percent toluene diisocyanates by weight (Jennings *et al.*, 1988).

Concentration Data

No data on non-industrial concentrations of toluene diisocyanates were found.

Emissions Data

No data on emissions of toluene diisocyanates from potential indoor sources were found.

Summary

There are no data on indoor concentrations or source emissions of toluene diisocyanates, and they are not included in an ongoing California field study. It is particularly important to obtain data on these compounds. In addition to being suspected human carcinogens, they are potent respiratory irritants and sensitizers, even at very low airborne concentrations (IARC, 1986). Because toluene diisocyanates are in CARB Group II, they should be given a high priority for study.

Toluene diisocyantes are considered to be semivolatile by the definition used in this report. Nevertheless, it is recommended that they be included in a study of emissions of minor constituents from products and materials because it is likely that useful information about indoor sources can be obtained in this manner. Some potential sources which are widely used in buildings are flexible polyurethane foams and polyurethane finishes. Although there are no data, it is suspected that emissions of toluene diisocyanates from these materials may occur under some circumstances. Source categories for a laboratory screening study of emissions should, therefore, include polyurethane carpet pads, foam furniture cushions, varnishes and caulks. It will be necessary to validate an analytical method for these compounds as part of this study.

It is also recommended that toluene diisocyanates be included in a field study conducted in a probability-based sample of homes. Since these compounds are highly reactive, methods for sampling and analysis that are suitable for use in indoor air must be developed and validated before this study can be undertaken.

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Dimethyl sulfate

Uses and Sources

Dimethyl sulfate is used as a solvent in the manufacture of dyes, perfumes and pharmaceuticals and for the separation of mineral oils. It is also used as a sulfating and methylating agent in the production of agrichemicals, fabric softeners, dyes and pharmaceuticals (HSDB, 1990). The extent to which any unreacted dimethyl sulfate is present as a contaminant in these products is unknown.

Concentration Data

No data on indoor concentrations of dimethyl sulfate were found.

Emissions Data

No data on emission of dimethyl sulfate from potential indoor sources were found.

Summary

There are no data on indoor concentrations or source emissions of dimethyl sulfate, and this compound is not included in an ongoing California field study.

Indoor concentrations of dimethyl sulfate are expected to be quite low because there are few probable indoor sources. It is possible, however, that dimethyl sulfate could be released from some finished products. This could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Dimethyl sulfate is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

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CHAPTER 5

Methods for Measuring Emissions of VOC

Introduction

A variety of methods were used to evaluate the potential emissions of some of the candidate compounds from their sources. These methods ranged in complexity from simple bulk analyses and static-headspace measurements of products to experiments conducted in large-scale environmental chambers. The data produced by the methods ranged from weight compositions and emissions expressed as mass of compound per mass of material to true emission rates. In one case, measured emission rates were used in a model to predict indoor concentrations of VOC.

In this chapter, various methods which have been used to estimate and measure emissions of VOC from materials and products are reviewed. The appropriate uses and the limitations of these methods are assessed. The chapter concludes with discussions of specific aspects of experiments conducted in environmental chambers, including the effects of environmental parameters on emission rates, the importance of sink effects, and methods of data analysis.

Bulk Analysis, Extraction and Headspace Techniques

The potential emissions of VOC from materials and products can sometimes be estimated by bulk analyses of the volatile components. A study was conducted for the U.S. EPA to provide information on the concentrations of six chlorinated solvents in approximately 1,200 common household products (Westat, Inc. and Midwest Research Institute, 1987). Measured aliquots of the products were added to water, and the compounds were analyzed by a purge and trap technique using GC/MS. In a follow-up study, the stored chromatograms were searched for 25 additional VOC (Sack and Steele, 1989). The purpose of these studies was to provide inputs for mathematical models of human lifetime exposures to these compounds. A national usage survey was conducted to provide additional inputs on the frequencies and durations of the uses of the products (Westat, Inc., 1987) For some products, use of composition data for this type of modeling is a valid approach. An example is aerosol sprays, for which the emissions and exposures primarily occur during the actual use of the product and are directly related to product composition (Girman and Hodgson, 1986). However, in other cases, use of bulk analyses for modeling may result in greatly overestimated emissions and exposures. Experiments conducted in a large-scale chamber showed this to be true for emissions of alcohol from liquid detergents (Wooley *et al.*, 1990).

Qualitative and semi-quantitative data on the composition of minor constituents in materials and products can be obtained by various extraction techniques. Thirty building-construction and interior-finish materials were screened for the emissions of VOC and semi-volatile compounds by vacuum extraction (Hodgson *et al.*, 1983). For a number of samples of adhesives which had been dried for one to two weeks, there was good qualitative agreement between the results obtained by vacuum extraction and by a small-chamber (3.8 L) technique. Another method for estimating emissions by direct product analysis is Soxhlet extraction using various organic solvents. New carpeting was examined for potential emissions of VOC using both Soxhlet extraction with dichloromethane and a dynamic-headspace technique (Pleil and Whiton, 1990). There was relatively good qualitative agreement between the methods for compounds with room-temperature equilibrium vapor pressures from about 0.05 to 25 torr.

Static-headspace measurements have commonly been used to evaluate potential emissions of VOC from materials and products. A major example is the NASA sponsored study of 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.

Emissions 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. Paints, other coatings and adhesives were first applied to both sides of aluminum plates. The containers were then heated to 49^{o} C for 72 hours, after which samples of headspace gas were collected and analyzed. The results were reported as μg of compound emitted per gram of material.

The static-headspace method served its purpose in the NASA study as a relatively simple screening tool for identifying high emitting materials among a large number of materials. However, since the method uses closed containers, the concentrations of VOC entering the gas phase are limited by equilibrium. Partitioning between organic and aqueous phases may also limit emissions. Therefore, gas-phase concentrations of VOC may not directly correspond to compositions of these compounds in the materials or to the emissions of these compounds under actual conditions in buildings. For example, one study reported that for certain materials and compounds, static-headspace results and environmental-chamber results did not agree (Colombo *et al.*, 1990). In this study, emissions of VOC from several household cleaners, waxes and polishes were measured using both a 7.5-L chamber and a static-headspace technique. The relative compositions of VOC in chamber and headspace air were compared for three products. Polar compounds generally had considerably higher relative abundances in chamber air. In fact, some of the major VOC components detected in the chamber experiments were below limits of detection in the headspace experiments.

Small-scale Chambers

Chambers are distinguished from static-headspace devices by a controlled flow of ventilation air. If the ventilation rate is sufficiently high, concentrations of VOC in the bulk air will be below their room-temperature equilibrium vapor pressures and emission rates (*e.g.*, mass of compound emitted per unit time) can be determined. Small-scale chambers ranging in volume from 0.08 L to one cubic meter, or more, have been used to measure the emissions and emission rates of VOC from a variety of materials and products. The design and operation of these chambers have varied considerably depending upon the objectives of the studies.

In their simplest form, small-scale chambers can be considered to be dynamic-headspace devices. These simple devices often have relatively small volumes and environmental parameters which are not necessarily scaled to rooms or buildings. Therefore, they are most appropriately used as a screening tool for qualitative and semi-quantitative analysis of emissions or for the relative ranking of materials with respect to emissions. For example, dynamic-headspace devices have been used in conjunction with building studies to help identify the sources of compounds found in air samples (Sheldon *et al.*, 1986; Hodgson and Girman, 1989). In these studies, samples of materials and products were collected from buildings and their emissions of VOC were examined in the laboratory using chambers with volumes of 0.08 or 4 L.

If precise environmental controls are provided, small-scale chambers can be used to examine the effects of environmental variables on emissions. Tichenor *et al.* (1990) measured the emission rates of p-dichlorobenzene (DCB) from moth crystal cakes as a function of temperature, relative humidity and ventilation rate using 166-L stainless-steel chambers. Emissions of DCB were found to vary considerably with temperature, less dramatically with ventilation rate and only slightly with relative humidity. Significant losses of DCB to the walls of the chamber were discovered.

If the factors which control emissions of VOC from a material are sufficiently well understood, data produced in small-scale chambers can be used in models to predict indoor concentrations of VOC with a high degree of accuracy. In the study of DCB cited above, a model was developed to estimate indoor concentrations in houses in which moth crystal cakes were used (Tichenor *et al.*, 1990). When appropriate values for source emission rates, air exchange rate, in-house air movement, and losses to sinks were provided, model predictions of concentrations were in close agreement with actual concentrations in a test house. However, it should be noted that the sink term, which is dependent upon the types of surfaces present, was determined in the same house.

The need for standardized designs and protocols for small-scale chambers is being addressed. An ASTM subcommittee on methods for indoor air (D22.05) has developed a document entitled, "Standard Guide for Small-scale Chamber Measurements of Organic Emissions." This document was approved by the subcommittee and full committee in April, 1990. An earlier version was published as a U.S. EPA report (Tichenor, 1989). The ASTM document is a guide not a method. As a guide, it primarily discusses the general considerations for making these types of measurements. There are chapters on mass-transfer considerations, facility design, sample collection, experimental design, experimental procedures, quality assurance and control, data analysis, and data reporting.

Although small-scale chambers are applicable for measuring emission rates of VOC from many types of materials and products, there are limitations to their use. Clearly, large assemblages of building materials or large pieces of furniture can not be placed into small chambers. Small-scale chambers are also not appropriate for evaluating emissions from consumer products if the highest emissions and exposures result from the actual application and use of these products. This may be true for a number of consumer products (*e.g.*, paints, polishes, and various aerosol sprays). Another problem is that it may be more difficult to properly scale air mixing and air velocities to rooms and buildings with small-scale chambers than with large-scale chambers. Finally, sink effects caused by losses of compounds to chamber walls are accentuated in small-scale chambers because of the relatively high surface-to-volume ratios.

Large-scale Chambers

For the purposes of this discussion, large-scale chambers are defined as environmental chambers with volumes of five cubic meters or more. Most large environmental chambers are on the scale of small residential rooms with volumes of 20-40 m^3. The considerations discussed in the ASTM standard guide for small-scale chambers are applicable to large-scale chambers as well. The design and materials of construction should be appropriate for experiments with VOC. For example, the construction materials should have low emissions of VOC and surface materials should be chosen to minimize sink effects. Adequate controls for ventilation rate, temperature and humidity must be provided to maintain these parameters within specified limits. This typically necessitates the use of elaborate air-handling systems and the placement of these chambers within temperature-controlled rooms.

Because room-size chambers are large enough to be occupied by a person, they are well suited for measuring emissions and exposures that occur during the actual use of consumer products. For example, exposures to dichloromethane from the use of paint removers and aerosol sprays were investigated using the 20-m^3 environmental chamber at Lawrence Berkeley Laboratory (Girman and Hodgson, 1986). Protocols were developed which simulated typical consumer use of these products. Experiments were conducted at two different ventilation rates, and a mass-balance model for exposure as a function of ventilation rate was developed. In a follow-up study, the utility of this model for predicting exposures in various residential environments was demonstrated (Hodgson and Girman, 1987). Using the same chamber, the release of ethanol to the atmosphere during the use of liquid laundry and dish-washing detergents was investigated (Wooley *et al.*, 1990). In these experiments, either a kitchen sink or a washing machine was set up and typical washing operations were conducted by a person in the chamber.

Large chambers can also be used to measure emissions of VOC from complete pieces of furniture and from large assemblages of building materials. If a material is not homogeneous with respect to emissions, then large material sizes can be used to provide a more representative sample.

Because large chambers are on the same scale as rooms in houses, some of the problems of scaling environmental variables are reduced. For example, if typical residential ventilation rates and material loading rates are used, the concentrations of VOC in the air should be similar to those measured in houses. Other parameters affecting mass transfer, such as air velocities at surfaces of materials, should also approach residential values.

Large-scale chambers can be used to help validate models for indoor air quality. Data generated in experiments in large-scale chambers can be compared to results predicted from experiments conducted in small-scale chambers. The advantage of this exercise is that the accuracy of small-chamber results and the efficacy of models are evaluated under carefully controlled environmental conditions. Validation experiments conducted in actual rooms and buildings may be considerably more difficult to control and characterize.

There are practical limitations to the use of large-scale chambers. There are in existence only several large-scale chambers that are appropriate for studies of VOC due, in part, to the large capital investment required for such a facility. Operating costs for large-scale chambers are also high relative to small-scale chambers because they must be contained within temperature-controlled rooms and considerable labor is needed to maintain them and keep them operating within specified limits for the environmental parameters.

In-situ Measurements of Source Strength

Emissions of VOC from sources can be sometimes be evaluated from *in-situ* measurements made in buildings. If the ventilation rate and indoor and outdoor concentrations of VOC in a building at near steady-state conditions are known, a single-equation mass-balance model can be used to calculate net specific sources strengths for VOC. This model assumes perfect mixing of air in the building. At steady-state conditions, the source strength, S (mg h^{-1}), of a pollutant is:

$$S = V\, a\, (C - C_0) \tag{5.1}$$

where V is the ventilated volume (m^3), a is the ventilation rate (h^{-1}), and C and C_0 are the indoor and outdoor concentrations (mg/m^3), respectively. Non-ventilation losses are assumed to be negligible.

This method was used to evaluate both long- and short-term variations in the source strengths of total VOC, classes of VOC and individual VOC in a large office building (Hodgson and Daisey, 1989). The method works best if the emissions from the sources being evaluated are characteristic and unique. In this case, total VOC was found to be dominated by emissions of a characteristic mixture of isoparaffinic hydrocarbons from wet-process photocopiers and plotters. The source strength for total VOC which was calculated with the model agreed well with an estimate of emissions based on the average usage of solvent in these machines. The same model was used to calculate the sink term for DCB in a test house (Tichenor *et al.*, 1990). Here, an effective emission rate was calculated from the indoor-air concentration of DCB and the ventilation rate. The difference between the emission rate calculated from the weight loss of the moth crystal cake source and the effective emission rate was attributed to losses to surfaces in the house.

Effects of Environmental Parameters

Environmental parameters have to be carefully considered and controlled in chamber experiments in order to produce data that can be reliably used in models to predict indoor concentrations. A good discussion of the effects of environmental parameters on mass-transfer processes as they relate to experiments conducted in chambers is provided by Tichenor (1989).

Temperature has large effects on mass-transfer processes. It determines the vapor pressures of the compounds, and therefore, the rates of evaporation of the compounds from materials. It affects the rates at which compounds sorb onto and desorb from surfaces. Since these rates are not necessarily equal, a change in temperature can alter the relative partitioning of VOC between the gas phase and sinks. Temperature also affects diffusion rates both in air, and perhaps more importantly, in the materials themselves.

The air exchange rate and the material loading ratio (L), which is the surface area of the material per unit of chamber volume (m^2/m^3), largely determine the concentration of VOC in the air in the chamber. Generally, chamber experiments should be conducted using a ratio of air-exchange rate (N) to loading ratio of material that approximates the N/L ratio in the building environment the investigator is trying to simulate. This should result in concentrations of VOC in chamber air that are similar to air concentrations in the building. A decrease in air exchange rate or an increase in loading will increase the concentration in air which decreases the diffusion gradient between the material and the bulk air. This decrease in the driving force can lower the emission rates of compounds if the emissions process is limited by mass-transfer effects.

Air velocity and mixing in the chamber are important because they affect the thickness of boundary layers of air at the surfaces of materials. It may be difficult to achieve the correct air velocity and mixing in experiments conducted in environmental chambers. The average air velocity in various buildings was found to be approximately 10 cm/sec (Kovanen *et al.*, 1987). Since chambers are typically maintained at nearly isothermal conditions, thermal gradients, which are a relatively large driving force for air movement in buildings, are minimized. Therefore, air velocities in chamber experiments that are conducted at ventilation rates that are typical for buildings are expected to be lower than 10 cm/sec. As a result, thick boundary layers can develop and emission rates can be suppressed. Often small mixing fans are added to chambers to overcome this problem. However, these fans can easily introduce too much turbulence and, therefore, artificially enhance emission rates.

The effects of water vapor on emission rates of hydrophobic organic compounds are generally minor compared to the effects of other environmental parameters. Water vapor can, however, modify sink effects. For example, an increase in humidity can reduce the number of available active sites on surfaces and reduce the amount of VOC sorbed onto these surfaces.

Sink Effects

The understanding and measurement of sink effects is essential if indoor air quality models are to be used to accurately predict concentrations of VOC in buildings. All types of materials in buildings can act as sinks. The magnitude of sorption onto these materials is determined by the composition of their surfaces and their surface areas. The amount of sorption is also dependent upon the compound. At this time, there are no general rules which can be used to predict sorption effects, except that compounds with low room-temperature equilibrium vapor pressures are expected to be most readily lost to surfaces. The net effect of sinks in a building is to spread emissions of VOC over longer time periods. The implication for human exposure, is dependent upon the behavior of the sinks and the time-activity patterns of the occupants.

Seifert and Schmahl (1987) investigated sorption effects for selected compounds and surfaces found in indoor environments. Two types of carpeting, plywood and the glass walls of the chamber were shown to remove VOC; but, the effects varied considerably for the different compounds that were examined. In experiments on the emission of DCB from moth crystal cakes, a substantial amount of DCB was sorbed onto the walls of stainless-steel chambers (Tichenor *et al.*, 1990). In subsequent experiments in a test house, 40 percent of the emissions of DCB were estimated to be lost to surfaces.

Data Analysis

The emission rates of VOC from materials and products are usually best expressed as mass of compound emitted per unit area or mass of source per unit time (*e.g.*, mg/m^2-h). The method for calculating emission rates depends on the emissions characteristics of the source.

The simplest case is a source which emits at a relatively constant rate over the time period of interest. In this case, the concentrations of VOC will initially exponentially increase from zero and reach and maintain a constant steady-state value. Assuming that the chamber is an ideal, continuously stirred tank reactor and that there are no losses to sinks, the steady-state source strength is calculated using Equation 5.1. The emission rate (mg/m^2-h) is then calculated by dividing the source strength by the area (or mass) of the source. If the rate of loss of VOC to sinks, such as chamber walls, can be measured, this loss term can be incorporated into the calculation by adding it to the ventilation rate in Equation 5.1.

The calculation and interpretation of emission rates is more difficult for sources with high initial emission rates that rapidly decrease with time. Emissions of VOC from paints and various coatings, adhesives, and other products with relatively high solvent contents typically exhibit this temporal behavior. It is important to carefully consider the study objectives when designing experiments to measure emission rates from these products. For example, an experiment to estimate the exposure to workers applying a product might dictate different protocols and methods of data analysis than an experiment to estimate the more long-term exposure to occupants of a building in which the product has been used. In the former case, the emission rate during the usage period is of most importance. It is during this period that maximum concentrations occur which are often strongly influenced by the worker's activities, for example, brushing or rolling of a paint.

Tichenor (1989) described a method of data analysis for calculating an emission rate for the initial, undisturbed drying period after applying a wet source such as a paint. Typically, the change in the emission rate, R, can be approximated by a first-order decay of the form:

$$R = R_o e^{-kt} \tag{5.2}$$

where R_o is the initial emission rate (mg/m^2-h), k is the first-order rate constant, and t is time (h). Using a non-linear, least squares regression of the concentration versus time data from the chamber, values of R_o and t are obtained. A similar method of data analysis is described by Colombo *et al.* (1990). This method empirically fits an equation to the data that describes concentrations in a chamber which increase from zero, pass through a maximum and then decline toward zero or some intermediate plateau.

For many products, calculation of emission rates during undisturbed drying may not provide a realistic estimate of exposures to VOC during actual usage by workers or consumers. For example, in chamber experiments in which paint removers and aerosol sprays containing dichloromethane were used by a worker, source strengths and personal exposures were found to be highest when brushing or spraying the products (Girman and Hodgson, 1986). Emissions during undisturbed drying of the products were relatively very low. In these experiments, concentrations of dichloromethane were continuously measured.

Exposures were calculated by integrating the areas under the concentration versus time curves. Theoretical estimates of concentration versus time were also developed from the measured average usage of the products during the experimental periods. Exposures obtained by integrating the theoretical curves closely agreed with the measured exposures.

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Glossary of Terms

Abbreviation	Definition
ABS	Acrylonitrile-butadiene-styrene plastic
BTU	British Thermal Unit
°C	degrees Celsius
C.C.	Contra Costa
C_n	n-carbon alkane
CARB	California Air Resources Board
cig.	cigarette
cm^2	square centimeter
conc.	concentration
CTCP	Clinical Toxicology of Commercial Products
2,4-D	an insecticide
DCB	p-dichlorobenzene
DEHP	di(2-ethylhexyl)phthalate
DFBA	decaflourobenzaldehyde azine
dia.	diameter
DNPH	2,4-dinitrophenyl hydrazine
EPA	Environmental Protection Agency
ETS	environmental tobacco smoke
g	gram
GC	gas chromatography
GC/ECD	gas chromatography / electron capture detection
GC/FID	gas chromatography / flame ionization detection
GC/MS	gas chromatography / mass spectrometry
GC/TEA	gas chromatography / thermal energy analysis
h	hour
h^{-1}	per hour
HPLC	high performance liquid chromatography
HSDB	Hazardous Substances Data Bank
IACP	Integrated Air Cancer Project
IARC	International Agency for Research on Cancer
kg	kilogram
l	liter
L.A.	Los Angeles
l/min.	liters per minute (flow rate)
LOD	limit of detection
m	meter
m^2	square meter
m^3	cubic meter
MDA	4,4'-methylenedianiline
µg	microgram
µg/g	microgram per gram (concentration)

Abbreviation	Definition
µg/h	microgram per hour (emission rate)
µg/l	microgram per liter (concentration)
µg/m^3	microgram per cubic meter (concentration)
µg/m^2-h	microgram per square meter per hour (specific emission rate)
µg/m^3-h	microgram per cubic meter per hour (specific emission rate)
mg	milligram
mg/cm^2-h	milligram per square centimeter per hour (specific emission rate)
mg/kg	milligram per kilogram (concentration)
mg/h	milligram per hour (emission rate)
mg/m^3	milligram per cubic meter (concentration)
mg/person-day	milligram per person per day (emission rate)
ml	milliliter
ml/min.	milliliters per minute (flow rate)
N	number of items in set
NASA	National Aeronautics and Space Administration
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
ng	nanogram
ng/kJ	nanogram per kilojoule
NMOR	N-nitrosomorpholine
No.	number
NVOC	National Volatile Organic Compound Database
PCP	pentachlorophenol
POM	particulate organic matter
pos.	positive
ppb	part per billion (by weight)
ppbv	part per billion by volume
ppm	part per million (by weight)
ppmv	part per million by volume
PTEAM	Particulate Total Exposure Assessment Methodology
PVC	polyvinyl chloride
SASS	Source Assessment Sampling System
SUMMA	passivation process for sampling containers
TCE	1,1,1-trichloroethane
TEA	thermal energy analysis
TEAM	Total Exposure Assessment Methodology
vent.	ventilation
VOC	volatile organic compound
% (w/w)	weight percent
XAD	styrene-divinylbenzene polymeric resin

APPENDIX

Bibliographic Database

The following 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 "Pro-Cite," a bibliographic software package developed by Personal Bibliographic Software, Inc. (Ann Arbor, MI). Most of the records contain abstracts, key words, and compound and subject index terms. The database can be searched and sorted by any of more than twenty fields for each record.

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