

EMISSIONS OF PERCHLOROETHYLENE FROM DRY CLEANED FABRICS

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Abstract—A study was conducted to evaluate the emissions of perchloroethylene (tetrachloroethylene) from dry cleaned fabrics to determine: (a) how the introduction of fresh dry cleaning into a home affects the indoor concentration of perchloroethylene, and (b) the effectiveness of 'airing out' dry cleaned clothes in reducing perchloroethylene emissions. Small chamber tests were conducted to determine perchloroethylene emission characteristics for three fabrics at several air exchange rates. Test house studies were conducted to determine the indoor concentration of perchloroethylene due to the placement of dry cleaned clothing in the house. Based on the study results, and assuming that test conditions were representative of normal dry cleaning and consumer practices, the following conclusions were reached.

- (1) Emissions from freshly dry cleaned clothing cause elevated levels of perchloroethylene in residences.
- (2) For the three fabrics tested, 'airing out' of dry cleaned clothing by consumers for short time periods (4–8 h) will not be effective in reducing perchloroethylene emissions.
- (3) Adsorptive surfaces (i.e. sinks) in residences may have a major impact on consumer exposure to perchloroethylene.

It is emphasized that these conclusions are based on the results of the study reported. Significant variations in dry cleaning practices and/or in the mix of fabrics and clothing being cleaned could provide different results and conclusions.

Key word index: Indoor air quality, perchloroethylene, dry cleaning, chamber testing, emission factors, mathematical models, sink effects, test house studies, indoor concentrations.

1. INTRODUCTION

1.1. Study objectives

The Indoor Air Branch (EPA's Air and Energy Engineering Research Laboratory) conducted a short term study to evaluate the emissions of perchloroethylene (tetrachloroethylene) from dry cleaned fabrics. Specifically, the study was designed to answer two questions: (a) to what extent does the residual perchloroethylene in dry cleaned fabric increase the concentration of perchloroethylene in residential environments? and (b) how effective is 'airing out' dry cleaning in reducing indoor perchloroethylene concentrations?

1.2. Factors affecting emissions and indoor concentrations

A number of factors may affect the amount of residual perchloroethylene in dry cleaned fabrics, including the following.

Type of fabric. Brodmann (1975) reports that the residual perchloroethylene after cleaning varies widely between fabrics. Table 1 provides Brodmann's evaluation

Table 1. Perchloroethylene retained by various fabrics after dry cleaning (Brodmann, 1975)

Fabric type	% Retained (immediate)	% Retained (after 24 h)
Arnel (triacetate)	0.80	0.41
Acetate (diacetate)	0.46	0.21
Polypropylene	0.82	0.20
Spun Dacron 54	0.18	0.12
Spun Dacron 64	0.07	0.07
Polyester double knit	0.09	0.05
Nylon 66	0.09	0.04
Orlon	<0.02	ND*
Acrilan	<0.02	ND*
Wool	<0.02	ND*
Fiberglass	<0.02	ND*

*Not detected.

of the perchloroethylene residuals (as per cent of fabric weight) immediately and 24 h after treatment in a coin operated machine.

Variability of treatment. Perchloroethylene residuals may be affected by the drying cycle and the

aeration step, as well as by such factors as age and condition of cleaning equipment, amount of material cleaned per load, operator technique and solvent purity/age. While data on the effects of such factors are unavailable, such variables could cause differences in perchloroethylene residuals between cleaning establishments and between loads at the same establishment.

Several additional factors are important with respect to the *emission rate* of perchloroethylene from dry cleaned fabrics.

Environmental variables. Temperature, humidity, ventilation (air exchange), and the concentration of perchloroethylene in the air may affect the rate at which residual perchloroethylene is emitted from fabrics.

Type of fabric. The rate of perchloroethylene emissions varies between fabric types. For example, Brodmann's data indicate that Spun Dacron 64 retained 100% of the residual perchloroethylene over a 24 h period, Nylon 66 retained less than 50%, and polypropylene retained less than 25%.

Storage/handling parameters. A number of variables associated with in-home storage or handling of dry cleaned fabrics may affect the perchloroethylene emission rate.

(a) Plastic storage bag retained or removed. Keeping the plastic bag on may reduce the rate of emission, but not the total emitted.

(b) The amount of dry cleaned fabric stored in a closet. The more material stored in a given closet, the greater the total emissions. The emission factor ($\text{mg m}^{-2} \text{h}^{-1}$) may be lower, however, due to the effect of vapor pressure suppression of evaporation. This will not occur if the emissions are limited by in-fabric diffusion.

(c) Pre-storage 'airing out'. Hanging the dry cleaned fabrics outdoors or in a well ventilated area prior to in-home storage may reduce indoor perchloroethylene emission rates.

(d) Time since treatment. The amount of residual perchloroethylene and subsequent emissions to the indoor environment will vary depending on the time between cleaning and placement in the home. Storage at the dry cleaners and transportation time will impact this variable.

Finally, several additional factors may affect the *indoor perchloroethylene concentrations*.

Air exchange rate. The air exchange rate (amount of outdoor air infiltration) determines the dilution and flushing indoors. For a given amount of dry cleaning, the higher the air exchange rate, the lower the indoor perchloroethylene concentration.

HVAC system. The operation of the HVAC (heating, ventilating, air conditioning) system in the home affects the mixing and movement of air. All rooms in residences are generally well-mixed when the HVAC fan is operating. This would cause the perchloroethylene concentrations to be fairly consistent from room

to room, except in the closet where the dry cleaning is stored.

Air movement. The amount of air movement between the closet and the adjoining room and between that room and the rest of the home will affect the perchloroethylene concentrations throughout the residence. Factors such as HVAC operation and open or closed doors are important in affecting air movement.

Sink effects. Materials in the home may adsorb perchloroethylene at higher concentrations and gradually release it over time. Such an effect would lower initial concentrations but extend the exposure time. Factors such as the amount of clothing in the closet (in addition to the dry cleaned items) could impact the sink effect.

1.3. Previous studies

In addition to the study by Brodmann (1975) on perchloroethylene residuals in dry cleaned fabrics, several other references deal with the issue of perchloroethylene exposure from dry cleaning. Several industry sponsored articles are available dealing with safe handling of perchloroethylene in dry cleaning establishments and methods for reducing occupational exposure (Fisher, 1976; HSIA, 1986; IFI, 1987). Fisher (1976) also provides data on perchloroethylene concentrations measured in dry cleaning plants. Data on non-occupational perchloroethylene exposure from dry cleaning are limited to studies conducted on alveolar (breath) air from people exposed to dry cleaning establishments. (Verberk and Scheffers, 1980; Wallace, pers. comm. 1988).

2. STUDY DESIGN

A study consisting of four components was conducted:

- (a) fabric/clothing selection;
- (b) emission factor determination (small chamber testing);
- (c) indoor air quality (IAQ) model analysis; and
- (d) evaluation of indoor concentrations (test house).

2.1. Fabric/clothing selection

Since the available data on perchloroethylene residuals in fabrics are over 10 years old, changes in types of fabrics and dry cleaning technologies may have occurred which would affect the perchloroethylene emissions. Thus, prior to the selection of the test fabrics, a 'screening study' was conducted. Twelve fabrics were purchased, cut into 50×100 cm subsamples, and dry cleaned. Using fabric pieces instead of clothing allowed appropriate sizes to be cut for use in the small chambers. These samples were placed in small test chambers and preliminary data on perchloroethylene emission rates were obtained. These

data were then used to select three fabrics for further evaluation.

For the test house studies, clothes made of the three selected fabrics were used, including: a man's suit, a woman's skirt, and two blouses.

2.2. Emission factor determination (small chamber testing)

Small environmental research chambers were used to develop data on emission factors. The effect of air exchange (air changes per hour [ACH]) on emission factors was investigated for each of three fabrics to determine the effect of 'airing out'. All testing was conducted at a temperature of 20°C and an r.h. of 50%. This test program was designed to provide emission factors for perchloroethylene ($\text{mg m}^{-2} \text{h}^{-1}$), information on the rate of decay of the emissions for the three fabrics, and information on the effect of air exchange.

2.3. IAQ model analysis

The chamber emission factor data were used in an IAQ model to predict expected perchloroethylene concentrations in the test house based on available data on the air exchange and air movement in the test house. These results were used to design the test house experiments. In addition the model enabled an evaluation of the 'sink' effect.

2.4. Evaluation of indoor concentrations (test house)

Based on the results of the chamber tests and subsequent model analyses, four 2-week test house experiments were conducted. Each test consisted of 1 week of testing followed by 1 week of data evaluation and house ventilation in preparation for the next test. Indoor air samples were collected at three locations in the house: (a) the closet where the clothing was hung (three elevations), (b) the adjacent bedroom, and (c) the den. Sampling frequency was determined based on the IAQ model analysis of the small chamber data. A set of background samples were collected prior to each test.

3. EXPERIMENTAL PROCEDURES

3.1. Fabric treatment

All fabrics (bolt material and clothing) were cleaned at a local dry cleaning establishment. The cleaner used a dry-to-dry machine with a 16 kg capacity operating at 60°C. Both utility and legger presses were available, with steam traps at 150°C. The fabric samples and the clothing were handled in a manner consistent with normal dry cleaning operation, including pressing. Protective plastic bags from the cleaners enclosed all cleaned material prior to testing. The cleaned fabrics were picked up from the cleaners within 1 h of being cleaned.

3.2. Small chamber testing

The environmental test chamber system used in the study consists of the following components: a clean air conditioning and delivery system, an incubator containing six 53 l

test chambers, sampling manifolds, and sample collection adsorbers using Tenax and charcoal. The environmental variables were monitored and controlled by a microcomputer. Perchloroethylene analyses were conducted by thermal desorption, concentration via purge and trap, and gas chromatography (GC) using flame ionization detection (FID). Adsorber traps were spiked with hexane, an internal standard, prior to analysis.

Within 1 h of being picked up at the dry cleaners, fabrics were cut to size, hung on wire racks, and placed in the test chambers. The first sample was collected within 30 min of the start of testing. Several samples were collected on the first day; a sampling frequency of one per day was continued until the end of the test period. Most tests were concluded within 5 days.

Samples were collected by pulling a portion of the chamber air stream through tandem glass cartridges filled with Tenax and Tenax/charcoal sorbents. The sampling flow rate was 0.1 l min^{-1} . Sampling time varied from 5 to 100 min providing sample volumes of 0.5–10 l. The sorbent cartridges were thermally desorbed at 220°C to the Tenax/charcoal concentrator column of a purge-and-trap unit. The concentrator column was rapidly heated, and the collected compounds were desorbed to the analytical column of a gas chromatograph (GC). Perchloroethylene was identified by retention time and quantified by FID response. The perchloroethylene peak on the chromatogram was clean and easily identified. The measured quantity of perchloroethylene was adjusted to account for the recovery of the internal standard.

The GC was calibrated by loading Tenax sample cartridges with known amounts of perchloroethylene. Liquid standards were prepared by serial dilution of a gravimetrically determined primary standard. Two microliters of stock solutions, ranging in concentration from 16 to 1600 $\text{ng } \mu\text{l}^{-1}$, were injected through the hot port of the purge-and-trap concentrator. Volatilized compounds were swept by a helium purge to the Tenax sample cartridges. The cartridges were then analyzed in the same manner as the chamber samples. A linear least squares fit ($R^2 = 0.99$) of the FID response (in area counts) provided a response factor which was used to convert FID response to mass units. The GC was checked daily to ensure the calibration had not shifted.

3.3. IAQ test house

A single-story frame house with three bedrooms, two baths, den, kitchen, and an open living/dining area is leased for use as an IAQ test house (Fig. 1). The house is 8 years old, has a forced-air gas heating/electric air conditioning system, and is insulated to be energy efficient (Jackson *et al.*, 1987). Available instruments included a GC with ECD (electron capture detector) that was used for determination of perchloroethylene concentrations.

A standard set of clothing consisting of a woman's wool skirt, two polyester/rayon blouses, and a man's two-piece wool blend suit was dry cleaned in a commercial facility. The clothes were transported to the house in the standard plastic bag provided by the dry cleaners. The clothes were placed in the closet of the corner bedroom and the closet doors were closed. All other interior doors were open. The house was closed, and the sampling initiated within 15 min. The house was maintained at a temperature of 20°C. The HVAC fan was operated in the normal mode, and the fan operating times were recorded.

Samples were collected at three locations for each test: (a) the closet in which the clothes were placed, (b) the corner bedroom (adjacent to the closet), and (c) the den. Samples were collected by gastight syringes for immediate injection into the GC. Samples were taken in the center of each room at a height of 160 cm from the floor. Samples were also collected at heights of 15 and 198 cm in the closet to check for stratification. A system was designed to allow sampling while the closet doors remained closed. This system also returned

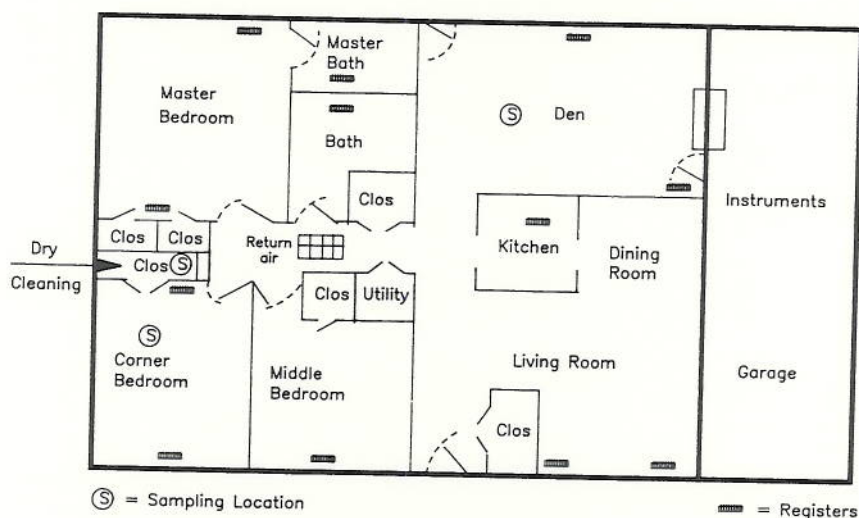


Fig. 1. IAQ test house.

the air to the closet to prevent the loss of perchloroethylene by dilution.

The GC was calibrated with liquid standards over a range of perchloroethylene concentrations. The GC was calibrated every morning before any samples were taken, and its performance was checked every 3 h during the day by injecting two liquid perchloroethylene standards. The sample chromatograms had well defined and easily identifiable perchloroethylene peaks. Only samples with responses within the linear portion of the calibration curve were acceptable.

The air exchange rate for the house, needed in the IAQ model analysis (see section 4.3), was determined on the first day of each test by use of SF_6 tracer gas. The gas was released at the start of the each run and collected in Tedlar bags at hourly intervals until eight samples were taken. The SF_6 was analyzed by GC with ECD and provided sufficient data quality.

After each test, all the windows in the house were opened and the house was allowed to ventilate for a minimum of 4 days and then was reclosed for 4 h before the start of the next run. A background check was performed to ensure that the perchloroethylene from the previous run was below detection limits. The detection limit for the sampling and analysis system used in the study was $1 \mu\text{g m}^{-3}$.

4. RESULTS

4.1. Chamber tests

Models have been developed to analyze the results of the chamber tests in order to provide emission rates (Dunn and Tichenor, 1988). The simplest model (i.e. neglecting sink and vapor pressure effects) assumes: (a) the chambers are ideal continuous stirred tank reactors (CSTRs) and (b) the change in emission factor can be approximated by a first order decay, as shown in Equation (1):

$$R = R_0 e^{-kt} \quad (1)$$

where

R is the emission factor ($\text{mg m}^{-2} \text{h}^{-1}$); R_0 is the initial emission factor ($\text{mg m}^{-2} \text{h}^{-1}$); k is the first order rate constant (h^{-1}); and t is the time (h).

The mass balance for the chamber over a small time increment, dt , is:

change in mass = mass emitted – mass leaving chamber.

This can be expressed as:

$$VdC = AR_0 e^{-kt} dt - QCd t \quad (2)$$

where

V is the chamber volume (m^3); C is the chamber concentration (mg m^{-3}); A is the area of the source (m^2); and Q is the flow through the chamber ($\text{m}^3 \text{h}^{-1}$).

Equation (2) can be rearranged:

$$dC/dt + (Q/V)C = (A/V)R_0 e^{-kt} \quad (3)$$

Equation (3) is a linear, non-homogeneous differential equation. Given that $C = 0$ when $t = 0$, the solution to Equation (3) is:

$$C = \frac{AR_0(e^{-kt} - e^{-Nt})}{V(N - k)} \quad (4)$$

where

N is the air exchange rate (h^{-1}), and is equal to Q/V .

Using a non-linear regression curve fit routine, implemented on a microcomputer, values of R_0 and k can be obtained by fitting the concentration vs time data from the chamber to Equation (4). To conduct such analyses, initial estimates of R_0 and k are required. A good initial estimate of k is:

$$k = Ne^{(k-N)t_{\max}} \quad (5)$$

where t_{\max} is the time of maximum concentration, C_{\max} .

Equation (5) is obtained by substituting C [Equation (4)] into Equation (3) and setting $dC/dt = 0$ at $t = t_{\max}$. Once an estimate of k is achieved from Equation (5), R_0 can be estimated from Equation (4). Figure 2

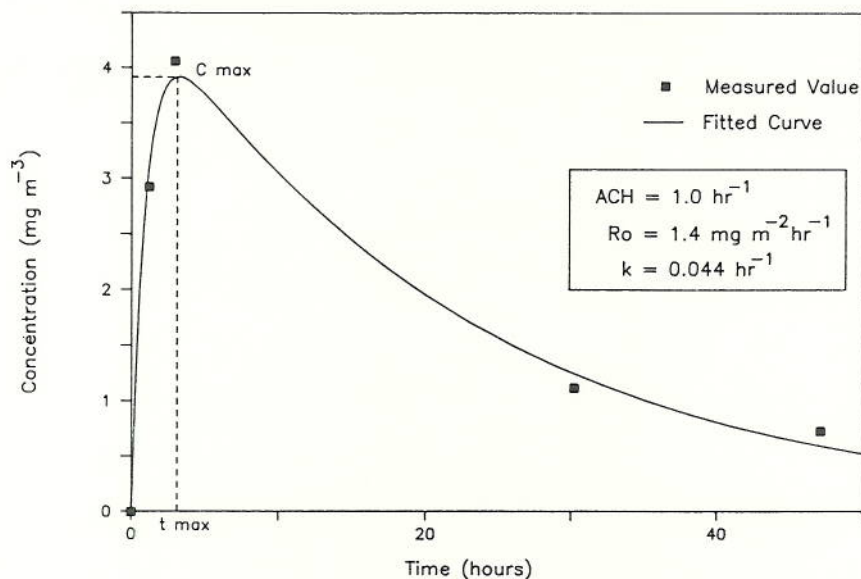


Fig. 2. Perchloroethylene emissions from dry cleaned polyester/rayon (modeling of small chamber data).

illustrates the curve fitting process for a polyester/rayon fabric chamber test at an air exchange rate of 1 h^{-1} ; the solid line is the 'best fit' of Equation (4), and the data points are shown as solid squares.

Data from all the test runs were analyzed using this procedure. The total available emissions (or source strength) per unit area is represented by R_o/k and is obtained by integrating Equation (1) from time zero to infinity. The half-life of the emission factor, $t(1/2)$, was also determined; $t(1/2)$ is the amount of time required for the emission factor to be reduced by 50%.

A preliminary screening study was conducted on 12 different fabrics (cleaned/unpressed). The fabrics were investigated in the 53 ℓ test chambers under the following conditions: air exchange rate = 1.0 h^{-1} , temperature 20°C , relative humidity = 50%, and sample area (one side) = 0.168 m^2 . The sample area was selec-

ted to provide a chamber loading (area of sample/volume of chamber) similar to what was expected in the test house closet.

It is emphasized that the results from this preliminary screening study are useful in a qualitative sense for comparing the emission characteristics of the fabrics tested. Only one short term test was conducted on each fabric, and only two or three data points were collected. Thus, the results of the curve fit procedure described above should be used with caution. These results are presented in Table 2 and show that the amount of perchloroethylene held on fabric surfaces varies greatly depending on fabric type. The total amount of perchloroethylene initially available for emission (R_o/k) ranges from 1.2 to 740 mg m^{-2} . Also, some fabrics hold perchloroethylene longer; $t(1/2)$ values range from 3.3 to 77 h. Again, the reader is

Table 2. Perchloroethylene emissions from various fabrics

Fabric	R_o ($\text{mg m}^{-2} \text{ h}^{-1}$)	k (h^{-1})	R_o/k (mg m^{-2})	$t(1/2)$ (h)
50% Polyester/50% rayon*	0.22	0.030	7.3	23
Rayon	0.055	0.034	1.6	20
Polyester knit	0.43	0.031	14	23
Acetate	6.7	0.009	740	77
Acrylic knit	0.056	0.039	1.4	18
55% Polyester/45% wool*	1.2	0.033	36	21
Wool blend†	0.99	0.080	12	8.7
Cotton	0.44	0.140	3.1	5.0
Linen	0.57	0.076	7.5	9.1
65% Polyester/35% cotton	0.35	0.210	1.7	3.3
85% Rayon/15% flax	0.18	0.150	1.2	4.6

*Selected for further testing.

†Composition unknown.

cautioned to use these results only in a qualitative way to compare one fabric to another. Use of these data to calculate emissions should be avoided.

Based on these preliminary results and an evaluation of the prevalence of materials used in clothing on the market that is normally dry cleaned, the following three fabrics were selected as the test materials.

(a) *A 55% polyester-45% wool blend.* This fabric had a relatively high emission rate and is widely used in men's suits.

(b) *A 50% polyester-50% rayon blend.* This fabric had a relatively low emission rate and is widely used in women's clothing.

(c) *A 100% wool.* Wool was not evaluated, but it is widely used and commonly sent to dry cleaners.

The three selected fabrics (cleaned/pressed) were investigated in the 53 ℓ test chambers under the following conditions: air exchange rates = 0.25, 1.0 and 2.0 h^{-1} ; temperature = 20°C; r.h. = 50%; and sample area (one side) = 0.168 m^2 . The results are shown in Table 3.

The results provided in Table 3 show variations of R_o , k , R_o/k , and $t(1/2)$ for each fabric at the three air exchange rates tested. (See section 6—QA/QC for a discussion of the differences.) Much of the variation is probably due to the changing amount of perchloroethylene retained at the time the fabrics were picked up from the dry cleaners. Four dry cleaning 'loads' were required over a 5 week period to complete the tests reported in Table 2. Whatever the cause of the variations, the data do not suggest that higher air exchange rates have a significant effect on the rate of decay of the emission rate, k , or on the half-life of the emission factor, $t(1/2)$.

4.2. Indoor concentrations (test house)

Evaluations of the impact of dry cleaned clothes on indoor concentrations of perchloroethylene were conducted in the IAQ test house. For each test, the following clothing was dry cleaned and brought to the test house.

A two piece man's suit (55% polyester/45% wool blend);

a woman's skirt (100% wool), fully lined (acetate), and

two women's blouses (50% polyester/50% rayon).

The total area of this mix of clothing, including linings, padding, pockets and accounting for seam overlap, is 8.6 m^2 .

Four tests were conducted.

(a) 'Bag off'—the plastic bag was removed prior to placing the clothes in the closet.

(b) 'Bag on'—the plastic bag was not removed.

(c) 'Aired out'—the plastic bag was removed, and the clothes were hung in an open carport for 4 h prior to being placed in the closet.

(d) A repeat of the first 'bag off' test.

The results of the test house evaluations are shown in Figs 3-5, which show the average daily concentrations for all four tests as measured in the closet, bedroom and den, respectively. The closet values are the average of the three sampling elevations, since no consistent stratification was observed in the closet.

The results show two consistent patterns: (a) on any given day, the concentrations are highest in the closet, followed by the bedroom, with the den having the lowest concentrations; and (b) the concentrations in all rooms generally decrease over time.

A wide variation in perchloroethylene concentrations was observed between the four tests for the first couple of days of each experiment. Since one would not expect that keeping the bag on or airing out the clothes would cause increases in emissions, these differences are not believed to be due to the experimental variables. Rather, it is assumed that the differences are due to the amount of perchloroethylene retained in the clothes at the dry cleaners. At any rate, under all test conditions, elevated levels of perchloroethylene were measured in the test house when freshly dry cleaned clothing was placed in the closet. Also, the perchloroethylene dropped to near or below the detection limit after the clothes were removed from the house.

4.3. IAQ model analysis

The EPA IAQ model (Sparks, 1988) was used to determine the consistency of the test house and cham-

Table 3. Effect of air exchange rate on perchloroethylene emissions

Fabric	Air exchange (h^{-1})	R_o ($\text{mg m}^{-2} \text{h}^{-1}$)	k (h^{-1})	R_o/k (mg m^{-2})	$t(1/2)$ (h)	Rep* (#)
Polyester/wool	0.25	1.50	0.028	54	27	6
	1.0	2.40	0.045	54	16	5
	2.0	0.80	0.028	29	25	1
100% wool	0.25	0.93	0.041	23	20	2
	1.0	1.20	0.028	43	26	4
	2.0	0.80	0.052	15	19	2
Polyester/rayon	0.25	0.56	0.022	26	34	2
	1.0	1.10	0.038	28	19	2
	2.0	0.47	0.027	17	25	1

*Number of replicate tests.

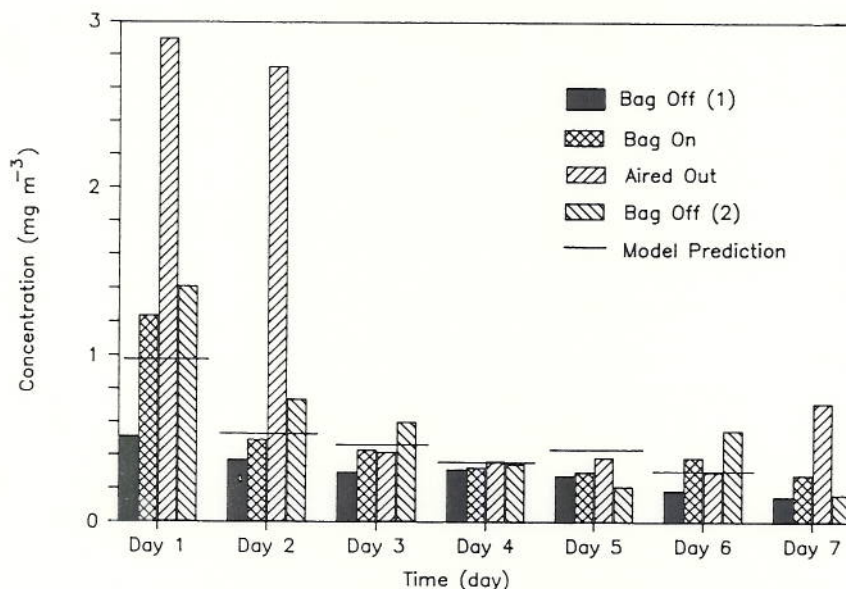


Fig. 3. Perchloroethylene in closet.

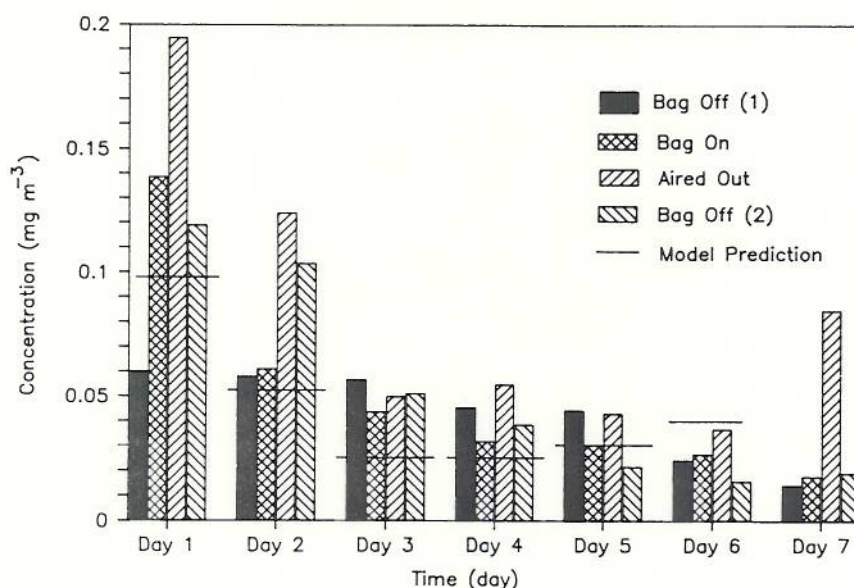


Fig. 4. Perchloroethylene in bedroom.

ber data. The model was also used to estimate sink effects.

The model estimates the effects of heating, ventilating, and air conditioning (HVAC) systems, air cleaning, room to room air movement, and natural ventilation on pollutant concentrations. It is based on conducting mass balances of pollutant and air flow between multiple well-mixed model rooms.

The source term used to model the perchloroethylene emission was based on the small chamber data

and is in the form:

$$E(t) = R_0 e^{-kt} A \quad (6)$$

where

$E(t)$ is the emission rate (mg h^{-1}) at time t ; R_0 is the initial emission factor ($\text{mg m}^{-2} \text{h}^{-1}$); k is a first order rate constant (h^{-1}); and A is the clothing area (m^2).

For the test house studies, $R_0 = 1.60 \text{ mg m}^{-2} \text{h}^{-1}$, $k = 0.03 \text{ h}^{-1}$, and $A = 8.6 \text{ m}^2$. These values were obtained by using a weighted average of the chamber test

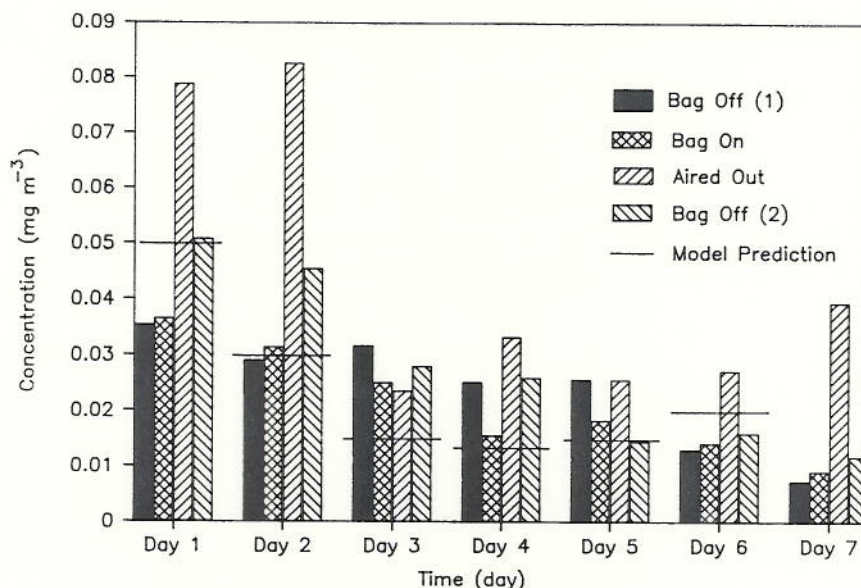


Fig. 5. Perchloroethylene in den.

results based on the measured areas of the fabric types for the clothing used in the test house experiments.

A re-emitting sink was used in the perchloroethylene modeling. The rate going to the sink was assumed to be:

$$R_s = k_s C_r A_s \quad (7)$$

where

R_s is the rate to the sink (mg h^{-1}); k_s is a constant (m h^{-1}); C_r is the concentration in the room (mg m^{-3}); and A_s is the area of the sink (m^2).

The value of k_s was estimated using data from a special perchloroethylene experiment, data from moth crystal cake experiments (Sparks *et al.*, 1988), and a theoretical analysis of mass transfer to walls in a well stirred reactor. The value used for k_s was 0.35 m h^{-1} .

The emission rate from the sink, E_s (mg h^{-1}), was assumed to be:

$$E_s = k_e M_s A_s (C_r - C_c), \text{ when } C_r > C_c \quad (8)$$

$$E_s = 0, \text{ when } C_r \leq C_c \quad (9)$$

where

k_e is the emission constant ($\text{m}^3 \text{ mg}^{-1} \text{ h}^{-1}$); M_s is the mass collected on the sink (mg m^{-2}); and C_c is the critical concentration (mg m^{-3}).

When $C_r > C_c$, emissions are possible, and when $C_r \leq C_c$, emissions are not possible. k_e was estimated to be $5000 \text{ m}^3 \text{ mg}^{-1} \text{ h}^{-1}$, and C_c was estimated to be 0.04 mg m^{-3} .

The results of the initial model runs with no sink effects did not provide good agreement with the measured test house perchloroethylene concentrations. The predicted concentrations were too high, and the predicted curves did not show the changes in slope noted in the experimental data. The likely explanation

for the differences between predicted and measured concentrations is the existence of a sink effect.

Model runs were then made with a re-emitting sink as described above. The model results for days 1–6, using a re-emitting sink, are shown in Figs 3–5. Note that the agreement between the model predictions and the measured data is good both in magnitude and in the shape of the decay curve. Also note that the model predictions, as well as the measured data, show plateaus of nearly constant perchloroethylene concentration, including slight increases, for days 3–6. These plateaus and small increases in perchloroethylene concentration are probably caused by re-emissions from the sink, because, without a re-emitting sink, the concentrations would have continued to decay. Stagnant volumes in the house could also result in similar perturbations in the decay curve, but the linearity of the semi-log plots of the SF_6 data used to determine air exchange rates suggests that such stagnant volumes are too small to account for the variations that were observed.

5. DISCUSSION AND CONCLUSIONS

5.1. Emission factors

Emission factors for perchloroethylene from dry cleaned fabrics were determined by testing in small environmental test chambers under controlled conditions. Evaluation of the data from these tests provides the following results.

(a) A preliminary screening evaluation showed that wide variations in initial emission factor, R_o , and emission factor half-lives, $t(1/2)$, occurred between different fabrics. Thus, the type of fabric is important in determining indoor emissions of perchloroethylene from dry cleaned clothes.

(b) Based on the screening study and on the prevalence of fabrics used in dry cleaned clothing, three fabrics were selected for investigation: 55% polyester/45% wool; 100% wool; and 50% polyester/50% rayon.

(c) The air exchange rate showed no effect on the emission factor or decay rate for the three fabrics investigated. This suggests that the emissions are limited by the diffusion of perchloroethylene within the fabric and are not controlled by evaporative processes. This also suggests that increasing the ventilation by airing out the clothes will not speed up the emission of perchloroethylene.

5.2. Effect of airing out

Since the three fabrics tested had emission factor half-lives of about a day, airing the clothes out for a few hours before hanging them in the home will do little to reduce the indoor perchloroethylene concentrations. For fabrics with faster perchloroethylene decay rates, airing out may be more practical. The per cent emitted during airing out is calculated by:

$$\% \text{ emitted during airing} = (\text{amount emitted} / \text{total available}) 100\%.$$

The amount emitted equals the integral of the emission rate function [Equation (1)] over the time aired out:

$$\text{amount emitted} = (R_0/k) (1 - e^{-ak}) \quad (10)$$

where

a is the airing out time (h).

As defined above, the total perchloroethylene available is R_0/k , thus:

$$\% \text{ emitted during airing} = (1 - e^{-ak}) 100\%. \quad (11)$$

The effect of airing out is illustrated in Fig. 6 which shows the per cent of perchloroethylene emitted during airing out as a function of the time aired out for a wide range of decay rates. Note that, for the decay rates determined for the three fabrics investigated in this study (from Table 3, k ranges from 0.022 to 0.052 h^{-1}), the per cent of perchloroethylene emitted over a 4 h airing out period would range from 8 to 19%; for an 8 h period, the range would be 16–34%.

5.3. Indoor concentrations

All the test house experiments showed that the introduction of dry cleaned clothing caused elevated levels of perchloroethylene in the house. Differences in concentration between the tests were probably due to differences in the amount of perchloroethylene retained at the dry cleaner.

5.4. Model results

The IAQ model, using emissions data developed in the small chambers, predicted indoor perchloroethylene concentrations which compared favorably with those measured in the test house. The effect of perchloroethylene 'sinks' in the test house was also demonstrated.

5.5. Conclusions

Based on the study results, and assuming that test conditions are representative of normal dry cleaning and consumer practices, the following conclusions are reached.

(a) Emissions from freshly dry cleaned clothing cause elevated levels of perchloroethylene in residences.

(b) For the three fabrics tested, 'airing out' of dry cleaned clothing by consumers for short time periods

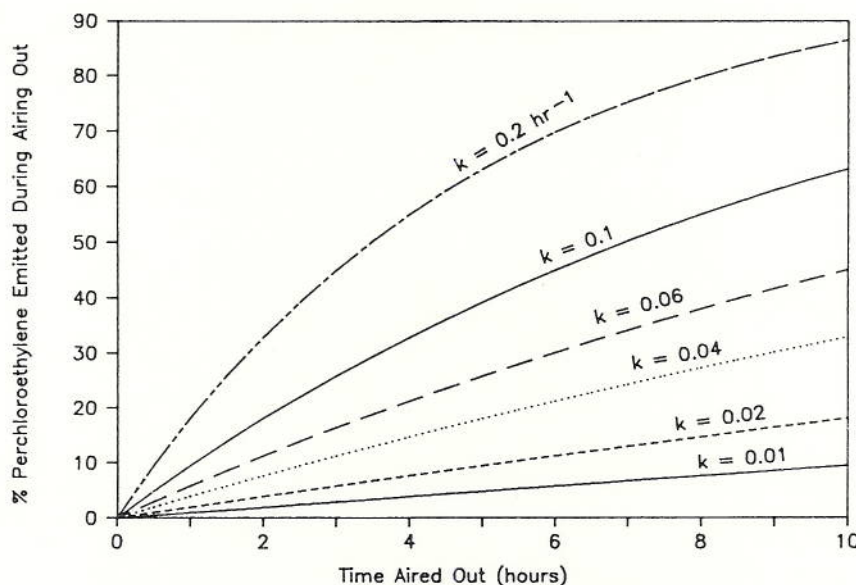


Fig. 6. Effect of airing out.

(4–8 h) will not be effective in reducing perchloroethylene emissions.

(c) Adsorptive surfaces (i.e. sinks) in residences can have a major impact on consumer exposure to perchloroethylene.

It is emphasized that these conclusions are based on the results of the study reported herein. Significant variations in dry cleaning practices and/or in the mix of fabrics and clothing being cleaned could provide different results and conclusions.

6. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

A number of QA/QC steps were implemented in the conduct of the study; the results are reported below. Accuracy (or bias) is reported as the average deviation from the true value:

$$\text{accuracy} = [(m - x_o)/x_o]100\% \quad (12)$$

where

m is the mean; and x_o is the true value.

Precision is reported as Relative Standard Deviation (RSD). RSD (also called the coefficient of variation) is calculated by:

$$\text{RSD} = (s/m) 100\% \quad (13)$$

where

s is an estimate of the standard deviation; and m is the mean.

6.1. Calibration audit for perchloroethylene

Two audit gas cylinders were obtained and analyzed for perchloroethylene in the chamber laboratory and at the test house. The results of the analyses are shown in Tables 4 and 5. In all cases, the goals of 20% accuracy and 15% precision were met.

6.2. QC for chamber laboratory

Variability of sample size, determined by comparing the mass of each fabric used in the individual experiments with the average mass in all tests, ranged from 1.2 to 4.2% for each fabric. The average test chamber temperature was controlled to within $\pm 1^\circ\text{C}$ of the setpoint for all but one experiment, which exceeded the expected range by 0.4°C . Relative humidity was controlled to within $\pm 15\%$ of the setpoint for all experiments. Uncertainty of chamber air flow, determined from the difference in measured flow at the beginning and end of each experiment, was $\pm 4\%$.

QC of the sorbent tubes included analysis of a randomly selected blank from each set of 14 tubes that were thermally desorbed for 'clean-up'. If the blank showed any perchloroethylene above the detection limit, another tube was selected. If both tubes failed the QC check, all 14 tubes were rejected.

Recovery of the internal standard, present in every sample, averaged $103 \pm 9.8\%$ for 270 samples, meeting the goal of 20%. The precision of duplicate samples averaged $7.4 \pm 4.7\%$ for 39 duplicate pairs; the goal was 10%.

Table 4. Audit gas analysis—chamber laboratory

Reported conc. (ppb)	Number of analyses	Ave. meas. conc. (ppb)	Accuracy (%)	Precision (%)
400	2	452	12.8	1.0
10.9	3	9.4	13.8	11.2

Table 5. Audit gas analysis—test house

Reported conc. (ppb)	Number of analyses	Measured conc. (ppb)	Accuracy (%)	Precision (%)
400	7	370	7.5	6.7
10.9	4	10.0	8.3	2.3

Table 6. Variability in R_o , k and $t(1/2)$ for polyester/wool

Air ex. (h^{-1})	No. of samples	R_o ($\mu\text{g m}^{-2} \text{h}^{-1}$)	k (h^{-1})	$t(1/2)$ (h)
0.25	6	1507 ± 529	0.0277 ± 0.0067	26.5 ± 6
1.0	5	2412 ± 495	0.0453 ± 0.0123	16.3 ± 3.9
2.0	1	798	0.0278	24.9

Table 7. Variability in R_o , k and $t(1/2)$ for 100% wool

Air ex. (h ⁻¹)	No. of samples	R_o ($\mu\text{g m}^{-2} \text{h}^{-1}$)	k (h ⁻¹)	$t(1/2)$ (h)
0.25	2	933 ± 95	0.0410 ± 0.0170	20.4 ± 8.4
1.0	4	1186 ± 539	0.0277 ± 0.0095	25.5 ± 3.7
2.0	2	2021 ± 18	0.0385 ± 0.0035	18.7 ± 0.9

Table 8. Variability in R_o , k and $t(1/2)$ for polyester/rayon

Air ex. (h ⁻¹)	No. of samples	R_o ($\mu\text{g m}^{-2} \text{h}^{-1}$)	k (h ⁻¹)	$t(1/2)$ (h)
0.25	2	562 ± 32	0.0220 ± 0.0060	34.0 ± 9.3
1.0	2	1072 ± 254	0.0380 ± 0.0041	18.5 ± 2.0
2.0	1	474	0.0274	25.3

Estimates of the variability of the R_o , k and $t(1/2)$ for all tests conducted at 20°C are shown in Tables 6, 7 and 8, where the mean and standard deviation for each of these parameters is given. The variability indicated in these tables includes load to load variation at the dry cleaners, experimental error, and statistical errors associated with the curve fitting of the data.

6.3. QC for test house

Duplicate samples were taken from each sampling location. A total of 69 pairs of duplicate samples were taken. The precision of the duplicate samples averaged $5.6 \pm 5.7\%$. The precision of seven of the 69 duplicate pairs exceeded the QC goal of 15%, which occurred during the first sampling in the house and may depict levels of perchloroethylene rising due to the recent introduction of the clothing into the house. These samples had a slight difference in collection time.

REFERENCES

- Brodmann G. L. (1975) Retention of chlorinated solvents in fabrics. *J. Amer. Ass. Textile Chem. Color.* **7**, 20-23.
- Dunn J. E. and Tichenor B. A. (1988) Compensating for sink effects in emissions test chambers by mathematical modeling. *Atmospheric Environment* **22**, 885-894.
- Fisher W. E. (1976) Safe handling of perchloroethylene: parts 1 and 2. *Focus on Drycleaning* **2**. International Fabricare Institute, Silver Springs, MD.
- HSIA (Halogenated Solvents Industry Alliance) (1986) The Safe Handling of Perchloroethylene Dry Cleaning Solvent, Washington, DC.
- IFI (International Fabricare Institute) (1987) Perchloroethylene vapor in drycleaning plants. *Focus on Drycleaning* **11**.
- Jackson M. D., Clayton R. K., Stephenson E. E., Guyton W. T. and Bunch J. E. (1987) EPA's indoor air quality test house, 1. Baseline Studies. Proceedings of the 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, EPA-600/9-87-010 (NTIS No. PB88-113402), 104-108.
- Sparks L. E. (1988) Indoor Air Quality Model Version 1.0 EPA-600-8-88-097a (NTIS No. PB89-133607).
- Sparks L. E., Jackson M. D. and Tichenor B. A. (1988) Comparison of EPA test house data with predictions of an indoor air quality model. Presented at ASHRAE IAQ 88, Atlanta, GA.
- Verberk M. M. and Scheffers T. M. L. (1980) Tetrachloroethylene in exhaled air of residences near dry-cleaning shops. *Envir. Res.* **21**, 432-437.