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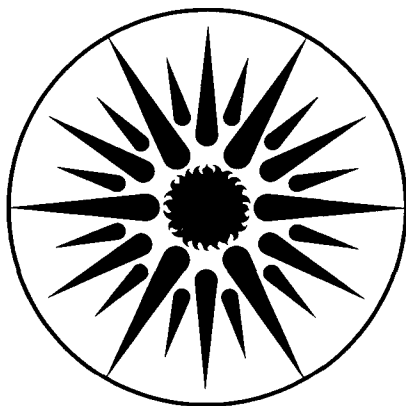
SOURCE CHARACTERIZATION AND PERSONAL EXPOSURE
TO METHYLENE CHLORIDE FROM CONSUMER PRODUCTS

J.R. Girman and A.T. Hodgson

March 1986

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Source Characterization and Personal
Exposure to Methylene Chloride from
Consumer Products

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ABSTRACT

A recently completed bioassay, which found methylene chloride (CH_2Cl_2) to be an animal carcinogen, has increased the concern about consumer exposure to this chemical. To provide information on exposures sufficient to conduct a health risk assessment, CH_2Cl_2 source strengths and personal exposures were characterized in a room-size (20 m^3) environmental chamber for representative applications of several paint removers and aerosol finishes as examples of the two major types of consumer products containing CH_2Cl_2 . For each product, experiments were conducted at ventilation rates of ~ 0.5 and ~ 3 air changes per hour. Altogether, including duplicate experiments, a total of 10 experiments were performed. Both the chamber concentration and the worker's breathing-zone concentration of CH_2Cl_2 were continuously monitored by infrared spectroscopy throughout each experiment. In addition, the source strength of CH_2Cl_2 was determined from product composition and the quantity of product used. Measured personal exposures resulting from the use of paint removers ranged from 1040 to 1200 $\text{ppm}\cdot\text{h}$ at the high ventilation rate and from 1970 to 2400 $\text{ppm}\cdot\text{h}$ at the low ventilation rate for work periods of ~ 90 min. Personal exposures from the use of aerosol finishes ranged from 32 to 35 $\text{ppm}\cdot\text{h}$ for a single coat of a polyurethane finish and 121 to 124 $\text{ppm}\cdot\text{h}$ for two coats of a metallic paint for work periods of 23 min or less. Several occupational standards and guidelines for CH_2Cl_2 concentrations were exceeded during experiments with paint removers. When chamber concentrations of CH_2Cl_2 were integrated over the work periods and compared to measured personal exposures, agreement was good at the low ventilation rate but measured personal exposures were higher by 21% at the high ventilation rate. Temporal profiles of CH_2Cl_2 concentrations were calculated from the source strengths, the ventilation rates and the chamber volume using single-equation, mass-balance models. These theoretical concentrations were in good agreement with measured concentrations. Exposure models based upon the concentration models were also developed and then evaluated by comparing theoretical and measured exposures for the experiments. The exposure models appeared to have sufficient accuracy and precision for use in assessment of consumer health risk from the use of consumer products containing CH_2Cl_2 .

Key Words: aerosol finish, consumer product, environmental chamber, exposure model, methylene chloride, modeling, paint remover, personal exposure

INTRODUCTION

Methylene chloride or dichloromethane (CH_2Cl_2) is a chemical widely used by consumers in the residential environment. In 1984, domestic production of CH_2Cl_2 in the United States was estimated by the U.S. International Trade Commission to be 607 million pounds (Greek, 1985). Approximately 30% of this CH_2Cl_2 was formulated into paint stripper/removers for both industrial and consumer use. A second major source of consumer exposure to CH_2Cl_2 occurs through its use in a variety of aerosol finishes which accounts for another 20% of CH_2Cl_2 end use.

There is concern about consumer exposure to CH_2Cl_2 from these products since CH_2Cl_2 retained in inhalation is metabolized to carbon monoxide leading to elevated levels of carboxyhemoglobin (Ratney *et al.*, 1974; Stewart *et al.*, 1972). At relatively high exposures, the resulting anoxic stress placed on individuals may pose a health hazard. In addition, a recent National Toxicology Program inhalation bioassay found "clear evidence of carcinogenicity" of CH_2Cl_2 in female rats and in both sexes of mice as well as "some evidence of carcinogenicity" in male rats (National Toxicology Program Board of Scientific Counselors Peer Review Panel, 1985).

Because information about consumer exposures to CH_2Cl_2 from the use of paint removers and aerosol finishes was inadequate, an investigation was undertaken to measure exposures under controlled conditions and to develop a theoretical model from the data which would allow extrapolation of exposures to other conditions. Experiments were conducted with several paint removers and aerosol finishes in a room-size environmental chamber at two ventilation rates. Exposures to CH_2Cl_2 were characterized from continuous measurements of both breathing-zone and chamber concentrations. The source strengths of CH_2Cl_2 were determined for the products and were applied to a single-equation, mass-balance model for predicting exposures. The resulting theoretical exposures were compared to measured exposures.

EXPERIMENTAL

Consumer Products

Two brands of non-flammable, semi-paste paint removers and two aerosol finishes (a metallic paint and a clear polyurethane finish) were selected as the sources of CH_2Cl_2 . For each product, all containers used for analyses and experiments were from the same manufacturer's lot.

The percent weight compositions of the non-volatile fractions of the products were determined by air drying aliquots of the products. For paint removers, ~40 g of product was weighed into an uncovered petrie dish and dried in a fume hood with occasional stirring until constant weight was obtained (10-15 days). For aerosol finishes, the product container was weighed and shaken; ~15 g of product was sprayed into an empty 35-L polyethylene bag; the container was reweighed; the bag was suspended in a fume hood in an open position; and the contents were dried for five days before re-weighing.

The major compounds comprising the volatile fractions of the products were identified by gas chromatography/mass spectrometry (GC/MS) analysis of gas phase samples. After identification of the major compounds, the percent weight compositions of these compounds were determined by analysis of gas-phase samples by capillary gas chromatography with flame ionization detection (GC/FID). For paint removers, ~50-100 mg of sample was weighed onto foil and immediately transferred to a 2-L flask with septum cap. The flask was heated at 65°C for 1 h. Samples were withdrawn from the flask with a gas-tight syringe. For aerosol finishes ~0.4 g of sample was sprayed, through a hypodermic syringe needle attached to the spray nozzle, into a preweighed, empty 8-L gas-sampling bag. The bag was reweighed, filled with a known volume of clean air, heated at 65°C for 30 min and sampled with a gas-tight syringe. Gas standards for quantitative analysis of volatile compounds were prepared by injecting aliquots of solvent mixtures into 2-L flasks with septum caps (Riggin, 1984). Partial pressures of analytes in all gas mixtures were kept well below their maximum values at room temperature.

The base substrates for application of products were 0.74-m² (1.22 m x 0.61 m) panels of 1.27 cm thick plywood. For application of paint removers, the panels were painted by roller on one side with a primer coat and two finish coats of an oil-based enamel. Panels for spray paint application were painted with a primer coat only. Unpainted panels were used for polyurethane finish application. All painted substrate panels were concurrently painted and dried at room conditions for over five months prior to use.

Environmental Chamber

Experiments were conducted in a 20-m³ environmental chamber located in an air-conditioned laboratory. The chamber, illustrated in Figure 1, has interior dimensions of 3.66 m (length) x 2.46 m (width) x 2.23 m (height). All interior surfaces are clad with stainless steel. The walls, floor and ceiling are insulated with a 10-cm layer of high-density polyurethane foam. The door and interior seams are sealed with silicone gasket material. Electrical and plumbing feedthroughs are also sealed. The ventilation rate of the chamber in air exchanges per hour due to natural ventilation is 0.03±0.01 h⁻¹. The chamber is equipped with a single-pass ventilation system. Inlet air is drawn from laboratory room air through a coarse filter by a variable speed blower. Volumetric flow rate is monitored with both orifice-plate and gas-turbine flowmeters (Model 2011-0, Daniel Industries, Inc., Houston, Texas) located in the air inlet downstream of the blower. Air enters the chamber through a diffuser positioned low at one end of a long wall and exits through an outlet located high at the opposite end of the same wall. This configuration is designed to promote mixing within the chamber while approximating typical ventilation patterns in residences. Air is exhausted outdoors. For these experiments, the chamber was operated at either ~0.5 or ~3 h⁻¹.

The volumetric flowrate of ventilation air entering the chamber was continuously monitored throughout each experiment with the gas turbine flowmeter. Calibration of this instrument was checked immediately before and after each experiment by measuring the pressure drop across the orifice-

plate flowmeter. Laboratory atmospheric pressure and the differential pressure between the turbine meter and atmosphere were also measured at these times. The temperature of the air entering the turbine meter was monitored with a thermocouple. Air temperature in the chamber was monitored with thermocouples located adjacent to five of the 15 points of the sampling grid described below. A chilled-mirror hygrometer (Model 911, EG&G, Inc., Waltham, Mass.) was used to monitor the dew point temperature of chamber air. The sampling point for the hygrometer was at the air outlet of the chamber; the sample flowrate was 1 L min^{-1} .

Air Sampling and Analysis

Chamber air was sampled continuously to obtain average volume concentrations of CH_2Cl_2 and other solvents during an experiment by drawing air from a 15-point sampling grid into a common mixing manifold and sampling line. The grid consisted of sampling points at three chamber heights: five points at the 0.31 m level; five points at the 1.14 m level; and five points at the 1.94 m level. At each height, each of four sampling points were located near a corner but more than 27 cm from any chamber surface, and the fifth sampling point was located near the center of the chamber. The total flowrate for the chamber sample was $\sim 25 \text{ L min}^{-1}$. The relative standard deviation of the flowrates among the 15 points of the sampling grid was 5%.

Air from near the breathing zone of the worker in the chamber was also continuously sampled for CH_2Cl_2 during an experiment. This air was drawn from the top of the worker's right shoulder through a single sampling line at a flowrate of $\sim 25 \text{ L min}^{-1}$. All sampling lines were Teflon®; mixing manifolds and fittings were stainless steel.

Both the chamber sample and the breathing-zone sample were continuously analyzed for CH_2Cl_2 with single-beam, variable-filter infrared (IR) spectrometers (MIRAN® IA, Foxboro Co., South Norwalk, Conn.). Spectrometers were set at an analytical wavelength of $13.3 \mu\text{m}$ and a cell pathlength of 0.75 m. Instrument cell pressures were regulated near 500 torr and were monitored with pressure transducers during calibrations and analyses. Cell temperatures were monitored with thermocouples.

The IR spectrometers were calibrated using certified-grade CH_2Cl_2 gas standards of 500 and 5000 ppm $\pm 1\%$ in air (Scientific Gas Products, Inc., South Plainfield, N.J.) dynamically mixed with dry air to desired concentrations by an electronic mass-flow-controlled dilution system. Multi-point calibrations over the required analytical range were performed immediately before and after each experiment.

Since toluene, with an analytical wavelength of $13.7 \mu\text{m}$, is found in many aerosol finishes, interference by toluene in the analysis of CH_2Cl_2 at $13.3 \mu\text{m}$ was evaluated. At a CH_2Cl_2 /toluene mass ratio of one, no interference in the analysis of CH_2Cl_2 was observed for the instrument used for the chamber sample, while a 5% positive interference was measured for the instrument used for the breathing-zone sample. No correction was made for this interference. Because the IR adsorption bands for water vapor are 2.66 , 2.74 and $6.27 \mu\text{m}$, water vapor was not expected to interfere. To confirm this, multi-point calibrations were conducted using a closed-loop calibration system over a CH_2Cl_2 concentration range of zero to 665 ppm and humidities ranging from 7 to 83% RH at room temperature. As expected, no interference by water vapor was observed.

The chamber sample was also periodically analyzed for CH_2Cl_2 , as well as for other major solvents, with a GC/FID (Model 3700, Varian Instrument Co., Palo Alto, Calif.) equipped with a 10-port heated sample valve, a glass capillary column (SPB-5, 30 m x 0.75 mm ID, $1.0 \mu\text{m}$ film; Supelco, Inc., Bellefonte, Penn.), and a chromatographic data system (Model 3000K, Nelson Analytical, Inc., Cupertino, Calif.). A portion of the sample gas stream was drawn through a sample loop (0.25 or 0.5 cm^3) at $90 \text{ cm}^3 \text{ min}^{-1}$ regulated by a downstream mass-flow controller. Samples were injected onto the chromatographic column at ~ 15 min intervals throughout an experiment. Sample loop temperature and pressure at the time of injection were recorded. Gas standards consisting of a mixture of the compounds of interest for a given experiment were prepared in 2-L flasks (Riggin, 1984). These standards were analyzed using the same procedure employed for samples. A multi-point calibration was performed immediately prior to each experiment, and at least one standard was analyzed at the conclusion of each experiment.

Data Acquisition

Analog output signals from the IR spectrometers and their associated pressure transducers and thermocouples were sampled with a data acquisition system (Series 500, Keithly/DAS, Boston, Mass.) at a rate of 1 point s^{-1} . Analog output signals from the turbine meter, dewpoint hygrometer, mass flow controllers and the other thermocouples were sampled with this system at a rate of 12 points min^{-1} . These data were stored on magnetic diskettes for subsequent analyses.

Safety

A pressure-demand breathing apparatus with full face mask (Model 801548-02, Scott Aviation, Lancaster, N.Y.) was worn during all experiments by the worker in the chamber. This mask was supplied by an air cylinder external to the chamber. The total breathing air usage was measured for each experiment. Disposable coveralls were worn during all experiments, and Viton[®] gloves were worn when working with paint removers.

Procedure

The environmental chamber was operated for at least 1 h prior to each experiment during which time it was stabilized at the desired temperature ($24 \pm 3^{\circ}C$), relative humidity ($50 \pm 10\%$), and ventilation rate (0.5 or 3 h^{-1}). Chamber temperature and humidity were controlled by adjusting laboratory conditions. During the stabilization period, the analytical instruments and the gas turbine meter were calibrated as described above. Preparations for product application were also completed during this time. The appropriate substrate panel was attached to a metal stand which held the panel horizontally at a 45° angle with its lower edge at waist level. The panel was positioned against the chamber wall opposite the air vents and with its face toward the center of the chamber (Figure 1). A 2-kg electronic balance (Model PE 2000, Mettler Instr. AG, Greifensee, Switzerland) was positioned in the chamber so that it was readable from the observation window in the chamber door. An unopened product container and, for experiments with paint removers, a 1-L can, a 7.6-cm wide brush, 7.6-cm

and 3.2-cm wide putty knives, cloths, and a thin polyethylene sheet, were taken into the chamber and individually weighed. The polyethylene sheet was placed under the work area. For experiments with aerosol finishes, both the chamber floor and the wall that the panel was positioned against were protected from overspray with an unweighed polyethylene sheet.

After calibrations were completed and the chamber had stabilized at the desired conditions, the worker entered the chamber and the door was sealed. Monitoring of the chamber concentration of CH_2Cl_2 by IR spectroscopy was initiated, and a sample of chamber air for GC-FID analysis was obtained. The worker's activities were monitored through the chamber window and recorded by an observer. At a signal from the observer, the worker put on the breathing apparatus and attached the breathing-zone sampling line. Monitoring of the breathing-zone sample for CH_2Cl_2 was initiated, and the worker began the application procedure.

All products were used according to the manufacturers' instructions printed on the container labels, except for minor deviations in the case of paint remover B. Paint remover B was left undisturbed for times as short as 10 min, rather than the 10-15 min recommended by the manufacturer. The manufacturer also recommended that the stripped surface be washed with a steel-wool pad dipped in a "paint remover wash". This was not done. These deviations were deemed minor and there was no observable difference in the performance of paint remover B relative to paint remover A.

For paint removers, the original 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 panel surface using single brush strokes in one direction only. The details of the entire paint removal procedure were as follows: (1) paint remover was applied to the first quarter of the panel, the can was covered and the can and brush were weighed; (2) after the remover had remained undisturbed on the first quarter for 10 min, remover was applied to the second quarter of the panel and the can and brush were weighed; (3) softened paint was scraped from the first quarter with the putty knives, and paint scrapings were collected on the polyethylene sheet. This sequence was repeated until each

quarter of the panel had been stripped twice. During the periods between scraping and the next application of product, the worker usually sat on a stool in the chamber corner near the air inlet. The vertical stratification of CH_2Cl_2 at the center of the chamber was measured during several experiments. For these measurements, the worker connected an extension to the breathing-zone sampling line and held it for 1-2 min each at the low, middle, and high grid points in the center of the chamber. Upon completion of the measurements, the sampling line extension was removed, and paint removal activities were resumed. At the conclusion of the final stripping, the worker wiped the panel with a cloth and weighed all containers and tools. The polyethylene sheet was folded with all paint scrapings inside and also weighed. The breathing-zone sampling line was disconnected, and laboratory air outside the chamber was monitored for CH_2Cl_2 concentration with the IR spectrometer previously used for the breathing-zone sample. The worker then gathered all containers, tools, and the folded sheet and quickly exited the chamber while the breathing apparatus supply line was disconnected. Monitoring of chamber air by IR spectroscopy and periodic analyses of chamber air by GC/FID continued until the chamber concentration of CH_2Cl_2 decayed to 10 ppm or for no more than 2 h after the worker exited the chamber. The sheet with the paint scrapings was spread out in an unused room with continuous mechanical ventilation. The scrapings were allowed to dry overnight, and the sheet with the dry scrapings was reweighed. The tools were also air dried overnight and reweighed.

For aerosol finishes, the product container was vigorously shaken for at least 1 min prior to use, and then the product was sprayed with even horizontal strokes onto the substrate surface from a distance of ~30 cm. Two coats of the metallic paint were applied with a 14-min drying period between coats. During this period, the worker weighed the product container and then sat on a stool near the air inlet. Only a single coat of the polyurethane finish was applied since the manufacturer's recommended drying time between successive coats was 3 h. Immediately, after each use of either product, the aerosol nozzle was cleared by inverting the container and spraying for several seconds. After the final application, the worker weighed the product container, waited from 3-12 min, then made preparations to exit the chamber. For two experiments, the vertical stratification of

CH₂Cl₂ was measured as described above just prior to the exit. All sampling and analytical procedures were the same as described for experiments with paint removers.

The work period for experiments with paint removers was defined as the time between the initial pouring of the product into the can and disconnecting the breathing-zone sampling line prior to the worker's exit from the chamber. For experiments with aerosol finishes, the work period was defined as the time between the initial shaking of the product container and disconnecting of the breathing-zone sampling line.

MODELING

A single-equation, mass-balance model which describes the average volume concentration of a pollutant in an enclosed space (Turk, 1963) was used to calculate theoretical temporal concentration profiles of CH₂Cl₂ in the chamber for all experiments. The model has been used in evaluating a variety of indoor air pollution sources (Traynor et al., 1985). It assumes that exfiltrating air and indoor air have the same average pollutant concentrations. The mathematical expression for the change in indoor pollutant concentration is:

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

where:

- C = indoor pollutant concentration (ppm or mL m⁻³);
- C_o = outdoor pollutant concentration (ppm or mL 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);
- V = volume (m³);
- k = net rate of removal processes other than ventilation (h⁻¹);
- t = time (h).

Assuming C_0 , P , S , a , and k are constant over the time period of interest, Equation 1 can be solved for $C(t)$ to give:

$$C(t) = \frac{PaC_0 + S/V}{a + k} [1 - e^{-(a+k)t}] + C(0) e^{-(a+k)t}. \quad (2)$$

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. Assuming that C_0 is negligible and that $C(0)$ 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:

$$\int_0^{t_1} C(t) dt = \frac{St_1}{(a+k)V} - \frac{S}{(a+k)^2 V} [1 - e^{-(a+k)t_1}] \quad (3)$$

which reduces to:

$$\int_0^{t_1} C(t) dt = \frac{St_1}{(a+k)V} - \frac{C(t_1)}{(a+k)} \quad (4)$$

The first term on the right side of Equations 3 and 4 is the exposure that would be received by the occupant at steady-state conditions, and the second term is a correction to the steady-state exposure which accounts for the time required to reach steady-state conditions and is, therefore, inversely proportional to the pollutant removal rate ($a+k$).

Equations 3 and 4 are only applicable for determining an occupant's exposure while the source term, S , remains constant, i.e., the source is still

actively emitting the pollutant. Once product application stops and the source term returns to zero, the pollutant concentration will begin to decay as determined by the pollutant removal rate. A general solution for exposure which covers the periods of both pollutant emission and decay is:

$$\int_0^{t_2} C(t)dt = \int_0^{t_1} C(t)dt + \int_{t_1}^{t_2} C(t)dt$$

$$= \frac{St_1}{(a+k)V} - \frac{C(t_1)}{(a+k)} e^{-(a+k)(t_2 - t_1)} \quad (5)$$

where the source is emitting at a constant rate from $t=0$ to $t=t_1$ with constant a and k and then immediately decreases to and remains at zero from $t=t_1$ to $t=t_2$.

RESULTS AND DISCUSSION

Product Composition

The percent weight compositions of the components of the four products are shown in Table 1. The compositions of the volatiles in paint removers are averages of three or four analyses; all other compositions are averages of duplicate analyses. Precision estimates are shown as standard deviations. As determined by our analysis, the percent weight composition of the volatile fraction of the metallic paint was 136%. For purposes of comparison, the percent weight compositions of the volatile compounds from the analysis of this product were multiplied by one minus the fractional composition of non-volatiles and divided by 1.36 to yield a total weight composition of 100% for the product. The relatively low precision and the inaccuracy in the analysis of the volatile compounds in the aerosol finishes were due, in part, to the small sample aliquots which were difficult to weigh accurately and which may not have been uniformly representative of the contents of the product containers. By our analyses, the two aerosol

finishes contained, by weight, 26-27% CH_2Cl_2 , 32-33% aliphatic hydrocarbon propellants (butanes), and differing percentages of toluene. The polyurethane finish also contained unquantified aliphatic hydrocarbon thinners. Product composition data printed on the aerosol container labels are presented in Table 1 for comparison. Our analytical results for the metallic paint agreed well with the manufacturer's data. However, by our analysis, the polyurethane finish contained toluene, which was not reported by the manufacturer, and higher percentages of CH_2Cl_2 and propellants.

The compositions of the two semi-paste paint removers were similar to each other. They contained 83-87% CH_2Cl_2 by weight and small percentages of several alcohols. The non-volatile component of the paint removers was only 3-4% of the total weight.

Environmental Data

A total of 10 exposure experiments were conducted in the environmental chamber. Each of the four products was used at both the high ($\sim 3 \text{ h}^{-1}$) and low ($\sim 0.5 \text{ h}^{-1}$) ventilation rates. In addition, duplicate experiments were conducted for one paint remover and one aerosol finish at the high ventilation rate.

The environmental data for the work periods of the 10 experiments are summarized in Table 2. Average values for mechanical ventilation rate, spatially-averaged air temperature, and relative humidity were calculated for each minute of each experiment from the raw data, and these were averaged over the work periods. An average volumetric respiration rate, in air changes per hour, was calculated for each experiment from the total volume and time of breathing air use. In Table 3, the respiration rates were added to the mechanical ventilation rates to obtain the total ventilation rates for the work periods.

Mechanical ventilation rates and air temperatures were stable during all experiments, and temperatures ($23.4\text{-}24.8^\circ\text{C}$) were similar in all experiments. However, considerable variation in relative humidity occurred both within and among experiments. This variation was due to changes in

atmospheric conditions, to limited humidity control and to differences in respiration and perspiration rates. The highest respiration and perspiration rates occurred during the use of paint removers because of the physical exertion of scraping paint. The result was high water vapor concentrations which, in low ventilation rate experiments, decayed slowly.

CH₂Cl₂ Concentrations

Quantitative data for CH₂Cl₂ were obtained by GC/FID from the periodic analyses of the chamber sample. All of the concentrations measured with GC/FID during the experiments were compared to concentrations measured concurrently with the IR spectrometer used for the chamber sample. The relationship between the two variables was defined with Bartlett's three-group method for regression (Sokal and Rohlf, 1969) which is an appropriate method when both variables are subject to measurement error. Concentration of CH₂Cl₂ measured by GC/FID, Y, was related to concentration measured by IR spectroscopy, X, by the equation $Y = 1.31X - 40.8$. The good fit of the regression line to the data was indicated by a 95% confidence interval of 1.30-1.32 for the slope. When the relationship between the variables was examined by product type, the concentrations were related by the equation $Y = 1.29X - 5.8$ for experiments with paint removers and by the equation $Y = 1.17X - 27.7$ for experiments with aerosol finishes. The better agreement between the analytical methods with aerosol finishes was due, in part, to the relatively low concentrations in these experiments.

Attempts to identify the source(s) of the difference between the analytical methods were unsuccessful. As a check on the accuracy of the IR data, the IR spectrometers were calibrated using the alternate method of injecting liquid standards into a closed-loop calibration system. Calibration curves obtained by this method were identical to those obtained by the dilution of the calibration gas standards. Because (1) these calibrations agreed, (2) the GC/FID was calibrated by a less direct method, and (3) the IR spectroscopic data were conservative, concentrations of CH₂Cl₂ in air measured by IR spectroscopy were used throughout this paper except where noted.

Temporal profiles of CH_2Cl_2 concentrations determined by IR spectroscopy are presented in Figures 2-4 for three representative experiments: Experiments 2 and 4 (Figures 2 and 3) with paint remover B at the high and low ventilation rates, respectively; and Experiment 6 (Figure 4) with the metallic paint at the high ventilation rate. Profiles of CH_2Cl_2 concentrations for all experiments are presented in Appendix A.

Concentration fluctuations in chamber air (nine for paint removers and one or two for aerosol finishes) created by the sequential use of the products were very evident in experiments involving the use of paint removers at the high ventilation rate and aerosol finishes at both ventilation rates. In the case of paint removers used under conditions of low ventilation, these fluctuations are much less evident, though still distinguishable, probably due to slower release of CH_2Cl_2 (true for paint removers in general) combined with better mixing of chamber air and slower decay at the low ventilation rate.

In general for all experiments, the breathing-zone concentrations of CH_2Cl_2 while the worker was applying or working with the product were higher than the chamber concentrations. However, during rest periods, when the worker usually sat on a stool near the air inlet for the chamber, the breathing-zone concentrations tended to converge on and track the chamber concentrations. Although not immediately evident from an examination of the figures due to differences in the vertical scale, breathing-zone concentrations during these rest periods were generally within 100 ppm of chamber concentrations; only rarely did the difference exceed 200 ppm. On a relative basis, differences were generally less than 10% and in some instances much less than 10% during rest periods.

Concentrations of CH_2Cl_2 produced by the use of aerosol finishes were much lower than those produced by the use of paint removers because much less CH_2Cl_2 was used (Table 3). Peak chamber concentrations were ~190 ppm for experiments with the polyurethane finish and ranged from 430 to 590 ppm for experiments with the metallic paint with peak breathing-zone concentrations averaging approximately 50% higher.

The peak chamber concentrations of CH_2Cl_2 produced by the use of paint removers were high and ranged from 950 ppm (Experiment 1) to 3000 ppm (Experiment 4). Peak breathing-zone concentrations averaged approximately 30% higher than peak chamber concentrations, reaching a maximum of 3300 ppm in Experiment 4.

However, it must be noted that these concentrations are specific to the chamber volume, the chamber ventilation rate and the amount of product used. In actual practice, the concentrations produced by consumer use of these products will depend upon variations in these parameters.

Ideally, the concentrations of CH_2Cl_2 in these experiments should be evaluated against established indoor air quality guidelines or standards. However, there are no non-occupational indoor air quality guidelines for CH_2Cl_2 . Because of this lack, concentrations of CH_2Cl_2 in this study were compared to occupational air quality standards. Such a comparison may not be appropriate due to differences in the composition of the population that is exposed, occupational versus consumer (Albert, 1983). Nevertheless, the comparison is useful because it lends perspective to the observed concentrations. The U.S. Occupational Safety and Health Administration (OSHA) has set occupational standards for CH_2Cl_2 : 500 ppm for the 8-h time-weighted average concentration; and 1000 ppm for the acceptable ceiling concentration with a maximum exposure of 5 min in any 2 h but never to exceed 2000 ppm (U.S. Government, 1985). The Threshold Limit Values (TLV) for CH_2Cl_2 are 100 ppm for the 8-h time-weighted average concentration (TLV-TWA) and 500 ppm for the 15 min time-weighted average concentration (TLV-STEL), not to be repeated more than four times per day with at least 60-min between exposures (American Conference of Governmental Industrial Hygienists, 1984). It should be noted that there currently is a proposal to delete the TLV-STEL for CH_2Cl_2 . It should also be noted that these guidelines were developed on the basis of acute health effects (American Conference of Governmental Industrial Hygienists, 1980) and do not reflect recent bioassays which have shown evidence of carcinogenicity.

As illustrated by Figures 2 and 3, both the 100-ppm and 500-ppm concentration levels were exceeded in all experiments involving the use of

paint removers. Once exceeded, concentrations remained above these levels throughout the remainder of the work periods. In addition, these levels were reached relatively quickly, e.g., at the low ventilation rate the 500-ppm level was reached less than 22 min after opening the product container and at the high ventilation rate in less than 27 min. Both the 1000 ppm and the 2000 ppm OSHA standards were exceeded in the low ventilation rate experiments and, again, once exceeded, remained above these levels for the remainder of the work periods.

In the case of aerosol finishes, the 100-ppm level was also quickly exceeded within minutes of the start of application. However, the 500-ppm level was exceeded only in experiments in which two coats of the metallic paint were applied. In addition, the durations in which personal concentrations remained above the 500-ppm level were short, less than 15 min.

The vertical stratification of CH_2Cl_2 at the center of the chamber was measured during three experiments with paint removers and two experiments with metallic paint (Figures 3 and 4, and Appendix A). In the high ventilation rate experiments with both a paint remover and the metallic paint, concentrations of CH_2Cl_2 were approximately 30% higher at the 0.31 m level than at the 1.14 m and 1.94 m levels which were similar. However, these differences were similar to the short-term temporal fluctuations in breathing-zone concentrations. Variations in CH_2Cl_2 concentration with chamber height were more pronounced at the low ventilation rate. For measurements made near the middle of the work period of experiments with the paint removers and near the end of the work period with the metallic paint, concentrations were 40-60% higher at the 0.31 m level than at the 1.14 m and 1.94 m levels which, again, were similar. In this case, these differences were larger than the temporal fluctuations in breathing-zone concentrations. However, near the conclusion of the work period with a paint remover, the vertical stratification had almost completely dissipated.

CH_2Cl_2 Exposures

Personal exposures to CH_2Cl_2 in the 10 experiments were determined by

integrating the temporal profiles of breathing-zone concentrations over the previously defined work periods. For these calculations, breathing-zone concentrations during the periods of stratification measurements (~4 min duration) were averages of the breathing-zone concentrations immediately preceding and following those measurements, rather than the concentrations from the stratification measurements. The personal exposures are shown in Table 3 along with the durations of the work periods and the masses of products and CH_2Cl_2 used. Exposures to CH_2Cl_2 were considerably higher from the use of paint removers than from the use of the aerosol products due to the longer work periods and the greater masses of CH_2Cl_2 used. The highest personal exposures (1970 and 2400 ppm·h) occurred as the result of paint remover use at the low chamber ventilation rate. Between the two aerosol finishes, application of two coats of the metallic paint resulted in the highest personal exposures; however, these exposures were approximately a factor of 10 lower than the personal exposures from the use of paint removers. The variation in personal exposures between duplicate experiments was 7% for the paint remover and 2% for the metallic paint.

Additionally, to determine whether chamber concentrations could be used to estimate personal exposures, the temporal profiles of chamber concentrations were integrated over the work periods to produce chamber exposures, and these were compared to the measured personal exposures (Table 3). At high ventilation rates, measured personal exposures were consistently higher than chamber exposures by an average of 21%, while at low ventilation rates, the two exposures were equivalent in three of four experiments. The mean of the ratio of personal exposure to chamber exposure for high ventilation rate experiments (1.21 ± 0.06 , $n=6$) was compared to this ratio for low ventilation rate experiments (1.05 ± 0.08 , $n=4$) with a Student's t-test and found to be significantly different ($t=2.48$, $0.05 > P > 0.02$).

The good agreement of personal exposures to exposures estimated from chamber concentrations in the low ventilation rate experiments presumably resulted from the relatively good mixing of air that occurred because of the long residence times for chamber air under these conditions. At higher ventilation rates, the air in the chamber may have been less well mixed,

producing the discrepancy between the measured and estimated personal exposures.

The effectiveness of increasing the ventilation rate as a means of reducing exposures to CH_2Cl_2 was evaluated for the two types of product. For the experiments with paint removers, the high ventilation rates were approximately five times greater than the low ventilation rates. However, the exposures calculated from the chamber concentrations of the high ventilation rate experiments averaged 43% of the exposures for the low ventilation rate experiments, far different from the 20% of the exposures predicted from simple steady-state assumptions. A similar effect of changes in ventilation was exhibited by the measured personal exposures which, in high ventilation rate experiments with paint removers, averaged 51% of the personal exposures in the low ventilation rate experiments.

The non-linear effect of ventilation on exposures for experiments with paint removers was due to the relatively short duration of the experimental work periods and the difference in the time required to reach steady-state concentrations at the two ventilation rates. At the high ventilation rate, steady-state concentrations at the conclusion of the work period were ~99% of steady-state values, assuming constant use of paint remover. In contrast, concentrations at the low ventilation rate were only ~64% of steady-state values at the conclusion of the work period. If the work periods had been prolonged, concentrations at the low ventilation rate would have been higher and the ratio of exposures at the two ventilation rates would more closely approach that predicted by simple steady-state assumptions. Thus, while increased ventilation should always lead to a reduction in exposure (and peak concentration), the magnitude of the reduction in exposure will be non-linear with ventilation rate and can only be predicted by the application of mass-balance principles. This is discussed further in the subsequent modeling section.

The situation with respect to the exposures resulting from the use of the aerosol finishes differed considerably in that steady-state considerations were not applicable to these experiments. When the aerosol finishes were used, they produced a nearly instantaneous injection of

volatile compounds. This large injection was followed by the slower evaporation of compounds as the finishes dried, but this release was relatively minor.

Initially, the chamber concentration of CH_2Cl_2 in the experiments with aerosol finishes was determined by the amount of product that was used in the first application and by the volume of the chamber. The ventilation rate had little effect on this concentration, since there was insufficient time during the application period for the concentration to decay by flushing the chamber. Because the experimental work periods were short, the exposures occurred predominantly while concentrations were near their peak values and not during the more prolonged decay periods when the effects of ventilation were important. Thus, despite ventilation rates that were higher by a factor of 5.8, the exposures estimated from the chamber concentrations in the high ventilation rate experiments averaged 71% of the exposures in low ventilation rate experiments. The personal exposures in the high rate ventilation experiments averaged 83% of those in the low ventilation experiments. As these percentages indicate, ventilation was not very effective at reducing exposures to CH_2Cl_2 from aerosols finishes when the work period was short.

CH_2Cl_2 Source Strengths

For each experiment with aerosol finishes, the source strength of CH_2Cl_2 was calculated from the mass of product used, the percent weight composition of CH_2Cl_2 , and the time and duration of product use (Appendix B).

Both time-averaged and time-dependent source strengths of CH_2Cl_2 were calculated for each experiment with paint removers. First, the mass of product used in an experiment was determined from the weights of the containers, all tools, and the polyethylene sheet, as follows: (1) the initial weights of the tools and the sheet were subtracted from their final dry weights to yield the weight of the paint that was removed from the chamber; (2) the weight of the paint was subtracted from the total weight of all items at the exit from the chamber, and this difference was subtracted from the total initial weight of all items to yield the weight of product

that was volatilized; and (3) the weight of the product volatilized was divided by the percent weight composition of the volatile fraction of the product to yield the total mass of product used. The time-averaged source strength was calculated from the total mass of product used, the percent weight composition of CH_2Cl_2 in the product (Table 3), and the duration of the work period (Table 4). The time-dependent source strength for each experiment with paint removers was estimated by normalizing the mass of product used in each successive application (determined from the sequential weighing of the brush and can) by the total mass of CH_2Cl_2 volatilized during an experiment and by assuming: (1) that the source strength of CH_2Cl_2 from a section of panel was the same during application and scraping of that section; and (2) that the source strength was negligible when the product was not being worked. The second assumption is based on the long drying times for relatively undisturbed paint removers as noted in the description of methods for determining the non-volatile fraction of these products.

Figure 5 shows the estimated time-dependent source strength of CH_2Cl_2 along with the time-averaged source strength for Experiment 2, a high ventilation rate experiment with paint remover B. The estimated mass of CH_2Cl_2 volatilized during an event is the product of the source strength and duration of the event. In Experiment 2, the coefficient of variation for the mass of CH_2Cl_2 used in the eight successive applications was 16%. For all five experiments, with paint removers the coefficient of variation for the mass of CH_2Cl_2 used in the eight applications ranged from 16 to 31%. In these experiments, the duration of each application was typically ~1 min; the time required for stripping averaged ~4 min and generally decreased during the second stripping event for a given quarter. The rest periods spent near the air inlet accounted for ~38% of the work periods. The mass of product removed with the polyethylene sheet and tools at the conclusion of the work periods was 106 ± 38 g; the dry mass of paint stripped from the panels was 201 ± 8 g. Stripping the panels once, removed most of the two finish coats, exposing the primer coat and traces of bare wood. The second stripping removed virtually all of the finish coats and left only traces of primer imbedded in the grain. Time-dependent and time-averaged source strengths for all experiments with paint removers are figuratively represented in Appendix B. Although there are noticeable variations in the

source strengths with time among the five experiments, the variations are not large and all experiments are generally characterized by the regular application of product and stripping of paint.

Modeling

The mass balance model (Equation 2) was used to predict theoretical chamber concentrations of CH_2Cl_2 for each minute of each experiment. For experiments with paint removers, these calculations were made using both time-averaged source strengths and time-dependent source strengths calculated to the nearest minute. Source strengths calculated to the nearest minute were also used to predict theoretical concentrations for experiments with aerosol finishes. An outdoor pollutant concentration (C_o) of zero was used in all calculations, since CH_2Cl_2 concentrations in chamber air before the work period began and in laboratory air immediately prior to the worker's exit from the chamber were less than 10 ppm. The net rate of removal processes other than ventilation, k , was determined to be $0.07 \pm 0.02 \text{ h}^{-1}$, the average difference between the calculated and the mechanical ventilation rates for the uniform portions of the decay periods of the four low ventilation rate experiments. The temporal profiles of theoretical concentrations for Experiments 2, 4, and 6 are shown in Figures 6 - 8. Figures of theoretical concentrations for all experiments are presented in Appendix C.

The temporal profiles of theoretical chamber concentrations of CH_2Cl_2 were integrated over the work periods to produce theoretical estimates of exposures. For experiments with paint removers, the integral solution of Equation 4 was used to calculate exposures from the time-averaged source strengths. These theoretical exposures are compared in Table 4 with the exposures derived from the measured chamber concentrations.

The theoretical exposures and the measured chamber exposures for experiments with paint removers were compared with paired Student's t-tests. The exposures derived from the theoretical estimates of concentrations based on the time-dependent source strengths were not significantly different from the chamber exposures ($t=2.29$, $0.10 > P > 0.05$). However, the exposure

estimates derived from concentrations based on the time-averaged source strengths using Equation 4 were statistically higher than the chamber exposure ($t=4.94$, $0.01 > P > 0.001$). Nevertheless, the average ratios of the theoretical exposures to the chamber exposures were identical: 1.13 ± 0.13 for the exposures from the time-dependent source model; and 1.13 ± 0.07 for the exposures from the time-averaged source model.

Although there were no significant differences between the theoretical estimates of exposure based on the time-dependent source strengths and the measured chamber exposures when all of the experiments with paint removers were compared, the relationship between the two estimates of exposure was affected by ventilation rate. For both paint removers, the theoretical estimates of exposures agreed closely with the chamber exposures at the low ventilation rate but exceeded the chamber exposures at the high ventilation rate by 9% for product A and ~25% for product B. Perhaps fortuitously, the theoretical exposures agreed extremely well with the measured personal exposures (within 1% on average), which were also affected by ventilation rate.

As noted previously, while increased ventilation reduced exposures, the effect was non-linear. Using the time-averaged source strength for experiments with paint removers, theoretical exposures for the high ventilation rate (3.2 h^{-1}) experiments averaged 45% of the exposures for the low ventilation rate (0.6 h^{-1}) experiments. This compares to a measured reduction to 43% for chamber exposures and a measured reduction to 51% for personal exposures. To reiterate, the non-linear effect of ventilation was due to the relatively short duration of the work periods and the fact that concentrations at the end of the work periods were much closer to steady-state conditions at the high ventilation rate than at the low ventilation rate. This is graphically illustrated in Figures 6 and 7 by the temporal profiles of theoretical concentration for the time-averaged source strength.

Similarly, in experiments with aerosol finishes, theoretical exposures for the high ventilation rate (3.1 h^{-1}) experiments averaged 71% of the theoretical exposures for the low ventilation rate (0.5 h^{-1}) experiments.

This compares to the measured reductions to 71% for chamber exposures and the measured reductions to 83% for personal exposures.

For aerosol finishes, the good agreement between average theoretical and measured exposure reductions with ventilation rate is due, in part, to offsetting errors. For experiments with the metallic paint, the theoretical exposures underestimated the chamber exposures by 15%, and for experiments with the polyurethane finish, the theoretical exposures were as much as 30% higher than the chamber exposures. These discrepancies may have resulted from differences in drying times for the two products and from inaccuracies in the GC/FID analyses of product compositions which were previously discussed. The combined effects of product drying times and accuracies of the product analyses were evaluated by comparing the percent weight compositions of the volatile components in aerosol finishes to the respective percent weight compositions of the volatile components in chamber air. These comparisons are made in Table 5 using the quantitative GC/FID data for the three components: aliphatic hydrocarbon propellant; CH_2Cl_2 ; and toluene. For both products, the propellant was more predominant in chamber air than in the product. In addition, for the polyurethane finish, the percent weight composition of CH_2Cl_2 was considerably reduced in chamber air relative to the composition of CH_2Cl_2 in the product.

If it is assumed that the GC/FID analyses of the products and of CH_2Cl_2 in air were accurate, the observed enrichment of the propellant in chamber air relative to the aerosol products may have been due to differences in the vapor pressures of the components. The propellant, which exists only as a gas at room conditions, would have immediately entered the air while the other components which are liquids and vapors at room conditions would have evaporated from the substrate panels at rates which relate to their vapor pressures (e.g., Bennett and Myers, 1974). The fact that the propellant was most enriched and CH_2Cl_2 was depleted in the experiments with the polyurethane finish may have been due to the relatively slow drying time for this product and possible inhibition of CH_2Cl_2 evaporation due to the formation of a surface layer of polymer.

Other Compounds

Average mass ratios of volatile components in chamber air were calculated from the quantitative GC/FID data for propellant, isopropanol, CH_2Cl_2 , toluene and xylenes. For experiments with paint remover A, the mass ratio of xylenes to CH_2Cl_2 was 0.023 ± 0.010 (n=21); and for experiments with paint remover B, the mass ratio of isopropanol to CH_2Cl_2 was 0.056 ± 0.010 (n=17). For aerosol finishes (Table 5), the mass ratio of propellant to CH_2Cl_2 was 1.57 ± 0.149 (n=11) for the metallic paint and 4.02 ± 0.273 (n=3) for the polyurethane finish. The mass ratio of toluene to CH_2Cl_2 was 0.983 ± 0.053 (n=11) for the metallic paint and 0.480 ± 0.027 (n=7) for the polyurethane finish.

Chamber exposures to compounds other than CH_2Cl_2 were estimated from the mass ratios of these compounds to CH_2Cl_2 in chamber air and the chamber exposures to CH_2Cl_2 . Since the mass ratios for a given product did not vary appreciably with ventilation rate, the maximum estimated exposures to these compounds occurred in the low ventilation rate experiments. The maximum exposure to xylenes was estimated to be ~36 ppm·h for paint remover A (Experiment 5), and the maximum exposure to isopropanol was estimated to be ~190 ppm·h for paint remover B (Experiment 4). Although exposures to methanol for both paint removers and to ethanol for paint remover A could not be estimated due to the lack of quantitative data for these compounds, they would not be expected to exceed several hundred ppm·h at the low ventilation rate since the compounds were only minor constituents of the products. For the aerosol finishes at the low ventilation rate, maximum exposures to propellant were estimated to be ~310 and ~210 ppm·h for the metallic paint and the polyurethane finish, respectively. Maximum exposures to toluene for these two products were estimated to be ~73 and ~15 ppm·h, respectively.

CONCLUSIONS

In a room-size (20 m^3) environmental chamber, we measured the concentrations and determined the exposures produced by the use of several consumer products which contain relatively large amounts of CH_2Cl_2 .

Experiments were conducted with two individual products of both paint remover/strippers and aerosol finishes at chamber ventilation rates of ~ 0.5 and $\sim 3 \text{ h}^{-1}$.

When paint removers and aerosol finishes were applied to identical areas during simulated typical use, the resulting CH_2Cl_2 concentrations were higher, by far, with paint removers because of the larger amounts of CH_2Cl_2 used. While occupational guidelines may not be directly applicable to residential use of consumer products for reasons stated previously, it is notable that concentrations of CH_2Cl_2 in experiments with paint removers quickly exceeded occupational guidelines. It should also be noted that these guidelines were developed on the basis of acute health effects and do not reflect recent animal studies which have shown evidence of carcinogenicity. Although the experiments were conducted with a limited range of ventilation rates in a single chamber volume and only while stripping a single size and type of substrate, the results strongly suggest that concentrations of CH_2Cl_2 produced by paint removers are likely to be significant under many conditions of use. Concentrations of CH_2Cl_2 resulting from the use of aerosol finishes are also strongly dependent upon the conditions of use and, in some instances, could be higher than those observed in these experiments. In addition, aerosol finishes often contain relatively large percentages of compounds other than CH_2Cl_2 (e.g., toluene), and the health risks from these compounds should also be considered.

The measured chamber concentrations of CH_2Cl_2 were integrated to provide estimates of personal exposure. These estimates agreed closely with the measured personal exposures when the ventilation rate was low. However, when the ventilation rate was high, the measured personal exposures averaged 21% higher than estimated exposures. Although some vertical stratification of concentrations occurred for both product types at both ventilation rates, this stratification did not appear to affect exposure estimates.

Exposures to CH_2Cl_2 were reduced by increasing the ventilation rate. However, the observed effect of ventilation rate on exposures was non-linear. When paint removers were used, increasing the ventilation rate by approximately a factor of five only reduced exposures derived from chamber

concentrations to 43% of the exposures at the low ventilation rate. When aerosol finishes were used, increasing the ventilation rate by approximately a factor of six only reduced exposures to 71% of the exposures at the low ventilation rate.

Further reductions in exposure would be achieved by the use of a ducted exhaust directly over the work area or by the use of the products outdoors. However, because the worker is so close to the source when using the products, significant reductions in exposure might be difficult to achieve. This was indicated in experiments with all products, in which increased ventilation had measurably less effect on personal exposures than on exposures derived from chamber concentrations. Further experimentation would be necessary to determine the effect of other use conditions on reducing exposures.

Single-equation, mass-balance ventilation models for predicting chamber concentrations were employed and evaluated. In the case of paint removers, two models were utilized. The first is based upon a time-averaged source strength for the entire work period. The second model is based upon a time-dependent source strength which accounts for variations in sequential applications of product. Concentrations appeared to be predicted within 10-15% with the first model when product applications were uniform and regular. The second model, which gave even better results, is most applicable when the condition of uniform and regular product use is not met.

We also developed and tested exposure models for predicting exposures from source strength data. These models are derived from the models for concentration. Again, the first model is based upon a time-averaged source strength and the second upon a time-dependent source strength. For paint removers, both models overestimated exposures calculated from chamber concentrations by an average of 13%, but, perhaps fortuitously, both models predicted personal exposures within $\pm 1\%$. The concentration and exposure estimates calculated by the models for aerosol finishes were less accurate than those calculated for paint removers. However, this appeared to be due to inaccuracies in the product analyses and the resulting estimates of source strengths rather than to deficiencies in the models. Reductions in

exposure by increased ventilation were predicted with good accuracy by application of the exposure model which uses the time-averaged source strength, indicating that the model can be used for other product use scenarios to predict reductions in exposure with ventilation increases.

Both models appeared to have sufficient accuracy and precision for use in the estimation of consumer exposure to CH_2Cl_2 from the use of consumer products containing CH_2Cl_2 . A field validation to confirm the applicability of the exposure models to the residential environment is currently underway. This study will examine the effects of variations in volume, ventilation patterns and rates, and product use patterns on the predictive capabilities of the models.

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Table 1. Composition of products by weight

Component	PERCENT WEIGHT COMPOSITION (%)					
	Paint Removers		Metallic Paint		Polyurethane Finish	
	A	B	Manufact.	Our Analysis	Manufact.	Our Analysis
Non-volatile	3.6±0.1 ^a	2.8±0.1	8.6	9.8±0.1	26.9	21.4±0.0
Aliphatic HC Propellant	--	--	35.0	31.7±4.4	23.3	33.2±4.2
Methanol	p ^b	P	--	--	--	--
Ethanol	7.5±0.5	--	--	--	--	--
Isopropanol	--	9.4±0.5	--	--	--	--
CH ₂ Cl ₂	83.0±5.9	86.6±4.0	26.3	25.8±4.0	20.8	26.9±3.4
Toluene	--	--	30.1	32.7±2.8	--	6.8±3.4
Xylenes	P	--	--	--	--	--
Aliphatic HC Thinner	--	--	--	--	28.9	P
TOTAL	>94.1	>98.8	100	100 ^c	99.9	>88.3

^aPrecision estimates are ±1 standard deviation.

^bP=present but not quantified

^cBy analysis percent composition of volatiles was 136%; percent compositions of individual volatiles were normalized to yield 100% total weight composition.

Table 2. Summary of environmental data during work periods

Product ^a	Exp. No.	Elapsed Time (min)	Ventilation Rate		Average Temp. (°C)	Atmos. Pressure (torr)	Relative Humidity (%)
			Mechanical (h ⁻¹)	Respiration ^b (h ⁻¹)			
PR-A	1	90	3.05±0.02 ^c	0.14	24.1±0.2	738.6	53.6±3.9
	5	86	0.52±0.01	0.10	24.8±0.4	739.7	56.5±10.6
PR-B	2 } ^d	89	3.05±0.01	0.18	23.6±0.1	741.2	52.7±4.5
	3 }	91	3.04±0.03	0.16	24.1±0.1	743.6	44.0±1.6
	4	88	0.51±0.01	0.12	24.7±0.4	745.9	68.3±10.4
MP	6 } ^d	23	3.05±0.01	0.05	23.6±0.1	742.0	39.3±0.9
	7 }	21	3.05±0.01	0.07	23.7±0.1	743.5	41.7±0.7
	8	23	0.50±0.01	0.04	23.4±0.2	740.0	48.0±3.7
PF	10	10	3.01±0.01	0.10	24.0±0.0	742.8	41.5±0.5
	9	14	0.50±0.00	0.03	24.1±0.1	742.4	44.6±0.7

^aPR=paint remover; MP=metallic paint; PF=polyurethane finish

^bAdditional ventilation contributed by breathing apparatus

^cPrecision estimates are ±1 standard deviation.

^dDuplicate experiments

Table 3. Personal and chamber exposures to CH₂Cl₂

Product ^a	Exp. No.	Total Vent. Rate (h ⁻¹)	Work Period (min)	Mass used Product ^b (g)	CH ₂ Cl ₂ (g)	Personal Exposure (ppm·h)	Chamber Exposure (ppm·h)	Pers.Exp./ Chamber Exp. (%)
PR-A	1	3.19	90	316 ^c	262 ^c	1040	889	117
	5	0.62	86	325	270	1970	1970	100
PR-B	2 } ^d	3.23	89	363	314	1120	921	122
	3 }	3.20	91	389	337	1200	1010	119
	4	0.63	88	385	333	2400	2350	102
MP	6 } ^d	3.10	23	151	38.9	124	103	120
	7 }	3.12	21	161	41.6	121	103	118
	8	0.54	23	150	38.6	160	137	117
PF	10	3.11	10	72.8	19.6	31.6	23.9	132
	9	0.53	14	58.5	58.5	35.2	35.5	99.2

^aPR=paint remover; MP=metallic paint; PF=polyurethane finish

^bAverage density of paint removers was 1.18 g cm⁻³.

^cApproximate value since some product was spilled during application

^dDuplicate experiments

Table 4. Theoretical exposures to CH₂Cl₂

Product ^a	Exp. No.	Total Vent. Rate (h ⁻¹)	CHAMBER EXPOSURE				
			Theoretical		Measured (ppm·h)	Theor. Exp./Meas. Exp.	
			Time-dependent Source (ppm·h)	Time-averaged Source ^b (ppm·h)		Time-dependent Source (%)	Time-averaged Source (%)
PR-A	1	3.19	972	944	889	109	106
	5	0.62	1900	2100	1970	96.4	107
PR-B	2 } ^c	3.23	1180	1110	921	128	121
	3 }	3.20	1240	1200	1010	123	119
	4	0.63	2530	2600	2350	108	111
MP	6 } ^c	3.10	88.5	--	103	85.9	--
	7 }	3.12	85.7	--	103	83.2	--
	8	0.54	120	--	137	87.6	--
PF	10	3.11	31.2	--	23.9	130	--
	9	0.53	45.0	--	35.5	127	--

^aPR=paint remover; MP=metallic paint; PF=polyurethane finish

^bBased on Equation 4 (see text)

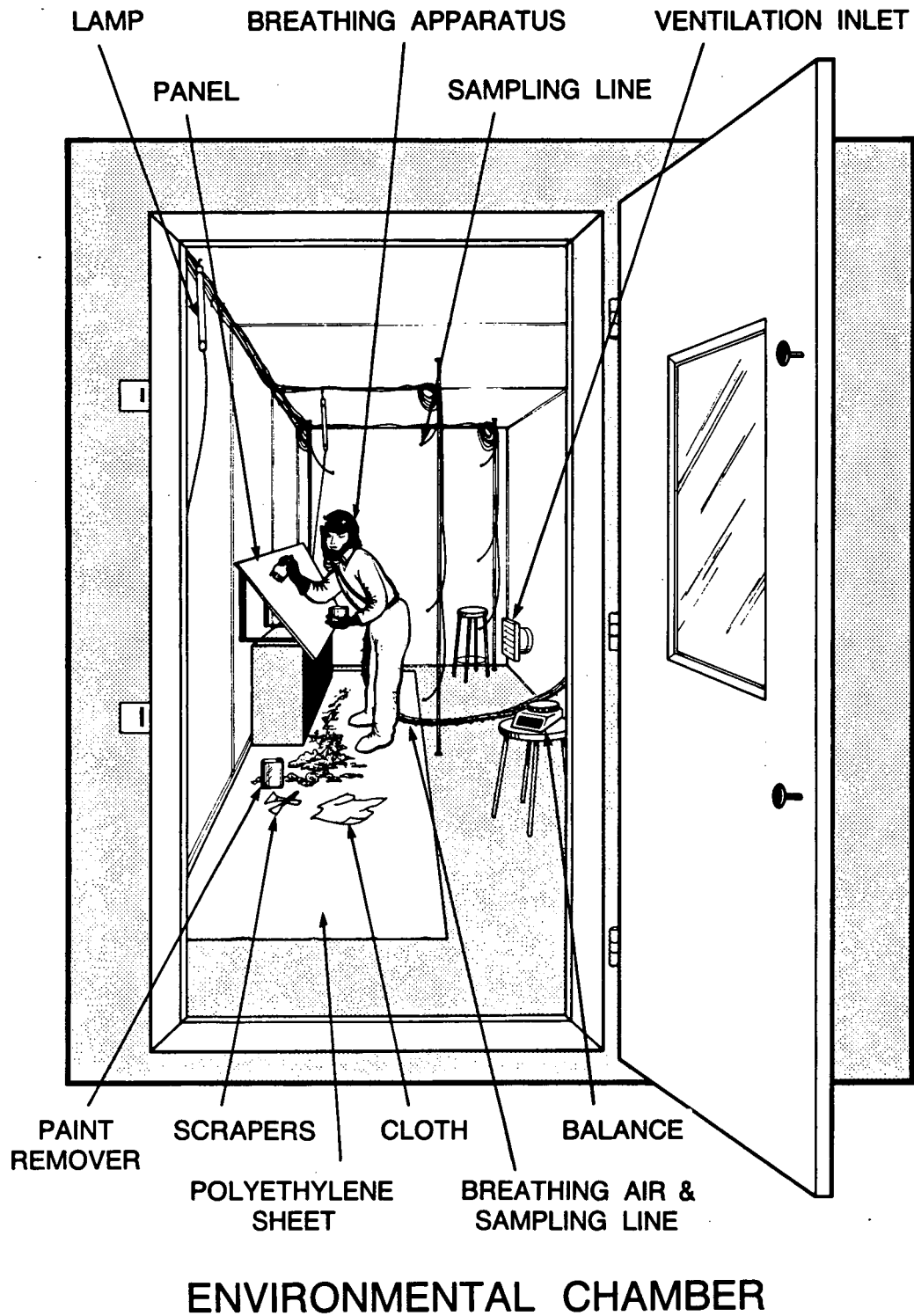
^cDuplicate experiments

Table 5. Percent weight compositions of propellant, CH₂Cl₂, and toluene in chamber air

Component	PERCENT WEIGHT COMPOSITION (%)			
	<u>Metallic Paint</u>		<u>Polyurethane Finish</u>	
	Product	Chamber air ^a	Product	Chamber Air ^a
Aliphatic HC Propellant	31.7±4.4 ^b	39.4±2.0	33.2±4.2	48.8±0.8
CH ₂ Cl ₂	25.8±4.0	25.2±1.3	26.9±3.4	12.1±0.6
Toluene	32.7±2.8	25.6±1.2	6.8±0.4	6.0±0.3
TOTAL	90.2	90.2	66.9	66.9

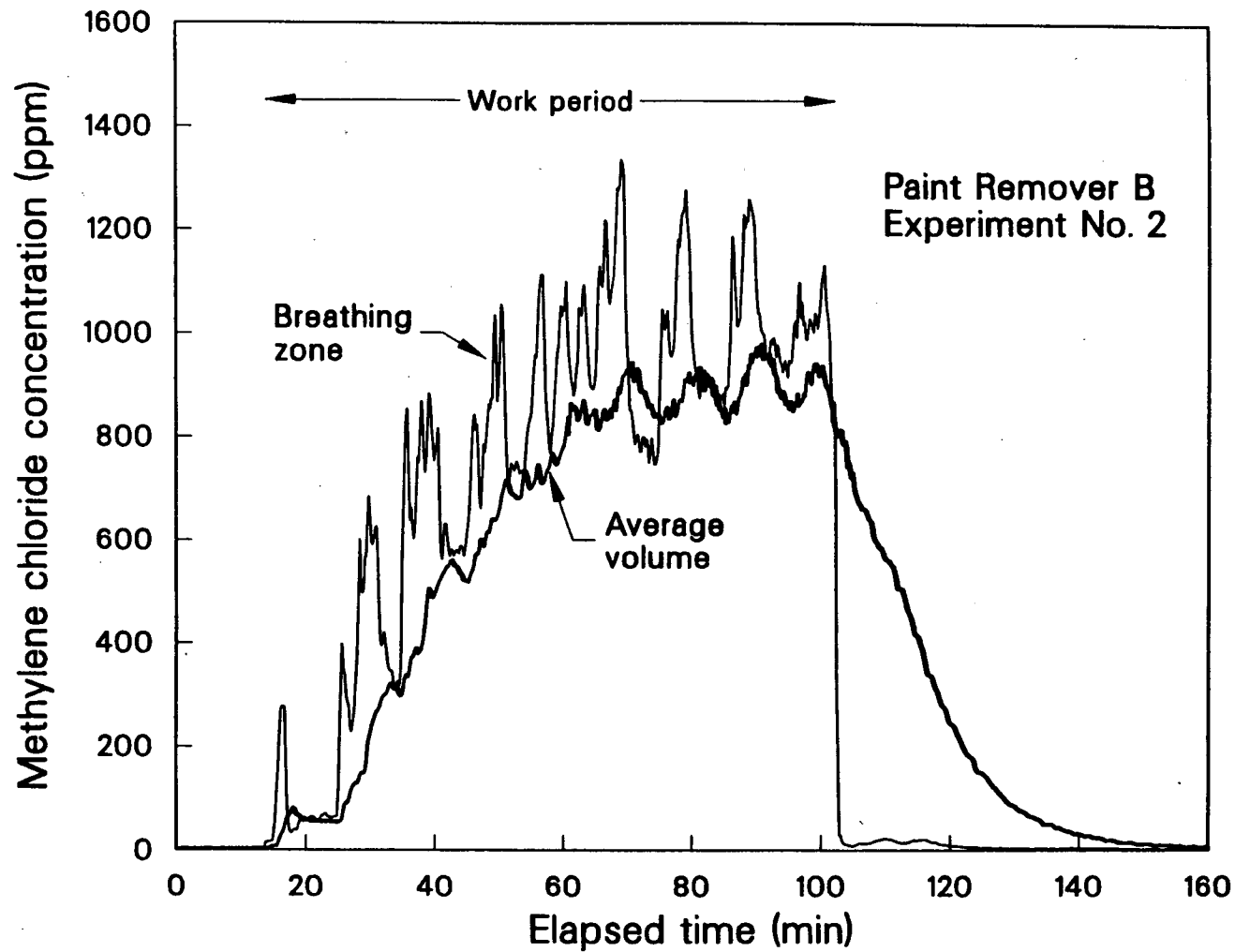
^aPercent compositions normalized to the total percent compositions of the three components in the product

^bPrecision estimates are ±1 standard deviation.



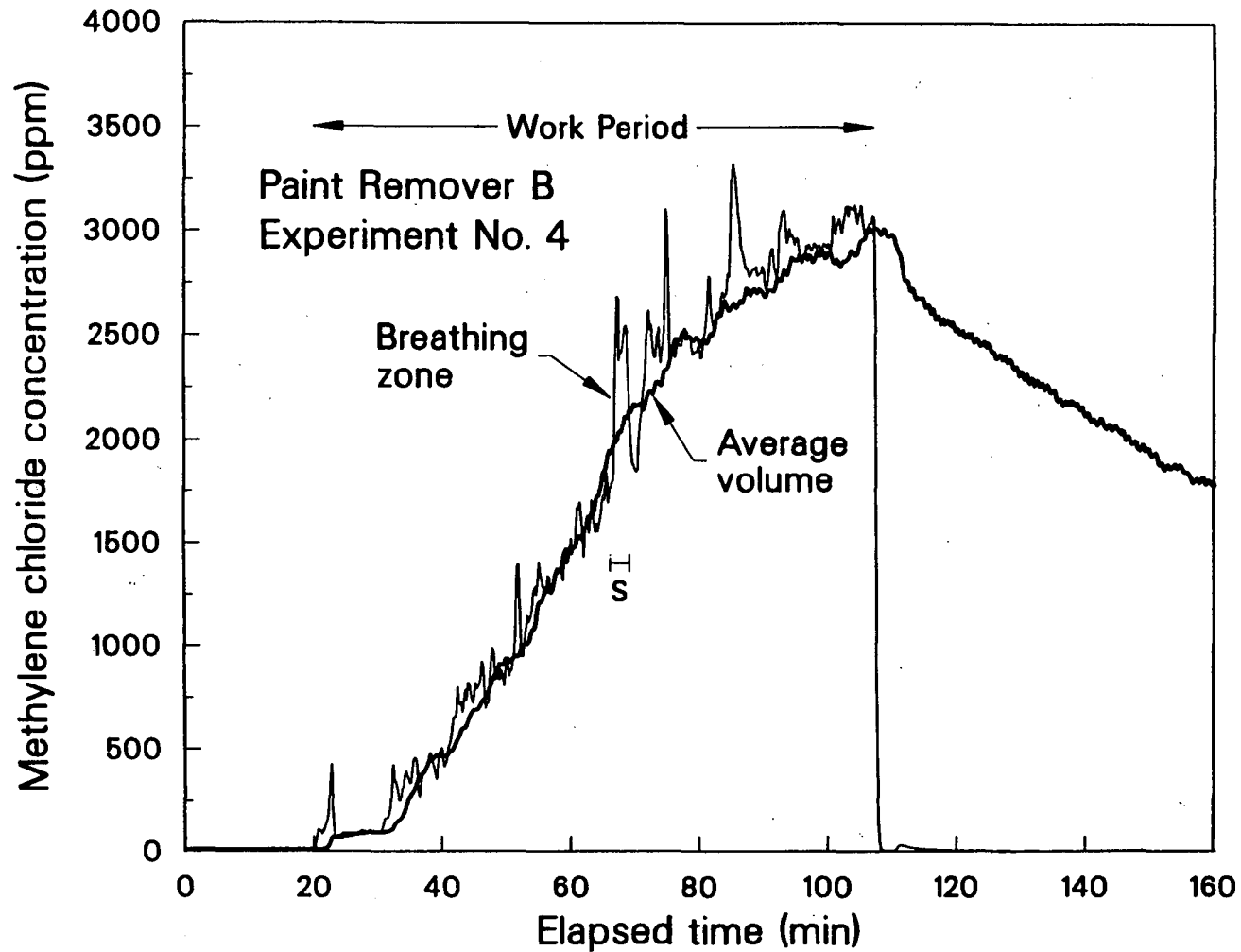
XBL 855-9537

Figure 1. Lawrence Berkeley Laboratory's 20-m³ environmental chamber setup for experiments with paint removers. For illustration, door with observation window is shown in open position and foreground sampling lines are omitted. Breathing-zone sampling line terminates at worker's right shoulder.



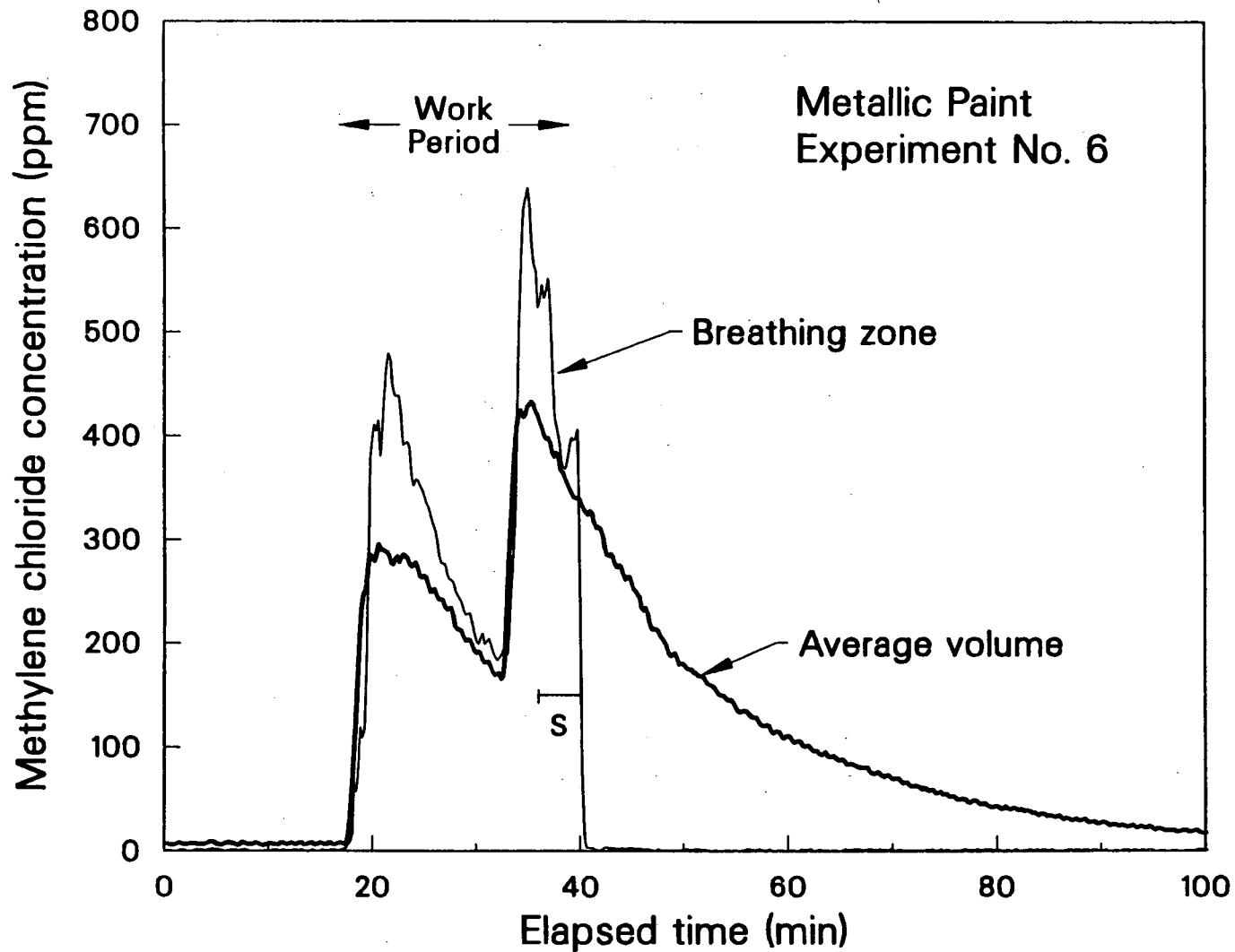
XCG 861-7054

Figure 2. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 2 with paint remover B at a ventilation rate of 3.23 h^{-1} . Duration of work period is shown above curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.



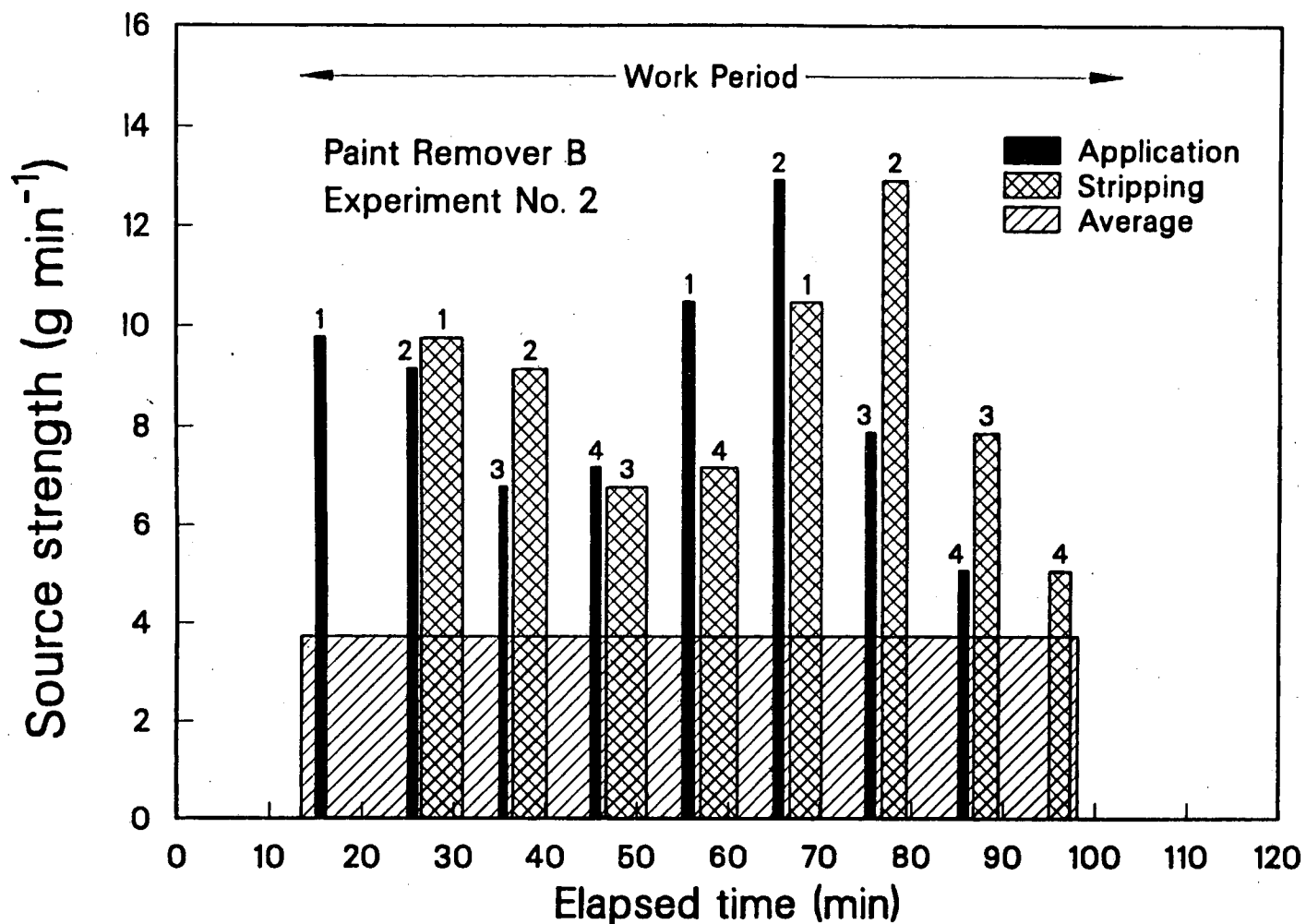
XCG 861-7055

Figure 3. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 4 with paint remover B at a ventilation rate of 0.63 h^{-1} . Duration of work period is shown above curves. Period of vertical stratification measurement (S) using breathing-zone sampling line is shown below curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.



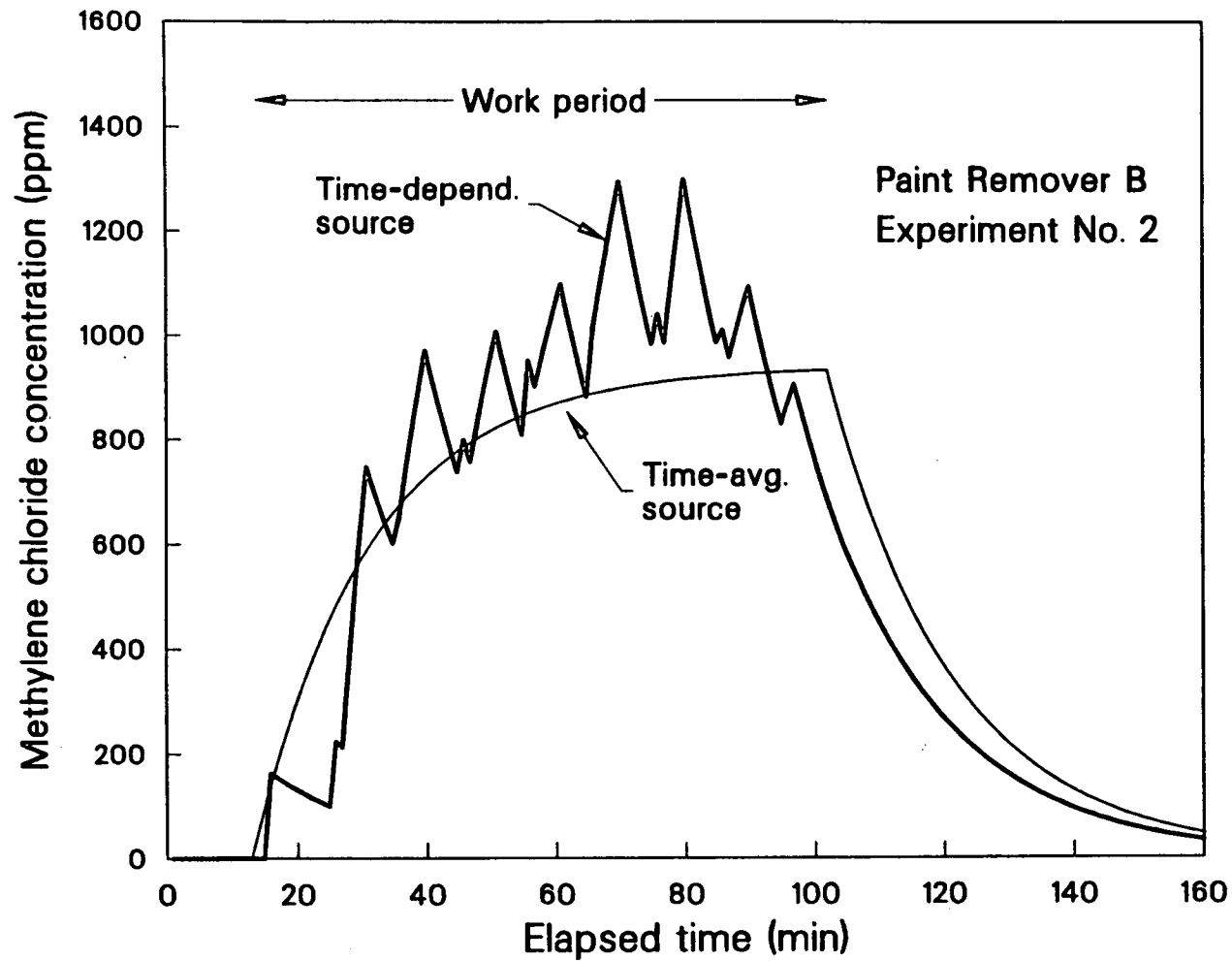
XCG 861-7056

Figure 4. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 6 with metallic paint at a ventilation rate of 3.10 h^{-1} . Duration of work period is shown above curves. Period of vertical stratification measurement (S) using breathing-zone sampling line is shown below curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.



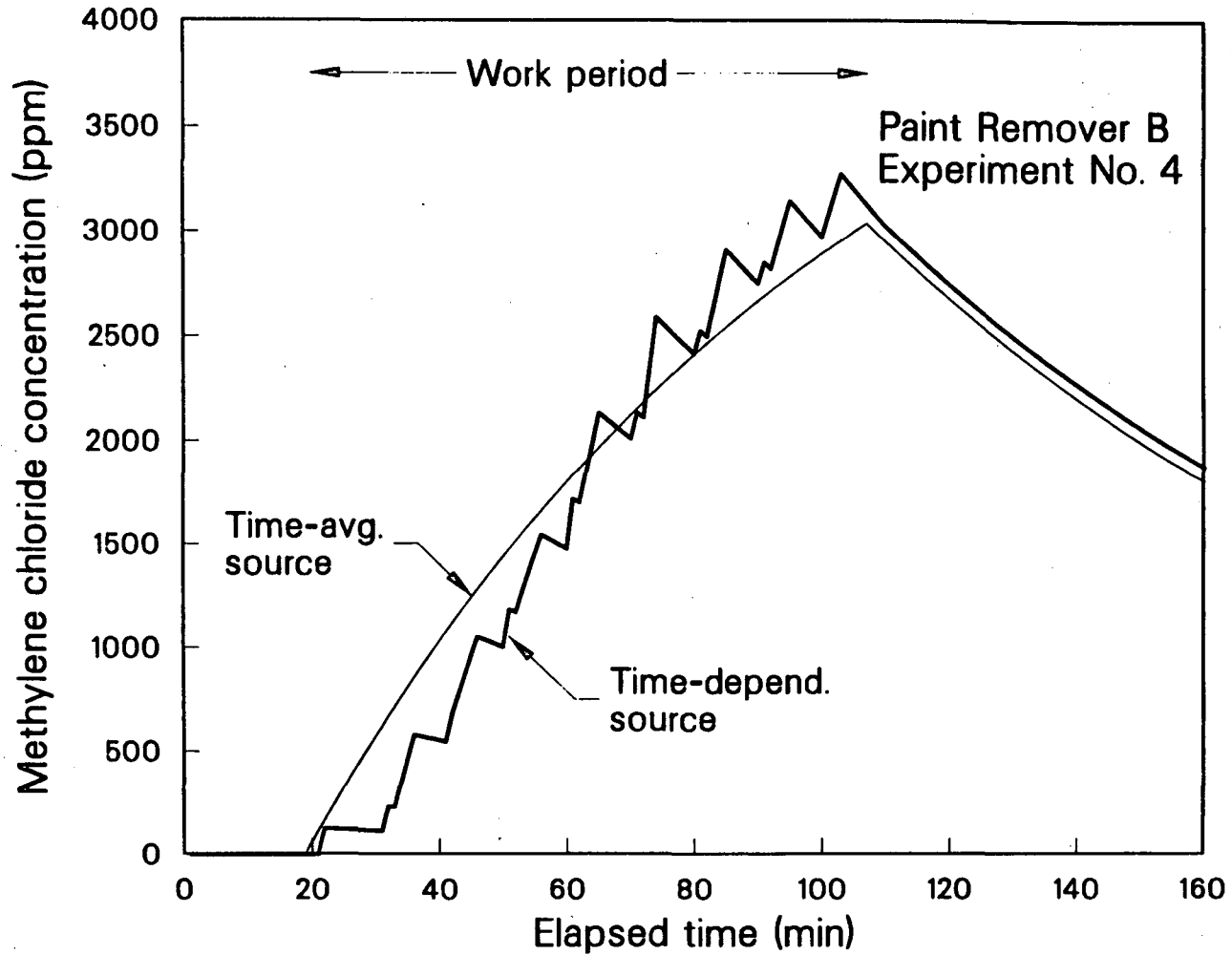
XCG 859-397

Figure 5. Estimated time-dependent source strength of CH_2Cl_2 , along with time-averaged source strength for Experiment 2 with paint remover B. The quarter of the panel to which an application or stripping event applies is identified above the representation of that event. The time-averaged source strength is for period between initial pouring of product into secondary container and wiping of panel at conclusion of stripping.



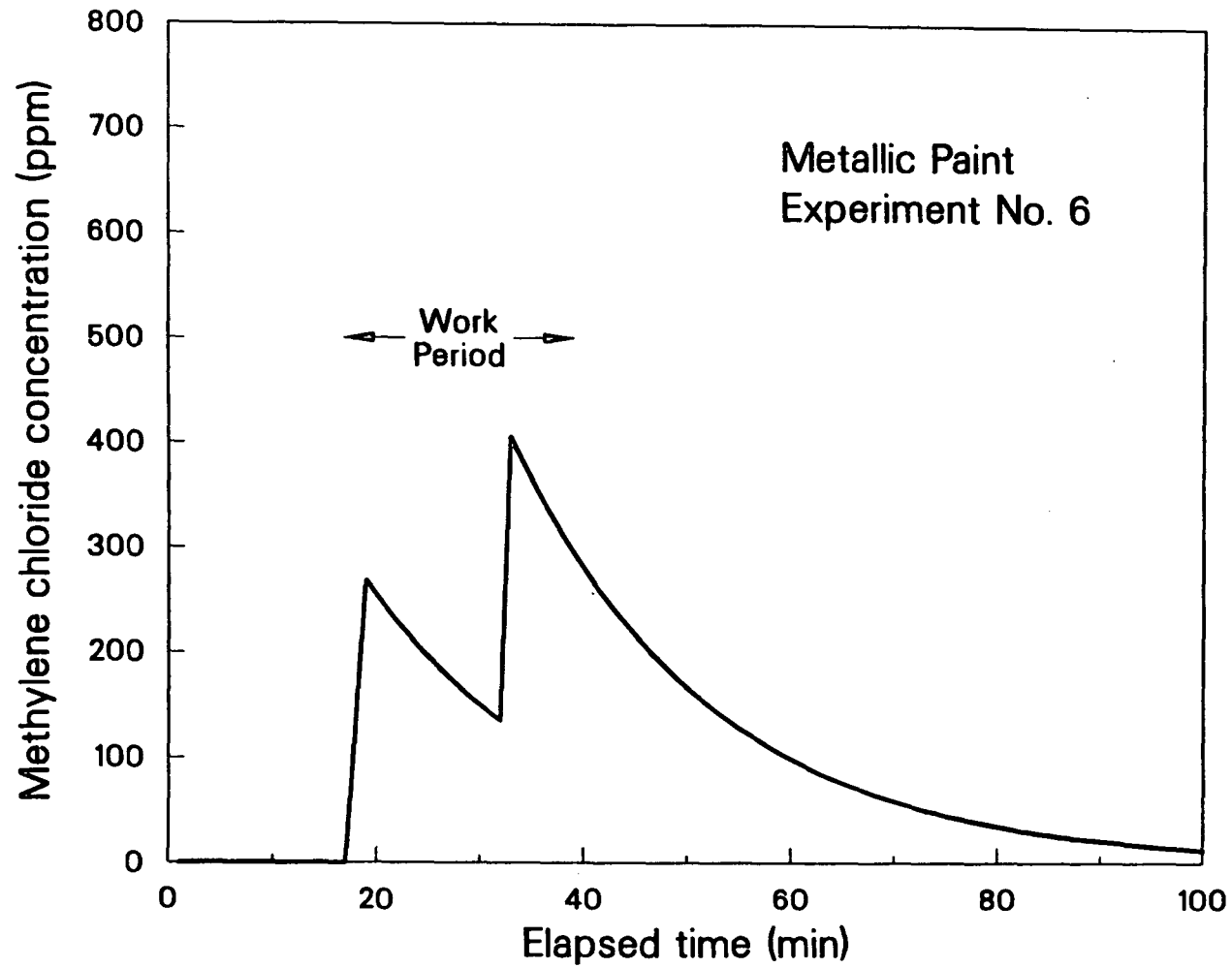
XCG 861-7057

Figure 6. Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for Experiment 2 with paint remover B at a ventilation rate of 3.23 h^{-1} . Concentrations were calculated using both time-dependent and time-averaged source strengths. Duration of work period is shown above curves.



XCG 861-7058

Figure 7. Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for Experiment 4 with paint remover B at a ventilation rate of 0.63 h^{-1} . Concentrations were calculated using both time-dependent and time-averaged source strengths. Duration of work period is shown above curves.



XCG 861-7059

Figure 8. Temporal profile of theoretical chamber concentration of CH_2Cl_2 for Experiment 6 with metallic paint at a ventilation rate of 3.10 h^{-1} . Duration of work period is shown above curves.

APPENDIX A

Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 for experiments with paint removers and aerosol finishes at two ventilation rates.

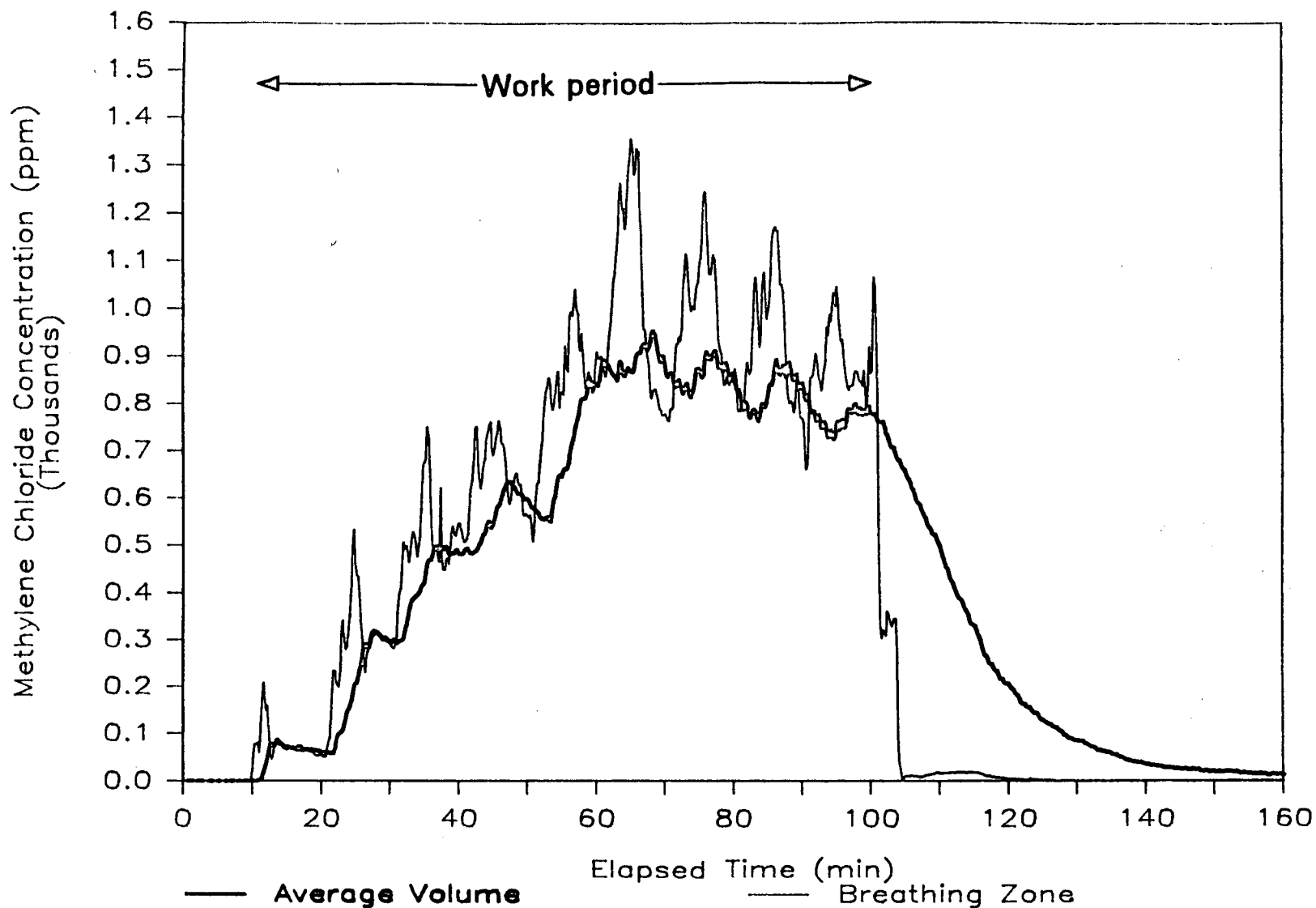


Figure A-1. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 1 with paint remover A at a ventilation rate of 3.19 h^{-1} . Duration of work period is shown above curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

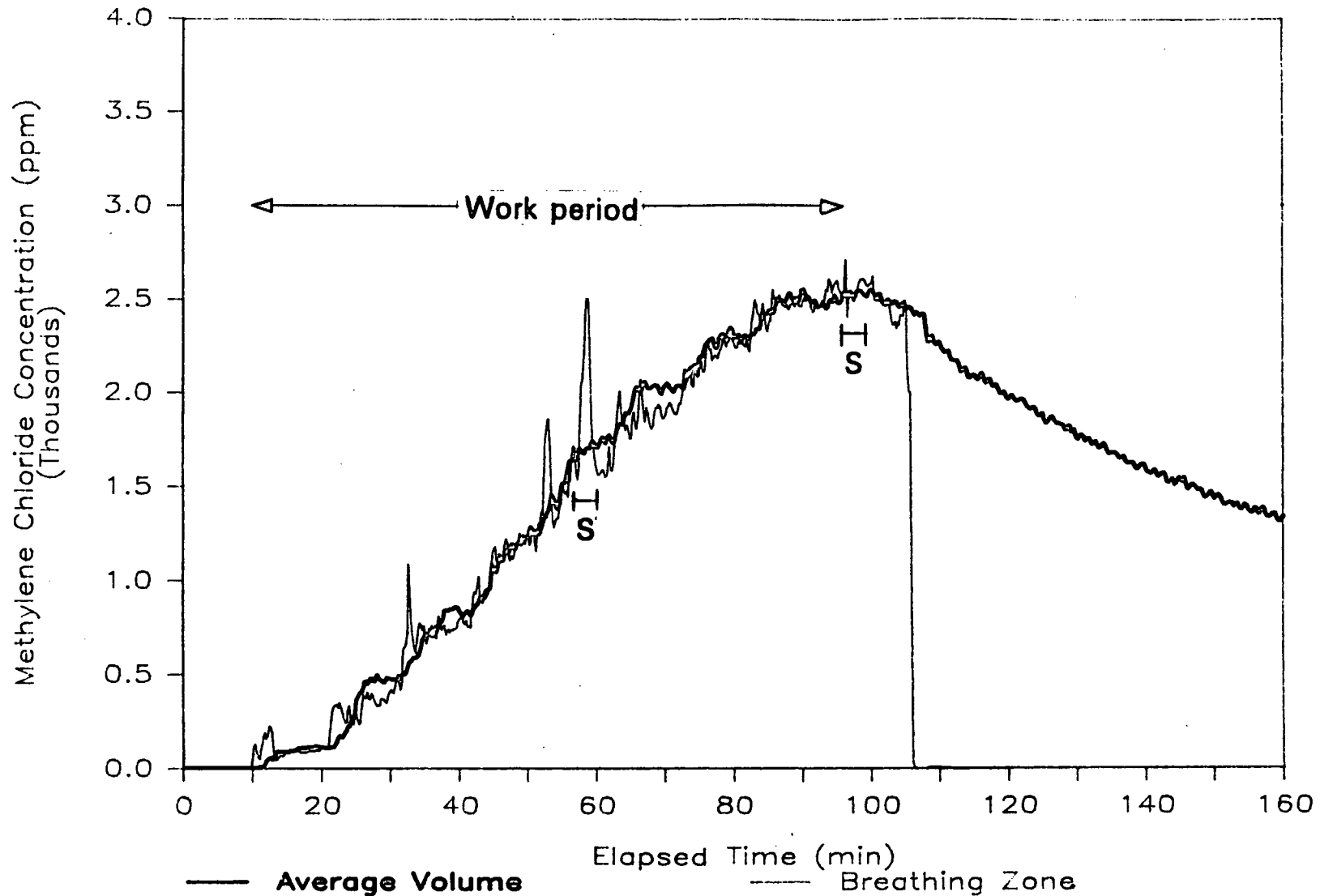


Figure A-2. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 5 with paint remover A at a ventilation rate of 0.62 h^{-1} . Duration of work period is shown above curves. Periods of vertical stratification measurement (S) using breathing-zone sampling line are shown below curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

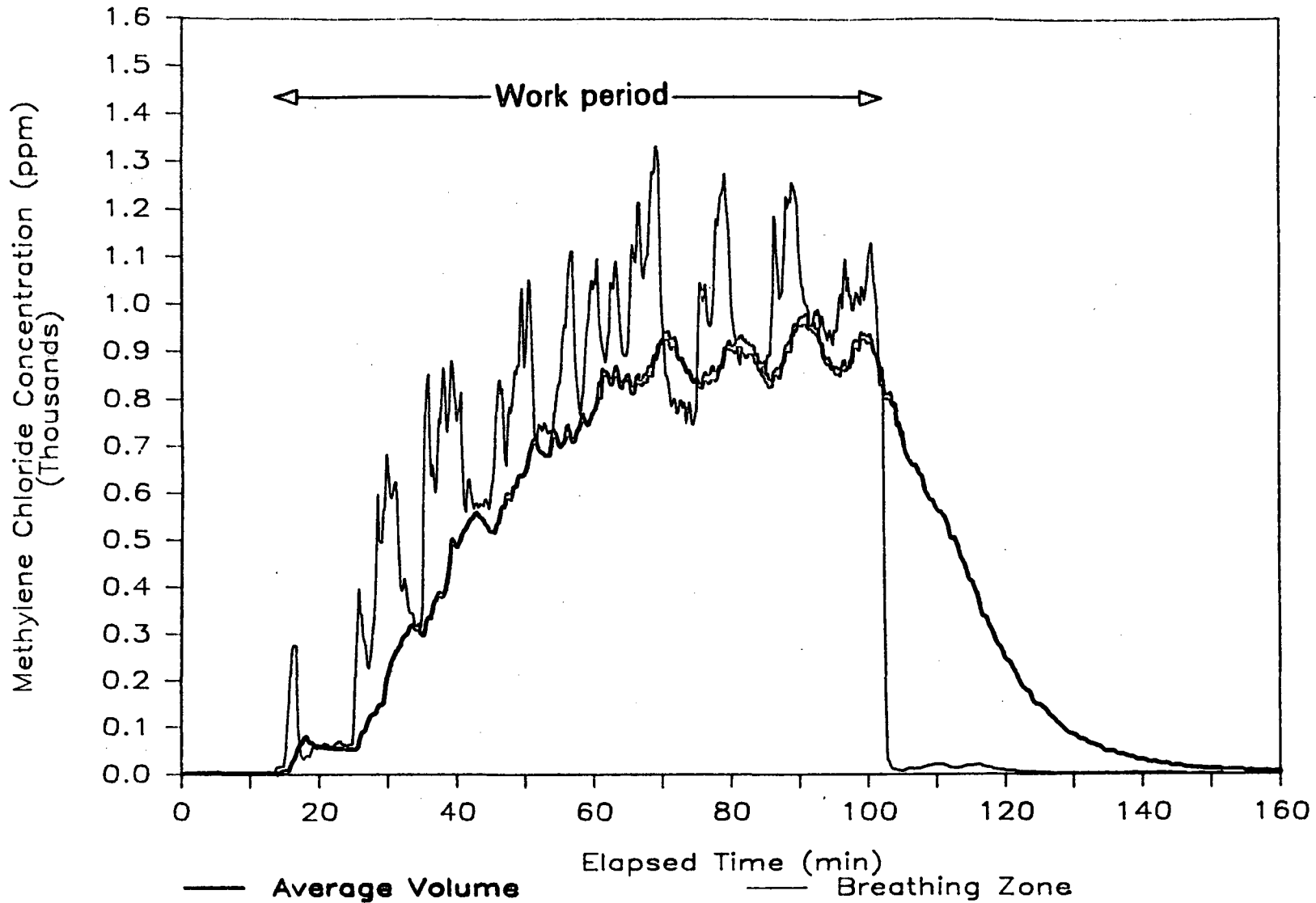


Figure A-3. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 2 with paint remover B at a ventilation rate of 3.23 h^{-1} . Duration of work period is shown above curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

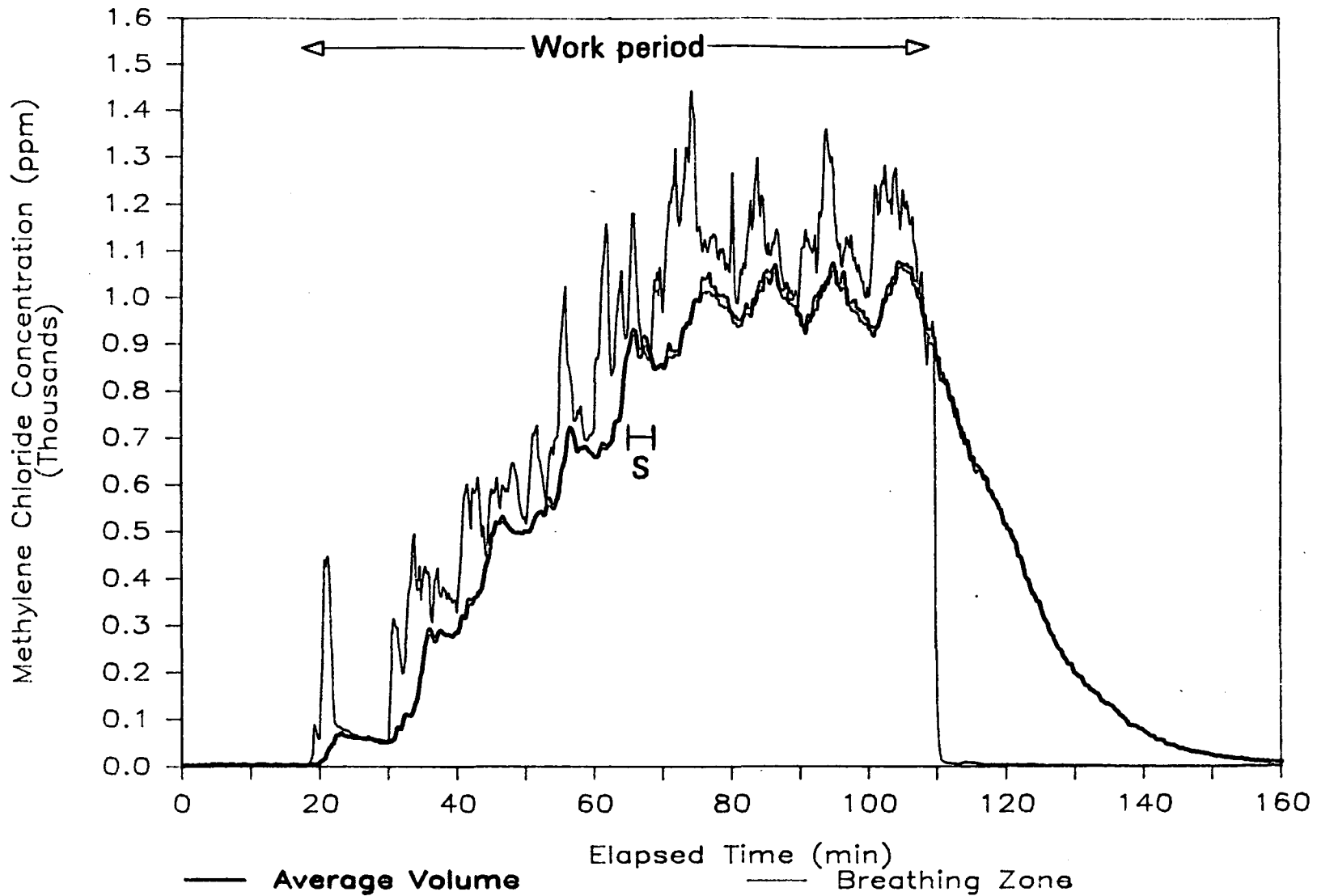


Figure A-4. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 3 with paint remover B at a ventilation rate of 3.20 h^{-1} . Duration of work period is shown above curves. Period of vertical stratification measurement (S) using breathing-zone sampling line is shown below curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

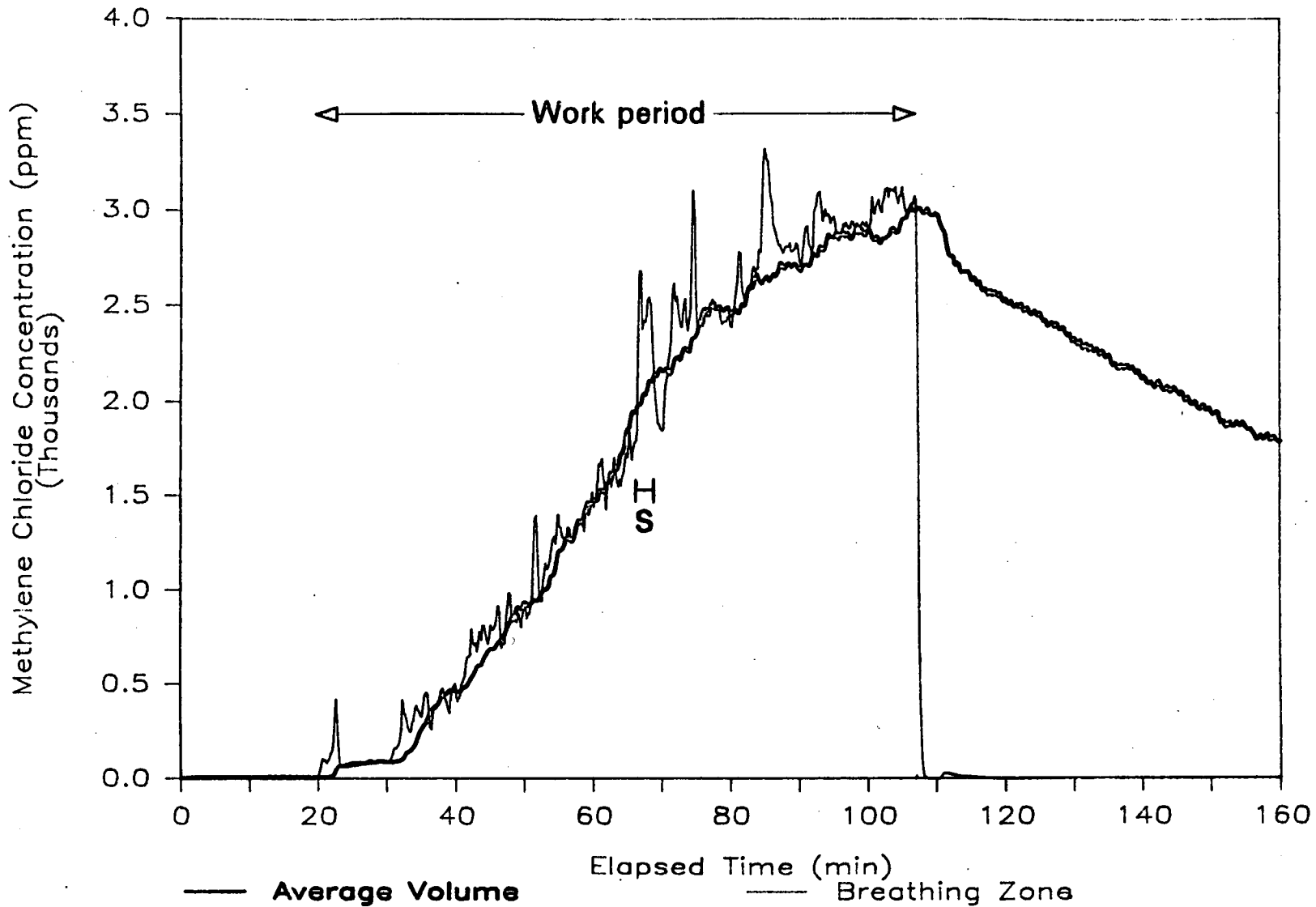


Figure A-5. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 4 with paint remover B at a ventilation rate of 0.63 h^{-1} . Duration of work period is shown above curves. Period of vertical stratification measurement (S) using breathing-zone sampling line is shown below curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

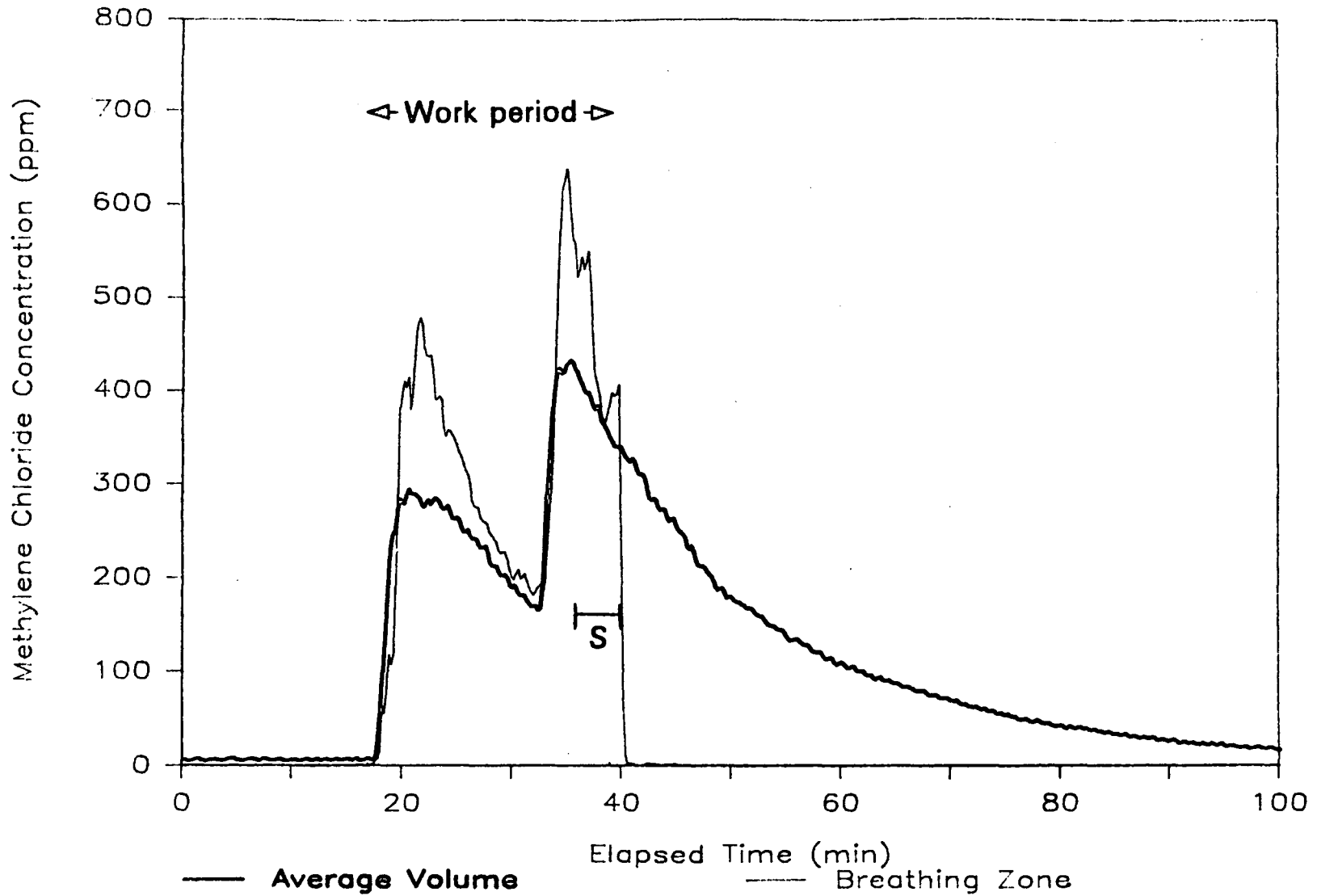


Figure A-6. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 6 with metallic paint at a ventilation rate of 3.10 h^{-1} . Duration of work period is shown above curves. Period of vertical stratification measurement (S) using breathing-zone sampling line is shown below curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

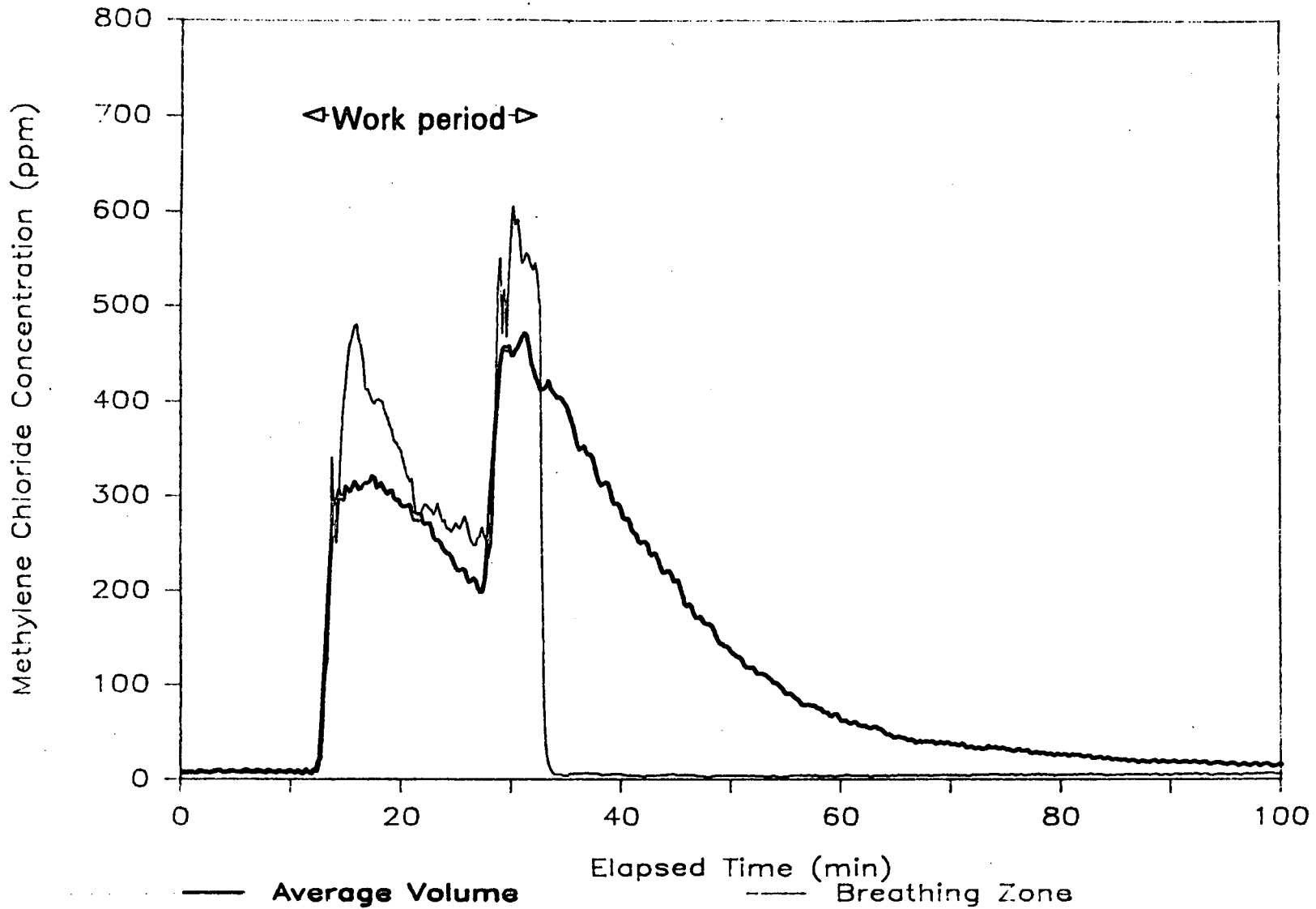


Figure A-7. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 7 with metallic paint at a ventilation rate of 3.12 h^{-1} . Duration of work period is shown above curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

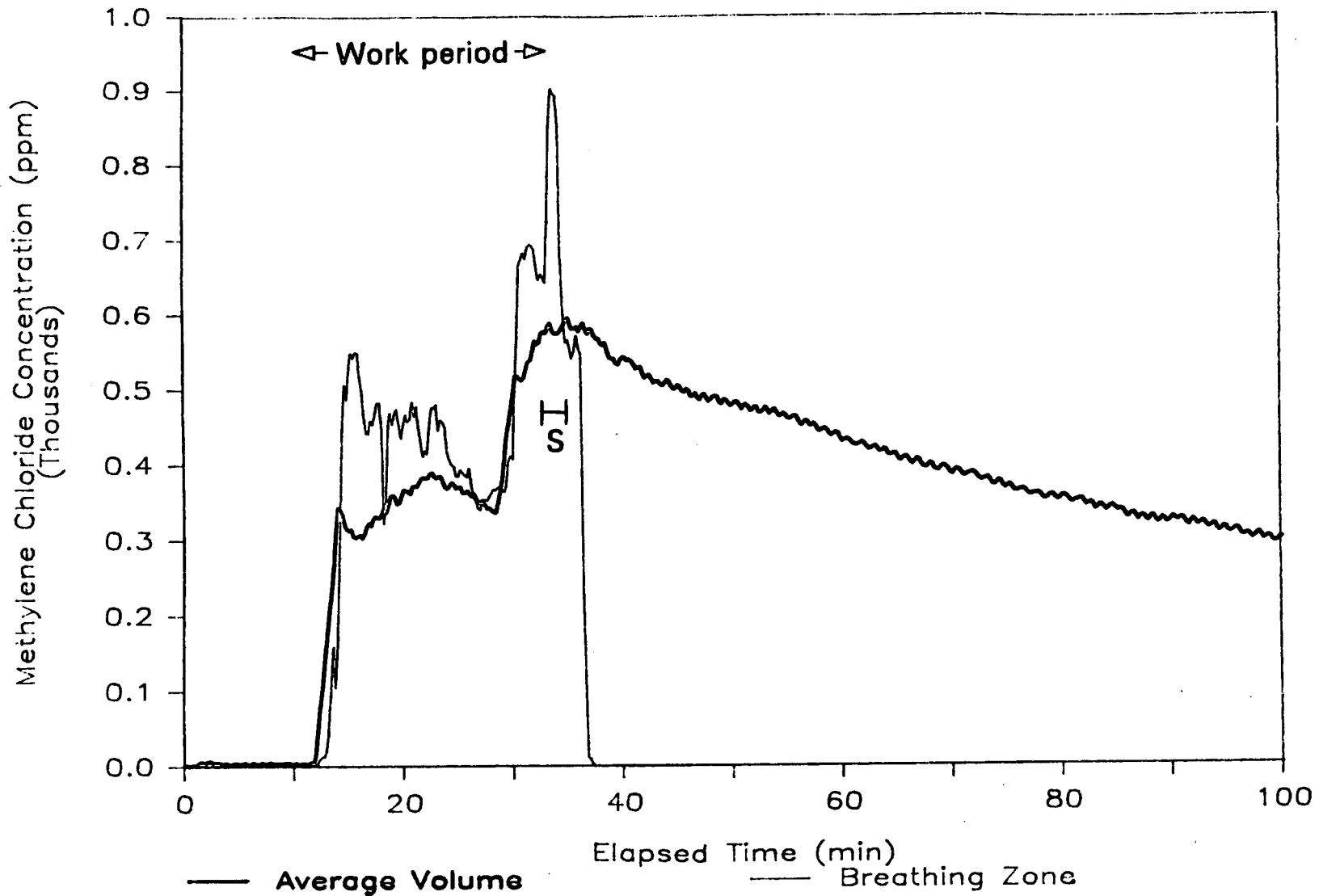


Figure A-8. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 8 with metallic paint at a ventilation rate of 0.54 h^{-1} . Duration of work period is shown above curves. Period of vertical stratification measurement (S) using breathing-zone sampling line is shown below curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

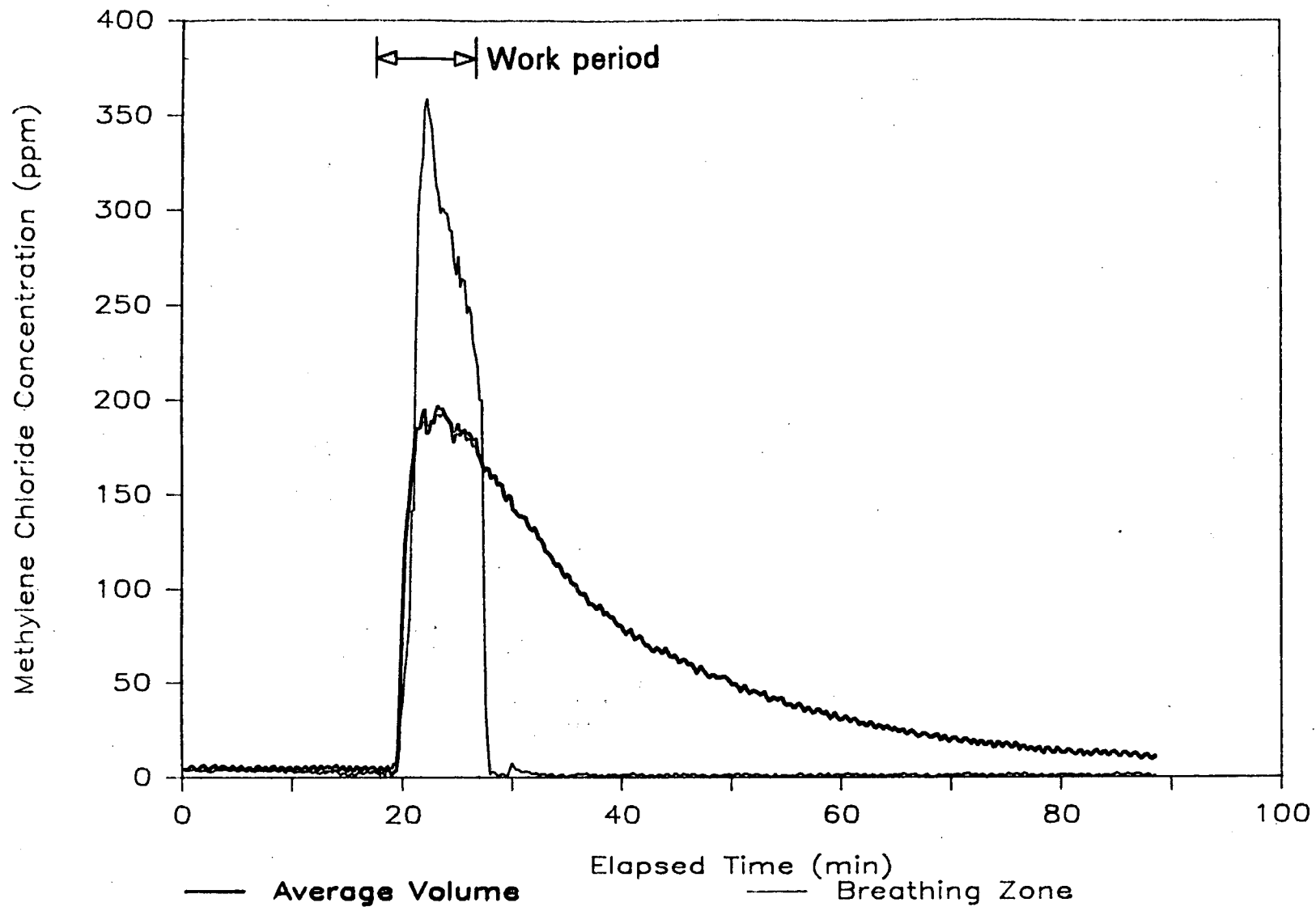


Figure A-9. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 10 with polyurethane finish at a ventilation rate of 3.11 h^{-1} . Duration of work period is shown above curves. At end of work period, breathing-zone sampling line was switched to laboratory air external to chamber.

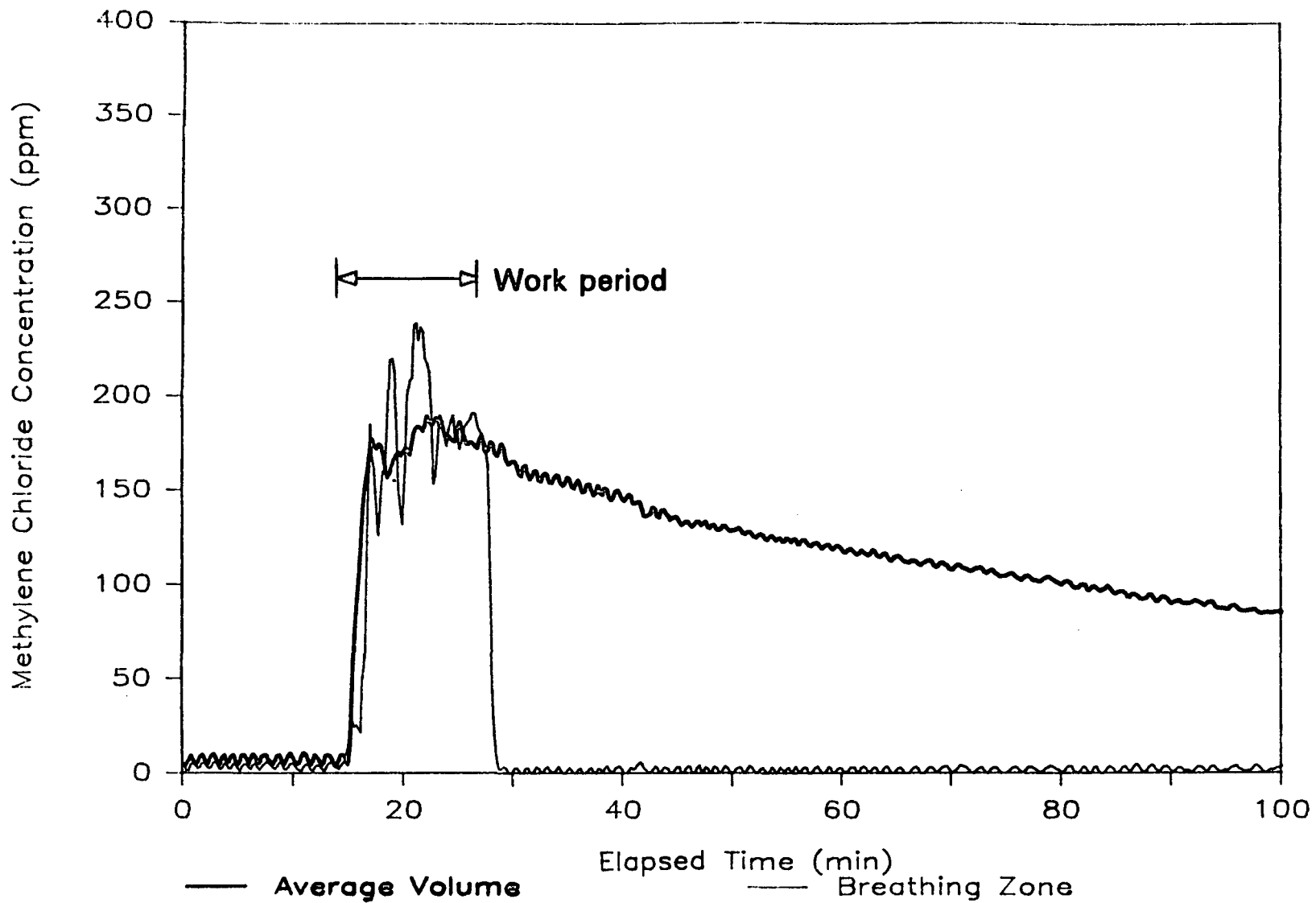


Figure A-10. Temporal profiles of chamber and breathing-zone concentrations of CH_2Cl_2 during Experiment 9 with polyurethane finish at a ventilation rate of 0.53 h^{-1} . Duration of work period is shown above curves. At end of work period, breathing-zone sampling line was switched to laboratory air external

APPENDIX B

Source strengths of CH_2Cl_2 for experiments with paint removers and aerosol finishes at two ventilation rates.

Table B-1. Source strengths of CH₂Cl₂ for experiments with aerosol finishes

Product ^a	Exp. No.	First Application			Second Application		
		Time		Source	Time		Source
		Start (min)	End (min)	Strength (g min ⁻¹)	Start (min)	End (min)	Strength (g min ⁻¹)
MP	6 } ^b	17.0	18.6	12.1	32.0	33.3	15.0
	7 }	12.0	13.2	17.8	27.0	28.2	16.8
	8	11.4	13.6	10.4	28.0	29.7	9.3
PF	10	19.0	20.2	16.3	--	--	--
	9	14.5	16.0	10.5	--	--	--

^aMP-metallic paint; PF-polyurethane finish

^bDuplicate experiments

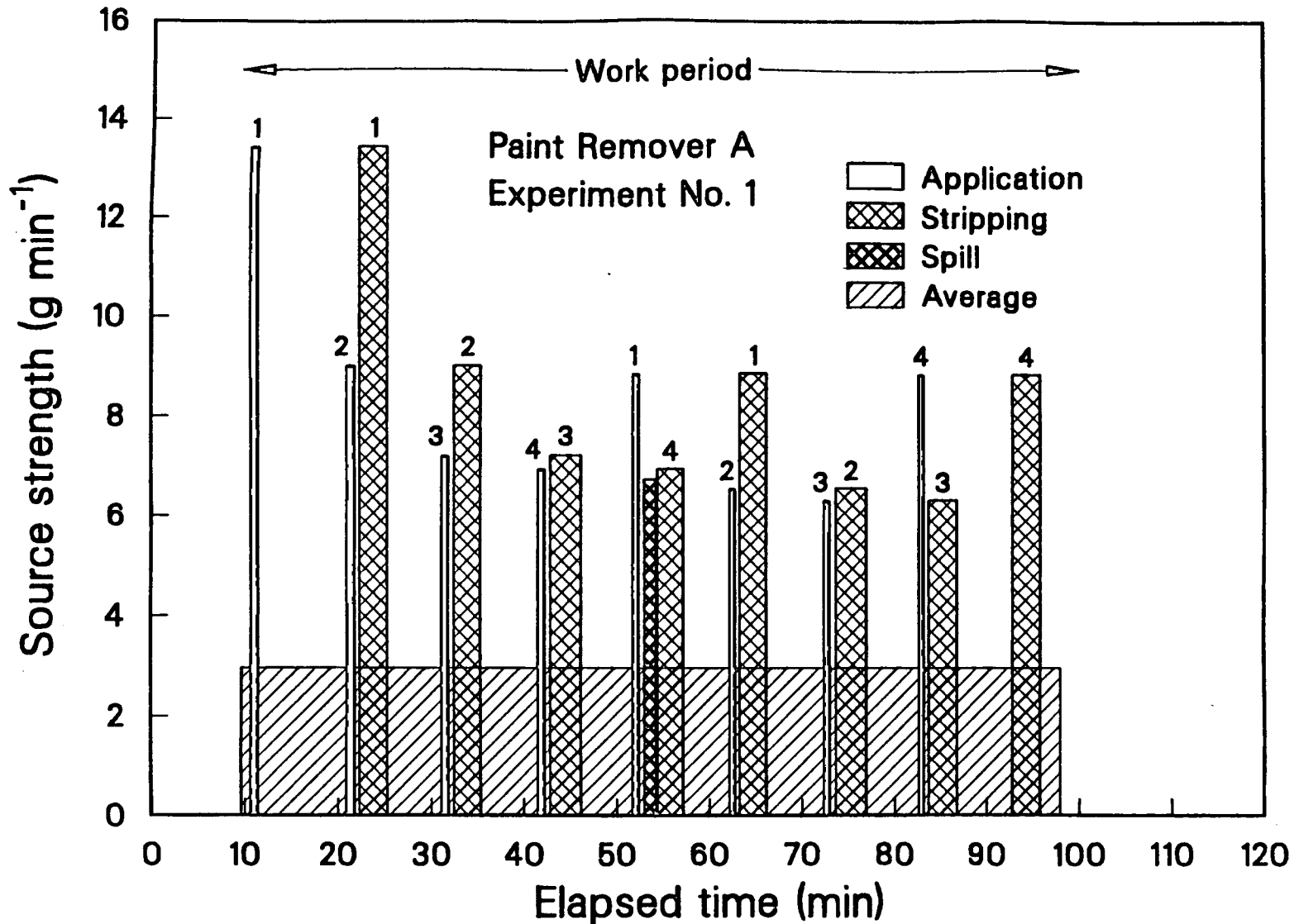


Figure B-1. Estimated time-dependent source strength of CH_2Cl_2 along with time-averaged source strength for Experiment 1 with paint remover A. The quarter of the panel to which an application or stripping event applies is identified above the representation of that event. The time-averaged source strength is for period between initial pouring of product into secondary container and wiping of panel at conclusion of stripping.

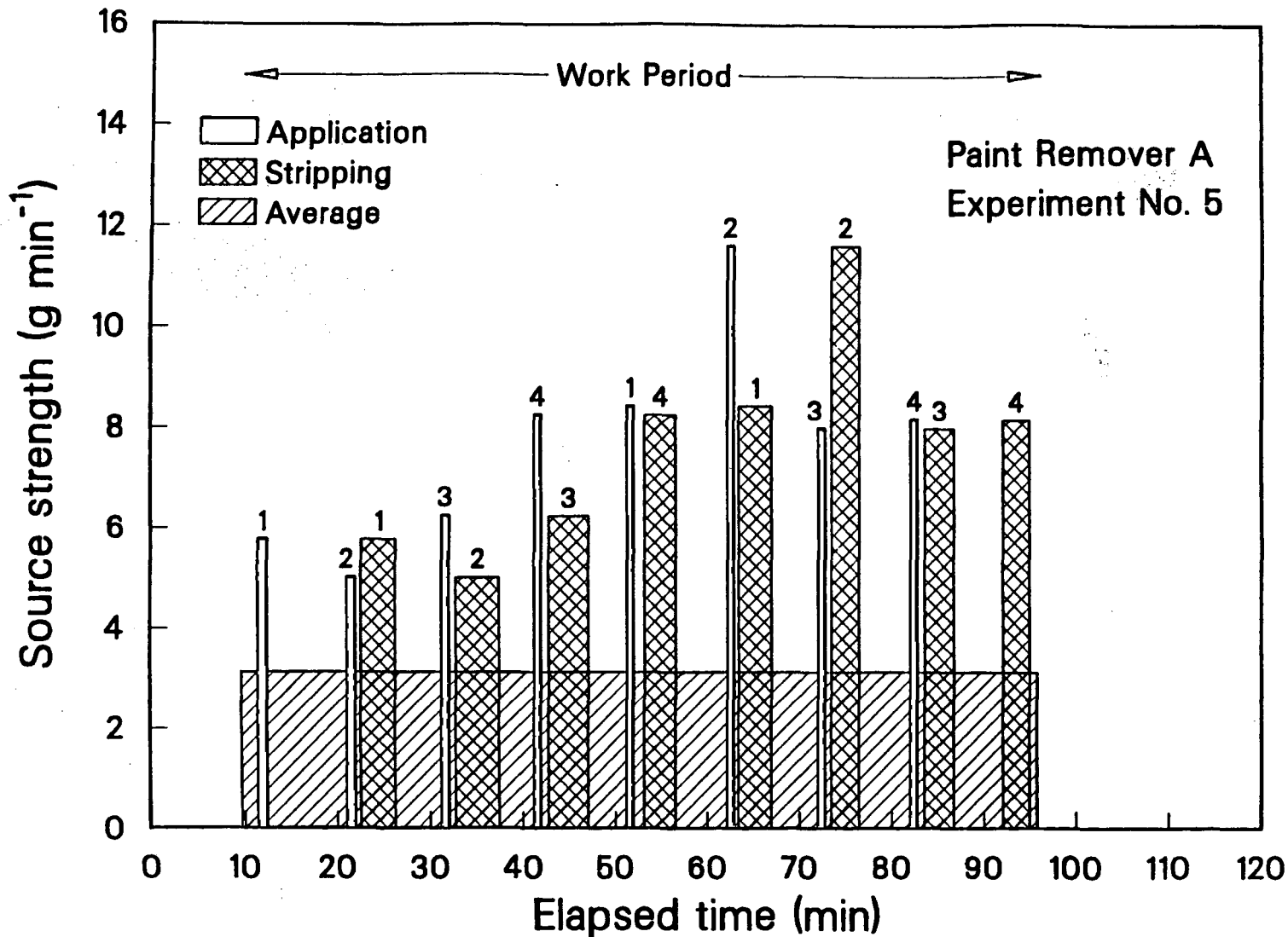
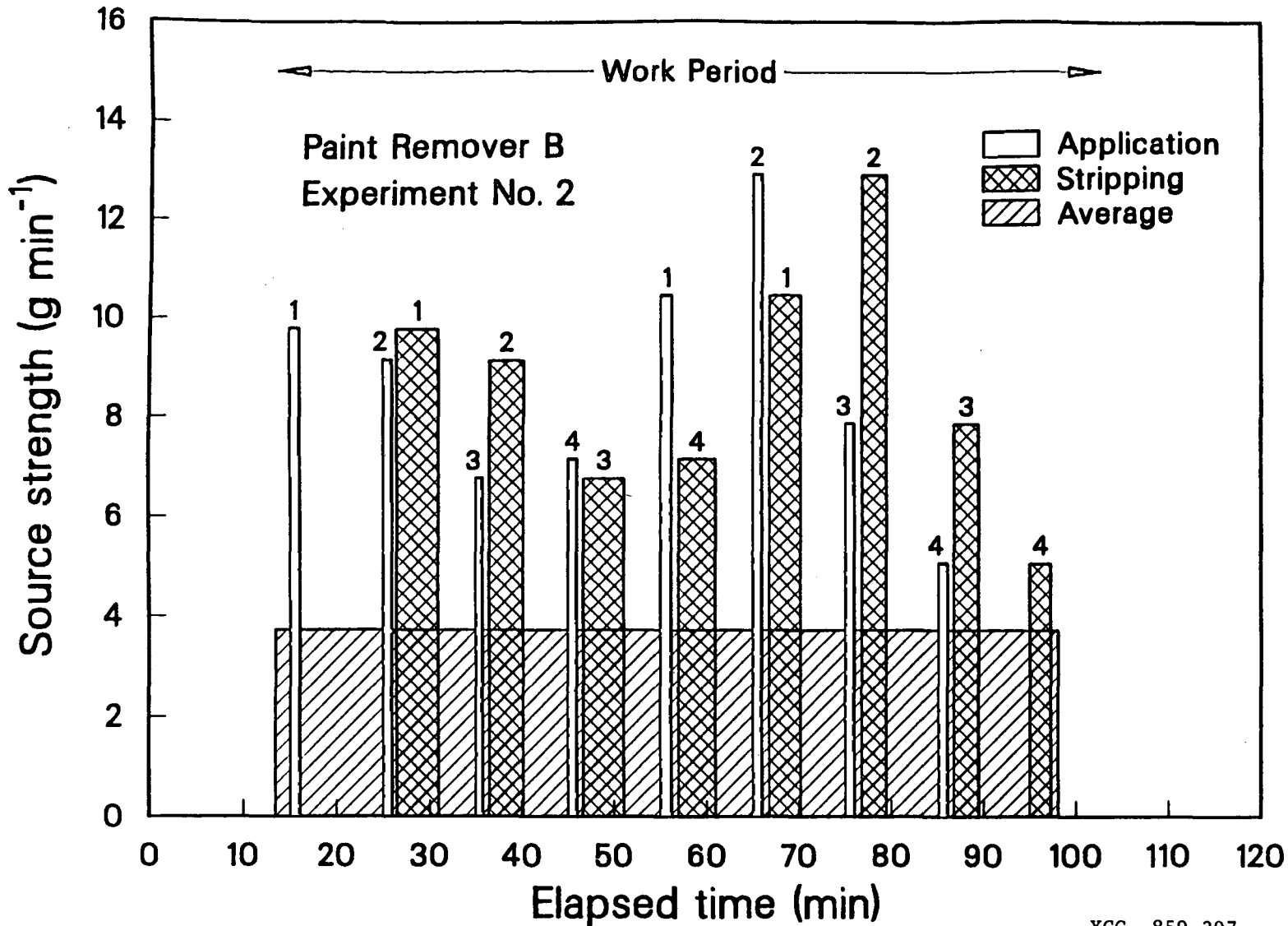


Figure B-2. Estimated time-dependent source strength of CH_2Cl_2 along with time-averaged source strength for Experiment 5 with paint remover A. The quarter of the panel to which an application or stripping event applies is identified above the representation of that event. The time-averaged source strength is for period between initial pouring of product into secondary container and wiping of panel at conclusion of stripping.



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Figure B-3. Estimated time-dependent source strength of CH_2Cl_2 along with time-averaged source strength for Experiment 2 with paint remover B. The quarter of the panel to which an application or stripping event applies is identified above the representation of that event. The time-averaged source strength is for period between initial pouring of product into secondary container and wiping of panel at conclusion of stripping.

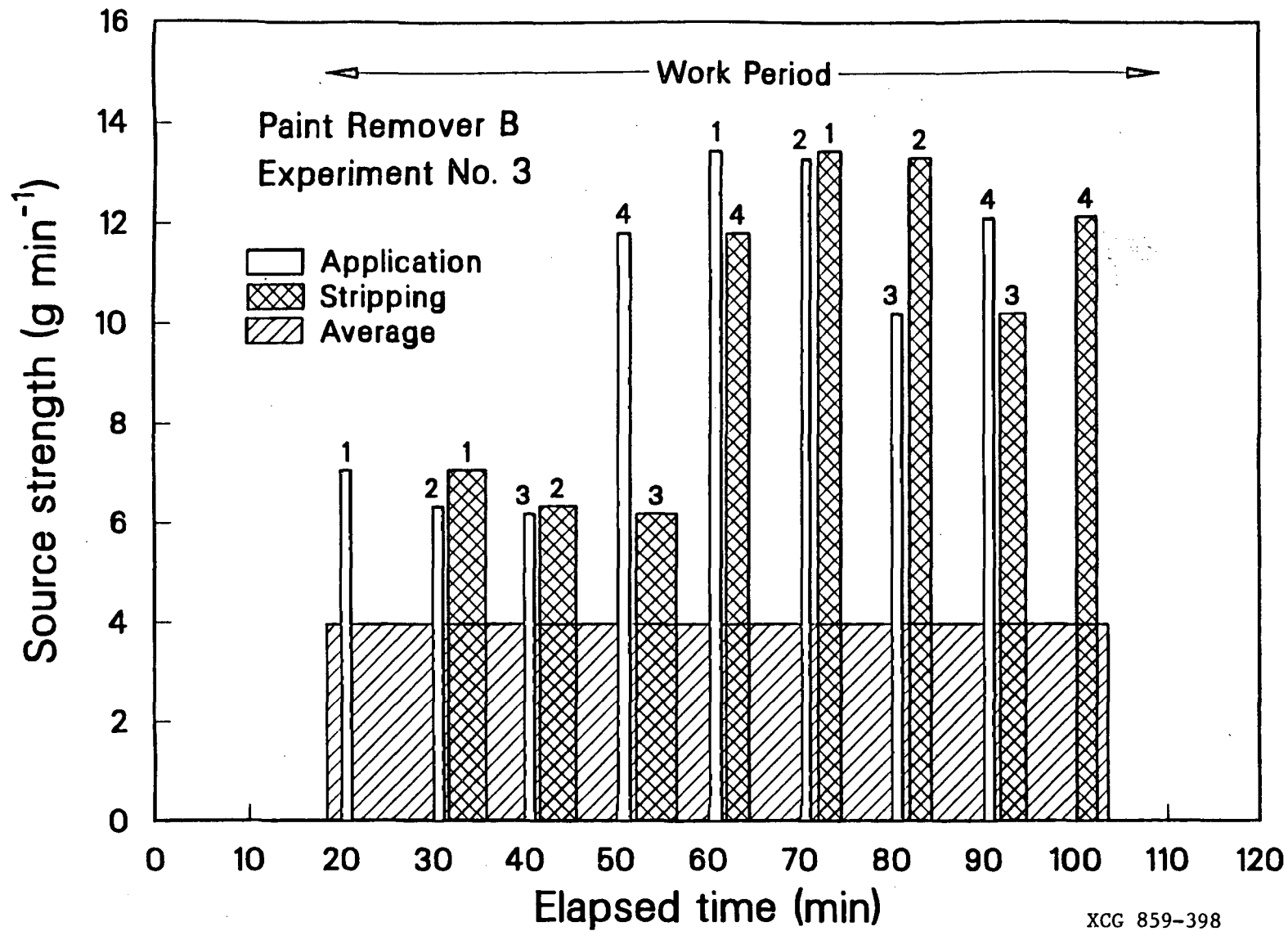


Figure B-4. Estimated time-dependent source strength of CH_2Cl_2 along with time-averaged source strength for Experiment 3 with paint remover B. The quarter of the panel to which an application or stripping event applies is identified above the representation of that event. The time-averaged source strength is for period between initial pouring of product into secondary container and wiping of panel at conclusion of stripping.

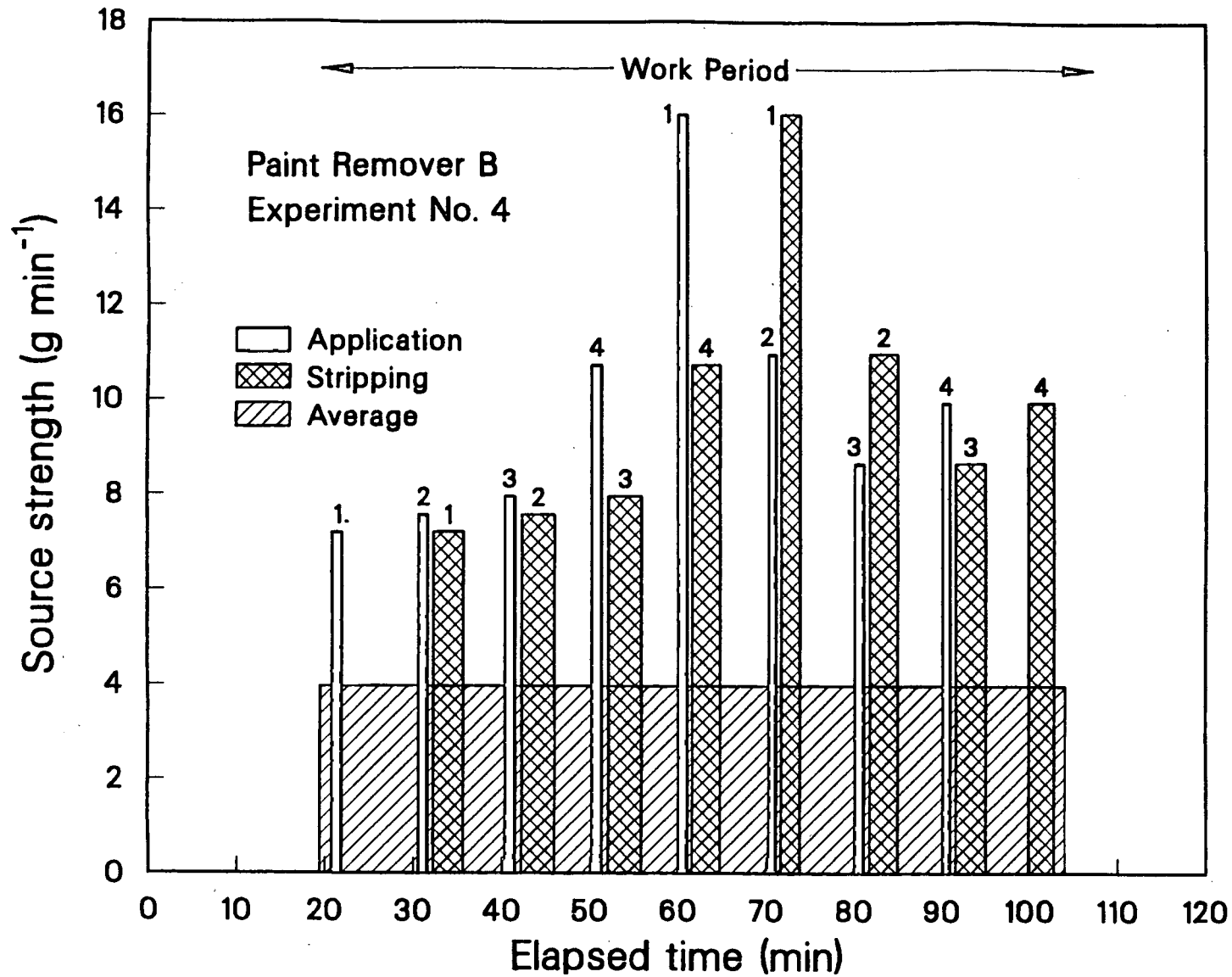


Figure B-5. Estimated time-dependent source strength of CH_2Cl_2 along with time-averaged source strength for Experiment 4 with paint remover B. The quarter of the panel to which an application or stripping event applies is identified above the representation of that event. The time-averaged source strength is for period between initial pouring of product into secondary container and wiping of panel at conclusion of stripping.

APPENDIX C

Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for experiments with paint removers and aerosol finishes at two ventilation rates.

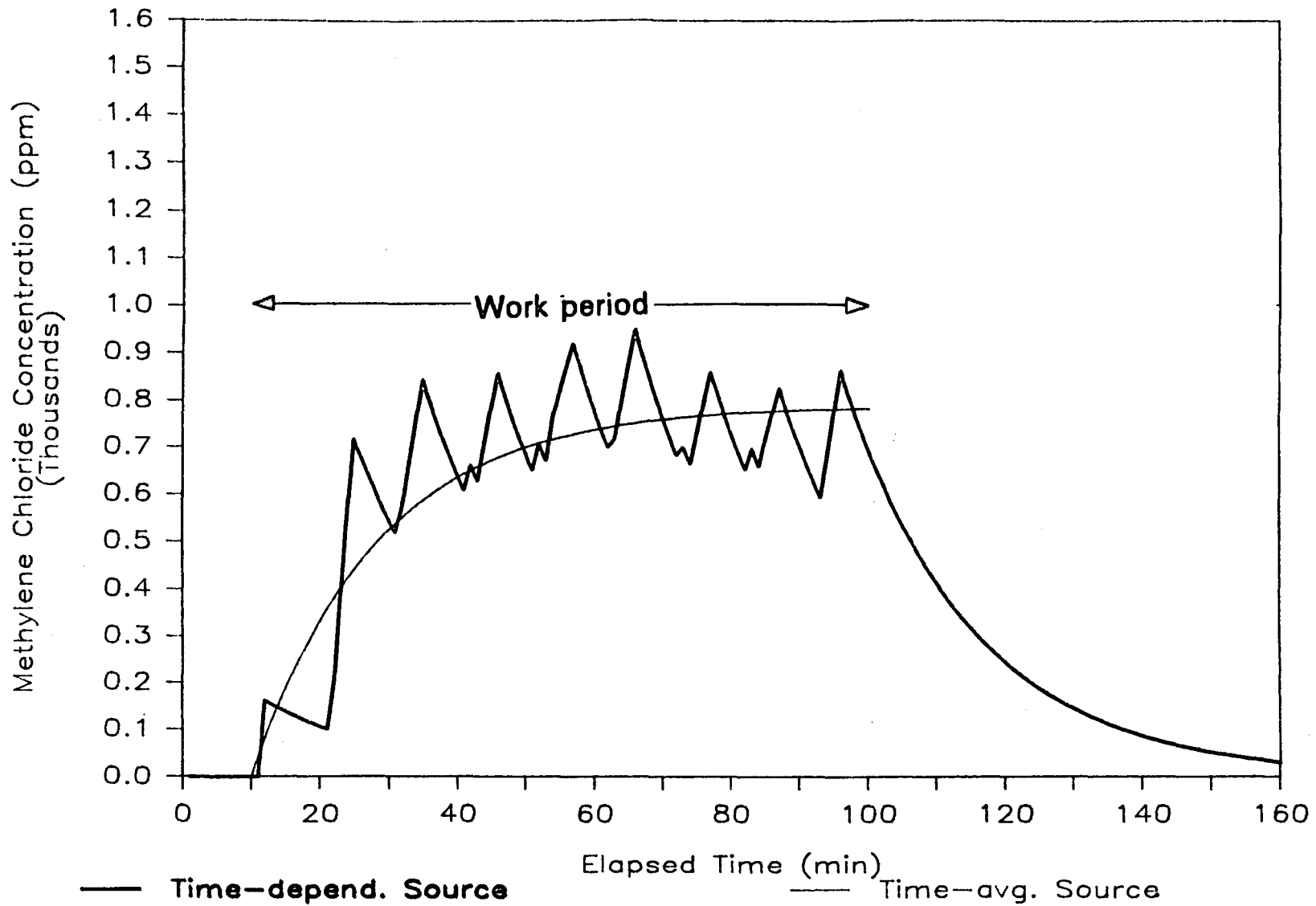


Figure C-1. Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for Experiment 1 with paint remover A at a ventilation rate of 3.19 h^{-1} . Concentrations were calculated using both time-dependent and time-averaged source strengths. Duration of work period is shown above curves.

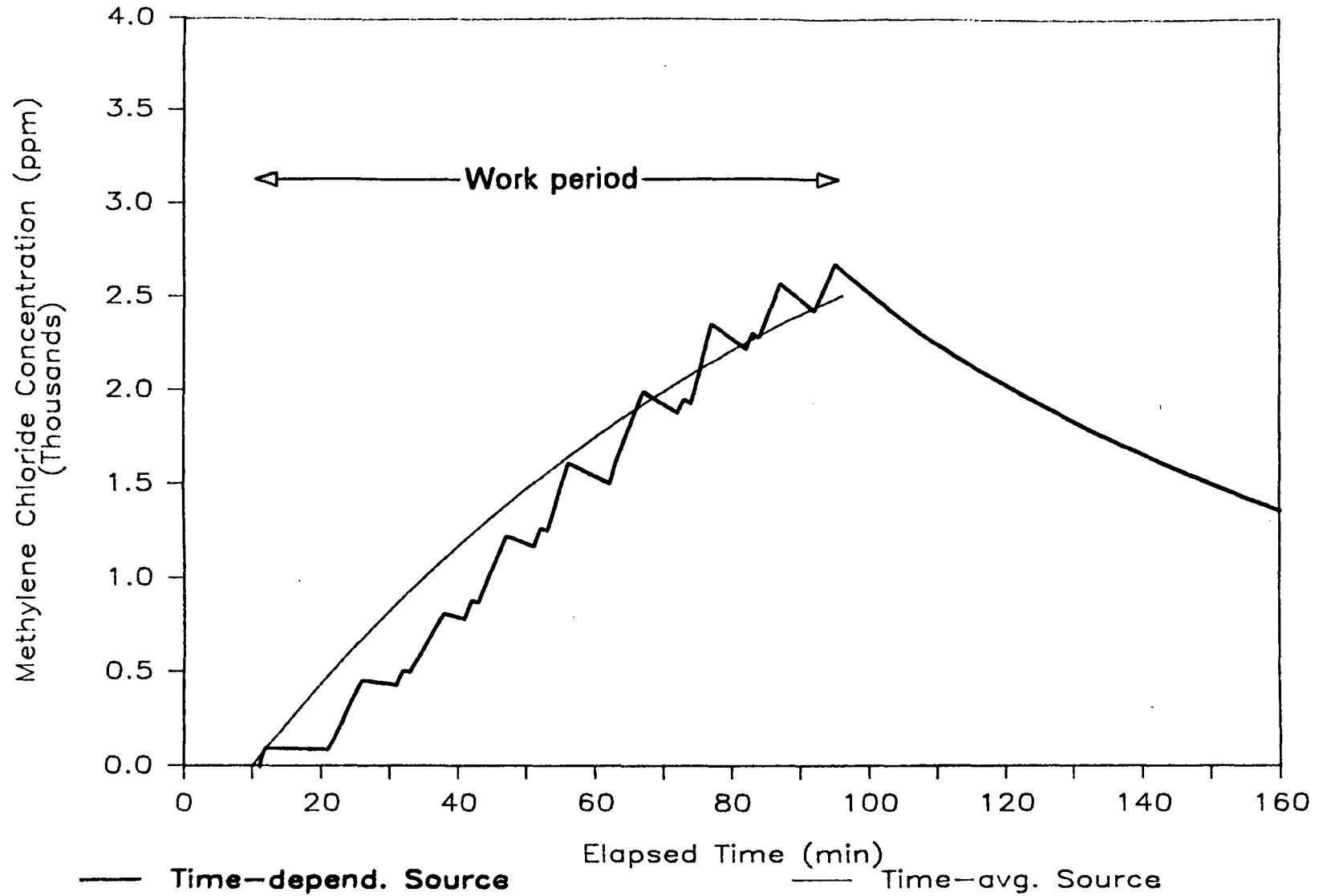


Figure C-2. Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for Experiment 5 with paint remover A at a ventilation rate of 0.62 h^{-1} . Concentrations were calculated using both time-dependent and time-averaged source strengths. Duration of work period is shown above curves.

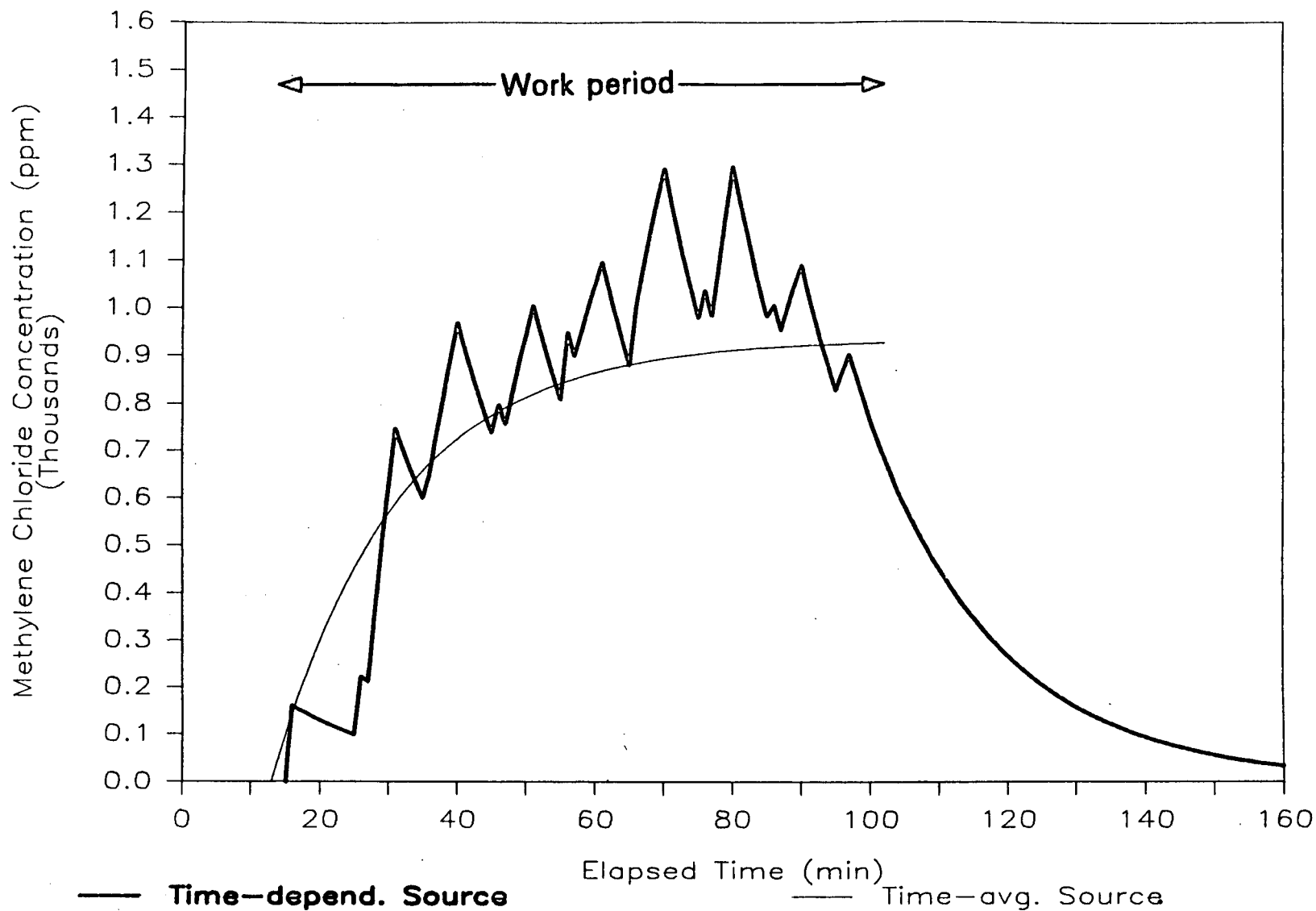


Figure C-3. Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for Experiment 2 with paint remover B at a ventilation rate of 3.23 h^{-1} . Concentrations were calculated using both time-dependent and time-averaged source strengths. Duration of work period is shown above curves.

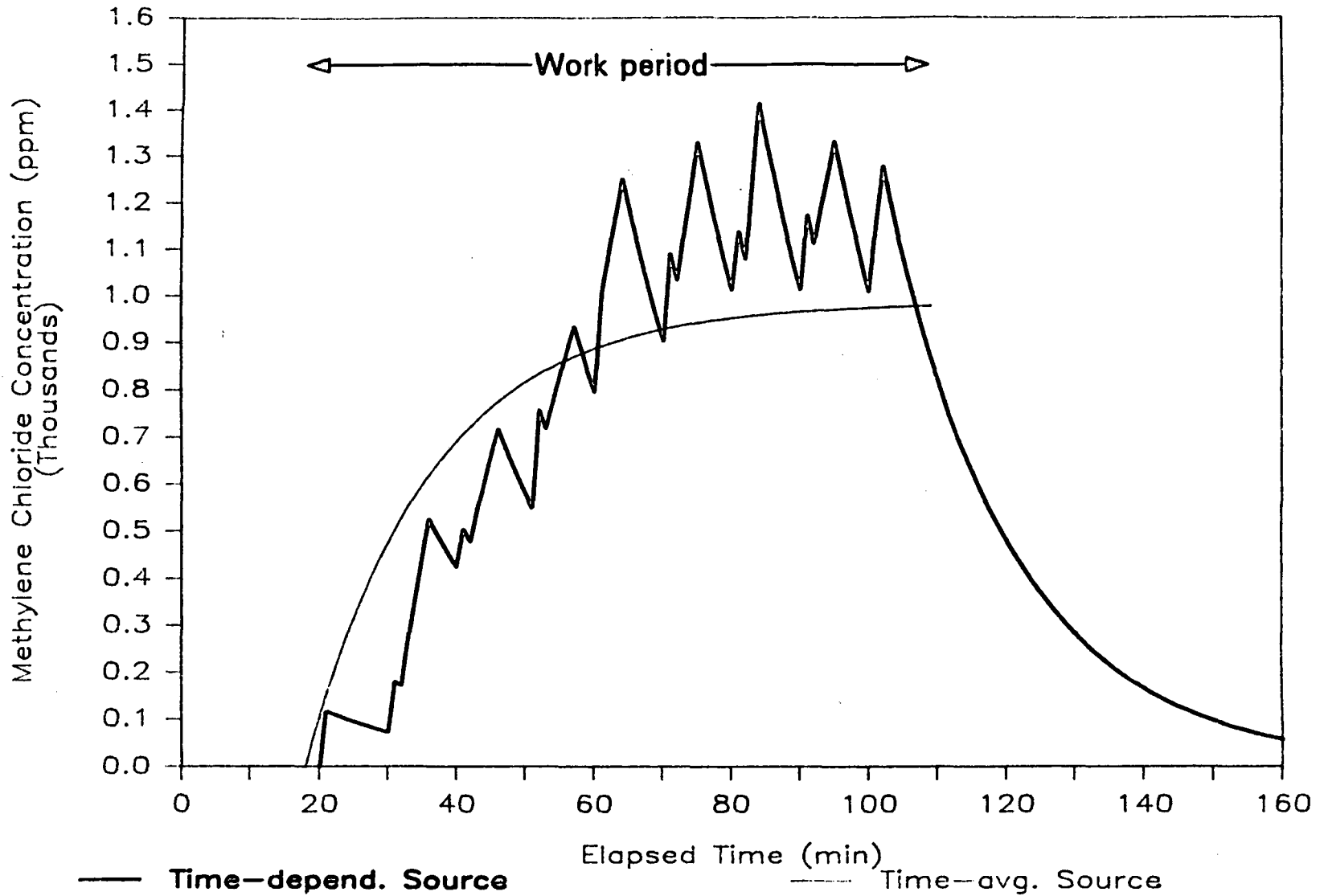


Figure C-4. Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for Experiment 3 with paint remover B at a ventilation rate of 3.20 h^{-1} . Concentrations were calculated using both time-dependent and time-averaged source strengths. Duration of work period is shown above curves.

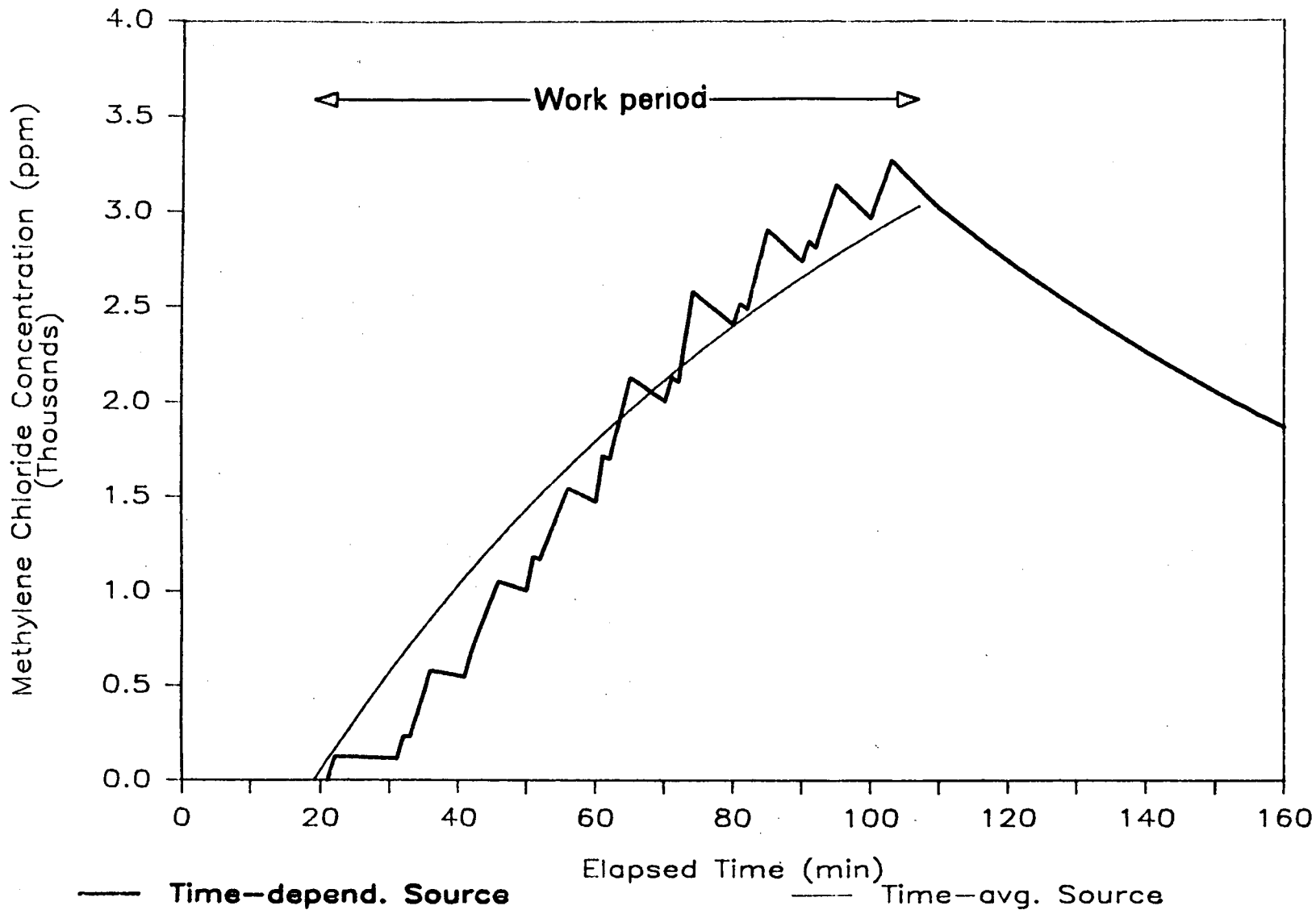


Figure C-5. Temporal profiles of theoretical chamber concentration of CH_2Cl_2 for Experiment 4 with paint remover B at a ventilation rate of 0.63 h^{-1} . Concentrations were calculated using both time-dependent and time-averaged source strengths. Duration of work period is shown above curves.

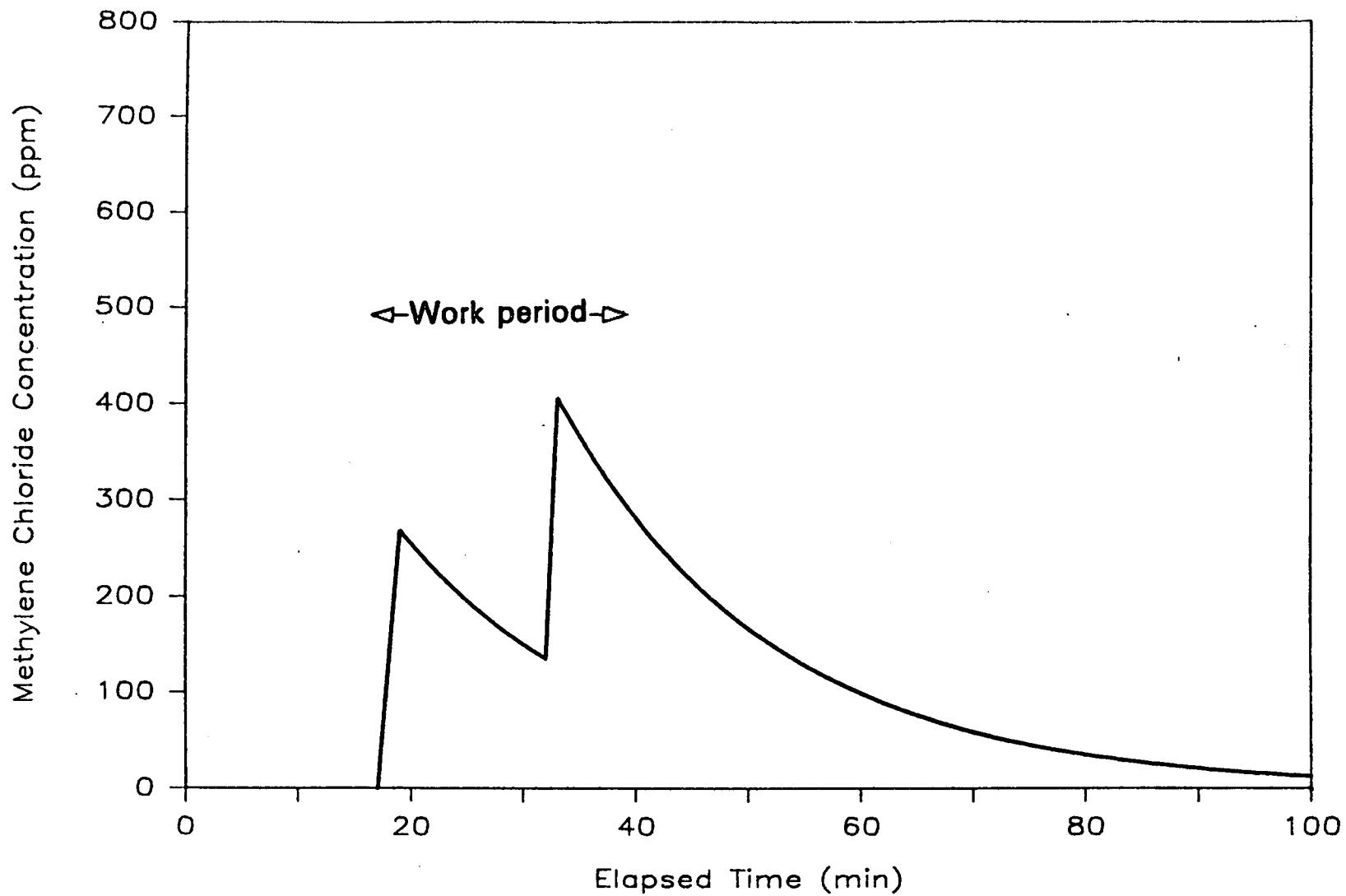


Figure C-6. Temporal profile of theoretical chamber concentration of CH_2Cl_2 for Experiment 6 with metallic paint at a ventilation rate of 3.10 h^{-1} . Duration of work period is shown above curve.

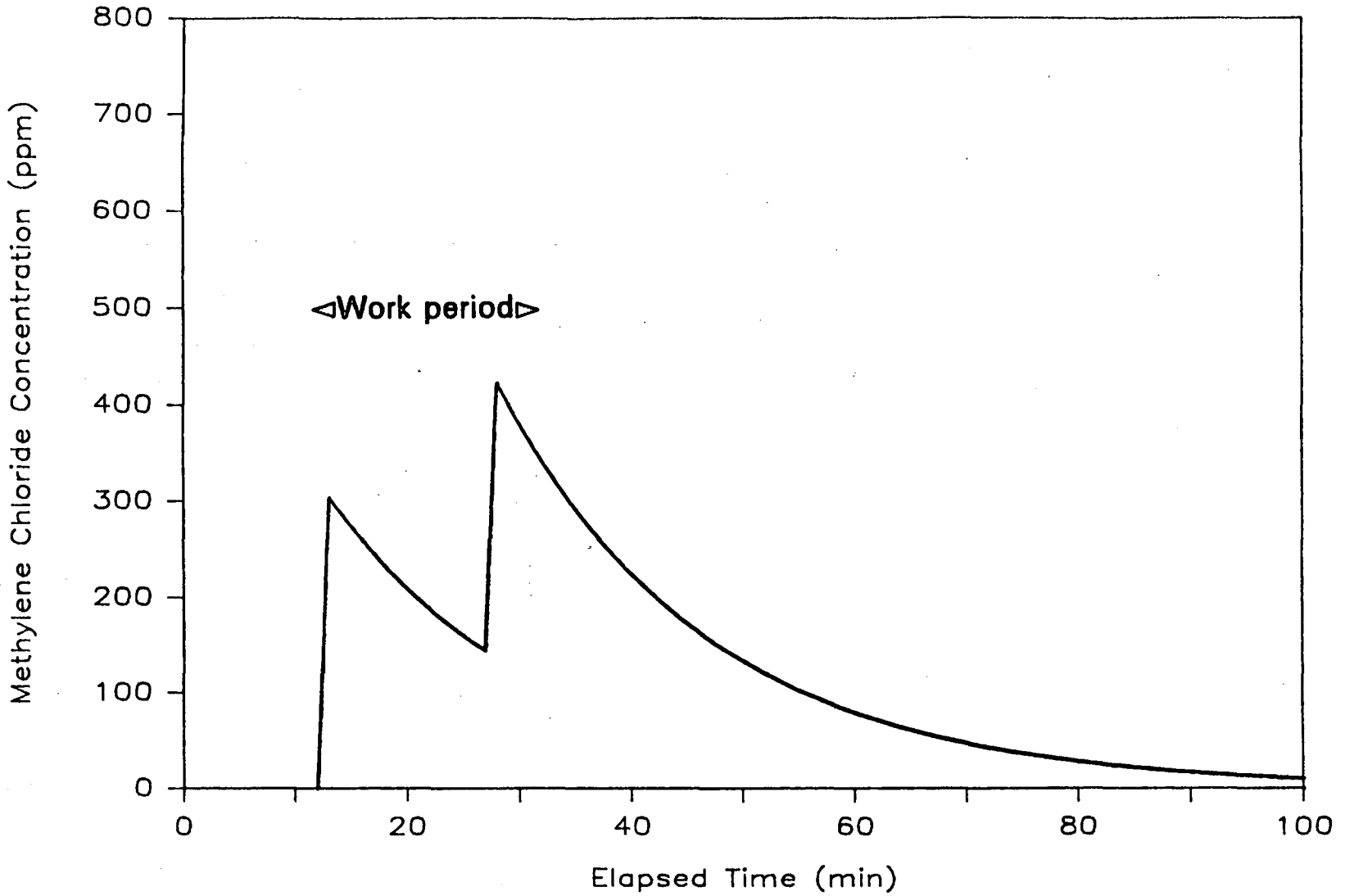


Figure C-7. Temporal profile of theoretical chamber concentration of CH_2Cl_2 for Experiment 7 with metallic paint at a ventilation rate of 3.12 h^{-1} . Duration of work period is shown above curve.

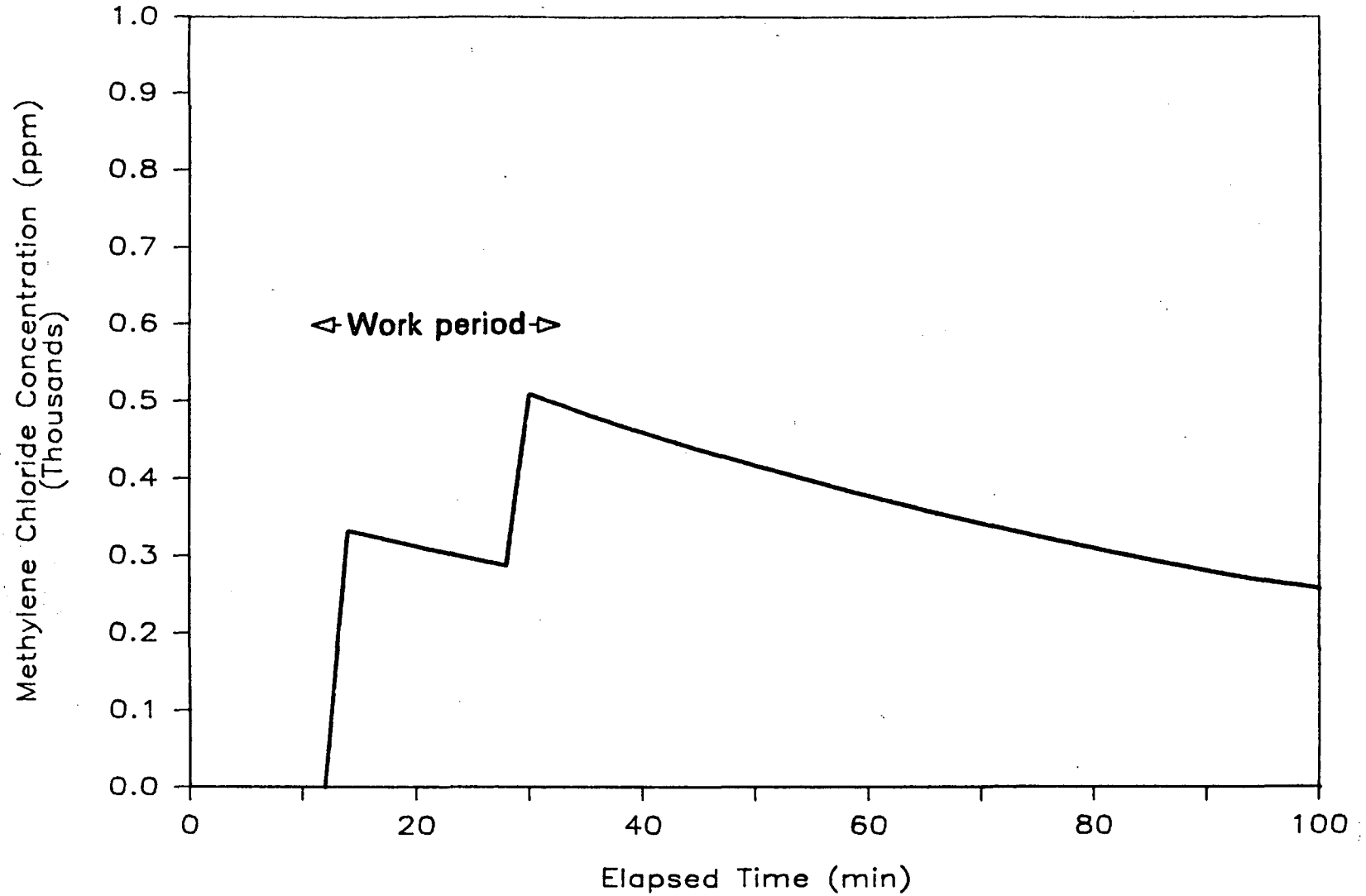


Figure C-8. Temporal profile of theoretical chamber concentration of CH_2Cl_2 for Experiment 8 with metallic paint at a ventilation rate of 0.54 h^{-1} . Duration of work period is shown above curve.

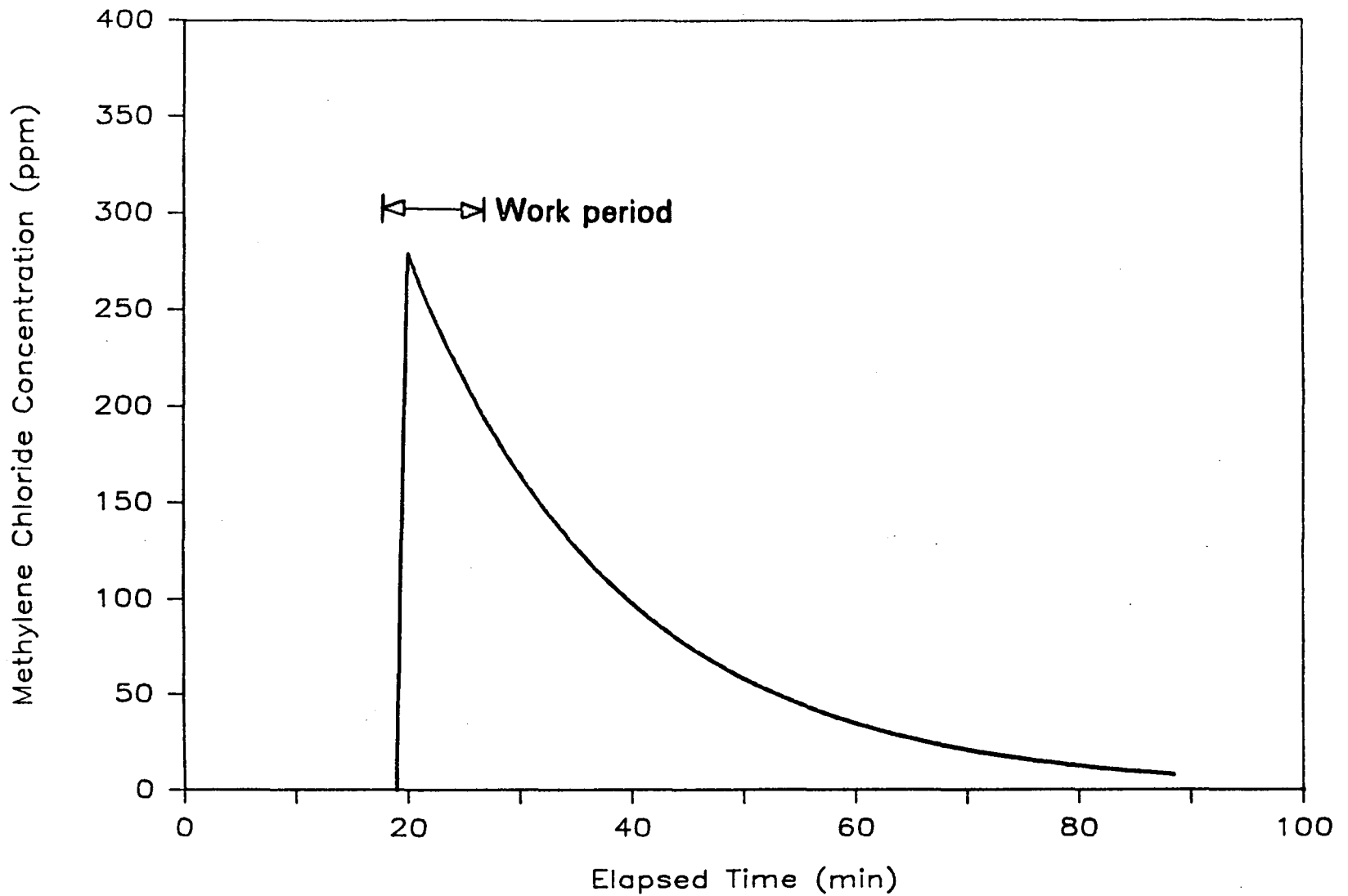


Figure C-9. Temporal profile of theoretical chamber concentration of CH_2Cl_2 for Experiment 10 with polyurethane finish at a ventilation rate of 3.11 h^{-1} . Duration of work period is shown above curve.

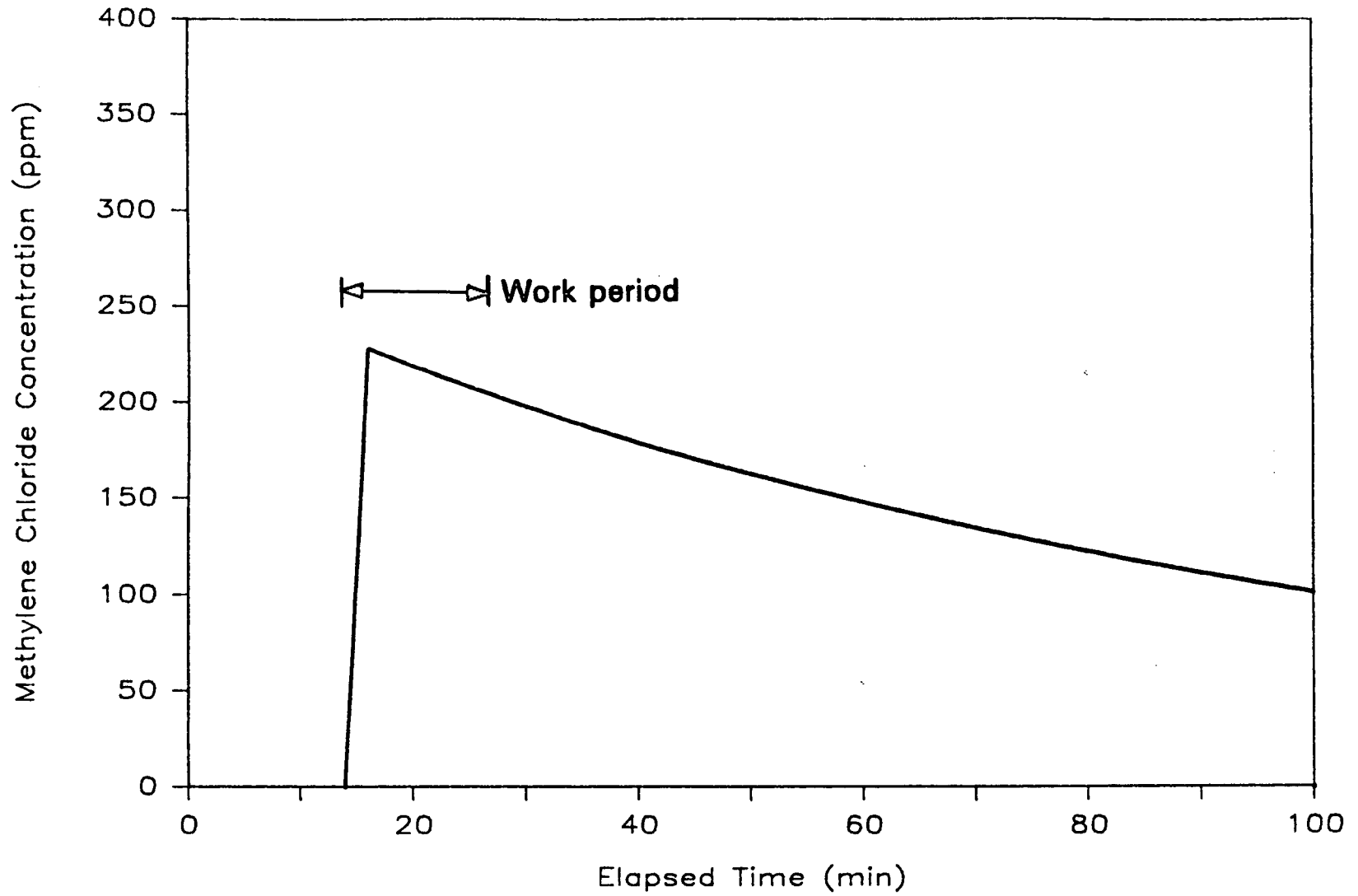


Figure C-10. Temporal profile of theoretical chamber concentration of CH_2Cl_2 for Experiment 9 with metallic paint at a ventilation rate of 0.53 h^{-1} . Duration of work period is shown above curve.

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