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EXPOSURE TO METHYLENE CHLORIDE FROM CONTROLLED USE OF A PAINT REMOVER IN RESIDENCES

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ABSTRACT

A recent laboratory investigation characterized personal exposures to methylene chloride (CH_2Cl_2) for simulated typical uses of paint removers and aerosol finishes containing CH_2Cl_2 in a room-size environmental chamber at two ventilation rates. Because paint removers produced relatively large exposures to CH_2Cl_2 in these experiments, the present investigation was undertaken to measure exposures to CH_2Cl_2 for standardized use of a paint remover in a variety of residential environments. A total of 21 experiments were conducted outdoors and indoors in a garage, a basement workshop, and large and small rooms of a house. In the indoor work areas, ventilation patterns and rates were varied by opening windows and doors and by the use of a household fan. Finishes were removed from uniformly-prepared panels and from chairs. The personal exposure of the worker was determined from the continuous measurement of CH_2Cl_2 concentration in a pumped breathing-zone sample.

Personal exposures resulting from the outdoor use of paint remover were very low (6-36 ppm·h). Exposures resulting from the use of paint remover indoors without mechanical exhaust ventilation were considerably higher (190-2090 ppm-h). In each indoor location, an open window or exterior door reduced exposures by one half relative to the closed condition. Exposures were greatly reduced by a fan placed near the work area and exhausting out through an open window or door (11-142 ppm·h).

A single-equation mass-balance model was used to produce estimates of theoretical exposures for experiments conducted indoors. The efficacy of the model for predicting exposures was evaluated by comparing theoretical and measured personal exposures. The model performed best for small-volume work areas with low ventilation rates. In general, the model had an accuracy of ±50 percent when applied to experiments conducted in enclosed work areas without an exhaust fan.

Key Words: Breathing zone, consumer product, indoor air quality, mass-balance model, methylene chloride, paint remover, personal exposure, residences, source strength, ventilation rate

INTRODUCTION

Methylene chloride, or dichloromethane (CH_2Cl_2), is used in many consumer products. It is the major constituent of most paint removers and is included in the formulation of a number of aerosol products such as paints, polyurethane finishes, pesticides, and lubricants.

There is concern about consumers' exposures to CH_2Cl_2 because of a variety of adverse health effects that can result from inhalation of high concentrations of this chemical. These health effects include neurologic toxicity (dizziness, nausea, headache), carbon monoxide poisoning leading to anoxic stress (Stewart *et al.*, 1972), and pulmonary edema (Buie *et al.*, 1986). In addition, a National Toxicology Program inhalation bioassay found "clear evidence of carcinogenicity" of CH_2Cl_2 in rats and mice (National Toxicology Program, 1985).

Paint removers probably have the highest potential for toxic exposure to CH_2Cl_2 among the various consumer products because they typically contain a high percentage of the chemical. For example, use of paint removers in poorly ventilated spaces was shown to result in concentrations of CH_2Cl_2 that exceeded occupational guideline concentrations of 100 and 500 ppm for 8-h work periods established by the American Conference of Governmental Industrial Hygienists and by the U.S. Occupational Safety and Health Administration, respectively (Otson *et al.*, 1981; Girman and Hodgson, 1986). This comparison of consumer product use to occupational guidelines lends perspective to the observed concentrations but is not considered a health assessment.

Since concentrations of CH_2Cl_2 during use of paint removers are often high and the work periods often have relatively long durations, the resulting personal exposures to CH_2Cl_2 can be quite high. Controlled use of paint removers on standard panels in a 20-m^3 (706-ft^3) environmental chamber at two ventilation rates produced exposures ranging from approximately 900 ppm·h to over 2000 ppm·h for 90-minute work periods (Girman and

Two different substrates were selected for finish removal to represent typical consumer refinishing projects. In the majority of the experiments, finish was removed from 0.74 m^2 (8 ft^2 with dimensions 2 ft x 4 ft) panels of plywood painted on one side with a primer coat and two finish coats of an oil-base enamel. These painted panels had been air dried for over ten months prior to use. A set of identical, straight-back, wood chairs were used in other experiments. These chairs, which were at least several years old, were finished with a clear varnish. For finish removal, a panel was attached to a stationary metal stand which held the panel horizontally at a 45° angle with its lower edge at waist level. A chair was placed directly on the floor of the work area and was rotated and inverted as needed during finish removal.

A common household fan was used to increase ventilation rates in some experiments. This fan was a three-speed, 51-cm (20-in), five-blade appliance designed primarily for use in windows or doorways. It was operated at its highest speed setting with a power consumption of ~225 watts. It was positioned near an open window or exterior door so that it exhausted air out of the work area.

A total of 21 experiments were conducted at several outdoor and four indoor environments. These environments were selected to represent work areas that consumers' typically use for refinishing projects. In three of the indoor work areas, ventilation rates were varied by opening windows and doors and by the use of the fan.

Two of the work areas were located in a single-story house. This three-bedroom, one-bath house had a volume based on interior dimensions of 249 m^3 (8790 ft^3). It was estimated that the furniture, appliances, and other household items occupied ten percent of the volume giving a ventilated volume of 224 m^3 (7910 ft^3). A floor plan of the house showing the two work areas and two experimental arrangements is presented in Fig. 1. All windows and

experiments. Both a panel and a chair were stripped with the basement window and the door leading to the stairway closed. Three additional experiments were conducted with panels. In one, the nearby window was open (dimensions 0.38 m x 0.84 m or 1.2 ft x 2.8 ft). In another, the fan was placed in front of the open window. In the final one, the window was closed and the stairway door leading to the first floor was open (dimensions 0.72 m x 1.8 m or 2.4 ft x 5.9 ft). In this experiment, the interzonal transport of CH_2Cl_2 between the basement and the central area of the first floor was measured.

The fourth indoor work area was a single-car garage with a volume based on interior dimensions of 85.0 m^3 (3000 ft^3). It was estimated that 20 percent of the volume was occupied giving a ventilated volume of 68.0 m^3 (2400 ft^3). The floor plan and an experimental arrangement for the garage are shown in Fig. 3. Four experiments were conducted in this work area. Both a panel and a chair were stripped with all exterior openings closed. Finish was also removed from a panel with the garage door open (dimensions 2.4 m x 2.1 m or 8.0 ft x 7.0 ft). In another experiment with a panel, both the rear door (dimensions 0.79 x 2.0 m or 2.6 ft x 6.7 ft) and the garage door were open and the fan was placed on the floor halfway between the worker and the garage door.

Ventilation rates in the indoor work areas were determined by measuring tracer-gas decays. Immediately prior to an experiment, the tracer gas (SF_6) was uniformly mixed in the work area by injecting pure gas with a syringe in front of a small, hand-held fan. Mixing was continued with the fan for approximately five minutes after the injection was completed. Experimental conditions were established by opening a window and/or doors if required; the fan was turned off; and concentrations of SF_6 in a sample drawn from a stationary point at a height of 1.5 m near the substrate were measured at 1-min intervals with a gas chromatograph equipped with an electron capture detector. Decay was measured over the dynamic range of the instrument or until the experiment was completed. In experiments with high ventilation rates, one or more decays were measured prior to initiation of the work period. However,

Analog output signals from the spectrometer and its associated pressure transducer and thermocouple were sampled with a data acquisition system (Series 500, Keithly/DAS, Boston, MA) at a rate of one point per second. Analog output signals from the other instruments were sampled with this system at a rate of twelve points per minute. These data were stored on magnetic diskettes for subsequent reduction and analyses.

Preparations for an experiment were made while the spectrometer and gas chromatograph were being calibrated. The substrate was positioned in the work area (see Figs. 1-3 for indoor environments). A 2-kg electronic balance was located so that it was readable by an observer. A product container, a 1-L can, a 7.6-cm wide brush, a 7.6-cm wide scraper, cloths, and a thin polyethylene sheet were taken into the work area and individually weighed. The polyethylene sheet was placed under the substrate to collect scrapings.

After calibrations and preparations were completed, tracer gas was injected (indoor work areas only) and ventilation-rate measurements and data acquisition were initiated. The worker put on disposable coveralls and entered the work area. The worker next put on a pressure-demand breathing apparatus with full face mask (Model 801548-02, Scott Aviation, Lancaster, NY) and Viton gloves. Monitoring of the breathing-zone sample for CH_2Cl_2 was initiated, and the worker began the application procedure. All of the worker's activities were recorded by an observer positioned outside of the work area.

Paint remover was used according to the instructions on the container label. The procedure was the same as that used in the previous laboratory investigation (Girman and Hodgson, 1986). The container was shaken; a portion of the product was transferred to the 1-L can: and the can and application brush were weighed. Thick coats of product were sequentially applied to the substrate using single brush strokes in one direction only. The details of the entire paint removal procedure for panels were as follows: (1) paint remover was applied to the first quarter of the panel, and the can and brush were weighed; (2) after the

$$dC = PaC_o\,dt + \frac{S}{V}dt - (a + k)\,C\,dt \qquad (1)$$

where: C = indoor pollutant concentration (ppm or mg m^{-3});

C_o = outdoor pollutant concentration (ppm or mg m^{-3});

P = fraction of the outdoor pollutant level that penetrates the enclosed space (unitless);

a = ventilation rate in air changes per hour (h^{-1});

S = indoor pollutant source strength (mL h^{-1} or mg h^{-1}, 1 mg h^{-1} = 1.67×10^{-5} g min^{-1});

V = volume (m^3);

k = net rate of removal processes other than ventilation (h^{-1});

t = time (h).

Assuming C_o, P, S, a, and k are constant over the time period of interest, Equation 1 can be solved for C(t) to give:

$$C(t) = \frac{PaC_o + S/V}{a + k}\left[1 - e^{-(a+k)t}\right] + C(0)\,e^{-(a+k)t} \qquad (2)$$

For the application of a consumer product in an enclosed space, the theoretical exposure (ppm·h) received by an occupant of the space to a pollutant emitted by the product can be derived from Equation 2 by a second integration over the time interval of the work period. Assuming that C_o is negligible and the C(0) equals zero at the start of product application, integration of Equation 2 with respect to time from the start of product application (t=0) to the completion of product application ($t=t_1$) with constant S, a, and k yields:

The bedroom had a ventilation rate of only 0.13 h^{-1} with the windows and interior door closed. In the experiment with the interior door open, there appeared to be a substantial flow of air between the bedroom and the rest of the house. This flowrate, which is driven primarily by temperature differentials, is difficult to determine, but can be greater than the flowrate of outdoor air supplied to the whole house (Sandberg, 1984). With the interior door closed and the window open, the ventilation rate for the room increased by a factor of twelve over the closed condition. The ventilation rate of 18.7 h^{-1} with the interior door open and the fan exhausting out through the open window was 144 times higher than the ventilations rate when the room was closed.

The closed basement workshop was a relatively leaky room with a ventilation rate of 1.6 h^{-1}. This relatively high ventilation rate may not be atypical for a basement since in many houses ventilation rates for basements exceed ventilation rates for the occupied floors (B. Turk, LBL, personal communication). The ventilation rate increased by a factor of three with the window open. With the fan exhausting out through the open window and no other window or door open, there was a seven-fold increase in ventilation rate over the completely closed condition.

The garage, which was also a leaky structure, had a ventilation rate of 2.1 h^{-1} with the garage and rear doors closed. With the garage door open, there was a factor of five increase in ventilation rate. With the rear door also open and the fan placed on the floor half-way between the garage door and the panel and exhausting out, there was a nine-fold increase in ventilation rate over the completely closed condition.

Changes in ventilation rate with changes in operating conditions were greatest in the bedroom primarily because of its small volume and low ventilation rate when closed. However, the ventilation rates achieved in the bedroom and the garage with the fan were nearly identical. The ventilation rate in the basement with the fan on was lower, perhaps,

these conditions approached or were lower than some exposures measured outdoors. The fan was less effective in reducing exposure in the basement where there was no large opening for cross ventilation.

In each indoor work area, personal exposures were always reduced by an increase in ventilation rate. However, the effect of ventilation rate on exposure was often nonlinear. This was particularly noticeable in the bedroom where a factor of twelve increase in ventilation because of the open window resulted in only a two-fold reduction in exposure. The nonlinear effect of ventilation rate in the bedroom was due to the short duration of the work period relative to the time required to reach steady-state concentrations particularly at the low ventilation rate (Girman and Hodgson, 1986). In locations where ventilation rates were higher, steady-state concentrations were quickly approached, and increased ventilation rate had a more linear effect on exposure. For example, in the basement workshop, the open window produced a factor of three increase in ventilation rate and a similar decrease in personal exposure.

In all four experiments conducted outdoors, exposures were low and generally inversely related to average wind speed with the lowest and highest exposures occurring at the highest and lowest wind speeds, respectively. The profile of breathing-zone concentration for the experiment which resulted in the highest outdoor exposure of 36 ppm·h is included in Fig. 4.

Modeling

The total mass of product applied to the substrate was calculated for each experiment (Tables 1-3). This mass was the sum of the differences between the before and after weights of the 1-L can plus brush for the eight applications of paint remover. The mean and standard deviation was 406 $\pm$ 35 g for the 17 experiments with panels and 382 $\pm$ 73g for the four experiments with chairs.

panels were derived from these concentrations and are presented in Table 1. Profiles of theoretical concentrations for indoor experiments with panels are shown in Fig. 5.

Theoretical exposures were compared to measured personal exposures. For the twelve experiments (including two chamber experiments) with panels in which ventilation-rate measurements were made, the difference between theoretical and measured exposures ranged from -381 to 278 ppm·h. The absolute errors were within 150 ppm·h for nine of these experiments and were within 100 ppm·h for six experiments. The largest absolute errors occurred in experiments in the dining area, the closed basement, and the bedroom with the window open. On a relative basis, three of the twelve experiments had theoretical exposures within 10 percent of personal exposures, five had theoretical exposures within 25 percent of personal exposures, and eight had theoretical exposures within 50 percent of personal exposures. The best relative agreement was obtained for experiments in the chamber and the closed bedroom. These three experiments were conducted in a small volume with a low or controlled ventilation rate. The worst relative agreement was obtained for experiments in the bedroom with the fan on and in the garage with the door open and the fan either on or off. However, the absolute differences between the theoretical and personal exposures were small ($\leq$100 ppm·h). The poor relative agreement for these experiments with high ventilation rates may have been largely due to a lack of good mixing. The model also did not do a good job of predicting personal exposure for the experiment conducted in the dining area when the volume and the ventilation rate for the whole house were used in the calculation probably because the gradient between breathing-zone concentration and the average-volume concentration for the whole house was large. Using the estimated ventilated volume of the dining area/family room/kitchen and assuming that the ventilation rate for this area was the same as the ventilation rate for the whole house, the theoretical exposure was 592 ppm·h which was 103 percent of the measured exposure.

Theoretical exposures were compared to measured personal exposures for the four experiments with chairs (Table 3). When the ventilated volume for the whole house was used in the calculation for the experiment in the dining area, the model significantly underpredicted exposure. However, when the ventilated volume of the dining area/family room/kitchen was used, the model results were 503 ppm·h and 115 percent of the measured exposure. Excluding the experiment in the dining area, the model on an absolute basis predicted exposures for two of three experiments within 50 ppm·h; on a relative basis, the model overpredicted exposures by 21 percent on average.

Interzonal Transport

Use of a paint remover in a residence can expose occupants other than the worker to CH_2Cl_2 if CH_2Cl_2 gets transported from the work area to the rest of the house. This interzonal transport was examined in the single-story and multi-story houses. In both houses, personal exposures that would have been received by occupants were compared to the personal exposures received by the worker.

In the multi-story house, paint removal was done in the basement workshop with the window closed and the stairway door leading to the first floor open. Concentrations at a height of 1.5 m were measured in a central location on the first floor near the stairway. The profile of breathing-zone concentration that an occupant might have been exposed to is shown in Fig. 8 along with the profile of breathing-zone concentration for the worker in the basement measured in another experiment with the window and the interior door closed (concentrations in the basement with the interior door open were not measured but would have been lower). It took approximately 20 minutes before measurable concentrations were recorded in the living area of the house. These concentrations seemed to peak at about 110 minutes. The personal exposure for this period was 67 ppm·h. If the decay portion of the

ventilation rates. The highest exposure of 2090 ppm·h was probably above the range of most consumers' exposures for a comparable work period since the irritant effects and odor from the high concentrations (>2000 ppm) may not be tolerable to most individuals without breathing protection. In the work areas included in this study, an open window or exterior door increased ventilation rates by a factor of three to twelve and reduced exposures by approximately one half relative to the closed condition. Exposures were greatly reduced by the use of a fan placed near the work area and exhausting out through an open window or door (range 11-142 ppm·h). Exposures when using the fan were similar to those measured in experiments conducted outdoors if a large-area opening for cross ventilation was provided. Although exposures were always reduced by an increase in ventilation rate, the relationship was often nonlinear with less reduction in exposure than would be predicted by assuming steady-state conditions. This nonlinearity was most evident in the work area with the lowest ventilation rate because the time required to achieve steady-state concentrations was long relative to the duration of the work period.

The effect of substrate type on exposure to CH_2Cl_2 was evaluated by removing finish from chairs and from flat panels. When small differences in ventilation rate, work period duration, and source strength were accounted for, there remained an unexplained difference in exposures resulting from the use of paint remover on chairs versus use on panels. Exposures from use of paint remover on chairs were 70 percent, on average, of exposures from equivalent use on panels.

The transport of CH_2Cl_2 from the work area to the rest of a house when interior doors were open was investigated to evaluate the potential exposure of occupants versus the exposure of the worker. In experiments conducted in a multi-story and a single-story house, occupants would have received exposures that were 16 and 37 percent, respectively, of the exposures received by the worker during the work period.

The biggest deficiency of the mass-balance model was that it greatly underpredicted exposures for experiments conducted in a relatively large-volume, open-area of a house. Theoretical exposures for finish removal from both a panel and a chair in the dining area of the house were only one-third of actual exposures. The model did not work well in this situation because the average volume concentration for the whole house was low and not representative of the concentration in the immediate work area. When the volume of the dining area/family room/kitchen was used in the calculations, the theoretical exposures agreed well with the measured exposures. However, since the exchange rates among areas of the house were unknown, it was assumed in these calculations that the work area had the same ventilation rate as the whole house. Even though the assumption seems to be valid in this case, it is not always justified. In the same house when the interior door was open to the bedroom, there appeared to be a substantial exchange between the room and the rest of the house.

In conclusion, the single-equation mass-balance model is most useful for predicting exposures in relatively small, enclosed work areas where concentrations and exposures will be the highest. These areas are typically well mixed so that average-volume concentrations are representative of breathing-zone concentrations. On the other hand, the model will underpredict, often significantly, exposures in relatively large, irregularly-shaped work areas and in work areas that are open to the large volume of a house. In these work areas, mixing is not uniform and concentrations in a given location are determined by interzonal air flowrates. A multi-chamber model could be used to predict concentrations in interconnected zones of a house. However, interzonal air flowrates must be known. These are difficult to determine and are inherently variable, but can be estimated from tracer-gas concentrations measured under controlled conditions (Maldonado and Woods, 1983).

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Table 2. Personal Exposure to CH_2Cl_2 from outdoor use of paint remover on panels.

Wind Speed ($m\ s^{-1}$)	Relative Wind Direction	Work Period (min)	Mass of Product Applied (g)	CH_2Cl_2 Source Strength ($g\ min^{-1}$)	Personal Exposure (ppm·h)
2.2	Rear	90	384	3.07	6
2.0	Side	87	441	3.57	16
1.8	Side	88	360	3.25	12
0.9	Front	87	458	3.03	36

Table 4. Composition of paint remover by weight.

Component	Weight Composition (%)
Non-volatile	4.0 ± 0.0[a]
Methanol	3.1 ± 0.3
Ethanol	7.4 ± 0.2
CH_2Cl_2	78.6 ± 10.4
Ethylbenzene	0.7 ± 0.1
Xylenes	2.9 ± 0.4
TOTAL	96.7

[a]Mean ± 1 standard deviation for triplicate analyses.

Fig. 8. Temporal profiles of breathing-zone concentrations of CH_2Cl_2 for a worker and an occupant in a multi-story and a single-story house. Each of the four experiments was conducted with a panel with an interior door open between the work area and the main living area of the house with the exception of the experiment with the worker in the multi-story house in which the interior door was closed.

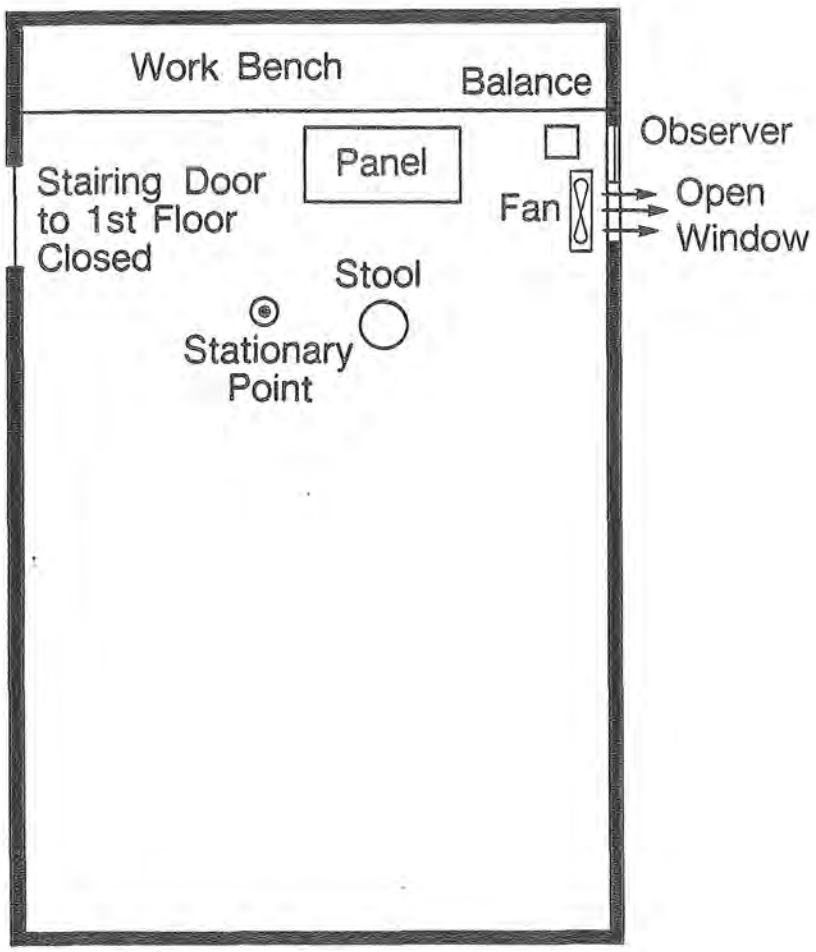

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Figure 2.

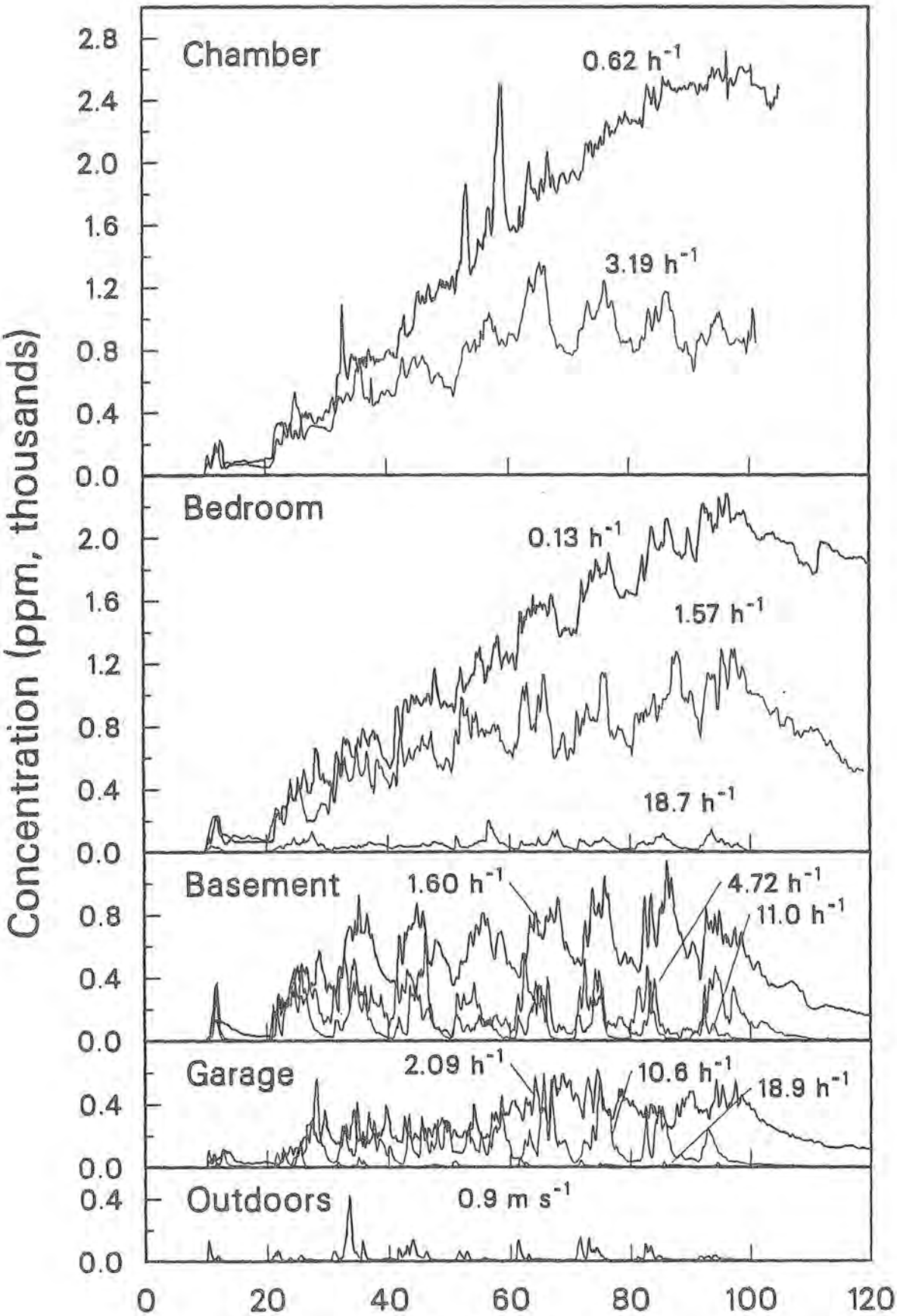

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Figure 4.

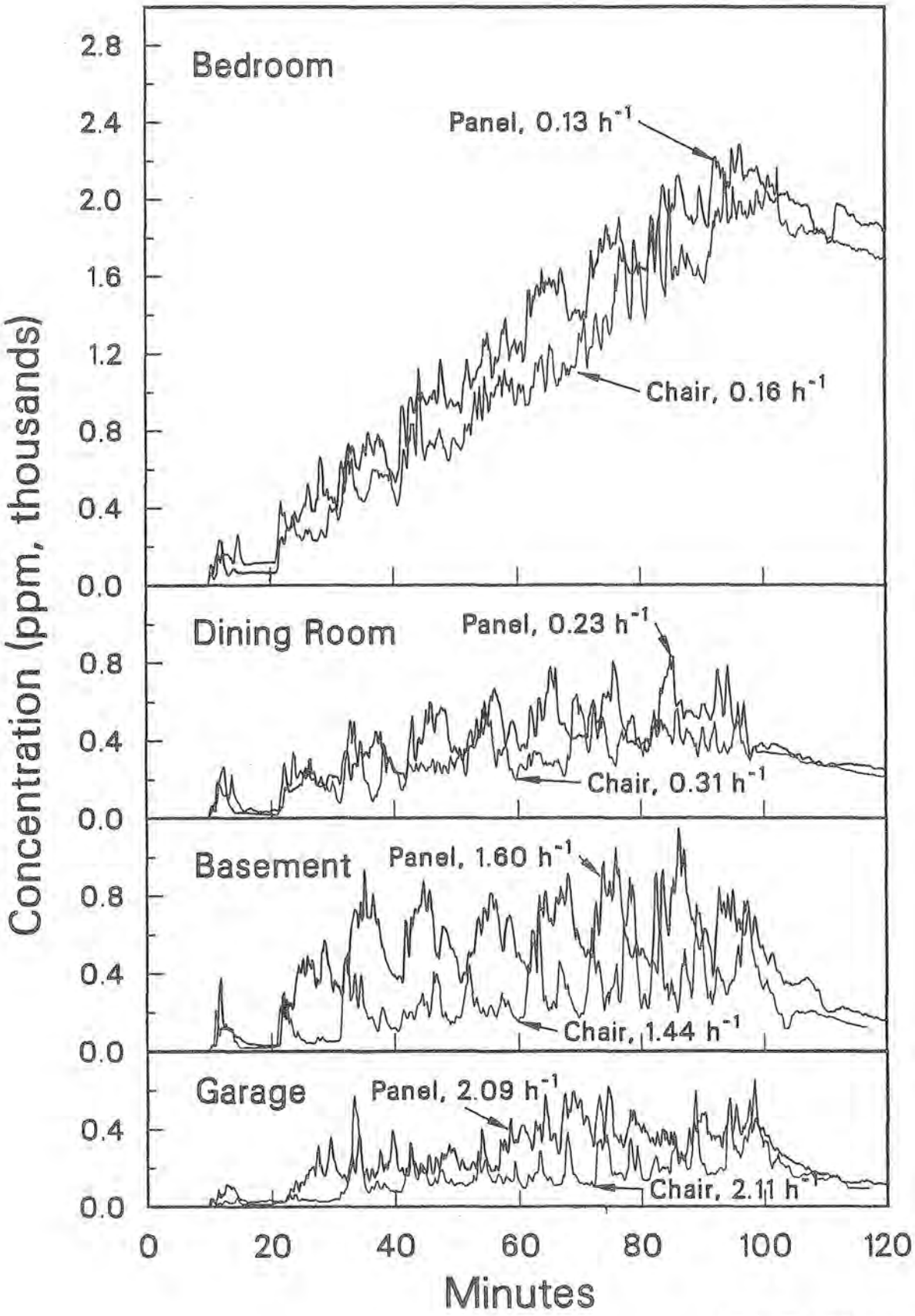

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Figure 6.

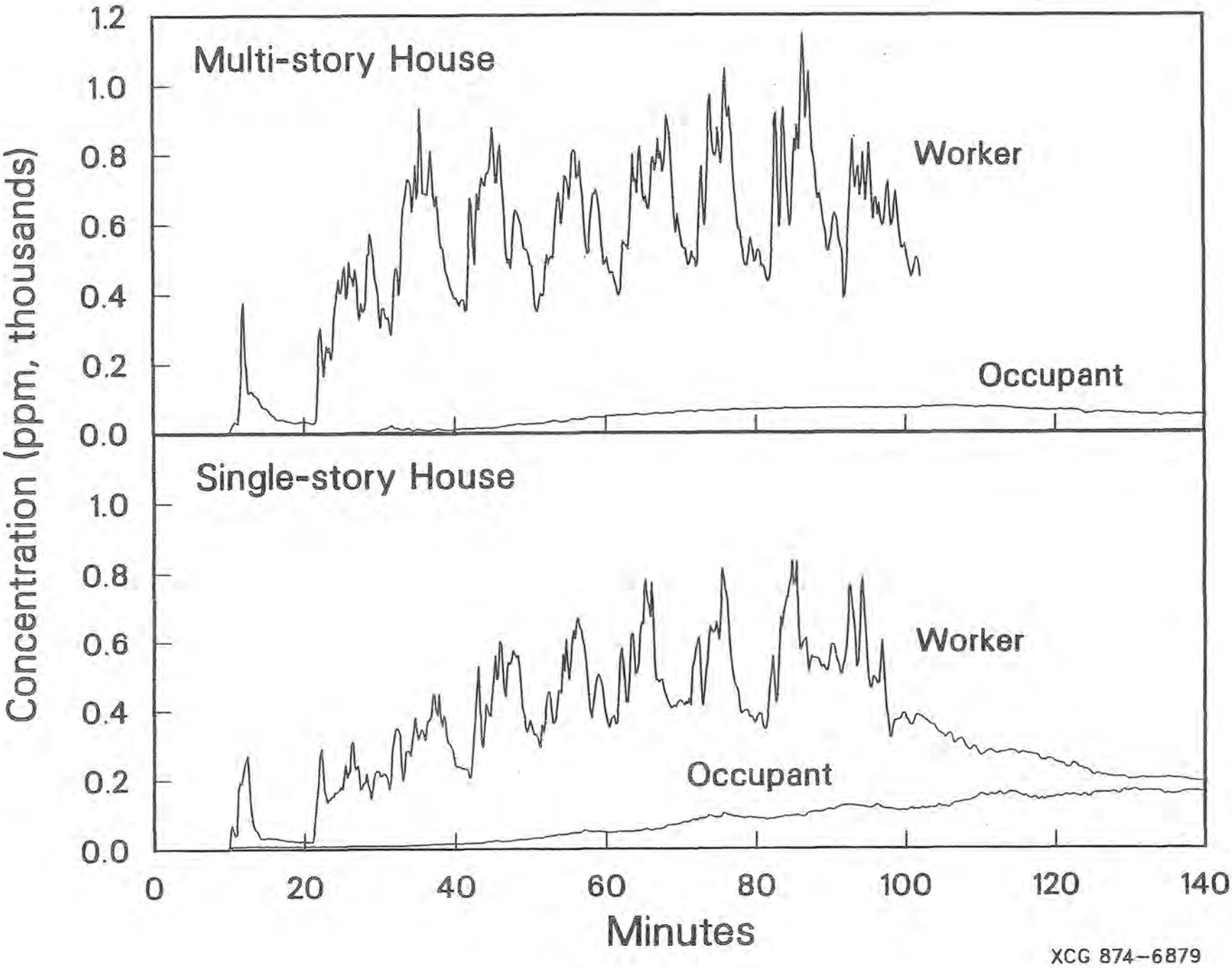
Multi-story House
Worker
Occupant
Single-story House
Worker
Occupant
Concentration (ppm, thousands)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
140
Minutes
XCG 874-6879

Figure 8.