

Evaluation of the Perfluorocarbon Tracer Technique for Determining Infiltration Rates in Residences



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■ A simple passive perfluorocarbon tracer (PFT) technique, for determining air infiltration rates into homes and buildings, was evaluated in a well-defined environmental chamber under experimental conditions of (1) constant temperature and ventilation rate, (2) constant temperature but variable ventilation rate, and (3) variable temperature but constant ventilation rate. Two PFT sources of known emission rate and temperature dependence produced chamber concentrations of 100–300 nL/m³ (parts per trillion). The average relative standard deviation for sampling and analysis of 16 paired samplers in experiment 1 was $\pm 1.9 \pm 1.0\%$, and there was negligible consequence of sampler orientation. For a 3-fold variation in ventilation rates (experiment 2), the passive samplers accurately measured the average chamber tracer concentration, but the PFT-determined ventilation rate had a 10% negative bias. Temperature cycling differences of as much as 8 °C were accommodated to provide essentially no bias in the PFT-determined ventilation rate. The PFT technique is applicable to the expected range of conditions in homes and buildings.

Introduction

Efforts to reduce energy consumption in residences have led to the construction of energy efficient homes and the undertaking of residential weatherization programs which, in turn, have raised concerns about the quality of indoor air. The reduction of air infiltration rates in residences is an effective way to conserve energy by reducing heating and air conditioning demands. Reductions in infiltration rates, however, could result in the occurrence of air contaminants indoors at concentrations that may result in human exposures in excess of health- and comfort-related standards. The determination of infiltration rates in residences is necessary in order to assess the effectiveness of weatherization programs and to develop and evaluate models for infiltration and assessment of indoor air contaminant levels. This paper presents an evaluation of a new tracer system for determining infiltration rates.

The only direct measure of air infiltration in residences under normal occupancy conditions is by the tracer gas technique, which is applied to assessing infiltration rates in two ways. The first method is generally referred to as the tracer gas decay method (1, 2) and the second is referred to as the steady-state tracer gas method (3–5).

Considering a residence as a well-mixed single chamber and letting C = concentration of tracer in chamber (nL/m³), V = volume of chamber (m³), S' = source strength of tracer (nL/h), $S = S'/V$ (nL/hm³), R_E = rate of air exfiltration or leakage (m³/h), and $n = R_E/V$ or number of air changes per hour (ach) (h⁻¹), a mass balance around the chamber gives

$$dc/dt = S - nC \quad (1)$$

Integrating from C_0 at $t = 0$ to C_t , the tracer concentration at time t , gives

$$C_t = \frac{S}{n} + \left(C_0 - \frac{S}{n} \right) e^{-nt} \quad (2)$$

For the tracer decay approach, in which a small amount of tracer is well-mixed into the chamber and the source is turned off ($S = 0$), eq 2 becomes

$$C_t = C_0 e^{-nt} \quad (3)$$

and hence

$$\ln C_t = \ln C_0 - nt \quad (4)$$

When the natural logarithm of the tracer concentration vs. time is plotted, the air changes per unit time, n , is obtained as the negative of the slope as shown by eq 4. In practice, the tracer gas concentration in the space is measured as a function of time via either continuous monitors or a series of grab samples transported to a laboratory for subsequent analysis. This method has employed a number of gases as tracers (SF₆, CH₄, N₂O, CO₂, CO, C₂H₆, He, etc.) which have been evaluated in a number of studies (6–8). The tracer gas decay method provides a short-term measurement of air exfiltration rates, usually on the order of a few hours.

The steady-state tracer gas method uses SF₆ or a perfluorocarbon tracer gas. The tracer gas is emitted into the space at a constant rate either via a mechanical or microprocessor system (3, 5, 9) or via a liquid permeation source (4). The tracer gas is allowed to come to steady-state conditions in the space and then is sampled in the space either continuously, periodically with a sequential sampling system into a collection media such as syringes or bags, or passively using adsorption tube samplers. The latter two collection methods require subsequent laboratory analysis. At steady state ($dC/dt = 0$), eq 1 becomes

$$n = \frac{S}{C} = \frac{S'}{VC} \quad (5)$$

The number of air changes per hour, n , is simply the known tracer source rate divided by the volume of the house and the measured steady-state average tracer concentration.

One steady-state tracer gas method for assessing air-exchange rates, developed at Brookhaven National Laboratory and called the Brookhaven National Laboratory Air Infiltration Measurement System (BNL/AIMS) (10), is being extensively employed in large field studies of indoor air quality and impact of weatherization (11–14). The BNL/AIMS method consists of miniature perfluorocarbon tracer (PFT) sources and miniature passive capillary ad-

sorption tube samplers (CATS). The sources and samplers are about the size of a cigarette. The PFT sources use one of four perfluorocarbon compounds: perfluorodimethylcyclohexane (PDCH); perfluoromethylcyclohexane (PMCH); perfluoromethylcyclopentane (PMCP); perfluorodimethylcyclobutane (PDCB). Vapors from the perfluorocarbon liquid in the PFT sources permeate through an elastomeric plug crimped into one end. The PFT sources emit the tracer gas at a constant rate for 2-7 years. The emission rate, however, does vary with temperature (15). The emission rates are determined gravimetrically.

The CATS device is a passive sampler utilizing about 50 mg of type XE-347 Amborsorb as the collection media. After sampling, the collected tracer gas is thermally desorbed into a gas chromatograph for determination of the PFT concentration. One type of PFT source can be used for a single-compartment model, while up to a four-compartment model (air-exchange rates between the space and outdoors as well as between compartments or rooms in the space) can be evaluated by using four different types of PFT sources, one type per compartment. This method is typically used to obtain integrated air-exchange rates over periods of 1 day to several weeks or months. Use of a programmable sampler with sampling pump will allow for multiple short-term (<1 h) sample collections for determinations of air exchange rates on a short-term basis. The small size of the sources and samplers, their passive nature (e.g., no pumps), wide range of sampling times (from hours to weeks or months), ease of analysis, and relative low cost have made the BNL/AIMS ideally suited to large-scale field studies of infiltration rates in residences and large buildings (16).

This paper presents the results of experiments conducted in an environmental chamber to evaluate the BNL/AIMS system for determining air-exchange rates. The accuracy of the BNL/AIMS system by comparison with CO₂ tracer decay, the impact of orientation of the CATS samplers with respect to flow direction, and the impact of variations in infiltration rate and temperature are evaluated under conditions of near ideal air mixing in the chamber.

Methods

Environmental Chamber. Figure 1 presents a schematic view of the environmental chamber with associated control equipment. The box on the right, actually a cross-sectional schematic of the 34-m³ chamber itself, displays within it the range of operating conditions. All ductwork and internal surfaces were constructed of aluminum. The floor, 11 m², consisted of uniformly perforated aluminum sheets overlaid with an aluminum grating. The perforated floor served as an air diffuser. Air entered the chamber via a plenum beneath the floor and flowed upward through the perforations to the ceiling. The design allowed a volume flow of up to 2000 cfm (1 m³/s) with low linear velocity and very rapid mixing. The volume flow (recirculation rate) could be varied from 400 to 2000 cfm (0.2-1.0 m³/s) which corresponded to 20-100 air changes per hour (ach) and a vertical velocity of 0.02-0.09 m/s. A variable percentage of the recirculated air could comprise fresh ventilation air. The fresh air brought into the chamber could be varied from 0 to 400 cfm (0-0.2 m³/s) which corresponded to 0-20 ach of fresh air. The chamber possessed excellent temperature and humidity control. Air cleaning could be accomplished by diverting the recirculated air through an electronic air cleaner or granular filter media. At no time during these experiments were the air cleaning capabilities of the chamber utilized.

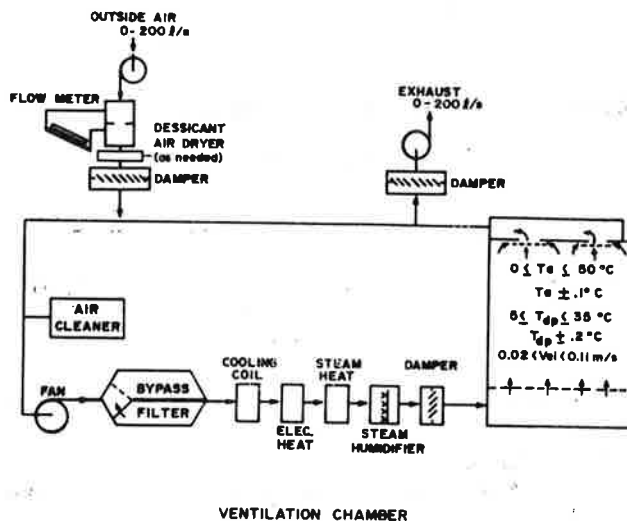


Figure 1. Schematic view of environmental chamber and control equipment. Arrows in box at right portray the flow of air from the plenum beneath the floor to the return ducts in the ceiling.

BNL/AIMS. The PFT sources and CATS were supplied by the Department of Applied Science, Brookhaven National Laboratory (BNL). Analysis of the passive samplers and emission rate determinations of the PFT sources were done by BNL. In this set of experiments, two perfluorodimethylcyclobutane (PDCB) PFT sources were used. The emission rates of these PFT sources were determined gravimetrically at a stabilized temperature of 25 °C. The PFT sources were shipped via mail to the chamber facility laboratory where they were stored at 23 °C for over 2 weeks prior to their use. The average PFT source strengths were adjusted to the 23 °C base temperature at which the experiments took place according to the following formula (15):

$$S'_t = S'_{25} e^{-4006(1/T - 1/298)} \quad (6)$$

where S'_t = PFT source strength at the average base temperature (t , °C) in nL/h, S'_{25} = PFT source strength at 25 °C (determined gravimetrically as 5688 ± 120 nL/h), and T = average base temperature (t , °C) in kelvin at which the PFT source is used. For short-term (less than 48 h) temperature changes, the exponential constant was found to be half that for long-term (greater than 10 days) changes (15). Thus, when the temperature of the chamber was varied for short-term changes

$$S'_t = S'_{23} e^{-2000(1/T - 1/296)} \quad (7)$$

where S'_t = PFT source strength at chamber temperatures in nL/h, S'_{23} = PFT source strength at 23 °C base temperature (from eq 6) in nL/h, and T = chamber temperature in K.

The CATS were delivered to this laboratory by hand and stored in a separate building prior to and after use in order to minimize contamination. Two unopened but deployed CATS were included as controls in this set of experiments. After use, the CATS were returned to BNL for analysis by gas chromatography. BNL was blind as to the placement of the passive samplers and chamber conditions for each experiment. A detailed description of the BNL/AIMS method can be found elsewhere (10, 15).

CO₂ Decays. Ventilation rates (n) throughout these experiments were determined by the tracer gas decay method using CO₂ as the tracer gas. At regular intervals during each experiment CO₂ was injected into the chamber until the concentration in the chamber reached 1%. The gas was then shut off and the decay of CO₂ recorded

Table I. Average Measured PDCB Concentrations for Paired CATS vs. Sampler Orientation and Chamber Location
 [Experiment 1: $av\ ach_{CO_2} = 0.601 \pm 0.011\ h^{-1}$, $S = 152.8 \pm 4.3\ nL/(h \cdot m^3)$ at 23 °C]

passive sampler orientation to flow	average PDCB concn of paired samplers \pm SD, ^a nL/m ³ (%), ^b at chamber location				CATS orientation average
	A	B	C	D	
1 (perpendicular)	246.3 \pm 3.4 (1.4)	243.3 \pm 3.0 (1.2)	237.7 \pm 3.0 (1.2)	244.1 \pm 8.3 (3.4)	242.9 \pm 5.0 (2.1)
2 (away)	231.3 \pm 1.4 (0.6)	240.0 \pm 2.2 (0.9)	235.3 \pm 1.4 (0.6)		235.5 \pm 4.1 (1.7)
3 (into)	244.9 \pm 3.0 (1.2)	237.9 \pm 5.3 (2.2)	234.6 \pm 9.9 (4.2)		241.5 \pm 4.6 (1.9) ^c
4 (shielded)	234.6 \pm 6.2 (2.7)	235.5 \pm 6.0 (2.5)	241.4 \pm 5.6 (2.3)		237.1 \pm 5.7 (2.4)
5 (perpendicular)	241.7 \pm 2.9 (1.2)	244.5 \pm 5.3 (2.2)	246.9 \pm 6.3 (2.6)		244.4 \pm 4.5 (1.9)
average	239.8 \pm 6.8 (2.8)	240.2 \pm 4.9 (2.0)	239.2 \pm 6.6 (2.7) ^c	244.1 \pm 8.3 (3.4)	240.4 \pm 5.7 (2.4) ^d

^aThe average of 16 paired standard deviations was $4.6 \pm 2.4\ nL/m^3$ ($1.9 \pm 1.0\%$) with a range of 1.4–9.9 (0.6–4.2%) and a median of 5.3 (2.2%). ^bQuantities in parentheses are the percent relative standard deviations. ^cOne concentration excluded from location C (orientation 3) in computation of the overall averages. ^dCalculated overall average PDCB concentration was 254.2 ± 12.8 (5.0%).

continuously on a Beckman LB-2 infrared CO₂ analyzer. Background CO₂ levels were also recorded. The CO₂ analyzer was calibrated before and after each experiment with NBS traceable gases. For each decay, background levels were subtracted. The natural logarithms of 11 concentrations per decay (5-min intervals) were plotted vs. time, and a least-squares linear regression was used to obtain the slope and hence ventilation rate (eq 4).

Experiments. Three experiments were conducted to evaluate the BNL/AIMS infiltration measurement method under controlled conditions in the environmental chamber, as outlined in Figure 2. The two PFT sources used throughout all experiments were placed in the center of the chamber 1.9 m above the floor. This ensured that the PDCB tracer gas was well mixed in the recirculation loop before exposure to the samplers. Although the PFT sources were stored at 23 °C before use, they were allowed to equilibrate at a temperature of 23 °C for 3 days in the chamber before the experiments began in order to ensure that a steady-state concentration of the PDCB tracer gas was achieved in the chamber under the conditions of an air recirculation rate of 60 ach and a fresh air ventilation rate of about 0.6 ach.

(a) Experiment 1. The impact of CATS orientation during sample collection and accuracy of the BNL/AIMS method at a known and constant ventilation rate were evaluated in the first experiment. A constant temperature of 23 °C, an air recirculation rate of 60 ach, and a fresh air rate of about 0.6 ach were maintained throughout the experiment. The CATS samplers were placed on four chairs, equidistantly spaced in the chamber. The five positions of the CATS samplers placed on each chair are shown in Figure 2. The open end (only one end during sampling) was facing up in position 2, down in position 3, and off the back of the chair in position 5. All samples were taken in duplicate. One of the chairs (location D) had CATS in position 1 only, for a total of 32 CATS samples in the chamber. Hour-long CO₂ decays were obtained at six equally spaced times during the course of this 44-h experiment.

(b) Experiment 2. The accuracy of the BNL/AIMS method in measuring the average ventilation rate over a period of time where the ventilation rate was varied in discrete steps was evaluated in this experiment. A constant temperature of 23 °C was maintained throughout the run while the ventilation rate was varied in a series of 11 steps among three levels of about 0.60, 1.29, and 1.64 ach. The chamber was well-mixed (recirculation rate greater than 60 ach) and duplicate CATS samples only for position 1 were obtained on all four chairs (eight CATS samples). A total of twenty 1-h CO₂ decays (one after each new ventilation rate was set and, generally, a duplicate run later)

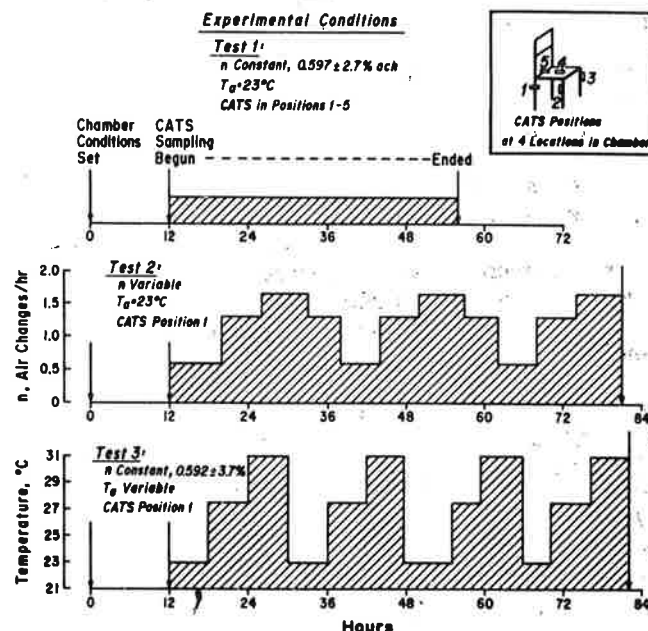


Figure 2. Experimental conditions in the environmental chamber for each of three tests for evaluating the BNL/AIMS method for determining ventilation rates. CO₂ decays performed throughout each of the three experiments served as the basis for comparison.

were obtained for this 69-h experiment.

(c) Experiment 3. The impact of varying temperature on the PFT source emission rate in determining ventilation rates was evaluated in this experiment. After the initial equilibration period at 23 °C, the temperature was cycled among three temperature settings (23, 27, and 31 °C) for a total of 12 steps as shown in Figure 2. The ventilation rate was constant at about 0.6 ach and the recirculation rate at 60 ach during this 72-h experiment. The standard temperature correction factor (eq 6) was applied to the PDCB PFT sources in calculating the emission rate at 23 °C and the short-term correction (eq 7) for the 27 and 31 °C rates. Sixteen hour-long CO₂ decays were obtained, one after each temperature change and an occasional repeat. Duplicate CATS samples were obtained in position 1 for all four chairs (eight CATS samples).

Results

Experiment 1. The average measured concentrations, standard deviations, and relative standard deviations of the 16 paired samplers are shown in Table I, arranged according to sampler orientation and location within the chamber. The average of the 16 paired standard deviations was $4.6 \pm 2.4\ nL/m^3$ which, for an overall average concentration of $240.4 \pm 5.7\ nL/m^3$, corresponded to an av-

Table II. Comparison of BNL/AIMS Measured vs. Calculated PCB Concentrations

experiment	conditions	no. of changes	average PCB concn, nL/m ³		measd/calcd
			measured ^a	calculated ^b	
1	constant temp, constant ach	0	240.4 ± 5.7	254.2 ± 12.8	0.946 ± 0.074
2	constant temp, variable ach	11	139.3 ± 2.5	149.2 ± 7.7	0.934 ± 0.068
3	variable temp, constant ach	12	290.5 ± 8.0	280.9 ± 19.3	1.034 ± 0.107

^a Measured concentrations were determined with CATS. ^b Calculated concentrations were obtained either from eq 5 (experiment 1) or from eq 9 (experiments 2 and 3), time-weighted over each measurement period.

average relative standard deviation of 1.9 ± 1.0% with a range of 0.6–4.2% and a median of 2.2%. Thus, the expected precision of duplicate samplers, ±2%, demonstrates that there is no need to perform duplicate sampling during actual field use, since the sampling rates, handling, and analytical procedures for the CATS are consistent and reproducible.

All 32 sampler analyses results are shown in Figure 3, where they are plotted vs. both sampler orientation and chamber location. Also included are the means (crosses) and standard deviations (bars) for all samplers in each orientation and location as well as the overall average and standard deviation for 31 samplers (one result at orientation 3 and location C, which had a value of 227.6 nL/m³, was statistically low and was excluded from all averaging).

Figure 3 clearly shows that the averages of the 10 samplers in each of the three chamber locations (A–C) were statistically identical. In fact, excluding location D because there were only two samplers, the maximum difference between the three averages was only 0.4%, indicating that the chamber concentration was uniformly identical at all locations.

Figure 3 does show that sampler orientation did affect the average sampling rate. Positions 1 and 5 both exposed the samplers at right angles to the chamber flow; their averages were identical within 0.7% and about 1.3% above the overall mean. Position 3, CATS facing into the direction of flow, had an average that was 0.5% above the overall average. The lowest mean concentrations were for positions 2 (facing away from the direction of flow) and 4 (shielded by the chair seat), probably because those positions prevent turbulence at the sampling end. Those means were 2.0 and 1.4% below the overall mean. As shown in the figure, only position 2 was statistically different (more than 1 standard deviation) from the overall average.

The average chamber ventilation rate, n , based on five of the six CO₂ decay measurements was 0.601 ± 0.011 h⁻¹. The tracer source strength, S' , based on gravimetric measurements at 25 °C was 5688 ± 120 nL/h. Substituting into eq 6 gave $S'_{23} = 5195 ± 145$ nL/h, and dividing by the chamber volume ($V = 34$ m³) gave $S = 152.8 ± 4.3$ nL/(h·m³). The PCB concentration can then be calculated from eq 5:

$$C = \frac{S}{n} = \frac{152.8 \pm 4.3}{0.601 \pm 0.011} = 254.2 \pm 12.8 \text{ nL/m}^3$$

which, as shown in Table II, is identical within the standard deviation of the average of the measured concentrations.

Experiment 2. Unlike experiment 1, which was conducted at steady-state conditions of constant temperature and ventilation rate, experiments 2 and 3 were performed over multiple periods in which the temperature and ventilation rate were constant during each period, but at least one of the two was changed from the previous period. The tracer concentration at any time, t , during the period is

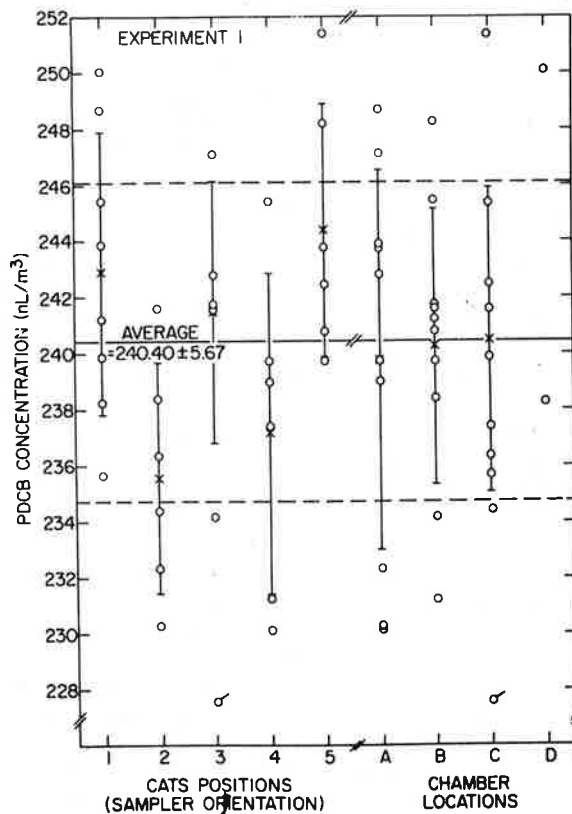


Figure 3. PCB concentrations (O), averages (X), and standard deviations (—) for 16 paired CATS vs. sampler orientation (position 1, 90° from into the wind; position 2, 180°; position 3, 0°; position 4, shielded; position 5, 90°) and chamber location.

given by eq 2 where C_0 is the concentration at the end of the previous period.

The average concentration during each period is given by

$$\bar{C} = \frac{1}{\tau} \int_0^{\tau} C_t dt \quad (8)$$

Substituting eq 2 into eq 8 and integrating give

$$\bar{C} = \frac{S}{n} - \left(\frac{C_0 - S/n}{n\tau} \right) (e^{-n\tau} - 1) \quad (9)$$

where τ = the duration of each period (h).

The ach (n) and duration (τ) for each period of experiment 2 (constant temperature and variable ach) are given in Table III and were used in eq 2 and 9 to compute the concentration as a function of time and the average concentration for each period as shown in Figure 4 (top). The series of exponential curves, when integrated over each period, gave the average concentrations listed in Table III; the calculated overall average concentration for the 69-h period was 149.2 ± 7.7 nL/m³.

Table IV lists the measured concentrations obtained with the eight CATS. The relative standard deviation of

Table III. Conditions and Calculated Results for Variable Infiltration Rate Experiment [Experiment 2: $S = 152.8 \pm 4.3$ nL/(h·m³) at 23 °C]

period	average ach _{CO₂} ± SD, h ⁻¹ (%) ^a	time of period, h		calcd av PDCB ^b concn, nL/m ³
		duration	from-to	
1	0.608 ± 0.004 (0.7)	8	0-8	251.3 ± 8.8
2	1.306 ± 0.069 (5.3)	6	8-14	134.1 ± 10.8
3	1.627	7	14-21	95.9 ± 6.2
4	1.312 ± 0.062 (4.7)	5	21-26	113.0 ± 8.5
5	0.599 ± 0.014 (2.4)	6	26-32	217.6 ± 11.4
6	1.298 ± 0.046 (3.5)	6	32-38	134.9 ± 9.0
7	1.623 ± 0.021 (1.3)	7	38-45	96.2 ± 4.3
8	1.263 ± 0.014 (1.1)	5	45-50	116.7 ± 4.7
9	0.567	6	50-56	227.3 ± 8.6
10	1.273 ± 0.001 (0.1)	6	56-62	138.9 ± 4.6
11	1.624 ± 0.070 (4.3)	7	62-69	96.4 ± 6.8
av ^c	1.190 ± 0.033 (2.8)			149.2 ± 7.7(5.1%)

^a Average of two measurements per period with standard deviation and percent relative standard deviation in parentheses. ^b Calculated from eq 9 including the error in S and ach_{CO₂} (n). ^c Time-weighted average.

Table IV. Measured PDCB Concentrations for Variable Infiltration Rate Experiment (Experiment 2: Calculated Time-Weighted Average PDCB Concentration = 149.2 ± 7.7 nL/m³)

chamber location	CATS sampler	PDCB concn, nL/m ³	
		measured	average ± SD (%) ^a
A	5621	142.2	142.0 ± 0.3 (0.2)
	5391	141.8	
B	5366	139.2	139.1 ± 0.2 (0.1)
	5655	138.9	
C	5332	131.4	133.4 ± 2.8 (2.1)
	5627	135.4	
D	4682	140.4	138.8 ± 2.3 (1.7)
	5379	137.1	
av ^b		139.3 ± 2.5 (1.8)	

^a Average of two measurements with standard deviation and percent relative standard deviation in parentheses. ^b CATS 5332 not included in overall average.

the four sets of duplicate measurements ranged from 0.1 to 2.1%, similar to the experiment 1 paired results. The overall average PDCB concentration was 139.3 ± 2.5 nL/m³ which, as shown in Table II, agrees with the calculated concentration for experiment 2 within the standard deviation of each determination.

Table V. Conditions and Calculated Results for Variable Temperature Experiment [Experiment 3: $S = 152.8 \pm 4.3$ at 23 °C, 167.2 ± 5.8 at 27 °C, 182.5 ± 7.5 nL/(h·m³) at 31 °C]^a

period	chamber temp, °C	av ach _{CO₂} ± SD h ⁻¹ ^b	time of period, h		calcd av PDCB ^c concn, nL/m ³
			duration	from-to	
1	23.0	0.577 ± 0.009	6	0-6	264.8 ± 11.8
2	27.0	0.566	6	6-12	286.7 ± 18.3
3	31.0	0.611	6	12-18	297.5 ± 22.3
4	23.0	0.593 ± 0.018	6	18-24	268.8 ± 17.9
5	27.0	0.567	6.75	24-30.75	285.7 ± 19.6
6	31.0	0.621	5.5	30.75-36.25	293.9 ± 22.0
7	23.0	0.588 ± 0.018	7.5	36.25-43.75	267.5 ± 17.5
8	27.0	0.585	4.25	43.75-48	276.4 ± 18.4
9	31.0	0.596	6.5	48-54.5	300.5 ± 22.5
10	23.0	0.626	4.5	54.5-59	264.7 ± 18.5
11	27.0	0.597	7	59-66	272.5 ± 18.6
12	31.0	0.621 ± 0.026	6	66-72	290.1 ± 23.7
av ^d	27.0	0.595 ± 0.022			280.9 ± 19.3

^a The time-weighted average S was 167.5 ± 5.9 nL/(h·m³). ^b A standard deviation of ±0.02 h⁻¹ was assumed for the single measurement periods. ^c Calculated from eq 9 including the error in S and ach_{CO₂} (n). ^d Time-weighted average.

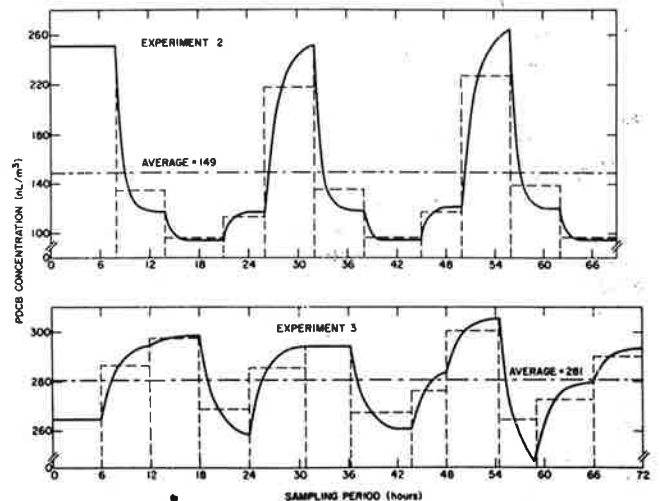


Figure 4. Calculated PDCB concentrations vs. sampling time: (top panel) effect of 11 step changes in ventilation rate; (bottom panel) effect of 12 temperature step changes (between 23 and 31 °C) and minor ventilation rate changes.

Experiment 3. The chamber temperature and its effect on the PDCB source strength term (S), the ach (n), and the duration (τ) for each period of this variable temperature experiment are given in Table V and were used in eq

Table VI. Measured PDCB Concentrations for Variable Temperature Experiment (Experiment 3: Calculated Time-Weighted Average PDCB Concentration = 280.9 ± 19.3 nL/m³)

chamber location	sampler	PDCB concn, nL/m ³	
		measured	av ± SD (%) ^a
A	5461	312.5	296.9 ± 22.1 (7.4)
	4678	281.3	
B	5251	292.4	298.6 ± 8.7 (2.9)
	5361	304.7	
C	5513	281.5	287.2 ± 8.1 (2.8)
	5641	293.0	
D	5476	292.4	290.3 ± 3.0 (1.0)
	5551	288.2	
controls	5656	0.33	
	5297	0.28	
average ^b		290.5 ± 8.0 (2.8)	

^a Average of two measurements with standard deviation and percent relative standard deviation in parentheses. ^b CATS 5461 (location A) and controls not included in average.

2 and 9 to compute the PDCB concentration vs. time and the average for each of the 12 periods as shown in Figure 4 (bottom) and listed in Table V; the time-weighted overall calculated average concentration was 280.9 ± 19.3 nL/m³ for the 72-h experiment.

Table VI lists the measured concentrations obtained with the eight CATS plus the levels from the two controls which were never opened; the controls showed levels of about 0.1% of the sampled values. The relative standard deviations of three pairs (locations B-D) ranged from 1.0 to 2.9%, similar to that of experiment 1; location A had a high difference for the CATS pair (±7.4%). Excluding the high value from the overall average gave a measured concentration of 290.5 ± 8.0 nL/m³ which, as shown in Table II, agreed with the calculated average for experiment 3 and was well within the standard deviation of each determination.

Discussion

As summarized in Table II, for each of the these experiments (constant temperature and ventilation rate, constant temperature but variable ventilation, and constant ventilation but variable temperature), the ratio of the PDCB concentration measured by the CATS samplers divided by the calculated concentration determined from CO₂ decay measured ventilation rates and known PDCB source strengths was equal to 1 within the standard deviation associated with some of the errors. Thus, the passive sampling method does give an accurate measure of the average concentration that existed during a measurement period.

The agreement was even more within the error bounds than indicated in Table II because certain errors in the

measurement technology were not included such as the error associated with the absolute sampling rate of the CATS (±2%) and the uncertainty in the gas calibration standards (±2%).

Experiment 1. The chamber recirculation rate in each experiment was 60 ach, equivalent to an upward air velocity of 0.052 m/s. Typical between-zone air-exchange rates can be as large as 200 m³/h (10). Assuming that CATS are sampling the air in a room near a doorway, that there are four doors per zone, and that the cross-sectional area for flow is about one-fourth the area of a doorway (i.e., about 0.4 m²), the maximum anticipated velocity in a home is of the order of 0.04 m/s, comparable to the chamber velocity. Some actual horizontal velocity measurements in a home showed levels from 0.05 to 0.2 m/s (17) in the more turbulent regime within 0.5 m of the ceiling.

The effect of wind speed and orientation into the wind was studied for a passive NO₂ sampler (18). From their data, the rate of sampling relative to still air for different orientations was correlated with wind speed and then used to calculate the effect at the chamber velocity of 0.052 m/s. As shown in Table VII, the agreement of the Palmes measurements with those from this study was very good and consistent, with the largest effect occurring at 90° to the wind, the next lowest effect at 0° (facing into the wind), and the least effect at 180° (facing away from the wind). It can be seen that the maximum bias in the sampling rate at velocities expected in homes and buildings is less than 2-3% and can be ignored. In fact, by placing the sampler on a flat surface within the room, any local wind effects can be blocked.

The ventilation rate computed by the BNL/AIMS technique using the computed source strength [$S = 152.8 \pm 4.3$ nL/(h·m³)] and CATS average measured concentration (240.4 ± 5.7 nL/m³) is given by eq 5 as

$$n = \frac{S}{C} = \frac{152.8 \pm 4.3}{240.4 \pm 5.7} = 0.636 \pm 0.034 \text{ h}^{-1}$$

in agreement with the CO₂-decay average value of 0.601 ± 0.011 h⁻¹. Thus, under constant ventilation rate and constant temperature conditions, there was no bias in the determination of the average ventilation rate with the BNL/AIMS approach.

Experiment 2. As shown in Figure 4 (top), the widely varying ventilation rate caused significant swings in the calculated PDCB chamber concentration vs. time. But, as expected, the CATS measured concentration of 139.3 ± 2.5 nL/m³ was in agreement with the calculated average value of 149.2 ± 7.7 nL/m³.

Although the passive samplers are capable of determining the correct average tracer concentration over a measurement period, it has been shown that the reciprocal of an average concentration, \bar{C} , the quantity measured, is close to but not identical with the average of reciprocal concentrations. For example, for conditions of constant temperature (S is constant) but multiple equal-duration

Table VII. Effect of Air Velocity and Direction on Passive Samplers (Experiment 1)

CATS orientation	angle from into wind	av PDCB concn, nL/m ³	PDCB concn relative to still air	
			from this study ^a	calcd from Palmes measurements ^b
1	90°	242.86 ± 5.04	1.024 ± 0.047	1.014 ± 0.038
2	180°	235.54 ± 4.09	0.993 ± 0.042	0.976 ± 0.010
3	0°	241.46 ± 4.65	1.018 ± 0.045	1.004 ± 0.027
4	shielded	237.14 ± 5.68		
5	90°	244.37 ± 4.53	1.030 ± 0.045	1.014 ± 0.038

^a The CATS shielded by the chair was assumed to be in still air. ^b Calculated from linear regression fit of data collected for wind velocity from 0.5 to 2.6 m/s (18) for the chamber velocity of 0.052 m/s.

periods (m) of different ventilation rates (i.e., different \bar{C}_k), eq 5 becomes

$$n = S \frac{1}{m} \sum_{k=1}^m \frac{1}{\bar{C}_k} \approx \frac{S}{\bar{C}} \quad (10)$$

Substituting the explicit values of S and \bar{C} from Table III gives

$$n \approx \frac{152.8 \pm 4.3}{149.2 \pm 7.7} \text{ or } 1.02 \pm 0.09 \text{ h}^{-1}$$

However, Table III shows that the actual time-weighted average ventilation rate was $1.19 \pm 0.03 \text{ h}^{-1}$. Thus, for a measurement period in which the ventilation rate varied about 2.7-fold on a cyclical basis, there was an explicit underestimate of the true average ventilation rate by about 14%.

Such periodic variation can occur in actual building measurements on a diurnal basis because the ventilation driving force, the inside-outside temperature difference, increases at night and decreases during the day; a 1.5-2-fold variation on a daily basis is not unreasonable. However, the cycle in experiment 2 as shown in Figure 4 (top) is biased somewhat by the constant rate in the first period (0-8 h). By looking at periods 2-9 inclusive in Table III, which includes exactly two complete up-down cycles, the average concentration would have been $141.2 \pm 7.9 \text{ nL/m}^3$ corresponding to an apparent ventilation rate of $1.08 \pm 0.10 \text{ h}^{-1}$, and the true average ventilation rate would have been $1.21 \pm 0.04 \text{ h}^{-1}$, for a rate underestimate of less than 11%. Thus, for measurement periods of several days or longer, it can be expected that the BNL/AIMS approach may underestimate the true ventilation rate by about 3-6%, a tolerable bias for this convenient technique.

Experiment 3. Figure 4 (bottom) showed that the 8 °C swing in chamber temperatures from 23 to 31 °C and down again caused less than a 1.2-fold variation in the concentration, and again, as shown in Table II, the CATS-measured concentration of $290.5 \pm 8.0 \text{ nL/m}^3$ was in agreement with the expected concentration of $280.9 \pm 19.3 \text{ nL/m}^3$.

Since both the source strength, S , and the PDCB concentration, C , are different for each period, for multiple equal-duration periods (m), eq 5 becomes

$$n = \frac{1}{k} \sum_{k=1}^m \frac{S_k}{C_k} \approx \frac{1}{\bar{C}} \frac{1}{k} \sum_{k=1}^m S_k \approx \frac{\bar{S}}{\bar{C}} \quad (11)$$

The reciprocal concentration term can be more accurately factored out in the case of the temperature cycling because the magnitude of the concentration swings is much less and more accurately represented by an average value than was the case for experiment 2.

The time-weighted averages of source strength and concentration were $167.5 \pm 5.9 \text{ nL/(h}\cdot\text{m}^3)$ and $280.9 \pm 19.3 \text{ nL/m}^3$, respectively (cf. Table V). Substituting in eq 11 gives

$$n = \frac{167.5 \pm 5.9}{280.9 \pm 19.3} \text{ or } 0.596 \pm 0.067 \text{ h}^{-1}$$

which is essentially identical with the measured average ventilation rate of $0.595 \pm 0.022 \text{ h}^{-1}$. Thus, the BNL/AIMS technique is not biased to any significant extent if the appropriate temperature for the source is known.

For these chamber experiments, the base temperature was 23 °C, the value at which the sources were conditioned before the experiment began. The source strengths for the two other temperatures, 27 and 31 °C, were computed from eq 7 because these were short-term temperature adjustments; the total duration of the experiment was only 3 days.

If these measurements had been conducted over a 2-week or longer period, then the average source strength could have been estimated from the time-weighted average source temperature and used in eq 6; this would be the procedure for a ventilation rate determination in a home, where the time-weight average thermostat setting would be used as the average base temperature. Assuming long-term equilibration at the chamber base temperature of 27 °C, eq 6 becomes

$$S'_{27} = \frac{5688 \pm 120}{34} e^{-4000(1/300-1/298)} = 182.9 \text{ nL/(h}\cdot\text{m}^3)$$

which, divided by the average concentration, gives

$$n = \frac{182.9}{280.9} = 0.651 \text{ h}^{-1}$$

This is about 9.4% higher than the true ventilation rate of 0.595 h^{-1} because the sources had not equilibrated at the experiment 3 base temperature of 27 °C in the 3-day period.

One can reverse the procedure and use the measured ventilation rate and average PDCB concentration from Tables V and VI, respectively, to compute the source strength and hence the estimated average chamber temperature. From eq 5

$$S_i = nC = (0.595 \pm 0.022)(290.5 \pm 8.0) = 172.8 \pm 11.3 \text{ nL/(h}\cdot\text{m}^3)$$

Equation 6 becomes

$$172.8 \pm 11.3 = \frac{5688 \pm 120}{34} e^{-(4000 \pm 300)(1/T-1/298)}$$

or $T = 298.9 \pm 2.2 \text{ K}$ ($25.7 \pm 2.2 \text{ °C}$). This average chamber temperature of 25.7 °C is, as expected, above the preexperiment base temperature of 23 °C and below the long-term time-weighted chamber temperature of 27 °C, confirming the applicability of the BNL/AIMS approach in variable temperature scenarios.

Conclusions

The relative standard deviation of multiple paired passive samplers is $\pm 1.9 \pm 1.0\%$, indicating that the reproducibility in the manufacture, handling, and analysis of the CATS is sufficiently good to preclude the necessity of duplicate sampling in field experiments.

For the low air movement velocities in homes ($<0.2 \text{ m/s}$, away from any forced air vents), the effect of sampler orientation is not consequential on the sampling rate, having less than a 2-3% positive bias in the worst case.

Under conditions of widely varying concentrations, the passive sampler accurately measures the correct time-weighted average tracer concentration. However, because the determination of ventilation ratios requires the determination of the average reciprocal tracer concentration rather than the reciprocal of the average tracer concentration, which is the item measured by the passive sampler, there is an estimated negative bias in the ventilation rate determination of about 3-6%, a tolerable bias for this convenient technique.

By use of a time-weighted average temperature for determining the estimated source strength, room temperature fluctuations or intentional cycling differences of as much as 8 °C (14 °F) can be accounted for in order to produce essentially no bias in the determination of ventilation rates.

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