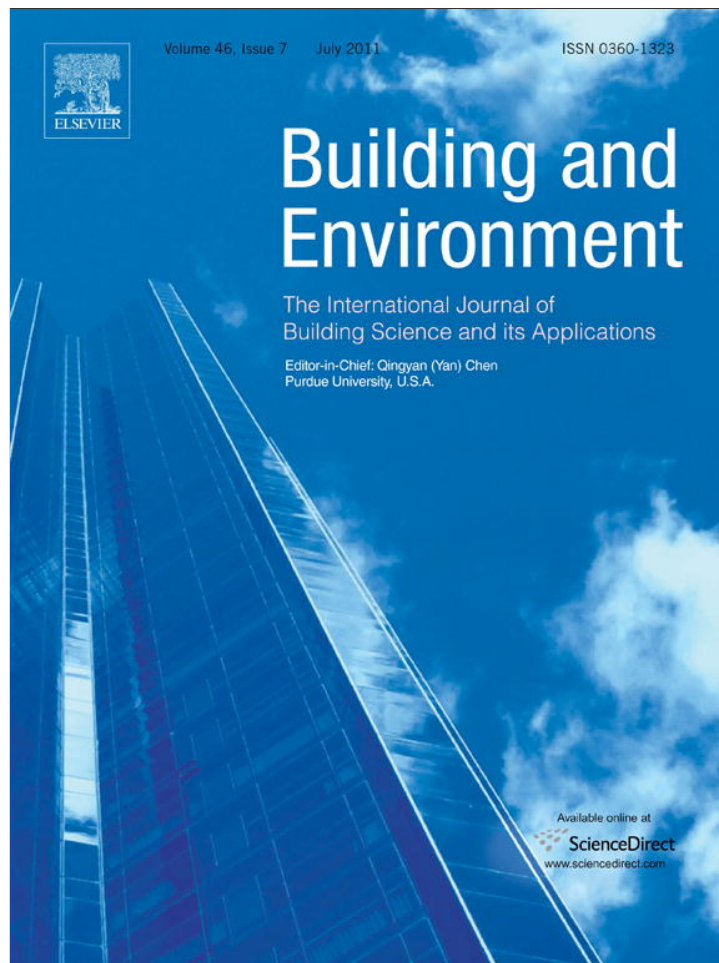


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

## Building and Environment

journal homepage: [www.elsevier.com/locate/buildenv](http://www.elsevier.com/locate/buildenv)

## Diffusion-controlled reference material for volatile organic compound emissions testing: Pilot inter-laboratory study

Cynthia Howard-Reed<sup>a,\*</sup>, Zhe Liu<sup>b</sup>, Jennifer Benning<sup>c</sup>, Steven Cox<sup>b</sup>, Daniel Samarov<sup>a</sup>, Dennis Leber<sup>a</sup>, Alfred T. Hodgson<sup>d</sup>, Stephany Mason<sup>e</sup>, Doyun Won<sup>f</sup>, John C. Little<sup>b</sup>

<sup>a</sup> National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, MD 20899, USA

<sup>b</sup> Virginia Tech, 405 Durham Hall, Blacksburg, VA 24061, USA

<sup>c</sup> South Dakota School of Mines and Technology, 501 E Saint Joseph St., Rapid City, SD 57701, USA

<sup>d</sup> Berkeley Analytical Associates, LLC, 815 Harbour Way, Richmond, CA 94804, USA

<sup>e</sup> Air Quality Sciences, Inc., 2211 New Market Parkway, Marietta, GA 30067, USA

<sup>f</sup> National Research Council Canada, 1200 Montreal Rd., Ottawa, Ontario K1A 0R6, Canada

### ARTICLE INFO

#### Article history:

Received 18 November 2010

Received in revised form

18 January 2011

Accepted 21 January 2011

#### Keywords:

Product emissions testing

Inter-laboratory study

Reference material

Volatile organic compounds

### ABSTRACT

To improve the reliability and accuracy of tests used to measure emissions of volatile organic compounds (VOCs) from samples of interior building products, the National Institute of Standards and Technology (NIST) and Virginia Tech (VT) have created a program to develop reference materials with independently predictable emission rates. A diffusive reference material and associated mechanistic model have been developed and are undergoing extensive evaluation. As part of this process, a pilot inter-laboratory study (ILS) was conducted with four laboratories using a polymer material loaded with toluene as the reference source. Results showed the prototype material to be a relatively stable, homogeneous source with consistent emissions both within and between production batches. A comparison of toluene emission rates determined by the laboratories showed relative standard deviations as low as 9%, which are significantly lower than inter-laboratory variations for most previous ILS exercises with VOC sources. At a sample time of 48 h, the mean measured toluene emission rate for all four laboratories was within 1% of the model predicted value. The success of this pilot ILS is a key step toward being able to provide a VOC reference material for independent validation of VOC emission tests conducted in small chambers.

Published by Elsevier Ltd.

### 1. Introduction

The market for interior building products with low emission rates of volatile organic compounds (VOCs) continues to grow with an increased demand for products that are compliant with a range of acceptance criteria. The most common procedure used to determine compliance is to test representative product samples in environmental chambers according to standard methods. A typical chamber test involves placing a prepared specimen in an inert chamber operated at standard conditions of airflow rate, temperature and

humidity that are selected to be representative of typical indoor conditions (e.g., an air change rate of  $1.0 \text{ h}^{-1}$ , temperature =  $23 \text{ }^\circ\text{C}$ , relative humidity = 50%). Concentrations of VOCs of interest are measured in chamber exhaust air at specified times. Using a mass balance on the air within the chamber, and assuming quasi-steady state conditions, the specimen's emission rate in units of mass per area per time is then calculated. The measured emission rate is dependent on multiple factors affecting chamber operation, air sampling and analysis that vary among laboratories. To date, it has not been possible to independently verify the performance of these environmental chamber measurements. The primary method available to assess laboratory performance is via an inter-laboratory study. Such studies can be expensive, time-consuming, and lead to inconclusive results, especially because there is no way to identify which laboratory's results are correct.

The first extensive inter-laboratory studies for product emissions testing were conducted in the 1990s [1,2]. These early studies showed significant variation among laboratories with relative standard deviations of individual VOC emission rates often around

\* Corresponding author. National Institute of Standards and Technology, MS 8633, Gaithersburg, MD 20899-8633, USA. Tel.: +1 301 975 8423; fax: +1 301 975 4409.

E-mail addresses: [chreed@nist.gov](mailto:chreed@nist.gov) (C. Howard-Reed), [liuzhe@vt.edu](mailto:liuzhe@vt.edu) (Z. Liu), [jennifer.benning@gmail.com](mailto:jennifer.benning@gmail.com) (J. Benning), [stcox2@vt.edu](mailto:stcox2@vt.edu) (S. Cox), [daniel.samarov@nist.gov](mailto:daniel.samarov@nist.gov) (D. Samarov), [dennis.leber@nist.gov](mailto:dennis.leber@nist.gov) (D. Leber), [ahodgson@berkeleyanalytical.com](mailto:ahodgson@berkeleyanalytical.com) (A.T. Hodgson), [smason@aqcs.com](mailto:smason@aqcs.com) (S. Mason), [doyun.won@nrc-cnrc.gc.ca](mailto:doyun.won@nrc-cnrc.gc.ca) (D. Won), [jcl@vt.edu](mailto:jcl@vt.edu) (J.C. Little).

50% and as high as 240% [3]. Lessons learned from these first studies included the need to use more homogeneous emission sources, increase standardization of test procedures, and independently check portions of the procedure (e.g., sampling methods and analytical performance). Recent studies have benefited from these lessons and have shown significant improvement in the variability among laboratories (less than 20% RSD for several compounds) [4,5]. However, achieving these improved results required the coordination of more than 30 laboratories over many months. In the end, it still is only possible to characterize laboratory performance based on a measured mean value and standard deviation, not a “true” reference value.

There is a need for a building-like material that has a reference, or known, VOC emission rate that can be used to independently verify a laboratory's performance. The National Institute of Standards and Technology (NIST) is working with Virginia Tech (VT) to develop a homogeneous material that mimics a real building material and has a known emission rate. As described by Cox et al. [6], a polymer film was selected as a substrate that can be loaded with a representative VOC through a diffusion process. The loaded polymer has an emission profile similar to a typical “dry” building material (e.g., sheet flooring) that can be measured in small chambers commonly used for emissions testing. The advantage of this polymer film reference material is the capability to independently predict the emission rate by first measuring key material properties (i.e., material-phase concentration and diffusion and partition coefficients) and then using a mechanistic emission model.

The development of this reference material has followed a multiple phase approach. In Phase I, proof of concept tests were conducted with results showing acceptable agreement between measured concentrations of toluene in the chamber and emission model predictions [6]. Phase II, a pilot inter-laboratory study (ILS) and the focus of this paper, was conducted with four laboratories to assess the prototype material's potential as a reference source and to evaluate scaled-up production of the material. The four participating laboratories were: Air Quality Sciences, Inc. (Atlanta, GA), Berkeley Analytical (Berkeley, CA), National Institute of Standards and Technology (Gaithersburg, MD), and National Research Council of Canada (Ottawa, Canada). Each laboratory was sent four reference material films that included two films from two different production batches. Specific study goals were to: 1) assess the variability of chamber test results within a single reference material production batch; 2) assess the variability of chamber test results between different production batches; 3) assess the variability of chamber test results among different laboratories; 4) evaluate the

ability of the mechanistic model to predict the emission rate of the reference material in different test chambers; and 5) gain experience for a larger study involving more laboratories.

## 2. Material and methods

### 2.1. Loading reference materials for ILS

The first steps included loading the polymer films at VT and distributing them to the participating laboratories. To load the polymer films with a specific amount of toluene, a gas calibrator with a mass flow controller was used to generate a continuous air stream with a constant toluene concentration. The toluene-laden air was passed through two 7-L stainless steel vessels connected in series, each holding several polymer films. The effluent air from the second vessel was passed through a high-resolution (0.1  $\mu\text{g}$ ) dynamic microbalance and then exhausted to a fume hood. As shown in Fig. 1, four polymer films ( $6\text{ cm} \pm 0.01\text{ cm} \times 6\text{ cm} \pm 0.01\text{ cm}$ ) were held in each vessel by aluminum screen fixtures so that they were fully exposed to the toluene in the air. One extra film ( $3.6\text{ cm} \pm 0.01\text{ cm} \times 3.6\text{ cm} \pm 0.01\text{ cm}$ ) was suspended in the microbalance and its mass was monitored throughout the loading process. All film samples were cut from a single, 0.0254-cm thick (as measured by the manufacturer), polymer (polymethyl pentene) sheet using a desktop rotary paper trimmer. During the loading process, toluene molecules were absorbed into the films until sorption equilibrium was reached between the material-phase and air-phase. Simultaneously, the film on the microbalance underwent the same mass transfer process and was representative of all of the film samples. Therefore, the mass change data recorded by the microbalance was used to assess the loading process and determine when sorption equilibrium was reached. The total mass increase of the film at the end of the loading process was divided by its volume to determine the material-phase concentration of toluene, which was assumed to be equal to the material-phase concentration of the films in the two loading vessels.

Two separate batches of eight films were loaded, resulting in the production of 16 samples in total. Each laboratory received two samples from each batch. Reproducibility between production batches was achieved by maintaining the same toluene concentration in the supply air. The mass change profiles recorded on the microbalance were nearly the same for each batch (Fig. 2). The total mass increase at the end of each loading process and consequently, the material-phase concentration of the loaded films in two batches had a relative difference of less than 3%.

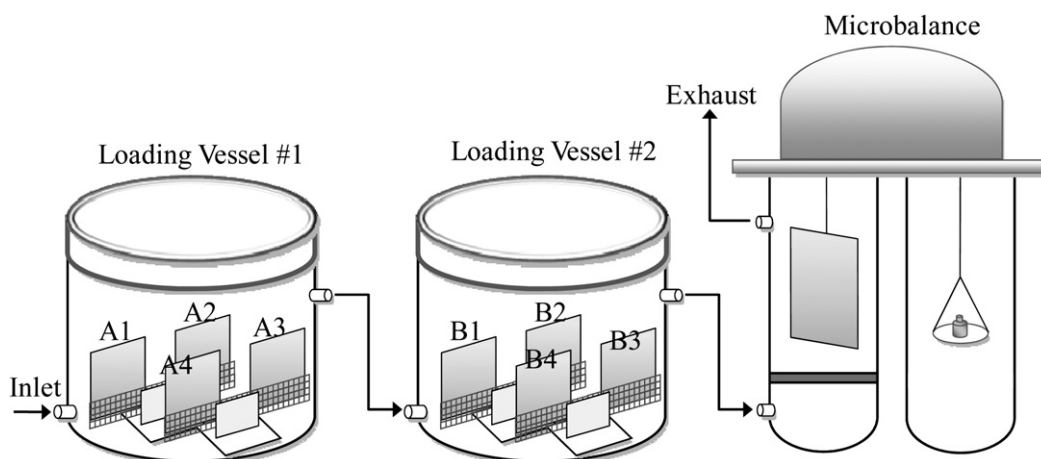


Fig. 1. Loading process for polymer films (not to scale).

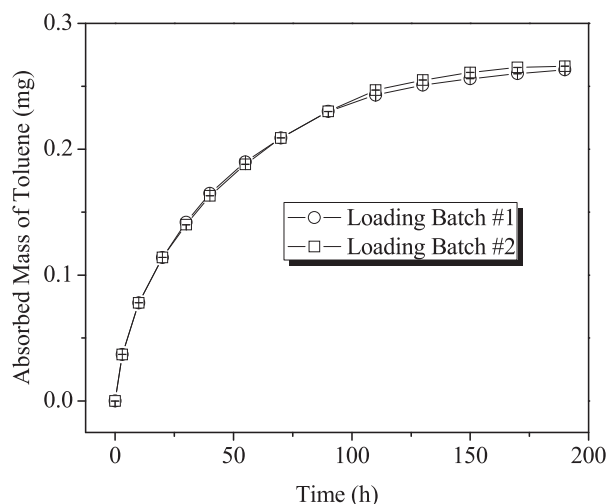


Fig. 2. Toluene mass loading for two batches of polymer films (uncertainty of mass measurements at equilibrium is  $\pm 0.0002$  mg).

When the microbalance data indicated that sorption equilibrium was reached, the films were considered loaded. The films were removed from a loading vessel one at a time for packaging, minimizing exposure to ambient air by limiting the time the vessel was opened. A random number generator was used to determine which samples were sent to each laboratory. Each laboratory received one sample from Loading Vessel #1 and a second sample from Loading Vessel #2 (see Fig. 1). The packaging procedure included wrapping each film in heavy-duty aluminum foil and placing it in a small sealable plastic bag, carefully evacuating air at each step. The bags were coded, placed in coolers with dry ice, and sent by overnight delivery to the laboratories.

Each laboratory received two aluminum specimen holders for use in their chambers. The polymer film was curved such that it would not lay flat naturally (Fig. 3a). The holder was designed to provide a level platform and a wire mesh cover to press the film flat against the platform (Fig. 3b). While this approach increased the film's contact area, it was discovered that an air gap still existed between portions of the sample film and the platform. As a result, variability was potentially introduced, as the exposed emission surface of each film likely was not consistent.

## 2.2. Chamber test method

NIST developed a test method and data entry spreadsheet for each participant. Several chamber set points were specified (Table 1). The laboratories were able to comply with the set point within 5% with the exception of the chamber airflow rate set point of  $0.065 \text{ m}^3/\text{h}$ . This value was selected based on the range of laboratory chamber volumes and a reference sample size of  $36 \text{ cm}^2$  to achieve an area specific flow rate of  $18.1 \text{ m}/\text{h}$ . However, not all laboratories operated their chambers at this set point (Table 2). As a result, it is not possible to compare "steady-state" chamber air concentrations among laboratories.

NIST asked each laboratory to follow specific procedures for sample preparation, sample loading, air sample collection and chemical analysis. Sample preparation instructions included removing the sample from the freezer, keeping the sample in the sealed bag for 5 min at room temperature, unwrapping the sample and placing it on the sample holder in the center bottom of the chamber with the film's shiny side (convex orientation) down, and finally sealing the chamber. Each lab was asked to record the time it took to complete each step. The experimental time zero was the time the sample was unwrapped.

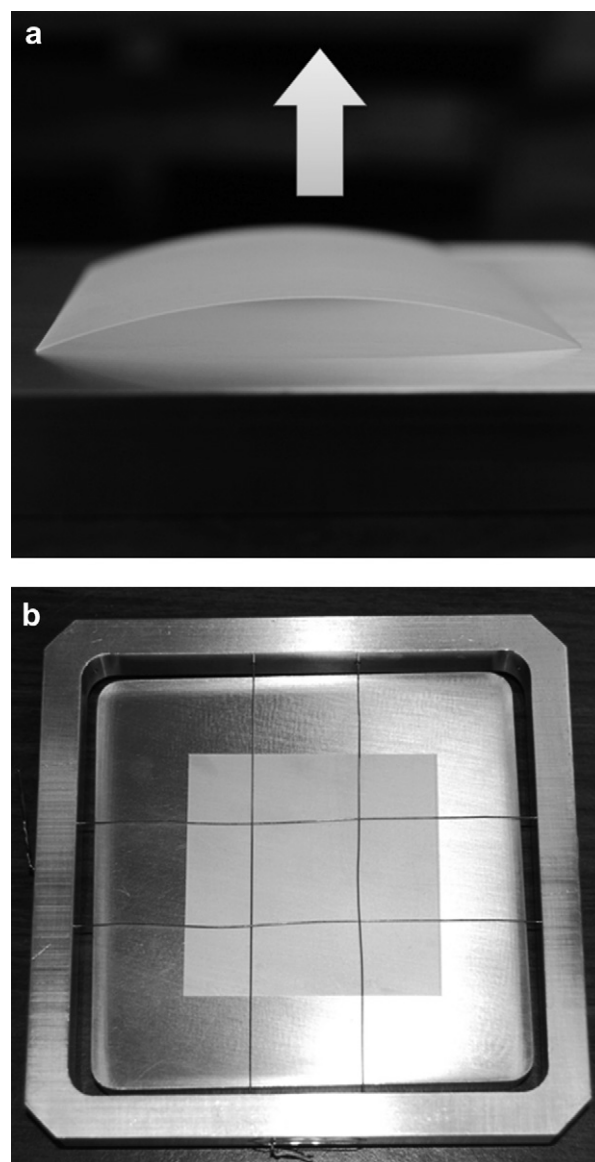


Fig. 3. a. Polymer film with convex curve. b. Film "flattened" by sample holder wires.

Laboratories were asked to collect chamber air samples at: 0.5 h, 1 h, 2 h, 4 h, 7 h, 24 h, 27 h, 30 h, 48 h, 51 h, and 54 h, with a minimum of 3 duplicate air samples. Two laboratories collected air samples at additional time points to those that were specified. NIST additionally distributed a liquid standard ( $100 \text{ ng}/\mu\text{L}$  toluene in methanol) to each laboratory for internal assessment of analytical performance.

Table 1  
Specified chamber set points.

Chamber parameter	Set point	Range of actual
Chamber temperature ( $^{\circ}\text{C}$ )	23	22.1 to 23.0 ( $\pm 0.5$ )
Chamber relative humidity (%)	50	50 to 51.0 ( $\pm 2.0$ )
Chamber airflow rate ( $\text{m}^3/\text{h}$ )	0.065	0.05 to 0.0862 ( $\pm 0.002$ )
Area specific airflow rate ( $\text{m}/\text{h}$ )	18.1	13.9 to 23.9 ( $\pm 0.002$ )
Chamber mixing fan	Off	True
Chamber conditioning prior to test	At least 4 h	True
Chamber background concentration of toluene	$<2 \mu\text{g}/\text{m}^3$	True

**Table 2**  
Chamber Set Points that Varied.

Chamber parameter	Range of actual
Volume (m <sup>3</sup> )	0.05 to 0.086 ( $\pm 0.001$ )
Air change rate (h <sup>-1</sup> )	1.0 to 1.3 ( $\pm 0.01$ )
Product loading factor (surface area of film/chamber air volume) (m <sup>2</sup> /m <sup>3</sup> )	0.042 to 0.072
Air velocity $\approx$ 1 cm above sample (m/s)	Not measured to < 0.05 m/s

Several parts of the test procedure were left to the discretion of each laboratory. For example, the sample age at the start of each test varied between laboratories from 2 days to 14 days after sample production (samples were stored in a freezer until tested). Three laboratories ran two reference samples simultaneously in two different chambers, whereas the fourth laboratory used a single chamber for all four tests. Laboratories collected and analyzed chamber air samples in the manner of their choice. Although not specified, all samples were collected on sorbent tubes and analyzed by thermal desorption gas chromatography/mass spectrometry (GC/MS). One laboratory used 1-bromo-4-fluorobenzene as an internal standard for analysis. Individual laboratory sampling and analytical performance was not assessed prior to the reference material testing. As a result, the laboratory results for this study reflect all potential sources of variability.

### 2.3. Emission profile prediction

The emission rate of toluene from the source can be predicted using a mechanistic mass transfer model. The mass transfer mechanisms and the corresponding model that predicts toluene emissions from the loaded films have been presented elsewhere [6]. The model and method used to obtain the model parameters are briefly summarized here.

The emission of a VOC from a homogeneous dry material to a well-mixed chamber includes internal diffusion within the material, characterized by diffusion coefficient  $D$ , and partitioning between the material-phase and air-phase at the material/air interface, characterized by partition coefficient  $K$ . Assuming a uniform initial VOC concentration in the material,  $C_0$ , the material-phase concentration can be calculated [6,7] as a function of the distance from the bottom of the material and time. Other parameters required for the model are  $A$ , the exposed material surface area,  $L$  the material thickness,  $Q$  the volumetric airflow rate, and  $V$ , the well-mixed chamber volume. If the VOC material-phase concentration at the surface of the material is known, then the chamber air concentration,  $y$ , which is in equilibrium with the material-phase concentration at the material surface, can be calculated using  $K$ , the partition coefficient.

The model parameters therefore include  $D$ ,  $K$ ,  $C_0$  and other directly measurable parameters such as  $A$ ,  $L$ ,  $V$  and  $Q$ .  $C_0$  is calculated from the total mass increase of the single film monitored by the microbalance during loading.  $D$  and  $K$  are determined via independent microbalance sorption and desorption tests [8]. By fitting a Fickian diffusion model to the sorption and desorption data,  $D$  of toluene in the polymer material was found to be  $3.6 \times 10^{-14} \text{ m}^2/\text{s} \pm 0.7 \times 10^{-14} \text{ m}^2/\text{s}$  [6]. Using the known gas-phase toluene concentration and the total toluene mass absorbed by the volume of polymer sample at gas-phase/material-phase equilibrium,  $K$  of toluene between the polymer material and air was  $(500 \pm 30) (\mu\text{g toluene}/\text{m}^3 \text{ material})/(\mu\text{g toluene}/\text{m}^3 \text{ air})$ . The deviations between  $K$  obtained in the present paper and that in previous work [6] is due to a recent modification on the microbalance system used to determine  $K$ , which is expected to improve accuracy substantially.

## 3. Results

### 3.1. ILS results

All 16 samples prepared for the ILS were successfully used by the four laboratories allowing for analysis of within batch variation of samples, between batch variation of samples, and emission rate variation among laboratories.

#### 3.1.1. Within batch variation

Each laboratory received two samples from the same batch of reference films. The initial concentration of toluene ( $C_0$ ) is presumed to be the same for each sample in a batch. Laboratories A, C and D ran the within batch samples simultaneously in two similar chambers, whereas Laboratory B ran the samples sequentially 7 days apart. Chamber air concentrations of toluene measured for each of the 8 samples in the first batch are shown in Fig. 4. Due to differences in chamber airflow rates, air concentrations cannot be compared directly between laboratories.

Uncertainties associated with each data point in Fig. 4 were calculated based on propagation of errors associated with the air sample volume and analytical calibration parameters required to determine the chamber concentration of toluene. The resulting expanded uncertainties (using a coverage factor of 2) for each measured concentration ranged from 3.3% to 16% across all laboratories.

Most paired concentrations were within each other's estimated error, and the agreement tended to improve at later sampling times. For example, percent differences between concentrations ranged from 3.2% to 22% for samples collected at 2 h, 3.8%–14% for samples collected at 24 h, and 1.3%–12% for samples collected at 48 h. Variations in sample handling prior to starting a test and/or incomplete mixing in the first few hours of a test are possible reasons for higher early discrepancy. It should be noted that the earliest sample time for most test methods is 24 h after the specimen is loaded in the chamber, and is often not until 72 h [9,10].

#### 3.1.2. Between batch variation

Each laboratory received two samples from two different batches of reference films. Samples from the same loading position (see Fig. 1) in each batch were sent to the same laboratory (e.g., Laboratory A received samples 2 and 7 from Batch 1 and Batch 2). A subset of between batch results is provided in Table 3. Relative standard deviations for the four samples across both batches within each laboratory ranged from 7.1% to 19% for samples collected at 2 h, 6.1%–17% for samples collected at 24 h, and 5.0%–11% for samples collected at 48 h. Again, there was a trend of improving consistency among measured concentrations with time. Although differences in chamber air concentrations between batches were small, there was a general trend of higher chamber concentrations for Batch 2. This result is consistent with a small difference in loaded toluene mass between batches. The initial concentration ( $C_0$ ) was  $7.86 \times 10^5 \text{ mg}/\text{m}^3 \pm 300 \text{ mg}/\text{m}^3$  for the first batch and  $8.03 \times 10^5 \text{ mg}/\text{m}^3 \pm 300 \text{ mg}/\text{m}^3$  for the second batch. Although it is possible to adjust a sample's reference emission value for a different  $C_0$ , additional work is planned to reduce the variations among production batches.

#### 3.1.3. Batch variation summary

The data were further assessed using an analysis of variance model that accounted for non-linear effects associated with the change in concentration over time (details of the model are available upon request). The statistical analysis revealed that the samples performed consistently within and between batches when differences in experimental conditions were taken into account.

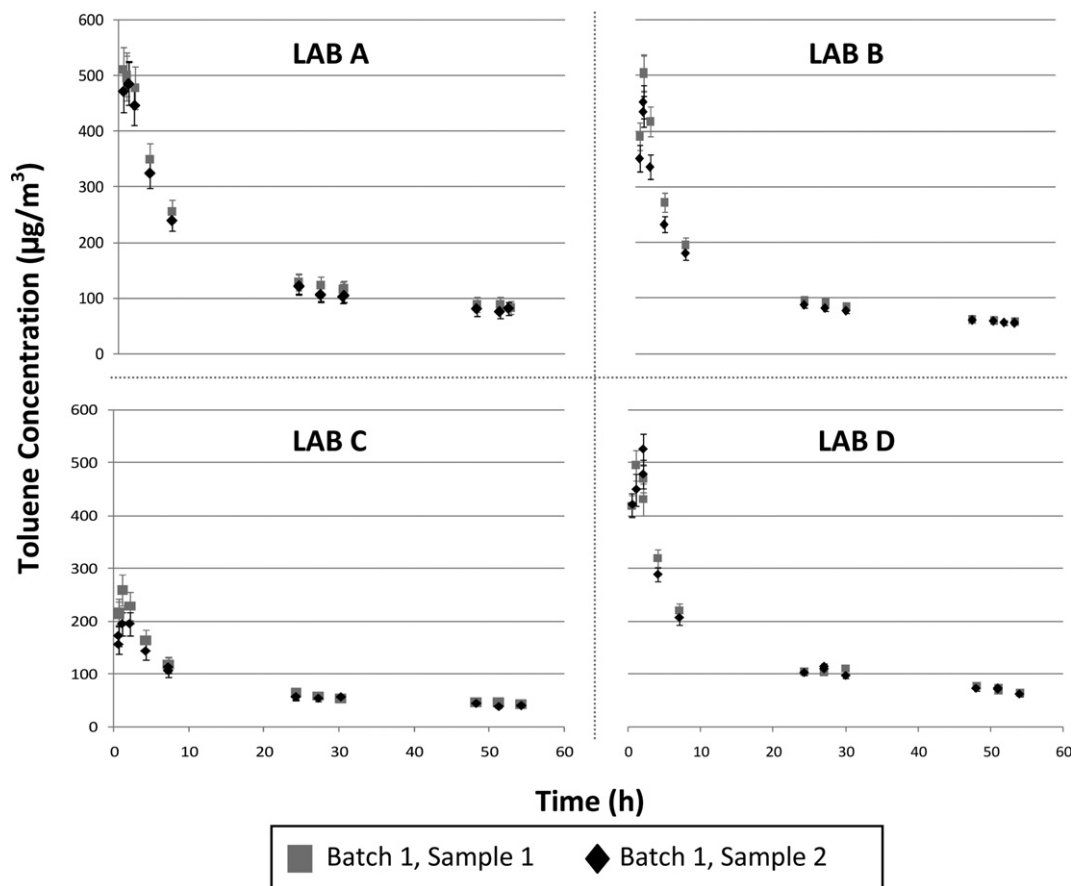


Fig. 4. Measured chamber concentrations of toluene for eight reference samples produced in first batch. Expanded uncertainties shown with a coverage factor of 2.

Specifically, there were no significant within batch effects for the three laboratories that ran both within batch samples simultaneously in two similar chambers. However, a slight within batch effect was detected for the fourth laboratory (Lab B), which ran the two samples in the same chamber on separate days (approximately 7 days apart).

In contrast, a slight between batch effect was detected for the three laboratories that ran batch samples simultaneously. For these laboratories the first batch of samples was run approximately 7 days later relative to sample production than the second batch.

No between batch effect was found for the fourth laboratory (Lab B), which ran the samples on the same post production days for each batch.

Based on these observed differences it appears that sample age (i.e., the older the sample the lower the measured chamber air concentrations) may be a more important variable than differences between the batches or among samples with a batch. However, as sample age is confounded with other differences in experimental conditions, further tests are required to determine the significance of this observation. What these results do show is that when

Table 3  
Toluene chamber concentrations across batches for each laboratory.

Lab	Sampling time (h)	Chamber toluene concentration (µg/m <sup>3</sup> )				Relative standard deviation (%)
		Batch 1 sample 1	Batch 1 sample 2	Batch 2 sample 1	Batch 2 sample 2	
A	2.0	478 ± 38 <sup>a</sup>	447 ± 36	486 ± 54	555 ± 61	9.3
A	7.0	257 ± 20	240 ± 19	270 ± 31	253 ± 29	4.8
A	24	129 ± 15	122 ± 14	141 ± 16	127 ± 14	6.2
A	48	88.5 ± 14	81.0 ± 13	101 ± 8.1	89.8 ± 7.2	9.2
B	2.0	417 ± 27	336 ± 22	408 ± 27	333 ± 21	12
B	7.0	196 ± 13	181 ± 12	213 ± 14	180 ± 12	7.8
B	24	95.7 ± 6.1	87.8 ± 5.6	101 ± 6.8	91.0 ± 5.9	6.1
B	48	61.2 ± 3.9	60.4 ± 3.9	67.1 ± 4.4	65.2 ± 4.2	5.0
C	2.0	229 ± 26	195 ± 22	304 ± 35	273 ± 32	19
C	7.0	118 ± 14	110 ± 13	164 ± 19	145 ± 17	19
C	24	66.2 ± 7.3	57.7 ± 6.3	85.1 ± 9.6	79.0 ± 8.9	17
C	48	46.9 ± 5.0	45.2 ± 4.8	53.4 ± 5.8	56.7 ± 6.2	11
D	2.0	451 ± 28	502 ± 28	428 ± 14	442 ± 22	7.1
D	7.0	220 ± 13	207 ± 13	247 ± 11	255 ± 9.9	9.7
D	24	106 ± 6.5	102 ± 5.3	126 ± 4.7	135 ± 5.6	14
D	48	77.9 ± 3.8	72.5 ± 3.3	69.6 ± 4.0	71.1 ± 3.2	5.0

<sup>a</sup> Uncertainties represent an expanded uncertainty with a coverage factor of 2.

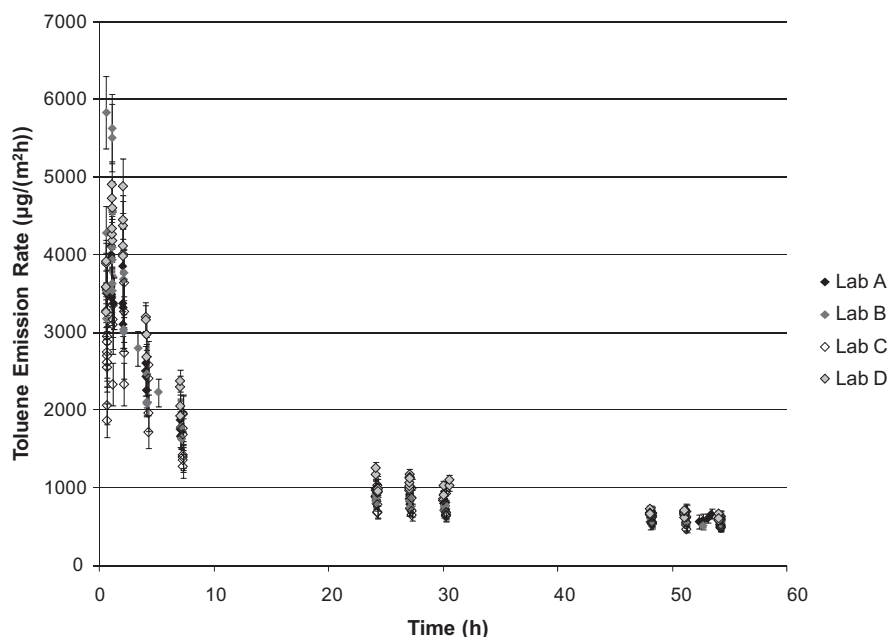


Fig. 5. Approximate steady-state emission rates estimated for all 16 reference films. Expanded uncertainties include chamber concentration measurement uncertainty, film size measurement uncertainty, and chamber airflow rate uncertainty with a coverage factor of 2.

samples were run under the same conditions, no observed batch or sample effects were detected.

### 3.1.4. Among laboratory variation

Since the chamber airflow rates were not identical, it was necessary to calculate toluene emission rates in order to compare results among laboratories. A pseudo-steady-state emission rate was estimated at a given time point ( $t$ ), using a simple mass balance model:

$$E_{ss,t} = QC_t/A \quad (1)$$

where,  $E_{ss,t}$  = approximate emission rate at time  $t$  ( $\mu\text{g}/(\text{m}^2\text{h})$ );  $Q$  = chamber airflow rate ( $\text{m}^3/\text{h}$ );  $C_t$  = chamber toluene concentration at time  $t$  ( $\mu\text{g}/\text{m}^3$ );  $A$  = surface area of the sample ( $\text{m}^2$ )

The calculated emission rates across all labs for all 16 samples are shown in Fig. 5. The relative standard deviations of toluene emission rates for all 16 samples were 17% at 2 h, 15% at 24 h, and

9.4% at 48 h. While there are apparent differences among laboratories (e.g., possible bias due to analytical performance), the overall results are relatively consistent, especially at the later sampling points.

### 3.1.5. Model predictions

Two model predictions of toluene chamber concentration are provided for each laboratory in Figs. 6–9. The intended procedure was to expose just one-side of the sample with the other side pressed flat against the platform. However, the results for the first sample batch for all laboratories showed chamber concentrations higher than the values predicted by the one-side model. It was then hypothesized (and later confirmed) that the samples were not laying flat on the sample holder, and that a portion of the second side of the film was exposed. Thus, the model prediction was re-run assuming both sides of the sample were exposed.

The uncertainty of the model prediction (shaded band) was estimated using a Monte Carlo method [6]. In summary,  $C_0$ ,  $K$  and  $D$

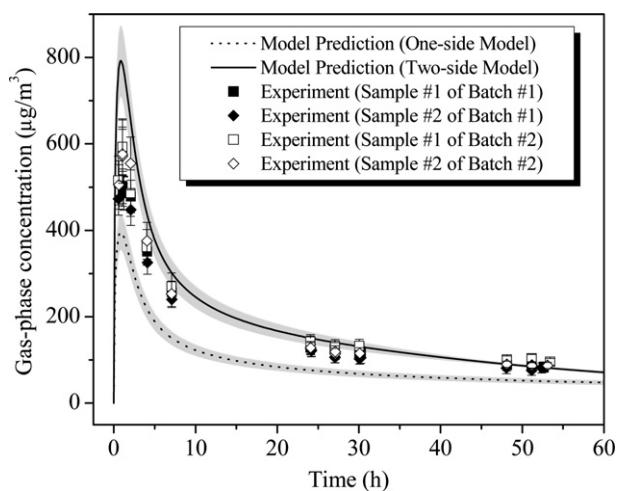


Fig. 6. Measured and predicted chamber concentrations for Laboratory A. Shaded area represents uncertainty associated with model.

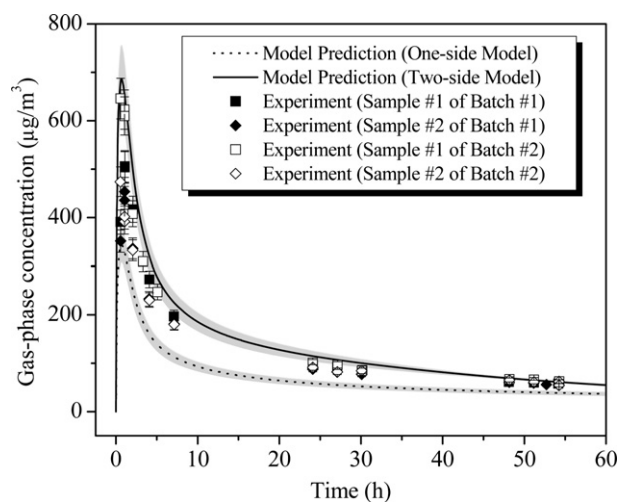


Fig. 7. Measured and predicted chamber concentrations for Laboratory B.

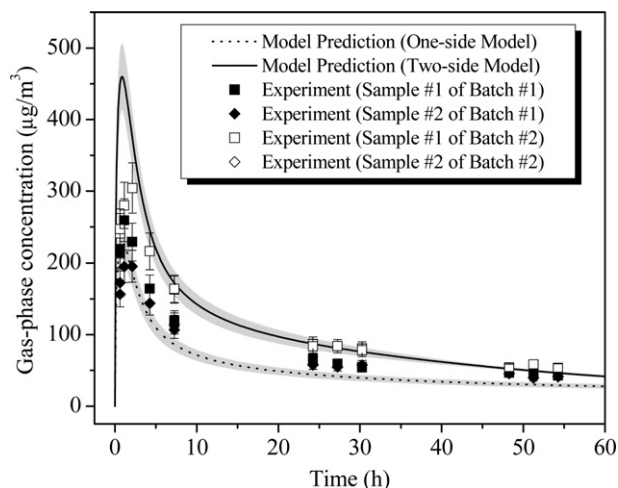


Fig. 8. Measured and predicted chamber concentrations for Laboratory C.

were all assumed to follow normal distributions, whose means and standard deviations were estimated from replicate measurements of the parameters. 10000 repeated model predictions were performed for each chamber test, with  $C_0$ ,  $K$  and  $D$  randomly sampled from their distributions, and other parameters ( $L$ ,  $A$ ,  $Q$ , and  $V$ ) fixed for each test. The results of all the 10000 predictions were then pooled to assess the expected variation in gas-phase chamber concentration as a function of time.

As shown in Figs. 6–9, the measured concentrations for all four laboratories were closer to the predictions from the two-side model, especially at the later time points. Despite the unknown surface area exposed, about half of the measured concentrations agreed with the two-side predicted values, within the measurement error for a given sampling time point.

### 3.2. Additional NIST test results

Additional tests were conducted at NIST to verify the two-side results. For these tests, the sample holder was modified to expose both sides of the polymer film. The first test was run as a replicate of the ILS tests with the only difference being the change in the sample holder. The second test additionally employed a mixing fan to potentially improve mixing during the initial time periods. The films for each test came from different production batches to allow the same sample age of one day.

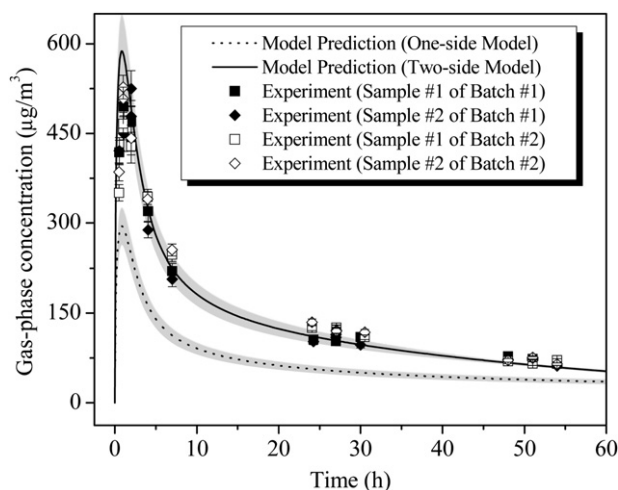


Fig. 9. Measured and predicted chamber concentrations for Laboratory D.

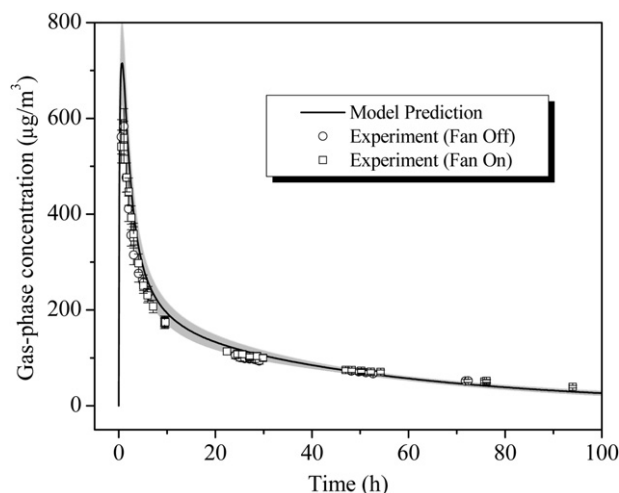


Fig. 10. Two-side chamber tests with mixing fan on and off.

The two-side model prediction matched the measured concentrations very well (Fig. 10). Measured concentrations are within the model's error bounds between 4 h and 54 h for both tests. The results from the test with the fan agreed with the model predictions as early as 2 h. Nevertheless, the measured chamber concentrations from the tests with and without the fan were within about 8% of each other at 2 h and 3% at 24 h, 48 h and 72 h, well within the expanded uncertainty for each sample point. Based on these results, the mixing fan may provide a more uniform concentration in the earliest sampling time periods, but it is not a significant factor beyond 24 h of testing time. Also, the small differences between the measured concentrations in each test further support the finding of low variability among production batches.

### 4. Discussion/conclusions

The results of the pilot ILS proved valuable from many perspectives. Firstly, the results demonstrated that the process used to create the reference material resulted in consistent loading of toluene within and between production batches. The results also showed that the loaded polymer film is a relatively stable, homogeneous emissions source for at least two weeks after production. Additional tests are being planned to investigate the impact of specific production variables (e.g., loading temperature, film thickness, and shelf-life), but no major changes to the production process are required.

Secondly, the measurement results produced by four laboratories at the later time points (24 h–57 h) were in good agreement both among laboratories and with the model predictions assuming both sides of the source were effectively exposed. Based on the ILS results alone, it is possible to define a reference emission rate value for the material. For example, the mean emission rate for all four laboratories at 48 h was  $620 \mu\text{g}/(\text{m}^2\text{h}) \pm 59 \mu\text{g}/(\text{m}^2\text{h})$ . This value was in good agreement with the 48 h, two-side model predicted emission rate value of  $627 \mu\text{g}/(\text{m}^2\text{h}) \pm 22 \mu\text{g}/(\text{m}^2\text{h})$ , a difference from the measured mean of only 1%.

The discrepancies between measured and modeled results at the earlier time period observed for all four laboratories are of interest both with respect to the performance of the model and to chamber operation and require further investigation. The most likely cause of the discrepancy is the difference between the surface area used by the model (2 sides) and the actual surface area exposed (somewhere between 1 and 2 sides due to the sample not



being completely flat). Another possible reason for the early scatter is incomplete mixing of the chamber air. Mixing may have varied among the laboratories due to differences in chamber design. Incomplete mixing is suggested as a contributing factor by one test conducted at NIST using a mixing fan which resulted in higher initial concentrations and a better fit to the mass transfer model predictions.

Based on the lessons learned during this study, several modifications to the procedures are envisioned. The sample holder needs to be redesigned to fully expose both sides of the film in the chamber. The ability to provide a range of exposed surface areas is needed to accommodate different chamber sizes and inlet flow rates. The time between production of the source and the start of chamber measurements should be more tightly controlled and duplicate tests should be required to run simultaneously. The sampling schedule may be modified to focus on the time points of most interest with respect to determining diffusion-controlled emission from dry product specimens, i.e., 24 h, 48 h, and 72 h.

Finally, several steps have been identified for moving closer to the production of a viable reference material for validation of VOC emission tests conducted in small-scale chambers. Most importantly, the material, the model and the procedures need to be evaluated for a larger set of laboratories and chambers. The source requires additional characterization, and measurements are being conducted by NIST and VT as described above. Possible modifications to the reference material include improving the packaging for distribution and adding a second VOC.

The primary advantage of this reference material is that it should allow laboratories to independently check their small-scale chamber measurements without the need for an organized ILS. If significant deviations are encountered between the measured and modeled results, the fact that the source is standardized and well-characterized by the mechanistic model, should facilitate the identification and resolution of problems in a laboratory's equipment and procedures.

## Acknowledgments

The authors would like to thank Caitlin McCrae, Segovia Shu, and Steven Nabinger for their laboratory assistance during this project. We also appreciate the thoughtful review comments provided by Andy Persily.

## References

- [1] ECA. European collaborative action indoor air quality and its impact on man. In: Determination of VOCs emitted from indoor materials and products—interlaboratory comparison of small chamber measurements; 1993. Report No. 13. Luxembourg.
- [2] De Bortoli M, Kephelopoulou S, Kirchner S, Schauenburg H, Vissers H. State-of-the-art in the measurement of volatile organic compounds emitted from building products: results of European interlaboratory comparison. *Indoor Air* 1999;9:103–16.
- [3] Howard-Reed C, Nabinger SJ. Developing a standard reference material for VOC emissions testing. In: proceedings of the indoor environmental quality: problems, research and solutions Conference, EPA/AWMA, Research Triangle Park, NC; July 2006.
- [4] BAM. Investigations for the improvement of the measurement of volatile organic compounds from floor coverings within the health-related evaluation of construction products; March 2009. Research- Number ZP 52-5-20.49.1-1251/07.
- [5] Horn W, Wilke O, Wiegner K. Results of RR-VOC-BAM\_2009, final report. Berlin, Germany: BAM: Federal Institute for Materials Research and Testing; 2010.
- [6] Cox SS, Liu Z, Little JC, Howard-Reed C, Nabinger SJ, Persily A. Diffusion-controlled reference material for VOC emissions testing: proof of concept. *Indoor Air* 2010;20:424–33.
- [7] Little JC, Hodgson AT, Gadgil AJ. Modeling emissions of volatile organic compounds from new carpets. *Atmos Environ* 1994;28:227–34.
- [8] Cox SS, Zhao D, Little JC. Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring. *Atmos Environ* 2001;35:3823–30.
- [9] ECA. European collaborative action indoor air quality and its impact on man, harmonisation of indoor material emissions labeling systems in the EU, inventory of existing schemes; 2005. Report No. 24, EUR 21891 EN.
- [10] CDPH. Standard method for the testing and evaluation of volatile organic chemical emissions from indoor sources using environmental chambers, Version 1.1. California Department of Public Health; 2010.