

LBL--31916

DE93 001581

VOLATILE ORGANIC CHEMICAL EMISSIONS FROM CARPETS

FINAL REPORT

Interagency Agreement CPSC-IAG-90-1256

Prepare for:

**Directorate for Health Sciences
U.S. Consumer Product Safety Commission
5401 Westbard Avenue
Bethesda, MD 20207**

Submitted by:

**Alfred T. Hodgson, John D. Wooley and Joan M. Daisey
Indoor Environment Program
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720**

APRIL 1992

This project was funded in part with Federal funds from the U.S. Consumer Product Safety Commission under interagency agreement number CPSC-IAG-90-1252 and by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract DE-AC03-76F00098.

MASTER

ED
REPRODUCTION OF THIS DOCUMENT IS RESTRICTED BY LAW

ABSTRACT

Carpets are known to emit a variety of volatile organic compounds (VOC). The potential impacts of VOC released from newly installed carpets on human health and comfort are of concern. Therefore, the primary objective of this research, was to measure the emission rates of selected individual VOC, including low molecular-weight aldehydes, released by samples of four new carpets that are typical of the major types of carpets used in residences, schools and offices. The carpet samples were collected directly from the manufacturers' mills and packaged to preserve their chemical integrity. The study compounds were selected from among the dominant VOC emitted by the carpet samples in preliminary screening measurements. The measurements of the concentrations and emission rates of these compounds were made under simulated indoor conditions in a 20-m³ environmental chamber designed specifically for investigations of VOC. The measurements were conducted over a period of one week following the installation of the carpet samples in the chamber. Duplicate experiments were conducted for one carpet. In addition, the concentrations and emission rates of VOC resulting from the installation of a new carpet in a residence were measured over a period of seven weeks.

The operating parameters for the chamber were highly reproducible. The average ventilation rate only varied between 0.98 and 1.00 h⁻¹ and the average temperature only varied between 22.8 and 23.5° C for the five experiments. The stabilities of the week-long ventilation rates and temperatures were one percent relative standard deviation.

The four carpets emitted a variety of VOC, 40 of which were positively identified. Twenty-one compounds were targeted for analysis during the chamber experiments. Eight of these were considered to be dominant. They were (in order of chromatographic retention time) formaldehyde, vinyl acetate, 2,2,4-trimethylpentane (isooctane), 1,2-propanediol (propylene glycol), styrene, 2-ethyl-1-hexanol, 4-phenylcyclohexene (4-PCH), and 2,6-di-*tert*-butyl-4-methylphenol (BHT). Styrene and 4-PCH were emitted by the two carpets with styrene-butadiene rubber latex adhesive. The 4-PCH produces the "new carpet" odor. Formaldehyde was emitted by a commercial "hard-back" carpet along with relatively high concentrations of vinyl acetate and 1,2-propanediol. With the exception of formaldehyde, only limited data are available on the toxicity and irritancy of these compounds at low concentrations. Therefore, it is difficult to determine at this time the potential magnitude of the health and comfort effects that may occur among the population from exposures to emissions from new carpets.

The concentrations and emission rates of most compounds decreased rapidly over the first 12 h of the experiments. The decays during this period were exponential and generally related to compound volatility with the most volatile compounds having the most rapid decays. The initial period was followed by a period of slower decay that did not fit a simple exponential form. At the end of the week-long experiments, the concentrations of all but one compound were 10 ppbv or less.

ACKNOWLEDGEMENTS

We appreciate the assistance and contributions of the Project Managers, Val Schaeffer and Lori Saltzman, of the U.S. Consumer Product Safety Commission.

This project was funded in part with Federal funds from the U.S. Consumer Product Safety Commission under interagency agreement number CPSC-IAG-90-1252 and by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

DISCLAIMER

The content of this publication does not necessarily reflect the views of the U.S. Consumer Product Safety Commission, nor does mention of trade names, commercial products, or organizations imply endorsement or sanction by the Commission.

TABLE OF CONTENTS

	Page
Abstract	1
Acknowledgements	2
Disclaimer	2
List of Tables	5
List of Figures	7
Summary and Conclusions	9
Study Objectives and Design	9
Evaluation of Experimental Methods	9
Emissions of VOC	11
Chamber Comparison and House Measurements	13
Health and Comfort Issues	15
Control Strategies	16
Introduction	17
Background	17
Study Objectives	18
Methods	20
Laboratory Experiments	20
Carpets	20
Screening Measurements	21
Environmental Chamber Facility	23
Preliminary Chamber Measurements	25
Experimental Protocol	27
Air Sampling and Analysis	27
Data Analysis	32
Field Study	35
Study Site and Carpet	35
Experimental Protocol	35
Chamber Experiment	36
Data Analysis	36

	Page
Results	38
Qualitative Analyses	38
Performance of the Environmental Chamber	41
Analytical Performance	42
Concentrations in the Environmental Chamber	43
VOC	43
Aldehydes	46
TVOC	46
Emissions	49
Chamber Comparison	51
Field Study	53
Ventilation Rates	53
Concentrations of VOC	53
Emissions	54
Discussion	56
Qualitative Analyses of Emissions	56
Quantitative Analyses of Emissions	59
Comparisons of Emissions in Different Environments	65
References	69
Tables	73
Figures	97

LIST OF TABLES

	Page
Table 1. Descriptions of the four carpets sampled by the CPSC.	73
Table 2. Collection dates and storage times for the carpet samples.	74
Table 3. Conditions specified for the operation of the small-volume chambers and the environmental chamber.	75
Table 4. Specifications and operating conditions for the analytical system used for the analysis of individual VOC.	76
Table 5. VOC emitted by Carpet 1 as determined by measurements of headspace emissions and emissions in the small-volume chambers and the environmental chamber.	77
Table 6. VOC emitted by Carpet 4 as determined by measurements of headspace emissions and emissions in the small-volume chambers and the environmental chamber.	78
Table 7. VOC emitted by Carpet 3 as determined by measurements of headspace emissions and emissions in the small-volume chambers and the environmental chamber.	79
Table 8. VOC emitted by Carpet 2 as determined by measurements of headspace emissions and emissions in the small-volume chambers and the environmental chamber.	81
Table 9. VOC selected for quantitation during the experiments in the environmental chamber.	82
Table 10. Environmental parameters for the experiments in the environmental chamber.	83
Table 11. Background concentrations of the target compounds for each experiment in the environmental chamber.	84
Table 12. Estimated limits of quantitation for the target compounds in the environmental chamber.	85
Table 13. Estimated uncertainties for single measurements of the concentrations of the target compounds for each experiment based on their calibration curves.	86

	Page
Table 14. Fractions of the total-ion-current (TIC) chromatographic areas accounted for by the sums of the chromatographic areas of the target compounds.	87
Table 15. Coefficients for the decays in the concentrations of the target compounds over 1-12 h and over 24-168 h in each experiment.	88
Table 16. Quasi steady-state specific emission rates of the target compounds at 24 and 168 hours after the start of each experiment.	90
Table 17. Specific mass emissions of the target compounds over the first 24 hours and the entire 168 hours of each experiment.	91
Table 18. Ventilation rates and concentrations of VOC in the field-study house.	92
Table 19. The 12 most frequently occurring VOC emitted by 19 SBR latex-backed carpets in small-scale environmental chambers (Data from Black <i>et al.</i> , 1991; and Hetes <i>et al.</i> , 1992) and their presence in the emissions from the two SBR latex-backed carpets in this study.	93
Table 20. Designations for the carpet samples included in this study and the corresponding designations for the carpet samples previously investigated by the CPSC for qualitative emissions of VOC.	94
Table 21. Average and maximum specific emission rates at 24 and 140 h for selected VOC emitted by 19 SBR latex-backed carpets in small-scale environmental chambers. Data from Black <i>et al.</i> (1991) and Hetes <i>et al.</i> (1992).	95
Table 19. Comparison of the maximum chamber concentrations of eight dominant compounds to reported irritant- and odor-effect levels.	96

LIST OF FIGURES

	Page
Figure 1. Schematic diagram of the vacuum-extraction apparatus.	97
Figure 2. Schematic diagram of the environmental chamber facility.	98
Figure 3. Ratio of the TVOC response to the actual mass of carbon added to a sampler for selected compounds and one mixture.	99
Figure 4a. Chamber concentrations of VOC emitted over one week by Carpet 1 in experiment a.	100
Figure 4b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 1 in experiment a.	101
Figure 5a. Chamber concentrations of VOC emitted over one week by Carpet 1 in experiment b.	102
Figure 5b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 1 in experiment b.	103
Figure 6a. Chamber concentrations of VOC emitted over one week by Carpet 4.	104
Figure 6b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 4.	105
Figure 7a. Chamber concentrations of VOC emitted over one week by Carpet 3.	106
Figure 7b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 3.	107
Figure 8a. Chamber concentrations of VOC emitted over one week by Carpet 2.	108
Figure 8b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 2.	109
Figure 9. Chamber concentrations of formaldehyde emitted by the carpets over one week.	110
Figure 10. Chamber concentrations of acetaldehyde emitted by the carpets over one week.	111

	Page
Figure 11. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 1 in experiment a.	112
Figure 12. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 1 in experiment b.	113
Figure 13. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 4.	114
Figure 14. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 3.	115
Figure 15. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 2.	116
Figure 16. Comparison of the small-volume and the environmental chamber concentrations at 1, 3 and 6 h of three selected VOC emitted by Carpet 1 in experiment b.	117
Figure 17. Comparison of the small-volume and the environmental chamber concentrations at 1, 3 and 6 h of three selected VOC emitted by Carpet 4.	118
Figure 18. Comparison of the small-volume and the environmental chamber concentrations at 1, 3 and 6 h of three selected VOC emitted by Carpet 3.	119
Figure 19. Comparison of the small-volume and the environmental chamber concentrations at 1, 3 and 6 h of three selected VOC emitted by Carpet 2.	120
Figure 20. Quasi steady-state specific emission rates of VOC emitted by a new carpet installed in a house.	121
Figure 21. Chamber concentrations of VOC emitted over one week by the field-study carpet.	122

SUMMARY AND CONCLUSIONS

Study Objectives and Design

The primary objective of this research was to measure the emission rates of selected volatile organic compounds (VOC) released by samples of new carpets that are typical of the major types of carpets used in residences, school classrooms and offices. The Consumer Product Safety Commission (CPSC) selected the carpet types for this study based on the results of previous screening studies they had conducted. Examples of four major types of carpets typically installed in residences, schools and offices were chosen. These included three "action-back" carpets, two with a styrene-butadiene rubber (SBR) latex adhesive on the secondary backing and one with a polyurethane foam secondary backing, and a "hard-back" carpet with a polyvinyl chloride secondary backing. Each of the selected carpets had distinctly different qualitative or quantitative emissions of VOC. The samples of these carpets were collected directly from the manufacturers' mills by CPSC field staff immediately prior to their use in the experiments. They were packaged in Tedlar bags to preserve their chemical integrity and shipped to the laboratory by air.

The study compounds were selected from among the dominant compounds emitted by the carpet samples in preliminary screening measurements conducted using headspace samples and small-scale chambers. Measurements of the concentrations and emission rates of these compounds were made under simulated indoor conditions in a 20-m³ environmental chamber designed specifically for investigations of VOC. The measurements were conducted over a period of one week following the installation of each carpet sample in the chamber. Duplicate experiments were conducted for one carpet. In addition, the concentrations and emission rates of VOC resulting from the installation of a new carpet in a residence were measured over a period of seven weeks.

Evaluation of Experimental Methods

Other investigators have demonstrated that the emissions of total VOC (TVOC) from carpets are low relative to other indoor sources. For example, the emissions of TVOC from adhesives used to bond commercial carpets to floors can be up to three

orders of magnitude higher than the emissions from the carpets themselves. Consequently, it was essential to have analytical methods for VOC with suitably low limits of quantitation. The sampling and analysis methods for VOC and low molecular-weight aldehydes that were selected for the study more than adequately fulfilled this requirement. The limits of quantitation for the measurements of individual VOC by gas chromatography-mass spectrometry were all less than one part per billion and often less than 0.1 ppbv. Formaldehyde and acetaldehyde, which were analyzed by high-performance liquid chromatography, had limits of quantitation of less than 2 ppbv. For most compounds including the aldehydes, these analyses were also highly precise with uncertainties for individual measurements often considerably less than one part per billion.

Concentrations of TVOC were also measured during the experiments to determine how well they compared to the summations of the concentrations of the individually quantified compounds. The results were dependent upon the composition of the mixture of VOC that was collected. Generally good agreement was obtained between TVOC and the sum of the individual VOC for the two carpets with SBR latex adhesive that primarily emitted hydrocarbons. The other two carpets had relatively high emissions of oxidized compounds, and the emissions of TVOC were lower than the sum of the individual compounds because the method has lower sensitivity to carbon in oxidized compounds relative to hydrocarbons. The uncertainty for individual measurements of TVOC averaged about 35 ug carbon m⁻³ (17 ppbv carbon) making the analysis of TVOC less precise than analyses of individual VOC. It can be concluded that the measurement of TVOC is most appropriately used as a screening tool for comparing the total mass emissions of VOC from similar carpets.

In order to conduct quantitative emissions experiments with very low sources of VOC, it is necessary to have reproducible and stable chamber conditions. The operating parameters for the environmental chamber were highly reproducible from experiment to experiment. As examples, the average ventilation rate only varied between 0.98 and 1.00 h⁻¹ and the average temperature only varied between 22.8 and 23.5° C for the five experiments that were conducted. These parameters were also very stable throughout the week-long measurement periods with relative standard deviations for ventilation rate and temperature of only one percent.

Emissions of VOC

The four carpets included in the laboratory study emitted a variety of VOC at concentrations significantly above their limits of quantitation, 40 of which were positively identified based on the analysis of authentic standards. Twenty-one of the identified compounds were selected for measurement during the chamber experiments. Eight of these target compounds were considered to be dominant based on high chamber concentrations or high total mass emissions. The two carpets with SBR latex adhesive primarily emitted styrene and 4-phenylcyclohexene (4-PCH). Both of these compounds derived from the SBR latex. The 4-PCH is the compound that produces the "new carpet" odor. The dominant compounds emitted by the "hard-back" carpet with a polyvinyl chloride secondary backing were formaldehyde, vinyl acetate, 2,2,4-trimethylpentane (isooctane), 1,2-propanediol (propylene glycol), and 2-ethyl-1-hexanol. It is possible that formaldehyde derived from urea-formaldehyde resin used as an adhesive. Alternately, formaldehyde may have been present as a contaminant of a polyvinyl acetal compound. The dominant compound emitted by the carpet with the polyurethane foam secondary backing was 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene or BHT).

The initial concentrations of styrene from the carpets with SBR latex adhesive ranged from about 10 ppbv to 180 ppbv, with the highest concentrations produced by the textured-loop carpet containing olefin fibers. The initial concentrations of 4-PCH were in the narrow range of 6-8 ppbv. In the experiment with the "hard-back" carpet, the initial concentrations of formaldehyde, vinyl acetate, 2,2,4-trimethylpentane, 1,2-propanediol, and 2-ethyl-1-hexanol were about 46, 290, 21, 120 and 8 ppbv, respectively. The maximum concentration of BHT emitted by the carpet with polyurethane foam backing was 14 ppbv.

The chamber concentrations of most compounds decreased rapidly over the first 12 h of the experiments. The decays during this period were exponential. The decay coefficients were generally related to compound volatility, with the most volatile compounds having the most rapid decays. These observations suggest that evaporation from the carpet surfaces may have been controlling the emissions rates during the initial period following installation. Simple exponential equations did not fit the decays in the concentrations of the VOC over a period of 24-168 h which suggests that other factors, such as diffusion within the materials and sorption and desorption from surfaces, were

influencing the emission rates over the longer period. Power functions were used to fit the data for this period. The concentrations of all compounds, except 1,2-propanediol emitted by the "hard-back" carpet, decreased to 10 ppbv, or less, by 168 h. The concentrations of a number of the target compounds were below their limits of quantitation at this time.

Good agreement was obtained for the concentrations of VOC between the replicate experiments with simultaneously collected samples of the Nylon cut-pile carpet with SBR latex adhesive. These experiments were conducted three weeks apart. The initial concentrations of 4-PCH were 6 ppbv in both experiments. At the end of the experiments, the concentrations of this compound differed by only 1 ppbv which was within the measurement uncertainty. The initial concentration of styrene was somewhat higher in the second experiment (16 ppbv vs. 10 ppbv). The storage bags were opened directly in the chamber for this one experiment, and the higher concentration was attributed to this procedural difference. The good agreement that was obtained between the replicate experiments was largely due to the reproducibility and stability of the chamber operating parameters. It also suggests that the sample packaging procedure, which utilized double, heat-sealed Tedlar bags, was successful in maintaining the chemical integrity of the samples over periods of at least weeks.

Quasi steady-state specific emission rates of the VOC at 24 and 168 h were calculated from the concentration data using a simple mass-balance model. The specific emission rates of styrene at 24 h from the carpets with SBR latex adhesive ranged from 25-35 $\mu\text{g m}^{-2} \text{ h}^{-1}$ for the Nylon cut-pile carpet to 260 $\mu\text{g m}^{-2} \text{ h}^{-1}$ for the olefin textured-loop carpet. By 168 h, the rates for styrene had decreased by 90-94 percent. On the other hand, the emission rates of 4-PCH were similar for both carpets. They ranged from an average of 75 $\mu\text{g m}^{-2} \text{ h}^{-1}$ for the Nylon cut-pile carpet to 82 $\mu\text{g m}^{-2} \text{ h}^{-1}$ for the olefin textured-loop carpet. The reductions in the emission rates of 4-PCH at 168 h were only 25-39 percent. Vinyl acetate and 1,2-propanediol were initially emitted by the "hard-back" carpet at respective rates of 850 and 690 $\mu\text{g m}^{-2} \text{ h}^{-1}$ with reductions of 88 and 72 percent at 168 h. Formaldehyde, 2,2,4-trimethylpentane and 2-ethyl-1-hexanol were all emitted at similar rates of about 60 $\mu\text{g m}^{-2} \text{ h}^{-1}$ at 24 h. These rates declined by 61-68 percent at 168 h. Butylated hydroxytoluene was the only compound that was emitted at a relatively high rate from the carpet with the polyurethane backing. At 24 and 168 h, the emission rates of BHT were 210 and 170 $\mu\text{g m}^{-2} \text{ h}^{-1}$, respectively.

This was the lowest percentage temporal reduction of all of the compounds that were measured.

The carpets were also compared based on the specific mass emissions of the target compounds. These mass emissions were calculated from the concentration versus time profiles. The masses of 4-PCH emitted by the two carpets with SBR latex adhesive were identical at 11 mg m⁻² over the 168-h experimental period. However, the mass emissions of styrene from these two carpets were considerably different at 2.8 mg m⁻² for the Nylon cut-pile carpet and 26 mg m⁻² for the olefin textured-loop carpet over the same time period. The "hard-back" carpet emitted 85 and 72 mg m⁻² of vinyl acetate and 1,2-propanediol, respectively, over 168 h. The total mass emissions of formaldehyde, 2,2,4-trimethylpentane and 2-ethyl-1-hexanol from the same carpet were 7, 8 and 7 mg m⁻², respectively. The carpet with the polyurethane backing emitted 28 mg m⁻² of BHT over 168 h.

Chamber Comparison and House Measurements

Measurements made in small-volume chambers (4 L) were compared to measurements made in the room-size environmental chamber to assess whether small-volume chambers can adequately characterize short-term emissions of VOC from carpets. The experiments in the small-volume chambers were conducted at a ventilation rate of 6 h⁻¹. However, the ventilation rate to loading ratio was the same as for the large chamber which facilitated the direct comparison of concentrations in the two chambers. The small-volume chambers had a surface-to-volume ratio 16 times that of the large chamber, while the air velocities in the small chambers were probably considerably lower than the 6-9 cm s⁻¹ velocities in the large chamber. Concentrations of selected compounds measured at 1, 3 and 6 h in both chambers were compared.

Significant differences between the chambers were observed for some compounds demonstrating the combined effect of differences in compound volatilities and experimental parameters on emissions. The least volatile compounds, 4-PCH and BHT, had consistently lower concentrations in the small-volume chambers, although, these concentrations were within a factor of two to three of the concentrations in the environmental chamber. The difference between the chambers was attributed to greater wall losses of these compounds in the small chambers with their high surface-to volume

ratio. Compounds with relatively high volatilities and relatively low concentrations had substantially lower concentrations in the small chambers versus the large chamber. As examples, the concentrations of 4-ethenylcyclohexene, styrene (from the Nylon cut-pile carpet) and hexamethylcyclotrisiloxane were about an order of magnitude lower in the small-volume chambers. These differences were attributed to volatilization losses during the handling of the small samples of carpet. At substantially higher styrene concentrations (from the olefin textured-loop carpet), the differences between the chambers were within experimental uncertainties.

Concentrations and emission rates of styrene and 4-PCH were also measured in a residence over a period of seven weeks following the installation of new Nylon cut-pile carpet with SBR latex adhesive on the secondary backing. The initial emission rate of 4-PCH in the house was several times higher than the 24-h emission rates measured in the environmental chamber for other SBR carpets. This rate declined by two thirds in a period of a week which was a more rapid decay than measured in the chamber. After four weeks, the emission rate of 4-PCH in the house was in the range of 30-60 ug m⁻² h⁻¹, which was almost the same as the emission rates measured in the chamber at 168 h. The long-term emissions of 4-PCH in the house demonstrate that there was a relatively large reservoir of this compound present in the SBR latex adhesive. It was emitted over a period of months at a slow rate that is probably controlled by processes in the carpet such as diffusion through the materials. The emission rates of styrene in the house were considerably lower than the rates for 4-PCH and similar to those measured in the chamber for the Nylon cut-pile carpet.

The chamber comparison and the house measurements illustrate the difficulties that can be encountered when attempting to extrapolate the results of environmental chamber experiments to buildings. The initial emissions of at least the more volatile VOC from carpets may be highly variable and considerably different in the real world than those from specially packaged and handled samples measured under constant, carefully controlled conditions. Factors such as carpet age, type of packaging, and handling procedures during installation will have an effect on the emissions of such compounds. Sink effects due to sorption and desorption of VOC onto surfaces may significantly alter the temporal profiles of the emissions of the less volatile VOC in buildings relative to their temporal profiles in chambers. These sink effects may lower the peak emissions and extend the emission periods of those compounds that are readily sorbed onto the complex surfaces that are typically found in buildings. The resulting

effects on occupant exposures will be dependent upon the buildings' operating parameters and on the temporal patterns of occupancy. To evaluate the magnitudes of these sources of variability, it would be instructive to conduct additional experiments that compared emission rates of VOC from carpets measured in small-volume chambers, a room-size environmental chamber and buildings.

Health and Comfort Issues

It is difficult to evaluate whether the emissions of VOC from carpets could constitute a public health or comfort problem. On the one hand, the emissions of TVOC from carpets are low relative to other sources of TVOC that are commonly found in buildings. On the other hand, the potencies of different VOC may vary over a number of orders of magnitude as evidenced by the ranges of Threshold Limit Values (TLVs) for industrial exposures to chemicals, irritancy as measured by a mouse bioassay that uses respiratory rate as the indicator, and odor thresholds. Since some compounds may have effects at very low concentrations, it is essential to identify and quantify the individual VOC that are emitted by carpets when attempting to evaluate the potential for health and comfort effects.

It is useful to focus on the compounds with relatively high emissions as identified above. Of these compounds, most is known about the toxicity and irritancy of formaldehyde. A recent epidemiology study of mobile-home occupants showed that significant irritant effects (burning/tearing eyes) occurred at a weekly average indoor concentration of 70 ppbv, assuming 60 percent of the time was spent at home. The maximum concentration of formaldehyde in the experiment with the commercial "hard-back" carpet was about half of this value, and the average weekly concentration was significantly lower. Higher concentrations would be expected at lower ventilation rates. Also, since other sources of formaldehyde are often present in buildings, the addition of a carpet source could result in concentrations that approached or exceeded lower limits for irritancy. Only very limited data are available on the toxicity and irritancy of the other compounds at low concentrations. However, it is possible that several of the dominant compounds, in addition to formaldehyde, may produce irritant effects at relatively low concentrations based on their structural similarity to known irritants. These compounds are vinyl acetate, 4-PCH, and BHT. It would be of value to determine the sensory and respiratory irritancy, as well as the neurotoxicity, of the

dominant chemicals emitted from the carpets, particularly if further emissions testing confirms their prevalence.

Odor is another important factor that influences people's acceptance of products. The 4-PCH produces a strong odor at low to sub part-per-billion concentrations that some people may find objectionable. In addition, the concentrations of vinyl acetate and of styrene in one experiment were high enough to produce an odor response in some people.

Control Strategies

If it is determined that control measures for reducing emissions of VOC from carpets are warranted based on an assessment of the potential for health and comfort effects, the identification and quantitation of individual VOC can be used to guide that effort. The compounds of interest may be introduced at different points in the manufacturing process. Therefore, engineering or process-control measures directed at these specific compounds should, in most cases, be the most effective and efficient means of reducing their emissions.

A relatively simple control strategy might be implemented at the time of installation. This strategy was suggested by the rapid decline in the emissions of many VOC over the first few hours after installation of the carpets in the chamber. It is likely that the emissions of these compounds in buildings could be reduced by airing out carpets for 12-24 h immediately prior to their installation either outdoors or in a well-ventilated space. The required time might be reduced by vacuuming the rolled-out carpets as this procedure would increase the flow of air through the fibers and possibly accelerate the emissions of compounds sorbed onto the fibers. Unfortunately, this strategy might not have a major impact on the emissions of some of the compounds, such as formaldehyde, 4-PCH and BHT, that did not decay rapidly and which are possibly more important with respect to health and comfort effects.

INTRODUCTION

Background

The potential impacts of newly installed carpets on human health and comfort are of concern. The U.S. Consumer Product Safety Commission (CPSC) has compiled data on health complaints related to carpets (Schachter, 1990). Complaints from 335 residents from 206 households were received from 1988 through early 1990 after the CPSC issued a news release about their interest in studying carpet-related health problems. About two thirds of the complainants reported that symptoms started immediately, or within a few days, following carpet installation. Most people reported upper respiratory problems in combination with other symptoms such as eye irritation, headache, rashes, and fatigue. Twenty-five of the complainants were hospitalized. It should be noted that this CPSC investigation was limited in scope and did not attempt to determine any direct relationship between these symptoms and emissions from carpets.

Remodeling of the Washington headquarters of the U.S. EPA focused attention on emissions of volatile organic compounds (VOC) from carpets. Many of the EPA employees complained of health and odor problems after new carpeting was installed in part of the building. Testing identified an individual compound, 4-phenylcyclohexene (4-PCH), as the predominant source of the "new carpet" odor (Van Ert *et al.*, 1987). This compound is a manufacturing by-product present in the styrene-butadiene rubber (SBR) latex which is frequently used to bind the secondary backing of a carpet. The National Federation of Federal Employees petitioned the EPA to regulate 4-PCH, which the union alleged was the cause of health problems suffered by the EPA employees. The petition was denied; however, the EPA initiated a one-year dialogue with carpet manufacturers to develop standard methodologies for measuring emissions of total VOC (TVOC) from carpets and to obtain commitments from industry for carpet testing (Federal Register, 1990). A Carpet Policy Dialogue Group was formed consisting of representatives from industry, the EPA, the CPSC, labor, public interest groups, and members of the scientific and research communities (Carpet Policy Dialogue, 1991). This group began meeting periodically in August, 1990. A laboratory method to measure the emissions of TVOC from small samples of carpets was developed as part of this effort. It is entitled, "Standard Test Method for Determining Total Volatile Organic

Compound Emission Factors from Carpet Under Defined Test Conditions Using Small Environmental Chambers" (Carpet Policy Dialogue, 1991).

Carpets have been shown to emit a variety of VOC including 4-PCH (Seifert *et al.*, 1989; Bayer and Papanicolopoulos, 1990; Black, 1990; Pleil and Whiton, 1990; Schröder, 1990; Davidson *et al.*, 1991; Hetes *et al.*, 1992). There have been several reports of the quantitative emissions of 4-PCH from carpets (Seifert *et al.*, 1989; Black, 1990; Black *et al.*, 1991a and b). It is suspected that 4-PCH or some other component(s) of these volatile emissions is the source of carpet-related health and comfort complaints. However, the effects of these compounds at low concentrations have generally not been investigated, and no specific etiological agent(s) has been identified.

Most of the measurements of the emissions of VOC and TVOC from carpets have been made in small containers or in small-volume chambers (typically 50 L). Few studies have been conducted to validate these results by comparisons with results obtained in large chambers and in buildings have generally not been conducted. Large (*i.e.*, room-size) environmental chambers should inherently produce more realistic data because they more closely replicate conditions in buildings. For example, larger sample sizes can be used to reduce the variability caused by material heterogeneity. Because large chambers are similar in size to rooms in houses, some of the problems of scaling environmental variables, such as air velocities at surfaces of materials, may be reduced. In addition, sink effects caused by losses of compounds to chamber walls may be lower because of the lower surface-to-volume ratios of large chambers.

Study Objectives

The primary objective of this research was to measure the emission rates of selected VOC released by samples of new carpets that are typical of the major types of carpets used in residences, school classrooms and offices. The carpet samples were to be collected directly from the manufacturers' mills and packaged to preserve their chemical integrity. The study compounds were to be selected from among the dominant compounds emitted by the carpet samples in screening measurements. The measurements of the concentrations and emission rates of these compounds were to be made under simulated indoor conditions in a 20-m³ environmental chamber designed specifically for investigations of VOC. The measurements were to be conducted over a period of one

week following the installation of the carpet samples in the chamber. Duplicate chamber experiments were to be conducted for one carpet. In addition, measurements of the concentrations and emission rates of VOC emitted by a new carpet were to be made directly in a residence over a period of several months following the installation of the carpet.

The carpets for the environmental chamber experiments were selected by the CPSC based on the results of previous headspace and small-volume chamber screening studies of similar carpets. Consequently, they were not a statistically representative sample of any population of carpet products. Because only a limited number of experiments could be conducted, the investigation of the range of variability in VOC emissions due to differences in manufacturing processes was not part of the study objectives.

METHODS

LABORATORY EXPERIMENTS

Carpets

The four carpets investigated in the laboratory were selected by the CPSC to be typical of the predominant types of carpets used in residences, school classrooms and offices. The selection was based on the results of previous screening studies of a number of carpets produced by several mills (Jarmer and Singh, 1990; Jarmer, 1991; Miller *et al.*, 1991). The study carpets have been designated Carpets 1-4. Their descriptions are presented in Table 1. Three had all Nylon yarn fibers, while Carpet 4 had a combination of olefinic and Nylon fibers. Carpets 1 and 2 were cut pile; the other two were textured loop. Carpet 1 was treated for static control. Carpet 3 was treated for stain resistance and to control microbial growth. Fiber treatments were not specified for Carpets 2 and 4. The yarn was woven onto an polypropylene primary backing in all cases. The secondary backings varied among the carpets. Carpets 1 and 4 were "action-back" carpets with a coarse polypropylene mesh bonded to the primary backing with styrene-butadiene rubber (SBR) latex adhesive. Carpet 2 was also an "action-back" carpet with a flexible polyurethane foam secondary backing, approximately 3-mm thick, bonded to the back with an outer synthetic fiber layer bonded to the polyurethane. Carpet 3 was a "hard-back" carpet with a 1.5-mm thick polyvinyl chloride secondary backing. The adhesives used in the construction of Carpets 2 and 3 were not specified. Carpet 3 was supplied in the form of 18 x 18 inch (46 x 46 cm) tiles. These tiles are designed to be directly glued down onto a floor. The other three carpets are intended to be conventionally installed over a pad.

The carpet samples were collected by staff from the CPSC field office in Atlanta GA. Arrangements were made with the manufacturers to collect the samples directly at the mills immediately following their production. The collection dates for the carpets are shown in Table 2. Two identical samples of Carpet 1 were simultaneously collected. These samples have been designated 1a and 1b.

Each sample of a rolled carpet consisted of an 8 x 12 ft (2.4 x 3.6 m) contiguous section of a large manufacturing run. This piece was cut into either two or three equal-

sized pieces for shipment. Each of the smaller pieces were individually rolled with the fibers on the outside. This roll was placed into a large Tedlar bag which was then heat sealed so that the amount of air in the bag was minimized. This bag was, in turn, placed into another Tedlar bag which was also heat sealed. Carpet 3, which was produced in the form of tiles, was packaged in double heat-sealed Tedlar bags with about ten tiles per bag. Several smaller pieces of each carpet (approximately 0.2 m²) were collected for use in the screening measurements. For Carpet 1, the smaller pieces were packaged in new, clean 1-gal (4-L) paint cans. For the other carpets, the smaller pieces were packaged in double heat-sealed Tedlar bags.

The bagged pieces of each carpet were placed into a large cardboard box and shipped by overnight air freight to the laboratory in Berkeley, CA. Upon arrival, the sample was stored at room conditions in an office or a non-chemistry laboratory. It was intended to initiate the environmental chamber experiment within approximately two weeks of sample collection. This period was required to conduct the screening measurements and evaluate their results. The actual storage times for the samples are shown in Table 2. Samples 1a, 2 and 4 were stored for approximately two weeks prior to use in the chamber. Sample 3 was stored for about 3 weeks, and sample 1b, the duplicate of sample 1a, was stored for 35 days.

Screening Measurements

Each carpet sample was screened for emissions of VOC using several techniques. These techniques included the analysis of headspace gas collected from the sample storage bags, the measurement of emissions using small-volume chambers, and the vacuum extraction of samples. In addition, samples for the qualitative analysis of emissions were collected throughout each environmental chamber experiment. The results of these qualitative and semi-quantitative measurements were used as the primary basis for the selection of the compounds to be quantitatively analyzed in the environmental chamber experiments.

Following the arrival of a carpet sample at the laboratory, samples of headspace gas for the analysis of individual VOC were withdrawn from one of the double-layered Tedlar bags. This was accomplished by attaching a Swagelok union fitted with a syringe needle to the inlets of the multisorbent samplers. The needle was inserted through the bags into the air space surrounding the carpet. Several samples of different volumes

were collected. These samples were collected and analyzed using the methods described below (see Air Sampling and Analysis).

The carpet samples were also initially screened for emissions of VOC using small-volume chambers (Hodgson and Girman, 1989). The chambers consisted of new, clean 1-gal (4-L) paint cans with lids equipped with two fittings. Dry nitrogen, supplied by a gas cylinder, was introduced near the bottom of a can through one fitting with a tubing extension. The flow rate was regulated with a needle valve and was measured with a calibrated rotameter. The gas exited and was sampled at the other fitting. The operating conditions specified for the small-volume chambers are presented in Table 3.

A 10 x 10 cm (100 cm²) piece of carpet was cut from a sample. The piece was weighed and placed into a stainless-steel holder which covered the bottom and cut edges of the carpet. The chamber was placed on its side, and the holder was positioned in the can midway between the ends with the top surface of the carpet exposed. The chamber was sealed and a ventilation rate of 6.3 h⁻¹ was established. The chamber was maintained at room temperature (20-25° C). Samples for VOC were obtained at approximately one, three and six hours after closing the chamber. These samples were collected and analyzed using the methods described below (see Air Sampling and Analysis).

A vacuum-extraction technique was used to detect the emissions of higher-boiling VOC and semi-volatile organic compounds (Hodgson *et al.*, 1983). Seven to ten grams of carpet in the form of 1-cm² pieces were cut from a sample. The pieces were weighed and inserted into a specially constructed vacuum apparatus (Figure 1). The cold-finger trap in the apparatus was cooled to liquid-nitrogen temperature, and the system was evacuated to a pressure of approximately 0.1 Pa. This pressure was maintained for four hours. The sample was warmed to 40-50° C with a heating mantle during this period to accelerate the emissions process. At the end of the extraction period, the cold-finger trap was isolated from the system and brought to atmospheric pressure. The condensed extract, which included some water, was collected by washing the trap with approximately 200 μ l of n-hexane. The organic fraction was retained and analyzed by GC-MS using syringe injection (see Air Sampling and Analysis for a description of the GC-MS instrumentation).

Environmental Chamber Facility

The environmental chamber facility is located in a laboratory with both heating and air conditioning. This facility is schematically shown in Figure 2. The chamber encloses a volume of 20 m³ with interior dimensions of 3.65 m (length) x 2.44 m (width) x 2.23 m (height). The walls, floor and ceiling are insulated with a 10-cm layer of high-density polyurethane foam. All interior surfaces are clad in stainless steel. The door and interior seams are sealed with a closed-cell silicone gasket material. Electrical and plumbing feed throughs are also sealed. The materials used throughout the construction of the chamber were selected, in part, for their low emissions of VOC.

The chamber is equipped with a single-pass ventilation system. Inlet air is drawn from outside the laboratory building by a variable-speed blower. The air then passes through a filter assembly (Model ECO Glide Pack, Farr Co.) containing a coarse filter, 12 charcoal filters, and a HEPA (high-efficiency particle accumulation) filter, in series. The desired dew-point and dry-bulb temperatures of the inlet air are established by a pre-heater, a humidifier, a chiller coil, and a re-heater in the air-handling system. The operation of these components is controlled by a microprocessor. The volumetric flow rate of air is monitored with a turbine flow meter (Model 2-2011, Daniel Industries, Inc.) located downstream of the air-conditioning components. Air enters the chamber through an inlet positioned high at one end of a long wall. Air is exhausted from the chamber to a laboratory hood through an outlet at the opposite lower corner of the same wall. A gate valve on the outlet is used to maintain the chamber at a slight positive pressure with respect to the laboratory. The natural ventilation rate of the chamber with the air inlet and outlet sealed is $0.03 \pm 0.01 \text{ h}^{-1}$.

For this study, the chamber was fitted with a 3-mm I.D. stainless-steel sampling line running from the middle of the chamber at a height of 1.2 m above the floor to a stainless-steel manifold on the outside of the chamber. The sampling line was kept as short as possible. The manifold allowed the simultaneous collection of replicate samples. Identical sampling hardware was installed on the air inlet duct immediately upstream of the chamber.

Prior to each experiment, the interior surfaces of the chamber were washed with an alkaline cleaning solution, thoroughly rinsed and dried.

The conditions specified for the operation of the 20-m³ chamber are presented in Table 3. The atmospheric pressure at the site is typically 745 ± 5 mm Hg. The air temperature in the chamber was maintained by controlling the temperatures of the inlet air and the laboratory. The relative humidity of the inlet air was controlled by the air-handling system. The ventilation rate was controlled by setting the speed of the blower.

The average air velocity at 5 cm above the floor in various buildings has been found to be 9.2 cm s⁻¹ with a standard deviation of 4.9 cm s⁻¹ (Kovanen *et al.*, 1987). Since the chamber is nearly isothermal, natural air velocities in the chamber are considerably lower than this value. Six small, variable-speed fans were used to increase air movement. These fans were positioned along the four walls of the chamber (two fans along each of the long walls) at a height of about 60 cm above the floor. Their speeds and orientations were adjusted so that the average velocity near the floor was close to the target value of 9 cm s⁻¹.

During each experiment, the air temperature in the chamber was continuously monitored at three locations with type T thermocouples. These thermocouples were positioned in the chamber near the air inlet, the air exhaust, and the mid-point of the chamber. The readings from these three thermocouples were averaged to obtain an average air temperature. Additional thermocouples were attached to the floor of the chamber to determine if the carpet sample was at the same temperature as the chamber air. The air temperature in the laboratory was also monitored. All thermocouples were calibrated against a precision thermometer.

The dew-point temperature of the inlet air as it entered the chamber was continuously monitored with a chilled-mirror dew-point-hygrometer (Model 911 Dew-All, EG&G, Inc.). This instrument was calibrated by the manufacturer.

The air velocity in the chamber was monitored with an omni-directional hot-wire anemometer (Model 8470, TSI, Inc.). This instrument was positioned in the center of the chamber with the tip approximately 5 cm above the surface of the carpet.

Atmospheric pressure in the chamber was continuously monitored with a pressure transducer readable to one torr (Model PDCP-20A-230, Columbia Research Laboratories, Inc.). The calibration of the transducer was checked against a mercury barometer.

The analog output signals from the thermocouples, the dew-point hygrometer, the air-velocity transducer, the pressure transducer, and the turbine flow meter were continuously sampled throughout an experiment with a data-acquisition system (Series 500, Keithly/DAS) at a rate of five points per minute. Data collection, processing and recording were controlled with an IBM PC compatible computer running a commercial data-acquisition software program (Labtech Notebook, Ver. 6.01, Laboratory Technologies Corp.). Average parameter values for consecutive ten-minute intervals were recorded on a hard disk. These files were backed up on diskettes.

Preliminary Chamber Measurements

Prior to the experiments with the carpets, experiments were conducted in the chamber to: validate the ventilation rate; evaluate the mixing of chamber air; measure background concentrations of particles in chamber air; and estimate the loss of styrene onto the walls of the chamber.

The chamber ventilation rate is determined by the volumetric flow rate of air into the chamber divided by the chamber volume:

$$a = Q/V \quad (1)$$

where a is the ventilation rate (h^{-1}); Q is the flow rate through the chamber ($\text{m}^3 \text{ h}^{-1}$); and V is the chamber volume (m^3). The ventilation rate based on the turbine flow meter measurement of Q was validated by a tracer-gas technique. In three separate measurements, an aliquot of sulfur hexafluoride (SF_6) was introduced into the chamber with the flow rate of inlet air set at $0.330 \text{ m}^3 \text{ h}^{-1}$ as indicated by the turbine flow meter. This flow rate is equivalent to a ventilation rate of 1.01 h^{-1} . The decay in the concentration of SF_6 was monitored at the mid point of the chamber at one-minute intervals using a gas chromatograph equipped with an electron-capture detector (GC-ECD). The measured concentration followed a simple exponential decay curve for a completely mixed chamber of the form:

$$C = C_i e^{-at} \quad (2)$$

where C is the concentration (ug m^{-3}) in the chamber at time t (h) and C_i is the initial chamber concentration (ug m^{-3}). The ventilation rate was calculated from Equation 2 by

a least-squares fit to a plot of $\log C$ versus t . This ventilation rate was 0.98 ± 0.01 (s.d.) h^{-1} . Since the difference between this value and the reading of the turbine flow meter was within the uncertainty of the tracer-gas technique, the turbine flow meter was considered to be accurate.

The mixing of chamber air was evaluated using the tracer-gas technique described by an ASTM Standard Guide (ASTM, 1990). With the chamber operating at the specified experimental conditions, SF_6 was introduced at constant concentration (190 ppbv) and flow rate (10.8 L min^{-1}) into the inlet air immediately upstream of the chamber. The concentration of SF_6 was measured in the chamber outlet at one-minute intervals by GC-ECD. A plot of the increase in measured concentration was compared to the theoretical curve for a completely mixed chamber:

$$C = C_0 (1 - e^{-at}) \quad (3)$$

where C is the outlet concentration (ug m^{-3}) and C_0 is the inlet concentration (ug m^{-3}). The actual increase in SF_6 concentration was indistinguishable from the theoretical increase, indicating that short circuiting of the air flow was not occurring and that the air in the chamber was well mixed.

The concentration of particles in the air in the chamber with the chamber empty and operating at the specified experimental conditions was measured with a condensation-nucleus counter (Model 3020, TSI, Inc.). After three complete air exchanges, the number concentration was $3,600 \text{ particles cm}^{-3}$. This was about four times lower than the concentration of particles in laboratory air.

An experiment was conducted to determine if styrene, one of the major compounds emitted by carpets with SBR latex, was lost by sorption onto the stainless-steel walls of the chamber. The procedure was similar to the that described above for evaluating the mixing of chamber air (Equation 3). With the chamber empty and operating at the specified conditions, styrene from a gravimetrically-calibrated diffusion source was introduced at a constant rate (3 ug min^{-1}) near the mid-point of the chamber. At one and six hours after introducing the source, air samples were collected at the chamber outlet, and the concentration of styrene in the samples was measured as described below (see Air Sampling and Analysis). The measured and predicted

concentrations agreed within five percent indicating that there was no significant loss of styrene to the chamber walls.

Experimental Protocol

The chamber was operated at the specified experimental conditions for at least three days immediately prior to an experiment. The chamber air temperature, humidity and ventilation rate were monitored throughout the preliminary period with the data-acquisition system. This period was used to stabilize the chamber at the operating conditions and to collect samples to determine if the chamber was a source of any of the compounds of interest (see Air Sampling and Analysis).

On the morning of the day that an experiment was to begin, the chamber was entered, and the carpet sample was quickly installed to cover the floor of the chamber. For all but one experiment, the pieces of carpet were removed from their bags in the hall outside of the chamber facility, unrolled and immediately carried into the chamber. For experiment b with Carpet 1, the pieces were removed from their bags inside the chamber. A sample was installed so that there were no gaps or overlaps between the individual pieces. The edges at the walls were trimmed as required to make the sample lay flat on the floor. The installed dimensions of the sample were measured. The loading ratio was typically about $0.44 \text{ m}^2 \text{ m}^{-3}$. Next, the hot-wire anemometer was positioned at the center of the chamber with the tip 5 cm above the surface of the carpet. The entire installation procedure took approximately 15 min. The chamber was then exited, and the chamber door was sealed. The door remained closed for the duration of the experiment. The closing of the chamber door established the initial time for the experiment (e.g., elapsed time = 0).

Air Sampling and Analysis

All samples for individual VOC and total VOC (TVOC) were collected on commercially available multisorbent samplers (Part No. ST032, Envirochem, Inc.) which are packed with glass beads at the inlet followed by Tenax-TA, Carboxen carbon molecular sieve, and activated charcoal, in series (Hodgson and Girman, 1989). These multisorbent samplers are reusable. Prior to each use, they were cleaned and conditioned by heating them to 300°C for 10 min with a helium purge flowing in the reverse direction of gas flow during sample collection. The samplers were capped at

both ends with Nylon Swagelok caps fitted with Teflon ferrules. The capped samplers were individually sealed in elongated culture tubes and were stored in a dedicated freezer at -10° C prior to use. Samples for low molecular-weight aldehydes were collected on C₁₈ Sep-Pak cartridges (Millipore Corp.) impregnated with an acid solution of 2,4-dinitrophenylhydrazine (DNPH) as described by Kuwata *et al.* (1983). The DNPH cartridges were prepared and supplied by Atmospheric Assessment Associates, Inc. (Chatsworth, CA). Each cartridge was fitted with a plug at the inlet and outlet and was sealed in a polyethylene vial. A batch of cartridges was stored in a metal paint can in a freezer at -10° C.

Replicate samples of chamber air were collected periodically over the course of a week-long chamber experiment for the quantitative analysis of individual VOC and TVOC. During the first day, samples were collected starting at elapsed times of approximately 1, 3, 6 and 12 h. Subsequent samples were collected at 24 h and at daily intervals, with the last samples being collected at 168 h. Duplicate samples for quantitative analysis were simultaneously collected at all sampling intervals, except 3, 24 and 168 h when triplicate samples were collected. An additional sample was collected at each sampling interval for qualitative analysis. Experiment b with Carpet 1 was an exception in that consecutive duplicate samples were collected over each 30 minute interval for the first 6.5 h of the experiment. Immediately following the collection of each set of chamber samples, a single sample was collected from the chamber inlet-air duct. On each of three days during the preliminary period proceeding the experiment, samples for the analysis of individual VOC and TVOC were simultaneously collected from the chamber and the chamber inlet. The samples were stored in a freezer at -10° C and were analyzed within one week of sample collection.

The chamber sampling line and manifold were flushed immediately prior to the collection of samples for the analysis of individual VOC and TVOC by pulling air through them at 1.0 L min⁻¹ for 30-60 min. The air flow rate for each VOC/TVOC sample was in the range of 50-200 cm³ min⁻¹. The sample collection times ranged from 25-50 min. Sample volumes ranged from 1.25-10 L. Generally the smaller volumes were used at the beginning of an experiment when the concentrations were highest. The volumes of the samples of inlet air and the chamber background were typically 10 L. The sample flow rates were regulated with electronic mass-flow controllers placed between the samplers and a house vacuum source. All mass-flow controllers were calibrated at standard conditions of 25° C and 760 mm Hg (1 atm). These calibrations

were performed at the start of the study using a bubble-flow meter. Potential contamination from the vacuum source was prevented by a charcoal filter inserted between the source and the mass-flow controllers.

During each chamber experiment, ten samples of chamber air were collected for the analysis of low molecular-weight aldehydes. On the first day, single samples were collected over elapsed time intervals of approximately 0-3, 3-6 and 10-13 h. A single sample was collected on each of the remaining days. Samples of inlet air were collected on three separate days. On each of two days during the preliminary period proceeding the experiment, samples for aldehydes were simultaneously collected from the chamber and the chamber inlet. The samples were stored in a freezer at -10° C and were analyzed within two weeks of sample collection.

The air flow rate for each aldehyde sample was regulated at 1.00 L min⁻¹ with a calibrated electronic mass-flow controller and an oil-less vacuum pump. The sample volumes were 180 L collected over 3 h, except for experiment 3 when the volumes were 90 L collected over 1.5 h.

The analytical procedures for VOC collected on multisorbent samplers have previously been described (Hodgson and Girman, 1989). In brief, a sample is thermally desorbed from a sampler, concentrated and introduced into a capillary gas chromatograph (GC) with a UNACON 810A (Envirochem, Inc.) sample concentrating and inletting system. This instrument passes the sample through dual sequential traps to concentrate the sample. Sample components are resolved with a GC (Series 5790A, Hewlett Packard Co.) equipped with liquid nitrogen sub-ambient cooling and a 30-m x 0.25-mm I.D. x 1.0-um thick film fused-silica capillary column (Model DB-1701, J&W Scientific, Inc.). The GC is connected via a direct capillary interface to a Series 5970B Mass Selective Detector (MSD) equipped with a Series 59970C workstation (Hewlett Packard Co.). The MSD is mass tuned using perfluorotributylamine. The specifications and standard operating conditions for the components of the analytical system are summarized in Table 4.

An internal standard consisting of approximately 50 ng of 1-bromo-4-fluorobenzene was added to all samplers, including standards, immediately prior to their analysis. The internal standard was generated by a gravimetrically-calibrated diffusion source. It was transferred from the source with a gas-tight syringe and introduced into

a helium gas stream flowing through a sampler in the direction of sample gas flow. The purpose of the internal standard was to provide a retention-time marker and an indicator for the mass calibration and sensitivity of the MSD.

For the analyses of the samples for the screening measurements and the qualitative analysis of samples collected from the environmental chamber, the MSD was operated to scan a mass range of m/z 33-250. Compounds were tentatively identified by comparing the unknown spectra with spectra contained in the EPA/NIH Mass Spectral Data Base (Heller and Milne, 1978). Whenever possible, these identifications were confirmed by analyzing authentic standards of the compounds under identical conditions. For the quantitative analysis of these samples, abundant and characteristic mass ions for the compounds of interest were extracted from the total-ion-current chromatograms and integrated. Calibration standards were prepared as described below.

For the quantitative analysis of the samples collected during the environmental chamber experiments, the MSD was operated to monitor multiple, individually selected mass ions. For each compound of interest, a mass ion with a high relative abundance was chosen as the quantitative ion, and a characteristic ion was chosen as a qualifying ion for confirmation of compound identity. The peak areas of the target mass ions were integrated using the MSD software.

Authentic standards used for compound identifications and for the calibrations were generally obtained from Aldrich Chemical Company (Milwaukee, WI). The Standard for 4-phenylcyclohexene (4-PCH) was produced by Wiley Organics (Columbus, OH).

Standard gas mixtures of VOC were prepared by injecting a several-microliter aliquot of a liquid mixture of the compounds of interest into a 2-L flask with septum cap which was then heated and maintained at 65°C (Riggin, 1984). A sample was withdrawn from the flask with a gas-tight syringe and was injected into a helium gas stream flowing through a conditioned multisorbent sampler in the direction of sample gas flow. The internal standard was also introduced onto the sampler at this time. The sampler was then analyzed using the same procedure as for the samples. Multi-point external calibrations were prepared by analyzing a range of volumes of the gas mixture. Fresh standard gas mixtures were prepared on each day of analysis.

For compounds with very low equilibrium vapor pressures at room temperature, a dilute standard was prepared in a low-boiling solvent such as n-hexane or benzene, and a 0.5-3 μ l aliquot of the liquid standard was injected directly onto the sorbent bed of an all-Tenax sampler (Part No. ST023, Envirochem, Inc.). The sampler was then purged with 3-5 L of dry helium. This removed much of the solvent but did not result in the breakthrough of the analytes. Following the purge, the Tenax sampler was analyzed using the normal procedure. Multi-point external calibrations were prepared by analyzing serial dilutions of the liquid standard.

Complete multi-point external calibrations for the compounds of interest were prepared at the start of the analysis of samples collected during a chamber experiment. In addition, at least one calibration standard for the compounds was analyzed on each day that samples from the experiment were analyzed. At the conclusion of the analysis of the samples for an experiment, all of the standards for each compound were incorporated into a single calibration which was used to calculate the masses of the compound in all of the samples.

During the thermal desorption procedure, approximately eight percent of each VOC sample was automatically split off and analyzed directly without chromatographic separation by a flame-ionization detector (FID) that is built into the UNACON sample concentrating and inletting system. This produced a measure of the total carbon in the sample over a boiling-point range encompassed by approximately C₃ - C₁₄ hydrocarbons (some C₁ and C₂ compounds are also included, depending on their functional groups). The results of this analysis were expressed as mass of carbon. The FID was calibrated with a mixture of C₆ - C₁₂ normal alkane hydrocarbons that was constituted so that each compound contributed an equal mass of carbon. A gas standard of this mixture was prepared in a 2-L flask and analyzed as described above for individual VOC. Fresh gas standards were prepared daily. Multi-point external calibrations were prepared for each experiment using the same strategy as for individual VOC.

The aldehyde samples collected on the DNPH cartridges during the chamber experiments with Carpet 1 were analyzed for formaldehyde and acetaldehyde by Atmospheric Assessment Associates, Inc. (Chatsworth, CA) using a published method (Fung and Grosjean, 1981). The samples collected during the other chamber experiments were analyzed in our laboratory using essentially the same method. Each sampler was eluted with glass-distilled acetonitrile and made up to volume in a 2-ml

volumetric vial. The analysis was performed with a high-performance liquid chromatograph (HPLC) equipped with a diode-array UV detector (Series 1090, Hewlett-Packard Co.). Ten microliter aliquots of the eluate were manually injected into the instrument. The compounds were separated on a 2.1-mm I.D. x 15-cm long, reverse-phase C₁₈ column (Vydac Model 201TP5215, The Separations Group) using an isocratic solvent program with a 63:35 v/v mixture of water and acetonitrile as the mobile phase. The peak-area responses of the formaldehyde and acetaldehyde hydrazone derivatives at a wavelength of 360 nm were integrated. Samplers from each chamber experiment were analyzed as a batch over a period of two days. Multi-point, external calibrations were prepared for each experiment by analyzing serial dilutions of purified formaldehyde and acetaldehyde hydrazone derivatives made up in acetonitrile.

Data Analysis

A linear calibration curve for a compound was determined by fitting a least-squares linear regression to all of the calibration points for the compound that were run during an experiment. The scatter in the points around the fitted line limits the precision with which the mass of a compound in a sample can be analyzed. This scatter was measured by the standard error of the fit which was then used to calculate 95 percent confidence intervals for the individual sample masses as described by Kolthoff and Elving (1978). The size of this interval is additionally affected by the number and spacing of the calibration points along the mass axis and by the slope of the instrumental response.

The limits of quantitation were estimated from the chamber-background and chamber-inlet samples for those compounds which were present in these samples. If the background concentrations were higher than the inlet concentrations for a compound, then only the background samples were considered. Otherwise, both sample sets were used. The limit of quantitation for a compound was estimated as three times the standard deviation of these measurements. For those compounds which were not detected in the background and inlet samples, the limits of quantitation were conservatively estimated to be less than 0.1-0.2 ppbv based on the sensitivity of the MSD and the sample volumes.

Chamber concentrations of the compounds of interest were corrected for any contamination introduced with the inlet air or due to background emissions from the

chamber. If the measurements of the chamber background of a compound and its inlet-air concentrations during an experiment were indistinguishable, the average of all of these values was subtracted from the concentrations measured in the chamber during the experiment. If the background concentrations were uniformly higher than the inlet-air concentrations, the average of the background concentrations was used to correct the chamber concentrations.

Curves were fit to the chamber concentrations of each compound in each experiment using standard curve-fitting routines executed with a graphics software package (KaleidaGraph, Ver. 2.0, Synergy Software). These curves were fit over time intervals of 1-12 h and 24-168 h. An exponential least-squares fit was used for the 1-12 h data, and a power least-squares fit was used for the 24-168 h data.

For each environmental chamber experiment, the quasi steady-state source strengths, S (ug h^{-1}), of the compounds of interest were calculated as:

$$S = V a (C - C_0) \quad (4)$$

where V is the chamber volume (20 m^3); a is the average ventilation rate (h^{-1}) for the experiment; C is the average of the replicate measurements of chamber concentration (ug m^{-3}) at a sampling interval; and C_0 is the average chamber background or the average background and inlet concentration (ug m^{-3}) for the experiment. Quasi steady-state specific emission rates ($\text{ug m}^{-2} \text{ h}^{-1}$) were calculated by dividing the source strengths by the area of the carpet (m^2). The steady-state assumption will tend to underestimate the source strengths and emission rates when the chamber concentrations are changing rapidly. This period of rapid change typically occurred over the first 0-12 or 0-24 h of a chamber experiment.

The use of non-steady state models to describe the emissions of VOC from carpets was also explored. The U.S. EPA has conducted research on the processes that affect the rate of emissions of VOC from consumer products and building materials. These experiments were performed in a small-scale chamber facility. Procedures were developed to model the results of the chamber experiments to provide emission rates (Tichenor and Guo, 1991). The simplest model, which is analogous to Equation 2, assumed that the chambers were continuous stirred tank reactors and that the change in emission rate could be approximated by a first-order decay. Sink and vapor pressure

effects were ignored. The mass balance for the chamber over a small time increment, dt , was expressed as:

$$VdC = AR_o e^{-kt} dt - QCdt \quad (5)$$

where V equals the chamber volume (m^3); C equals the chamber concentration ($\mu g m^{-3}$); A equals the area of the source (m^2); R_o is the initial emission rate ($\mu g m^{-2} h^{-1}$); k is the first-order rate constant (h^{-1}); t is time (h); and Q equals the air flow rate through the chamber ($m^3 h^{-1}$). By rearrangement of Equation 5 and assuming that $C = 0$ when $t = 0$, the solution is:

$$C = AR_o (e^{-kt} - e^{-at}) / V (a-k) \quad (6)$$

where a equals the ventilation rate (h^{-1}). Values of R_o and k were obtained by fitting Equation 6 to the concentration versus time data from the chambers.

Colombo *et al.* (1990) attempted to refine this approach by fitting a double exponential non-steady state equation to the chamber concentrations of VOC emitted from several materials. This approach was used to model emissions which, like the emissions of many VOC from carpets, had an initial period of rapid decay followed by a period of relatively slow decay.

The total masses of the compounds of interest that were emitted per square meter of carpet over 0-24 h and 0-168 h were estimated from the concentration data. For each compound, the trapezoidal areas resulting from a linear interpolation of the average concentrations at each interval were integrated and summed for the two time intervals starting with time zero when there was no emission. These sums were multiplied by Va and divided by the area of the carpet. This method introduces several types of errors. The mass emitted from time zero to the first sampling interval will be underestimated if the maximum chamber concentration was achieved prior to the collection of the first sample. The linear interpolation tends to overestimate the emitted mass for intervals over which chamber concentrations are declining since the decrease in concentration is best described by fits of exponential or power curves to the data. Finally, the mass of any compound sorbed onto the stainless-steel walls of the chamber at the end of the week-long experiment will not be included. Based on the sorption experiment with styrene, wall losses are unlikely to have a major effect on results for compounds with

equilibrium vapor pressures similar to, or less than, that of styrene. Some loss of the less volatile compounds, such as 4-PCH, to the walls of the chamber is likely. These losses, which were not quantified, should be less than what would occur in buildings.

FIELD STUDY

Study Site and Carpet

The field study was conducted at a town house in the San Francisco Bay Area that was occupied by one of the researchers. The house had three floor levels with a total floor area of about 132 m² (1,400 ft²) and a volume of about 402 m³ (14,200 ft³). The carpeted area was approximately 93 m² (1,000 ft²). The new carpet was cut-pile Nylon with a secondary backing bonded with SBR latex adhesive. The carpet was shipped by over-night freight from the manufacturer to the installer on the day that production was completed. Installation of the carpet began on the following day, a Friday. The existing wall-to-wall carpet and pad were removed, and the new carpet was placed over a virgin polyurethane pad using tack strips to secure it. The installation was completed on the following Monday.

Pieces of carpet left over from the installation were collected at the site immediately following the installation. The pieces were packaged in two layers of new polyethylene bags. The bagged pieces were kept at room temperature in an office prior to their use in an environmental chamber experiment.

Experimental Protocol

Samples for the analysis of individual VOC were collected in the house prior to installation of the new carpet, immediately after installation, and with time after installation over a period of seven weeks. There were a total of nine sample collection times over this period which started in October and ended in December. The sampling method was similar to that described above for the laboratory experiments. However, small peristaltic pumps were used to collect time-integrated samples over either 12 or 24 h. The sampling air flow rate was 5 cm³ min⁻¹. Duplicate samples were simultaneously collected on the middle level of the house which contained the main living spaces. These samples were analyzed for VOC using the methods described above

for the laboratory screening measurements in which the MSD was operated in the scan mode. The samples were quantified for styrene and 4-PCH, two compounds characteristically emitted by carpets with SBR latex adhesive.

Ventilation rates in the house were determined in conjunction with the collection of samples for VOC using a tracer-gas technique. Known amounts of sulfur hexafluoride (SF₆) were continuously injected into the lower and upper levels of the house with small peristaltic pumps. These pumps drew pure SF₆ from gas-sampling bags and released it in front of fans to produce a concentration in the house of about 60 ppbv, or less. Injection of the tracer gas began at least several hours prior to the collection of the samples for VOC. Samples of air for analysis of SF₆ were collected over the same time periods and at the same locations as the samples for VOC by drawing air into gas-sampling bags with peristaltic pumps. The concentrations of SF₆ in these samples were measured in the laboratory by a GC equipped with an electron-capture detector.

Chamber Experiment

The emission rates of VOC from the carpet pieces collected at the house were measured in the environmental chamber using procedures nearly identical to those described above for the laboratory experiments. This was the first chamber experiment for the entire study and was conducted for the primary purpose of evaluating the protocols. Almost five months had elapsed between the initiation of the field study and this experiment as considerable time was required to set up the chamber and conduct the preliminary chamber measurements. Only the chamber concentrations of styrene and 4-PCH were quantified.

Data Analysis

The average ventilation rates in the house over the sampling intervals were calculated from the SF₆ concentrations using Equation 4. The house was treated as a single volume and perfect mixing of air was assumed. Average source strengths of styrene and 4-PCH in the house over the sampling intervals were also calculated with Equation 4 using the computed ventilation rates and the measured concentrations. The concentration of styrene measured prior to the installation of the carpet was used as the background concentration in the computation. No 4-PCH was detected prior to the

installation. Specific emission rates were calculated by dividing the source strengths by the area of the carpet (93 m²).

Data analysis for the chamber experiment was the same as described above for the laboratory study.

RESULTS

QUALITATIVE ANALYSES

The identifications of the individual VOC emitted by each of the carpets are shown in Tables 5-8. These identifications were determined from the GC-MS scan analyses of samples collected from the Tedlar storage bags, from the small-volume chambers and from the environmental chamber during the first few hours of each experiment. An identification of a compound was considered to be "confirmed" if its spectrum and retention time matched those of an authentic standard analyzed under identical conditions. An identification was considered to be "probable" if the unknown compound had a spectrum that closely matched a probable hit in the EPA/NIH Mass Spectral Data Base (typically, a match quality of at least 90 percent) and a retention time that was realistic with respect to its volatility. Some compounds, such as the branched-alkane hydrocarbons which have numerous isomers, were identified only to the class level. In many cases, these class identifications were assigned a "probable" confidence level because of the distinctiveness of their spectra. Identifications which were less certain were considered to only be "tentative." In an attempt to resolve the identities of these compounds, other references such as the The Eight-Peak Index (Mass Spectrometry Data Centre, 1983) and McLafferty (1980) were consulted. Some unknowns were impossible to identify.

A chromatogram of a sample often contained nearly a hundred, or more, discernable peaks. The areas of some peaks clearly dominated the sample, while many of the individual peak areas were insignificant relative to the total-ion-current area. The concentrations of the individual compounds represented by the peaks were semi-quantitatively estimated to provide a basis for the elimination of insignificant compounds and the categorization of the more abundant compounds. First, the masses of the individual compounds were estimated by comparing their peak areas to the peak area of the internal standard that had been added to the sample. It was assumed that the total-ion-current responses of all compounds, including the internal standard, were similar and linear with mass. Concentrations were then estimated from the sample volume. The more abundant compounds were grouped into several approximate concentration ranges as indicated in Tables 5-8. Higher concentrations were used to delineate categories for the static headspace measurements than for the chamber measurements. Compounds

with very low concentrations were judged to be relatively insignificant and were not included in the tables. Dominant compounds with distinctly high concentrations have been indicated.

The identifications of about 40 of the individual VOC emitted by the four carpets were confirmed by the analysis of authentic standards. The identifications of a number of other compounds were judged to be probable. The compounds emitted by each carpet are listed in the tables in the order of their chromatographic retention time, which is an approximate indicator of compound volatility. Generally, the headspace samples contained the most volatile compounds. These compounds have high equilibrium vapor pressures at room temperature and can achieve relatively high concentrations in a static container. In addition, they are rapidly volatilized from materials under dynamic conditions in chambers.

The results for Carpet 1, the Nylon cut-pile carpet with SBR latex adhesive, are presented in Table 5. There were eight volatile compounds which were present in the headspace sample that were not detected at significant concentrations in the samples from the small-volume and environmental chambers. Of these, propane and 2-methyl-1-propene (isobutylene) were by far the most abundant. The N,N-dimethylacetamide, which was present in all samples, is a residual from the production of Tedlar as indicated in the Material Safety Data Sheet for this product (Dupont Co.). The storage bags were presumed to be the source of this compound. The other abundant compounds emitted by Carpet 1 were cyclohexanol, 1-dodecanol and the aromatic compounds, 4-ethenylcyclohexene, styrene, and 4-phenylcyclohexene (4-PCH). Additional aromatic compounds and a group of related unsaturated hydrocarbons were also emitted.

Table 6 presents the results for Carpet 4, the olefin textured-loop carpet with SBR latex adhesive. Again, there were a number of volatile compounds which were only present at significant concentrations in the headspace sample. As with Carpet 1, isobutylene was dominant. The most abundant compounds detected in the chamber samples were 2-propanone (acetone), 4-ethenylcyclohexene, styrene and 4-PCH. Other aromatic compounds and some alkane hydrocarbons were also emitted.

Carpet 3 was a Nylon textured-loop carpet with a polyvinyl chloride secondary backing. The compounds emitted by this carpet are presented in Table 7. Carpet 3 had the highest number of significant compounds emitted. The dominant compounds that

occurred in at least one of the samples were vinyl acetate, acetic acid, 2,2,4-trimethylpentane (isooctane), and 1,2-propanediol. The other abundant compounds were acetaldehyde, 2-ethyl-1-hexanol, n-undecane, *E*-caprolactum, a C₁₁ unsaturated hydrocarbon, various alkane hydrocarbons, and several unidentified oxidized compounds. Only a few aromatic compounds were emitted.

The qualitative results for Carpet 2 are presented in Table 8. This was a Nylon cut-pile carpet with a polyurethane secondary backing. The headspace sample contained six abundant volatile compounds; the dominant compound was isobutylene, and the others were acetone, 2-propanol (isopropyl alcohol), 1-propanol, trimethylsilanol, and 1,1,1-trichloroethane. The additional dominant or abundant compounds in the samples were 2,2,5-trimethylhexane, hexamethylcyclotrisiloxane, and 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT). The carpet also emitted 1-butanol, toluene, several siloxanes, isomers of dipropylene glycol methyl ether, and 1,2-dichlorobenzene.

The vacuum extraction technique was used to detect the emissions of higher-boiling VOC and semi-volatile organic compounds that might not be adequately sampled by the multisorbent air sampling method. The results of the analyses of the vacuum extracts of all of the carpets were negative in that no additional abundant compounds were detected. For the carpets with SBR latex adhesive, 4-PCH was confirmed to be the single most abundant low-volatility compound. Butylated hydroxytoluene was the most abundant low-volatility compound emitted by carpet 2.

Compounds were selected for quantitative analysis during the environmental chamber experiments based on the results of the screening measurements. Five to seven compounds were selected for each experiment (Table 9). Generally, these compounds were the dominant and abundant compounds identified in the screening samples collected from the small-volume and environmental chambers. Other compounds of interest were also included. For example, several less-abundant aromatic hydrocarbons were targeted for analysis in the experiments with carpets which had SBR latex adhesive. Screening measurements were not made for the aldehydes. Therefore, formaldehyde and acetaldehyde were targeted for analysis in all of the environmental chamber experiments.

PERFORMANCE OF THE ENVIRONMENTAL CHAMBER

The performance of the environmental chamber during the five, week-long experiments is summarized in Table 10. There were approximately 3,000 individual measurements of chamber air temperature during a week (the outputs of three thermocouples were recorded at each time interval). For the parameters of ventilation rate, relative humidity, air velocity, and atmospheric pressure, there were approximately 1,000 measurements. The mean parameter values and their standard deviations can be compared to the specified operating conditions and quality assurance objectives (Table 3). The mean ventilation rates were within 0.02 h^{-1} of the specified value of 1.0 h^{-1} and had relative standard deviations of one percent. The mean chamber temperatures were within 0.5° C of the specified value of 23° C and had standard deviations of 0.3° C , or less. Temperatures at the floor of the chamber were the same as the chamber air temperatures within the uncertainty of the measurement. The mean relative humidities were within 3.5 percent of the specified value of 50 percent and had standard deviations of 0.8 percent relative humidity, or less. The mean air velocities at the floor ranged between 6.5 and 9.0 cm sec^{-1} and had standard deviations of 1.4 cm sec^{-1} , or less. The air velocity was not measured during experiment 4, but was undoubtedly similar since the fans were operated in the same manner as in the other experiments. The mean atmospheric pressures in the chamber ranged between 743 and 747 mm Hg for the five experiments.

The mean inlet air and/or background concentrations of the target compounds for each experiment in the environmental chamber are shown in Table 11. The chamber is suspected to be the source of the low concentrations of 1,1,1-trichloroethane, hexamethylcyclotrisiloxane and styrene that were detected. The very low concentrations of 4-PCH were probably due to a small amount of surface contamination that was not removed by the cleaning and ventilation processes. Inlet air was probably the source of the other compounds. The concentration of TVOC in outdoor air at the site was not measured during the experiments, but is typically in the range of 100-200 ug carbon m^{-3} . Therefore, the filtration system was probably reducing the concentration of TVOC in the inlet air by a factor of two or more.

ANALYTICAL PERFORMANCE

The estimated limits of quantitation for the target compounds in the environmental chamber are shown in Table 12. For a compound which was detected in the inlet air and/or the chamber background, the limit of quantitation was calculated as three times the standard deviation of the mean concentration for these measurements. For the remaining compounds, the limits of quantitation were estimated from the sensitivity of the instrument to the compounds and the sample volumes. The limits of quantitation for all of the VOC analyzed by GC-MS were below 1 ppbv. The alcohols, 1-butanol and 2-ethyl-1-hexanol, had somewhat higher limits of quantitation than the other compounds because of their lower analytical sensitivities. The limits of quantitation for the aldehydes were in the range of 1-2 ppbv.

The scatter in the calibration data for a compound around the least-squares linear regression fit to these data is a major determinant of the precision with which the concentration of the compound can be measured. Using the method of Kolthoff and Elving (1978), uncertainties were estimated from the calibration curves for single measurements of the concentrations of the target compounds in each experiment (Table 13). The concentrations of the aldehydes were determined with high precision because of the high linearity of the calibration data for these compounds. The 95 percent confidence intervals for many of the VOC analyzed by GC-MS were less than 1 ppbv. However, there were exceptions. Vinyl acetate and styrene in one experiment had relatively high confidence intervals primarily because their concentrations spanned a very broad range (the values in parentheses are the range of the confidence interval from low to high concentrations). Propanediol was another compound which had a high confidence interval. It also occurred at high concentrations, and the calibration data were of relatively low quality. The other compounds for which there was a relatively large amount of scatter in the calibration data were 2,2,4-trimethylpentane, 2-ethyl-1-hexanol and BHT.

Researchers have used various methods to measure TVOC. The results that are obtained are dependent upon the methods that are used to sample and analyze the compounds. The TVOC method used in this study was relatively simple in that the compounds collected on the multisorbent samplers were directly analyzed by an FID without chromatographic separation. The method was calibrated with a mixture of C₆ - C₁₂ normal alkane hydrocarbons constituted so that each compound contributed an

equal mass of carbon. The results for TVOC were expressed as mass/volume concentrations of carbon since the detector responds to carbon.

The TVOC response for several selected compounds and one mixture of compounds was measured. To evaluate the accuracy of the method, the TVOC response for the compound(s) was compared to the actual mass of carbon added to a sampler. The results are shown in Figure 3. The method predicted the mass of carbon in styrene with a high degree of accuracy. However, it significantly under-predicted the masses of carbon by as much as 50 percent for the oxidized compounds, vinyl acetate and propanediol. The carbon masses of 4-PCH and hexamethylcyclotrisiloxane were over-predicted. The Carpet Policy Dialogue (1991) developed a method for measuring TVOC emitted by carpets which utilized a calibration mixture containing equal parts by weight of 1-hexanol, toluene, cyclohexane and n-decane. The TVOC method used here under-predicted the mass of carbon for this mixture by about ten percent probably due to the presence of the oxidized compound, 1-hexanol, in the mixture. The TVOC response of BHT was not measured; however, it is suspected that the mass of carbon in this compound is under-predicted.

CONCENTRATIONS IN THE ENVIRONMENTAL CHAMBER

VOC

The environmental chamber concentrations of the VOC analyzed by GC-MS in each of the five experiments are shown in Figures 4-8. The concentrations are presented in molar-volume concentration units (ppbv) and are plotted on a logarithmic scale so that all of the compounds emitted by a carpet could be shown in the same figure. The use of the same scale for all figures (0.1-500 ppbv) facilitates comparisons among the carpets. The VOC concentration data for an entire week-long experiment are plotted in part a of each figure. The data for the first 12 h of an experiment are plotted in part b. All of the individual measurements for duplicate and triplicate samples are plotted rather than the averages. The scatter in the points for a compound at each time interval is an indication of the precision of the analysis. For individual points, this is often less than the imprecision due to the scatter in the calibration data (Table 13). Curves were fit to the concentration data primarily as an aid to the visualization of the

data. Exponential curves were fit to the data for 1-12 h. Power curves provided better fits to the data for 24-168 h.

The chamber concentrations for experiment a with Carpet 1, the Nylon cut-pile carpet with a SBR backing, are shown in Figure 4. Initially, styrene had the highest concentration of 10 ppbv. The initial concentration of 4-PCH was about 6 ppbv. The concentrations of the three xylene isomers were combined as C₂ alkyl benzenes. Their initial concentration was 3 ppbv. The concentrations of styrene and the alkyl benzenes decayed rapidly relative to 4-PCH. After 48 h, the concentrations of the alkyl benzenes were below the limit of quantitation. Styrene approached the limit of quantitation at 144 h. The concentration of 4-PCH remained relatively constant, only declining to 4 ppbv by the end of the week.

Figure 5 shows the chamber concentrations for experiment b with Carpet 1. The carpet sample for this experiment had been stored 21 days longer than the sample for experiment a. The other procedural difference between this and the previous experiment was that the sample was removed from its storage bags inside the chamber rather than outside. Samples were collected every half hour during the first 6.5 h of this experiment in an attempt to better define the initial concentration profiles. Styrene had the highest initial concentration of about 16 ppbv. The somewhat higher concentrations of styrene throughout this experiment may have been due to the unpacking of the sample directly in the chamber. The initial concentration of 4-PCH was again about 6 ppbv. The concentrations of ethyl benzene and the three xylene isomers were combined as C₂ alkyl benzenes. Their initial concentration was 5 ppbv. An additional compound, 4-ethenylcyclohexene, was analyzed in this experiment. Its initial concentration was 6 ppbv. The concentrations of styrene, the alkyl benzenes and 4-ethenylcyclohexene decayed rapidly. The alkyl benzenes were near their limit of quantitation at 72 h. Ethenylcyclohexene was at its detection limit at 120 h. At the end of the experiment, the concentration of 4-PCH was 3 ppbv. The concentration of 4-PCH was generally 1 ppbv lower throughout this experiment than during the previous experiment. This difference is within the uncertainty due to the scatter in the calibration curves (Table 13).

The concentrations of VOC emitted by Carpet 4, the olefin textured-loop carpet with a SBR backing, are presented in Figure 6. This carpet had much higher emissions of styrene than Carpet 1. The initial styrene concentration was 180 ppbv. The

compound with the next highest initial concentration was 4-ethenylcyclohexene at 18 ppbv. The initial concentration of 4-PCH was 8 ppbv. The concentrations of the three xylene isomers and n-propylbenzene were combined as alkyl benzenes. Their initial concentration was 7 ppbv. Again, the concentrations of all compounds except 4-PCH decayed rapidly. By 72 h, the concentrations of 4-Ethenylcyclohexene and the alkyl benzenes were less than 1 ppbv. The concentration of styrene at the end of the experiment was less than 2 ppbv. The concentration of 4-PCH at this time was about 3.5 ppbv.

Figure 7 shows that concentrations of VOC emitted by Carpet 3, the Nylon textured-loop carpet with a polyvinyl chloride backing. The highest concentrations of VOC occurred during this experiment. The one-hour data for vinyl acetate are missing because the samplers were overloaded with this compound. At 3 h, the concentration of vinyl acetate was 290 ppbv. Propanediol also had a relatively high initial concentration of about 120 ppbv. The initial concentrations of 2,2,4-trimethylpentane, 2-ethyl-1-hexanol, and methyl acetate were 21, 8 and 2 ppbv, respectively. The concentration of methyl acetate decayed to below its limit of quantitation within 24 h. The other compounds were still quantifiable at the end of the experiment. At this time, the concentration of propanediol was 20 ppbv, and the concentration of vinyl acetate was 10 ppbv. The final concentrations of 2,2,4-trimethylpentane and 2-ethyl-1-hexanol were less than 2 ppbv.

Carpet 2 was the Nylon cut-pile carpet with a polyurethane backing. The chamber concentrations for the experiment with this carpet are shown in Figure 8. Butylated hydroxytoluene had the highest initial concentration of about 15 ppbv. The initial concentrations of the other compounds were all less than 10 ppbv. By 24 h or less, the concentrations of hexamethylcyclotrisiloxane, 1,1,1-trichloroethane and toluene had decayed to below their limits of quantitation. The concentration of BHT remained relatively constant at about 8-10 ppbv over much of the experiment. The concentration of 1-butanol declined from 9 to 1 ppbv over the course of the experiment. The combined concentration of the three isomers of dipropylene glycol methyl ether declined from 3 to 1 ppbv. The concentrations of 1,2-dichlorobenzene were very low. An exponential curve provided a better fit than a power curve to the 24-168 h data for dichlorobenzene.

Aldehydes

Formaldehyde and acetaldehyde concentrations were measured throughout all of the environmental chamber experiments. The formaldehyde data for these experiments are plotted together in Figure 9, and the acetaldehyde data are plotted in Figure 10. The data are plotted on arithmetic scales. Curves were fit to the concentrations of formaldehyde and acetaldehyde measured during the experiment with Carpet 3. Exponential curves were used for the 1-12 h data, and power curves were used for the 24-168 h data.

Formaldehyde was detected above the limit of quantitation of about 2 ppbv in all experiments except the one with Carpet 2. The concentrations during the experiments with Carpets 1 and 4 were low with maximum values of 3-5 ppbv. In all three of these experiments, the concentrations declined to below the limit of quantitation before the end of the week. Carpet 3 was the only carpet with significant emissions of formaldehyde. The initial concentration of formaldehyde was about 46 ppbv. The concentration decayed to 20 ppbv by 24 h. At the end of the experiment, the concentration was 6 ppbv.

Acetaldehyde was detected at concentrations slightly above the limit of quantitation of about 1 ppbv in experiment a with Carpet 1 and in experiments with Carpets 4 and 2. These concentrations declined to below the limit of quantitation within 6 h. As for formaldehyde, the experiment with Carpet 3 was the only one with elevated concentrations of acetaldehyde. The initial concentration in this experiment was 17 ppbv. At 24 h, the concentration was about 6 ppbv. By 96 h, the concentration was near the limit of quantitation.

TVOC

The environmental chamber concentrations of TVOC analyzed by FID in each of the five experiments are shown in Figures 11-15. The data are presented as mass/volume concentrations of carbon (ug C m⁻³). The concentrations are plotted on a logarithmic scale of 10-5,000 ug C m⁻³. For each experiment, the TVOC concentrations are compared to the sum of the concentrations of carbon contributed by the VOC that were individually quantified, exclusive of formaldehyde and acetaldehyde. All of the

individual measurement data are plotted. Exponential curves were fit to the data for 1-12 h. Power curves provided better fits to the data for 24-168 h.

The concentrations of TVOC for experiment a with Carpet 1 are shown in Figure 11. The initial TVOC concentration was 280 $\mu\text{g C m}^{-3}$. This compares to the initial concentration of 90 $\mu\text{g C m}^{-3}$ for the sum of the quantified VOC (QVOC). At 24 h, the concentrations of TVOC and QVOC were 100 and 45 $\mu\text{g C m}^{-3}$, respectively. The relatively large difference between these measures during the first 12-24 h of the experiment indicates that VOC which were not individually quantified made up a significant portion of the mass of carbon emitted by the carpet during this period. By the end of the experiment, the concentration of TVOC had decayed to about 30 $\mu\text{g C m}^{-3}$, and the difference between TVOC and QVOC was relatively small.

The TVOC results for experiment b with Carpet 1 that are shown in Figure 12 are in generally good agreement with the results for experiment a. The initial concentrations of TVOC and QVOC of 320 and 140 $\mu\text{g C m}^{-3}$, respectively, were somewhat higher in this experiment perhaps due to the unpacking of the sample directly in the chamber. From 24-168 h, the concentrations of TVOC were slightly lower during experiment b, while the concentrations of QVOC were nearly identical to those in experiment a.

The TVOC results for Carpet 4, which also had a SBR latex adhesive and emitted practically the same compounds as Carpet 1, are presented in Figure 13. Initially, the concentration of TVOC was about 1,500 $\mu\text{g C m}^{-3}$. Much of the sample mass was contributed by styrene. At 24 h, the concentration had decayed to 180 $\mu\text{g C m}^{-3}$. By the end of the experiment, the concentration was 40 $\mu\text{g C m}^{-3}$ which was near the final concentration for the experiments with Carpet 1. From 24-168 h, the results for TVOC and QVOC were in good agreement, with TVOC being somewhat elevated over QVOC. The good agreement between the measures indicates that the VOC which were individually quantified made up a significant portion of the mass of carbon emitted over this period.

Carpet 3 produced the highest sustained concentrations of TVOC (Figure 14). The initial concentrations of TVOC and QVOC were similar at about 880 $\mu\text{g C m}^{-3}$. At 24 h, the concentration of QVOC was 300 $\mu\text{g C m}^{-3}$, which exceeded the concentration of TVOC by about 90 $\mu\text{g C m}^{-3}$. At the end of the experiment, the concentrations for

both measures were 60 ug C m⁻³. Throughout the experiment, the concentrations of QVOC either exceeded or were very similar to the concentrations of TVOC. This result was largely due to the underestimation by the TVOC method of the masses of carbon contributed by the oxidized compounds, vinyl acetate and 1,2-propanediol (Figure 3). The difference between the measures would have been even greater if there were not other unquantified compounds present in the samples contributing to the mass of carbon.

The measured concentrations of TVOC during the experiment with Carpet 2 were low. The initial concentration was 100 ug C m⁻³. At 24 h, the concentration was 35 ug C m⁻³, and by the end of the experiment, the concentration was 15 ug C m⁻³. The concentrations of TVOC were significantly under-estimated since the concentrations of QVOC were consistently higher. This was probably due to the underestimation by the TVOC method of the mass of carbon in BHT and the other oxidized compounds that dominated the samples. In addition, there is considerable uncertainty in these TVOC values since they were somewhat below the estimated limit of quantitation during much of the experiment.

The measurements of TVOC for at least the two carpets that emitted oxidized compounds were obviously inaccurate. As a result, these measurements could not be reliably used to estimate the fractions of TVOC accounted for by the target compounds.

The fractions of the total mass-volume concentrations accounted for by the target compounds were estimated using an alternate method. For each sample collected from the chamber at approximately 24 and 168 h and analyzed by GC-MS in the scan mode, the individual peaks comprising the total-ion-current (TIC) chromatogram were integrated and summed. The summed area was normalized by the area of the internal standard in the sample, and the area of the internal standard was subtracted. Then, the summed area was adjusted to represent a 10-L sample volume. The TIC chromatograms of background chamber samples were similarly treated. For each experiment, the respective background area was subtracted from the areas of the samples collected at 24 and 168 h. The normalized and volume-adjusted peak areas of the target compounds in these samples were separately summed. The fractions of the TIC chromatographic areas accounted for by the sums of the areas of the target compounds are presented in Table 14. (Samples for GC-MS scan analysis were not collected during experiment a with Carpet 1.) These values are approximate estimates of the fractions of the total mass-

volume concentrations accounted for by the quantified compounds. However, the TIC area responses of individual compounds are expected to differ (Wallace *et al.*, 1990).

Table 14 shows that the target compounds only accounted for 0.3 of the TIC area at 24 h in experiment b with Carpet 1. The fraction at the early sampling period was higher for the experiments with the other carpets. For all experiments except the one with Carpet 1, the fractions declined by the end of the week-long sampling period. The relatively low values at the end of the experiments with carpets 3 and 4 suggest that only about 25 percent of the mass in these samples was accounted for. The high values for Carpet 2 at 24 and 168 h indicate that the target compounds accounted for most of the mass during this experiment.

EMISSIONS

The curves that were fit to the concentration data for 1-12 h and 24-168 h provide numerical measures of how fast the concentrations of the compounds decayed under the conditions of the experiments. Exponential curves in the form of Equation 2 provided a good fit to the concentration data for 1-12 h. Power curves in the form:

$$C = C_i t^{-k} \quad (7)$$

where C is the concentration in the chamber at time t (h) and C_i is the initial concentration, provided a good fit to the concentration data for 24-168 h. Values of the exponential and power-curve coefficients for the quantified compounds in all experiments are presented in Table 15. For each experiment, the compounds are listed in the order of their chromatographic retention times which is an approximate indicator of volatility. The vapor pressures of the compounds at 20° C and 760 mm Hg pressure were determined from several sources. No vapor-pressure data were found for some compounds.

It is apparent that there was a general decrease in the exponential decay coefficients for the compounds that was directly related to their volatilities or vapor pressures. With the exception of the aldehydes, the most volatile compounds decayed most rapidly over the first 12 h of an experiment. The least volatile compounds, such as 4-PCH and BHT, decayed most slowly. The relationship between the power-curve

coefficients and the volatilities of the compounds was not as strong. However, the least volatile compounds had the lowest power-curve coefficients.

The decay coefficients for the compounds emitted by the carpets with SBR latex adhesive can be compared. The exponential and power-curve decay coefficients for the alkyl benzenes, styrene and 4-PCH were generally in good agreement between experiments a and b with Carpet 1. In comparing the experiments for Carpet 1 with the experiment for Carpet 4, there was good agreement in the exponential decays for 4-ethenylcyclohexene and the alkyl benzenes. However, styrene and 4-PCH emitted by Carpet 4 decayed more rapidly over the first 12 h. The longer-term power-curve decays of the compounds were similar for both carpets.

Using Equation 4 divided by the carpet areas, quasi steady-state specific emission rates in $\text{ug m}^{-2} \text{ h}^{-1}$ were calculated for the target compounds that were quantified at 24 and 168 h after the start of the experiments (Table 16). The mean values and their 95 percent confidence intervals were calculated from the triplicate concentration measurements made at these times. The fractional reductions in the specific emission rates that occurred from 24 to 168 h were also determined. Emission rates have not been reported for measurements made prior to 24 h since the steady-state assumption tends to underestimate emission rates when the chamber concentrations are changing rapidly.

Vinyl acetate and 1,2-propanediol emitted by Carpet 3 had the highest emission rates at 24 h of 853 and 690 $\text{ug m}^{-2} \text{ h}^{-1}$, respectively. Other compounds with relatively high 24-h emission rates were styrene from Carpet 4 (260 $\text{ug m}^{-2} \text{ h}^{-1}$), BHT from Carpet 2 (214 $\text{ug m}^{-2} \text{ h}^{-1}$) and 4-PCH from Carpets 1 and 4 (64-85 $\text{ug m}^{-2} \text{ h}^{-1}$). At 168 h, all of these compounds, except styrene, still had high emission rates relative to the other compounds.

There was a general relationship between compound volatility and the observed reductions in the specific emission rates over the period of 24 to 168 h. The emission rates of the most volatile compounds decayed most rapidly. Some of the compounds were no longer present at 168 h, and the emission rates of many of the other compounds had decreased by more than half at 168 h. The exceptions were 4-PCH emitted by Carpets 1 and 4 (0.25-0.39 reduction), and BHT and the three isomers of dipropylene glycol methyl ether emitted by Carpet 2 (0.19 and 0.45 reduction, respectively).

An attempt was made to fit the non-steady state model given by Equation 6 to the concentrations of the VOC measured during the experiments in the environmental chamber. As described above, the concentrations from 1-12 h declined exponentially; however, there were an insufficient number of data points over the initial hours of the experiments to define R_0 . The concentrations over 1-168 h clearly did not fit simple exponential decays. Therefore, an attempt was made to fit a double exponential equation to the concentrations of the VOC measured over this time period. Although a double exponential decay provided a better fit to the data than a single decay, it still did not provide an accurate fit to the data over the middle portion of the experiments.

The specific mass emissions of the target compounds in mg m^{-2} of carpet are presented in Table 17. These emissions were determined for both the first 24 h and the entire 168 h of each experiment. The ratio of the mass of a compound emitted over the first 24 h to the total mass emitted is another measure of the rate at which the emissions of the compounds declined.

For Carpets 1 and 4, more than half of the total masses of 4-ethenylbenzene, the C_2 alkyl benzenes and styrene were emitted during the first 24 h, while only 0.18-0.20 of the 4-PCH was emitted during this initial period. The first-day emissions of the compounds from Carpet 3 were in the range of 0.27-0.45 of their total 168-h emissions, exclusive of methyl acetate which was completely emitted within 24 h. Hexamethylcyclotrisiloxane and 1,1,1-trichloroethane emitted by Carpet 2 also disappeared within 24 h. For the other compounds from Carpet 2, the first-day emissions accounted for 0.18-0.34 of their total emissions. The fractional reduction was the lowest for BHT, the compound with the lowest equilibrium vapor pressure.

CHAMBER COMPARISON

The operating conditions for the small-volume chambers were selected so that the ratio of the ventilation rate to the material loading (a/L) in these chambers would be nearly identical to this ratio for the experiments in the environmental chamber. The a/L ratio for the small-volume chamber was $2.4 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$, and the ratio for the environmental chamber was $2.3 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ for all experiments except the one with Carpet 3, for which the ratio was $2.9 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$.

The small-volume chambers were sampled at approximately one, three and six hours after initiation of the screening measurements. The concentrations of selected compounds that were measured in the small-volume chambers for each carpet were compared to their respective concentrations for samples collected in the environmental chamber experiments at approximately one, three and six hours (Figures 16-19).

For Carpet 1, the concentrations of 4-ethenylcyclohexene, styrene and 4-PCH that were measured during the small-volume and environmental chamber experiments with sample b are compared in Figure 16. In this case, the sample of carpet used in the small chamber was cut from the center of the large sample immediately after it was rolled out on the floor of the environmental chamber. Both the small-volume and the environmental chamber experiments were started at the same time. The environmental chamber concentrations of all three compounds were higher than their respective small chamber concentrations. The differences were large for the volatile compounds, 4-ethenylcyclohexene and styrene.

The same three compounds were compared for Carpet 4 (Figure 17). For this and the remaining carpets, the samples used in the small chambers were cut from the small pieces of carpet that were separately packaged, and the screening measurements were conducted prior to the environmental chamber experiments. As previously noted, the emissions of styrene from Carpet 4 were relatively high. There was good agreement between the concentrations of this compound measured in the two chambers, while the concentrations of 4-ethenylcyclohexene and 4-PCH were higher in the environmental chamber.

For Carpet 3, the concentrations of vinyl acetate, 2,2,4-trimethylhexane and 1-ethyl-2-hexanol were compared between the small-volume and environmental chambers (Figure 18). The results for the environmental chamber were multiplied by 1.2 to correct for the lower loading ratio that was used for this experiment. The agreement between the concentrations in the two chambers was relatively good for all three of the compounds.

The concentrations of hexamethylcyclotrisiloxane, the three isomers of dipropylene glycol methyl ether, and BHT emitted in the small-volume and environmental chambers by Carpet 2 are compared in Figure 19. The concentrations of the dipropylene glycol methyl ethers in the two chambers were in excellent agreement.

However, the concentrations of hexamethylcyclotrisiloxane in the small-volume chamber were very low relative to the concentrations in the environmental chamber. The concentrations of BHT were also lower in the small-volume chamber.

FIELD STUDY

Ventilation Rates

The ventilation rates measured in the house in conjunction with the collection of the samples for VOC are shown in Table 18. Prior to the installation of the carpet and over the first few days after installation, the large sliding glass doors on all three levels of the house were left open. This resulted in very high ventilation rates of approximately $7\text{-}10\text{ h}^{-1}$. There is considerable uncertainty in these high measurements because it is not known how well the air in the house mixed under these conditions. In the subsequent sampling intervals, the house was maintained in a more closed condition. This resulted in ventilation rates of $0.4\text{-}1.3\text{ h}^{-1}$. The lowest ventilation rates occurred near the end of the experiment when the outdoor temperature was relatively low.

Concentrations of VOC

Screening measurements that were made using the small-volume chambers showed that the carpet only emitted two major VOC, styrene and 4-PCH. Based on these results, it was decided to only quantify styrene and 4-PCH in the house. The concentrations of TVOC in the house contributed by the carpet were estimated to be low relative to background concentrations of TVOC in the house.

The concentrations of styrene and 4-PCH measured in the house are shown in Table 18. The first samples were collected on the day prior to the start of the installation of the carpet. The concentration of styrene at this time was 0.23 ppbv, while 4-PCH was not detected. Samples were subsequently collected in the house on eight days over a period of 52 days after the installation of the carpet was completed. The maximum concentrations of styrene of about 1 ppbv and of 4-PCH of about 5 ppbv occurred on the fourth and sixth days after installation when the ventilation rate was close to 1 h^{-1} . The concentration of 4-PCH was about 3 ppbv at the end of the measurement period when the ventilation rate was the lowest. The concentration of

styrene at this time was about 0.7 ppbv. This compares to a median indoor air concentration of styrene of 0.3 ppbv reported in the national VOC data base (Shah and Singh, 1988).

Emissions

Quasi steady-state specific emission rates were calculated for styrene and 4-PCH using Equation 4 divided by the area of the carpet (93 m²). The concentration of styrene measured prior to the installation was used as the background concentration in the calculation. The background concentration of 4-PCH was assumed to be zero. The specific emission rates are plotted in Figure 20. Two days after installation, the emission rate of 4-PCH was estimated to be 320 ug m⁻² h⁻¹; however, there is considerable uncertainty in this value because of the uncertainty in the ventilation rate noted above. On the sixth day, the emission rate of 4-PCH was 150 ug m⁻² h⁻¹, and near the end of the measurement period, it had declined to about 30-60 ug m⁻² h⁻¹. The emission rate of styrene two days after installation was 28 ug m⁻² h⁻¹. On the sixth day, the emission rate of styrene was 13 ug m⁻² h⁻¹, and by the end of the measurement period, it was about 3-5 ug m⁻² h⁻¹. The emission rates of styrene after 12 days have larger uncertainties than those measured earlier because the indoor concentrations were only slightly elevated above the background concentration and the outdoor concentrations were not measured. There may also have been other sources of styrene present in the house, and it is possible that the estimated emission rates were not due solely to emissions from the carpet.

It is instructive to compare the emissions of styrene and 4-PCH in the house to the emissions of these compounds in the chamber during experiments with similar new carpets. The initial emission rate of 4-PCH in the house was several times higher than the 24-h emission rates measured in the chamber for Carpets 1 and 4 (Table 16). The emission rate of 4-PCH in the house declined by almost two thirds in a period of a week which was considerably more rapid than the decays observed in the week-long experiments with Carpets 1 and 4. As expected from the chamber results, 4-PCH continued to be emitted over a relatively long time period in the house. Near the end of the measurement period in the house, the emission rates of 4-PCH were similar to those measured in the chamber at 168 h. The emission rates of styrene in the house on the first few days of measurement were similar to the 24-h emission rates of this compound from Carpet 1. Near the end of the measurement period in the house, the emission rates

of styrene were similar to the low emission rates measured in the chamber for Carpets 1 and 4.

The concentrations of styrene and 4-PCH over the week-long environmental chamber experiment with the field-study carpet are plotted in Figure 21. This experiment was conducted almost five months after the production and installation of the carpet. During this time, the samples of the carpet were packaged and stored in two layers of polyethylene bags. It can be assumed that the emissions of styrene and 4-PCH declined over this extended storage period, particularly since a "carpet odor" was detectable at the exterior of the bags. Because of styrene's greater volatility, it is probable that the emissions of styrene declined more than the emissions of 4-PCH.

The chamber concentrations of styrene and 4-PCH can be compared to the concentrations of these compounds in experiments with Carpets 1 and 4, which were also constructed with SBR latex adhesive (Figures 4-6). The initial concentration of 4-PCH was similar to the initial concentrations in the experiments with Carpet 1 and about 3 ppbv lower than the initial concentration produced by Carpet 4. The final concentration of 4-PCH at 168 h was about 1-2 ppbv lower than the final concentrations in the other experiments. The initial concentration of styrene produced by the field-study carpet was considerably lower than the initial concentration produced by Carpet 1, which had relatively low emissions of styrene compared to Carpet 4. At the end of the experiment, the concentration of styrene was near the limit of quantitation.

The quasi steady-state specific emission rates of styrene and 4-PCH in the chamber at 24 and 168 h were calculated using Equation 4 divided by the area of the carpet (8.7 m^2). The emission rate of styrene at 24 h was $3 \text{ ug m}^{-2} \text{ h}^{-1}$. At 168 h, the styrene emission rate was less than $2 \text{ ug m}^{-2} \text{ h}^{-1}$. These rates are less than those measured near the end of the experimental period in the house probably due to the continuous loss of styrene during the extended storage period. At 24 h, the emission rate of 4-PCH was $48 \text{ ug m}^{-2} \text{ h}^{-1}$, and at 168 h it was $34 \text{ ug m}^{-2} \text{ h}^{-1}$. These rates are similar to the rates that were measured in the house from four to seven weeks after the installation of the carpet.

DISCUSSION

QUALITATIVE ANALYSES OF EMISSIONS

This study comprehensively identified the significant compounds emitted by four new carpets. The qualitative results for these carpets can be compared to results reported for other carpets.

Seifert *et al.* (1989) presented data on the dynamic headspace emissions of a Nylon carpet with a laminated fabric backing. The ten most abundant compounds were identified based on the relative areas of their chromatographic peaks. The most abundant compound was 4-PCH, and the next most abundant compound was styrene. The other compounds included C₁₁ and C₁₂ normal alkane hydrocarbons, several alkyl benzenes, 2-ethyl-1-hexanol, and two unidentified compounds. Bayer and Papanicolopoulos (1990) listed 32 compounds which they detected in the emissions from unspecified carpets. The list includes 4-PCH, styrene, alkyl benzenes and chlorinated hydrocarbons. Pleil and Whiton (1990) semi-quantitatively determined the emissions of VOC from seven new carpets. One carpet was specified as having a stiff plastic backing. The major headspace emissions from this carpet consisted of styrene, chlorinated butadiene, 4-PCH and a C₉ alkyl benzene. The major compounds emitted by five unspecified carpets included toluene, styrene, 2-ethyl-1-hexanol, and 4-PCH. In the current study, Carpets 1 and 4 with SBR latex adhesive emitted 4-PCH, styrene, and other aromatic compounds; Carpet 3 emitted 2-ethyl-1-hexanol.

Nineteen different SBR latex-backed carpets were evaluated for emissions of VOC for the Carpet and Rug Institute (Black *et al.*, 1991a). The samples were obtained directly from the manufacturing finish lines. The data were used to model exposures to individual VOC in a typical office and a house (Hetes *et al.*, 1992). The report of the modeling study presents a list of compounds that were emitted by the 19 carpets in small-scale environmental chambers. A total of 69 compounds were identified. Of these, 35 were observed in only a single carpet product. The 12 most frequently occurring compounds are listed here in Table 19. Carpets 1 and 4 with SBR latex adhesive emitted eight of these compounds plus alkane hydrocarbons in the volatility range of n-decane and n-undecane. The 2-butoxyethanol, and 1-ethyl-3-methylbenzene were not among the significant compounds emitted by these two carpets.

Davidson *et al.* (1991) measured emissions from a Nylon carpet with a polyurethane secondary backing. The primary compound emitted by this carpet was BHT. The carpet also emitted 1,2-dichlorobenzene. One carpet analyzed by Pleil and Whiton (1990) was specified as having a soft foam backing. The major compounds identified in the headspace of this carpet were trimethyl silanol, toluene, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, triethylphosphate, and BHT. All of these compounds were emitted by Carpet 2, which had a polyurethane secondary backing.

The CPSC and the National Center for Toxicological Research (NCTR) qualitatively determined the emissions of VOC from samples of 17 new carpets (Jarmer and Singh, 1990; Jarmer, 1991; Miller *et al.*, 1991). These samples were collected at various manufacturing mills during the Winter of 1989-90 and the Spring of 1990. Compounds were identified from headspace analyses and measurements made in small-volume chambers. The sample set included carpets of the same type and from the same manufacturers' mills as the four carpets included in the present study. The identifications of the corresponding carpets are shown in Table 20.

The major compounds emitted by sample 1R were styrene, 4-PCH, and an unidentified long-chain compound which may have been 1-dodecanol (1,4-dichlorobenzene was reported but is known to have been a system contaminant). Carpet 1 emitted the same compounds. The emissions from sample 4R were dominated by toluene, styrene, 4-PCH, and several unidentified aliphatic hydrocarbons (the phthalate ester is believed to have been a system contaminant). Minor compounds emitted by the sample included 4-ethenylcyclohexene, ethylbenzene, n-propylbenzene, and isopropylbenzene (cumene). All of the identified compounds were among the significant compounds emitted by Carpet 4. Samples 7C was judged to emit compounds in only minor or trace amounts. The emissions from Carpet 2 were dominated by BHT, which was not mentioned in the earlier study. There were several unresolved and unidentified mixtures of compounds emitted by sample 6C. The relative retention time and the mass spectrum of the most abundant of these is consistent with a mixture of vinyl acetate and 2,2,4-trimethylpentane which were emitted by Carpet 3. The 1,2-propanediol and the other major compounds emitted by Carpet 3 were not identified in the earlier study.

The source of the 4-ethenylcyclohexene, styrene, 4-PCH and several alkyl benzenes emitted by Carpets 1 and 4 was the SBR latex adhesive used to bond the secondary backing (Van Ert *et al.*, 1987). The 4-PCH, which is the principal ingredient of "new carpet" odor, is a unwanted manufacturing byproduct present in the SBR latex. It is formed by the Diels-Alder reaction of styrene and 1,3-butadiene. The 4-ethenylcyclohexene is formed by the reaction of two molecules of 1,3-butadiene. Styrene is present in the SBR latex as an unreacted monomer. No unreacted 1,3-butadiene was detected in the screening measurements of the carpets with SBR latex adhesive, although it was specifically looked for. Cyclohexanol is an intermediate in the production of adipic acid which is an intermediate in the manufacture of Nylon-6,6 (Sax and Lewis, 1987). Cyclohexanol is also used in textile finishing, as is 1-dodecanol (*ibid.*). Both Carpets 1 and 4 emitted a compound identified as 3-hexenedinitrile based on a good match of the unknown spectra to the spectra of this compound in the computerized mass spectral data base. However, the identity was not confirmed by the analysis of an authentic standard. The compound could be a related isomer, such as 1,4-dicyano-1-butene, which is an intermediate in the production of adiponitrile for the manufacture of Nylon-6,6 (Kirk *et al.*, 1978).

Vinyl acetate was the most abundant compound emitted by Carpet 3. The primary use of vinyl acetate is as a monomer for making polyvinyl acetate which, with vinyl acetate copolymers, are used in adhesives (*ibid.*). Vinyl chloride-vinyl acetate copolymers are widely used in flooring products. These resins are formulated to contain 3-20 percent vinyl acetate (*ibid.*). Therefore, the source of the vinyl acetate is the PVC secondary backing or, possibly, an adhesive. A major use of 1,2-propanediol is in the production of thermoset polyester resins (Kirk *et al.*, 1978). It is also used as a solvent in the production of vinyl acetate (*ibid.*) and as a dye solvent (Sax and Lewis, 1987). The 2-ethyl-1-hexanol is used as a dye solvent (Budavari, 1989). This compound is also used in the manufacture of di-2-ethylhexyl phthalate which is a primary PVC plasticizer (Kirk *et al.*, 1978). The 2,2,4-trimethylpentane is a common solvent which may have been used as a carrier for a coating or an adhesive that was applied to the carpet (Sax and Lewis, 1987). *E*-Caprolactam is used to manufacture Nylon-6 and was probably present in the fibers as a residual monomer (*ibid.*). It is possible that formaldehyde may have derived from urea-formaldehyde resin used as an adhesive. Alternately, both formaldehyde and acetaldehyde may have been present as contaminants of a polyvinyl acetal (PVA) compound (Kirk *et al.*, 1978). The PVAs are used as textile water-proofing and stain-resist coatings and in hot-melt adhesives. Acetaldehyde is also used

in the production of 2-ethyl-1-hexanol and may have been present as a contaminant of this compound (*ibid.*).

The 1,1,1-trichloroethane, 1-butanol, toluene, and glycol ethers emitted by Carpet 2 are all solvents used in various aspects of textile manufacturing (Sax and Lewis, 1987). The glycol ethers were probably components of a commercially available mixture of these compounds. Toluene also could have been present as a residual in the polyurethane secondary backing as it is used in the production of toluene diisocyanates (*ibid.*). The several siloxanes emitted by this carpet suggest that the fibers were treated with silicone fluids (Kirk *et al.*, 1978). Silicones provide oxidative stability and resistance to weathering. Hexamethylcyclotrisiloxane is not commercially produced for this purpose but could have been present as a contaminant in a less-volatile silicone product. The 1,2-dichlorobenzene is a solvent carrier used in dyes and in the production of toluene diisocyanates for polyurethane foam (Sax and Lewis, 1987). Butylated hydroxytoluene is commonly added to plastics and other materials as an antioxidant (*ibid.*).

QUANTITATIVE ANALYSES OF EMISSIONS

Some data on the emission rates of individual VOC from carpets are available for comparison with the results of this study. Black (1990) presented a figure showing the emission rate of 4-PCH from a "typical SBR latex carpet" over a period of six days. The measurements were made in a 50-L chamber operated at 25° C and a ventilation rate of 1 h⁻¹. The initial emission rate of 4-PCH was about 50 ug m⁻² h⁻¹. By 24 h, the rate had declined to about 22 ug m⁻² h⁻¹, and by 144 h it was 12 ug m⁻² h⁻¹.

As noted above, 19 different SBR latex-backed carpets were evaluated for emissions of VOC for the Carpet and Rug Institute (Black *et al.*, 1991a). Measurements of emission rates of individual compounds and TVOC were made over a period of six days in 50-L chambers operated at 25° C, 50 percent relative humidity, a ventilation rate of 1 h⁻¹, and a loading ratio of 0.41 m² m⁻³. The data on the emission rates of 13 compounds from these carpets are presented by Hetes *et al.* (1992). The average and maximum emission rates at 24 and 140 h of 4-ethenylcyclohexene, combined C₂ and C₃ alkyl benzenes, styrene and 4-PCH are reproduced in Table 21. The fractional reductions in the emission rates over this period are also shown. These data can be

compared to the data presented in Table 16. The emission rates at 24 h of ethenylcyclohexene from Carpets 1 and 4 were in the range between the average and maximum values from the small-scale chamber study. However, small amounts of this compound were still being emitted at 168 h in the large-scale environmental chamber. The 24-h emission rate of styrene from Carpet 4 was higher than the maximum value from the small-scale chamber study while the fractional reductions in the emission rates of styrene over the measurement periods were approximately equal for both studies. The 24-h emission rates of 4-PCH from Carpets 1 and 4 were similar to the average value for the other study. However, the fractional reductions in the emission rate of 4-PCH over 24-168 h for Carpets 1 and 4 were in the range of 0.25-0.39 which was considerably less than the average reduction of 0.62 over 24-140 h for the small-scale chamber study. The relatively small reductions in the emission rate of 4-PCH observed in the current study suggest that detectable amounts of 4-PCH would continue to be emitted from carpets over a relatively long period of time. The prolonged emissions of 4-PCH were demonstrated by the field study.

In general, the emissions of TVOC from carpets are relatively low compared to the emissions of TVOC from many other products and materials that are commonly used indoors. Davidson *et al.* (1991) compared the emission rate of TVOC from a carpet with the emission rate of TVOC from the adhesive used to bond the carpet to the floor. At 24 h, the emission rate from the adhesive alone was up to two orders of magnitude higher than the emission rate from the carpet. Black *et al.* (1991b) compared the emission rates of TVOC from carpets alone with the emission rates of TVOC from carpet systems in which adhesives were used. The emission rates from the carpet systems at 24 h were up to three order of magnitudes higher than the emission rates from only the carpets.

The measurement of TVOC is useful as a tool to compare mass emissions of similar products, such as SBR latex-backed carpet. However, TVOC is probably not adequate as a standard to protect health. In order to evaluate the potential for acute health and comfort problems resulting from exposure to emissions from carpets, it is necessary instead to measure the emissions of individual VOC since there are large differences among compounds with respect to their potencies. For example, Alarie (1981) showed that there was up to five orders of magnitude difference in the irritant effects of common VOC as determined by a mouse bioassay which measures the reduction in respiratory rate in response to short-term exposures to irritants. Of the

compounds reported by Alarie, the toluene diisocyanates were the most irritating and acetone was the least irritating. The threshold limit values (TLVs) for industrial exposures to common VOC, many of which are based on irritancy, also vary widely (ACGIH, 1991).

Odor is another parameter that undoubtedly influences people's response to and acceptance of, products and materials that are used indoors. Like irritancy, odor cannot be adequately addressed by the measurement of TVOC. Odor thresholds for VOC vary over many orders of magnitude depending upon the compound. The annoyance potentials of odors also vary greatly among individual VOC.

This study measured the emissions of relatively abundant individual VOC from four new carpets; but, many of the compounds selected for analysis had low emissions resulting in chamber concentrations over part of the week-long period that were near, or below, 1 ppbv. Such low concentrations would not be expected to be of significance with respect to acute health and comfort effects, with the possible exception of strongly irritating or toxic compounds, such as the toluene diisocyanates. There were a few compounds, however, that either produced relatively high chamber concentrations or had relatively high mass emissions over the week-long experiment. It is these dominant compounds which should be examined with respect to their potential to produce health and comfort effects.

Only three compounds produced initial chamber concentrations in excess of 100 ppbv. These were styrene emitted by Carpet 4 and vinyl acetate and 1,2-propanediol emitted by Carpet 3. The mass emissions of the compounds over the week-long experiments are compared in Table 17. The only compound released by Carpet 1 which had relatively high total emissions was 4-PCH. The average total emissions of 4-PCH for the two experiments with this carpet were 11 mg m⁻². The total emissions of 4-PCH from Carpet 4 were the same, while the total emissions of styrene were higher at 26 mg m⁻². Five compounds released by Carpet 3 had total emissions in excess of 5 mg m⁻². These compounds were formaldehyde, vinyl acetate, 2,2,4-trimethylpentane, 1,2-propanediol and 2-ethyl-1-hexanol. The emissions of vinyl acetate and 1,2-propanediol were dominant at 85 and 72 mg m⁻², respectively. The only compound released by Carpet 2 with relatively high total emissions was BHT at 28 mg m⁻².

Four of the eight dominant compounds identified above have TLVs for industrial exposures (ACGIH, 1991). These TLVs are: 2,2,4-trimethylpentane as octane, 300 ppmv; styrene, 50 ppmv; vinyl acetate, 10 ppmv; and formaldehyde, 1 ppmv. The TLV for cresols, which are related to BHT, is 5 ppmv.

Alarie (1981) showed that a mouse respiratory-rate bioassay could be used to make reasonable predictions of effects in humans over a wide range of concentrations and durations of exposures. He multiplied the concentrations that produced a 50 percent reduction in respiratory rate (RD₅₀) by 0.03 (the midpoint on a logarithmic scale between 0.01 and 0.1 RD₅₀) to put them on approximately the same scale as the corresponding TLVs. This mouse bioassay is an ASTM standard method (ASTM, 1984).

Irritancy has been measured by the mouse bioassay for three of the dominant compounds. Octane is a relatively non-irritating compound. Its irritancy level was estimated to be approximately 600 ppmv by the mouse test (Kristiansen and Nielsen, 1988). This compares to the irritancy level of acetone of 2,320 ppmv (*ibid.*). Styrene is a moderately irritating compound with a 0.03 RD₅₀ value of 29 ppmv (*ibid.*). Formaldehyde is more than two orders of magnitude more irritating than styrene with a 0.03 RD₅₀ value of 90 ppbv (Alarie, 1981). Data have not been reported for the five other dominant compounds; however, data are available for some related compounds. For example, allyl acetate (2-propenyl acetate), which is similar to vinyl acetate, was found to be highly irritating as were other allyl compounds (Nielsen *et al.*, 1984). The 0.03 RD₅₀ value for this compound was 90 ppbv. Nielsen and Alarie (1982) found that the sensory irritation of the alkyl benzenes increased with chain length and that their potency could be predicted from their equilibrium vapor pressures. The 0.03 RD₅₀ value for a C₆ alkyl benzene was about 4 ppmv. Since both 4-PCH and BHT are aromatic compounds with relatively low equilibrium vapor pressures, they would be predicted to be relatively potent irritants.

It is of interest to compare the maximum concentrations of the dominant compounds that were measured in the environmental chamber to their corresponding TLV or mouse irritancy values (Table 22). The maximum concentration of formaldehyde of 46 ppbv that occurred during the experiment with Carpet 3 is five percent of the TLV and one-half of the mouse irritancy value. The maximum concentration of vinyl acetate of 290 ppbv during the same experiment is three percent of the TLV. The initial concentration of styrene in the experiment with Carpet 4 was

180 ppbv. This is less than one percent of the TLV and the mouse irritancy values. The maximum concentration of 2,2,4-trimethylpentane of 23 ppbv that occurred during the experiment with Carpet 3 is far below the TLV and mouse irritancy values for octane.

Of these compounds, most is known about the effects of formaldehyde. Formaldehyde is a strong human irritant (Gupta *et al.*, 1982). A recent epidemiology study reported the irritant effects associated with formaldehyde exposures in mobile homes (Liu *et al.*, 1991). Formaldehyde concentrations were measured in a random sample of over 500 mobile homes. Irritant effects, in particular burning/tearing eyes, were found to be associated with formaldehyde exposure after controlling for personal variables. Significant responses were found at exposure levels as low as 7 ppm-hour. This translates into an exposure to a weekly average concentration of 70 ppbv for a person who spends 60 percent of his or her time at home. The maximum concentration of formaldehyde measured during the experiment with Carpet 3 approached this value. However, the concentration over 24-168 h during that experiment was 3.5-10 times lower.

The dermal sensitization potential and inhalation toxicology of 4-PCH has been investigated (Nitschke *et al.*, 1991). Under the conditions of the study, application of 4-PCH to the skin of guinea pigs did not produce delayed contact hypersensitivity. Also, inhalation of concentrations of 4-PCH up to 50 ppmv by rats produced no exposure-related hematologic or histopathologic effects. From these results, it was concluded that the low concentrations of 4-PCH that are found in homes and offices have no toxicologic significance. It is important, however, to note that these tests are not sensitive. It is possible that irritant and respiratory effects may occur at lower concentrations without observable histopathologic effects. The potency of 4-PCH with respect to irritant and respiratory effects could be measured using the more sensitive mouse respiratory-rate bioassay discussed above. This would put 4-PCH on a common scale with the large number of compounds that have been measured by this method.

Amoore and Hautala (1983) reviewed the literature on the odor thresholds of over 200 industrial chemicals. They tabulated the geometric mean of the values reported for each of the compounds. Odor thresholds for four of the eight dominant compounds were given. These were: 2,2,4-trimethylpentane as octane, 48 ppmv; formaldehyde, 0.83 ppmv; vinyl acetate, 0.50 ppmv; and styrene, 0.32 ppmv. The standard deviations

for these thresholds indicate that 68 percent of the people tested, on average, will have a personal threshold that lies within the range of one-fourth of the mean, to four times the mean threshold for the population (*ibid.*). Ruth (1986), in another review article, listed the odor thresholds for 1,2-propanediol as 60-90 ppmv and for 2-ethyl-1-hexanol as 0.08-0.14 ppmv. Van Ert *et al.* (1987) stated that the odor threshold for 4-PCH, the source of "new carpet" odor, is probably below 0.5 ppbv.

The concentrations of the compounds in the chamber experiments can be compared to these values (Table 18). A relatively low odor threshold for 4-PCH is supported by the observation of a distinct "new carpet" odor at the end of the week long experiments with Carpets 1 and 4 when the concentrations of 4-PCH were 3-4 ppbv. Among the other compounds, only styrene and vinyl acetate at the beginning of experiments with Carpets 3 and 4 had concentrations that were near their odor thresholds and would have been detected by some people.

To predict the concentrations of the compounds emitted by carpets over extended periods in buildings, it is necessary to apply models to the experimental emissions data. An attempt was made to fit single and double exponential decay equations to the concentration data over 1-168 h. The double exponential decay equation provided the better fits; however, the results were not entirely acceptable. It is likely that an arbitrary equation of another form could be found which would provide more acceptable fits. Unfortunately, this empirical approach may be of limited use for extrapolating the experimental results to buildings because it does not describe the physical phenomena that control emission rates. Carpets are multi-component materials, and the emissions process is presumably complex. For example, VOC originating in the secondary-backing adhesive may diffuse through and sorb and desorb from several layers of materials prior to their release to air. The effects of sinks on emission rates were examined by Tichenor *et al.* (1991) who experimentally determined adsorption and desorption rate constants for ethylbenzene and tetrachloroethylene on carpet fibers. In the case of emissions from a carpet, the carpet would serve as its own sink. The rate constants were put into a mass-balance equation to describe the change in the chamber concentration of a compound due to emissions of the compound from a source in the presence of a sink. A Langmuir adsorption process was assumed. It was concluded that sinks were important in controlling concentration levels but that the desorption kinetics of assemblages, such as carpets, were complex and appeared to be governed by non-Langmuir processes.

The complexity of the emissions of VOC from carpets was demonstrated by this study. Figures 4-8 show that the concentrations of the compounds decayed exponentially over the first 1-12 h. The exponential decay constants were generally related to compound volatility which suggests that the emissions during the first hours of an experiment may be largely the result of evaporation from surfaces. However, chamber concentrations from 24-168 h generally did not fit simple exponential decays. This suggests that factors other than evaporation, such as diffusion within the materials and repeated sorption and desorption from surfaces, were influencing the emission rates of VOC over the longer period. Dichlorobenzene was the only compound that decayed exponentially over 24-168 h.

COMPARISONS OF EMISSIONS IN DIFFERENT ENVIRONMENTS

When Equation 4 is divided by the area of the carpet, A in m^2 , to obtain the quasi steady-state specific emission rate, the units of V_a/A are $m^3 m^{-2} h^{-1}$. This is equivalent to the a/L ratio which can be substituted for V_a/A . Therefore, at constant emission rate, the chamber air concentrations of a compound should approach an identical level for experiments conducted at the same a/L ratio provided that all of the other factors which affect the emission rate are also the same. However, these factors often differ. As examples, small samples may not be representative of larger materials because of material inhomogeneity or differences in handling; air velocities at the surfaces of materials which affect the mass transfer coefficient may be different between small and large chambers; and surface area to volume ratios which may determine the magnitude of sorptive wall losses are higher for a small chamber. There is the added complicating factor that the emission rates of many VOC from carpets decay rapidly during the first hours of an experiment. Therefore, the rate at which the VOC concentrations change with time may vary significantly for chambers operated at different ventilation rates.

The experiments in the two chambers were conducted at approximately the same a/L ratio; but, other important parameters were different. The measurements in the small-volume chamber were made closer to steady-state conditions since the ventilation rate was a factor of six higher. In the environmental chamber, the air velocity above the carpet was maintained at $5-10 \text{ cm sec}^{-1}$, while the velocity in the small-volume

chamber was estimated to be significantly lower even at the higher ventilation rate. Additionally, the exposed interior surface area of the chamber per unit area of carpet sample was about ten times greater for the small-volume chamber. The difference in the relative humidity between the two chambers would be expected to have, at most, a minor impact on the emission rates of the compounds selected for comparison.

Although the comparison of emissions of VOC in the small-volume and environmental chambers was not rigorous for the reasons cited above, the differences that were observed clearly demonstrated that experimental parameters can have a dramatic impact on measured emission rates.

For Carpet 1, the concentrations of 4-ethenylcyclohexene and styrene in the environmental chamber were much higher than their respective concentrations in the small-volume chamber even though the small sample was obtained from the large piece of carpet and the experiments were run simultaneously. Other screening measurements, not reported here, corroborated this result. It is suspected that the difference was, at least in part, due to the extra handling of the small sample. It was cut from the large piece, trimmed, and fit into a holder before being inserted into the chamber. This handling could have resulted in considerable ventilation of the sample since the cut-pile fibers were relatively long and loose. In the experiment with Carpet 4, which emitted the same compounds, the concentrations of 4-ethenylcyclohexene in both chambers were in much better agreement, and the concentrations of styrene were in excellent agreement. This was a tightly-woven loop carpet, and it is possible that there was less loss of these moderately volatile compounds while handling the small sample. In addition, the emissions of styrene were an order of magnitude higher than for Carpet 1 so a small absolute loss of this compound would have a minor relative effect. For both carpets, the environmental chamber concentrations of 4-PCH were higher than the small-volume chamber concentrations by a factor of two to three. This compound has a low equilibrium vapor pressure at room conditions and is readily sorbed onto surfaces. Greater losses could have occurred in the small-volume chamber because of its higher surface-to-volume ratio.

The comparison of the small-volume and environmental chamber concentrations of the three compounds selected for Carpet 2 demonstrated the combined effect of compound volatility and experimental parameters on emissions. The concentrations of hexamethylcyclotrisiloxane, the most volatile of the compounds, were considerably lower

in the small-volume chamber perhaps due to losses during the handling of the small sample of this cut-pile carpet. The concentrations of BHT, the least volatile compound, were about a factor of two lower in the small-volume chamber possibly reflecting higher losses to the walls. The concentrations of the dipropylene glycol methyl ethers, which have relatively low volatility, were in good agreement between the two chambers.

Surprisingly, the concentrations of the three compounds selected for Carpet 3 were in good agreement between the small-volume and environmental chambers even though their volatilities differed considerably. The good agreement for vinyl acetate, the most volatile of the compounds, may possibly be explained, at least in part, by its high emission rate since a volatilization loss due to the handling of the small sample of this loop carpet might be apparent as only a minor relative loss.

The environmental chamber experiments with Carpets 1 and 4 and the field-study carpet produced emission rates of 4-PCH that were very similar to those measured in the field-study house from three to seven weeks after the installation of the carpet. However, the initial emission rate of 4-PCH in the house was considerably higher and even exceeded the maximum rate measured for 19 carpets in small-scale chambers.

REFERENCES

ACGIH (1991) *Threshold Limit Values and Biological Exposure Indices for 1990-1991*. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

Alarie, Y. (1981) Dose-response analysis in animal studies: Prediction of human responses. *Environmental Health Perspectives* 42: 9-13.

Amoore, J.E. and Hautala, E. (1983) Odor as an aid to Chemical safety: Odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. *J. Applied Toxicology* 3: 272-290.

ASTM (1984) Standard Method for Estimating Sensory Irritation of Airborne Chemicals, E 981. American Society for Testing and Materials, Philadelphia, PA.

ASTM (1990) Standard Guide for Small-Scale Chamber Measurements of Organic Emissions, D 5116. American Society for Testing and Materials, Philadelphia, PA.

Bayer, C.W. and Papanicopoulos, C.D. (1990) Exposure assessments to volatile organic compound emissions from textile products. *Indoor Air '90, Proceedings of the 5th International Conference on Indoor Air Quality and Climate*, Toronto, Canada, July 29 - Aug. 3, Vol. 3, pp 725-730.

Black, M. (1990) Environmental chamber technology for the study of volatile organic compound emissions from manufactured products. *Indoor Air '90, Proceedings of the 5th International Conference on Indoor Air Quality and Climate*, Toronto, Canada, July 29 - Aug. 3, Vol. 3, pp 713-718.

Black, M.S., Pearson, W.J. and Work, L.M. (1991a) Volatile organic compound emissions from carpet and associated products, Appendix R, Carpet Policy Dialogue Compendium Report. R.W. Leukrothe, Jr., Ed., Office of Toxic Substances, U.S. EPA, Washington, D.C., Sept. 27.

Black, M.S., Pearson, W.J. and Work, L.M. (1991b) A methodology for determining VOC emissions from new SBR latex-backed carpet, adhesives, cushions, and installed systems and predicting their impact on indoor air quality. *Proceedings IAQ '91, Healthy Buildings*, Washington, D.C., Sept. 4-8, pp 267-272. American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA.

Budavari, S. Ed. (1989) *The Merck Index, Eleventh Edition*. Merck & Co., Inc., Rathway, N.J.

Carpet Policy Dialogue (1991) Carpet Policy Dialogue Compendium Report. R.W. Leukrothe, Jr., Ed., Office of Toxic Substances, U.S. EPA, Washington, D.C., Sept. 27.

Colombo, A., De Bortoli, M., Pecchio, E., Schauenburg, H., Schlitt, H. and Vissers, H. (1990) Chamber testing of organic emission from building and furnishing materials. *The Science of the Total Environment* 91: 237-249.

Davidson, J.L., Black, M.S., Pearson, W.J., Work, L.M. and Miller, D.P. (1991) Carpet installation during renovation and its impact on indoor VOC concentrations. *Proceedings IAQ '91, Healthy Buildings*, Washington, D.C., Sept. 4-8, pp 299-303. American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA.

Federal Register, Vol. 55, No. 79, April 24, 1990, p 17404.

Fung, K. and Grosjean, D. (1981) Determination of nanogram amounts of carbonyls as 2,4-dinitrophenylhydrazones by high-performance liquid chromatography. *Anal. Chem.* 53: 168-171.

Gupta, K.C., Ulsamer, A.G. and Pruess, P.W. (1982) Formaldehyde in indoor air: Sources and toxicity. *Environment International* 8: 349-358.

Heller, S.R. and Milne, G.W.A. (1978) EPA/NIH mass spectral data base, U.S. Nat. Bur. Stand., Nat Stand. Ref. Data Ser., 63, U.S. Govern. Printing Off., Washington D.C.

Hetes, R.G., Womack, D.S., Pierson, T.K. and Naugle, D.F. (1992) Evaluation of Exposures to Volatile Organics Offgassing from New Carpets, U.S. EPA Contract No. CR-815509. Report 4479-001/12-F, Research Triangle Institute, Research Triangle Park, NC.

Hodgson, A.T., Girman, J.R., Newton, A.S. and Winkes, A.W. (1983) Emissions of volatile organic compounds from architectural materials with indoor applications. Report LBL-17130, Lawrence Berkeley Laboratory, Berkeley, CA.

Hodgson, A.T. and Girman, J.R. (1989) Application of a multisorbent sampling technique for investigations of volatile organic compounds in buildings. *Design and Protocol for Monitoring Indoor Air Quality, ASTM STP 1002*, N.L. Nagda and J.P. Harper, Eds., American Society for Testing and Materials, Philadelphia, PA, pp 244-256.

Jarmer, M.A. (1991) U.S. CPSC Health Sciences Laboratory Testing Report. Results of the Qualitative Analysis of Volatile Organic Compounds in Eight Commercial Carpet Samples. U.S. Consumer Product Safety Commission, Washington, D.C.

Jarmer, M.A. and Singh, H. (1990) U.S. CPSC Health Sciences Laboratory Testing Report. Qualitative Analysis of VOCs in Residential Carpet Samples. U.S. Consumer Product Safety Commission, Washington, D.C.

Kirk, R.E., Othmer, D.F., Grayson, M. and Ecroth, D., Eds. (1978) *Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition*. John Wiley & Sons, Inc., New York, NY.

Kolthoff, I.M. and Elving, P.J., Eds. (1978) *Treatise on Analytical Chemistry, Part 1, Theory and Practice, Second Edition*. John Wiley & Sons, Inc., New York, NY.

Kovanen, K., Seppänen, O., Sirén, K. and Majanen, A. (1987) Turbulent air flow measurements in ventilated spaces. *Indoor Air '87, Proceedings of the 4th International Conference on Indoor Air Quality and Climate*, Berlin, West Germany, Aug. 17-21, Vol. 3, pp 329-333.

Kristiansen, U. and Nielsen, G.D. (1988) Activation of the sensory irritant receptor by C7-C11 n-alkanes. *Arch. Toxicology* 61: 419-425.

Kuwata, K., Uebori, M. and Yamasaki, Y. (1983) Determination of aliphatic and aromatic aldehydes in polluted airs as their 2,4-dinitrophenylhydrazones by high performance liquid chromatography. *J. Chromatographic Science* 17: 264-268.

Liu, K., Huang, F. Hayward, S.B., Weslowski, J. and Sexton, K. (1991) Irritant effects of formaldehyde exposure in mobile homes. *Environmental Health Perspectives* 94: 91-94.

Mass Spectrometry Data Centre (1983) *Eight Peak Index of Mass Spectra, Third Edition*. The Royal Society of Chemistry, Nottingham, UK.

Miller, D.W., Heinze, T. and Beland, F.A., (1991) Qualitative Evaluation of Volatile Organic Compounds from Commercial and Residential Carpets. National Center for Toxicological Research, Jefferson, AR. Report (CPSC-IAG-89-2036 & CPSC-IAG-90-1212) prepared for the U.S. Consumer Product Safety Commission, Washington, D.C.

McLafferty, F.W. (1980) *Interpretation of Mass Spectra, Third Edition*. University Science Books, Mill Valley, CA.

Nielsen, G.D. and Alarie, Y. (1982) Sensory irritation, pulmonary irritation, and respiratory stimulation by airborne benzene and alkylbenzenes: Prediction of safe industrial exposure levels and correlation with their thermodynamic properties. *Toxicology and Applied Pharmacology* 65: 459-477.

Nielsen, G.D., Bakbo, J.C. and Holst, E. (1984) Sensory irritation and pulmonary irritation by airborne allyl acetate, allyl alcohol, and allyl ether compared to acrolein. *Acta Pharmacol. et Toxicol.* 54: 292-298.

Nitschke, K.D., Mizell, M.J., Beekman, M.J. and Lomax, L.G. (1991) Dermal sensitization potential and inhalation toxicological evaluation of 4-phenylcyclohexene. *Am. Ind. Hyg. Assoc. J.* 52: 192-197.

Pleil, J.D. and Whiton, R.S. (1990) Determination of organic emissions from new carpeting. *Appl. Occup. Environ. Hyg.* 5: 693-699.

Riggin, R.M. (1984) Compendium of methods for the determination of toxic organic compounds in ambient air, U.S. EPA report EPA-600/4-84-041, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

Ruth, J.H. (1986) Odor thresholds and irritation levels of several chemical substances: A review. *Am. Ind. Hyg. Assoc. J.* 47: A142-A151.

Sax, N.I. and Lewis, R.J., Sr., Eds. (1987) *Hawley's Condensed Chemical Dictionary*. Van Nostrand Reinhold Co. Inc., New York, NY.

Schachter, L. (1990) Carpet related health complaints, Report, U.S. Consumer Product Safety Commission, Washington D.C., July.

Schröder, E. (1990) Textile floor coverings and indoor air quality. *Indoor Air '90, Proceedings of the 5th International Conference on Indoor Air Quality and Climate*, Toronto, Canada, July 29 - Aug. 3, Vol. 3, pp 719-723.

Seifert, B., Ullrich, D. and Nagel, R. (1989) Volatile organic compounds from carpeting. *Man and his Ecosystem, Proceedings of the 8th World Clean Air Congress*, L.J. Brasser and W.C. Mulder, Eds., The Hague, Netherlands, Sept. 11-15, Vol. 1, pp 253-258.

Shah, J.J and Singh, H.B. (1988) Distribution of volatile organic chemicals in outdoor and indoor air, a national VOCs data base. *Environ. Sci. Technol.* 22: 1381-1388.

Tichenor, B.A. and Guo, Z. (1991) The effect of ventilation on emission rates of wood finishing materials. *Environment International* 17: 317-323.

Tichenor, B.A., Guo, Z., Dunn, J.E., Sparks, L.E. and Mason, M.A. (1991) The interaction of vapour phase organic compounds with indoor sinks. *Indoor Air* 1: 23-35.

Van Ert, M.D., Clayton, J.W., Crabb, C.L. and Walsh, D.W. (1987) Identification and characterization of 4-phenylcyclohexene - an emission product from new carpeting, U.S. EPA-OTS report, January.

Wallace, L., Pellizzari, E. and Wendel, C. (1990) Total organic concentrations in 2,500 personal, indoor, and outdoor air samples collected in the U.S. EPA TEAM studies. *Indoor Air '90, Proceedings of the 5th International Conference on Indoor Air Quality and Climate*, Toronto, Canada, July 29 - Aug. 3, Vol. 2, pp 639-644.

Table 1. Descriptions of the four carpets sampled by the CPSC.

PARAMETER	Carpet			
	1	2	3	4
Construction	Cut pile	Cut pile	Textured loop	Textured loop
Fiber type	100% Nylon	100% Nylon	100% Nylon-6	75% Olefin 25% Nylon
Pile height, mm	14	6	5	5
Dye method	Piece dyed	Beck dyed	Solution dyed	Solution dyed
Fiber treatments	Static control	NS*	Scotchguard, antimicrobial	NS
Primary backing	Polypropylene	Polypropylene	Polypropylene	Polypropylene
Secondary backing	Polypropylene	Polyurethane	Polyvinyl chloride	Polypropylene
Backing adhesive	SBR latex	NS	NS	SBR latex
Total weight, kg m ⁻²	3.0	2.6	5.5	2.0
Form	Roll	Roll	Tiles, 46 x 46 cm	Roll
Installation	Over pad	Over pad	Glue down	Over pad

*NS = Not specified by manufacturer.

Table 2. Collection dates and storage times for the carpet samples. Experiment numbers correspond to carpet numbers in Table 1.

EXPERIMENT	Sample Collection Date	Experiment Start Date	Storage Time Days
1a	Apr 16	Apr 30	14
1b	Apr 16	May 21	35
2	Aug 27	Sep 11	15
3	Jun 18	Jul 10	22
4	Jul 23	Aug 5	13

Table 3. Conditions specified for the operation of the small-volume chambers and the environmental chamber.

PARAMETER	Chamber Type	
	Small-volume	Environmental
Volume, m ³	3.78 x 10 ⁻³	20.0
Ventilation rate, h ⁻¹	6.3	1.0 ± 0.1*
Temperature, °C	Room (20-25)	23 ± 1
Relative humidity, %	Dry N ₂	50 ± 5
Loading ratio, m ² m ⁻³	2.65	0.44
Air velocity, cm sec ⁻¹	<1	5-10

*Uncertainties are quality-assurance objectives shown as ± one standard deviation.

Table 4. Specifications and operating conditions for the analytical system used for the analysis of individual VOC.

COMPONENT	Specifications and Operating Conditions
Column	J&W DB-1701 30 m x 0.25 mm I.D. x 1.0 μ m film
Carrier gas	Helium @ \sim 1 $\text{cm}^3 \text{ sec}^{-1}$
Concentrator	UNACON 810A Init. carrier flow time: 1 min Tube chamber heat: 4 min @ 275°C Second. carrier flow time: 5 min Trap 1 heat: 20 sec @ 275°C Trap to trap transfer: 2 min Trap 2 heat: 20 sec @ 275°C
GC Oven	HP 5790A 1°C (18 min) - 100°C @ 12°C min^{-1} 100 - 125°C @ 4°C min^{-1} 125 - 225°C @ 12°C min^{-1} 225°C (2 min)
MSD	HP 5970B On at 14.5 min SCAN mode: <i>m/z</i> 33-250 SIM mode: 3-4 cycles sec^{-1}

Table 5. VOC emitted by Carpet I as determined by measurements of headspace emissions and emissions in small-volume chambers and the environmental chamber.

COMPOUND	RT (min)	Head- space	Small Chmbr.	Environ. Chmbr.	Match Quality
n-Propane	14.6	+++			Probable
2-Methyl-1-propene	15.3	+++			Probable
2-Propanone (Acetone)	18.3	+			Confirmed
Dichloromethane	20.0	+			Confirmed
1,1,1-Trichloroethane	23.5	+			Confirmed
n-Pentanal	24.8	+			Confirmed
Toluene	26.4	+			Confirmed
C ₉ Alkane	27.4	+			Probable
4-Ethenylcyclohexene	27.6	++	+	++	Confirmed
Ethylbenzene	28.3	+	+	+	Confirmed
m-,p-Xylene	28.4	+	+	+	Confirmed
N,N-Dimethylacetamide	28.5	++	++	++	Confirmed
Cyclohexanol	28.8	++	++	++	Confirmed
Styrene	29.0	++	++	+++	Confirmed
o-Xylene	29.1	+	+		Confirmed
Phenol	31.4	+			Confirmed
Dihydro-4,4-dimethylfuranone	31.5		+		Tentative
Unsaturated HCs, C ₁₀ H ₁₈	30.4-33.0	+	+	+	Probable
3-Hexenedinitrile	34.1	+			Probable
Unsaturated HCs	33.0-37.2	+	+	+	Probable
Alkane HC	38.1	+	+		Probable
4-Phenylcyclohexene	39.3	++	+++	+++	Confirmed
1-Dodecanol	40.8	+		++	Confirmed

Headspace: + = Present at ~100 ug m⁻³ or greater.
 ++ = Present at ~250 ug m⁻³ or greater.
 +++ = Dominant compound.

Small Chmbr: + = Present at ~10 ug m⁻³ or greater.
 ++ = Present at ~25 ug m⁻³ or greater.
 +++ = Dominant compound.

Environ. Chmbr: + = Present at ~20 ug m⁻³ or greater.
 ++ = Present at ~50 ug m⁻³ or greater.
 +++ = Dominant compound.

Table 6. VOC emitted by Carpet 4 as determined by measurements of headspace emissions and emissions in small-volume chambers and the environmental chamber.

COMPOUND	RT (min)	Head- space	Small Chmbr.	Environ. Chmbr.	Match Quality
2-Methyl-1-propene	15.4	+++			Probable
2-Methylbutane	17.1	+			Probable
2-Propanone (Acetone)	18.1	++	+	++	Confirmed
Carbon disulfide	19.6	+			Confirmed
Dichloromethane	19.8	+			Confirmed
Methylcyclopentane	22.8	+			Confirmed
1,1,1-Trichloroethane	23.3	+			Confirmed
1,2-Diethylcyclobutane	26.0	+			Tentative
Alkane HC	27.1	+			Probable
Hexamethylcyclotrisiloxane	27.2	+	+	+	Confirmed
Alkane HC	27.3	+	+	+	Probable
4-Ethenylcyclohexene	27.7	+	++	++	Confirmed
C ₉ Alkane HC	28.2	+			Probable
Ethylbenzene	28.3	+	+	+	Confirmed
m-,p-Xylene	28.5	+	+	+	Confirmed
Styrene	29.1	+	+++	+++	Confirmed
o-Xylene	29.2	+	+	+	Confirmed
Isopropylbenzene (Cumene)	29.9	+	+	+	Confirmed
Alkane HC	30.8	+	+	+	Probable
n-Propylbenzene	30.8		+	+	Confirmed
Alkane HCs	31.1-32.9	+			Probable
Alkane HC	33.5	+			Probable
3-Hexenedinitrile	34.0			+	Probable
Alkane HC	34.7			+	Probable
Alkane HC	38.1		+	+	Tentative
4-Phenylcyclohexene	39.3	+	+	++	Confirmed
Nonanedioic acid, dibutyl ester	43.7			+	Tentative

Headspace: + = Present at ~100 ug m⁻³ or greater.
 ++ = Present at ~250 ug m⁻³ or greater.
 +++ = Dominant compound.

Small Chmbr: + = Present at ~10 ug m⁻³ or greater.
 ++ = Present at ~25 ug m⁻³ or greater.
 +++ = Dominant compound.

Environ. Chmbr: + = Present at ~20 ug m⁻³ or greater.
 ++ = Present at ~50 ug m⁻³ or greater.
 +++ = Dominant compound.

Table 7. VOC emitted by Carpet 3 as determined by measurements of headspace emissions and emissions in small-volume chambers and the environmental chamber.

COMPOUND	RT (min)	Head- space	Small Chmbr.	Environ. Chmbr.	Match Quality
Chloromethane	15.1	+			Probable
2-Methyl-1-propene	15.4	+			Probable
Acetaldehyde	15.4	+	++	+	Confirmed
Methyl acetate	19.9	+	+		Confirmed
Vinyl acetate	21.6	+++	+++	+++	Confirmed
Acetic acid	23.3	+++	++		Confirmed
Alkane HC	23.8	+			Probable
2,2,4-Trimethylpentane	24.3	+++	+++	++	Confirmed
C ₈ Alkane HC	25.3	+	++	+	Probable
Alkane HC	25.4	+	++	+	Probable
1,2-Propanediol	25.7		+	+++	Confirmed
Alkane HC	25.7	+	++		Probable
Alkane HC	25.9	+	++		Probable
Alkane HC	26.0		+		Probable
Unsaturated HCs	27.4-28.8		+		Probable
3-Heptanone	28.7		++	+	Probable
Isopropylbenzene (Cumene)	29.9		+	+	Confirmed
Unsaturated HCs	29.9-30.2		+	+	Probable
Oxidized cmpd.	30.5		+	+	Unident.
Alkane HC	30.7		++	+	Probable
Unsaturated HC	30.8		+		Probable
Benzaldehyde	31.0		+		Confirmed
Alkane HC	31.1		+		Probable
1-Methylethenylbenzene	31.5		+		Confirmed
Alkane HC	31.6		+		Probable
Alkane HC	31.7		+	+	Probable
Alkane HC	32.5		++	+	Probable
2-Ethyl-1-hexanol	32.6		++	++	Confirmed
Alkane HCs	32.7-33.6		++	+	Probable
Phenylethanone	34.0		+	+	Confirmed
Alkane HC	34.0		++	+	Probable
C ₁₁ Unsaturated HC	34.3		++	++	Probable
n-Undecane	34.5		++	++	Confirmed
E-Caprolactam	37.9			++	Confirmed
Oxidized cmpds.	39.5-40.5		++	++	Unident.
Unsaturated HC	40.8			+	Probable
Alkane HC	41.0			+	Probable
Hydrocarbon, C ₁₅ H ₂₄	41.2			+	Tentative
2,6-Di- <i>tert</i> -butyl-4-methylphenol (BHT)	41.6			+	Confirmed

Table 7. Continued.

Notes:

Headspace: + = Present at ~10 ug m⁻³ or greater.
+++ = Dominant compound.

Small Chmbr: + = Present at ~10 ug m⁻³ or greater.
++ = Present at ~25 ug m⁻³ or greater.
+++ = Dominant compound.

Environ. Chmbr: + = Present at ~20 ug m⁻³ or greater.
++ = Present at ~50 ug m⁻³ or greater.
+++ = Dominant compound.

Table 8. VOC emitted by Carpet 2 as determined by measurements of headspace emissions and emissions in small-volume chambers and the environmental chamber.

COMPOUND	RT (min)	Head- space	Small Chmbr.	Environ. Chmbr.	Match Quality
2-Methyl-1-propene	15.1	+++			Probable
2-Propanone (Acetone)	18.0	++		+	Confirmed
2-Propanol	18.4	++			Confirmed
1-Propanol	20.9	++			Confirmed
Trimethyl silanol	21.3	++	+	+	Probable
1,1,1-Trichloroethane	23.2	++	+	+	Confirmed
C ₇ Alkane HC	23.7	+			Probable
1-Butanol	23.8	+	+	+	Confirmed
C ₇ Alkane HC	24.0	+			Probable
Hexamethyldisiloxane	24.2	+			Probable
C ₇ Alkane HC	24.6	+			Probable
Alkane HC	25.8		+		Probable
Toluene	26.2	+	+	+	Confirmed
2,2,5-Trimethylhexane	26.4		++		Confirmed
Siloxane	26.5	+		+	Probable
C ₈ Unsaturated HCs	26.6-27.1		+		Probable
Hexamethylcyclotrisiloxane	27.1	++	++	+++	Confirmed
Octamethyltrisiloxane	28.4	+			Probable
Alkane HC	28.5		+		Probable
Octamethylcyclotetrasiloxane	31.3	+			Probable
Dipropylene glycol methyl ether	31.8	+	+	+	Confirmed
Dipropylene glycol methyl ether	31.9	+	+	+	Confirmed
Dipropylene glycol methyl ether	32.2	+	+	+	Confirmed
Dipropylene glycol methyl ether	32.4	+			Probable
1,2-Dichlorobenzene	33.3	+	+	+	Confirmed
Decamethyltetrasiloxane	33.4	+			Probable
Triethylphosphate	35.1	+	+		Probable
Glycol ether	35.8	+	+	+	Probable
Glycol ether	35.9	+	+	+	Probable
Hydrocarbon, C ₁₅ H ₂₄	41.2	+	+	+	Probable
2,6-Di- <i>tert</i> -butyl-4-methylphenol (BHT)	41.6	+++	+++	+++	Confirmed

Headspace: + = Present at ~50 ug m⁻³ or greater.
 ++ = Present at ~125 ug m⁻³ or greater.
 +++ = Dominant compound.

Small Chmbr: + = Present at ~10 ug m⁻³ or greater.
 ++ = Present at ~25 ug m⁻³ or greater.
 +++ = Dominant compound.

Environ. Chmbr: + = Present at ~20 ug m⁻³ or greater.
 +++ = Dominant compound.

Table 9. VOC selected for quantitation during the experiments in the environmental chamber.

EXPERIMENT	COMPOUND
1a	Ethylbenzene m-,p-Xylene* Styrene o-Xylene 4-Phenylcyclohexene
1b	4-Ethenylcyclohexene Ethylbenzene m-,p-Xylene* Styrene o-Xylene 4-Phenylcyclohexene
4	4-Ethenylcyclohexene m-,p-Xylene* Styrene o-Xylene n-Propylbenzene 4-Phenylcyclohexene
3	Methyl acetate Vinyl acetate 2,2,4-Trimethylpentane 1,2-Propanediol 2-Ethyl-1-hexanol
2	1,1,1-Trichloroethane 1-Butanol Toluene Hexamethylcyclotrisiloxane Dipropylene glycol methyl ethers 1,2-Dichlorobenzene 2,6-Di- <i>tert</i> -butyl-4-methylphenol

*These two isomers of xylene were not chromatographically resolved.

Table 10. Environmental parameters for the experiments in the environmental chamber.

EXPERIMENT	Ventilation Rate (h ⁻¹)	Air Temperature (°C)	Relative Humidity (%)	Air Velocity (cm sec ⁻¹)	Loading Ratio (m ² m ⁻³)
1a					
Mean ± std. dev.*	1.00 ± 0.01	23.5 ± 0.3	46.5 ± 0.8	6.5 ± 0.9	0.43
Range (min - max)	0.97-1.03	22.7-24.3	44.8-49.0	4.3-9.5	
1b					
Mean ± std. dev.	1.00 ± 0.01	23.5 ± 0.1	48.5 ± 0.8	8.9 ± 0.6	0.43
Range (min - max)	0.97-1.01	23.0-24.1	45.4-51.5	6.8-11.3	
2					
Mean ± std. dev.	1.00 ± 0.01	23.0 ± 0.2	49.6 ± 0.6	9.0 ± 1.4	0.44
Range (min - max)	0.97-1.03	22.7-23.6	39.6-52.0	5.8-12.3	
3					
Mean ± std. dev.	0.98 ± 0.01	22.8 ± 0.2	50.2 ± 0.5	8.9 ± 0.7	0.34
Range (min - max)	0.96-1.01	22.3-23.2	49.0-53.5	6.7-11.8	
4					
Mean ± std. dev.	1.00 ± 0.01	23.0 ± 0.2	49.5 ± 0.4	NM**	0.44
Range (min - max)	0.97-1.03	22.5-23.7	48.0-51.7		

*Uncertainties are shown as ± one standard deviation.

**NM = Not measured.

Table 11. Background concentrations of the target compounds for each experiment in the environmental chamber.

COMPOUND	Background Concentration in ppbv (Mean \pm 95% CI)				
	Experiment				
	1a	1b	4	3	2
Formaldehyde	NM*	NM	1.5 \pm 0.6	1.8 \pm 0.5	2.1 \pm 0.4
Acetaldehyde	NM	NM	0.9 \pm 0.4	0.7 \pm 0.1	0.9 \pm 0.3
1,1,1-Trichloroethane					0.8 \pm 0.1
2,2,4-Trimethylpentane				0.9 \pm 0.1	
Hexamethylcyclotrisiloxane					0.4 \pm 0.1
Ethylbenzene	<0.1	<0.1		ND**	
m-,p-Xylene	0.1 \pm 0.02	<0.1	0.2 \pm 0.01		
Styrene	0.2 \pm 0.1	0.2 \pm 0.02	0.2 \pm 0.03		
o-Xylene	<0.1	<0.1	<0.1		
4-Phenylcyclohexene	<0.1	0.1 \pm 0.02	<0.1		
TVOC (ug carbon m ⁻³)	25 \pm 8.6	49 \pm 12	61 \pm 13	75 \pm 15	56 \pm 12

*NM = Not measured.

**ND = Not detected.

Table 12. Estimated limits of quantitation for the target compounds in the environmental chamber.

COMPOUND	Limits of Quantitation (ppbv)
Formaldehyde	1.8*
Acetaldehyde	1.2*
Methyl acetate	<0.1
Vinyl acetate	ND**
1,1,1-Trichloroethane	0.7*
1-Butanol	<0.4
2,2,4-Trimethylpentane	0.5*
1,2-Propanediol	ND
Hexamethylcyclotrisiloxane	0.7*
4-Ethenylcyclohexene	<0.1
Ethylbenzene	<0.1*
m-,p-Xylene	<0.1*
Styrene	0.3*
o-Xylene	<0.1*
Propylbenzene	<0.1
Dipropylene glycol methyl ethers (3)	<0.1
2-Ethyl-1-hexanol	<0.2
1,2-Dichlorobenzene	<0.1
4-Phenylcyclohexene	<0.1*
2,6-Di- <i>tert</i> -butyl-4-methylphenol	ND
TVOC (ug carbon m ⁻³)	50*

*Calculated as 3 x standard deviation of the background concentration.

**ND = Not determined.

Table 13. Estimated uncertainties for single measurements of the concentrations of the target compounds for each experiment based on their calibration curves.

COMPOUND	Uncertainty in ppbv (\pm 95% CI) Experiment				
	1a	1b	4	3	2
Formaldehyde	ND*	ND	0.20	0.28	0.05
Acetaldehyde	ND	ND	0.11	0.07	0.03
Methyl acetate				0.61	
Vinyl acetate				15 (6.8-20)**	
1,1,1-Trichloroethane					ND
1-Butanol					0.47
2,2,4-Trimethylpentane				2.9	
1,2-Propanediol				25 (11-46)	
Toluene					ND
Hexamethylcyclotrisiloxane					1.5
4-Ethenylcyclohexene		0.19	0.40		
Ethylbenzene	0.15	0.10			
m-,p-Xylene	0.15	0.10	0.12		
Styrene	0.45	0.30	8.6 (3.2-20)		
o-Xylene	0.15	0.10	0.11		
Propylbenzene			0.14		
Dipropylene glycol methyl ethers (3)					0.58
2-Ethyl-1-hexanol				2.5	
1,2-Dichlorobenzene					0.19
4-Phenylcyclohexene	1.3	0.41	0.70		
2,6-Di- <i>tert</i> -butyl-4-methylphenol					3.6
TVO _C (ug carbon m ⁻³)	19.7	42.6	36.8	70.1	13.6

*ND = Not determined.

**Values in parentheses are the range.

Table 14. Fractions of the total-ion-current (TIC) chromatographic areas accounted for by the sums of the chromatographic areas of the target compounds at 24 and 168 h after the start of each experiment.

EXPERIMENT	Area of Quant. VOC/TIC Area	
	24 h	168 h
1b	0.30	0.45
4	0.48	0.25
3*	0.47	0.23
2	0.88	0.78

*Fractions calculated for 12 and 144 h.

Table 15. Coefficients for the decays in the concentrations of the target compounds over 1-12 h and 24-168 h in each experiment. The exponential curves for 1-12 h have the form: $y = ae^{-k_1 t}$, where a is a constant and t = time in hours. The power curves for 24-168 h have the form: $y = at^{-k_2}$.

EXPERIMENT/COMPOUND	Vapor Pres. ^a (mm Hg)	Decay Coefficient	
		k_1 1-12 h	k_2 24-168 h
1a			
C ₂ Alkyl benzenes	6	0.124	1.56
Styrene	5	0.0678	1.33
4-Phenylcyclohexene	ND ^b	0.0022	0.152
1b			
4-Ethenylcyclohexene	ND	0.134	1.27
C ₂ Alkyl benzenes	6	0.122	1.55
Styrene	5	0.0842	1.19
4-Phenylcyclohexene	ND	0.0041	0.149
4			
4-Ethenylcyclohexene	ND	0.138	1.15
Alkyl benzenes	5	0.132	0.842
Styrene	5	0.116	1.45
4-Phenylcyclohexene	ND	0.0265	0.259
3			
Formaldehyde	760	0.0417	0.630
Acetaldehyde	740	0.0637	1.01
Methyl acetate	170		---
Vinyl acetate	83	0.0923	1.07
2,2,4-Trimethylpentane	39 ^c	0.112	0.551
1,2-Propanediol	0.2	0.184	0.654
2-Ethyl-1-hexanol	0.05	0.0523	0.451
2			
1,1,1-Trichloroethane	100	0.586	---
Toluene	22	0.380	---
1-Butanol	4.4	0.0685	0.634
Hexamethylcyclotrisiloxane	ND	0.229	---
Dipropylene glycol methyl ethers (3)	ND	0.0122	0.312
1,2-Dichlorobenzene	1	0.0343	0.0128 ^d
2,6-Di- <i>tert</i> -butyl-4-methylphenol	0.002 ^e	0.0231	0.107

Table 15. Continued.

Notes:

- a**Vapor pressures at 20° C. All values from Verschueren (1977) *Handbook of Environmental Data on Organic Chemicals*, unless otherwise noted.
- b**ND = No data.
- c**From *Lange's Handbook of Chemistry* (1985).
- d**Exponential decay coefficient.
- e**Calculated from Stull (1947) *Vapor Pressure of Pure Substances*.

Table 16. Quasi steady-state specific emission rates of the target compounds at 24 and 168 hours after the start of each experiment.

EXPERIMENT/COMPOUND	Specific Emission Rate in $\mu\text{g m}^{-3} \text{h}^{-1}$ (Mean \pm 95% CI)		Fractional Reduction 1-(168/24 h)
	24 h	168 h	
1a			
C ₂ Alkyl benzenes	4.1 \pm 0.3	0.0	1.00
Styrene	24.7 \pm 1.0	2.0 \pm 0.2	0.92
4-Phenylcyclohexene	85.1 \pm 2.3	64.0 \pm 2.5	0.25
TVOC as carbon	213 \pm 9.6	71.2 \pm 9.9	0.67
1b			
4-Ethenylcyclohexene	7.3 \pm 0.3	0.6 \pm 0.1	0.91
C ₂ Alkyl benzenes	6.5 \pm 0.4	0.0	1.00
Styrene	34.7 \pm 2.0	3.5 \pm 0.2	0.90
4-Phenylcyclohexene	64.5 \pm 3.1	48.5 \pm 2.4	0.25
TVOC as carbon	178 \pm 15.9	51.2 \pm 15.0	0.71
4			
4-Ethenylcyclohexene	24.2*	2.7 \pm 0.1	0.89
Alkyl benzenes	12.4*	3.1 \pm 0.2	0.75
Styrene	260*	16.1 \pm 0.6	0.94
4-Phenylcyclohexene	81.9*	50.2 \pm 1.9	0.39
TVOC as carbon	399*	93.9 \pm 14.1	0.76
3			
Formaldehyde	57.2**	18.2**	0.68
Acetaldehyde	26.7**	4.6**	0.83
Methyl acetate	0.8 \pm 0.2	0.0	1.00
Vinyl acetate	853 \pm 41.5	103 \pm 20.2	0.88
2,2,4-Trimethylpentane	60.0 \pm 7.7	21.4 \pm 2.9	0.64
1,2-Propanediol	690 \pm 67.5	193 \pm 40.3	0.72
2-Ethyl-1-hexanol	58.0 \pm 0.6	22.6 \pm 2.0	0.61
TVOC as carbon	602 \pm 23.5	192 \pm 48.4	0.68
2			
1-Butanol	25.2 \pm 3.3	6.9 \pm 2.3	0.73
Dipropylene glycol methyl ethers (3)	26.3 \pm 0.8	14.4 \pm 0.1	0.45
1,2-Dichlorobenzene	10.2 \pm 1.0	1.6 \pm 0.1	0.84
2,6-Di- <i>tert</i> -butyl-4-methylphenol	214 \pm 20.5	173 \pm 8.1	0.19
TVOC as carbon	83.3 \pm 25.0	32.5 \pm 12.5	0.61

*Two replicate samples.

**Single sample.

Table 17. Specific mass emissions of the target compounds over the first 24 hours and the entire 168 hours of each experiment.

EXPERIMENT/COMPOUND	Specific Emissions in mg m ⁻²		
	0-24 h	Total 0-168 h	Ratio 0-24 h/Total
1a			
C ₂ Alkyl benzenes	0.33	0.40	0.83
Styrene	1.24	2.20	0.56
4-Phenylcyclohexene	2.19	12.5	0.18
TVOC as carbon	8.31	28.5	0.29
1b			
4-Ethenylcyclohexene	0.47	0.80	0.60
C ₂ Alkyl benzenes	0.39	0.64	0.62
Styrene	1.89	3.41	0.55
4-Phenylcyclohexene	1.80	9.80	0.18
TVOC as carbon	8.36	22.3	0.38
4			
4-Ethenylcyclohexene	1.47	2.62	0.56
Alkyl benzenes	0.62	1.37	0.45
Styrene	16.6	25.9	0.64
4-Phenylcyclohexene	2.22	11.2	0.20
TVOC as carbon	26.4	51.9	0.51
3			
Formaldehyde	2.37	6.61	0.36
Acetaldehyde	1.08	2.52	0.43
Methyl acetate	0.08	0.08	1.00
Vinyl acetate	38.6	85.3	0.45
2,2,4-Trimethylpentane	2.67	7.55	0.35
1,2-Propanediol	22.1	72.0	0.31
2-Ethyl-1-hexanol	1.93	7.20	0.27
TVOC as carbon	27.8	85.8	0.32
2			
1,1,1-Trichloroethane	0.02	0.02	1.00
1-Butanol	0.65	2.08	0.31
Hexamethylcyclotrisiloxane	0.35	0.35	1.00
Dipropylene glycol methyl ethers (3)	0.66	2.70	0.24
1,2-Dichlorobenzene	0.25	0.71	0.35
2,6-Di- <i>tert</i> -butyl-4-methylphenol	5.01	27.9	0.18
TVOC as carbon	2.24	8.06	0.28

Table 18. Ventilation rates and concentrations of VOC in the field-study house.

Elapsed Time* Days	Vent. Rate (h ⁻¹)	Styrene Conc. (ppbv)	4-PCH** Conc. (ppbv)
-1	9.6	0.23	0
2	7.3	0.44	1.6
4	1.0	1.12	4.7
6	1.1	0.89	5.1
12	0.8	0.62	4.1
18	1.3	0.30	2.1
25	0.8	0.50	2.4
40	0.4	0.68	3.2
52	0.7	0.66	3.2

*Elapsed time = days relative to the installation of the new carpet.

**4-PCH = 4-phenylcyclohexene.

Table 19. The 12 most frequently occurring VOC emitted by 19 SBR latex-backed carpets in small-scale environmental chambers (Data from Black *et al.*, 1991; as reported by Hetes *et al.*, 1992^a) and their presence in the emissions from the two SBR latex-backed carpets in the current study.

COMPOUND	Occurrence	Emitted by SBR Carpets in Current Study
Styrene	19	Yes
4-Phenylcyclohexene	19	Yes
4-Ethenylcyclohexene	16	Yes
Undecane	13	Yes ^b
Propylbenzene	12	Yes
Decane	11	Yes ^b
Ethylbenzene	9	Yes
2-Butoxyethanol	9	No
Isopropylbenzene	8	Yes
1-Ethyl-3-methylbenzene	7	No
Toluene	7	Yes
p-Xylene	7	Yes

^aThe data sources are: 1) Black, M.S., Pearson, W.J. and Work, L.M. (1991) Volatile organic compound emissions from carpet and associated products, Appendix R, Carpet Policy Dialogue Compendium Report. R.W. Leukrothe, Jr., Ed., Office of Toxic Substances, U.S. EPA, Washington, D.C., Sept. 27; and 2) Hetes, R.G., Womack, D.S., Pierson, T.K. and Naugle, D.F. (1992) Evaluation of Exposures to Volatile Organics Offgassing from New Carpets, U.S. EPA Contract No. CR-815509. Report 4479-001/12-F, Research Triangle Institute, Research Triangle Park, NC.

^bAlkane hydrocarbons present in the volatility range of n-decane and n-undecane.

Table 20. Designations for the carpet samples included in the current study and the corresponding designations for the carpet samples previously investigated by the CPSC for qualitative emissions of VOC.

Current Study		Previous CPSC Study
Carpet No.	New No.	Old No.
1	1R	CAC-8
2	7C	SWC-125
3	6C	WLC-143
4	4R	SAC-89

Table 21. Average and maximum specific emission rates at 24 and 140 h for selected VOC emitted by 19 SBR latex-backed carpets in small-scale environmental chambers. These data are from Black *et al.* (1991), as reported by Hetes *et al.* (1992).*

COMPOUND	Specific Emission Rate in ug m ⁻² h ⁻¹				Fractional Reduction ^b 1-(140/24 h)	
	24 h		140 h			
	Avg.	Max.	Avg.	Max.		
4-Ethenylcyclohexene	3	27	<1	<1	1.00	
C ₂ -C ₃ Alkyl benzenes ^c	5	39	1	8	0.80	
Styrene	37	173	3	18	0.92	
4-Phenylcyclohexene	64	152	25	73	0.62	

*The data sources are: 1) Black, M.S., Pearson, W.J. and Work, L.M. (1991) Volatile organic compound emissions from carpet and associated products, Appendix R, Carpet Policy Dialogue Compendium Report. R.W. Leukrothe, Jr., Ed., Office of Toxic Substances, U.S. EPA, Washington, D.C., Sept. 27; and 2) Hetes, R.G., Womack, D.S., Pierson, T.K. and Naugle, D.F. (1992) Evaluation of Exposures to Volatile Organics Offgassing from New Carpets, U.S. EPA Contract No. CR-815509. Report 4479-001/12-F, Research Triangle Institute, Research Triangle Park, NC.

^bCalculated using average emission rates.

^cData for propylbenzene, ethylbenzene, cumene, m-ethyltoluene and xylene were summed.

Table 22. Comparison of the maximum chamber concentrations of eight dominant compounds emitted by the carpets to reported irritant- and odor-effect levels.

COMPOUND	Concentration in ppmv				Max. Chamber Conc.
	Industrial Workplace TLV*	Mouse Bioassay 0.03 RD ₅₀ *	Odor Threshold*		
Formaldehyde	1	0.09	0.83		0.046
Vinyl acetate	10	---	0.50		0.29
2,2,4-Trimethylpentane	300**	600**	48**		0.023
1,2-Propanediol	---	---	60-90		0.13
Styrene	50	29	0.32		0.18
2-Ethyl-1-hexanol	---	---	0.08-0.14		0.008
4-Phenylcyclohexene	---	---	<0.0005		0.008
2,6-Di- <i>tert</i> -butyl-4-methylphenol	---	---	---		0.014

*See text for literature citations.

**Value for n-octane.

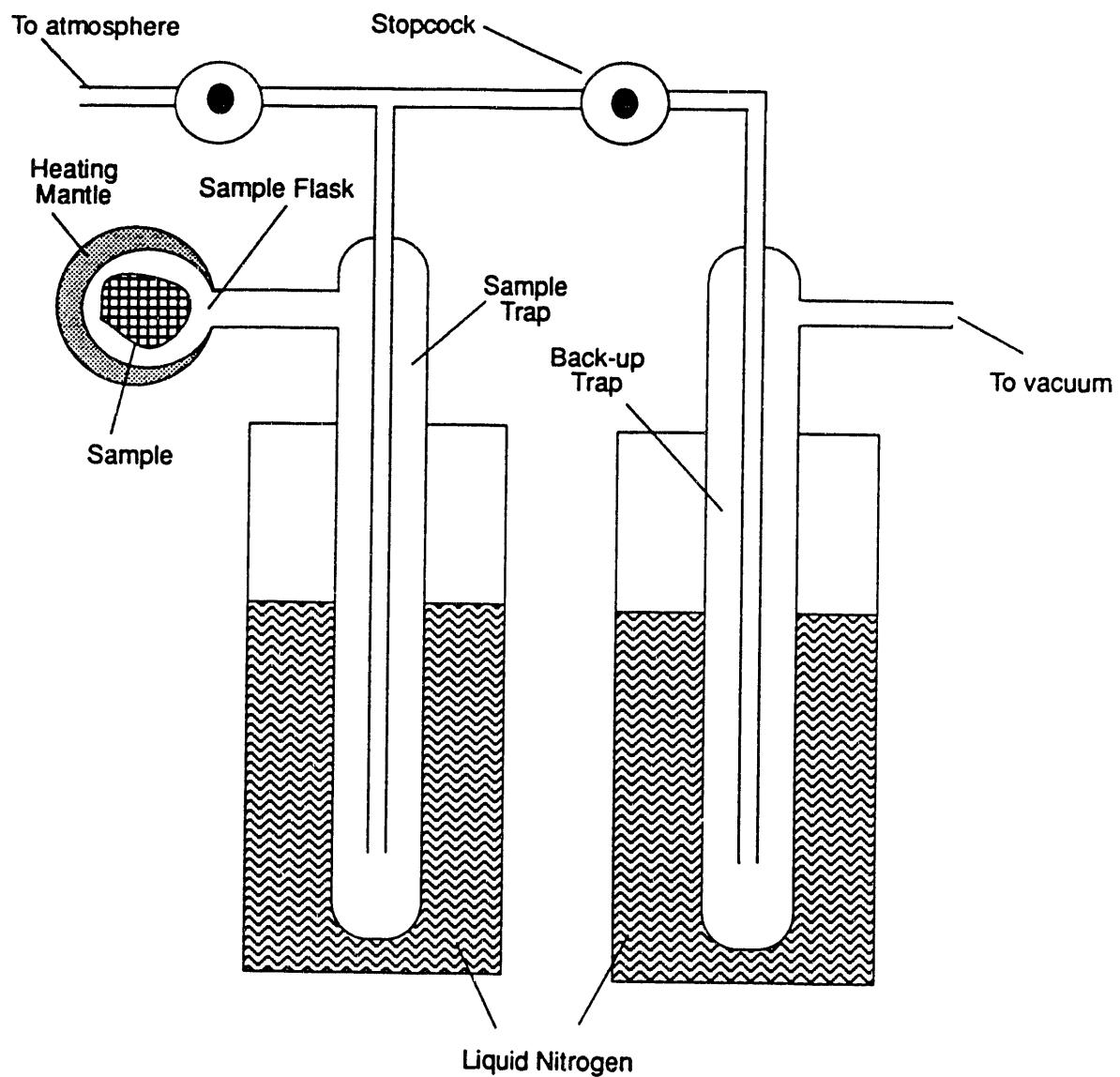


Figure 1. Schematic diagram of the vacuum-extraction apparatus.

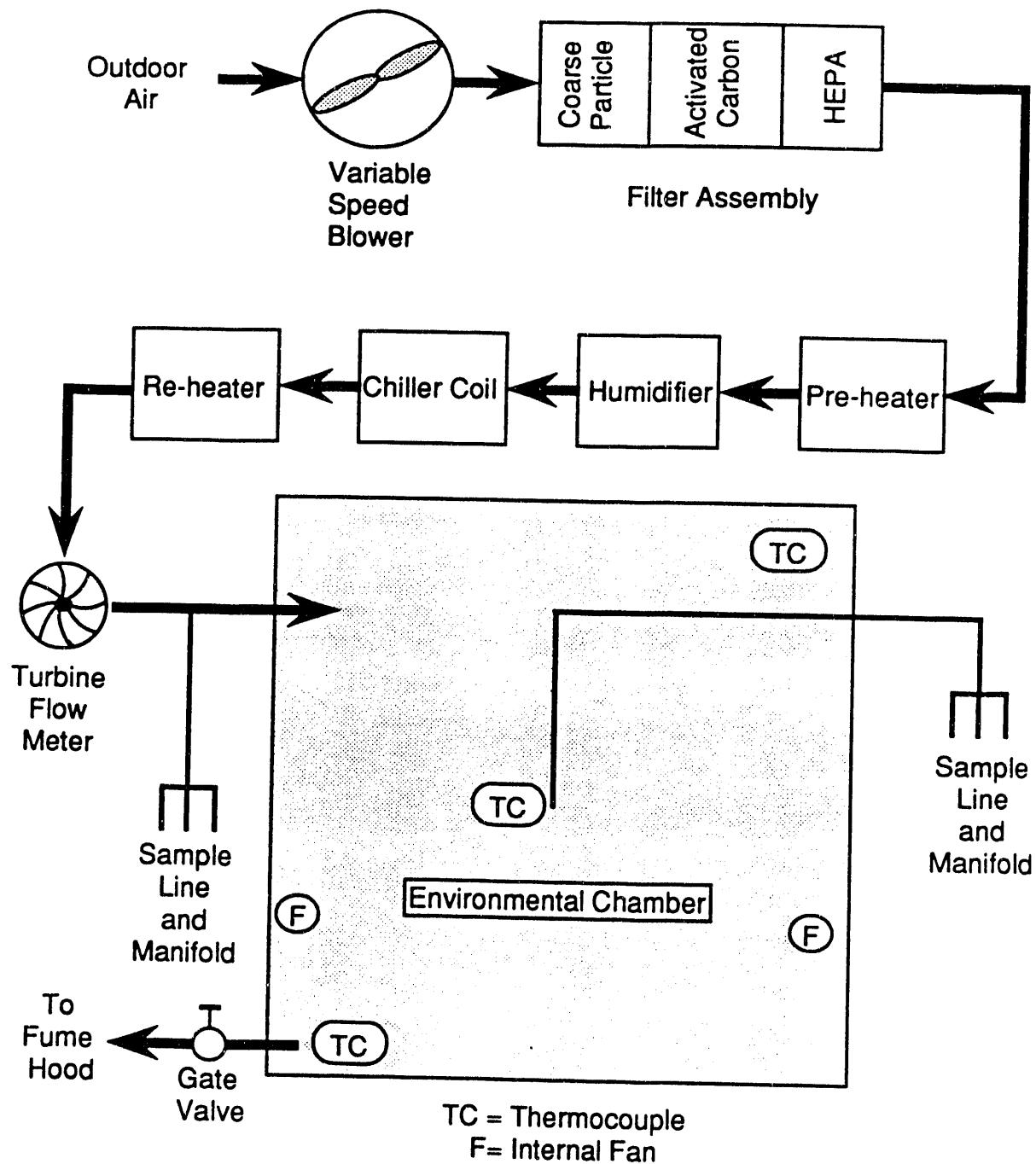


Figure 2. Schematic diagram of the environmental chamber facility.

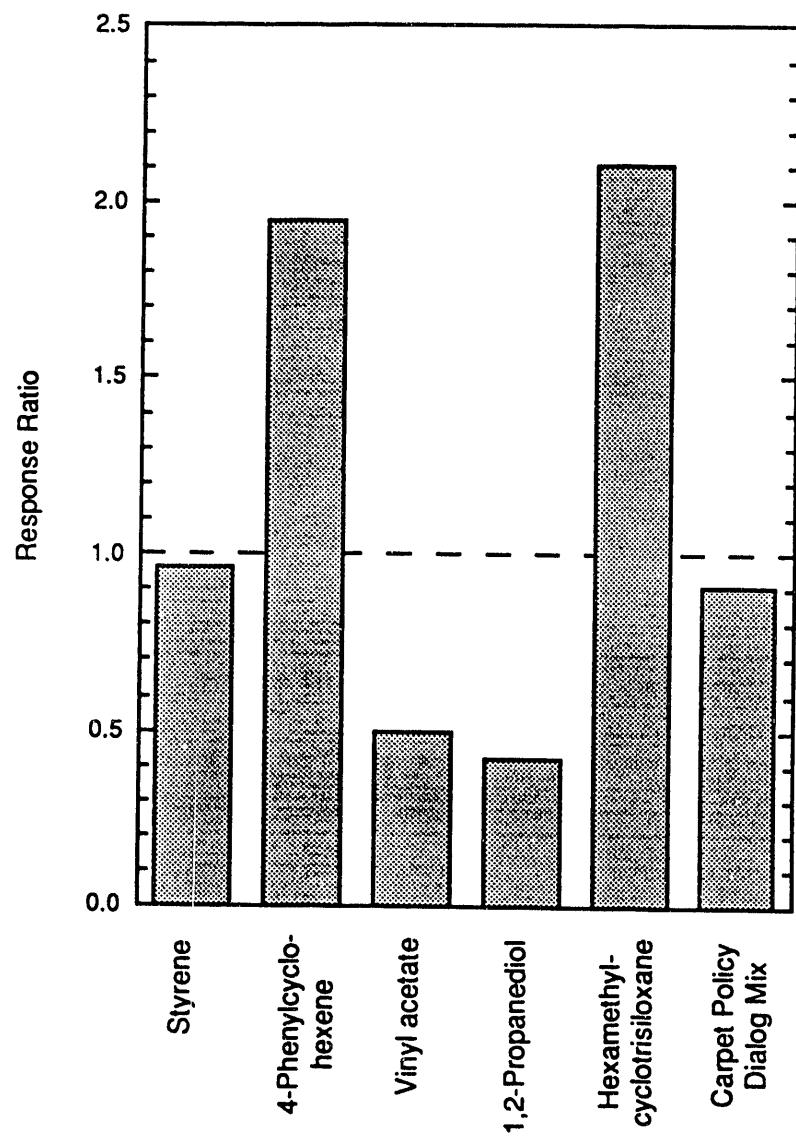


Figure 3. Ratio of the TVOC response to the actual mass of carbon added to a sampler for selected compounds and one mixture.

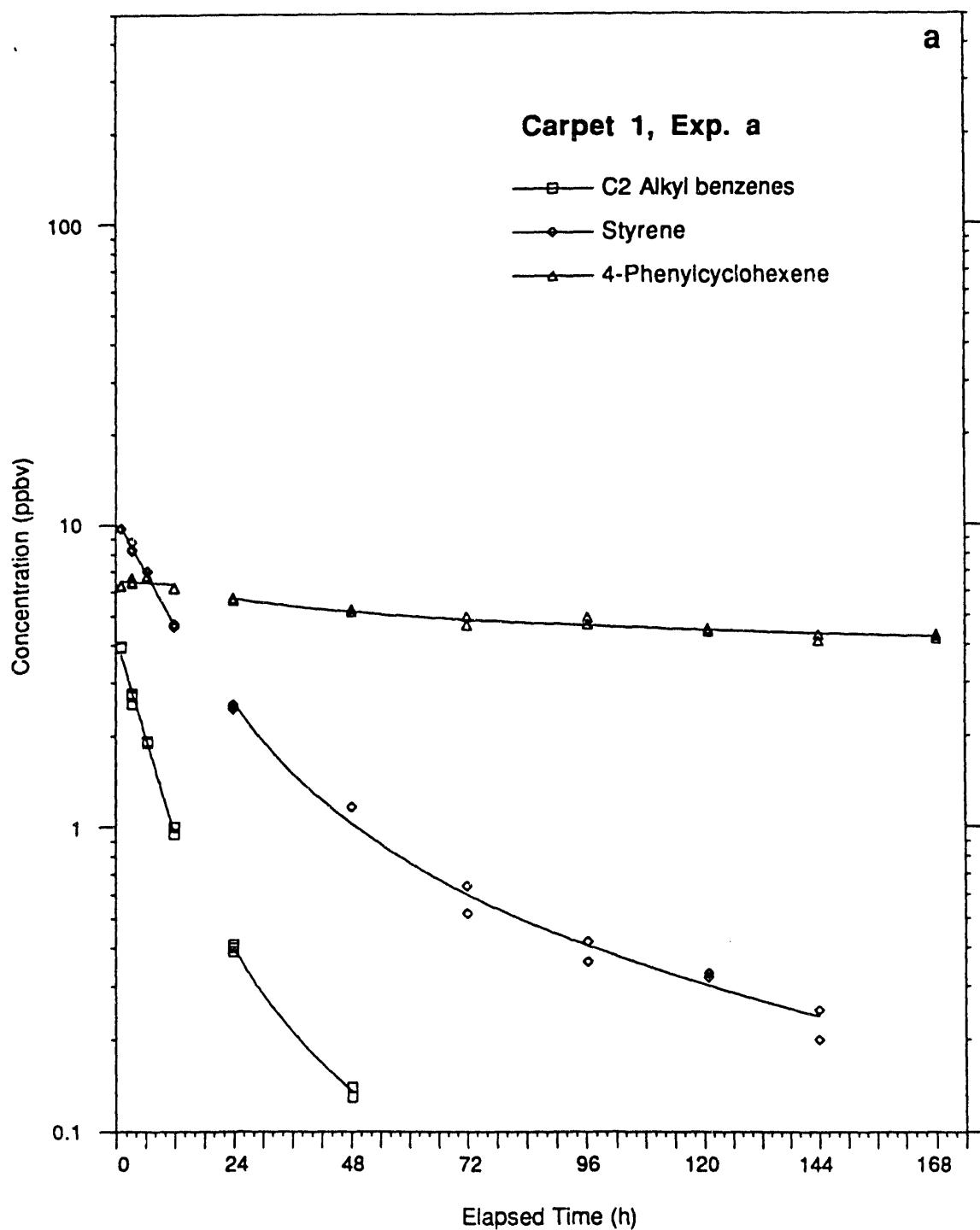


Figure 4a. Chamber concentrations of VOC emitted over one week by Carpet 1 in experiment a.
 C2 Alkyl benzenes = ethylbenzene + xylene isomers.

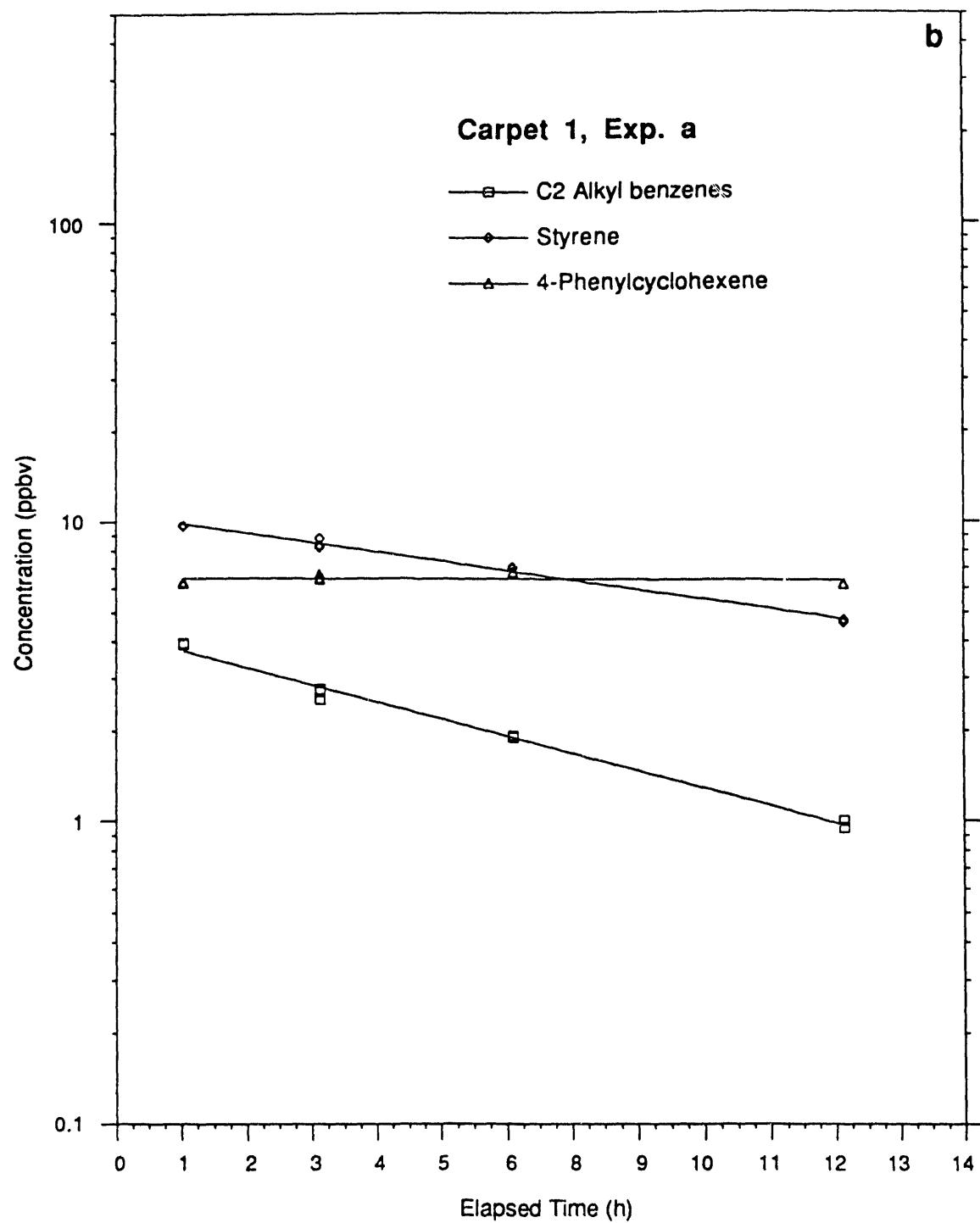


Figure 4b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 1 in experiment a.
C2 Alkyl benzenes = ethylbenzene xylene isomers.

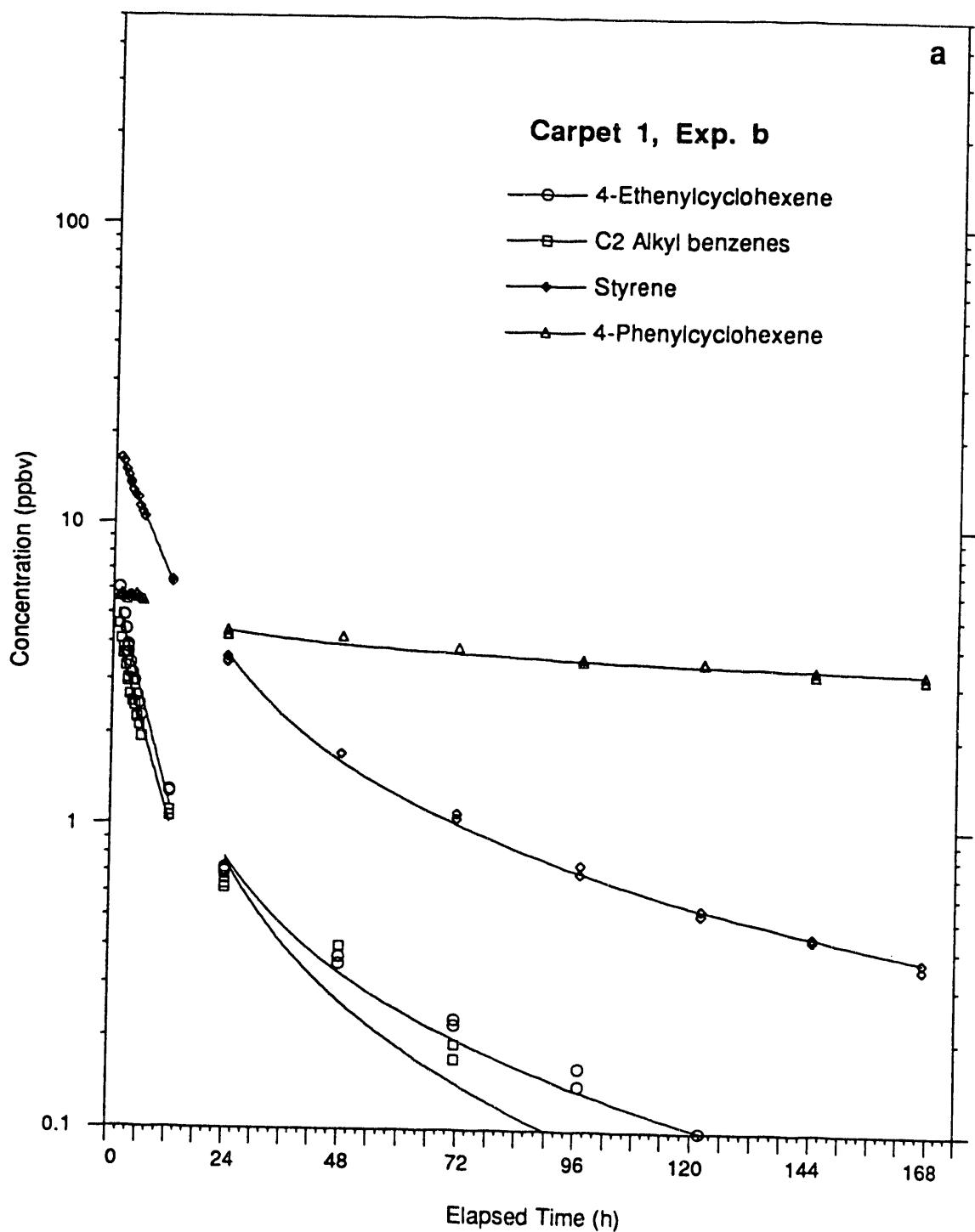


Figure 5a. Chamber concentrations of VOC emitted over one week by Carpet 1 in experiment b.
 C2 Alkyl benzenes = ethylbenzene + xylene isomers.

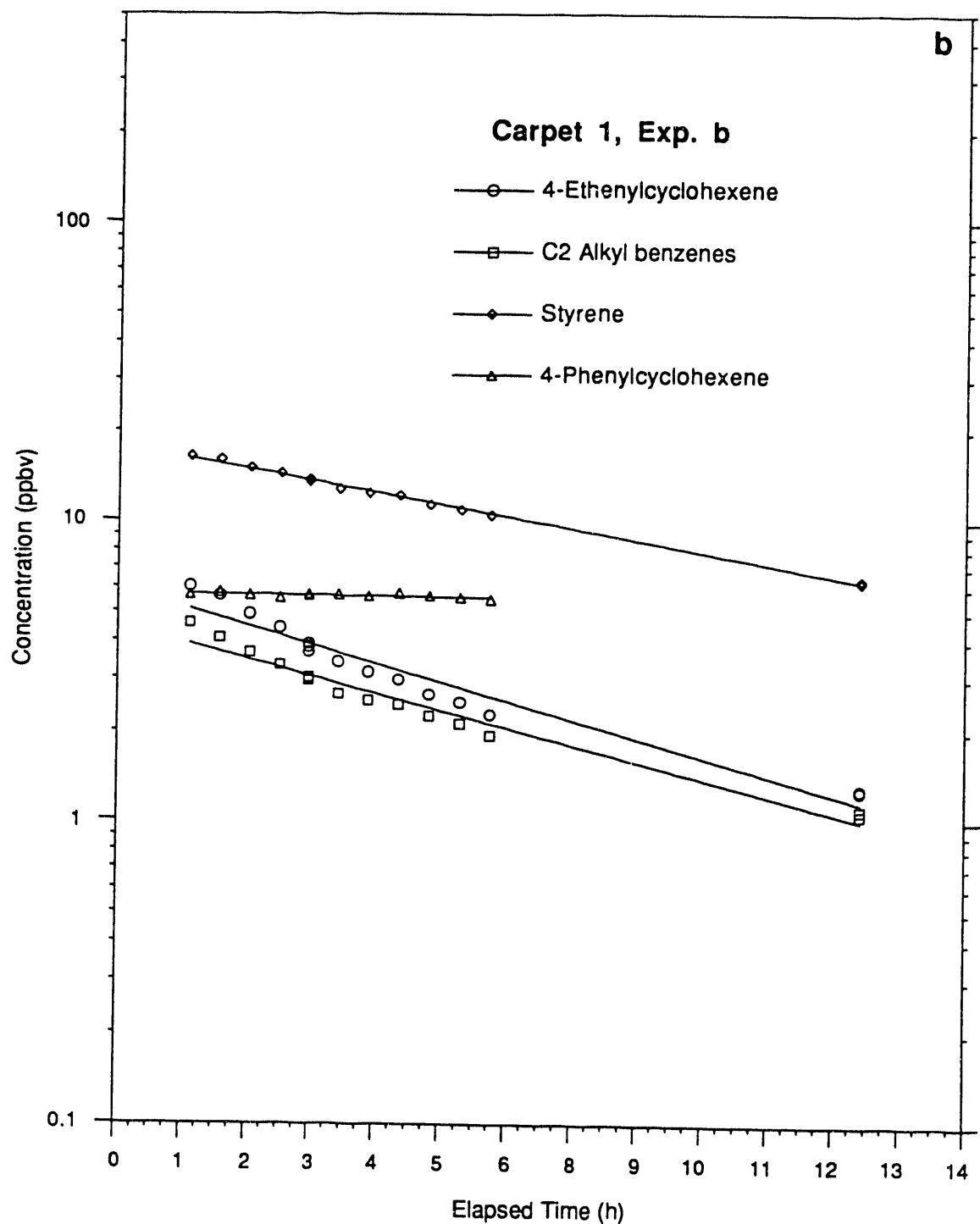


Figure 5b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 1 in experiment b.
C2 Alkyl benzenes = ethylbenzene + xylene isomers.

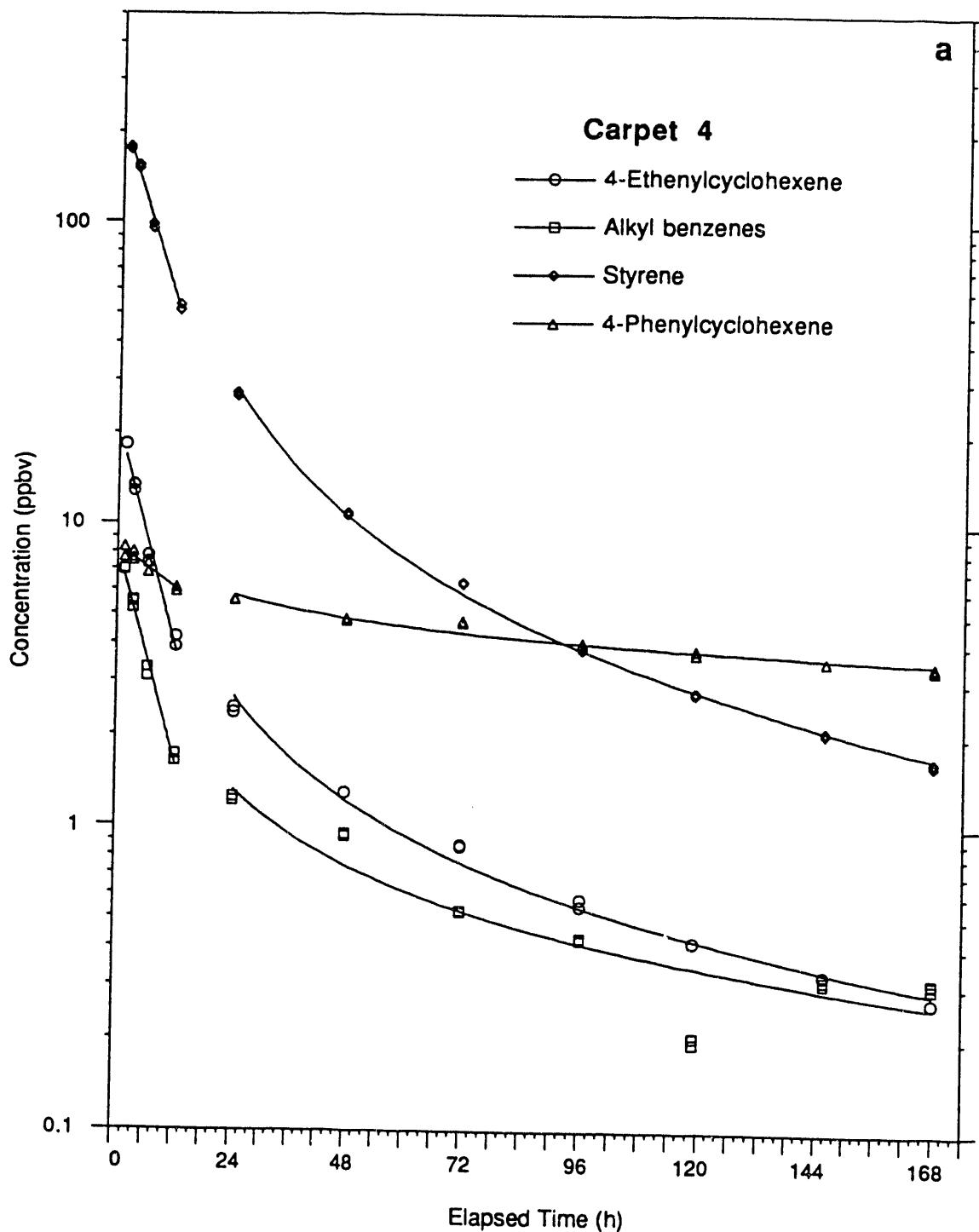


Figure 6a. Chamber concentrations of VOC emitted over one week by Carpet 4.
 Alkyl benzenes = xylene isomers + n-propylbenzene.

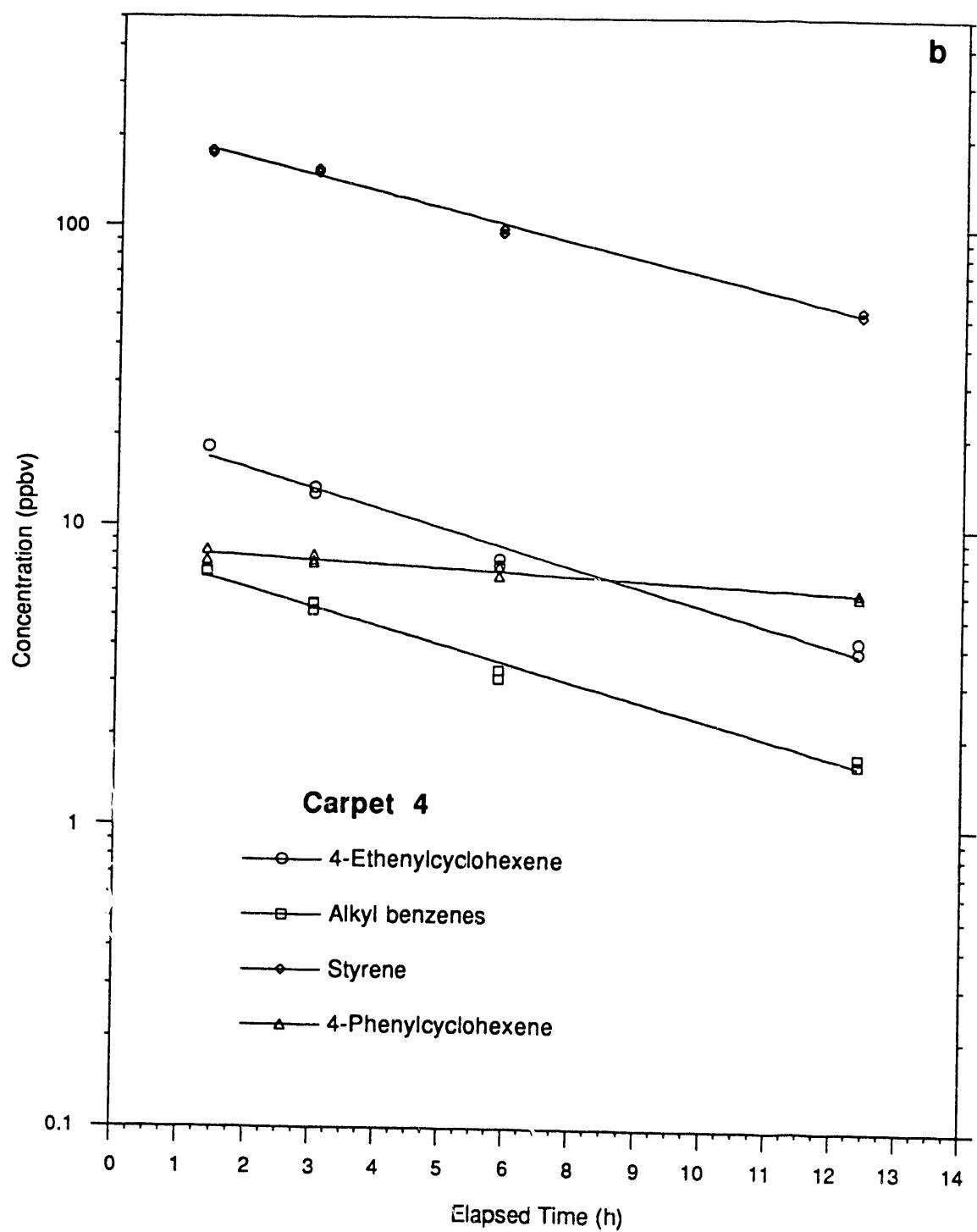


Figure 6b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 4.
 Alkyl benzenes = xylene isomers + n-propylbenzene.

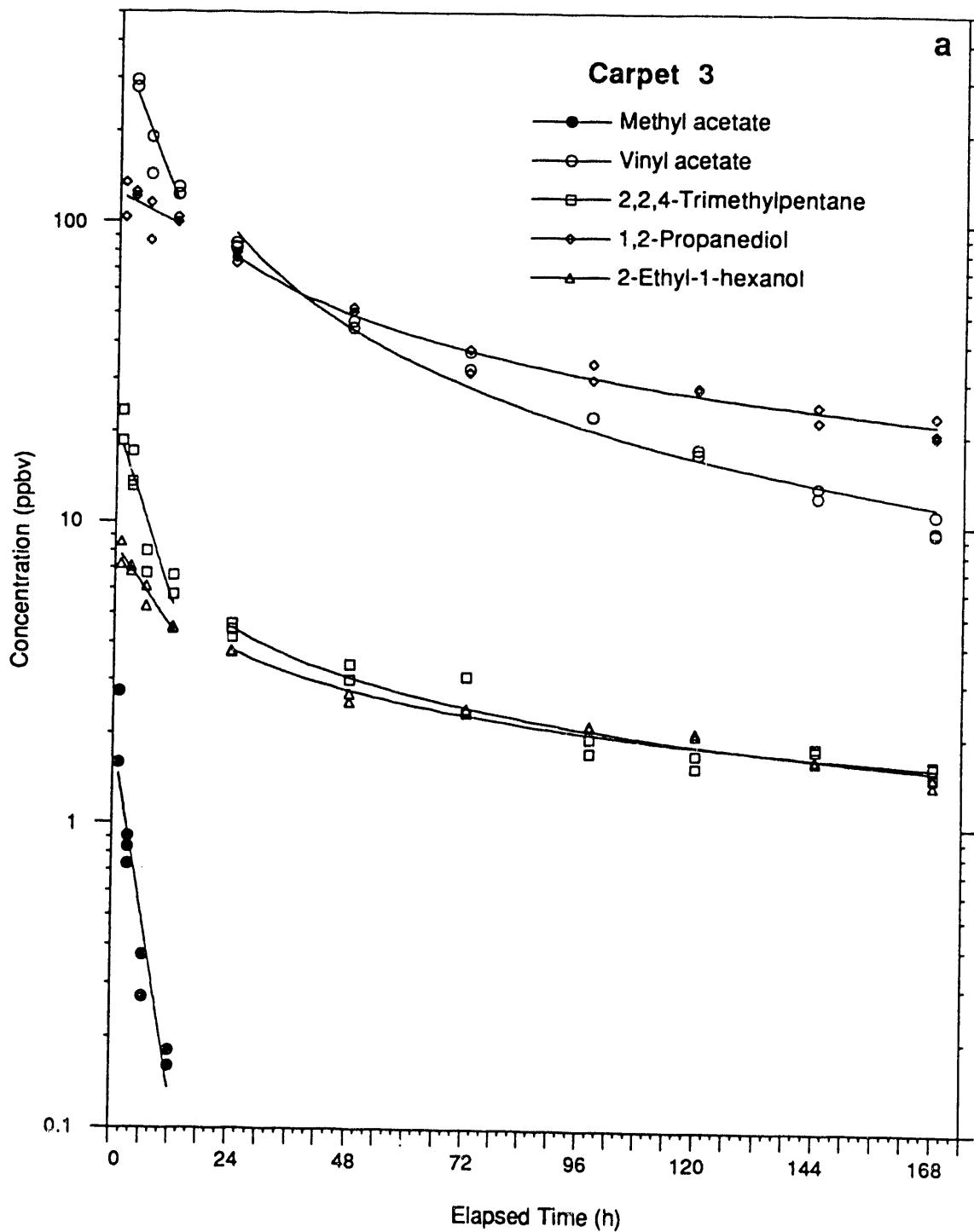


Figure 7a. Chamber concentrations of VOC emitted over one week by Carpet 3.

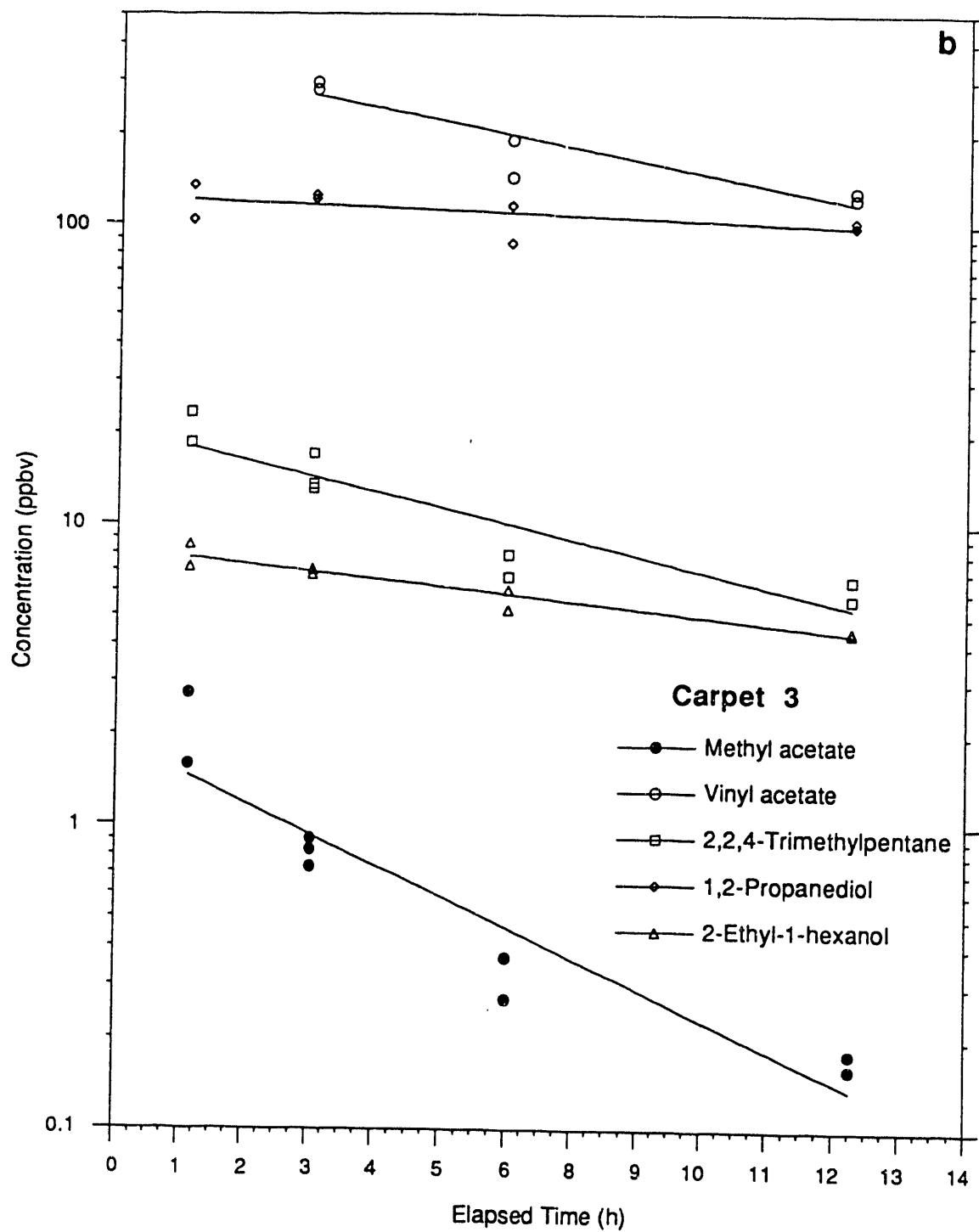


Figure 7b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 3.

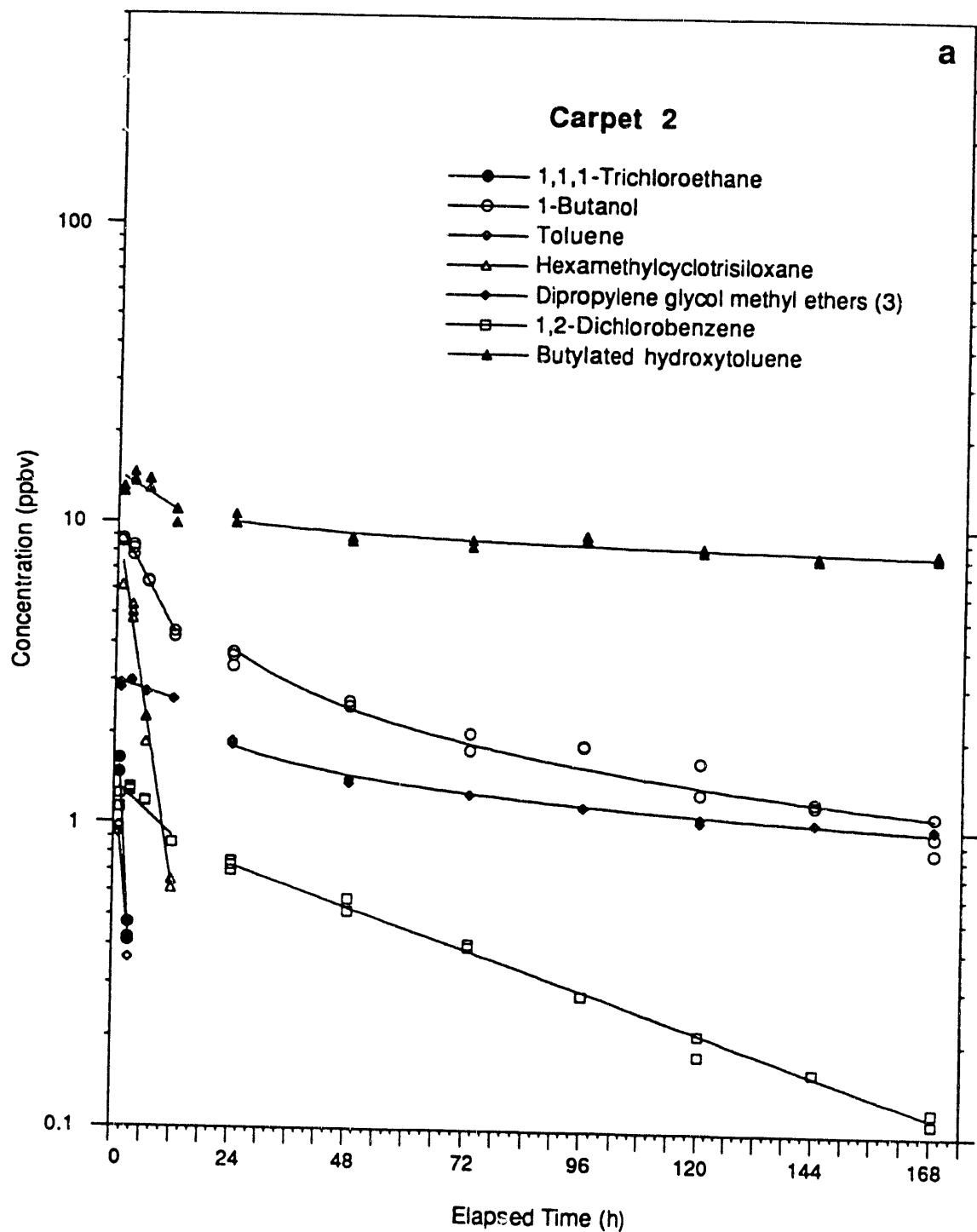


Figure 8a. Chamber concentrations of VOC emitted over one week by Carpet 2.

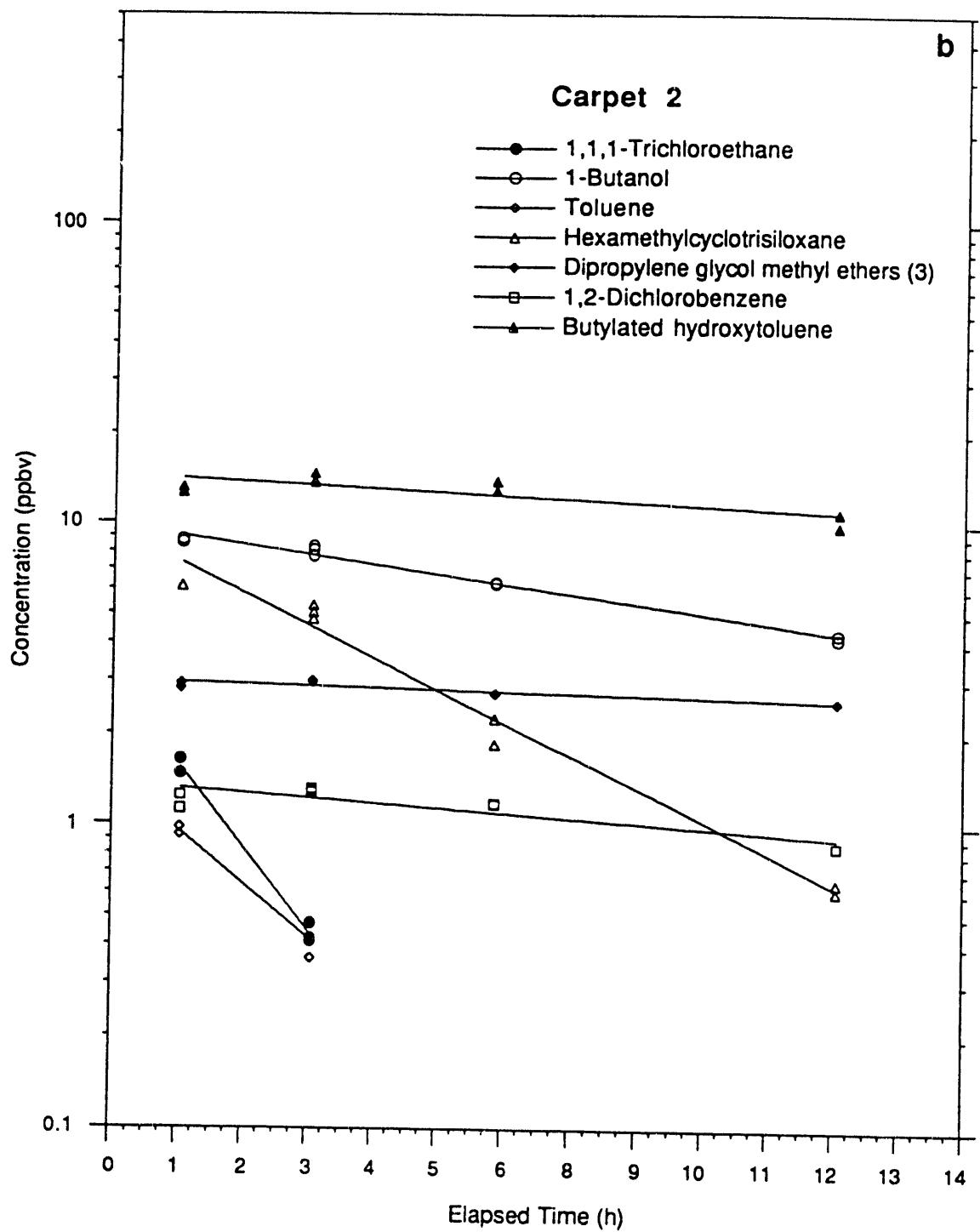


Figure 8b. Chamber concentrations of VOC emitted over 1-12 h by Carpet 2.

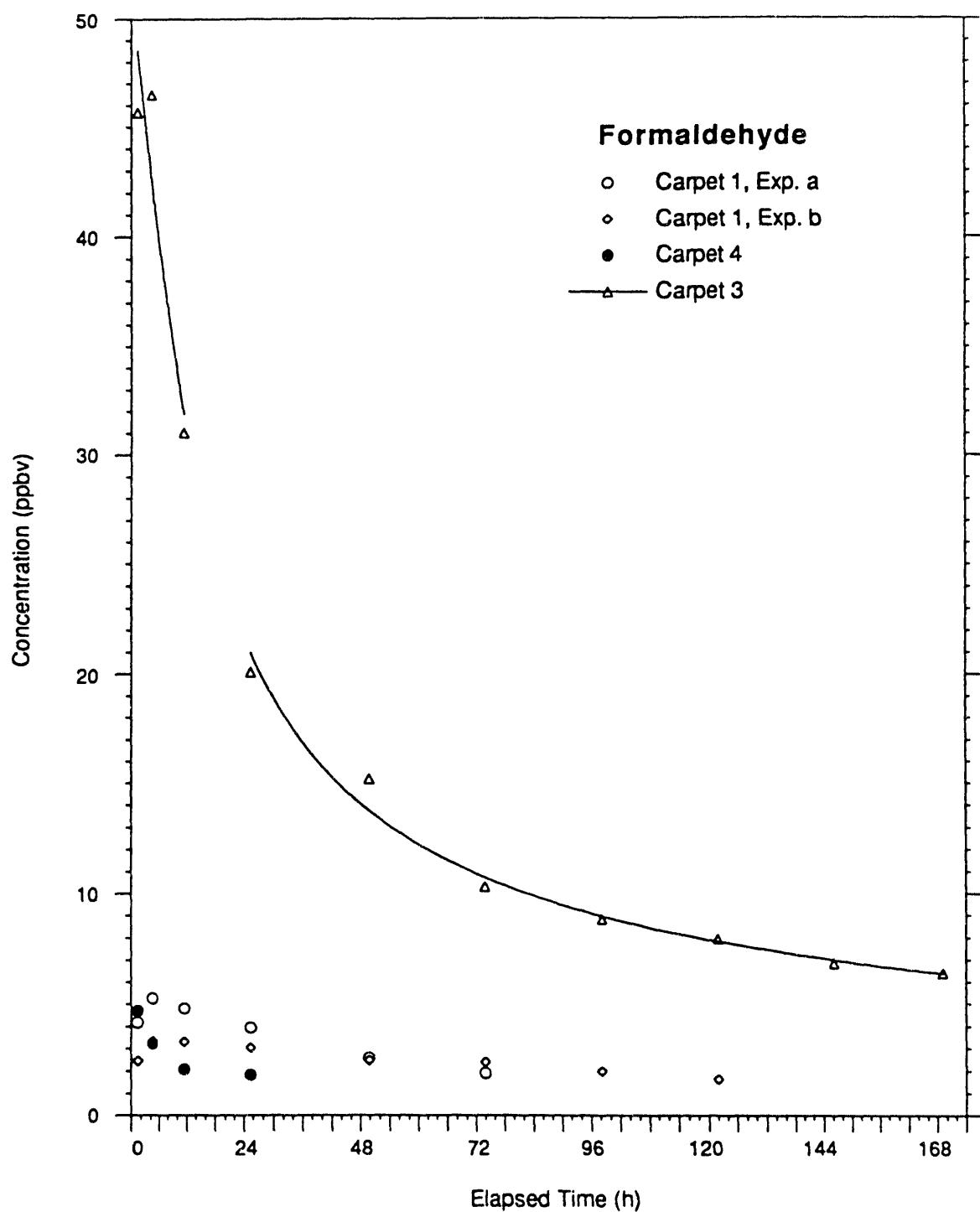


Figure 9. Chamber concentrations of formaldehyde emitted by the carpets over one week.

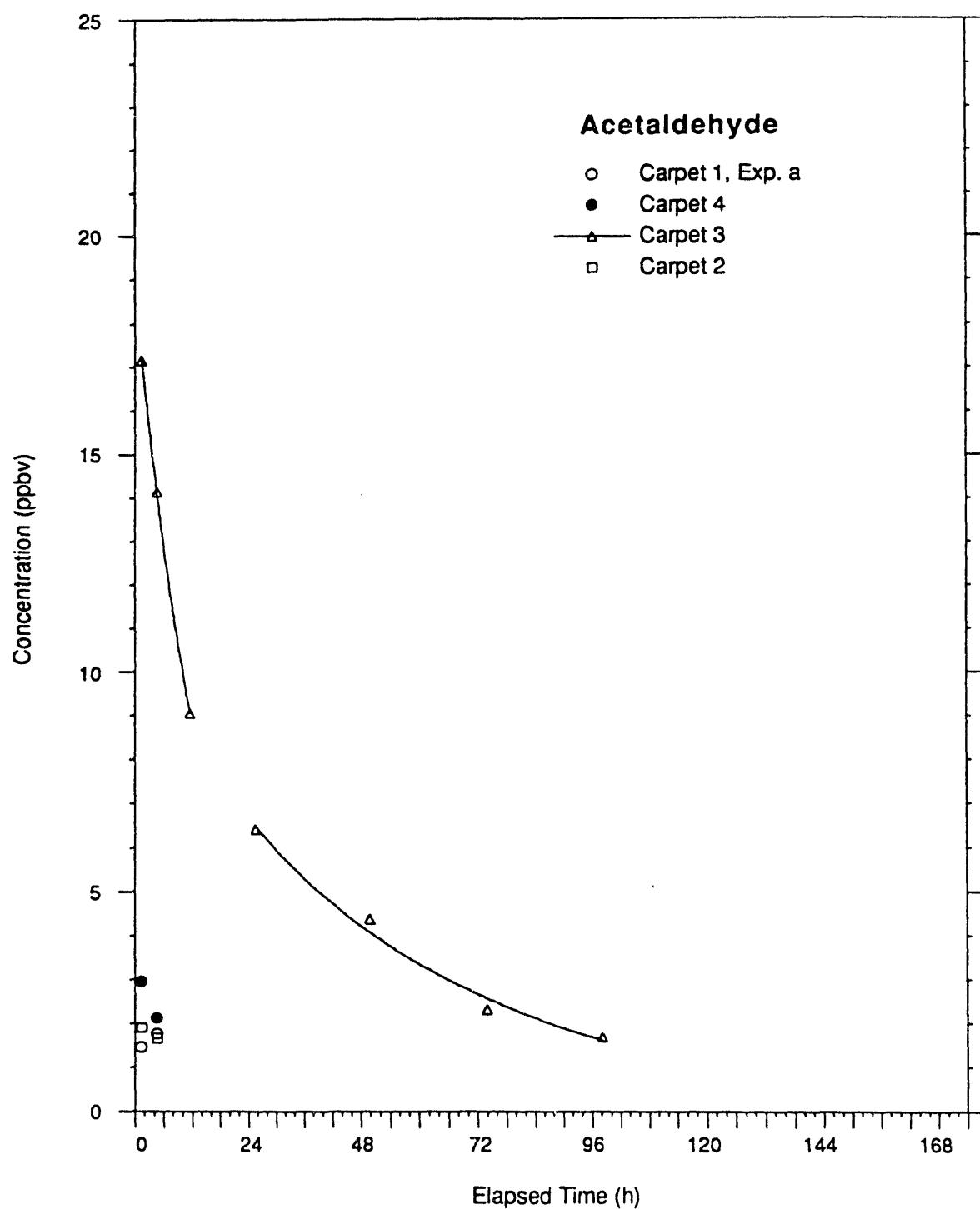


Figure 10. Chamber concentrations of acetaldehyde emitted by the carpets over one week.

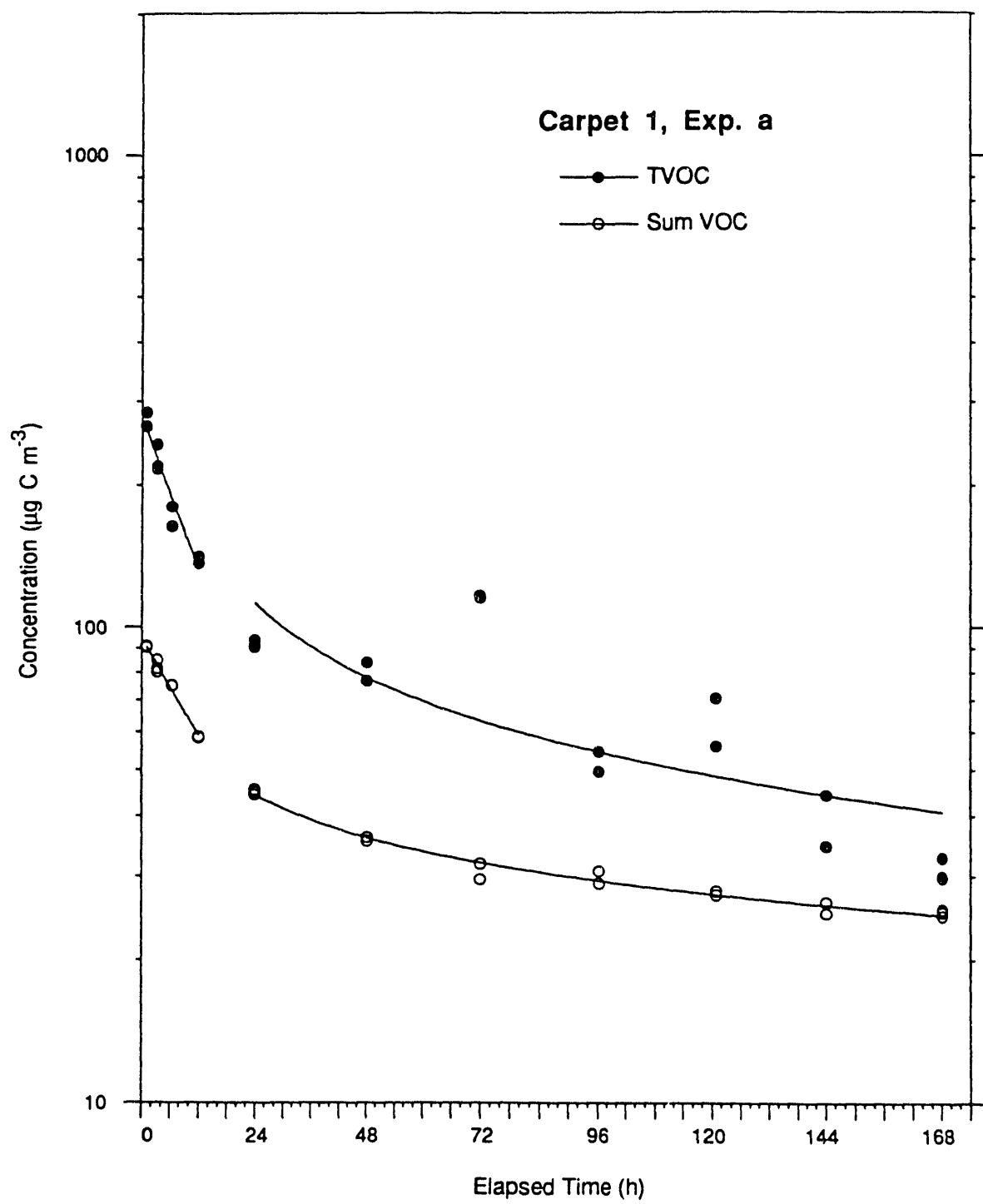


Figure 11. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 1 in experiment a.

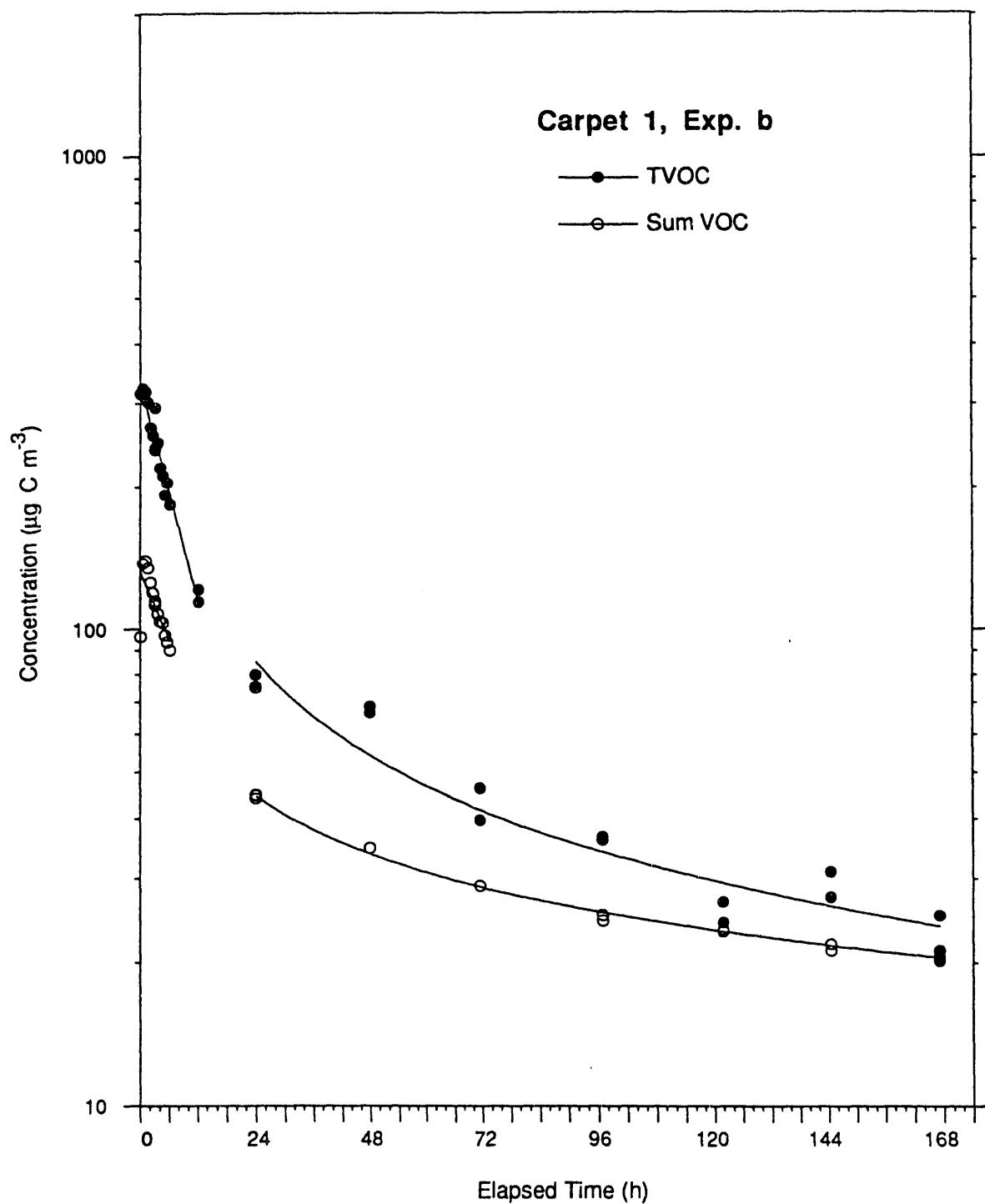


Figure 12. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 1 in experiment b.

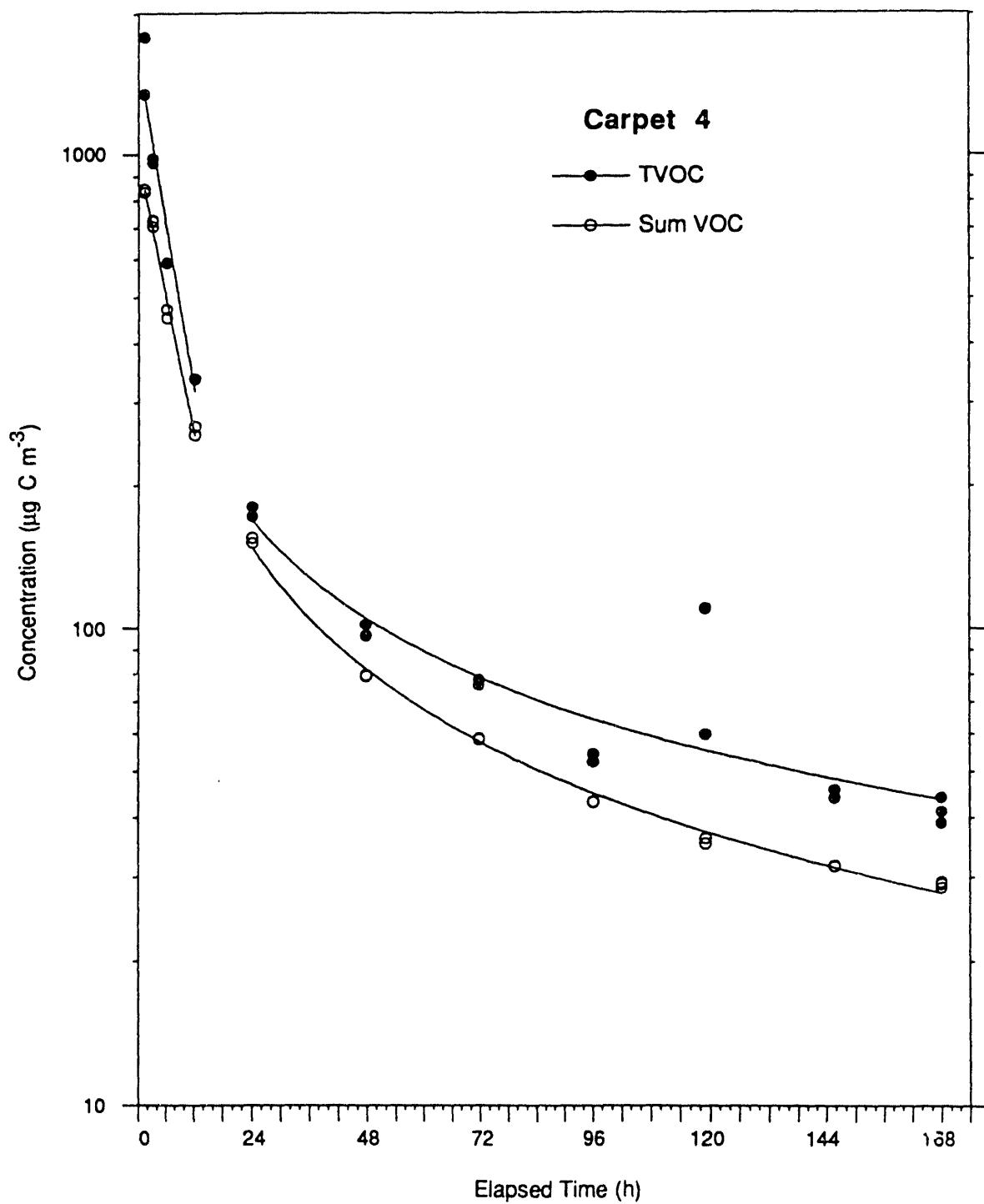


Figure 13. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 4.

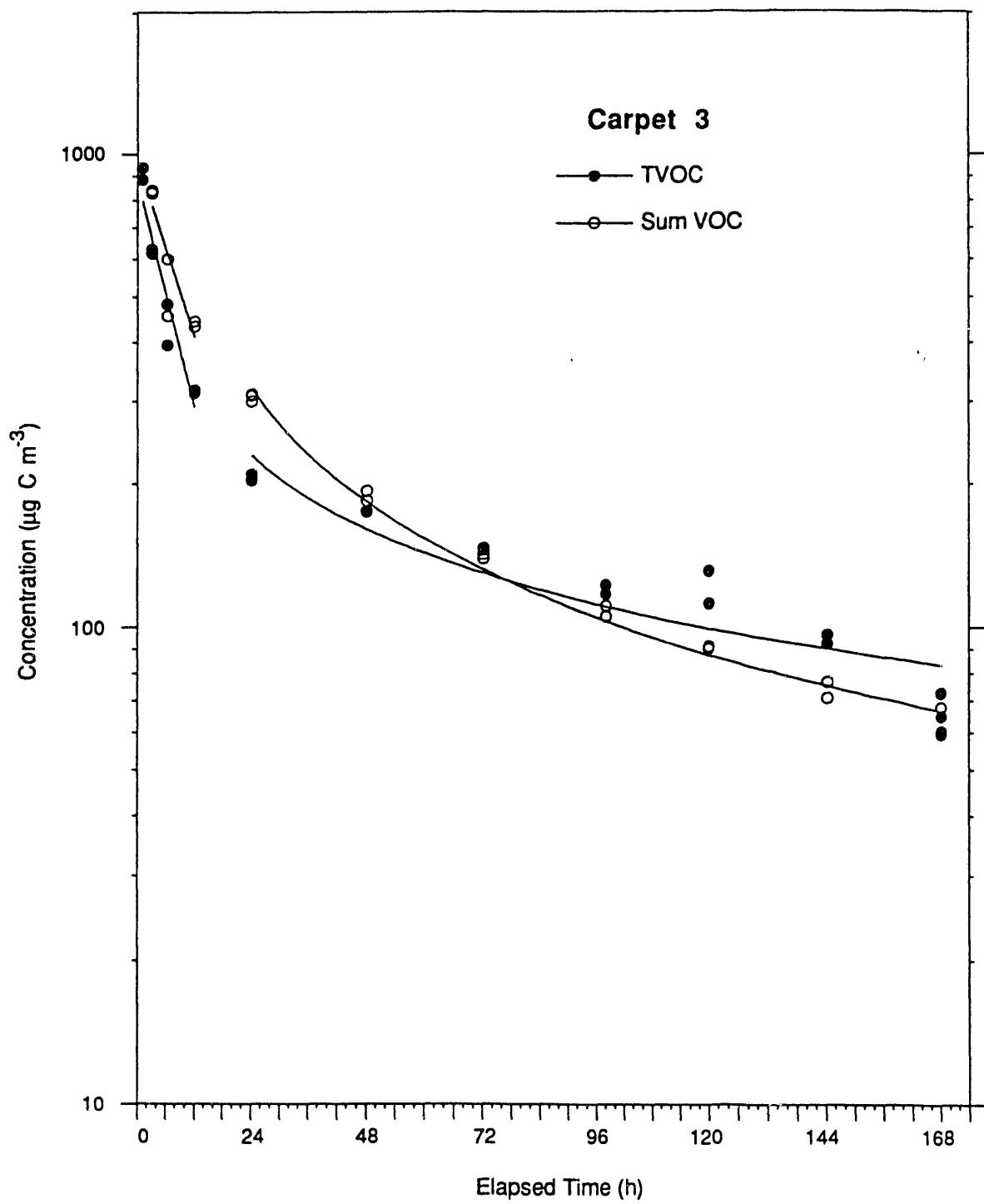


Figure 14. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 3.

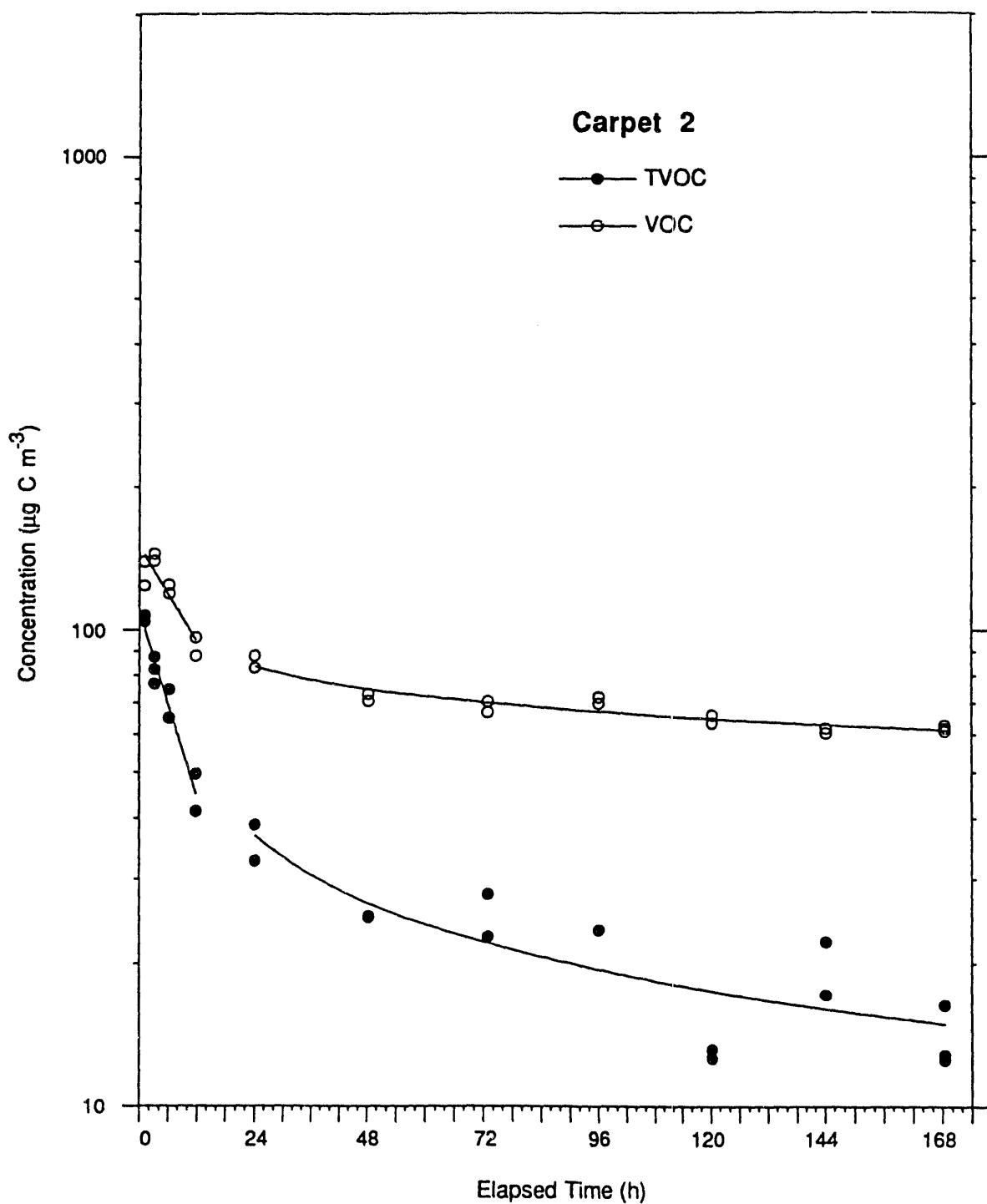


Figure 15. Chamber concentrations of TVOC and the sum of the individual VOC emitted over one week by Carpet 2.

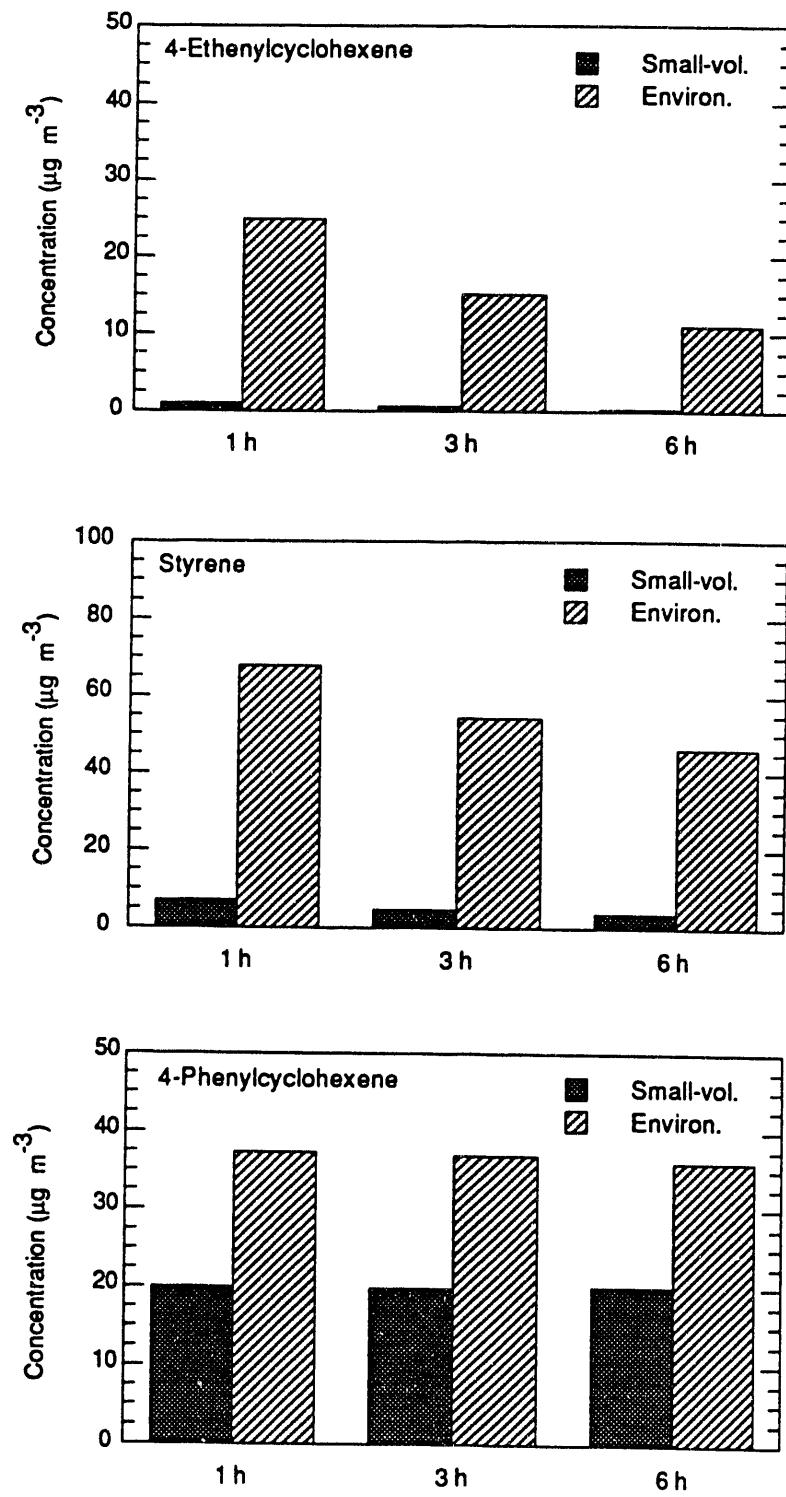


Figure 16. Comparison of the small-volume and environmental chamber concentrations at 1, 3, and 6 hours of three selected VOC emitted by Carpet 1 in experiment b.

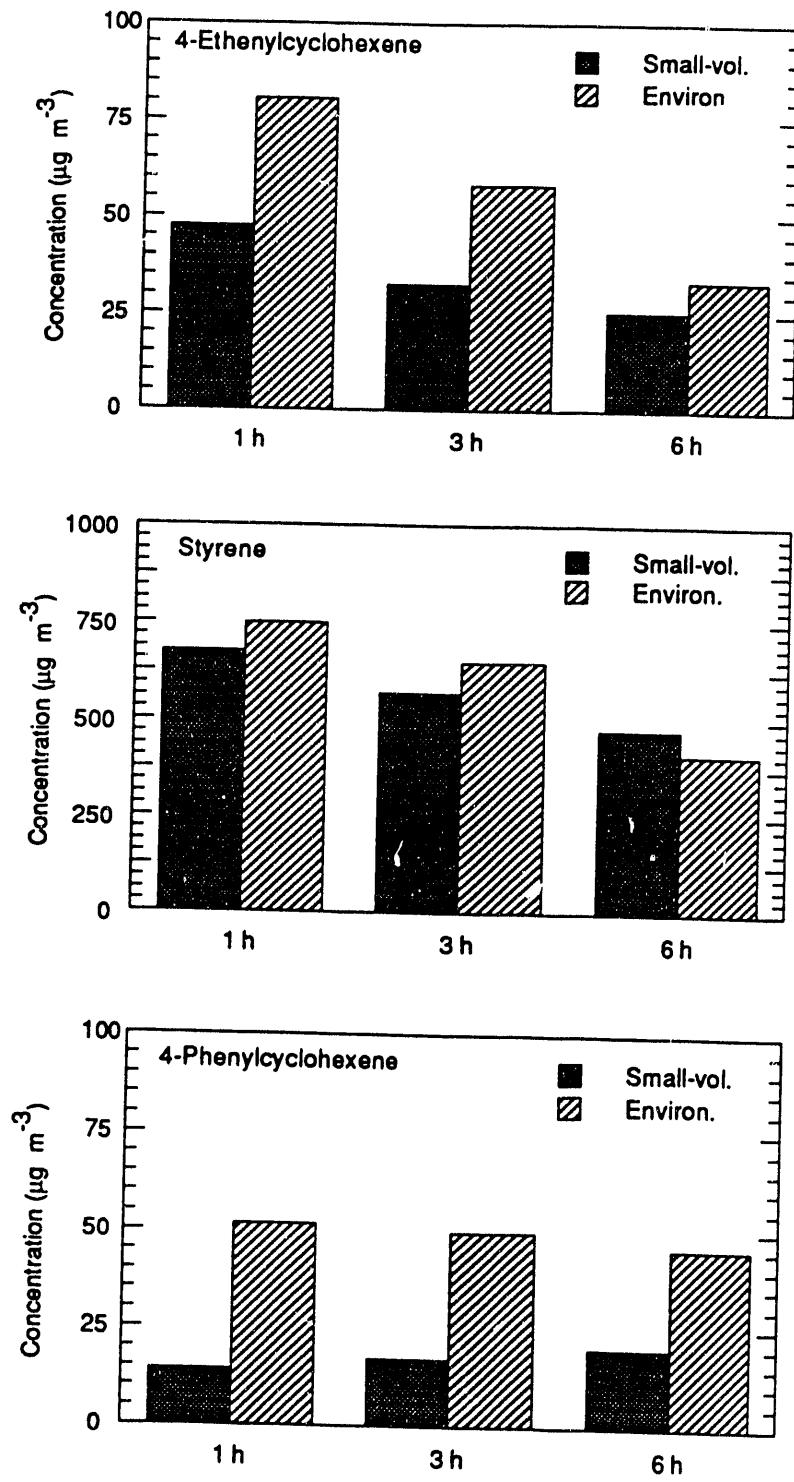


Figure 17. Comparison of the small-volume and environmental chamber concentrations at 1, 3, and 6 hours of three selected VOC emitted by Carpet 4.

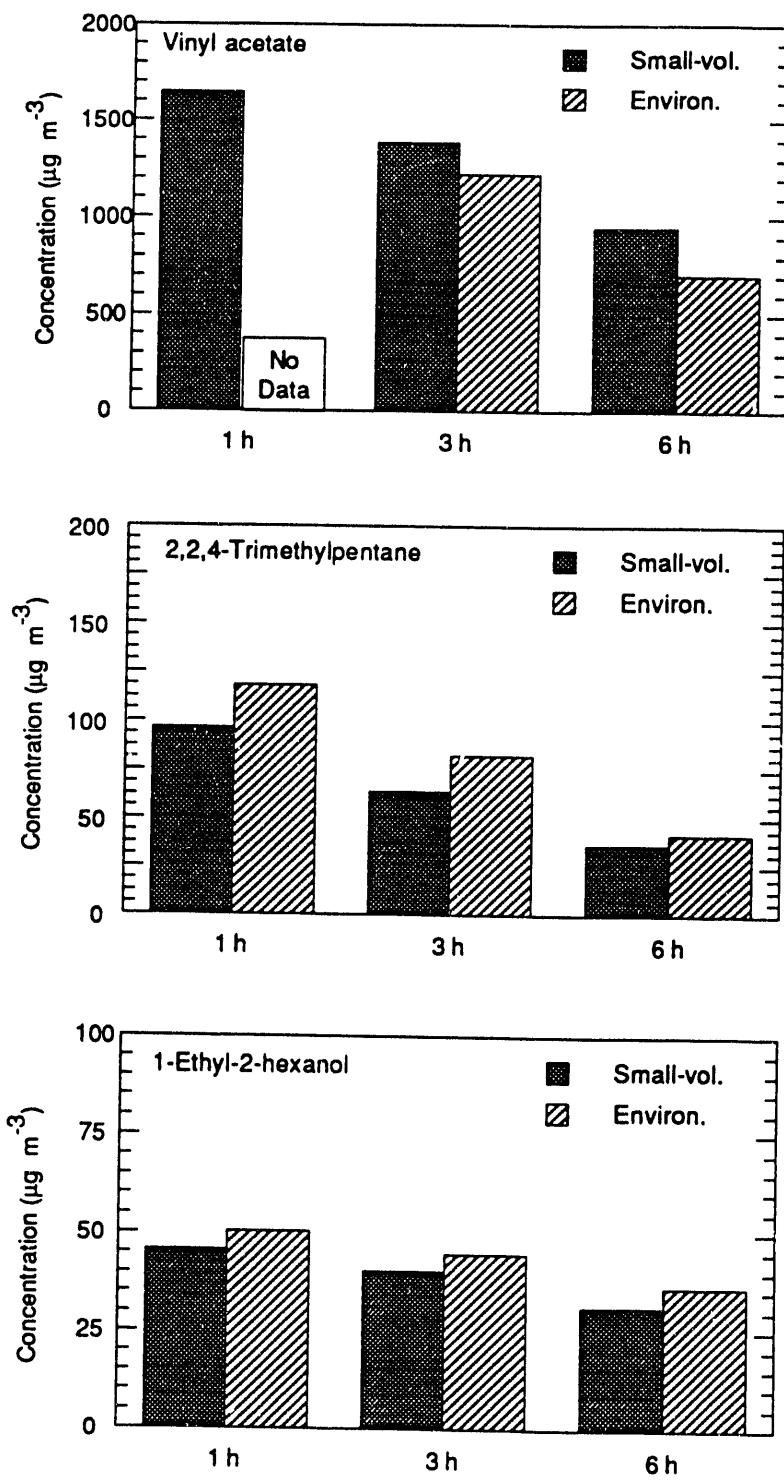


Figure 18. Comparison of the small-volume and environmental chamber concentrations at 1, 3, and 6 hours of three selected VOC emitted by Carpet 3. The environmental chamber concentrations have been multiplied by 1.2 (see text).

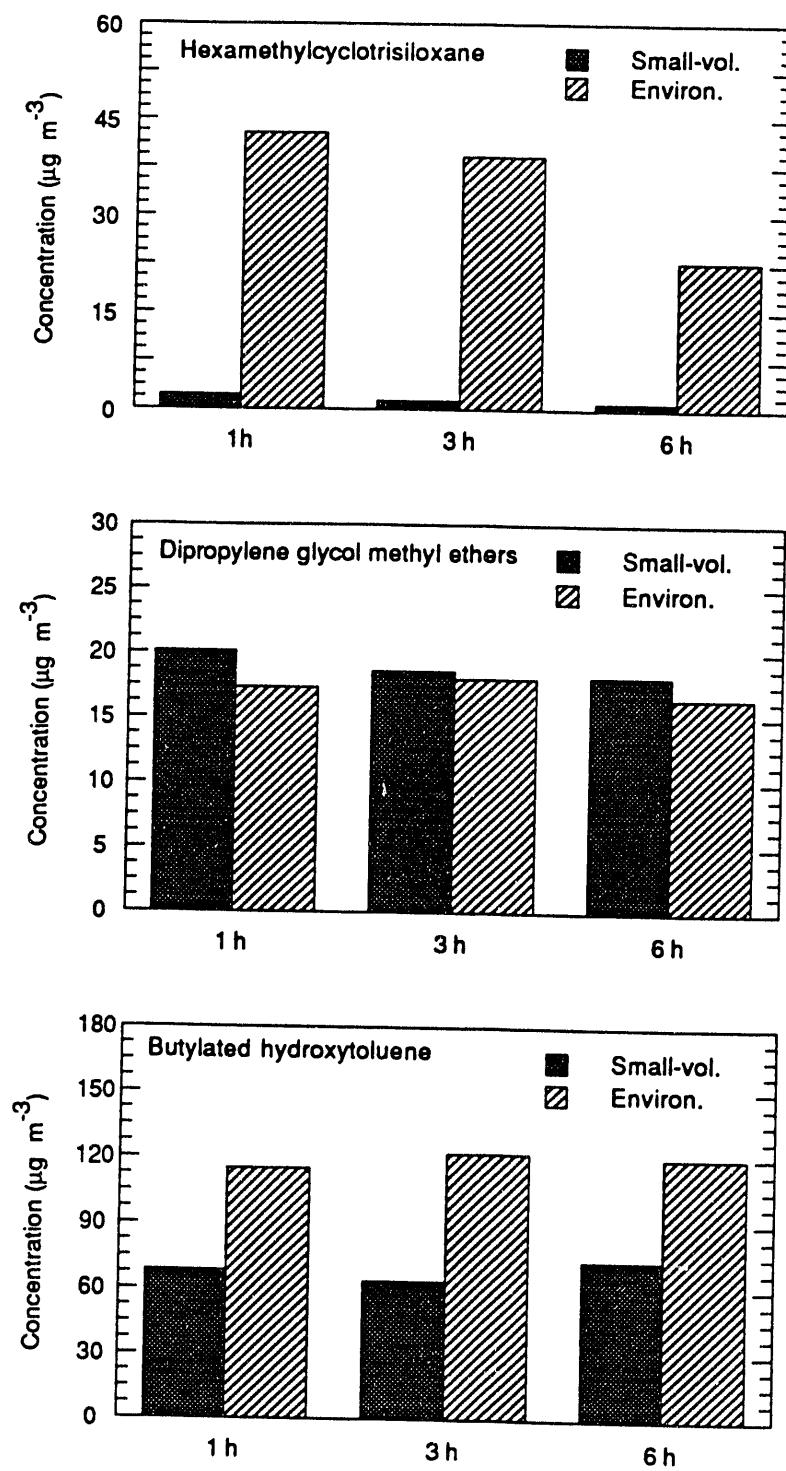


Figure 19. Comparison of the small-volume and environmental chamber concentrations at 1, 3, and 6 hours of three selected VOC emitted by Carpet 2.

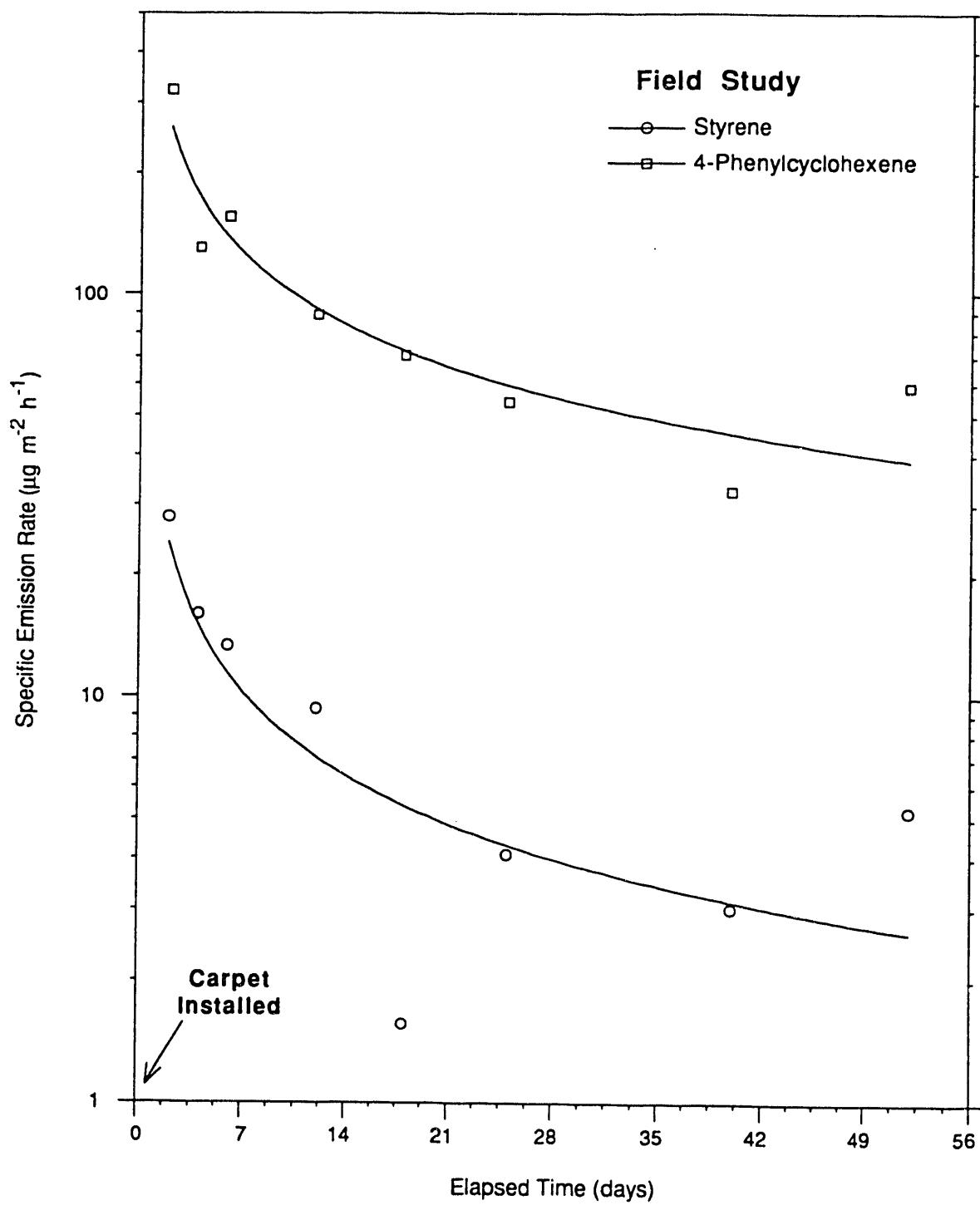


Figure 20. Quasi steady-state specific emission rates of VOC emitted by a new carpet installed in a house.

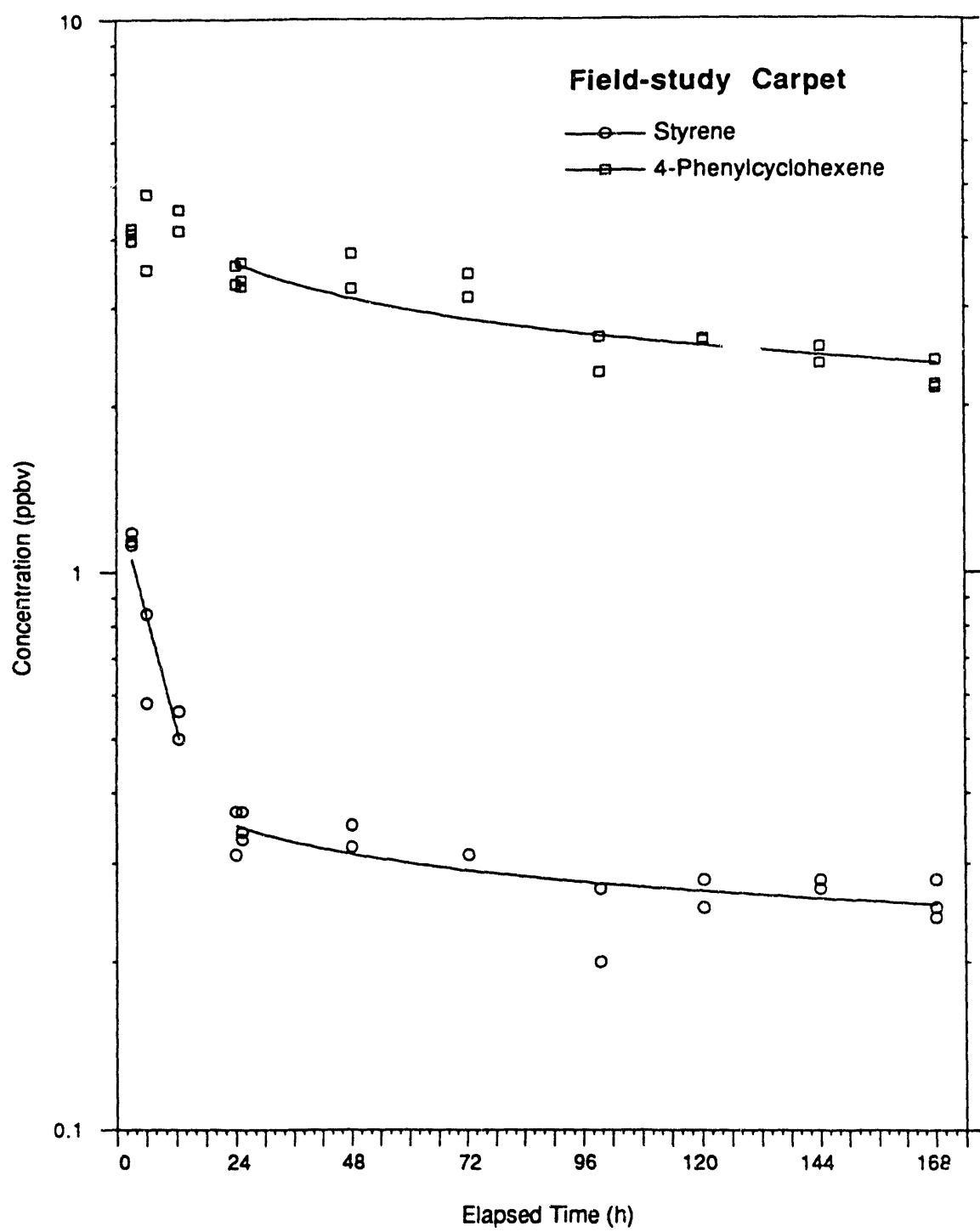


Figure 21. Chamber concentrations of VOC emitted over one week by the field-study carpet.

END

DATE
FILMED

12 / 8 / 92

