Developing a Reference Material for Formaldehyde Emissions Testing

Final Report

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DISCLAIMER

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EXECUTIVE SUMMARY

Exposure to formaldehyde has been shown to produce broad and potentially severe adverse human health effects. With ubiquitous formaldehyde sources in the indoor environment, formaldehyde concentrations in indoor air are usually higher than outdoors, ranging from 10 to 4000 $\mu g/m^3$. As a result, industry and government are taking actions to minimize formaldehyde exposure in the indoor environment. A critical step toward mitigating formaldehyde exposure in the indoor environment is assessing the potential of building materials and indoor furnishings to emit formaldehyde. These assessments usually involve emissions measurements obtained using environmental chambers. However, some variability currently exists with respect to chamber testing results. A formaldehyde emissions reference material could be used to identify and eliminate or minimize the root causes of formaldehyde emissions measurement variability. The objective of this research project was to create and evaluate such a reference material.

The formaldehyde emissions reference material development progressed through the following major steps: (1) identifying a suitable polymer film for use as a reference material and characterizing its mass-transfer properties; (2) loading formaldehyde into the selected polymer film; (3) predicting formaldehyde emissions from the pre-loaded polymer films through the use of a fundamental emission model; and, (4) measuring formaldehyde emissions from the pre-loaded films in small-scale environmental chambers. The reference material was evaluated by (1) comparing actual formaldehyde emission profiles measured using small-scale emission chambers to model predictions; (2) evaluating the effect of storage duration; (3) evaluating the effect of the packaging material; and, (4) investigating how reference material formaldehyde emissions were affected by humidity.

Polycarbonate film was selected as a suitable reference material substrate due to its relatively large partition coefficient with respect to formaldehyde. Using measured mass-transfer coefficients and chamber parameters, the emissions model was used to predict formaldehyde concentration profiles during small-scale chamber testing. Although measured chamber concentrations tended to be lower than model predictions in early time periods and higher than model predictions in later time periods, the measured emission profiles were overall quite similar to model predictions.

Subsequent chamber tests were conducted to evaluate the effect of reference material storage duration. Results suggested that some formaldehyde was lost from the reference materials over time but also showed good agreement with model predictions over the course of 144-hour tests when samples had been kept in storage for periods of less than 2 weeks.

The last two evaluations included testing the effect of the foil packaging material and the effect of humidity on formaldehyde emissions. Results of the packaging material test indicate that a tight aluminum foil wrap reduces but does not eliminate formaldehyde loss from the reference material. Although the results of the humidity evaluation were not consistent, the data suggests that formaldehyde emissions from the reference material are

possibly affected by humidity. This could be due to water molecules plasticizing the polymer film or possibly facilitating formaldehyde chemical reactions.

Recommendations for future work include further investigation of formaldehyde chemistry and reaction pathways and mass-transfer behavior, packaging materials and storage methods, evaluation of additional substrates for use as emissions reference materials, scale-up for use in large chambers, and additional testing for overall method evaluation.

SYMBOLS

A	exposed surface area of the material (m^2)
C	material-phase formaldehyde concentration (g/m^3)
C_0	initial uniform material-phase formaldehyde concentration (g/m^3)
D	diffusion coefficient of the VOC in the material (m^2/s)
K	partition coefficient of the VOC between the material and air (dimensionless)
L	thickness of the material (m)
Q	volumetric air flow rate (m^3/h)
r	correlation coefficient
t	time (s)
V	well-mixed chamber volume (m^3)
x	distance from the base of the material (m)
y	gas-phase formaldehyde concentration in the bulk chamber air (g/m^3)
y_{in}	gas-phase formaldehyde concentration in the influent air (g/m^3)

ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BDL	below detection limit
DAD	diode array detector
DCC	daily calibration check
DNPH	2,4-dinitrophenylhydrazine
EPA	United States Environmental Protection Agency
HPLC	high performance liquid chromatography
IAP	Internal Audit Program
IARC	International Agency for Research on Cancer
ILS	inter-laboratory study
NIST	National Institute of Standards and Technology
NMSE	normalized mean square error
PC	polycarbonate
PMP	polymethylpentene
QAPP	quality assurance project plan
QAQC	quality assurance and quality control
RH	relative humidity
TSCA	Toxic Substances Control Act
UF	urea-formaldehyde
UV	ultraviolet
VOCs	volatile organic compounds
VT	Virginia Tech

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1 INTRODUCTION AND OBJECTIVES

1.1 Introduction

Formaldehyde ($H_2C=O$), the simplest member of the aldehyde family, is a flammable, colorless gas with a pungent odor at room temperature. Since the 1880s, formaldehyde has been produced commercially and in recent years, annual global industrial production of formaldehyde is estimated at more than 21 million tonnes (Bizzari, 2009).

One of the primary uses of formaldehyde is for producing synthetic resins, such as urea-formaldehyde (UF), phenol-formaldehyde, melamine-formaldehyde and polyacetal resins, which are used as adhesives and impregnating resins in wood products, curable moulding products, and textile, leather, rubber and cement industries (IARC, 2006). These products may emit formaldehyde during the use phase although the emission rate may vary greatly (Kelly et al., 1999; Meyer and Boehme, 1997; Weigl et al., 2009).

Due to the ubiquitous presence of formaldehyde emission sources indoors as well as the slow removal rate in the indoor environment (outdoor formaldehyde is readily removed by photolysis and reaction with hydroxyl radicals in the presence of sunlight to produce carbon dioxide), formaldehyde concentration in indoor air (10 to 4000 $\mu g/m^3$) is usually much higher than outdoors (3 to 70 $\mu g/m^3$) (ATSDR, 2008; IARC, 2006; Salthammer et al., 2010; WHO, 1989).

Due to the potential health risks associated with indoor formaldehyde exposure, various guidelines, standards, and recommendations have been established around the world (Salthammer et al., 2010). The Formaldehyde Standards for Composite Wood Products Act, enacted as Title VI of the Toxic Substances Control Act (TSCA), was signed into law by President Barack Obama in July 2010. TSCA Title VI requires formaldehyde emissions testing in chambers to demonstrate compliance with these standards.

Inter-laboratory studies are often used to evaluate chamber testing performance. However, these studies can be costly and time-consuming and may lead to inconclusive results. The creation of a well characterized reference material for formaldehyde emissions testing is therefore critical for validating and calibrating emissions testing procedures.

In collaboration with the National Institute of Standards and Technology (NIST), researchers at Virginia Tech (VT) have developed a prototype reference material for VOCs emissions testing (Cox et al., 2010; Howard-Reed et al., 2011). It consists of a thin polymethylpentene (PMP) film that is loaded with toluene to equilibrium using a carrier gas stream containing a known gas-phase toluene concentration. Extensive chamber tests at NIST and other emissions testing laboratories have shown that the emissions behavior of the reference material resembles actual homogenous building materials with emission profiles that can be accurately predicted by a mechanistic model. The model predicted emission profiles therefore serve as true reference values and can be compared to emissions testing results of individual laboratories. This is of considerable benefit because the model not only provides reference emission values for validating individual

laboratories' performance, but also can provide insight into the likely causes of variability and experimental errors. VT's recent work shows that the same approach using PMP is applicable to n-butanol, a more polar compound than toluene.

In this project, a similar procedure was employed to create a reference material for formaldehyde following the same basic steps (Figure 1): (1) identifying a suitable polymer substrate and determining its mass-transfer properties; (2) loading formaldehyde into the polymer film; (3) predicting formaldehyde emissions from the pre-loaded polymer films employing a fundamental emission model; (4) measuring formaldehyde emissions from the pre-loaded films in small-scale environmental chambers; and, (5) comparing the predicted emission profiles to the measured results.
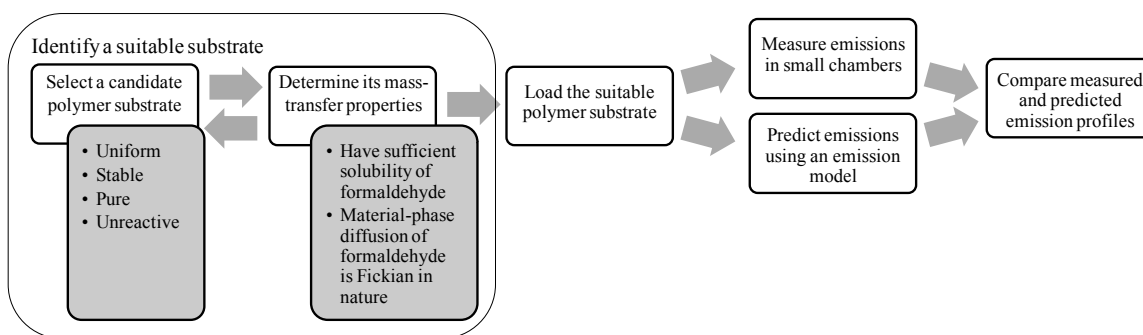
Figure 1. Strategy to develop a reference material for formaldehyde emissions testing.

1.2 Objectives

The specific objectives of this research project were to:
- develop a method to reliably generate a dry gas stream containing a controllable concentration of formaldehyde;
- evaluate different polymer films for use as a formaldehyde source and select the most suitable material for use as a reference material substrate;
- measure the diffusion coefficient, D, and partition coefficient, K, of formaldehyde for the selected polymer film;
- validate the overall approach in (1) small-scale chamber testing, (2) formaldehyde mass balance analysis, and (3) comparison of measurements with model predictions;
- investigate the effectiveness of packaging and storage methods; and
- investigate the effect of temperature and humidity on formaldehyde emission characteristics.

2 MATERIALS AND METHODS

2.1 Selecting polymer substrates

As outlined in Figure 1, identifying a suitable polymer substrate was the first step in creating a viable reference material. An ideal polymer should be uniform and stable so that the material's properties do not change. It should neither react with formaldehyde nor contain any reactive or volatile impurities (additives or contaminants) that may confound mass-transfer of formaldehyde within the material. Furthermore, the success of this method depends on two key criteria: first, formaldehyde needs to be sufficiently soluble in the polymer substrate so that an adequate amount of formaldehyde can be loaded into and then allowed to diffuse from the substrate; and second, the diffusion of formaldehyde in the polymer substrate must be ideal or Fickian in nature.

Although the encouraging application of PMP for both toluene and n-butanol suggests that diffusion of formaldehyde within PMP, a non-polar polymer, may be ideal, its solubility is rather low given that formaldehyde is quite polar. It is expected that formaldehyde has higher solubility in polar matrices. For example, the solubility in polycarbonate (PC) is reported to be about 150 times higher than in polypropylene (Hennebert, 1988). However, additional attention should be paid when selecting polar polymers because formaldehyde may react with hydroxyl ($-OH$) or amine ($-NH_2$) groups in polymers by forming a methylol ($-CH_2OH$) group with the active hydrogen (Walker, 1975). Such reactions have been observed in cellulose, paper, nylon, latex and polyester, rendering formaldehyde's transport within these materials non-ideal (Hennebert, 1988). Therefore, PMP material with a thickness of 0.025 cm and two polycarbonate materials of thicknesses 0.025 and 0.051 cm, respectively, were evaluated for potential use as a formaldehyde emissions reference material. These polymeric materials are commercially available and were purchased directly from manufacturers in large sheets.

2.2 Generating gas-phase formaldehyde

As described later, a continuous gas stream with a constant formaldehyde concentration was needed to characterize mass-transfer properties of candidate polymers and to load formaldehyde into the polymer substrate. The formaldehyde gas generating system consisted of a diffusion vial placed in a temperature-controlled calibration gas generator (Dynacalibrator Model 190, VICI Metronics Inc., Santa Clara, CA) with a purge clean air flow regulated by a mass-flow controller (Model FC-280S, Tylan General, Carson, CA). Solid paraformaldehyde (97%, Alfa Aesar, Ward Hill, MA) contained in the diffusion vial depolymerized to monomeric formaldehyde gas at elevated temperatures in the oven of the calibration gas generator (Röck et al., 2010), which then diffused into the purge flow of dry and clean air (UN1002, Airgas Inc., Radnor, PA). While maintaining constant purge gas flow rate, formaldehyde concentration in the generated gas stream was varied by adjusting the oven temperature and using diffusion vials with different diffusion path lengths. The formaldehyde gas generation parameters are summarized in Table 1.

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To determine the rate of formaldehyde emissions from the diffusion vial containing paraformaldehyde, the vial was weighed using a mechanical balance (with a precision of ~10 μg) over appropriate time intervals. The linearity between the measured weight and time can be examined to determine whether the formaldehyde release rate was constant. The formaldehyde concentration in the generated gas stream can then be calculated by dividing the formaldehyde release rate by the purge flow rate. The true gas flow rate was measured using a bubble flowmeter (mini-Buck Calibrator, A.P. BUCK Inc., Orlando, FL).

For comparison, the formaldehyde concentration in the gas stream was also directly measured by visible absorption spectrometry, following NIOSH Analytical Method 3500 (NIOSH, 1994). Briefly, an appropriate volume of the gas stream was passed through two impingers in series containing 20 mL 1% sodium bisulfite solution so that the gas-phase formaldehyde was completely absorbed by the solution, forming $HOCH_2 \cdot SO_3Na$. The backup impinger was used to check collection efficiency. Then aliquots of the impinger solution were transferred to a flask and mixed with 0.1 mL 1% chromotropic acid and 6 mL concentrated sulphuric acid. After heating the sample solution at 95 ^{o}C for 15 minutes and maintaining it at room temperature for 2 hours so that the chromophore was fully developed, the absorbance at 580 nm was measured using a spectrophotometer (Spectronic 20D+, Thermo Scientific, West Palm Beach, FL). Meanwhile, a blank and six calibration standard solutions prepared from a formaldehyde standard aqueous solution (1000 μg/mL, AccuStandard, New Haven, CT) were also treated with the reagents and analyzed by the spectrophotometer for absorbance at 580 nm. A calibration line (absorbance versus formaldehyde concentration of the calibration standard) was constructed and the formaldehyde concentration in the tested solution sample was obtained from the calibration line. Finally, formaldehyde concentration in the gas stream was calculated using an appropriate aliquot factor and the gas sample volume.

Table 1. Generating gas-phase formaldehyde

Test ID	Vial ID	Diffusion path length (mm)	Temp. (°C)	Test duration (h)	Avg. flow rate (mL/min)	Avg. emission rate (μg/min)
VT 1	Vial 1	76	85	140	250	61
VT 2	Vial 1	76	95	310	250	120
VT 3	Vial 2	38	95	290	250	230
VT 4	Vial 3	25	95	70	250	320
VT 5	Vial 3	25	100	140	250	450
VT 6	Vial 3	25	105	65	250	640

Note: VT 1 – VT 6 were conducted by VT.

2.3 Determining mass-transfer properties of selected polymers

The key VOC mass-transfer parameters of a given polymeric material include the diffusion coefficient of the VOC in the material (D) and the partition coefficient of the VOC between the material and air (K) (Cox et al., 2010; Xiong et al., 2011a; Xiong et al., 2011b). To determine D and K, a microbalance sorption/desorption method was

employed (Cox et al., 2001). As shown in Figure 2(a), the mass of a polymer film sample was continuously measured using a high-resolution (0.1 μg) dynamic recording microbalance (Thermo Cahn D-200, Thermo Fisher Scientific, Waltham, MA). During the sorption test, as air containing a known concentration of formaldehyde was passed across the film, formaldehyde sorbed into the material and the mass gain of the film was recorded, generating a sorption curve. Once the film had reached sorption equilibrium with the formaldehyde-containing gas stream, a desorption curve was created by passing clean air across the film while again using the microbalance to monitor formaldehyde mass loss. When Fickian diffusion controls the sorption and desorption process, D can be determined by fitting a Fickian diffusion model to the sorption and desorption curves. Under the experimental configuration, the mass change caused by Fickian diffusion of formaldehyde inside the film is given by (Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4H^2}\right\} \tag{1}$$

where M_t is the total formaldehyde mass that has entered or left the film via diffusion in time t, M_∞ is the formaldehyde mass in the film when partition equilibrium is reached between the film and the air, and H is the diffusion pass length. Furthermore, K can be derived by dividing M_∞ by the volume of the film sample and the gas-phase formaldehyde concentration. The selected films and parameters are summarized in Table 2.

Table 2. Determining mass-transfer properties of selected polymer by microbalance sorption/desorption test.

Test ID	Selected polymer	Film dimensions (cm × cm × cm)	Test duration (h)	Avg. flow rate (mL/min)	Avg. gas-phase formaldehyde concentration (g/m^3)	Avg. emission rate (μg/min)
VT 7	PMP	3.6×3.6×0.025	840	250	1.70	430
VT 8	PC	3.6×3.6×0.051	410	250	1.70	430
VT 9	PC	3.6×3.6×0.025	340	250	1.70	430

Note: VT 7 – VT 9 were conducted by VT.

2.4 Loading the identified polymer substrate with formaldehyde

After a suitable polymer substrate was identified, reference materials were created by loading precisely-cut film samples with formaldehyde. As shown in Figure 2(b), formaldehyde was infused into the films by passing air containing formaldehyde through a loading vessel containing several films and allowing material-phase/gas-phase sorption equilibrium to be reached. The effluent from the loading vessel was passed across an additional film installed on the microbalance so that formaldehyde mass gain could be continuously monitored during the loading process. Because the film on the microbalance was subject to the same mass-transfer process as the films in the loading vessel, the microbalance data were used to determine when material-phase/gas-phase equilibrium was reached. Furthermore, the material-phase concentration in the loaded

films, C_0, can be obtained from the microbalance data, by dividing the final measured mass of formaldehyde infused into the film by the film sample volume.

(a)   (b)
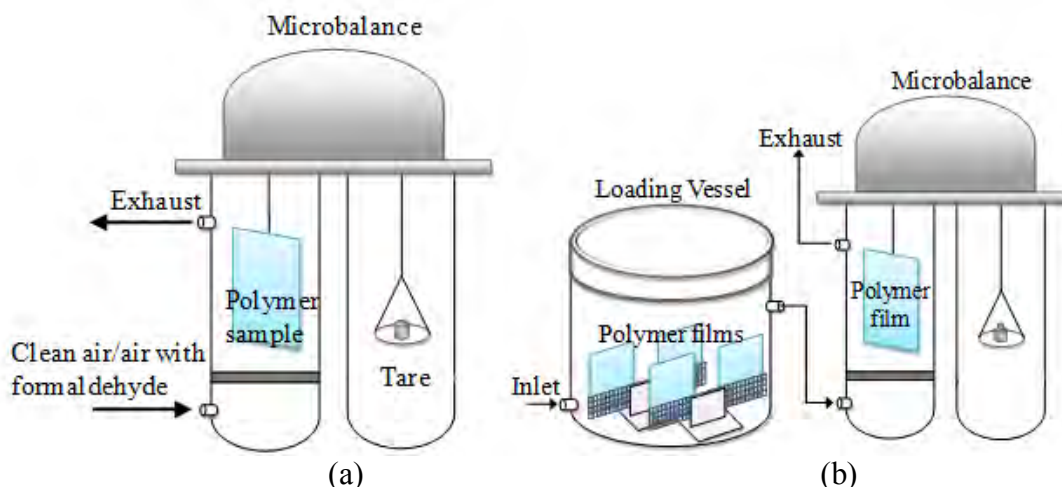
Figure 2. (a) Microbalance sorption/desorption test: air with a constant formaldehyde concentration is swept across the film for the sorption test and clean air is swept across the sample for the desorption test; (b) the microbalance and loading vessel system.

Table 3. Loading the identified polymer substrate with formaldehyde.

Test ID	Loading batch ID	Material (quantity)	Adsorption duration (day)	Avg. temp. (℃)	RH (%)	Avg. flow rate (mL/min)	Avg. gas-phase concentration (g/m^3)
VT 10	Batch 1	PC (3)	5	25	0	250	0.90
VT 11	Batch 2	PC (11)	6	25	0	250	0.90
VT 12	Batch 3	PC (9)	5	25	0	250	0.91

Note: VT 10 – VT 12 were conducted by VT.

2.5 Measuring formaldehyde emissions from pre-loaded films in small chambers

After material-phase/gas-phase absorption equilibrium had been reached in the loading vessel, films were quickly removed from the loading vessel, wrapped in aluminium foil, sealed in zip-loc bags, and placed in insulated containers that were then packed with dry ice. The containers were shipped via overnight mail to EPA for emissions testing. Once received, the films were retained in the original package and stored at -12 °C prior to being tested in small chambers. Formaldehyde emissions were measured by the EPA at 23 ºC using a 53-L stainless steel chamber with an air change rate of 1 h^{-1}, following the guidelines of ASTM International *Standard Guide for Small-scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products* (ASTM Standard D5116-2010) (ASTM 2010). Emissions measurement was also conducted by another participating laboratory (Lab A) at 25 ℃ using a 21 L stainless steel chamber with an air exchange rate of 2.9h^{-1}. During chamber testing both sides of the film were fully exposed to the chamber air using a custom fabricated sample holder. The chamber

air was sampled at appropriate time intervals to measure the gas-phase formaldehyde concentration development in the chamber, according to EPA standard method *Determination of Formaldehyde and Other Aldehydes in Indoor Air Using a Solid Adsorbent Cartridge* (EPA method IP-6A) (US EPA, 1990). Briefly, the chamber air was pulled through a cartridge containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) so that the gas-phase formaldehyde was collected on the cartridge by forming hydrazones with DNPH. After sampling, the cartridge was eluted with acetonitrile to extract the hydrazones, which were then analyzed by high performance liquid chromatography (HPLC) and ultraviolet (UV) spectroscopy. Small chamber test conditions are summarized in Table 4.

Table 4. Measuring formaldehyde emissions from pre-loaded films in small chambers.

Test ID	Film dimension (cm × cm × cm)	Test duration (h)	Inlet RH (%) ±STD	RH (%) ±STD	Temp. (°C)± STD	ACH (h^{-1}) ±STD	Chamber volume (L)
AT 1	8.5×8.5×0.025	140	50	50	25	2.9	21
AT 2	8.5×8.5×0.025	140	50	50	25	2.9	21
AT 3	8.5×8.5×0.025	140	50	50	25	2.9	21
AT 4	8.5×8.5×0.025	140	50	50	25	2.9	21
AT 5	8.5×8.5×0.025	140	50	50	25	2.9	21
ET 1	10×10×0.025	130	50±0.03	47±1.2	24±0.08	1.1±0.03	53
ET 2	10×10×0.025	100	BDL	BDL	24±0.04	1.1±0.01	53
ET 3	10×10×0.025	53	BDL	BDL	24±0.09	1.1±0.01	53
ET 4	10×10×0.025	150	BDL	BDL	25±0.03	1.0±0.007	53
ET 5	10×10×0.025	150	BDL	BDL	25±0.02	1.0±0.008	53
ET 6	10×10×0.025	150	BDL	BDL	25±0.03	1.0±0.005	53
ET 7	10×10×0.025	150	BDL	BDL	25±0.02	1.0±0.003	53
ET 8	10×10×0.025	150	BDL	BDL	25±0.17	1.0±0.007	53
ET 9	10×10×0.025	150	BDL	BDL	25±0.22	1.0±0.008	53
ET 10	10×10×0.025	150	BDL	BDL	25±0.02	1.0±0.001	53
ET 11	10×10×0.025	150	BDL	BDL	25±0.02	1.0±0.002	53
ET 12	10×10×0.025	170	BDL	BDL	25±0.02	1.0±0.002	53
ET 13	10×10×0.025	170	BDL	BDL	25±0.03	1.0±0.002	53
ET 14	10×10×0.025	1700	BDL	BDL	25±0.17	1.0±0.00	53
ET 15	10×10×0.025	150	51±0.35	50±0.34	25±0.03	1.0±0.002	53
ET 16	10×10×0.025	150	50±0.70	49±0.65	25±0.03	1.0±0.003	53
ET 17	10×10×0.025	150	BDL	BDL	25±0.04	1.0±0.004	53
ET 18	10×10×0.025	150	71±0.91	69±1.4	25±0.05	1.0±0.005	53

Notes: AT 1 – AT 5 were conducted by Lab A; ET 1 – ET 18 were conducted by EPA.

2.6 Predicting formaldehyde emissions from pre-loaded films

Figure 3 shows the mechanisms governing the emission of formaldehyde from a homogeneous solid material slab in a test chamber. If it is assumed that the external convective mass-transfer rate is much faster than internal diffusion, then a simple fundamental model can predict the emission profile. The following derivation applies to emissions from a single-sided source, however the solution can easily be adjusted and applied to a double-sided source by considering the source to be two single-sided sources.
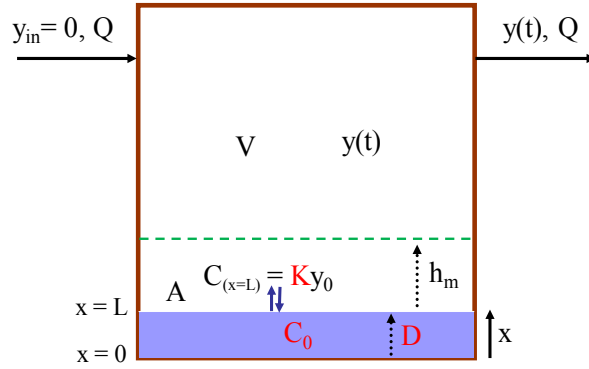
Figure 3. Schematic representation of a formaldehyde-containing source in a test chamber showing mechanisms controlling the emission rate.

The transient diffusion equation in the material slab is given by Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{2}$$

where t is time, x is the distance from the base of the slab, and C is the material-phase concentration of formaldehyde as a function of t and x. The initial condition assumes a uniform material-phase concentration of formaldehyde in the slab, C_0. The boundary condition at the base of the slab assumes there is no mass flux through the bottom surface. The boundary condition at the exposed surface is imposed via a mass balance on formaldehyde in the chamber air, or

$$\frac{dy}{dt} \cdot V = Q \cdot y_{in} - A \cdot D \cdot \frac{\partial C}{\partial x}\Big|_{x=L} - Q \cdot y \tag{3}$$

where y_{in} and y are the gas-phase formaldehyde concentration in the influent air and the bulk chamber air respectively, Q is the volumetric air flow rate, V is the well-mixed chamber volume, A is the exposed surface area of the slab, and L is the thickness of the slab. A linear and instantaneously reversible equilibrium relationship is assumed between the slab surface and the chamber air, or

$$K = C\big|_{x=L} \Big/ y \tag{4}$$

Equation (4) implies that the convective mass-transfer resistance through the boundary layer at the exposed surface is negligible compared to internal diffusion, which is common for compounds with small values of D (Cox et al., 2010). Assuming y_{in} and the initial chamber concentration are zero, an analytical solution to these equations was given by Little et al. (1994):

$$C(x,t) = 2C_0 \sum_{n=1}^{\infty} \left\{ \frac{\exp\left(-Dq_n^2 t\right)\left(h - kq_n^2\right)\cos(q_n x)}{[L\left(h - kq_n^2\right)^2 + q_n^2(L+k) + h]\cos(q_n L)} \right\} \tag{5}$$

where

$$h = Q/(ADK) \tag{6}$$

$$k = V/(AK) \tag{7}$$

and the q_ns are the positive roots of

$$q_n \tan(q_n L) = h - kq_n^2 \tag{8}$$

When key model parameters, D, K and C_0 are determined as described above and other parameters (V, Q, L, and A) are obtained from the chamber test configuration, C can be obtained using Equation (5) and y can be simply calculated using Equation (4). In addition, when the model is used to predict emissions from a pre-loaded film with both sides exposed to the chamber air, L should be half of the film thickness and A should be the total surface area of both sides. The Matlab code for emissions models are attached in Appendix F, with model parameters summarized in Table 5.

Table 5. Predicting formaldehyde emissions from pre-loaded films.

Test ID	C_0 (g/m^3) ±STD	Film dimension (cm × cm ×cm)	Chamber volume (m^3)	Avg. flow rate (m^3/h)	Duration (h)
VT 13	190±27	10×10×0.025	0.053	0.053	144
VT 14	160±8.9	10×10×0.025	0.053	0.053	144
VT 15	170±19	10×10×0.025	0.053	0.053	144
VT 16	170±19	8.5×8.5×0.025	0.021	0.061	144

Note: VT 13 – VT 16 were conducted by VT.

2.7 Task allocation

The work described in this report was created through the combined efforts of three organizations, EPA, Lab A, and VT. This specific work completed by each organization is summarized in Table 6.

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Table 6. Task allocation summary.

Organization	Experiment content	RH (%)	Test ID	Film ID	Film dimension (cm×cm×cm)	Loading batch
EPA	Small-scale chamber preliminary test	50	ET 1	B1F1	10×10×0.025	1
		10	ET 2	B1F2	10×10×0.025	1
		0	ET 3	B1F3	10×10×0.025	1
	0-week shelf-life test	0	ET 4	B2FA1	10×10×0.025	2
		0	ET 5	B2FA2	10×10×0.025	2
	2-week shelf-life test	0	ET 6	B2FA4	10×10×0.025	2
		0	ET 7	B2FA5	10×10×0.025	2
	4-week shelf-life test	0	ET 8	B2FA6	10×10×0.025	2
		0	ET 9	B2FA7	10×10×0.025	2
	6-week shelf-life test	0	ET 10	B2FB1	10×10×0.025	2
		0	ET 11	B2FB2	10×10×0.025	2
	10-week shelf-life test	0	ET 12	B2FB3	10×10×0.025	2
		0	ET 13	B2FB4	10×10×0.025	2
	Packaging test	0	ET 14	B2FA3	10×10×0.025	2
	ILS EPA	50	ET 15	B3FA1	10×10×0.025	3
		50	ET 16	B3FC2	10×10×0.025	3
	ILS Lab A	50	AT 1	B3FB1	8.5×8.5×0.025	3
		50	AT 2	B3FB2	8.5×8.5×0.025	3
		50	AT 3	B3FB3	8.5×8.5×0.025	3
		50	AT 4	B3FB4	8.5×8.5×0.025	3
		50	AT 5	B3FB5	8.5×8.5×0.025	3
	RH test	0	ET 17	B3FA2	10×10×0.025	3
		50	ET 15	B3FA1	10×10×0.025	3
		50	ET 16	B3FC2	10×10×0.025	3
		70	ET 18	B3FC1	10×10×0.025	3
VT	Generating gas-phase formaldehyde	0	VT 1	None	10×10×0.025	None
		0	VT 2	None	10×10×0.025	None
		0	VT 3	None	10×10×0.025	None
		0	VT 4	None	10×10×0.025	None
		0	VT 5	None	10×10×0.025	None
		0	VT 6	None	10×10×0.025	None
	Microbalance sorption/ Desorption test	0	VT 7	None	3.6×3.6×0.025	None
		0	VT 8	None	3.6×3.6×0.051	None
		0	VT 9	None	3.6×3.6×0.025	None
	Loading films for chamber test	0	VT 10	Note[a]	10×10×0.025	1
		0	VT 11	Note[b]	10×10×0.025	2
		0	VT 12	Note[c]	10×10×0.025[d]	3
	Emissions profiles model prediction	0	VT 13[e]	Note[l]	10×10×0.025	1
		0	VT 14[f]	Note[j]	10×10×0.025	2
		0	VT 15[g]	Note[k]	10×10×0.025	3
		0	VT 16[h]	Note[l]	8.5×8.5×0.025	3

Notes: [a]Films B1F1, B1F2 and B1F3;

[b]Films B2FA1, B2FA2, B2FA3, B2FA4, B2FA5, B2FA6, B2FA7,B2FB1, B2FB2, B2FB3, B2FB4;

[c]Films B3FA1, B3FA2, B3FB1, B2FB2, B3FB3, B3FB4, B3FB5, B3FC1, B3FC2;

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[d]10 cm × 10 cm × 0.025 cm film size for EPA, 8.5 cm × 8.5 cm × 0.025 cm film size for Lab A;

[e]VT 13 is the emission model prediction for films loading in Batch 1;

[f]VT 14 is the emission model prediction for films loading in Batch 2;

[g]VT 15 is the emission model prediction for films loading in Batch 3 with the size of 10 cm × 10 cm × 0.025 cm (EPA);

[h]VT 15 is the emission model prediction for films loading in Batch 3 with the size of 8.5 cm × 8.5 cm × 0.025 cm (Lab A);

[i]Films B1F1, B1F2 and B1F3;

[g]Films B2FA1, B2FA2, B2FA3, B2FA4, B2FA5, B2FA6, B2FA7,B2FB1, B2FB2, B2FB3, B2FB4;

[k]Films B3FA1, B3FA2, B3FC1, B3FC2;

[l]Films B3FB1, B2FB2, B3FB3, B3FB4, B3FB5;

3 RESULTS AND DISCUSSION

3.1 Generating gas-phase formaldehyde

By weighing the diffusion vial containing paraformaldehyde at certain time intervals, the formaldehyde release rate could be determined. Figure 4 shows the measured weight change of diffusion vials (Vial 1, 2 and 3) containing paraformaldehyde maintained at different temperatures (85, 95, 100, and 105 ºC). It is found that the weight decrease in all cases followed a linear pattern: when linear regression is performed between weight and time in each case, coefficients of determination (R^2) for all six cases are larger than 0.999. Therefore, the formaldehyde release rate in each case, derived from the slope of the corresponding linear regression, was constant over time. The difference in diffusion vials (Vial 1, 2, and 3) is that Vial 1 has the longest diffusion path, Vial 3 has the shortest diffusion path, and Vial 2 lies somewhere between the two extremes. As shown in Figure 4, at a fixed temperature, the formaldehyde release rate and thus the concentration in the generated gas stream increases when the diffusion path length decreases (from Vial 1 to 3). Moreover, Figure 4 also shows the formaldehyde release rate from a diffusion vial increases with temperature, which is due to the faster depolymerization rate of solid paraformaldehyde at higher temperatures.
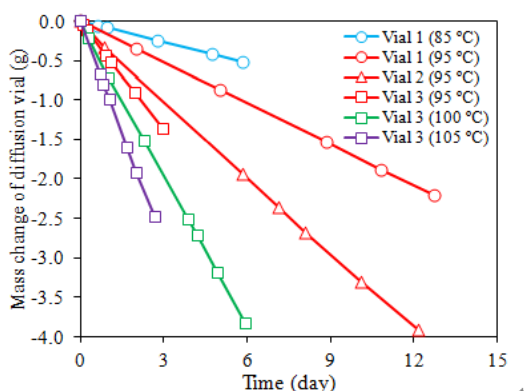
Figure 4. Measured weight decrease of diffusion vials over time: marker color indicates temperature and marker shape indicates emission vials with different diffusion path length.
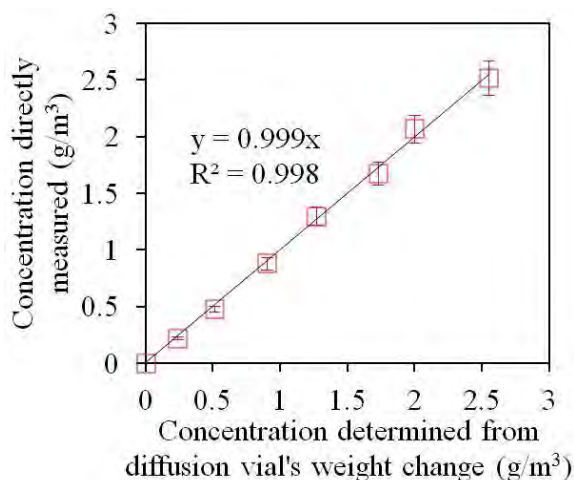
Figure 5. Comparison of directly measured formaldehyde concentration with that calculated from diffusion vial weight change.

Figure 5 compares the directly measured formaldehyde concentration in the generated gas stream using visible absorption spectrometry with that determined from the corresponding diffusion vial's weight change. It is found that the gas-phase formaldehyde concentrations obtained by these two approaches match well (a paired t-test yields a P value of 0.66), suggesting that either approach is able to determine the concentration accurately. Overall, the results in Figure 4 and 5 prove that a gas stream with a constant formaldehyde concentration at different levels can be achieved using the formaldehyde gas generating system.

3.2 Evaluating mass-transfer properties of selected polymer films

Considering the criteria in Figure 1, one PMP film with a thickness of 0.025 cm and two different PC films with thicknesses of 0.025 and 0.051 cm, respectively, were chosen as candidate substrates. To determine their mass-transfer properties, small film samples were cut from the original large sheets for the microbalance sorption/desorption tests. The measured mass gain of a 0.025 cm thick PMP sample (3.6 cm × 3.6 cm) during a sorption/desorption test is shown as blue circles in Figure 6(a). The gas-phase formaldehyde concentration for the sorption test was 1.70 g/m^3.

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(a)   (b)
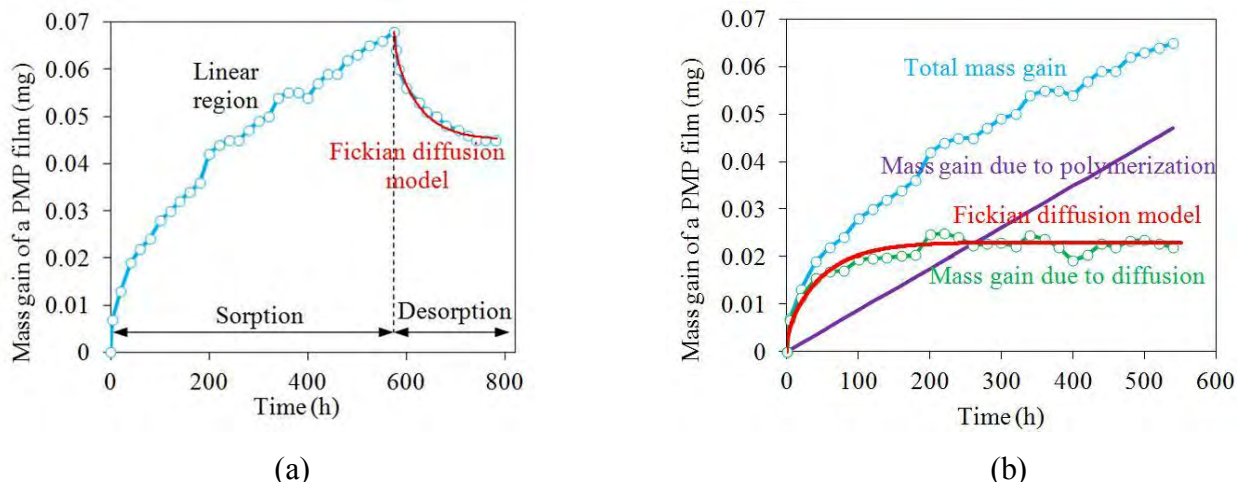
Figure 6. Sorption/desorption data and analysis for the 0.025 cm thick PMP.

If simple Fickian diffusion governs the sorption process, the mass would level off when reaching sorption equilibrium, as demonstrated for toluene/PMP and phenol/vinyl flooring (Cox et al., 2001; Cox et al., 2010). However, in contrast to what would be expected for simple Fickian diffusion, the mass of the PMP film continued to increase indefinitely as shown in Figure 6(a). Meanwhile, the mass desorbed from the PMP film during the desorption period (~0.025 mg) was less than the mass sorbed by the film during the sorption period (~0.07 mg). A possible explanation is that formaldehyde adsorption and polymerization or other chemical reaction occurred on the film surface, with overall mass gain during the sorption cycle due to both Fickian diffusion inside the film (absorption) and polymerized formaldehyde accumulating on the film surface. It has been shown that surfaces such as glass and stainless steel adsorb formaldehyde, with the amount being dependent on the nature of the surface, relative humidity, gas-phase formaldehyde concentration, and exposure time (Braswell et al., 1970). As demonstrated in the work of Braswell et al. (1970), surface polymerization may occur even at very low humidity levels because trace amounts of water (and many other nucleophilic surface contaminants) induce polymerization, building polyoxymethylene on surfaces (Walker, 1975). Moreover, the linear mass increase possibly due to polymerization implies that the surface polymerization rate would be relatively constant throughout the sorption period. As shown in Figure 6(b), if surface polymerization was occurring, the rate of mass gain due to polymerization would be linear and could be estimated from the slope of the overall mass gain (blue line) at later times (after 200 hours). Assuming that the rate of surface polymerization is constant and began at t=0, the linear mass gain due to polymerization (purple line) could be subtracted from the total mass gain (blue line), yielding the net mass gain due to diffusion (green line) which can be described by the Fickian diffusion model given in Equation (1). Assuming that polymerization at the film surface and Fickian diffusion inside the film are independent and using the method described above, D and K can be determined to be $(3.5\pm0.2)\times10^{-14}$ m^2/s and 40 ± 5, respectively. K of formaldehyde between PMP and air is much smaller than that of toluene, which is 500 ± 30 (Howard-Reed et al., 2011), indicating that formaldehyde has rather low solubility in PMP. During the desorption period, the mass decrease should be due to Fickian diffusion from within the film and possibly depolymerization of

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polyoxymethylene from the film surface. However, as shown in Figure 6(a), it is found that the Fickian diffusion model (Equation (1)), with D and K obtained from the sorption test, predicts the overall mass decrease well.

(a)   (b)
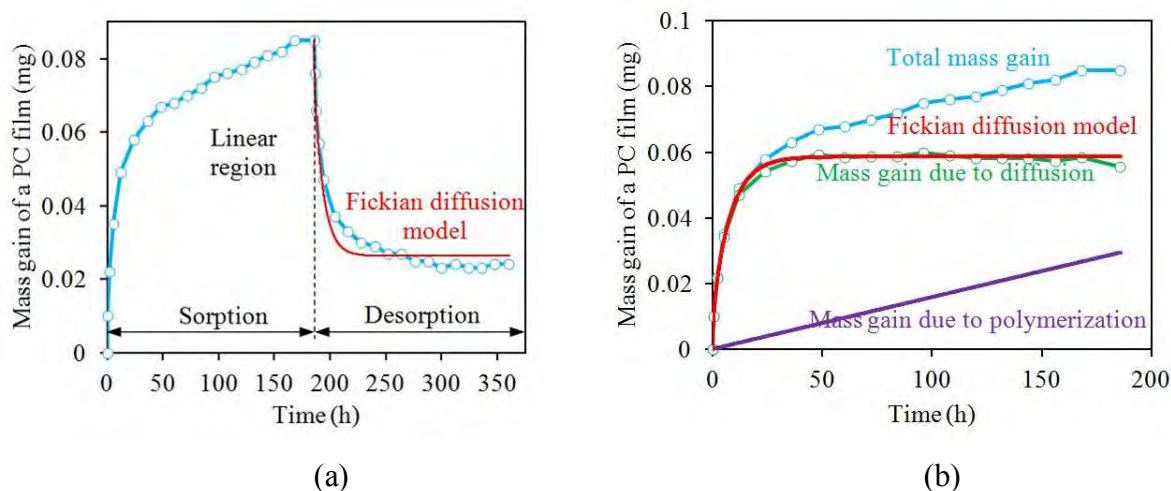
Figure 7. Sorption/desorption data and analysis for the 0.025 cm thick PC.

Figure 7 and 8 show the microbalance sorption/desorption results for a 0.025 cm thick PC sample (3.6 cm × 3.6 cm) and a 0.051 cm thick PC sample (3.6 cm × 3.6 cm). The gas-phase formaldehyde concentration for these sorption tests was 0.86 g/m^3. The mass increase of these two films during the sorption period followed a trend similar to PMP, as a result of the combined effect of polymerization or other chemical reactions at the film surface and Fickian diffusion inside the film. Based on the net mass gain due to diffusion during the sorption period (green lines in Figure 7(b) and 8(b)), D and K at 25℃, 0% RH for the two PC films can be determined. D and K were found to be $(1.9\pm0.3)\times10^{-13}$ m^2/s and 230±40 respectively for the 0.025 cm thick PC, and $(3.9\pm0.2)\times10^{-13}$ m^2/s and 170±20 respectively for the 0.051 cm thick PC. Therefore, these two PC films are slightly different in nature, but both of them have much greater formaldehyde solubility than PMP. In addition, the desorption curves of these two film samples can also be well predicted using the Fickian diffusion model with D and K obtained from the sorption tests.

In addition to Figures 6-8, replicate sorption/desorption tests were also performed and are summarized in Appendix A.

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(a)   (b)
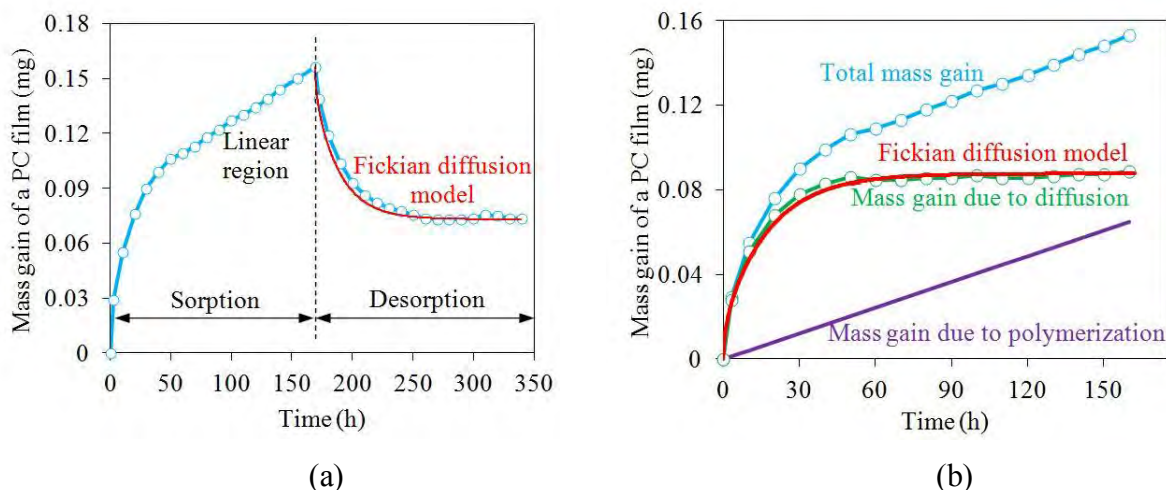
Figure 8. Sorption/desorption data and analysis for the 0.051 cm thick PC.

In summary, the sorption/desorption tests of the polymeric materials suggest that the total mass uptake during the sorption period was a combined result of constant-rate polymerization or irreversible chemical reactions involving formaldehyde at the film surface and Fickian diffusion inside the film. Because diffusion appears to dominate the desorptive mass-transfer process, the mass of formaldehyde emitted from the film can be predicted solely based on Fickian diffusion. Finally, the 0.025 cm thick PC was selected for use as a formaldehyde emissions reference material for this project due to the higher K value and the reduced time to reach gas-phase/solid phase equilibrium.
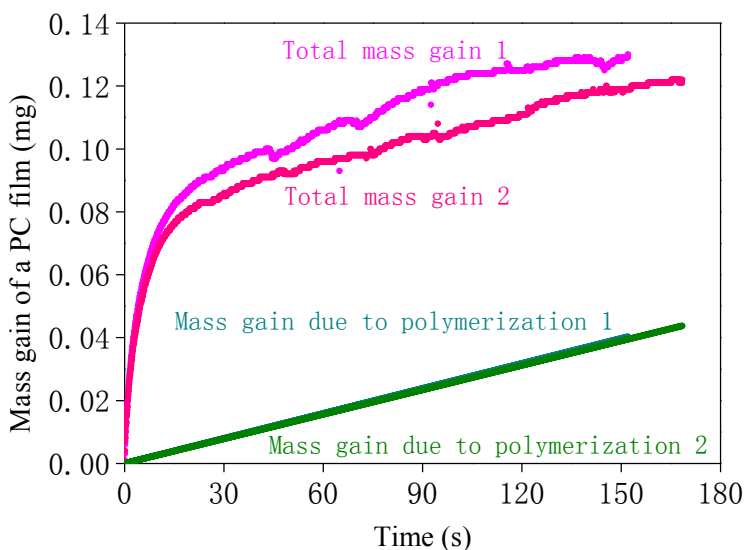
Figure 9. Comparison of duplicated analysis for 0.025 cm PC.

Figure 9 compares duplicate sorption tests of 0.025 cm PC films under similar conditions suggesting that the irreversibly-sorbed formaldehyde fractions are consistent.

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3.3 Validating overall approach by small-scale chamber testing

3.3.1 Preliminary approach by small-scale chamber testing.

Three 10 cm × 10 cm films were cut from the 0.025 cm thick PC sheet and loaded in Batch 1 using a gas stream containing ~0.90 g/m^3 formaldehyde (VT 10). The duration of the loading process was five days, long enough for the films to reach absorption equilibrium with the gas stream. Using the same analysis as in Figure 7(b), the net uptake of formaldehyde into the films through diffusion can be obtained and the formaldehyde concentration in the films was determined to be 190 ± 27 g/m^3. The loading process data and C_0 calculations are summarized in Appendix B. The films were then shipped to EPA and tested in small-scale chambers. Figure 10 shows the chamber test results of the three pre-loaded films as well as the test conditions (shelf-life and humidity level). The emission profiles are very similar, although the age effect and different humidity conditions may explain some of the difference. The small-scale chamber data are attached in Table C1, Table C2 and Table C3 in Appendix C.

Because the desorbed (emitted) mass of formaldehyde from the PC films are primarily due to diffusion, the emission model based on diffusion introduced earlier is applicable for formaldehyde with D and K values determined to be $(1.9 \pm 0.3) \times 10^{-13}$ m^2/s and 230 ± 40 (25 ℃, 0% RH) from the net mass gain due to diffusion during the sorption period. C_0 has been determined based on the net uptake of formaldehyde into pre-loaded films through diffusion, which is 190 ± 27 g/m^3. Therefore, Equation (4) and (5) can be used to predict the formaldehyde concentration profile in the chamber air during the emission tests.

To further estimate the uncertainties in model predicted concentrations associated with the uncertainties of D, K and C_0, the Monte Carlo method (Kim et al., 2004) was employed. 10,000 repeated model simulations were carried out with D, K and C_0 randomly sampled from their probability distributions, while the other parameters (L, A, Q, and V) were fixed for each individual run. The results of the 10,000 model predictions were then pooled to assess the expected variation in y as a function of time. Figure 10 shows the model prediction, with the black solid line indicating the mean of the transient gas-phase formaldehyde concentration in the chamber air and the shaded area indicting the range of mean ± one standard deviation of the transient gas-phase concentration. Compared with the measured results, the model overestimates emissions during the first 20 hours. Possible reasons include: (1) formaldehyde escaped from the pre-loaded films during packaging, shipping, and storage (shelf-life) period, especially when they were removed from the loading vessel and were wrapped; and, (2) the chamber tests were carried out at 24 ℃ while the D and K used in the model prediction were obtained from sorption/desorption tests performed at 25 ℃. Higher temperature will tend to increase D and reduce K, thus accelerating emissions (Deng et al., 2009; Zhang et al., 2007). The longer-term predicted concentrations nevertheless compare reasonably well with the measured results.
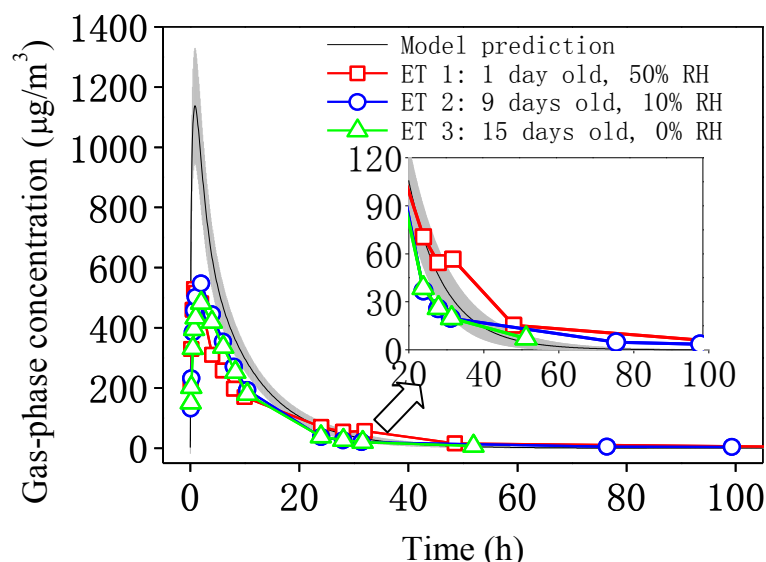
Figure 10. Comparison of the measured and predicted formaldehyde emission profiles.

3.3.2 Inter-laboratory study

To validate the formaldehyde reference material, an inter-laboratory study (ILS) was conducted with EPA laboratories and Lab A. Six 8.5 cm × 8.5 cm PC films and six 10 cm × 10 cm PC films were loaded in Batch 3 for six days (VT 12). The loading process data are summarized in Figure B3 in Appendix B. Based on microbalance data the formaldehyde concentration in the films was determined to be 170±19 g/m^3. Five of the 8.5 cm × 8.5 cm PC films were used by Lab A and two of the 10 cm × 10 cm PC films were used by EPA for the ILS. The ILS chamber tests conducted by EPA and Lab A were carried out at 50% RH and a temperature of 25 ℃.

(a)

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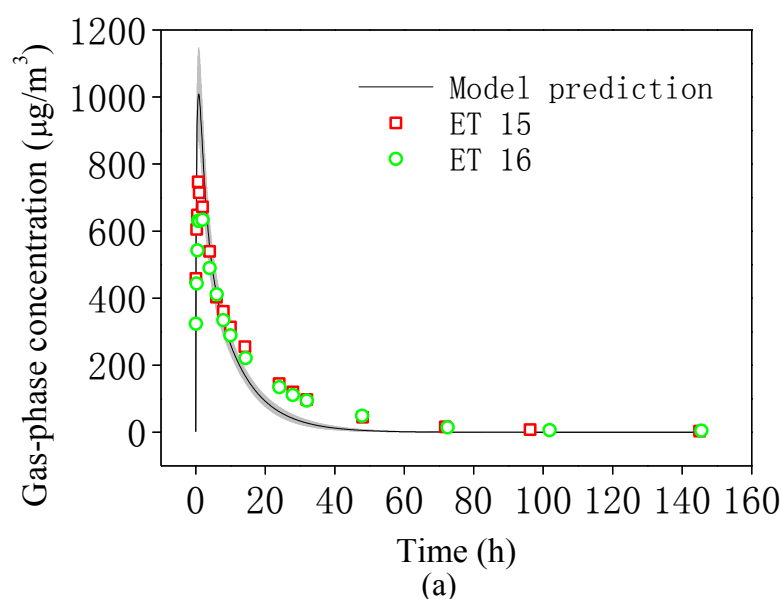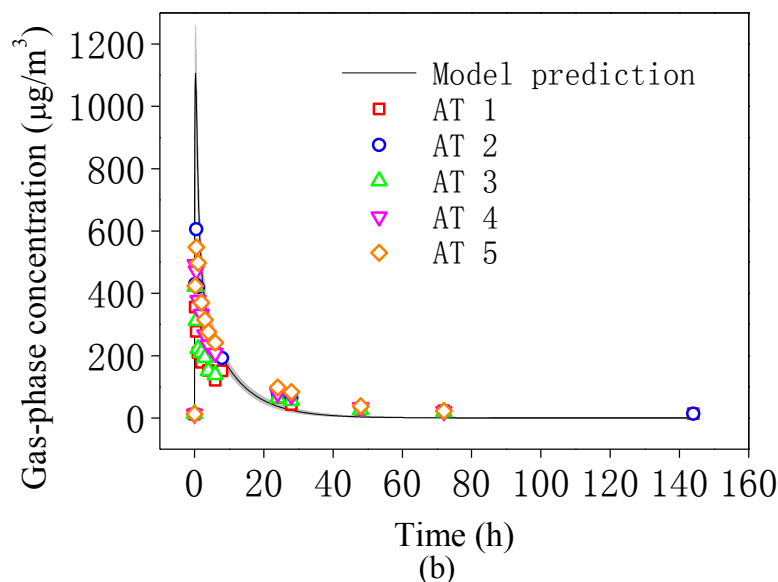
Figure 11. Comparison of measured and model predicted emission profiles in the ILS.

Direct comparison of the ILS test results generated by the two laboratories is not possible because they employed different chamber characteristics and air flow rates (Table 4 and Table 6) and have different emission profiles. However, the test results of each laboratory can be compared to the emissions model predictions based on the appropriate chamber characteristics. Figure 11 shows the measured formaldehyde concentrations and model predicted concentration profiles for each laboratory (raw data are summarized in Table C17-Table C19 in Appendix C), with Figure 11(a) comparing the test results of EPA to the model prediction and Figure 11(b) comparing the Lab A test results to the model prediction. The measured data and the model prediction of both EPA and Lab A show some deviation, although the deviations are similar in some respects. With respect to both EPA and Lab A, measured formaldehyde concentrations during the first 10 hours of testing are lower than model predictions, while measured formaldehyde concentrations after that period tend to be higher than the model predictions. The longer-term predicted concentrations nevertheless compare reasonably well with the measured results.

The lower concentrations during the early period could be explained by some loss of formaldehyde from the pre-loaded films during packaging, shipping, and storage, while higher concentrations during the later period might be explained by some formaldehyde depolymerization during the chamber test. It is also possible that the chamber conditions themselves do not correspond with the model assumptions. The model assumes that the air in the chamber is well mixed, and these conditions may not have been obtained by Lab A in reality. The overall deviation might also be explained by some impact of RH on formaldehyde emission profiles. The ILS chamber tests were conducted at 50% RH while the D and K values used in the model were obtained at 0% RH conditions. It is well known that RH affects formaldehyde emissions from composite wood products manufactured with UF (Parthasarathy, 2011). UF polymerization is a water-producing condensation reaction, and ambient moisture will naturally displace the reaction

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equilibrium with ambient moisture effectively reversing the polymerization reaction to release formaldehyde. In contrast, the potential effect of RH on formaldehyde emissions from PC films would be different.   Sorbed water can catalyze formaldehyde polymerization/depolymerization, but reaction rates will vary with many possible acidic or basic species (Brown, 1967). Finally, while the test results for the two laboratories differed with respect to the model predictions, the tests results of each laboratory are quite consistent.

3.3.3 Mass balance analysis

To further validate the overall approach, a formaldehyde mass balance analysis was conducted using data obtained during selected chamber tests.   The formaldehyde emission rate was estimated using the chamber flow rate and the measured gas-phase concentration data.   The emission rate was then integrated over the duration of each chamber test using a simple trapezoidal method of numerical integration. The emissions model was used to predict the mass emitted from each PC film during the same duration of the respective chamber test. The full integration results are contained in Appendix D and summarized in Table 7.

Table 7. Formaldehyde mass balance analysis.

Film ID	Model prediction ID	Measured emissions (µg)	Predicted emissions (µg)	Recovery[1]
B2FA1	VT 14	570	410	139%
B2FA2	VT 14	580	410	141%
B3FA2	VT 15	570	430	133%
B3FC1	VT 15	620	430	144%
B3FC2	VT 15	580	430	135%
B3FA1	VT 15	615	430	143%
B3FB2	VT 16	340	310	110%
B3FB4	VT 16	290	310	94%
B3FB5	VT 16	330	310	110%

[1] Recovery of adsorbed formaldehyde fraction only.

As shown in Table 7, measured formaldehyde mass emitted from each PC film is generally greater than the mass of formaldehyde monomer estimated to have diffused into the film during initial loading. This could be explained by polymerized formaldehyde on the film surface depolymerizing during chamber testing. However, according to previous tests by EPA, depolymerization rate is usually positively correlated with temperature. Further study will be necessary to more accurately describe formaldehyde polymerization and depolymerization chemistry.

3.4 Measuring effectiveness of foil packaging and storage materials and methods

To investigate the effectiveness of the packing material and storage methods, a series of small-scale chamber emissions tests were conducted. Several 10 cm × 10 cm films were cut from a 0.025 cm thick PC sheet and loaded in Batch 2 for five days using a gas stream containing ~0.91 g/m^3 formaldehyde (VT 11). The loading process data are summarized in Figure B2 in Appendix B.   The formaldehyde concentration in the films was

determined to be 160 ± 8.9 g/m^3. All films were packaged in aluminium foil, packed in dry ice, and shipped to EPA.

3.4.1 Packaging material evaluation

To investigate the effectiveness of the packing material, small-scale chamber emissions testing was conducted using a film tightly wrapped in the original aluminium foil packaging. The test was conducted at 0% RH with a chamber temperature of 25 ℃. Figure 12 shows the measured formaldehyde emission profiles with the film placed in the chamber, either with or without the aluminum foil wrapping. The gas-phase formaldehyde concentration without the foil wrapping is obviously much higher than that with the foil wrapping. What the results clearly show is that films wrapped in foil do lose formaldehyde at room temperature, although the foil wrapping reduces the formaldehyde loss rate.
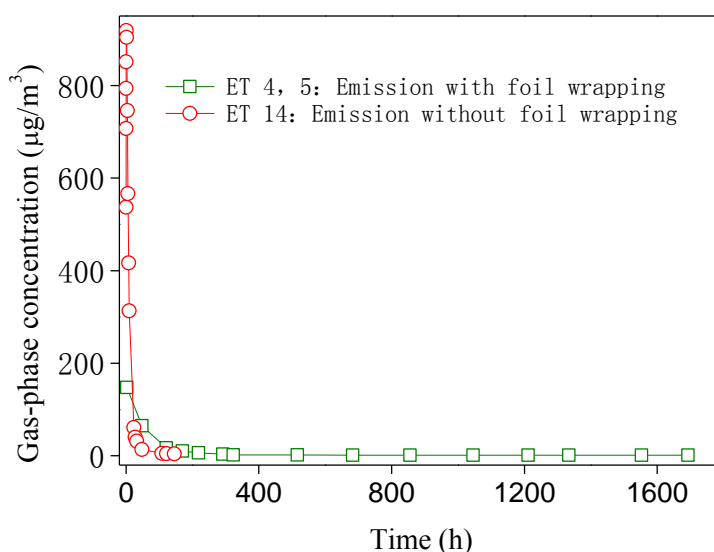
Figure 12. Comparison of the measured formaldehyde emission profiles in chamber tests using films with and without foil wrapping.

3.4.2 Shelf-life evaluation

To study formaldehyde emission profiles with respect to film storage duration, a series of chamber tests were conducted using PC films that had been stored for time periods of between 0 and 10 weeks. All films used for this evaluation were simultaneously loaded with formaldehyde in Batch 2. All of the tests were conducted in duplicate.
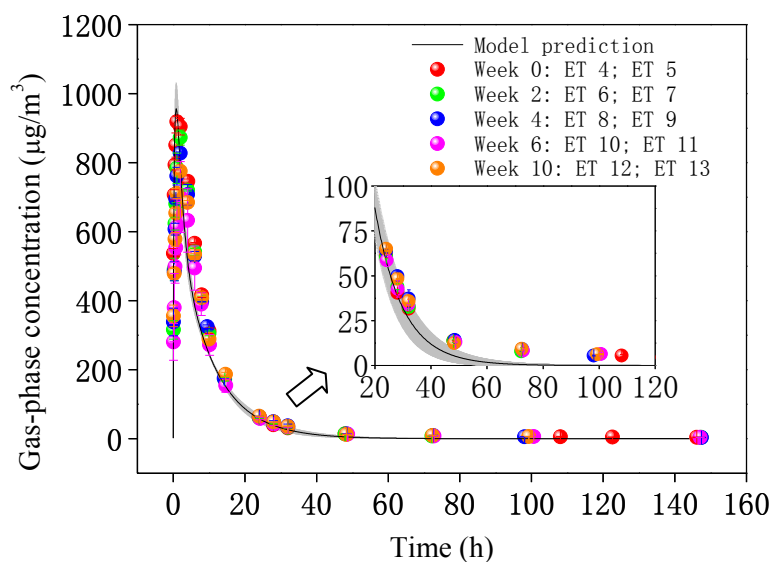
Figure 13. Comparison of the measured formaldehyde emission profiles in chamber tests of different shelf-life and the model prediction.

(a)

(b)

(c)

(d)

(e)
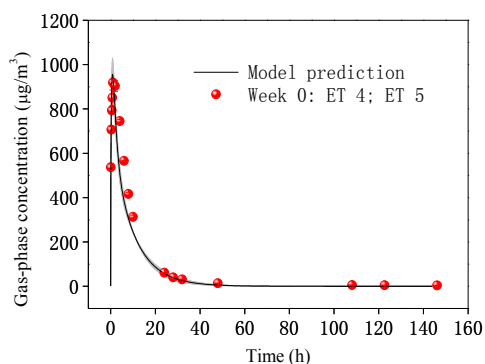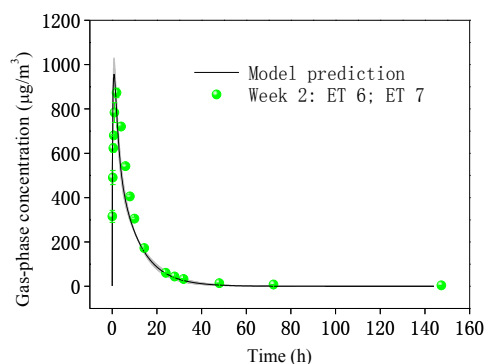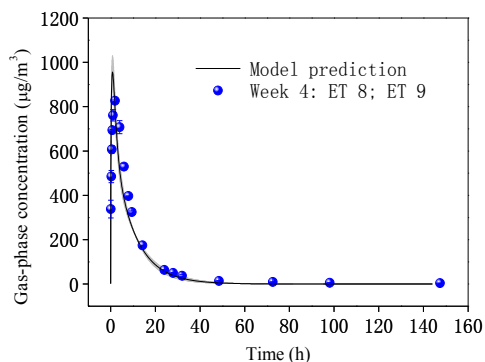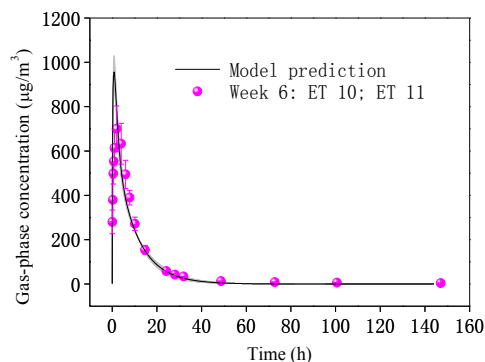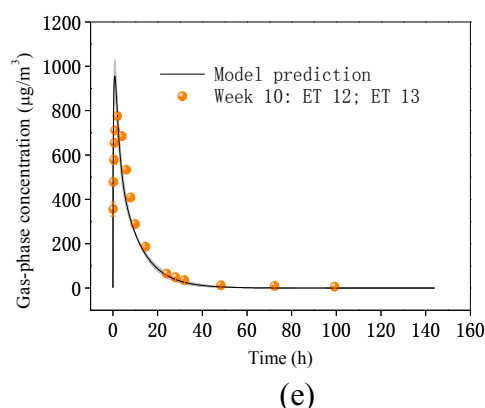
Figure 14. Comparison of model-predicted and measured formaldehyde emission profiles from films stored for different durations.

Figure 13 summarizes shelf-life test results compared to the model prediction, with the points showing the average value of duplicate tests and the error bars showing the deviation of duplicate tests (raw data is attached in Table C4-Table C13 in Appendix C). All gas-phase formaldehyde concentration measurements fit the model well, however emissions from films with shorter storage duration fit the model even better during the first 20 hours of testing. The grey shaded area provides an expression of the uncertainty of the mean at $\pm$ one standard deviation associated with estimates of D, K and C_0 using the Monte Carlo method (Kim et al., 2004). D, K and C_0 are respectively $(1.9\pm0.3)\times10^{-13}$ m^2/s, 230 ± 40 and 160 ± 8.9 g/m^3 (25 ℃, 0% RH). Figure 14 shows the results of each shelf-life test in a separate figure where the effect of storage duration can be seen more clearly.
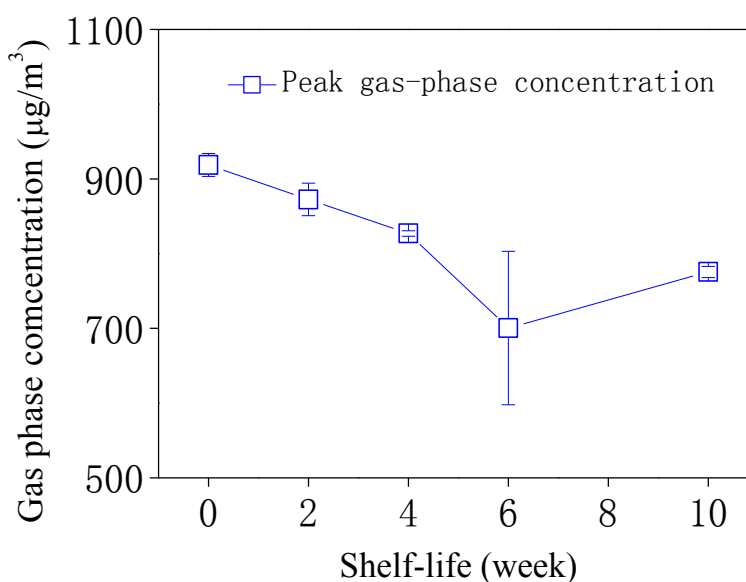
Figure 15. Peak gas phase concentration values of different shelf-life chamber tests.

Figure 15 shows that the peak values of gas phase formaldehyde concentration decrease with longer shelf life. The results suggest that some formaldehyde is lost from films even during storage at -12 $^\circ$C. The detailed view in Figure 13 also shows that the gas-phase formaldehyde concentrations after the first 40 hours were somewhat higher than the model predictions. A possible reason could be slow depolymerization of formaldehyde from the film surface during chamber testing, or the underestimation of C_0 caused by the deficiencies of the model. Despite these small deviations, the results presented in Figure 13 show very good agreement with the emissions model, particularly for films stored for shorter durations.

3.5 Measuring emissions at different relative humidity (RH) levels

To further investigate the impact of humidity on formaldehyde emission profiles, four 10 cm × 10 cm films loaded in Batch 3 for six days (VT 12) were employed for an emission test at different humidity levels (0% RH, 50% RH and 70% RH). Based on microbalance data the formaldehyde concentration in the films was determined to be 170±19 g/m^3. Figure 16 shows the test results and model prediction using a D value of (1.9±0.3)×10^{-13} m^2/s and a K value of 230±40. All of the RH tests were conducted at a chamber temperature of 25°C. The RH test raw data is attached in Table C15 and Table C16 in Appendix C.
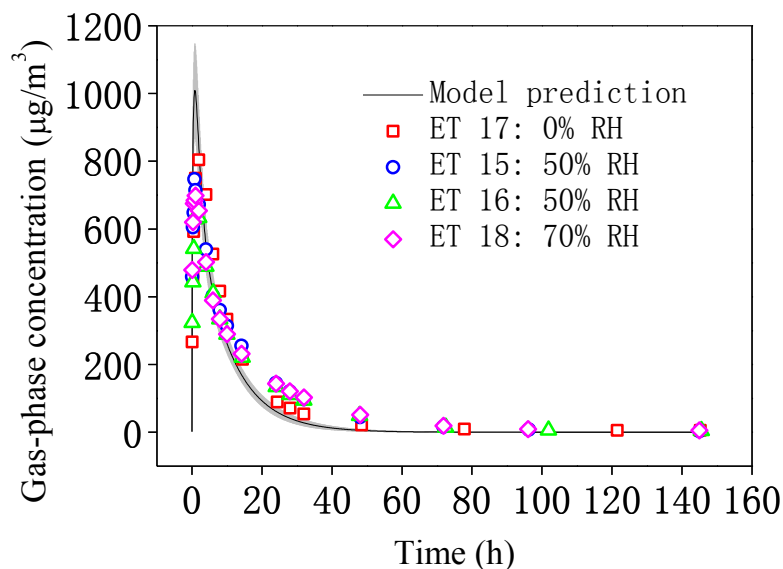
Figure 16. Emission profiles at different RH levels.

As with earlier small-scale chamber studies that indicated that humidity had an effect on some VOC emission characteristics for some materials (Wolkoff, 1998; Fang, 1999), this study suggests that formaldehyde emission profiles from the PC films may also be affected by humidity, as shown in Figure 16. The deviation increases somewhat as humidity increases. The test results generated from duplicate 50% RH tests showed good consistency, indicating that formaldehyde has the same emission profile at a specific RH level. Humidity may impact either the D or K values through a "plasticizing" effect of

the PC film material or with water molecules potentially competing for sorption sites. A recent study also shows that higher RH tends to increase both D and K values (Xu et al., 2012). A 35% increase in RH could increase formaldehyde emissions by a factor of 1.8 – 2.6 (Parthasarathy, 2011). The results could also be explained by a combination of these factors.

3.6 Statistical evaluation of measured and model-predicted concentrations

Differences between chamber-measured and model-predicted gas-phase formaldehyde concentrations result from 1) errors associated with the measurement procedure, 2) model construction and use, and 3) inaccuracies in model parameters. Two statistical analyses were used to assess the degree of agreement between model predictions and chamber measurements for the small-scale chamber testing conducted during this project. In the first analysis, the correlation coefficient, r, was calculated for each data set. The correlation coefficient is a measure of the strength of the relationship between measured and predicted concentrations. The second analysis, normalized mean square error (NMSE), is a measure of the magnitude of the prediction error relative to measured and predicted concentrations. ASTM D5157-97 advises that an r value of 0.9 or greater and a NMSE of 0.25 or lower generally indicate acceptable agreement between model-predicted and chamber-measured gas-phase concentrations (ASTM 2008). The results of the analysis are summarized in Table 8.

Table 8. Statistical analysis summary.

Test ID	r	NMSE
ET 1	0.99	1.0
ET 2	0.90	1.1
ET 3	0.85	1.4
ET 4	0.97	0.058
ET 5	0.97	0.061
ET 6	0.91	0.20
ET 7	0.92	0.17
ET 8	0.92	0.20
ET 9	0.92	0.17
ET 10	0.89	0.29
ET 11	0.88	0.52
ET 12	0.91	0.23
ET 13	0.92	0.19
ET 15	0.98	0.15
ET 16	0.96	0.34
ET 17	0.90	0.27
ET 18	0.99	0.17
AT 1	0.96	3.0
AT 2	0.96	0.9
AT 3	0.96	2.1
AT 4	0.96	0.93
AT 5	0.92	0.76

The statistical analysis shows that the agreement between the model and chamber-measured concentrations represented by r, is relatively strong for all tests indicating that the model predictions compare well to the experimental observations. The prediction error represented by NSME is within an acceptable range for most of the chamber tests conducted in accordance with ASTM 5116-10. The root cause of deviation between model-predicted and chamber-measured concentrations could be formaldehyde reactivity. Polymerization, depolymerization and other formaldehyde reaction pathways affect measurements of the model parameters D and K, as well as measurements of gas-phase formaldehyde concentrations during chamber testing. The relatively large prediction error associated with Tests ET 1 – ET 3 could be due to the length of time films from Batch 1 were exposed to air, and consequential loss of formaldehyde, during the packaging process at VT while preparing films for shipment. Employing experience gained from packaging Batch 1 films, the exposure time between removal from the loading chamber and packaging was reduced for Batch 2 and Batch 3 films. The NSME for Tests AT1-AT5 could be due to incomplete mixing in the chambers during the measurement process, while model condition is that the chambers are well-mixed.

4 QUALITY ASSURANCE AND QUALITY CONTROL

4.1 VT quality assurance and quality control

Work on this project was performed in accordance with *Quality Assurance Project Plan – Developing a Reference Material for Formaldehyde Emissions Testing* attached in Appendix F. Six microbalance data sets were used to obtain estimates of the mean D and K for formaldehyde in the 0.025 cm PC films. Each microbalance data set used to determine D, K, and C_0 consisted of a minimum of 600 data points. All the PMP/PC film samples were obtained from a single roll of additive-free film purchased directly from the manufacturer. Flow rates were verified using a flow meter calibrated to a NIST-traceable primary standard. The microbalance was calibrated before each test using standard weights that had been verified using mass standards whose calibrations are NIST-traceable.

4.2 EPA quality assurance and quality control

Quality assurance (QA) and quality control (QC) procedures were implemented in this project by following guidelines and procedures detailed in the approved Category III Quality Assurance Project Plan (QAPP), *Indoor Source Emissions and Sink Effect Study of Formaldehyde, Addendum 4 – Procedure for Evaluation of Reference Material for Formaldehyde Emissions Testing using Small Environmental Chambers* (Appendix G).

The Agilent 1200 High Performance Liquid Chromatography (HPLC) with a Diode Array and Multiple Wavelength Detector (DAD) was calibrated using an external standard method with formaldehyde in the range of 0.04-15 μg/mL. The Internal Audit Program (IAP) was implemented to minimize the systematic errors. Chamber environmental system components such as Gilibrator, temperature sensors, relative humidity sensors, and mass flow controllers were calibrated annually in EPA's Metrology Laboratory. Quality control samples, including background, field blank, and duplicate, all met the data quality indicator goals for critical measurements listed in the QAPP. On each day of analysis, at least one daily calibration check (DCC) sample was analyzed to document the performance of the instrument. The recoveries met the criterion of 85 to 115% recovery for acceptable performance of the HPLC instrument.

5 CONCLUSIONS

This project investigated the feasibility of creating a reference material for use in formaldehyde emissions testing by loading formaldehyde into a suitable polymer substrate and predicting the emission rate from pre-loaded films.

Gas-phase formaldehyde can be controllably generated through depolymerization of paraformaldehyde at elevated temperatures. Consistent carrier gas flow rate and formaldehyde gas generator temperature produced a consistent gas-phase formaldehyde concentration in the carrier gas. The gas-phase formaldehyde concentration could be regulated by adjusting the gas generator temperature, the length of the diffusion vial, or by adjusting the carrier gas flow rate.

During sorption/desorption testing of a PMP material and two types of PC material, it was found that the formaldehyde sorption process is complicated due to simultaneous Fickian diffusion inside the polymer and possible formaldehyde polymerization or other irreversible chemical reactions on the polymer surface. However, Fickian diffusion appears to dominate desorption and emissions, allowing the emission profiles to be predicted using a diffusion-based emission model. Prototype reference materials were then created using 0.025 cm thick PC films loaded with known quantities of formaldehyde. The D and K values for the formaldehyde/PC system were determined to be $(1.9\pm0.3)\times10^{-13}$ m^2/s and 230 ± 40 respectively for the 0.025 cm thick PC according to sorption/desorption test under 0 RH condition at 25 $^{\circ}$C.

Although some deviation existed between chamber-measured and model-predicted concentrations, overall the ASTM D-5116-10 small-scale chamber testing of formaldehyde emissions reference materials suggests that formaldehyde emissions could be predicted by a fundamental emissions model.

Tests showed that the aluminium foil packaging and dry-ice shipping and storage methods could successfully retard the loss of formaldehyde from the polymer films, although loss of formaldehyde was not completely prevented.

A series of shelf life tests showed that emission chamber measurements agreed well with the model predicted emission profiles, except that the model tends to underestimate the formaldehyde concentrations after the first 40 hours. This observation could be due to slow depolymerisation of formaldehyde from the surface of the film or some inconsistency in the model parameters. When reference materials are tested in small chambers by different laboratories, the reference emission profiles predicted by the model can be compared to the observed emission profiles to validate different emissions testing methods, to evaluate the test performance of individual laboratories, and to help identify the root causes of variability.

Although the effect was weak, RH test results indicated that the presence of water could affect the formaldehyde emission rate. This could be due to water molecules plasticizing

the PC film resulting in an increase in both K and D. Another possible reason might be that moisture affected formaldehyde polymerization on the PC film surface.

While further refinement and testing is needed, particularly with regard to the chemistry of formaldehyde, the results obtained in this study suggest that it is possible to create a viable reference material for formaldehyde emissions testing using the proposed approach.

6 RECOMMENDATIONS

Based on the results of this project, there are four recommendations for further work:

First, additional work is needed to identify and quantify the behavior of formaldehyde in PC films and in test chamber systems. Specifically the chemical behavior that affects formaldehyde mass-transfer on and within the PC films and chamber surfaces is not sufficiently understood. Because this behavior may be influenced by moisture and temperature, the relationship between humidity, temperature, and formaldehyde mass-transfer warrants further investigation. Although the idea that formaldehyde diffuses into and from the PC film as well as adsorbs to the surface is consistent with experimental results, the effect of formaldehyde reactivity and the conditions that facilitate formaldehyde reactions need to be further investigated and quantified.

Second, additional work is needed to evaluate packaging materials, storage methods, and other conditions that affect the shelf-life of the reference materials. The results suggest that a small amount of formaldehyde is emitted from the PC films, albeit at a slow rate, even while tightly wrapped in foil and stored at -12 $^{\circ}$C. A packaging method and/or sealing technique that could extend the shelf life and avoid the need for shipping in the presence of dry-ice would be of real value.

Third, experience has shown that substantial testing and evaluation is needed to perfect the development of such reference materials and build confidence in their practical application. Although the initial results are promising, it is nevertheless necessary to further test the procedures to develop and validate the current formaldehyde reference material for small-scale chambers, including more substantial inter-laboratory studies.

Finally, the reference material should be scaled-up for use in large chambers with larger or more numerous films subject to similar extensive testing and inter-laboratory studies.

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APPENDIX A: MICROBALANCE SORPTION/DESORPTION TEST RESULTS

In addition to Figure 6-8, replicate sorption/desorption tests were also performed. The results and analysis of all the sorption/desorption tests for PC and PMP are shown below. The legend in all the figures is the same as Figure 6-8: blue dots are the microbalance measured weight of the film during the sorption/desorption cycle; purple lines show the linear mass gain due to polymerization; green dots show the mass gain of monomer formaldehyde due to diffusion; and red lines are the model prediction based on Equation (1).

(a) sorption
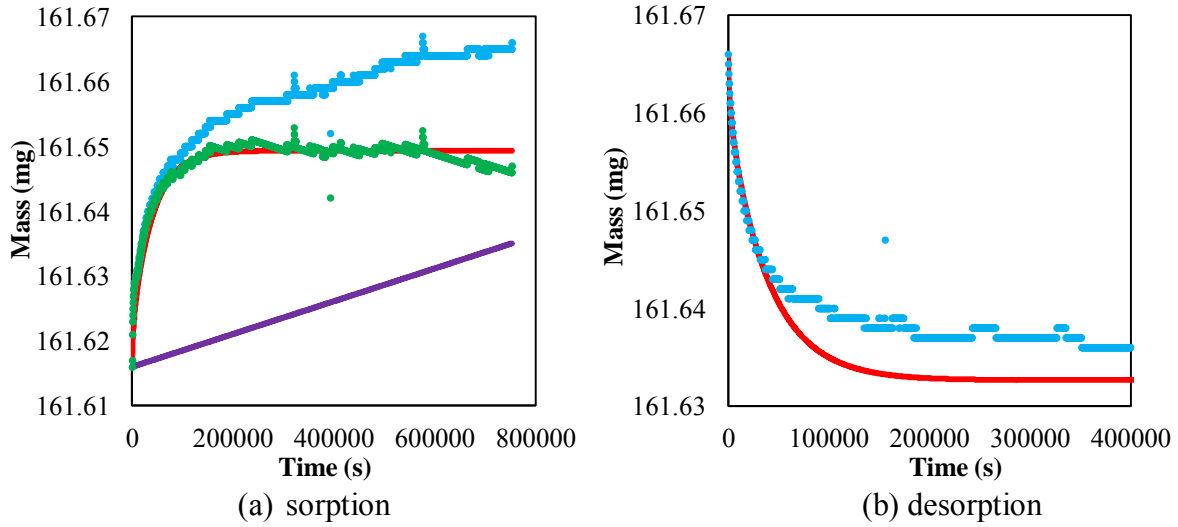
(b) desorption

Figure A1. Sorption/desorption data and analysis for a 0.025 cm thick PC (y_{in}: 0.48 g/m^3, D: 1.6×10^{-13} m^2/s, K: 210).

(a) sorption
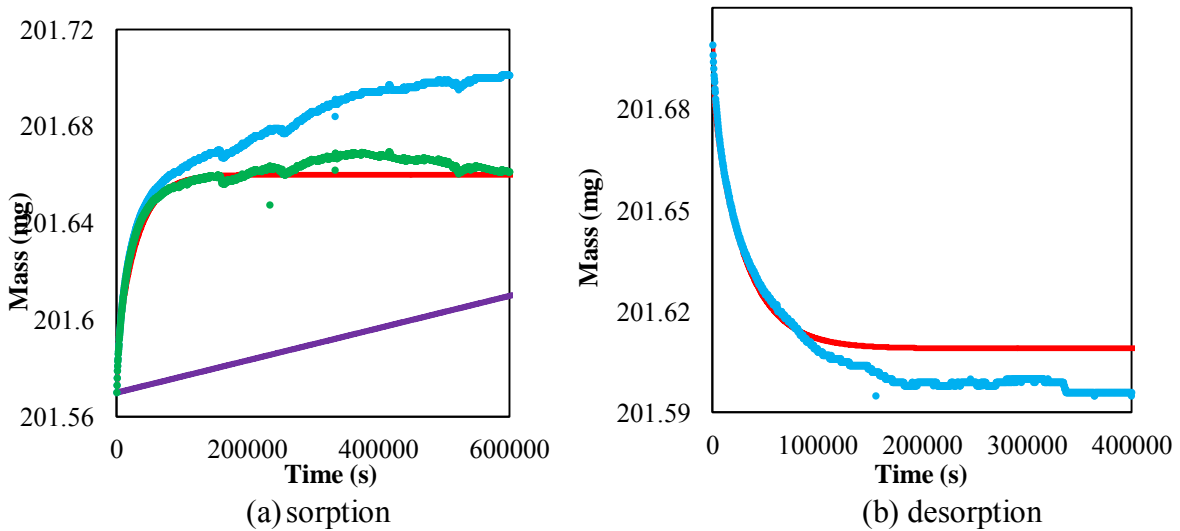
(b) desorption

Figure A2. Sorption/desorption data and analysis for a 0.025 cm thick PC (y_{in}: 1 g/m^3, D: 2.1×10^{-13} m^2/s, K: 270).
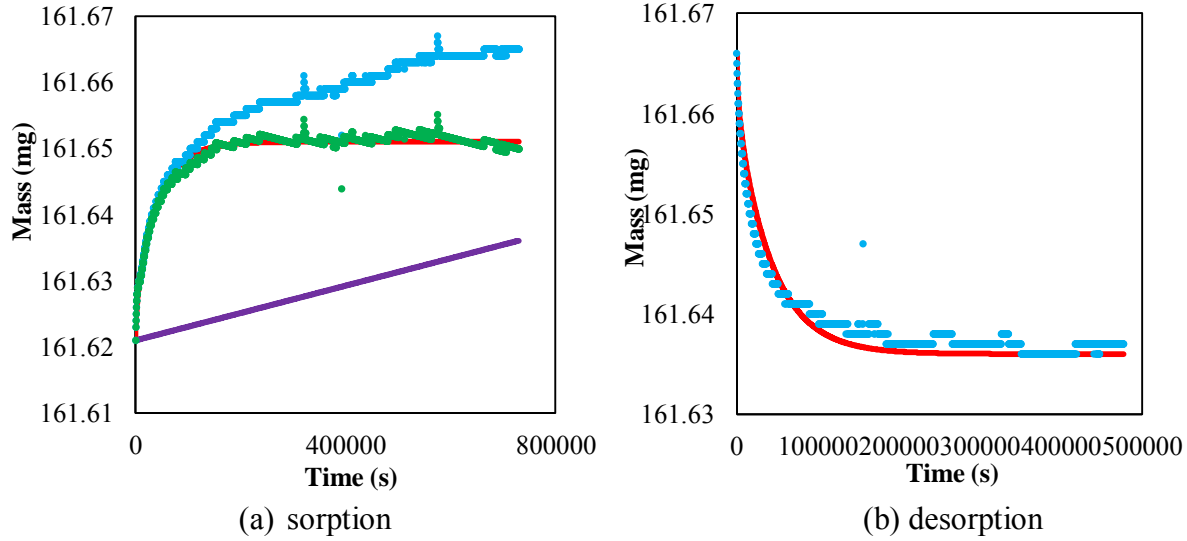
Figure A3. Sorption/desorption data and analysis for a 0.025 cm thick PC (y_{in}: 0.48 g/m^3, D: 1.5×10^{-13} m^2/s, K: 190).
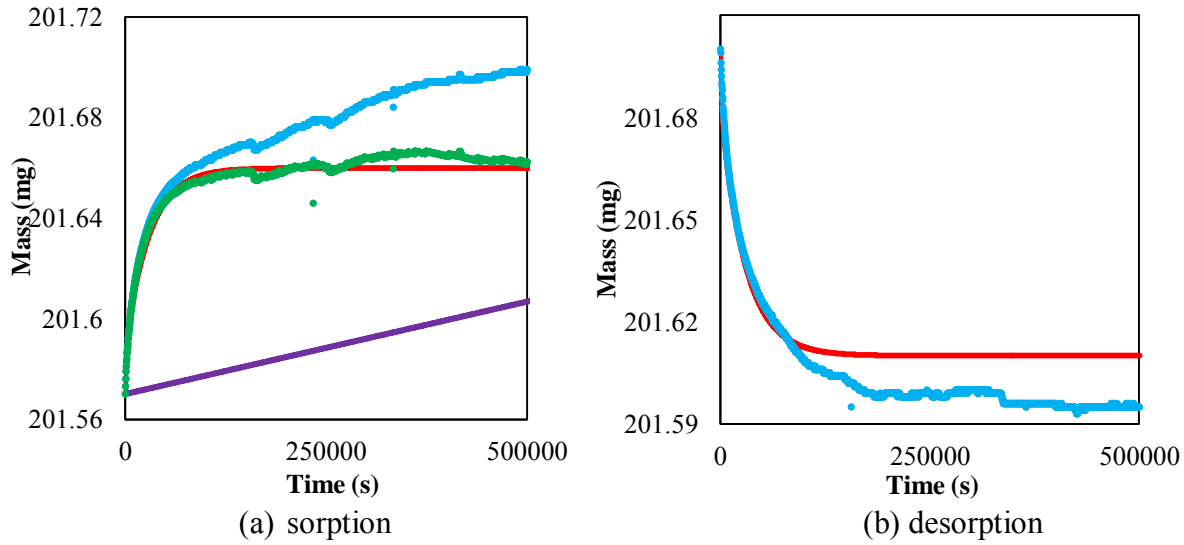
Figure A4. Sorption/desorption data and analysis for a 0.025 cm thick PC (y_{in}: 0.96 g/m^3, D: 2.2×10^{-13} m^2/s, K: 280).

(a) sorption
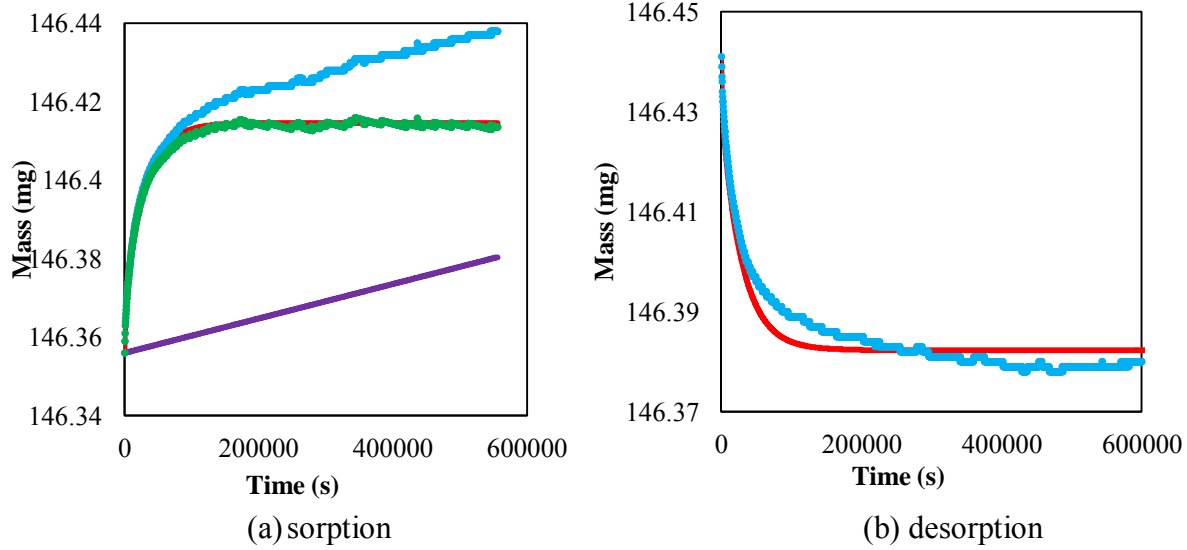
(b) desorption

Figure A5. Sorption/desorption data and analysis for a 0.025 cm thick PC (y_{in}: 0.86 g/m^3, D: 2.2×10^{-13} m^2/s, K: 210).

(a) sorption
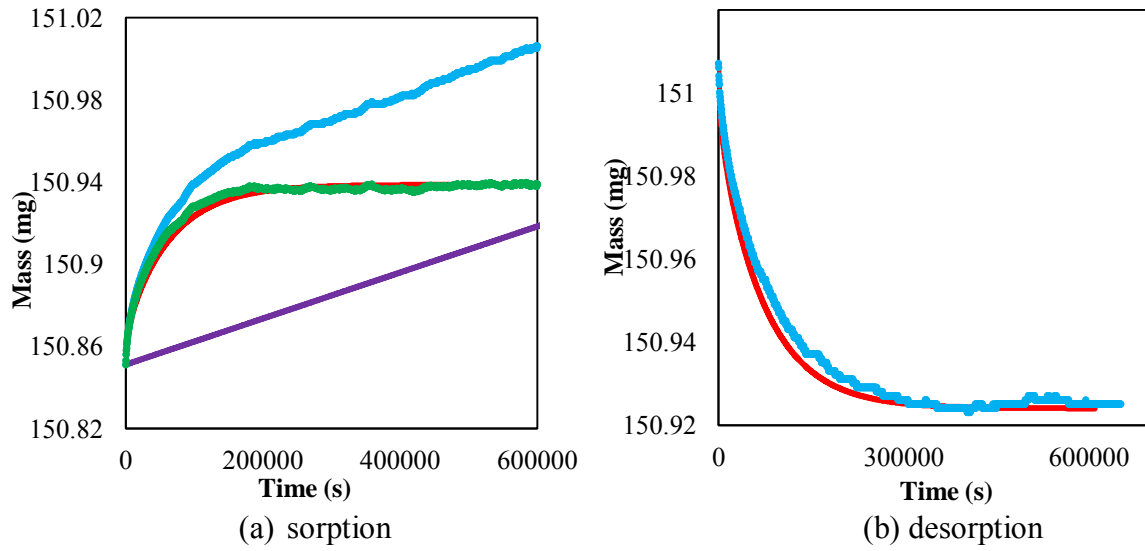
(b) desorption

Figure A6. Sorption/desorption data and analysis for a 0.051 cm thick PC (y_{in}: 0.86 g/m^3, D: 4.0×10^{-13} m^2/s, K: 155).

(a) sorption
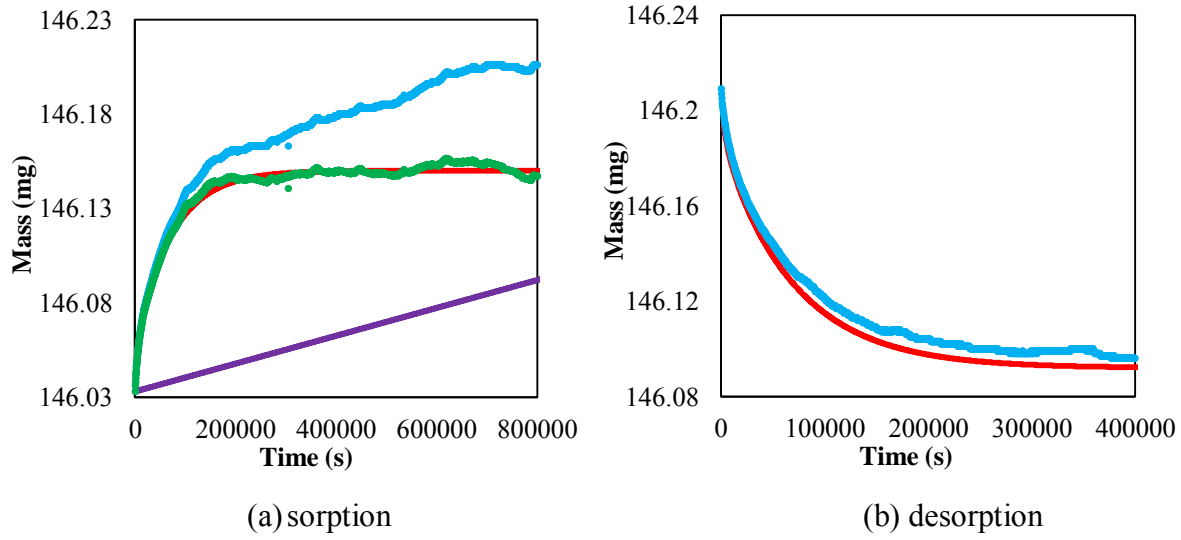
(b) desorption

Figure A7. Sorption/desorption data and analysis for a 0.051 cm thick PC (y_{in}: 0.97 g/m^3, D: 3.7×10^{-13} m^2/s, K: 180).

(a) sorption
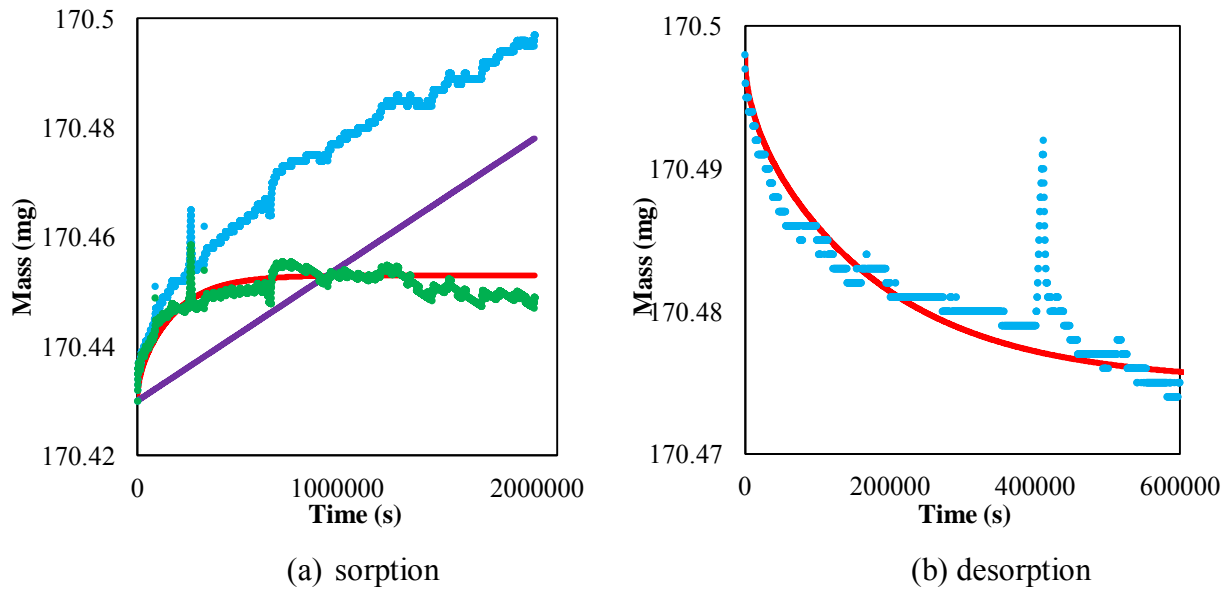
(b) desorption

Figure A8. Sorption/desorption data and analysis for a 0.025 cm thick PMP (y_{in}: 1.73 g/m^3, D: 3.5×10^{-14} m^2/s, K: 40).

APPENDIX B: MICROBALANCE SORPTION DATA FOR EMISSION TEST

Microbalance sorption data

The microbalance sorption data of loading process for Batch 1, Batch 2 and Batch 3 is shown below. Blue dots are the microbalance measured weight of the film during the sorption process; purple lines show the linear mass gain due to polymerization; green dots show the mass gain of monomer formaldehyde due to diffusion; and red lines are the model prediction based on Equation (1) using $D = 1.9 \times 10^{-13}$ m^2/s.
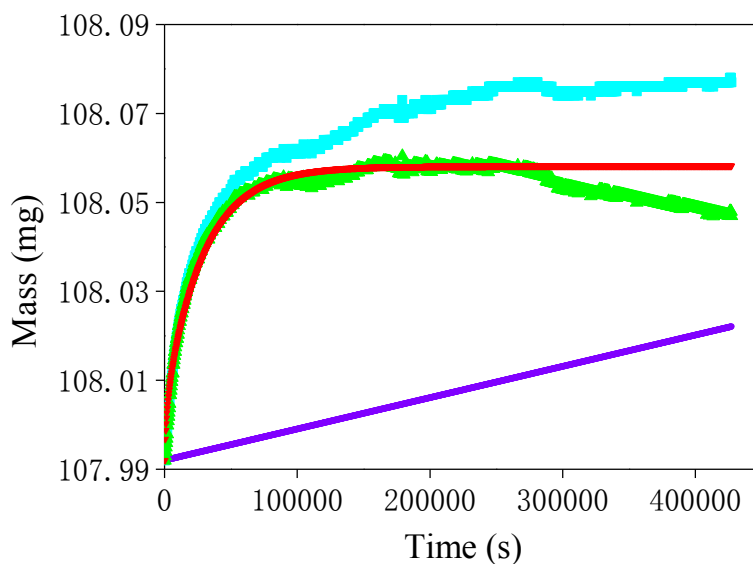
Figure B1. Sorption data of loading process for VT 10 (Batch 1).
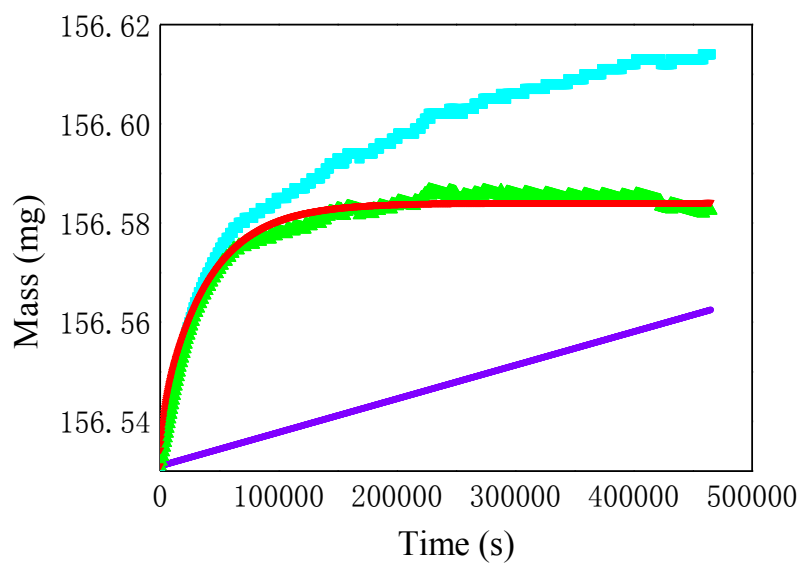
Figure B2. Sorption data of loading process for VT 11 (Batch 2).
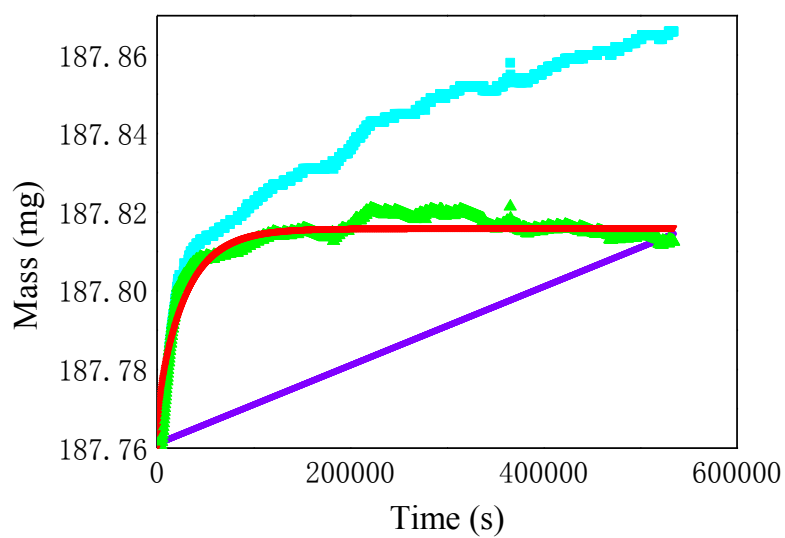
Figure B3. Sorption data of loading process for VT 12 (Batch 3).

Calculation of C_0

The size of the PC films used in microbalance testing was 3.6 cm × 3.6 cm and the thickness was 0.025 cm. Thus the volume of the film was 3.3×10^{-7} m^3 and the surface area was 2.6×10^{-3} m^2 (double sides). Using data obtained with the microbalance (Figure B1, B2 and B3), the mass gain due to diffusion of these three loading processes was 0.056 – 0.068 mg, 0.052 – 0.056 mg and 0.052 – 0.060 mg; the mass gain due to polymerization was 0.030 mg, 0.031 mg and 0.053 mg. Based on data above, the C_0 resulting from these three loading processes was 190±27 g/m^3, 160±8.9 g/m^3 and 170±19 g/m^3.

APPENDIX C: SMALL-SCALE CHAMBER TEST RAW DATA

Table C1. Preliminary small-scale chamber raw data for Batch 1 — film B1F1.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air ($\mu g/m^3$)
ID3622	SES-SCH-F1-0.1hr	0.08	6.83	209.03
ID3623	SES-SCH-F1-0.2hr	0.21	3.38	329.41
ID3624/ID3625	SES-SCH-F1-0.5hrA/B	0.50	3.44	459.84
ID3628	SES-SCH-F1-0.7hr	0.74	3.45	528.70
ID3626	SES-SCH-F1-1hr	1.03	7.04	515.79
ID3629	SES-SCH-F1-2hr	2.00	6.92	480.89
ID3630/ID3631	SES-SCH-F1-4hrA/B	4.01	7.41	309.77
ID3632	SES-SCH-F1-6hr	6.01	7.58	257.69
ID3633	SES-SCH-F1-8hr	8.06	46.71	197.49
ID3634	SES-SCH-F1-10hr	10.00	41.56	169.30
ID3635	SES-SCH-F1-24hr	24.00	41.89	70.51
ID3636/ID3637	SES-SCH-F1-28hrA/B	28.01	41.77	54.38
ID3640	SES-SCH-F1-32hr	32.02	43.54	56.66
ID3642	SES-SCH-F1-48hr	48.52	85.07	15.41
ID3645	SES-SCH-F1-123hr	122.91	180.35	1.75

Table C2. Preliminary small-scale chamber raw data for Batch 1 — film B1F2.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air ($\mu g/m^3$)
ID3700	SES-SCH-F2-0.1hr	0.08	7.00	131.33
ID3703	SES-SCH-F2-0.2hr	0.21	3.50	231.40
ID3704/ID3705	SES-SCH-F2-0.5hrA/B	0.48	3.47	384.86
ID3706	SES-SCH-F2-0.7hr	0.72	3.49	457.54
ID3707	SES-SCH-F2-1hr	0.99	7.00	501.54
ID3708	SES-SCH-F2-2hr	1.99	6.99	546.78
ID3710/ID3711	SES-SCH-F2-4hrA/B	3.99	7.00	444.29
ID3715	SES-SCH-F2-6hr	5.99	6.97	353.30
ID3716	SES-SCH-F2-8hr	7.99	41.84	270.57
ID3717	SES-SCH-F2-10hr	10.46	41.79	193.06
ID3721	SES-SCH-F2-24hr	24.03	41.61	36.78
ID3722/ID3723	SES-SCH-F2-28hrA/B	28.02	42.88	25.84
ID3728	SES-SCH-F2-31hr	31.45	42.83	19.79
ID3729	SES-SCH-F2-76hr	76.41	41.94	4.79
ID3733	SES-SCH-F2-99hr	99.33	54.43	3.48

Table C3. Preliminary small-scale chamber raw data for Batch 1 — film B1F3.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m^3)
ID3738	SES-SCH-F3-0.1hr	0.10	4.26	151.25
ID3737	SES-SCH-F3-0.2hr	0.20	3.50	202.13
ID3760/ID3761	SES-SCH-F3-0.5hrA/B	0.47	3.49	331.68
ID3762	SES-SCH-F3-0.7hr	0.72	3.50	395.28
ID3763	SES-SCH-F3-1hr	0.99	6.99	433.28
ID3764	SES-SCH-F3-2hr	1.99	6.97	482.72
ID3766/ID3767	SES-SCH-F3-4hrA/B	3.99	6.96	419.71
ID3768	SES-SCH-F3-6hr	6.07	13.93	336.04
ID3772	SES-SCH-F3-8hr	8.30	67.28	252.78
ID3773	SES-SCH-F3-10hr	10.46	41.73	179.42
ID3790	SES-SCH-F3-24hr	23.96	41.99	38.53
ID3791/ID3792	SES-SCH-F2-28hrA/B	28.06	41.21	26.13
ID3793	SES-SCH-F3-31hr	31.61	41.77	19.70
ID3794	SES-SCH-F3-52hr	51.92	45.17	7.06

Table C4. Small-scale chamber raw data for Batch 2 — film B2FA1.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m^3)
ID4115	SES-SCH1-FA1-W0-0.10hr	0.11	3.20	527.19
ID4120	SES-SCH1-FA1-W0-0.25hr	0.30	3.50	696.70
ID4123	SES-SCH1-FA1-W0-0.50hr	0.50	3.54	803.92
ID4125/ID4126	SES-SCH1-FA1-W0-0.75hr A/B	0.70	3.53	825.94
ID4129	SES-SCH1-FA1-W0-1.0hr	1.00	3.52	929.58
ID4134/ID4145	SES-SCH1-FA1-W0-2.0hr A/B	2.00	7.01	886.83
ID4138	SES-SCH1-FA1-W0-4.0hr	4.12	6.94	740.58
ID4140	SES-SCH1-FA1-W0-6.0hr	6.00	7.23	564.39
ID4144/ID4145	SES-SCH1-FA1-W0-8.0hr A/B	8.00	7.04	411.42
ID4148	SES-SCH1-FA1-W0-10hr	10.00	7.05	307.23
ID4150	SES-SCH1-FA1-W0-24hr	24.00	21.01	60.42
ID4152	SES-SCH1-FA1-W0-28hr	28.00	20.82	40.32
ID4154/ID4155	SES-SCH1-FA1-W0-32hr A/B	32.00	20.83	32.58
ID4158	SES-SCH1-FA1-W0-48hr	48.00	42.15	13.96
ID4161	SES-SCH1-FA1-W0-108hr	108.08	63.67	5.97
ID4164/ID4165	SES-SCH1-FA1-W0-123hrA/B	122.60	145.92	4.47
ID4175	SES-SCH1-FA1-W0-146hr	146.11	64.30	4.93

Table C5. Small-scale chamber raw data for Batch 2 — film B2FA2.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m^3)
ID4116	SES-SCH5-FA2-W0-0.10hr	0.11	3.20	547.14
ID4122	SES-SCH5-FA2-W0-0.25hr	0.30	3.51	717.16
ID4124	SES-SCH5-FA2-W0-0.50hr	0.50	3.52	783.08
ID4125/ID4126	SES-SCH5-FA2-W0-0.75hr A/B	0.70	3.46	875.49
ID4130	SES-SCH5-FA2-W0-1.0hr	1.00	3.53	907.80
ID4134/ID4145	SES-SCH5-FA2-W0-2.0hr A/B	2.00	6.96	921.13
ID4139	SES-SCH5-FA2-W0-4.0hr	4.12	6.92	750.39
ID4141	SES-SCH5-FA2-W0-6.0hr	6.00	7.21	567.66
ID4146/ID4147	SES-SCH5-FA2-W0-8.0hr A/B	8.00	7.05	422.20
ID4149	SES-SCH5-FA2-W0-10hr	10.00	7.05	318.50
ID4151	SES-SCH5-FA2-W0-24hr	24.00	21.21	61.94
ID4153	SES-SCH5-FA2-W0-28hr	28.00	20.76	40.56
ID4154/ID4155	SES-SCH5-FA2-W0-32hr A/B	32.00	21.19	30.59
ID4159	SES-SCH5-FA2-W0-48hr	48.00	41.66	13.71
ID4162	SES-SCH5-FA2-W0-108hr	108.08	63.58	4.95
ID4166/ID4167	SES-SCH5-FA2-W0-123hrA/B	122.60	145.94	4.60
ID4176	SES-SCH5-FA2-W0-146hr	146.11	64.38	3.81

Table C6. Small-scale chamber raw data for Batch 2 — film B2FA4.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m^3)
ID4201	SES-SCh1-FA4-W2-0.10hr	0.10	3.48	296.52
ID4205	SES-SCh1-FA4-W2-0.25hr	0.30	3.48	467.97
ID4207/ID4208	SES-SCh1-FA4-W2-0.50hrA/B	0.50	3.48	610.29
ID4211	SES-SCh1-FA4-W2-0.75hr	0.70	3.50	677.94
ID4213	SES-SCh1-FA4-W2-1.0hr	1.00	3.49	752.40
ID4215/ID4216	SES-SCh1-FA4-W2-2.0hrA/B	2.00	6.95	857.25
ID4219	SES-SCh1-FA4-W2-4.0hr	4.00	6.93	718.47
ID4221	SES-SCh1-FA4-W2-6.0hr	6.00	6.95	534.76
ID4223/ID4224	SES-SCh1-FA4-W2-8.0hrA/B	8.00	6.98	399.88
ID4227	SES-SCh1-FA4-W2-10hr	10.00	6.94	300.20
ID4232	SES-SCh1-FA4-W2-14hr	14.37	6.97	168.65
ID4234	SES-SCh1-FA4-W2-24hr	24.00	20.83	59.83
ID4238	SES-SCh1-FA4-W2-28hr	28.00	20.90	42.89
ID4241/ID4242	SES-SCh1-FA4-W2-32hrA/B	32.00	21.11	31.63
ID4242	SES-SCh1-FA4-W2-32hrB	32.00	21.07	32.46
ID4245	SES-SCh1-FA4-W2-48hr	48.00	42.15	13.11
ID4250	SES-SCh1-FA4-W2-72hr	72.22	42.44	7.79
ID4257/ID4258	SES-SCh1-FA4-W2-147hrA/B	147.39	82.25	3.75

Table C7. Small-scale chamber raw data for Batch 2 — film B2FA5.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m³)
ID4202	SES-SCh5-FA5-W2-0.10hr	0.10	3.51	334.56
ID4206	SES-SCh5-FA5-W2-0.25hr	0.30	3.51	513.53
ID4209/ID4210	SES-SCh5-FA5-W2-0.50hrA/B	0.50	3.50	636.25
ID4212	SES-SCh5-FA5-W2-0.75hr	0.70	3.52	682.99
ID4214	SES-SCh5-FA5-W2-1.0hr	1.00	3.51	815.26
ID4217/ID4218	SES-SCh5-FA5-W2-2.0hrA/B	2.00	6.98	887.86
ID4220	SES-SCh5-FA5-W2-4.0hr	4.00	7.00	721.73
ID4222	SES-SCh5-FA5-W2-6.0hr	6.00	6.99	549.05
ID4225/ID4226	SES-SCh5-FA5-W2-8.0hrA/B	8.00	7.02	410.56
ID4228	SES-SCh5-FA5-W2-10hr	10.00	6.99	309.66
ID4233	SES-SCh5-FA5-W2-14hr	14.37	7.01	175.30
ID4235	SES-SCh5-FA5-W2-24hr	24.00	21.00	61.35
ID4239	SES-SCh5-FA5-W2-28hr	28.00	20.93	45.17
ID4243/ID4244	SES-SCh5-FA5-W2-32hrA/B	32.00	21.13	33.40
ID4244	SES-SCh5-FA5-W2-32hrB	32.00	21.07	33.68
ID4246	SES-SCh5-FA5-W2-48hr	48.00	42.22	14.10
ID4251	SES-SCh5-FA5-W2-72hr	72.22	42.38	7.90
ID4259/ID4260	SES-SCh5-FA5-W2-147hrA/B	147.39	82.01	4.04

Table C8. Small-scale chamber raw data for Batch 2 — film B2FA6.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m³)
ID4281	SES-SCh1-FA6-W4-0.10hr	0.10	3.48	310.14
ID4283	SES-SCh1-FA6-W4-0.25hr	0.30	3.48	465.38
ID4287/ID4288	SES-SCh1-FA6-W4-0.50hrA/B	0.50	3.49	595.07
ID4291	SES-SCh1-FA6-W4-0.75hr	0.70	3.48	696.31
ID4293	SES-SCh1-FA6-W4-1.0hr	1.00	3.49	742.76
ID4295/ID4296	SES-SCh1-FA6-W4-2.0hrA/B	2.00	6.96	824.35
ID4299	SES-SCh1-FA6-W4-4.0hr	4.00	6.94	686.63
ID4301	SES-SCh1-FA6-W4-6.0hr	6.00	6.93	519.83
ID4303/ID4304	SES-SCh1-FA6-W4-8.0hrA/B	8.00	6.94	396.87
ID4309	SES-SCh1-FA6-W4-10hr	9.50	6.99	328.22
ID4312	SES-SCh1-FA6-W4-14hr	14.23	6.94	174.65
ID4314	SES-SCh1-FA6-W4-24hr	24.00	20.88	63.11
ID4319	SES-SCh1-FA6-W4-28hr	28.00	20.94	47.93
ID4321/ID4322	SES-SCh1-FA6-W4-32hrA/B	32.00	20.95	40.79
ID4325	SES-SCh1-FA6-W4-49hr	48.50	41.85	15.12
ID4330	SES-SCh1-FA6-W4-73hr	72.57	44.64	9.87
ID4336	SES-SCh1-FA6-W4-98hr	98.10	80.35	5.70
ID4340/ID4341	SES-SCh1-FA6-W4-147hrA/B	147.47	74.43	3.39

Table C9. Small-scale chamber raw data for Batch 2 — film B2FA7.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m³)
ID4282	SES-SCh5-FA7-W4-0.10hr	0.10	3.48	366.39
ID4284	SES-SCh5-FA7-W4-0.25hr	0.30	3.49	504.25
ID4289/ID4290	SES-SCh5-FA7-W4-0.50hrA/B	0.50	3.47	619.56
ID4292	SES-SCh5-FA7-W4-0.75hr	0.70	3.49	692.09
ID4294	SES-SCh5-FA7-W4-1.0hr	1.00	3.50	779.09
ID4297/ID4298	SES-SCh5-FA7-W4-2.0hrA/B	2.00	6.95	829.66
ID4300	SES-SCh5-FA7-W4-4.0hr	4.00	6.95	728.25
ID4302	SES-SCh5-FA7-W4-6.0hr	6.00	6.94	539.11
ID4305/ID4306	SES-SCh5-FA7-W4-8.0hrA/B	8.00	6.93	396.53
ID4310	SES-SCh5-FA7-W4-10hr	9.50	7.01	320.83
ID4313	SES-SCh5-FA7-W4-14hr	14.23	6.97	174.57
ID4315	SES-SCh5-FA7-W4-24hr	24.00	20.88	64.60
ID4320	SES-SCh5-FA7-W4-28hr	28.00	20.99	51.50
ID4323/ID4324	SES-SCh5-FA7-W4-32hrA/B	32.00	21.00	33.79
ID4326	SES-SCh5-FA7-W4-49hr	48.50	42.04	13.22
ID4331	SES-SCh5-FA7-W4-73hr	72.57	44.49	8.46
ID4337	SES-SCh5-FA7-W4-98hr	98.10	80.36	5.41
ID4342/ID4343	SES-SCh5-FA7-W4-147hrA/B	147.47	74.40	4.09

Table C10. Small-scale chamber raw data for Batch 2 — film B2FB1.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m³)
ID4370	SES-SCh1-FB1-W6-0.10hr	0.10	3.51	317.91
ID4375	SES-SCh1-FB1-W6-0.25hr	0.30	3.53	449.48
ID4377/ID4378	SES-SCh1-FB1-W6-0.50hrA/B	0.50	3.52	532.40
ID4381	SES-SCh1-FB1-W6-0.75hr	0.70	3.52	583.46
ID4383	SES-SCh1-FB1-W6-1.0hr	1.00	3.52	671.11
ID4385/ID4386	SES-SCh1-FB1-W6-2.0hrA/B	2.00	7.03	773.03
ID4390	SES-SCh1-FB1-W6-4.0hr	4.00	7.03	697.80
ID4393	SES-SCh1-FB1-W6-6.0hr	6.00	7.03	539.90
ID4395/ID4396	SES-SCh1-FB1-W6-8.0hrA/B	7.83	7.02	413.03
ID4399	SES-SCh1-FB1-W6-10hr	10.12	7.01	293.04
ID4401	SES-SCh1-FB1-W6-14hr	14.65	7.00	167.74
ID4403	SES-SCh1-FB1-W6-24hr	24.22	23.90	61.04
ID4405	SES-SCh1-FB1-W6-28hr	28.10	25.01	45.94
ID4407/ID4408	SES-SCh1-FB1-W6-32hrA/B	31.97	23.12	34.06
ID4411	SES-SCh1-FB1-W6-49hr	48.72	41.74	13.20
ID4420	SES-SCh1-FB1-W6-73hr	72.82	44.08	7.88
ID4414	SES-SCh1-FB1-W6-101hr	100.63	62.60	5.63
ID4422/ID4423	SES-SCh1-FB1-W6-147hrA/B	147.10	102.17	3.86

Table C11. Small-scale chamber raw data for Batch 2 — film B2FB2.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (µg/m^3)
ID4371	SES-SCh5-FB2-W6-0.10hr	0.10	3.51	242.67
ID4376	SES-SCh5-FB2-W6-0.25hr	0.30	3.53	310.10
ID4379/ID4380	SES-SCh5-FB2-W6-0.50hrA/B	0.50	3.48	465.08
ID4382	SES-SCh5-FB2-W6-0.75hr	0.70	3.52	523.37
ID4384	SES-SCh5-FB2-W6-1.0hr	1.00	3.51	556.52
ID4387/ID4388	SES-SCh5-FB2-W6-2.0hrA/B	2.00	6.99	627.76
ID4391	SES-SCh5-FB2-W6-4.0hr	4.00	7.03	567.57
ID4394	SES-SCh5-FB2-W6-6.0hr	6.00	7.03	449.50
ID4397/ID4398	SES-SCh5-FB2-W6-8.0hrA/B	7.83	6.99	366.67
ID4400	SES-SCh5-FB2-W6-10hr	10.12	7.01	250.40
ID4402	SES-SCh5-FB2-W6-14hr	14.65	7.02	140.06
ID4404	SES-SCh5-FB2-W6-24hr	24.22	23.93	56.33
ID4406	SES-SCh5-FB2-W6-28hr	28.10	25.03	39.48
ID4409/ID4410	SES-SCh5-FB2-W6-32hrA/B	31.97	23.13	33.79
ID4412	SES-SCh5-FB2-W6-49hr	48.72	41.67	13.01
ID4421	SES-SCh5-FB2-W6-72hr	72.82	43.80	8.57
ID4419	SES-SCh5-FB2-W6-101hr	100.63	62.65	7.00
ID4424/ID4425	SES-SCh5-FB2-W6-147hrA/B	147.10	102.24	4.34

Table C12. Small-scale chamber raw data for Batch 2 — film B2FB3.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (µg/m^3)
ID4445	SES-SCh1-FB3-W10-0.10hr	0.10	3.49	333.76
ID4447	SES-SCh1-FB3-W10-0.25hr	0.30	3.49	468.15
ID4449/ID4450	SES-SCh1-FB3-W10-0.50hrA/B	0.50	3.49	563.62
ID4455	SES-SCh1-FB3-W10-0.75hr	0.70	3.49	643.53
ID4457	SES-SCh1-FB3-W10-1.0hr	1.00	3.50	700.60
ID4461/ID462	SES-SCh1-FB3-W10-2.0hrA/B	2.00	6.97	780.82
ID4463	SES-SCh1-FB3-W10-4.0hr	4.00	6.96	680.84
ID4465	SES-SCh1-FB3-W10-6.0hr	6.00	6.95	536.23
ID4467/ID4468	SES-SCh1-FB3-W10-8.0hrA/B	8.00	6.92	411.01
ID4473	SES-SCh1-FB3-W10-10hr	10.03	6.91	287.34
ID4475	SES-SCh1-FB3-W10-15hr	14.64	6.80	182.00
ID4478	SES-SCh1-FB3-W10-24hr	24.00	20.87	65.18
ID4480	SES-SCh1-FB3-W10-28hr	28.01	21.20	48.41
ID4482/ID4483	SES-SCh1-FB3-W10-32hrA/B	32.00	20.84	35.04
ID4486	SES-SCh1-FB3-W10-48hr	48.33	43.46	12.84
ID4490	SES-SCh1-FB3-W10-72hr	72.36	43.47	8.80
ID4492	SES-SCh1-FB3-W10-99hr	99.28	64.18	6.16
ID4498/ID4499	SES-SCh1-FB3-W10-172hrA/B	171.52	73.60	3.59

Table C13. Small-scale chamber raw data for Batch 2 — film B2FB4.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air ($\mu g/m^3$)
ID4446	SES-SCh5-FB4-W10-0.10hr	0.10	3.49	378.09
ID4448	SES-SCh5-FB4-W10-0.25hr	0.30	3.49	489.24
ID4453/ID4454	SES-SCh5-FB4-W10-0.50hrA/B	0.50	3.48	592.31
ID4456	SES-SCh5-FB4-W10-0.75hr	0.70	3.50	664.11
ID4458	SES-SCh5-FB4-W10-1.0hr	1.00	3.50	721.07
ID4460/ID4459	SES-SCh5-FB4-W10-2.0hrA	2.00	6.97	770.16
ID4464	SES-SCh5-FB4-W10-4.0hr	4.00	6.94	689.26
ID4466	SES-SCh5-FB4-W10-6.0hr	6.00	6.95	530.87
ID4469/ID4470	SES-SCh5-FB4-W10-8.0hrA/B	8.00	6.94	405.52
ID4474	SES-SCh5-FB4-W10-10hr	10.03	6.91	289.24
ID4476	SES-SCh5-FB4-W10-15hr	14.64	6.75	190.93
ID4479	SES-SCh5-FB4-W10-24hr	24.00	20.77	65.01
ID4481	SES-SCh5-FB4-W10-28hr	28.01	21.12	48.13
ID4484/ID4485	SES-SCh5-FB4-W10-32hrA/B	32.00	20.93	36.66
ID4487	SES-SCh5-FB4-W10-49hr	48.33	43.45	12.03
ID4491	SES-SCh5-FB4-W10-72hr	72.36	43.49	9.69
ID4493	SES-SCh5-FB4-W10-99hr	99.28	64.20	6.25
ID4501/ID4500	SES-SCh5-FB4-W10-172hrA/B	171.52	73.60	4.23

Table C14. Small-scale chamber raw data for Batch 3 — film B3FA3.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air ($\mu g/m^3$)
ID4117/ID4121	SES-SCH6-PF-2.5hrA/B	2.50	104.19	147.49
ID4160	SES-SCh6-PF-48hr	48.00	104.70	64.86
ID4168	SES-SCh6-PF-122hr	121.77	102.77	17.24
ID4184	SES-SCh6-PF-170hr	169.74	115.85	10.56
ID4186	SES-SCh6-PF-218hr	218.28	104.05	6.20
ID4195/ID4196	SES-SCH6-PF-264hrA/B	292.05	104.20	3.53
ID4240	SES-SCh6-PF-312hr	323.50	416.42	2.05
ID4268	SES-SCh6-PF-516hr	516.03	448.81	1.87
ID4318	SES-SCh6-PF-683hr	682.60	471.57	1.27
ID4353/ID4354	SES-SCH6-PF-855hrA/B	855.42	578.27	1.27
ID4413	SES-SCh6-PF-1046hr	1045.90	538.23	1.12
ID4431	SES-SCh6-PF-1212hr	1211.53	508.25	1.11
ID4435	SES-SCh6-PF-1334hr	1334.04	518.28	1.60
ID4440	SES-SCh6-PF-1553hr	1552.97	499.62	1.36
ID4488/ID4489	SES-SCH6-PF-1693hrA/B	1692.69	508.67	1.11

Table C15. Small-scale chamber raw data for Batch 3 — film B3FA2.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air ($\mu g/m^3$)
ID4614	SES-SCH1-FA2-071612-0%RH-0.10hr	0.10	3.47	266.76
ID4615	SES-SCH1-FA2-071612-0%RH-0.25hr	0.30	3.48	454.80
ID4616/ID4617	SES-SCH1-FA2-0%RH-0.50hrA/B	0.50	3.48	592.42
ID4618	SES-SCH1-FA2-071612-0%RH-0.75hr	0.70	3.47	638.81
ID4619	SES-SCH1-FA2-071612-0%RH-1.0hr	1.00	3.47	749.78
ID4620/ID4621	SES-SCH1-FA2-0%RH-2.0hrA/B	2.00	6.95	803.93
ID4624	SES-SCH1-FA2-071612-0%RH-4.0hr	4.00	6.93	701.81
ID4625	SES-SCH1-FA2-071612-0%RH-6.0hr	6.01	7.33	526.20
ID4627/ID4628	SES-SCH1-FA2-0%RH-8.0hrA/B	8.00	6.95	416.21
ID4629	SES-SCH1-FA2-071612-0%RH-10hr	10.00	6.94	333.35
ID4630	SES-SCH1-FA2-071612-0%RH-14hr	14.47	6.84	215.23
ID4632	SES-SCH1-FA2-071612-0%RH-24hr	24.37	41.76	89.46
ID4634/ID4635	SES-SCH1-FA2-0%RH-28hrA/B	28.01	21.12	71.06
ID4636	SES-SCH1-FA2-071612-0%RH-32hr	32.00	20.76	54.02
ID4637	SES-SCH1-FA2-071612-0%RH-48hr	48.47	45.78	21.57
ID4639	SES-SCH1-FA2-071612-0%RH-78hr	77.83	71.56	9.37
ID4642/ID4643	SES-SCH1-FA2-0%RH-122hr A/B	121.50	62.57	5.54
ID4646	SES-SCH1-FA2-071612-0%RH-145hr	145.28	63.39	5.28

Table C16. Small-scale chamber raw data for Batch 3 — film B3FC1.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air ($\mu g/m^3$)
ID4545	SES-SCH1-FC1-071612-70%RH-0.10hr	0.10	3.46	479.00
ID4547	SES-SCH1-FC1-071612-70%RH-0.25hr	0.30	3.48	620.44
ID4549/ID4550	SES-SCH1-FC1-071612-70%RH-0.50hrA/B	0.50	3.48	675.37
ID4453	SES-SCH1-FC1-071612-70%RH-0.75hr	0.70	3.47	683.92
ID4555	SES-SCH1-FC1-071612-70%RH-1.0hr	1.00	3.47	698.49
ID4557/ID4558	SES-SCH1-FC1-071612-70%RH-2.0hrA/B	2.00	6.93	654.22
ID4561	SES-SCH1-FC1-071612-70%RH-4.0hr	4.00	6.93	502.65
ID4563	SES-SCH1-FC1-071612-70%RH-6.0hr	6.00	6.91	389.25
ID4565/ID4566	SES-SCH1-FC1-071612-70%RH-8.0hrA/B	8.00	6.99	334.05
ID4569	SES-SCH1-FC1-071612-70%RH-10hr	10.00	6.93	289.51
ID4571	SES-SCH1-FC1-071612-70%RH-14hr	14.17	6.92	231.78
ID4574	SES-SCH1-FC1-071612-70%RH-24hr	24.00	20.76	143.21
ID4576/ID4577	SES-SCH1-FC1-071612-70%RH-28hrA/B	28.00	20.80	120.73
ID4580	SES-SCH1-FC1-071612-70%RH-32hr	32.00	20.78	102.69
ID4582	SES-SCH1-FC1-071612-70%RH-48hr	48.02	41.60	51.94
ID4586	SES-SCH1-FC1-071612-70%RH-72hr	71.83	41.52	19.45
ID4590/ID4591	SES-SCH1-FC1-071612-70%RH-96hr A/B	96.00	62.40	9.66
ID4593	SES-SCH1-FC1-071612-70%RH-145hr	144.99	63.20	5.51

Table C17. Small-scale chamber raw data for Batch 3 — film B3FC2.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m³)
ID4546	SES-SCH5-FC2-071612-50%RH-0.10hr	0.10	3.45	458.99
ID4548	SES-SCH5-FC2-071612-50%RH-0.25hr	0.30	3.47	604.71
ID4551/ID4552	SES-SCH5-FC2-071612-50%RH-0.50hrA/B	0.50	3.47	648.17
ID4554	SES-SCH5-FC2-071612-50%RH-0.75hr	0.70	3.47	746.50
ID4556	SES-SCH5-FC2-071612-50%RH-1.0hr	1.00	3.47	714.31
ID4559/ID4560	SES-SCH5-FC2-071612-50%RH-2.0hrA/B	2.00	6.93	672.03
ID4562	SES-SCH5-FC2-071612-50%RH-4.0hr	4.00	6.92	539.61
ID4564	SES-SCH5-FC2-071612-50%RH-6.0hr	6.00	6.91	403.13
ID4567/ID4568	SES-SCH5-FC2-071612-50%RH-8.0hrA/B	8.00	6.95	360.90
ID4570	SES-SCH5-FC2-071612-50%RH-10hr	10.00	6.92	313.83
ID4572	SES-SCH5-FC2-071612-50%RH-14hr	14.17	6.90	254.97
ID4575	SES-SCH5-FC2-071612-50%RH-24hr	24.00	20.76	145.33
ID4578/ID4579	SES-SCH5-FC2-071612-50%RH-28hrA/B	28.00	20.80	119.98
ID4581	SES-SCH5-FC2-071612-50%RH-32hr	32.00	20.71	97.75
ID4583	SES-SCH5-FC2-071612-50%RH-48hr	48.02	41.44	44.83
ID4587	SES-SCH5-FC2-071612-50%RH-72hr	71.83	41.57	16.43
ID4588/ID4589	SES-SCH5-FC2-071612-50%RH-96hr A/B	96.25	62.45	8.03
ID4594	SES-SCH5-FC2-071612-50%RH-145hr	145.03	64.82	3.53

Table C18. Small-scale chamber raw data for Batch 3 — film B3FA1.

Tube ID	Description	Elapsed time (h)	Sample volume (L)	Formaldehyde in air (μg/m³)
ID4597	SES-SCH6-FA1-071612-50%RH-0.10hr	0.10	3.51	324.08
ID4599	SES-SCH6-FA1-071612-50%RH-0.25hr	0.30	3.50	443.45
ID4600/ID4601	SES-SCH6-FA1-50%RH-0.50hrA/B	0.50	3.49	542.31
ID4603	SES-SCH6-FA1-071612-50%RH-0.75hr	0.70	3.49	630.45
ID4602	SES-SCH6-FA1-071612-50%RH-1.0hr	1.00	3.66	629.62
ID4604/ID4605	SES-SCH6-FA1-50%RH-2.0hrA/B	2.00	6.95	633.46
ID4606	SES-SCH6-FA1-071612-50%RH-4.0hr	4.03	8.34	489.47
ID4607	SES-SCH6-FA1-071612-50%RH-6.0hr	6.03	7.02	410.94
ID4608/ID4609	SES-SCH6-FA1-50%RH-8.0hrA/B	8.00	6.95	334.09
ID4610	SES-SCH6-FA1-071612-50%RH-10hr	10.00	6.96	289.22
ID4611	SES-SCH6-FA1-071612-50%RH-14hr	14.37	6.80	221.01
ID4613	SES-SCH6-FA1-071612-50%RH-24hr	24.07	22.39	134.69
ID4622/ID4623	SES-SCH6-FA1-50%RH-28hrA/B	28.00	20.86	110.84
ID4626	SES-SCH6-FA1-071612-50%RH-32hr	32.00	20.85	94.18
ID4633	SES-SCH6-FA1-071612-50%RH-48hr	47.92	20.85	49.23
ID4638	SES-SCH6-FA1-071612-50%RH-73hr	72.52	45.92	14.73
ID4640/ID4641	SES-SCH6-FA1-50%RH-102hrA/B	101.88	71.71	5.95
ID4644	SES-SCH6-FA1-071612-50%RH-146hr	145.55	62.30	4.67

Table C19. Small-scale chamber raw data for Lab A.

Elapsed time (h)	Formaldehyde in air (µg/m^3)	Formaldehyde in air (µg/m^3)	Formaldehyde in air (µg/m^3)	Formaldehyde in air (µg/m^3)	Formaldehyde in air (µg/m^3)
	B3FB1	B3FB2	B3FB3	B3FB4	B3FB5
0	12.0	12.2	14.0	13.1	12.7
0.25	355.3	429.3	422.0	492.7	424.0
0.5	278.0	605.9	312.3	472.7	548.3
1	209.2	419.4	222.7	377.7	497.3
2	178.9	330.6	210.3	332.7	370.0
3			194.3	267.3	315.3
4	152.4	254.5	151.7	234.3	275.7
6	120.8	212.0	139.0	208.0	242.0
8	151.2	192.4			
24	65.5	84.1	64.4	79.5	97.8
28	43.2	64.1	56.2	71.8	83.9
48	27.6	33.9	26.7	34.3	38.3
72	22.3	21.6	20.0	21.3	22.7
144	14.0	13.9			

APPENDIX D: FORMALDEHYDE MASS BALANCE ANALYSIS

To evaluate the soundness of the overall approach to predicting and measuring formaldehyde emissions from the PC films, a mass balance analysis was performed by comparing the actual monomer formaldehyde to the model predicted monomer formaldehyde emitted during the first 144 hours of each chamber test. Table D1 shows the monomer formaldehyde loaded into each film as measured using the microbalance.

Total formaldehyde in the films as measured using the microbalance

Table D1. Total formaldehyde in the film as measured using the microbalance.

Test ID	Formaldehyde mass (μg)
VT 10	480
VT 11	410
VT 12 (10 cm × 10 cm)	430
VT 12 (8.5 cm × 8.5 cm)	310

Total formaldehyde in the films according to experimental data

Table D2. Formaldehyde mass-balance calculation using chamber test data.

Film ID	Total formaldehyde mass in the film (μg)	Emitted formaldehyde mass in small chamber tests (μg)	Recovery
B1F1	480	360	75%
B1F2	480	360	75%
B1F3	480	310	65%
B2FA1	410	570	140%
B2FA2	410	580	140%
B2FA4	410	510	120%
B2FA5	410	530	130%
B2FA6	410	520	130%
B2FA7	410	520	130%
B2FB1	410	500	120%
B2FB2	410	440	110%
B2FB3	410	520	130%
B2FB4	410	530	130%
B3FA1	430	580	130%
B3FA2	430	570	130%
B3FB2	310	340	110%
B3FB4	310	290	94%
B3FB5	310	330	110%
B3FC1	430	610	140%
B3FC2	430	620	140%

APPENDIX E: MATLAB PROGRAMS OF MODELS

Sorption/desorption model program

```
close all;
clear all;
T=3600*24*20;
time_step=300;
n=0;
L=0.0254*0.01;
D=2.1*10^-13;
N=T/time_step+1;
ratio=zeros(N,1);
for time=0:time_step:T
    n=n+1
    i=0;
    sum=0;
    step_step=8/((2*i+1)^2*3.141592654^2)*exp(-
1*D*(2*i+1)^2*3.141592654^2*time/L^2);
    sum=sum+step_step;
    while (abs(step_step)/sum>0.00001)
        i=i+1;
        step_step=8/((2*i+1)^2*3.141592654^2)*exp(-
1*D*(2*i+1)^2*3.141592654^2*time/L^2);
        sum=sum+step_step;
    end
    ratio(n,1)=1-sum;
end

for i=1:1:(T/time_step+1)
   xaxis(i)=300*(i-1);
end

induceddata=load('checkeddata.csv');
plot(induceddata(:,1),induceddata(:,4), 'r', xaxis,ratio, 'b')
```

Emission model program

```
clear all;
Q=0.001/60;
V=0.0209;
```

```
L=0.0254/100/2;
A=8.5/100*8.5/100*2;
D=1.9*10^(-13);
K=233;
Cinitial=1.628E+08;
h=Q/A/D/K;
k=V/A/K;
x=L;
T=24*3600*6;
time_step=360;
time_index=0;

for t=0:time_step:T
time_index=time_index+1
i=1;
sum=0;
root(i)=qiuun(h,k,L,i);
term_for_sum(i)=exp(-D*root(i)*root(i)*t)*(h-
k*root(i)*root(i))*cos(root(i)*x)/(L*(h-k*root(i)*root(i))*(h-
k*root(i)*root(i))+root(i)*root(i)*(L+k)+h)/cos(root(i)*L);
sum=sum+term_for_sum(i);
while (abs(term_for_sum)/sum>0.0001)
   i=i+1;
   root(i)=qiuun(h,k,L,i);
    term_for_sum(i)=exp(-D*root(i)*root(i)*t)*(h-
k*root(i)*root(i))*cos(root(i)*x)/(L*(h-k*root(i)*root(i))*(h-
k*root(i)*root(i))+root(i)*root(i)*(L+k)+h)/cos(root(i)*L);
    sum=sum+term_for_sum(i);
end
y(time_index)=2*Cinitial*sum/K;
clear sum;
clear term_for_sum;
clear root;
end
```

qiuun
```
function root=qiuun(h,k,L,m)
if m==1
    LB=0.5*pi/(2*L);
    UB=1*pi/(2*L);
else
```

```
    LB=(2*m-3)*pi/(2*L);
    UB=(2*m-1)*pi/(2*L);
end


root=LB;
DX=UB-LB;
error=1;
while (abs(error)>0.000000001)&&(abs(DX)>0.000000000000001)
    DX=DX/2;
    QN=root+DX;
    error=tan(QN*L)-(h/QN)+(k*QN);
    if error<0
        root=QN;
    end
end
```

Uncertainty of emission model program

```
clear all;
L=0.0254/100/2;
A=8.5/100*8.5/100*2;
Q=0.001/60;
V=0.0209;


Cinitial_mean=1.701E+08;
D_mean=1.9*10^(-13);
K_mean=233;
Cinitial_sd=1.916068973E+07;
D_sd=0.3*10^(-13);
K_sd=40;


Time=3600*24*6;
tt=360;


for i=1:1:10000
    Cinitial(i)=0;
    D(i)=0;
    K(i)=0;
    while ((Cinitial(i)<=0)|(D(i)<=0)|(K(i)<=0))
    Cinitial(i)=normrnd(Cinitial_mean, Cinitial_sd);
    D(i)=normrnd(D_mean, D_sd);
```

```
    K(i)=normrnd(K_mean, K_sd);
    end
    cci=Cinitial(i);
    dd=D(i);
    kk=K(i);
    i
    gas_conc(i,:)=steve(dd,kk, cci, L, A, Q, V,Time, tt);
end
```

steve
```
function y=steve(dd,kk, cci, L, A, Q, V,T, time_step)

h=Q/A/dd/kk;
k=V/A/kk;
x=L;


for t=0:time_step:T
i=1;
sum=0;
root(i)=qiuun(h,k,L,i);
term_for_sum(i)=exp(-dd*root(i)*root(i)*t)*(h-
k*root(i)*root(i))*cos(root(i)*x)/(L*(h-k*root(i)*root(i))*(h-
k*root(i)*root(i))+root(i)*root(i)*(L+k)+h)/cos(root(i)*L);
sum=sum+term_for_sum(i);
while (abs(term_for_sum)/sum>0.001)
   i=i+1;
   root(i)=qiuun(h,k,L,i);
    term_for_sum(i)=exp(-dd*root(i)*root(i)*t)*(h-
k*root(i)*root(i))*cos(root(i)*x)/(L*(h-k*root(i)*root(i))*(h-
k*root(i)*root(i))+root(i)*root(i)*(L+k)+h)/cos(root(i)*L);
    sum=sum+term_for_sum(i);
end
time_index=t/time_step+1;
y(time_index)=2*cci*sum/kk;
clear sum;
clear term_for_sum;
clear root;
end
```

APPENDIX F: VT QUALITY ASSURANCE PROJECT PLAN

Quality Assurance Project Plan

Developing a Reference Material for Formaldehyde Emissions Testing
(ver. 2)

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Date: August 30, 2011

TITLE AND APPROVAL PAGE

QAPP - Developing a Reference Material for Formaldehyde Emissions Testing (ver. 2)
Document Title

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Date
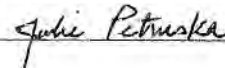
Project Manager: _____
Signature

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1.   PROJECT DESCRIPTION AND OBJECTIVES

1.1   Background

Wood and composite wood products usually emit formaldehyde (Meyer and Boehme, 1997) with emission rates that vary greatly and even unpredictably (Weigl et al., 2009). Formaldehyde is classified as a known carcinogen and various international guidelines and recommendations for formaldehyde in indoor air have been established (Salthammer et al., 2010) including new legislation recently passed by the US Congress and signed by the President. To demonstrate compliance with these regulations, manufacturers and independent laboratories conduct formaldehyde emissions testing in chambers with environmental conditions similar to a real building. Unfortunately, there are substantial uncertainties involved in chamber measurements, with published inter-laboratory studies for emissions of volatile organic compounds (VOCs) showing coefficients of variation between measured emission rates on the order of 50 % and as large as 300 % (Howard-Reed et al., 2007). For formaldehyde alone, standard emission testing methods vary substantially in different countries (Risholm-Sundman et al., 2007). Inter-laboratory studies can be expensive and time-consuming, and may lead to inconclusive results, especially since there is no way to identify which laboratory's results are correct. Therefore a well characterized reference material for formaldehyde emissions testing is a critical prerequisite for improving formaldehyde emissions measurement methods.
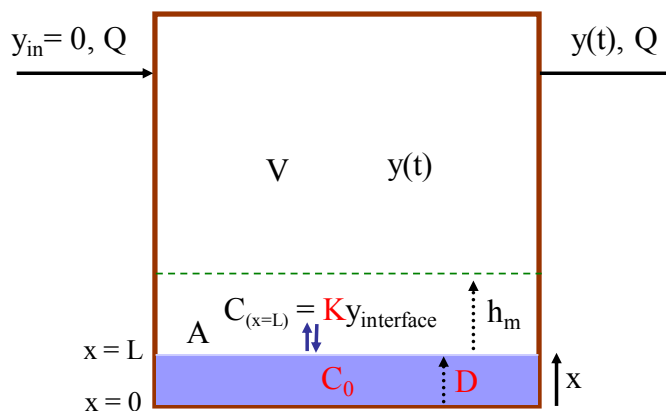
Figure 1. VOC source in test chamber showing mechanisms and parameters controlling the emission rate.

In collaboration with the National Institute of Standards and Technology (NIST), the PI has been developing reference materials for emissions testing of VOCs, whose emissions can be accurately predicted by a fundamental emission model. The project began with the development of a reference material for toluene (Cox et al., 2010; Howard-Reed et al., 2011), and is currently being extended to include n-butanol, a polar and more difficult VOC to handle experimentally. The emission model on which the reference materials are based is shown in Figure 1. The mechanisms of VOC emissions from the material include (1) internal diffusion within the material, characterized by material-phase diffusion coefficient, D (m^2/s), and initial material-phase concentration, C_0 (g/m^3); (2) partition at the material/air interface, characterized by partition coefficient between the material and air, K (dimensionless); and (3) convective mass transfer through the boundary layer near the material surface, characterized by convective mass-transfer coefficient, h_m (m/s). But

for diffusion controlled materials, external convective mass-transfer resistance is relatively small compared to that due to internal diffusion and therefore, the emission rate is largely controlled by internal diffusion and partition at the material/air interface while convective mass transfer through the boundary layer is negligible. To predict the emission rate and resulting gas-phase concentration profile in a well-mixed chamber, we simply need to measure the three parameters (C_0, D and K) and apply the emission model (Cox et al., 2002).

The development of the reference material for toluene has been described in detail by Cox et al. (2010) and Howard Reed et al. (2011), and involves the following basic steps: (1) polymethyl pentene (PMP) was selected as the polymer substrate; (2) thin-film samples of the PMP were loaded with toluene using small loading vessels held at a constant gas-phase toluene concentration (the toluene diffused into the polymer film until the material-phase toluene concentration in the polymer reached equilibrium with the gas-phase toluene concentration in the vessels); (3) the mass-transfer properties for toluene/PMP (the material-phase diffusion coefficient, D, the material/air partition coefficient, K, and the material-phase toluene concentration of the loaded samples, C_0) were measured gravimetrically using a recording microbalance; (4) a small well-mixed environmental chamber was used to measure gas-phase toluene emissions from the pre-loaded PMP films; (5) a fundamental emissions model was used together with the independently measured toluene/PMP parameters (C_0, K and D), the dimensions of the PMP film (thickness, L, and surface area, A) and the chamber operating configuration (air flow rate, Q, and chamber volume, V) to predict the toluene concentration profile; and, (6) the measured emissions profiles were compared to the predicted emissions profile.

The initial results for toluene and n-butanol are very promising and a similar procedure is proposed for the development of a reference material for formaldehyde. This will involve the following experimental steps: (1) create a constant gas-phase concentration using a diffusion vial containing paraformaldehyde (which depolymerizes into formaldehyde (Röck et al., 2010)) so that PMP films can be loaded with formaldehyde in a small loading vessel, (2) measure the formaldehyde/PMP parameters (C_0, K and D) using a microbalance, (3) test the reference material by placing the pre-loaded PMP samples into a small emissions chamber and comparing the measured formaldehyde concentration profile with that predicted by the model. The success of this method depends on two key criteria: (a) the formaldehyde needs to be sufficiently "soluble" in the PMP (a large enough K) so that C_0 is high enough for the formaldehyde emissions profile to be at the desired concentration; and (b) the diffusion of formaldehyde in the PMP needs to be ideal or "Fickian" in nature.

Although monomeric formaldehyde should be somewhat soluble in the PMP polymer matrix, more will dissolve into polar matrices such as nylon, polyacrylamide, polycarbonate (PC) and polyvinyl chloride (PVC), as reported by Hennebert (1988). While the –OH or –NH groups in nylon and polyacrylamide would react with the formaldehyde monomers by forming a –CH_2OH group, PC and PVC should not be reactive. If PMP does not absorb sufficient formaldehyde, PC and PVC represent viable alternatives, and the fact that it is not reactive, suggests that diffusion in PC and PVC

may be ideal (Hennebert, 1988). We will focus on PMP and PC in the development of the formaldehyde reference material. Because the presence of humidity creates the potential for formaldehyde to polymerize, we will initially use dry conditions in developing and deploying the reference material. We are optimistic that this will enable emissions to be predicted using our simple modeling approach, as proven for toluene in PMP. Although humidity does not appear to affect either the toluene/PMP or butanol/PMP systems, it may be that the presence of humidity will cause formaldehyde to behave in a non-ideal fashion, given that it tends to promote polymerization. We will therefore do a careful check of the influence of humidity on the performance of the formaldehyde reference materials (both PMP, which absorbs little water, and PC, which is expected to absorb a fair amount of water). It may be that we will have to change to a non-ideal diffusion mechanism to predict the emission rate of formaldehyde in the presence of water vapor. Either way, the emissions process should still be highly reproducible, which is the essential nature of a reference material.

1.2   Project objectives
The purpose of this project is to develop a reference material for formaldehyde using similar procedure to those we have developed for reference materials for toluene and n-butanol. Our specific research objectives are to:
   1) Develop a procedure to create a range of constant gas-phase concentrations of formaldehyde using solid paraformaldehyde (which depolymerizes into formaldehyde) in temperature controlled diffusion vials;
   2) Investigate the potential for two polymer materials (PMP and PC) to be used as reference materials for formaldehyde by measuring the diffusion coefficient (D) and partition coefficient (K) in a microbalance over a range of gas-phase concentrations;
   3) Determine the impact of humidity on the mass transfer of formaldehyde in PMP/PC using microbalance sorption/desorption tests;
   4) Develop the test protocol and test the overall performance of the reference materials. This will be performed in two steps: firstly, EPA and VT will establish a test protocol for the reference material and then PMP/formaldehyde and PC/formaldehyde will be tested by measuring formaldehyde emissions in small chambers at EPA and comparing the observed concentration profiles with model predicted values; and secondly, emission chamber tests will be conducted at both EPA and NIST to further evaluate the test protocol and the performance of the prototype reference materials.

2.   ORGANIZATION AND RESPONSIBILITIES
2.1   Personnel
Dr. John Little will serve as the principal investigator (PI) at Virginia Tech (VT) and is responsible for leading the work at VT, and submitting monthly reports documenting progress and the final project report. Dr. Julie Petruska, the Environmental Laboratory Supervisor for the Environmental Engineering Program at VT, will serve as the VT project QA Officer and ensure that the project is implemented according to the QAPP and that the data collected meet project objectives. Dr. Steven Cox, a Senior Research Associate at VT, will be responsible for laboratory infrastructure and will direct and

supervise the overall laboratory safety and the quality of the analytical and experimental data. Mr. Zhe Liu, a Graduate Research Assistant, will be responsible for the day-to-day activities including carrying out the experimental work, analyzing experimental data, developing models and preparing the draft report summarizing the results. Dr. Little will meet with Dr. Cox, Dr. Petruska and Mr. Liu weekly to review progress and discuss the results. In addition, Dr. Charles Frazier, Professor of Wood Science and Forest Projects and Director of the Virginia Tech Wood-Based Composites Center (a National Science Foundation Industry/University Cooperative Research Center), will serve as a consultant to this project, providing advice on polymer properties and formaldehyde chemistry, as well as acting as liaison with the representatives of the Wood-Based Composites Industry.

In addition to the project team at VT, a team at EPA will work with the VT team for object 4 to develop a test protocol for the reference material and test the PMP/formaldehyde and PC/formaldehyde in small emission chambers. The EPA team will be responsible for conducting emission tests, analyzing the emission testing data, and evaluating the test protocol. A team at NIST will be then involved to test the prototype reference materials and NIST team will report data to the EPA team for data analysis. During the project period working on objective 4, a conference call will be held weekly between the VT and EPA teams to discuss the test protocol, emissions testing plans, and testing results. The following project organizational chart illustrates the group hierarchy.
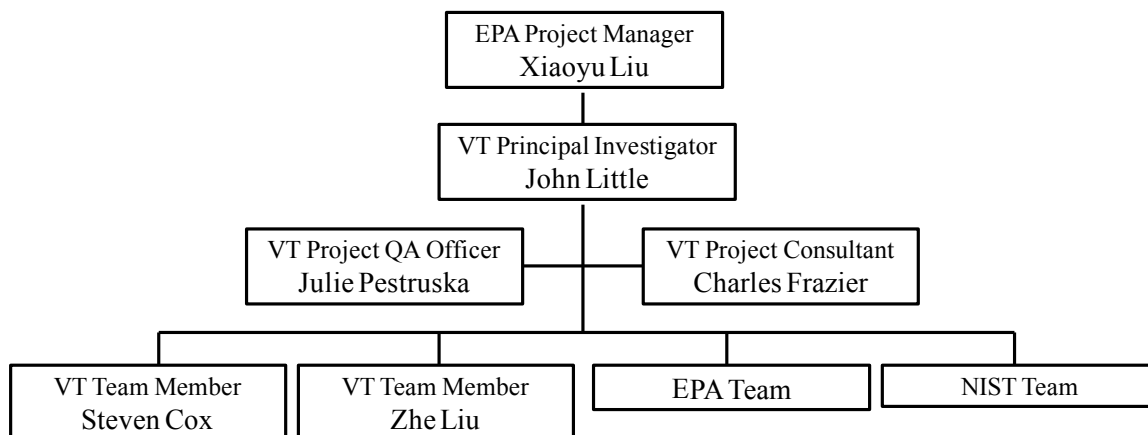
2.2 Project schedule

The following chart shows the project schedule in terms of the specific project objectives outlined in section 1.2. The project duration is from June 1, 2011 to February 15, 2012.

Tasks	Qtr 1	Qtr 2	Qtr 3
1	▓		
2	▓	▓	
3			▓
4			▓

Dr. Little (PI) and the VT team plan to visit EPA and NIST during the project period. It is also anticipated that representatives from EPA and NIST will visit VT during the project

to further familiarize themselves with the procedures being used at VT. Dr. Little will be responsible for submitting monthly reports documenting progress. Dr. Little will ensure completing the development of the formaldehyde reference material and submitting the preliminary results to the EPA Project Officer by January 15, 2012. A final project report that includes a data quality review will be submitted to the Project Officer by February 15, 2012.

3.   SCIENTIFIC APPROACH

3.1   Analyte of interest and matrices under study

To load either PMP or PC with formaldehyde, we will create a continuous gas stream with constant formaldehyde concentrations using a dynamic formaldehyde generation system (objective 1). The system consists of diffusion vials maintained at elevated temperatures with purge flow and dilution flow regulated by mass-flow controllers (accurate flow rate confirmed by bubble meters). Solid paraformaldehyde contained in the diffusion vials depolymerizes into monomeric formaldehyde and enters the purge gas (dry and clean air). The purge gas containing formaldehyde is then mixed with dilution air. The concentration of formaldehyde in the gas stream is adjusted by controlling the temperature of the diffusion vials and the flow rate of the dilution gas. The humidity of the gas stream will be adjusted by changing the humidity of the dilution air flow (e.g. 0% RH for D and K determination in objective 2 and infusing formaldehyde into PMP/PC in objective 4; 50% RH for objective 3). This gas stream will then pass through PMP and PC samples in loading vessels to infuse formaldehyde into the PMP and PC films. It will also enable us to conduct sorption/desorption tests using the microbalance system to determine D and K.

PMP and PC films will be purchased without any additives. Their purity will be checked by a dynamic microbalance. Before each test, dry and clean air will be passed through the microbalance on which the samples are suspended for at least 24 hours to check for volatile contaminants. All the samples will be obtained from a single roll/batch of material from the manufacturers to ensure they are identical and uniform.

3.2   Analytical approach

3.2.1   Measure formaldehyde gas stream

The gas-phase formaldehyde concentration from the dynamic formaldehyde generation system will be determined by three different approaches: gravimetric method, visible absorption spectrometry, and electrochemical sensor. Their principles and procedures are described below. Although the first two measurement methods are not continuous, the gravimetric method is expected to provide a quantifiable release rate from the diffusion vials while the spectrometry method can provide direct and accurate measurement of the formaldehyde concentration in the gas stream. The results of these two methods will be compared with each other and used to assess the performance of the dynamic formaldehyde generation system. The continuous monitoring data employing an electrochemical sensor will confirm the consistency of the concentration throughout the test periods.

Gravimetric method: The diffusion vials containing paraformaldehyde will be weighed by a high-resolution electronic balance over appropriate time intervals to determine the release rate of formaldehyde. The gas-phase formaldehyde concentration from the dynamic generation system can thus be calculated by dividing the release rate by the total flow rate of purge flow and dilution flow.

Visible absorption spectrometry: The formaldehyde concentration in the gas stream from the dynamic generation system will be measured directly by visible absorption spectrometry, following the NIOSH Analytical Method 3500. Briefly, an appropriate volume of gas stream will be pumped through two impingers in series containing 20 mL 1% sodium bisulfite solution so that gas-phase formaldehyde will be completely absorbed by the aqueous solution (the backup impinger will be used to check the collection efficiency); then 4-mL aliquots of impinger solution will be transferred to a flask and 0.1 mL 1% chromotropic acid and 6 mL concentrated sulfuric acid will be added to the sample solution; the sample solution will heated at 95°C for 15 min and then maintained at room temperature for 2 hours so that the chromophore can be fully developed; and finally the absorbance at 580 nm of the sample solution will be measured using a spectrophotometer. Meanwhile, at least six calibration standards with different known formaldehyde concentrations and a blank will be treated with the reagents and analyzed by the spectrophotometer for absorbance at 580 nm. Therefore, a calibration curve (absorbance versus formaldehyde concentration in the sample solution) can be constructed and the formaldehyde concentration in the tested solution sample can be obtained from the calibration curve. Finally, formaldehyde concentration in the gas stream can be derived using appropriate aliquot factor and gas sample volume.

Electrochemical sensor: The gas stream is continuously monitored using commercially available formaldehyde detection and measurement instrument based on electrochemical sensors (Formaldehyde Meter Z-300XP, Environmental Sensors Co., FL). The measured data of formaldehyde concentration in the gas stream will be recorded automatically.

3.2.2   Infuse formaldehyde and determine C_0

To infuse formaldehyde into PMP and PC samples, formaldehyde gas stream from the dynamic generation system will be passed into a stainless steel loading vessel, with several PMP or PC samples secured on stainless steel screen fixtures (Figure 2). Gas-phase formaldehyde in the gas stream will diffuse into the samples until sorption equilibrium is reached between the material phase and the gas phase. To determine the material-phase concentration of the samples, a microbalance is connected downstream with effluent from the loading vessel passing across an additional PMP or PC sample on the microbalance. Therefore, the material-phase concentration of formaldehyde at the end of the loading process (C_0) can be determined gravimetrically using the final mass increase of the extra sample and then dividing by its volume. The loading vessels will be maintained at 23 ^{o}C to eliminate variations in C_0 caused by temperature.
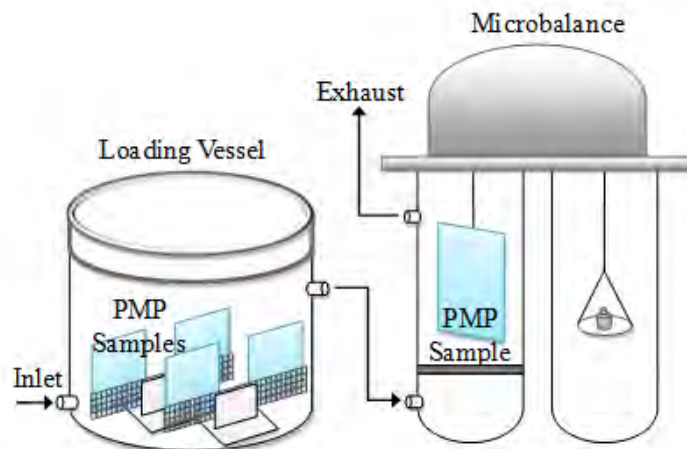
Figure 2. Infusing formaldehyde in loading vessels and measuring C_0
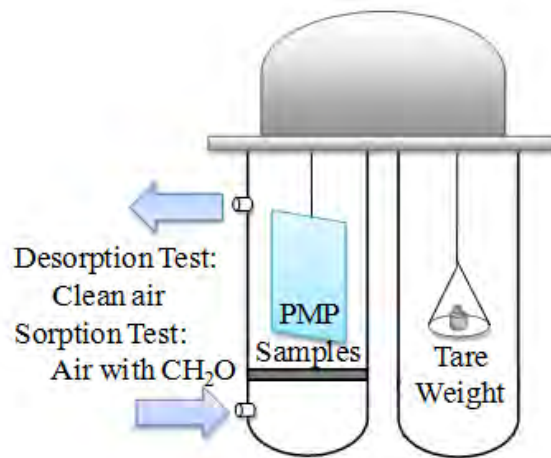
Figure 3. Microbalance sorption/desorption tests

3.2.3   Determine D and K

To determine D and K, a well-developed microbalance method will be employed (Cox et al., 2001a). As shown in Figure 3, a test sample (a PMP film here) is continuously measured gravimetrically by a microbalance. During the sorption test when the air stream containing formaldehyde (from the dynamic formaldehyde generation system) is passed across the clean sample, formaldehyde diffuses into the material and the gain in mass of the sample is recorded by the microbalance, generating a sorption curve. Once the sample has reached equilibrium with formaldehyde in the gas stream, then clean air is passed through the sample for the desorption test and a desorption curve is generated by measuring the mass loss from the sample over time. The sorption/desorption tests will be performed under at least three different formaldehyde concentrations.
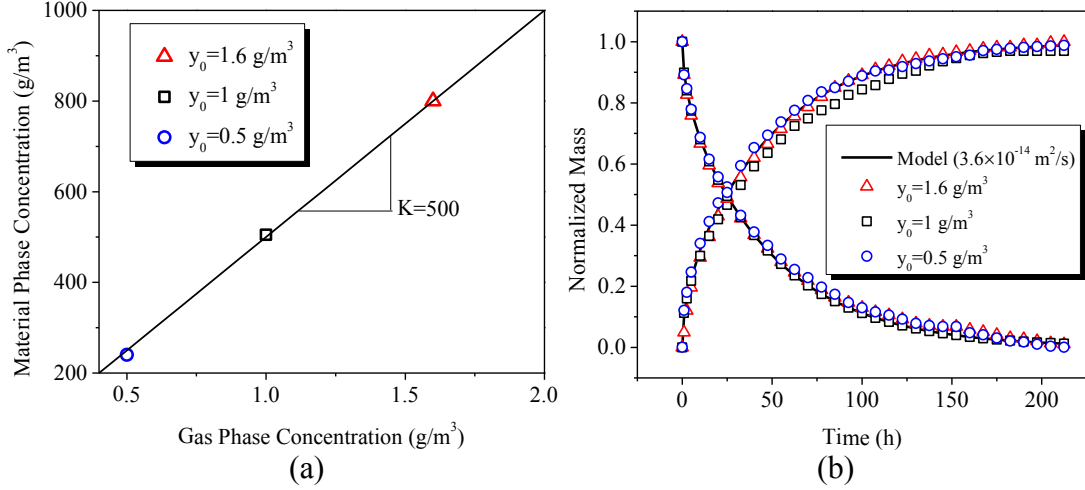
Figure 4. Determining K and D using microbalance data (toluene). (a) linear regression of material-phase concentration and gas-phase concentration in equilibrium to determine K (b) diffusion model fitted to sorption/desorption data to determine D

As shown in Figure 4(a) for toluene, a linear correlation can be constructed for the gas-phase formaldehyde concentration in the gas stream and the material-phase concentration in equilibrium, and the slope of the linear regression line is K. D will be determined by fitting a Fickian diffusion model to the sorption and desorption data. Under the experimental conditions, the mass change caused by Fickian diffusion of formaldehyde into the film is given by (Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right\} \tag{1}$$

where M_t (mg) is the total formaldehyde mass that has entered or left the film in time t (s), M_∞ (mg) is the formaldehyde mass in the film when air-phase/material-phase partition equilibrium is reached, and $2L$ (m) is the film thickness. Figure 4(b) shows the example of fitting the Fickian diffusion model to the normalized sorption/desorption data of toluene to obtain D.

All the sorption/desorption tests will be carried out at 23 °C to eliminate temperature dependence of D and K. The sorption/desorption tests will be carried out first at 0% RH for determining D and K under dry condition (objective 2), and then at 50% RH to evaluate the impacts of humidity on mass transfer (objective 3).

3.3   Modeling approach

The fundamental model describing VOC emissions from a homogeneous, diffusion-controlled source is briefly reviewed. Figure 1 shows the mechanisms governing emissions of VOCs from a material source in a test chamber. If we assume that the external convective mass-transfer rate is fast, the chamber wall sink-effect is negligible, and that the initial material-phase VOC concentration is uniform with depth (C_0) then we can develop a fundamental emission model to predict the chamber concentration. The transient diffusion equation in the material slab is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

where C (mg/m^3) is the material-phase concentration of a VOC, D (m^2/s) is the material-phase diffusion coefficient, t (s) is time, and x (m) is distance from the base of the slab. The initial condition assumes a uniform material-phase concentration of the VOC in the slab, C_0 (mg/m^3). The first boundary condition assumes there is no flux from the base of the slab. The second boundary condition is imposed via a mass balance on the VOC in the chamber air, or

$$\frac{\partial y}{\partial t} \cdot V = Q \cdot y_{in} - D \cdot \left. \frac{\partial C}{\partial x} \right|_{x=L} - Q \cdot y \qquad (3)$$

where y_{in} (μg/m^3) and y (μg/m^3) are the concentrations of the VOC in the influent and chamber air respectively, Q (m^3/s) is the volumetric air flow rate, V (m^3) is the well-mixed chamber volume, A (m^2) is the exposed surface area of the slab, and L (m) is the thickness of the slab. A linear and instantaneously reversible equilibrium relationship is assumed to exist between the slab surface and the chamber air, or

$$K = \frac{C|_{x=L}}{y} \qquad (4)$$

where K (dimensionless) is a material/air partition coefficient with units of mass per volume/mass per volume. The instantaneously reversible assumption implies that resistance to mass transfer between the material surface and the bulk chamber air is negligible, which has been shown to be the case for the PMP/toluene system (Cox et al., 2010). Assuming y_{in} is zero and D and K are independent of concentration, an analytical solution to these equations was given by Little et al. (1994):

$$C(x,t) = 2C_0 \sum_{n=1}^{\infty} \left\{ \frac{\exp(-Dq_n^2 t)(h - kq_n^2)\cos(q_n x)}{[L(h - kq_n^2)^2 + q_n^2(L + k) + h]\cos(q_n L)} \right\} \qquad (5)$$

where

$$h = \frac{Q}{ADK} \qquad (6)$$

$$k = \frac{V}{AK} \qquad (7)$$

and the q_n are the roots of

$$q_n \tan(q_n L) = h - kq_n^2 \qquad (8)$$

When material-phase concentration over time is given by equation (5), gas concentration is the chamber can be simply obtained by equation (4). This model has proven to be effective for predicting emissions of VOCs from vinyl flooring (Cox et al., 2002). The three key model parameters (C_0, K, and D) were measured completely independently of the chamber experiments (Cox et al., 2001a; Cox et al., 2001b).

3.4   Method performance metrics
3.4.1   Measure formaldehyde gas stream
As described in section 3.2.1, a continuous gas stream with constant formaldehyde concentration will be generated from a dynamic generation system. Three different approaches, including gravimetric method, visible absorption spectrometry, and

electrochemical sensor, will be used to determine the formaldehyde concentration and evaluate the performance of the dynamic generation system.

The gravimetric method will be performed over appropriate time intervals to determine the release rate of formaldehyde from each diffusion vial in the dynamic generation system. A high-resolution electronic balance (±10 µg) will be used for the gravimetric method. The electronic balance will be externally calibrated every day and maintained according to its manual. Briefly, the calibration procedure includes setting the zero and establishing the full capacity weight for the balance using certified calibration weights provided by the manufacturer of the balance. For each generation period during which gas stream with a constant formaldehyde concentration is generated continuously, the diffusion vial will be weighed at least five times, e.g. one measurement at the beginning and one at the end, and three during the period. Since the weight decrease rate is exactly the formaldehyde release rate from the diffusion vial, the linearity between the measured weight and time will be examined to evaluate whether the release rate is constant during the period. The average release rate (slope of the linear regression line for weight versus time) will be used to calculate the average formaldehyde concentration during the period.

The spectrometry method will be used to measure the formaldehyde concentration of the gas stream directly. It will be carried out at least five times during each generation period, e.g. one measurement at the beginning and one at the end, and three during the period. The visible absorption spectrometry standard method (NIOSH Analytical Method 3500) will be followed strictly and quality control procedures will be performed. For example, dual impingers will be used in series to absorb gas-phase formaldehyde to ensure efficient collection of formaldehyde; and at least six working standards and blanks will be tested by the spectrophotometer every time to construct the calibration line. Since the purge gas and dilution gas is clean air, there will be no oxidizable organic compounds other than formaldehyde in the gas stream and therefore no interferences for the spectrometry measurement.

The gas stream will also be continuously monitored using a commercially available formaldehyde detection and measurement instrument based on electrochemical sensors (Formaldehyde Meter Z-300XP, Environmental Sensors Co., FL). The instrument will be maintained according to its manual and sent to the manufacturer for calibration using standard calibration gas routinely (every few months).

3.4.2 Infuse formaldehyde and determine C_0

As shown in Figure 2, PMP and PC samples will be loaded with formaldehyde in stainless steel loading vessels and the mass change of a representative sample during the loading process will be continuously monitored by a high-resolution microbalance (±0.1 µg). The mass of the representative sample will be measured and recorded every 5 minutes throughout the loading process. Although gas streams with different formaldehyde concentration can be generated from the dynamic generation system, a high concentration gas stream is preferred for loading to achieve greater mass gain of the samples and higher material-phase concentration of formaldehyde (C_0). Greater mass gain can be more accurately measured by the microbalance (with high signal-to-noise

ratio) and higher C_0 leads to higher emission rates of the reference materials, facilitating the measurement of formaldehyde in the emission tests. For the same reasons and better control on the loading process, loading will last until partition equilibrium has been reached between the materials and loading gas stream, i.e., after the mass measured by the microbalance becomes stable.

3.4.3   Determine D and K

As described in section 3.2.3, microbalance sorption/desorption tests will be carried out to determine D and K for PMP and PC. The mass of samples will be measured and recorded every 5 minutes during the tests. As for the toluene case shown in Figure 4, sorption/desorption tests will be performed under at least three different concentration levels and the sorption/desorption cycle will be repeated three times as replicates under each concentration level. As shown in Figure 4(a), the linearity between gas-phase formaldehyde concentration and corresponding material-phase concentration in equilibrium will be examined statistically to test the assumption that the simple linear sorption isotherm (equation 4) is applicable for PMP/formaldehyde and PC/formaldehyde system and that K is constant within the tested concentration range. From the linear regression, the uncertainty of K will also be evaluated. As Figure 4(b) shows, the Fickian diffusion model will be fitted to the sorption/desorption data under different concentration levels. The assumption that D is constant over the tested concentration range will be examined statistically. Uncertainty of D will also be estimated from the model fitting.

3.4.4   Ship and store the reference materials

The validity and performance of the formaldehyde reference materials can only be tested in very rigorous emission chamber tests. For this purpose, loaded PMP/PC samples infused with known amounts of formaldehyde will be sent to EPA and later to NIST for emission chamber tests. To prevent or minimize the potential loss of formaldehyde during the shipping and handling procedures, three packaging approaches will be tried and tested: sealed aluminum zip bags, a cryogenic package, and an equilibrium container.

Sealed aluminum zip bag: Each loaded PMP/PC sample will be removed rapidly from the loading vessels and placed in a small sealed aluminum zip bag. Air will be evacuated from the bag before sealing the bag to minimize the headspace inside. The package will be delivered by express mail to EPA and NIST and then stored at room temperature prior to the emission tests.

Cryogenic package: The aluminum zip bags containing PMP/PC samples will be put into coolers with dry ice and then shipped to EPA and NIST. When received, samples in zip bags will be stored in freezers at -20°C until the emission tests. Low temperature during the shipping and storage period will reduce D and increase K of formaldehyde significantly and this reduces the volatile loss of formaldehyde from the samples. However, low temperature may also change the properties of the PMP/PC matrices and promote polymerization of formaldehyde.

Equilibrium container: Each PMP/PC sample will be placed in a sealed aluminum case which is filled with air containing formaldehyde (from the dynamic generation system) and kept at ambient temperature during the shipping. When received, the sample will be retained in the original package and maintained for a period at 23 $^{\circ}$C. Because the material-phase concentration of the sample is always at equilibrium with the gas-phase as in the loading vessel, it should remain in its original condition when taken out for the emission tests. The equilibrium container also eliminates cryogenic conditions.

3.4.5   Compare chamber tests and model predictions
A detailed test protocol for reference material will be developed by EPA and VT. The PMP/formaldehyde and PC/formaldehyde will be tested by EPA in small emission chambers following the test protocol. After the test protocol is developed by EPA and VT, the reference materials will also send to NIST for testing and comparison. At least three batches of PMP and three batches of PC will be produced by VT team with six identical samples in a single batch (three for NIST and three for EPA with different packaging approaches). PMP/PC samples will be tested in small-scale chambers for emissions at NIST and EPA. Emission tests will be carried out following standard test method for formaldehyde emissions from wood products (ASTM D 6007-02, 2008) and the test protocol developed by EPA and VT. Chamber air samples will be collected at 0.5 h, 1 h, 2 h, 4 h, 8h, 24h, 32 h, 48h, 54 h, and 72 h in each test, with a minimum of 3 duplicate air samples. Other procedures and chamber operating configurations, such as chamber volume, chamber airflow rate and mixing fan will not be specified to validate the reference material under various chamber configurations. The chamber test results will be analyzed by the EPA team to determine within-batch and between-batch variations, and evaluate the test protocol.

Model prediction will be performed for each chamber test, with parameters obtained from chamber tests (Q, V, and A) or microbalance data (D, K and C_0). Uncertainties associated with each model parameters will be taken into account in the prediction using the Monte Carlo Method (Cox et al., 2010). The chamber concentrations predicted by the model will be statistically compared (for example, using paired t-test) to the measured concentrations in corresponding chamber test to determine whether the model prediction matches the experimental results. Furthermore, the comparison between model predictions and chamber test results will help to diagnose problems and uncertainties in the development of the formaldehyde reference material.

4.   SAMPLING PROCEDURES
4.1   Requirements for samples
Samples in this project may involve various matrices in different processes, including: gas samples of formaldehyde from the dynamic generation system (throughout the entire project); PMP/PC samples for microbalance sorption/desorption tests (objectives 2 and 3); and PMP/PC samples loaded with formaldehyde for chamber tests (objective 4).

Gas samples of formaldehyde from the dynamic generation system: The gas samples are obtained from the continuous stream from the dynamic generation system and passed through impingers for determining the gas-phase concentration of formaldehyde in the

gas stream (see section 3.2.1, visible absorption spectrometry method for determining formaldehyde concentration). As described in section 3.4.1, at least five samples will be obtained during each generation period. The volume of each gas sample will be calculated by gas stream flow rate and collection time. The concentration of formaldehyde in the samples is expected to be relatively constant during a single generation period but will vary significantly in different generation periods (from 100 ppm to 1000 ppm level).

PMP/PC samples for microbalance sorption/desorption tests: PMP/PC samples will be obtained from a single roll/batch of PMP/PC purchased from manufacturers without any additives. For consistency, samples will have a uniform size (for example, 3.6 cm × 3.6 cm × 0.0254 cm of PMP will be used). Before being tested, each sample will be put on the microbalance and swept by clean air until its weight is stable (indicating no volatile contaminants remaining in it). During sorption/desorption tests, the mass change of each sample will be monitored by the microbalance.

PMP/PC samples loaded with formaldehyde for chamber tests: PMP/PC samples will be obtained from the same single roll/batch as those for sorption/desorption tests. The size of each sample can vary to accommodate specific requirements of the chamber tests. The formaldehyde concentration in the samples is proportional to the gas-phase concentration of formaldehyde in the gas stream for loading but a high concentration is preferred to facilitate the accurate determination of C_0 and the subsequent emission chamber tests.

4.2   Preparation of samples

As detailed in section 3.1 and 4.1, gas samples of formaldehyde are obtained and processed in the laboratory from the continuous gas stream and the dynamic generation system. As in section 4.1, PC/PMP samples are obtained from a single roll/batch of pristine materials purchased from the manufacturer and then prepared and processed in the laboratory (infused with formaldehyde). The loaded PC/PMP samples need to be sent to EPA and NIST for chamber tests according to the procedures described in section 3.4.4.

4.3   Sample preservation

As detailed in section 3.1 and 4.1, the continuous gas stream containing formaldehyde is generated from the dynamic generation system. It will be instantly measured for formaldehyde concentration (see section 3.2.1) or used (passed to loading vessels for infusing formaldehyde into PMP/PC or to microbalance for sorption/desorption tests). No preservation is required.

Loaded PMP/PC samples will be packed and sent to EPA and NIST once removed from the loading vessels. The shipping and storage requirements are described in section 3.4.4. In addition, samples will be tested in emission chambers as soon as possible after being received by EPA and NIST to minimize shelf-life and potential volatile loss of formaldehyde.

4.4   Sample numbering

Gas samples of formaldehyde from the dynamic generation system will be labeled according to specific generation information, sampling time, and sample volume. PMP/PC samples for microbalance sorption/desorption tests will be numbered according to specific testing information and time. Loaded PMP/PC samples will be labeled according to the loading information (time and gas-phase concentration of formaldehyde), positions in loading vessels, and shipping and storage procedures.

5.   MEASUREMENT PROCEDURES

Measurements involved in this project mainly include: gas-phase concentration of formaldehyde from the dynamic generation system (section 3.2.1); and weight of PMP/PC samples by microbalance for determining D, K and C_0 (sections 3.2.3 and 3.3.3). The sample preparation, calibration, measurement and quality control procedures for visible absorption spectrometry will be carried out following the NIOSH Analytical Method 3500. Other measurements require routine laboratory procedures and instruments (for example, bubble meters for gas flow rate, electronic balance for weight of diffusion vials, electrochemical sensors for direct formaldehyde measurement, and microbalance for PMP/PC mass), which are generally calibrated and operated according to product manuals.

6.   METHOD PERFORMANCE METRICS

Method performance metrics have been provided in section 3.4. The two most important steps involved in the reference material development are: determining whether constant formaldehyde concentrations can be generated from the dynamic generation system (section 3.4.1); and whether sorption/desorption of formaldehyde in PMP/PC is governed by Fickian diffusion (section 3.4.3). These are the two key challenges that we have to address in this project. Formaldehyde concentration generated from the dynamic generation system will be measured by three methods over a period of time and the concentration measurements by each method will be statistically tested to determine whether the concentration varies over time. For example, the linearity of the weight of diffusion vial will be checked by assessing the R^2 value of the linear regression, i.e., if R^2 is larger than 0.99, the release rate from the diffusion vial is regarded constant and the formaldehyde concentration can be calculated from the slope of the linear regression line. The direct measurement of formaldehyde concentration data will be compared to the value calculated from the release rate of the diffusion vial to determine whether they are statistically equal at significance level of 0.05 (t-test). If significant variation of concentration occurs or significant difference is found between results by two methods, the system will need modification and improvement until the requirement of constant concentration is met. The second challenge will be evaluated by fitting the Fickian diffusion model to the microbalance sorption/desorption data (as in Figure 4 for toluene). According to ASTM Standard D5157-97, a correlation coefficient (R) of 0.9 or greater generally indicates adequate model performance and it is therefore regarded that the sorption/desorption data can be described by Fickian diffusion principles. If the sorption/desorption data do not match the Fickian diffusion model statistically, implying that mass transfer of formaldehyde in PMP/PC does not follow Fickian diffusion, we will have to resort to other approaches or other polymer substrates.

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In validating the reference material using emission chamber tests, two criteria should be met. Firstly, the same reference material samples should generate the same emission profiles under identical chamber testing configurations (chamber concentration at a certain time should be the same across all the tests). This repeatability will be tested by comparing the measured chamber concentration of different runs using paired t-test. Secondly, the model should be able to predict the emission test results reasonable well. Paired t-test can be used to determine whether model predicted chamber concentration is equal to measured value but a maximum percent difference of 10% between the model predicted concentration and measured value is also acceptable.

7.   DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

7.1   Data reporting requirements

The primary parameters to be determined in this study include diffusion coefficient (D), the partition coefficient (K), and the initial material-phase concentration (C_0) for developed formaldehyde reference materials (with PMP and PC as substrate). The gas-phase concentration of formaldehyde under which PMP/PC substrate samples are loaded and microbalance sorption/desorption tests are performed will be also reported. SI units will be used throughout this project.

Data reduction procedures mainly involve determination of D, K and C_0. D and K will be determined from microbalance sorption/desorption data and detailed methods and equations have been provided in section 3.2.3. C_0 will be determined from the total mass gain measured by microbalance, which is then divided by sample volume (section 3.2.2).

7.2   Data validation

The gas-phase concentration of formaldehyde under which PMP/PC substrate samples are loaded and microbalance sorption/desorption tests are performed will be measured by three methods to ensure accuracy and reliability (section 3.2.1). D, K and C_0 will be used as model parameters to predict emission profiles of formaldehyde reference materials in emission chamber tests (section 3.3). The model predictions will be compared to emission chamber results to validate the values of D, K and C_0.

7.3   Data summarization

During the determination of D, K and C_0, associated uncertainties will be analyzed. Mean and standard error of D, K and C_0 will be reported.

7.4   Data storage

A dedicated laboratory notebook will be maintained for all the experimental effort. All the data will be transcribed to EXCEL spreadsheets each day that they are generated. The EXCEL files will be backed-up to electronic media on a weekly basis and also sent to Dr. Little for separate storage on a weekly basis.

8.   REPORTING

Monthly reports documenting progress will be submitted during the projection period. Detailed methodologies and preliminary results will be reported in a final report to EPA. Quality assurance results will be included as an appendix to the final report. During the

project period for objective 4, a conference call will be planned weekly to discuss shipping reference materials issues and chamber tests with the EPA team.

In addition to the final report to EPA, the methodologies and results will be summarized into one or two manuscripts for journal publication.

9.   REFERENCES

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APPENDIX G: EPA QUALITY ASSURANCE PROJECT PLAN

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Green Building Research: Indoor Source Emissions and Sink Effect Study of Formaldehyde

Quality Assurance Project Plan
Category III / Measurement Project
Revision: A4-1.1

QAPP Addendum 4: July 2012

Procedure for Evaluation of Reference Material for Formaldehyde Emissions Testing using Small Environmental Chambers

ARCADIS

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Document Revisions

Version	Author	Date	Description
1.0	EPA	7/21/2008	Initial release
1.1	EPA	10/27/2008	Revision:
			Editorial correction based on QA comments;
			Order of tests (Table 3-3, 3-7);
			Number of pieces of wallboard for sink tests (Section 3.1.4);
			Sampling location for large chamber baby crib tests (Section 3.3.2);
			Test schedule;
			Addition:
			Large chamber air velocity measurement (Appendix 1);
			FLEC measurement for baby crib tests (Section 3.3.2);
			High temperature chamber method to determine formaldehyde content in solid materials (Section 3.1.5);
			Dr. David Marr as a participant.
1.2	EPA	12/11/2009	Revision:
			Editorial correction based on Ronald Rogers' comments
			Section 3.3.1 deleted gypsum wallboard tests in the large chamber
			Section 3.3.3, changed baby furniture test condition to be conducted under different air exchange rate; reduced number of tests
A1-1.0	ARCADIS	8/31/2010	Addendum 1 Initial release: August 23, 2010
			EPA comments: September 21, 2010, QTRAK No. 08028, QA Category III "Document has EPA QA requirements that must be addressed before the QAPP can be approved."
			Response to comments: September 30, 2010
	ARCADIS	11/16/2010	Resubmitted: November 16, 2010
			EPA Comments: 11/30/2010, QLOG. A-00241/QTRAK 08028, QA Category III." The revised quality assurance project plan (QAPP)addendum is acceptable with minor revisions."
			Response to comments: December 27, 2010
			Resubmitted: December 30, 2010
A3-1.0	ARCADIS	7/29/2011	Initial release 1.0
			Addendum 3 "Measurement of Henry's Law Constants of Aqueous Formaldehyde Solutions using a Novel Headspace Extraction Method"
A2-1.0	ARCADIS	06/20/2011	Initial release: June 20, 2011 To Libby Nessley and Xiaoyu Liu
			Procedure for Air Resources Board (ARB) Interlaboratory
			Comparison of Composite Wood Product Third Party Certifiers
			Resubmitted: December 20, 2011

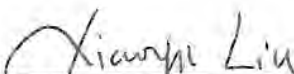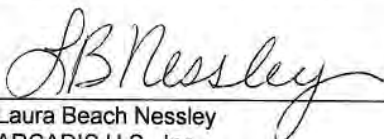|	ARCADIS	3/28/2012	Revision: Comments from QA - Liu, received July 15, 2011, QLOG No. A-00241 / QTRAK 08028, QA Category III. "acceptable with minor revisions". Changes made including changing to ARCADIS format and resubmitted to WAM 3/30/2012
	ARCADIS	2/30/2012	Added Appendix D: "Test Plan for Repeat of Secondary Test Method for iHWPW
A4-1.0	ARCADIS	4/4/2012	Initial release 1.0 April 4, 2012 Procedure for Evaluation of Reference Material for Formaldehyde Emissions Testing using Small Environmental Chambers
A4-1.1	ARCADIS	July 11, 2012	Response to EPA QA comments, QLOG No. A-00241 / QTRAK 08028, QA Category III (May 3, 2012), with the recommendation "acceptable with minor revisions" which allows data collection to start in parallel with the revision of the QAPP Addendum.

Distribution List

NRMRL	Xiaoyu Liu	(PI/WA Manager)
	Robert Wright	(QA Officer)
	Robert Thompson	(IEMB Chief)

Contractor Staff	Nancy Roache	(WA Leader)
	Corey Mocka	(Chemist)
	Robert Pope	(Chemist)
	Russell Logan	(Technician)
	Libby Nessley	(QA Officer)

List of Acronyms

ACH	Air changes per hour
C_0	Initial formaldehyde concentration
COC	Chain of Custody
CWP	Composite wood product
DAD	Diode array detector
DAS	Data acquisition system
DNPH	2,4-Dinitrophenylhydrazine
EPA	U.S. Environmental Protection Agency
FSCWA	Formaldehyde Standard for Composite Wood Products Act
HLPC	High-performance liquid chromatography
HTC	High temperature chamber
IARC	International Agency for Research on Cancer
IEMB	Indoor Environment Management Branch
µ-CTE	Markes Micro-Chamber / Thermal Extractor
NIST	National Institute for Standards and Technology
NRMRL	National Risk Management Research Laboratory
PI	Principal investigator
ppm	parts per million
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RH	Relative Humidity
RTP	Research Triangle Park
SOP	Standard operating procedure
TCSA	Toxic Substances Control Act
TPC	Third-party certifier
VT	Virginia Polytechnic Institute and State University
VOC	Volatile organic compound
WA	Work Assignment
WAL	Work Assignment Leader
WAM	Work Assignment Manager

Contents

1. Project Description and Objectives

The U.S. Environmental Protection Agency (EPA) has collaborated with Virginia Polytechnic Institute and State University (Virginia Tech, VT) to develop and test the emission characteristics of a polymer film being developed as a carrier for a formaldehyde reference material. This reference material will be used for improving the quantification of uncertainties associated with formaldehyde emission measurements in environmental chambers for the purpose of validation of source emission characteristics.

1.1 Background

Formaldehyde is produced on a large scale worldwide. One major use includes the production of wood-binding adhesives and resins. One of the major sources of exposure is inhalation of formaldehyde emitted from composite wood products (CWP) containing urea-formaldehyde resins. The International Agency for Research on Cancer (IARC) reclassified formaldehyde from "probably carcinogenic to humans" to "carcinogenic to humans" in 2004, based on the increased risk of nasopharyngeal cancer.

On July 7, 2010, President Obama signed the Formaldehyde Standard for Composite Wood Products Act (FSCWA) Senate Bill 1660 into law. [1] This Act amends the Toxic Substances Control Act (TSCA) as Title VI and requires EPA, by July 1, 2011, to promulgate regulations that ensure compliance with the standards. For industry to comply with the regulations, both internal and independent testing of formaldehyde emissions from the manufactured products must be conducted. The primary and secondary methods for evaluation of formaldehyde emissions involve the use of both large and small environmental chambers. This reference material would then be used to validate chamber testing methods including those used by third-party certifiers (TPCs) to confirm compliance of manufacturers of CWPs to these new regulations.

1.2 Project Objectives

The overall objective of this project is to collaborate with Virginia Tech researchers to test the emission characteristics of the polymer film that will be developed as a carrier for a formaldehyde reference material. Virginia Tech has developed the process for loading a known concentration of formaldehyde onto a polymer film. The final product needs to be tested and evaluated using small environmental chambers to determine its usefulness as a reference material for validating formaldehyde emissions in small chamber effluents. This Addendum outlines the responsibilities of ARCADIS for

conducting tests in the EPA small chamber laboratory to assess the performance of
the reference material film during environmental chamber testing. Details of the
preparation of the films are presented in the approved QAPP by Dr. John Little,
Developing a Reference Material for Formaldehyde Emissions Testing (ver. 2) [2],
Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA. All
of the materials to be tested on this project will be prepared and supplied to EPA by
Virginia Tech. All questions about the films and how they are prepared should be
addressed in the VT QAPP.

The resources of the small chamber include the 53-L small environmental chambers,
the Markes Micro-Chamber / Thermal Extractor (μ-CTE), the EPA high temperature
chamber (HTC), and a modified EPA Method 8315a for liquid extraction of
formaldehyde to evaluate the initial concentration (C_0) on the film, the effectiveness of
the packaging (shelf-life), and actual small environmental chamber emission rates from
the supplied reference materials. An interlaboratory comparison with at least one other
laboratory may also be conducted once the procedure has been established.

This addendum is a continuation of the approved October 2008 Quality Assurance
Project Plan (QAPP) "Green Building Research: Indoor Source Emissions and Sink
Effect Study of Formaldehyde" located in the following directory:
L:\Lab\NRML_Public\HCHO_2008\QA Documents\QAPP.

1.3 Facility Location and Description

The EPA Indoor Environment Management Branch (IEMB) small chamber laboratory is
located at the EPA Research Triangle Park (RTP), North Carolina campus in room
E378A. The proposed research will be conducted in this laboratory (E378A). The
sections below detail the chamber systems that are located in E378A, which will be
used for this project.

1.3.1 Small Environmental Chamber

The small environmental chamber system (Figure 1-1) consists of two large
temperature-controlled incubators, which house a total of eight 53-liter stainless steel
environmental chambers, a clean air system consisting of high pressure Volatile
Organic Compound (VOC) and oil-free compressed house air, an AADCO 737-11 Pure
Air generator, an OPTO 22 data acquisition system (DAS), and a Blue M temperature-
controlled water bath for controlled humidification. The support laboratory facilities are

located in rooms E383, E375A and E377A. These laboratories contain equipment such as a large drying oven, micro-balance, and deionized water system. The Agilent 1200 High Performance Liquid Chromatography (HPLC) with a Diode Array & Multiple Wavelength Detector (DAD) in room E383A will be used for the 2,4-Dinitrophenylhydrazine (DNPH - Silica Gel Cartridge (Waters Sep-Pak®) – Short Body, 55-105µm) extract analysis. The detailed description of the small chamber system is documented in the *Facility Manual for the Small Chamber Laboratory* (August 2003) (L:\Lab\NRML_Public\APPCD Facility Manuals\Small Chamber).

Figure 1-1. Small Chamber

1.3.2   Markes Micro-Chamber / Thermal Extractor

The µ-CTE system (Figures 1-2 and 1-3) consists of six micro-chambers that allow surface or bulk emissions to be tested simultaneously from up to six samples at the same temperature and flow rate. Each micro-chamber consists of an open-ended cylinder (cup) constructed of Silicosteel® (silicone-coated stainless steel) measuring 30-mm deep with a diameter of 45 mm and a volume of 44 mL. The system has temperature control that allows the tests to be conducted at ambient temperature or at elevated temperatures up to 120 °C. The chamber's flow distribution system maintains a constant flow of air through each sample chamber, independent of sorbent-tube impedance and whether or not a sorbent tube is attached. The flow rate is controlled by the source air pressure and the flow distribution device in the unit. For all of the evaluation tests, the high flow-rate option (50 mL/min to 500 mL/min) will be selected. According to the vendor, surface air velocities are roughly uniform across the surface of the sample, and these surface air velocities range from approximately 0.5 cm/s at an

inlet gas flow rate of 50 mL/min to approximately 5 cm/s at an inlet gas flow of 350 mL/min..

Figure 1-2. Markes Micro-Chamber / Thermal Extractor (μ-CTE)
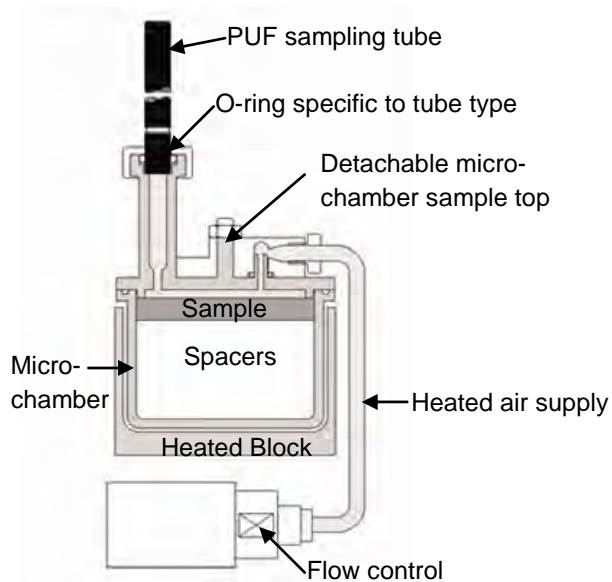
Figure 1-3. Diagram of a Single Micro-Chamber

1.3.3   EPA High Temperature Chamber

The high temperature chamber (HTC), also located in room E378A, is made of electro-polished stainless steel with the size of 17.8 cm (depth) by 2.5 cm (height) by 25.4 cm (width) (Figure 1-4). The HTC is designed to have well-distributed air flow and well-mixed exhaust across a test coupon and to provide heating up to 220 °C. The test coupon rests on the bottom of the chamber. A front drawer is held in place by two cam-activated clamps. The drawer is sealed to the chamber body by a Teflon-encased Viton O-ring. The entire unit is encased in an insulated aluminum case. A 122-cm long air heater is at the inlet to the chamber. The line heater heats the incoming air stream independently. Zero-percent relative humidity (RH) air is generated by the small chamber clean air generation system. A mass flow controller is used to regulate the air flow through the chamber. Relative humidity is monitored at the exhaust and recorded to the OPTO DAS. The temperature is set and maintained by the control panel of the apparatus at 60 °C for the liquid and film tests. The temperature of the effluent is monitored and recorded to the OPTO DAS. Figure 1-4 shows a picture of the HTC.
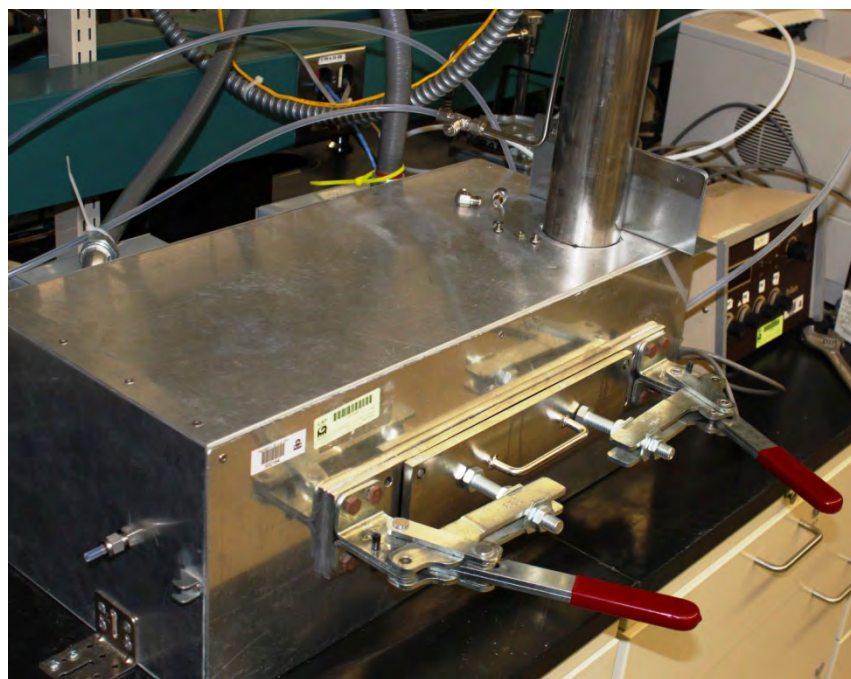
Figure 1-4. High Temperature Chamber

2. Project Organization

The organizational table for this project, presented in Table 2-1, tabulates the key points of contact for this project along with email and phone contact information. The roles and responsibilities of the project personnel are discussed in the following paragraphs. Virginia Tech is responsible for production and delivery of the formaldehyde reference material for these tests, therefore, the EPA PI for this project will be responsible for communication with Virginia Tech. The contact will be Dr. John Little (jcl@vt.edu), Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA.

Table 2-1. Key Points of Contact

Affiliation and Project Role	Contact	Phone Number	Email Address
EPA PI (This Task)	Xiaoyu Liu	541-2459	Liu.Xiaoyu@epa.gov
EPA QA Officer	Bob Wright	541-4502	Wright.Bob@epa.gov
ARCADIS QA Officer	Libby Nessley	328-5588	Libby.Nessley@arcadis-us.com
ARCADIS (WAL)	Nancy Roache	541-0365	Nancy.Roache@arcadis-us.com
ARCADIS Chemist	Corey Mocka	541-2862	Corey.Mocka@arcadis-us.com
ARCADIS Chemist	Robert Pope	541-2013	Robert.Pope@arcadis-us.com
ARCADIS Technician	Russell Logan	541-3810	Russell.Logan@arcadis-us.com

2.1 EPA Staff

Principal Investigator (PI), Dr. Xiaoyu Liu: Dr. Liu will serve as the PI and has the responsibility for developing the work plan, experimental design, data analysis, reporting, project management and communication with Virginia Tech.

QA Representative, Mr. Bob Wright: Mr. Wright will be responsible for review and approval of the QA project plan (QAPP) and other deliverables of this project and provide assistance on all QA-related issues.

2.2 In-house Contractor (ARCADIS) Staff

ARCADIS Work Assignment Leader (WAL), Nancy Roache: Ms. Roache is responsible for writing this addendum, setup and monitoring of all large and small chamber tests, the initial review of HPLC data for formaldehyde from samples collected from the small chamber and large chamber tests, preparing test materials, and collecting air samples

for both small chamber and large chamber tests. In addition, she is responsible for communicating any delays in scheduling or changes in cost to the EPA as soon as possible.

ARCADIS Chemist, Corey Mocka: Mr. Mocka is responsible for the operation and calibration of the HPLC analytical system for formaldehyde analysis. He will perform solvent extraction and derivatization of formaldehyde from DNPH cartridges, analyze sample extractions, and report data. Mr. Mocka will report directly to the WAL, Nancy Roache.

ARCADIS Chemist, Robert H Pope: Mr. Pope is responsible for setting up the small chamber system to monitor the formaldehyde emissions from formaldehyde sources, preparing test materials, and collecting air samples from the small chamber tests. He will prepare test notebooks for all small chamber tests. Mr. Pope will report directly to the WAL, Nancy Roache.

ARCADIS Technician, Russell Logan: Mr. Logan is responsible for staff support. Mr. Logan will report directly to the WAL, Nancy Roache.

ARCADIS Quality Assurance Officer (QAO), Laura Nessley: Ms. Nessley will review the QAPP and be responsible for ensuring that the contractor staff adheres to the procedures described therein.

3. Experimental Approach

The experimental design of this project consists of the following five tasks to be performed by ARCADIS:

1. Initial scouting small chamber testing of reference material – December 2011

2. Evaluation of three unique methods for the experimental determination of the initial HCHO concentration (C_0) on the film to validate the film loading concentration determined by VT.

3. Additional small chamber testing with emphasis on the evaluation of the integrity of the packaging and determination of shelf life of the reference material

4. Evaluation of formaldehyde emission rates from the reference material at varying values of RH.

5. Conduct an interlaboratory comparison with at least one other laboratory (possibly NIST).

The initial small chamber testing was performed in December with reference material supplied by Virginia Tech. These small chamber tests were performed at 23 °C, 1 air exchange rate (ACH). One test was conducted at 50% RH, and two tests were conducted at approximately 0% RH. The results of these test initiated the need to conduct follow-on testing of C_0, shelf life, and variations in RH.

3.1 Test Materials

The reference materials to be tested on this project have been developed and prepared by Virginia Tech. All of the materials to be tested on this project will be prepared and supplied to the EPA PI by Virginia Tech.

According to the EPA PI, the date and time the film is removed from the loading vessel is considered as time zero. Each film that is supplied to the EPA PI will be numbered with the loading date and time as well as the position in the loading vessel. Films from each loading batch are considered equal; however, the films from different loading batches may vary slightly. The initial films for the December tests were packaged for shipping wrapped individually in aluminum foil and placed in individual plastic zip bags. The bags were placed into a cooler with dry ice and overnight shipped to EPA RTP. This protocol will be followed for these tests.

Upon receipt of the films from VT, the packaged films will be removed from the cooler (remaining in their original packaging), photographed then placed in the freezer located in E383A. The chain of custody (COC) form received with the samples will be dated, initialed and placed with the samples. The freezer that will be used for this project is on the EPA Metrology Laboratory monitoring program and is equipped with a HOBO® thermocouple that records the temperature every hour. The data are downloaded by the Metrology Laboratory every three months. A weekly spot check of the temperature will be made while the films are being stored and the data will be recorded in the laboratory notebook # 2287.

3.2 Test Procedures and Sampling Schedules

3.2.1   Task 1: Initial Small Chamber Testing

Three small chamber tests were conducted with reference material supplied by Virginia Tech in December 2011. A set of three polycarbonate films measuring 10 cm x 10 cm x 0.0254 cm was received from Virginia Tech on December 6, 2011. The predicted monomer formaldehyde initial concentration on the surface (C_0) was estimated to be 188 g/m^3 as reported by VT. Table 3-1 details the test parameters of each film tested.

Table 3-1. Chamber Parameters for Initial Small Chamber Tests

Test ID	Start date End date	Age, days[a]	ACH	Temp, ºC	RH, %
SES-SCh-F1	12/7/2011 12/12/2011	2	1	23	50
SES-SCh-F2	12/15/2011 12/19/2011	8	1	23	<11.3[b]
SES-SCh-F3	12/21/2011 12/23/2011	14	1	23	<11.3[b]

[a.] The age of the film is the number of days from removal from the loading vessel.
[b.] This reading for RH is below the lowest calibration point of 11.3% RH for the probe

The resulting data are presented in Figure 3-1. The chamber data show a measurable difference between the predicted value and the measured concentrations from the chamber data. There is also a noticeable difference in the emission rate between 50% RH and 0% RH. These are issues that are being investigated with this study.
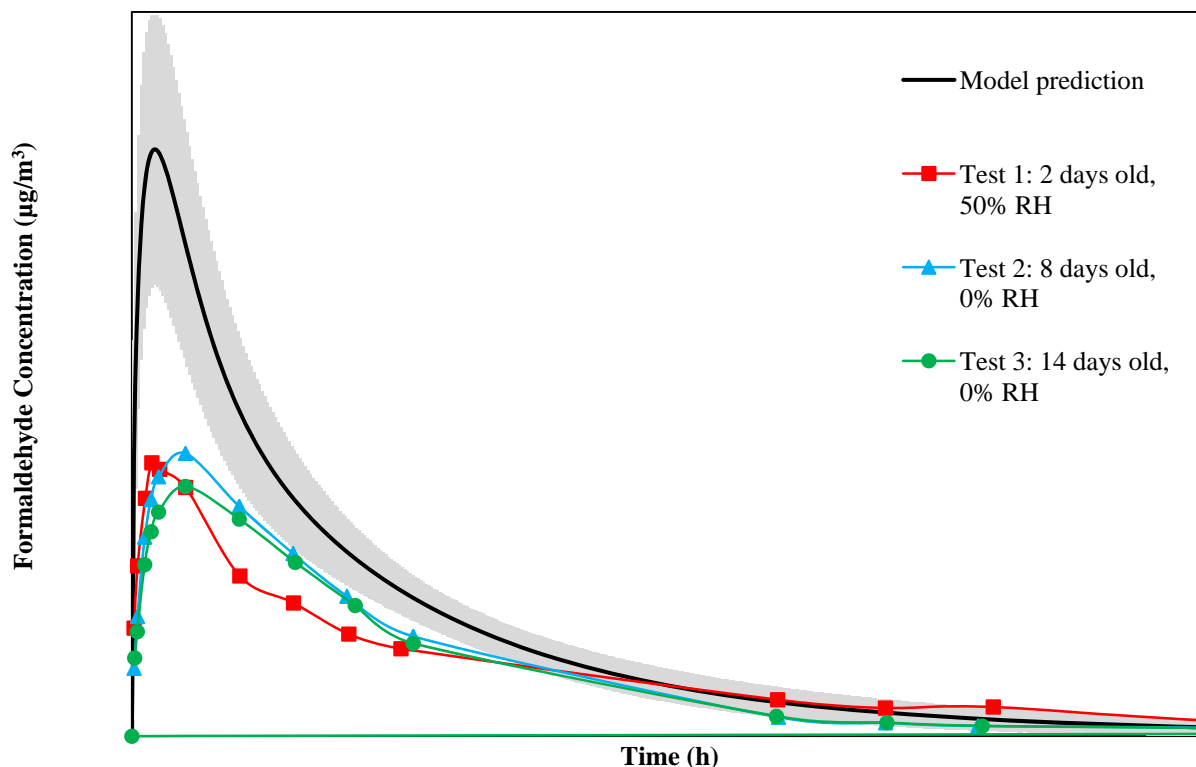
Figure 3-1. Results of Initial Small Chamber Tests

3.2.2   Task 2: Evaluation of Methods to Determine Experimental C_0

Virginia Tech will send six films (3.5 cm x 3.5 cm x 0.0254 cm) to EPA. The predicted monomer formaldehyde initial concentration on the surface, C_0 is estimated to be 190 g/m^3; the polymerized formaldehyde concentration, C_P on the film is estimated to be 0.034 g/m^2. The total loading mass is 73 μg. These films will be divided in half and will be used to evaluate methods for the experimental determination of C_0 on the film. It is assumed that at room temperature, formaldehyde depolymerization will not occur. At 25°C, the measured monomer formaldehyde on the film surface using selected methods will be C_0. At higher temperature, e.g. 40C and 60C, the measured formaldehyde on the film will be the total loading of formaldehyde mass. Three methods will be evaluated: liquid extractions (EPA Method 8315A http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8315a.pdf), the Markes μ-

CTE at three temperatures (25 °C, 40 °C, and 60 °C), and the EPA HTC at 60 °C. One of the methods will then be selected to determine the experimental C_0 and the total loading mass of formaldehyde on the reference materials that will be used for source emission tests in the future. The selection criteria will be based on the recovery efficiency of the monomer formaldehyde concentration as compared the initial C_0 and the procedure simplicity.

Tests will be conducted using a formaldehyde standard solution with a concentration similar to the expected concentration of the film to determine the recovery efficiency of each method. The expected mass of the monomer formaldehyde in the film will be calculated using Equation 1 below:

$$C_{m0} = L \times W \times T \times C_0 \times 1000000 \qquad \{1\}$$

Where:
C_{m0} = Experimentally determined mass of the monomer formaldehyde on the film (µg)
L = Length of the film subsample (m)
W = Width of the film subsample (m)
T = Thickness of the film subsample (m)
C_0 = Initial dosed concentration of monomer formaldehyde on the parent film, provided by Virginia Tech (g/m^3)

The expected mass of the polymerized formaldehyde in the film will be calculated using equation 2 below.

$$C_{mP} = L \times W \times C_P \times 1000000 \qquad \{2\}$$

Where:
C_{mP} = Experimentally determined mass of the polymerized formaldehyde on the film (µg)
L = Length of the film subsample (m)
W = Width of the film subsample (m)
C_P = concentration of polymerized formaldehyde on the parent film, provided by Virginia Tech (g/m^2)

The total mass of formaldehyde on the film will be the sum of the mass of the monomer formaldehyde on the film (C_{m0}) + the mass of the polymerized formaldehyde on the film (C_{mP}).

Percent recovery of C_0 will be calculated using Equation 3:

$$\% \text{ Recovery} = \frac{\sum_{i=1}^{N}(Ci*V)}{C_0} * 100 \qquad\qquad \{3\}$$

Where:

C_i = Liquid concentration of the integrated DNPH sample (µg/mL)
V = Final volume of the DNPH extract (mL)
C_0 = Initial concentration (provided by VT) of the film subsample (µg)
N = Number of DNPH samples

The formaldehyde standard solution tests will be followed by testing with the reference material. The following sections will give a description of each method and the proposed test procedure.

3.2.2.1 Liquid Extraction Procedure

The liquid extractions of the films will follow a modified version of EPA Method 8315A. Initially, a HCHO standard solution with a concentration of 3.2 mg/mL will be tested to evaluate the proposed method. For the C_0 evaluations the films will be removed from the freezer and placed immediately into the extraction vessel with no temperature equilibration period. The physical extraction of the HCHO from the film will be accomplished by submerging a subsample of the film (1.75 cm x 3.5 cm) into a 60-mL amber bottle (Figure 3-2) containing 60 mL of Honeywell Burdick & Jackson High Purity Water for HPLC, Cat.# 365-4.

Figure 3-2. Liquid Extraction of Film

The bottle will be shaken vigorously using a VWR Model 3500 standard shaker in a temperature-controlled incubator maintained to 23 °C initially for a period of 3.5 hours. The resulting solution will be derivatized (yielding the hydrazone) using the modified version of EPA Method 8315A, then analyzed by HPLC. If the results of this initial extraction period show a lower concentration than expected, then the procedure will be repeated extending the extraction period until 100% recovery is achieved, or the recovery results are the same after two extended extraction periods. Procedure for the modified EPA Method 8315A is listed below.

1. Extract the film by submerging a subsample of the film (1.75 cm x 3.5 cm) in the 60 mL bottle containing 60 mL of water

2. Shake vigorously shake using a VWR Model 3500 standard shaker in a temperature-controlled incubator maintained at 23 °C initially for a period of 3.5 hours. (This time will be extended if the recovery is less than 100 %)

3. Immediately after extraction, transfer 10 mL of the solution from the jar to a 125-mL Erlenmeyer flask

4. Add 4 mL of citrate buffer (pH 5.0) and 3 mL of DNPH solution (3.00 mg/mL)

5. Cover and return to the orbital shaker inside the incubator at a temperature of 23 °C for exactly 1 hour

6. Add 20 mL of dichloromethane to the flask containing the HCHO solution and separate the solvent portion containing the derivatized HCHO from the water using a 250-mL separatory funnel; repeat three (3) times.

7. Dry the solution using sodium sulfate.

8. Transfer the samples to a 100-mL blow-down tube; wash the flask four (4) times with 10-mL portions of methylene chloride and add the washes to the blow-down tube.

9. Insert the samples into the RapidVap and blow the solutions down to approximately 1.5 mL. The RapidVap settings are 12 psi nitrogen gas, 50 to 90% speed (start at 50%, after 10 minutes increase to 90%), at 40 °C. The entire blow-down process takes 35 minutes.

10. Pipette the solution from the blow-down tube into a 10-mL volumetric flask; wash the blow-down tube seven (7) times with approximately 1 mL of acetonitrile and add the washes to the flask

11. Bring the solution to volume with acetonitrile and aspirate the solution 20 times with a pipette

12. Transfer approximately 1.5 mL to a 2-mL amber vial

13. Analyze the sample on the Agilent 1200 HPLC/DAD (MOP 826 L:\Lab\NRML_Public\APPCD MOPs and Facility Manuals\APPCD MOPS and Facility manuals\800-Small Chamber\Appendix B - Operating Procedures)

3.2.2.2   Markes µ-CTE Procedure

The ease of use and versatility of air flow rate, temperature, and sample size makes the Markes µ-CTE procedure ideal for determining C_0 using elevated temperature air extraction. Each of the six chambers on the µ-CTE will be evaluated individually with the HCHO standard solution at 60 °C before testing the reference material. Operation and detailed setup procedures are outlined in SOP 6962, *Operation of the Markes Micro-Chamber Thermal Extractor* (L:\Lab\NRML_Public\APPCD MOPs and Facility Manuals\APPCD MOPS and Facility manuals\6900-PCP MOPs). The specific procedures for the HCHO standard solution test are listed below:

1. Prepare a HCHO solution with a concentration of 75 µg/mL and a HCHO standard solution with a concentration of 3.21 mg/mL.

2. Set the µ-CTE to the desired temperature.

3. Set up µ-CTE for high flow and adjust pressure to achieve the highest possible steady air flow rate of approximately 300 to 450 mL/min (approximately 48 psi)

4. Attach a test DNPH (Silica Gel Cartridge (Waters Sep-Pak®) – Short Body, 55-105µm) to chamber 1 and measure the air flow through the DNPH cartridge using a Gilibrator; record measurement in notebook.

5. Repeat step 4 for chambers 2 through 6.

6. Open each chamber lid.

7. Attach a new DNPH silica gel cartridge to the lid of each of the chambers that will be used for the test

8. Close each lid and record time

9. Collect empty chamber background sample for 60 min, remove, record time and extract for analysis by HPLC

10. Attach a new DNPH cartridge to each of the six chambers' lids

11. Spike 1 mL of the 75-µg/mL HCHO solution directly into each chamber 2 through 6

12. Immediately close the lid and record time

13. Spike 1 mL of the 3.21-mg/mL HCHO solution directly into chamber 1

14. Immediately close the lid and record time

15. Collect an integrated sample for 150 min on chamber 2, remove and immediately attach a second DNPH to collect for an additional 60 min; remove, record time, and extract for analysis by HPLC

16. Collect integrated samples on chambers 3 through 6 for 200 min; remove, record time, and extract for analysis by HPLC

17. Collect a time series of DNPH samples from chamber 1 following the sample schedule in Table 3-3

18. After sampling is complete, clean µ-CTE according to SOP 6962

The basic sampling scheme for collecting samples in the µ-CTE during the HCHO standard solution test is to collect DNPH according to the procedure detailed in MOP 812 (L:\Lab\NRML_Public\APPCD MOPs and Facility Manuals\APPCD MOPS and Facility manuals\800-Small Chamber\Appendix B - Operating Procedures) The sampling schedule should be a 30-second sample every 10 minutes for the first 30 minutes, then a 60-second sample every 10 minutes for the next 2 hours changing to a 10-minute sample every hour for the next 3 hours. The test duration will be 6.5 hours with 20 samples and 1 field blank.

After results from the HCHO standard solution tests have been reviewed, a series of film tests will be defined. Table 3-2 details the proposed film tests for determination of experimental C_0. The setup and operation of the μ-CTE will be the same as for the HCHO standard solution tests (steps 2 through 10 above). The procedure for the film test continues by placing the subsample of the film in the desired chamber and closing the lid – record the start time in the laboratory notebook. For the integrated samples, the chamber effluent will be collected onto a DNPH cartridge (MOP 812) for a minimum of 5 hours. After removing the DNPH, a second DNPH cartridge is connected to the lid and the chamber effluent is collected onto the cartridge for an additional 16 to 20 hours. The procedure for the time-series tests will follow the sampling schedule outlined in Table 3-3. All DNPH cartridges will be extracted with acetonitrile using the method outlined in MOP 812 and analyzed by HPLC (MOP 826).

Table 3-2. Proposed Film Tests for Determination of Experimental C_0

Type of test	μ-CTE temp., ºC	Air flow rate, mL/min	Size of film	μ-CTE #	Duplicate
Time series	60	350	1.75 cm x 3.5 cm	1	
Integrated	60	350	1.75 cm x 3.5 cm	1 and 2	yes
Integrated	40	350	1.75 cm x 3.5 cm	1 and 2	yes
Integrated	25	350	1.75 cm x 3.5 cm	1 and 2	yes

Table 3-3. Proposed Schedule for Collection of DNPH Cartridge Samples for the Film μ-CTE Time Series Method at 60 ºC

Elapsed Time (Hrs)	Sample Duration, min	Sample Volume (L)
-1 Empty Chamber Background	150	50
0.042 (2.5 min)	5	1.8
0.2 (12 min)	5	1.8
0.4 (24 min)	5	1.8
0.5 (30 min)	5	1.8
0.7 (42 min)	5	1.8
0.9 (54 min)	5	1.8
1	5	1.8

1.5	10	3.6
2	10	3.6
3	30	11
Total number of samples	11	
Field blanks (daily)	1	
Total number of samples per test	12	

3.2.2.3   EPA HTC Procedure

The EPA HTC has been used successfully in previous research to collect emissions from solid material at an elevated temperature. The proposed tests for this chamber will be limited to one HCHO standard solution at 60 °C and one reference material test. An SOP has not been written for the operation of this chamber. The specific procedures for the HCHO standard solution test are listed below:

1. Prepare a HCHO solution with a concentration of 75 µg/mL

2. Attach clean air supply to pre-heat tube and set air flow rate to approximately 150 to 200 mL/min

3. Set the HTC to the desired temperature

4. Open the chamber door and place a new small Al dish on the floor of the chamber

5. Close and seal the door

6. Let system flush at set temperature for at least 1 hour before collecting a background sample

7. Attach a test DNPH cartridge to the chamber effluent and measure the air flow through the DNPH cartridge using a Gilibrator; record measurement in notebook

8. Attach a new DNPH cartridge to chamber exhaust point; record time

9. Collect empty chamber background sample for 200 minutes, remove the DNPH cartridge, record time, and extract for analysis by HPLC

10. Open the door and quickly spike 1 mL of the 75-µg/mL HCHO solution into the Al dish

11. Seal the door quickly; record the time

12. Collect an integrated sample for 200 min , remove the DNPH cartridge, and immediately attach a second DNPH to collect for an additional 60 min, remove the DNPH cartridge, record time, and extract for analysis by HPLC

13. After sampling is complete, clean the HTC with deionized water; elevate heat and flush with clean dry air.

The procedure for the reference material film will follow steps 2 through 9 removing the Al dish and replacing it with a film holder. The film will be placed in the chamber on the film holder, and the door will be sealed immediately. The DNPH sample will be collected for a minimum of five hours, and a second DNPH cartridge will be attached to the exhaust and collected for an additional 16 to 18 hours. All DNPH cartridges will be extracted with acetonitrile and analyzed by HPLC.

3.2.3   Task 3: Evaluation of Packaging Integrity and Shelf Life

3.2.3.1   Small Chamber Procedure

Task 3 will use the small environmental chamber systems set up in the six-chamber incubator. The small chambers will be operated in accordance with approved MOPs 801, 802, 803, 804, and 806, located in L:\Lab\NRML_Public\APPCD MOPs and Facility Manuals\APPCD MOPS and Facility manuals\800-Small Chamber. Three chambers will be set up in the six-chamber So-Low Incubator with the following parameters: 0% RH, 1 ACH, and 25 °C. Eleven (11) 10-cm x 10-cm films and five (5) 3.5-cm x 3.5-cm films will be requested from Virginia Tech. Table 3-4 outlines the proposed tests for this task. The duration of each test will be a minimum of 96 hrs.

Table 3-4. Proposed Small Chamber Tests for Reference Material

Time	Test ID	Proposed small chamber tests and C_0 determination
Week 0	SES-SCH#-F4&5-W(0)- SES-SCH#-F6-W(0)-Packaging- SES- MCH#-C_0-F4&5-W(0)-	(2) SCh tests with 10-cm x 10-cm films – Duration 96 hours (1) SCh test with 10-cm x 10-cm wrapped and sealed film – Duration 2 weeks (2) C_0 test with 3.5-cm x 3.5-cm film divided in half – µ-CTE
Week 2	SES-SCH#-F7&8-W(2)- SES- MCH#-C_0-F7&8-W(2)-	(2) SCh tests with 10-cm x 10-cm films – Duration 96 hours (2) C_0 test with 3.5-cm x 3.5-cm film divided in half – µ-CTE
Week 4	SES-SCH#-F9&10-W(4)- SES- MCH#- C_0-F9&10-W(4)-	(2) SCh tests with 10-cm x 10-cm films – Duration 96 hours (2) C_0 test with 3.5-cm x 3.5-cm film divided in half – µ-CTE
Week 6	SES-SCH#-F11&12-W(6)- SES- MCH#-C_0-F11&12-W(6)-	(2) SCh tests with 10-cm x 10-cm films – Duration 96 hours (2) C_0 test with 3.5-cm x 3.5-cm film divided in half – µ-CTE
Week 10	SES-SCH#-F13&14-W(10)- SES- MCH#-C_0-F13&14-W910)-	(2) SCh tests with 10-cm x 10-cm films – Duration 96 hours (2) C_0 test with 3.5-cm x 3.5-cm film divided in half – µ-CTE

3.2.3.1.1 Shelf Life Tests

Table 3-5 outlines the proposed sampling schedule for the small chamber tests evaluating the shelf life of the films.   These tests will be conducted with duplicated identical environmental parameters. Upon completion of the small chamber emissions test the 10 cm x 10 cm film will be removed. A photograph will be taken on a grid surface, and two small sections will be removed from the film (Figure 3-4). The picture will be available to determine the surface area of each section using Auto CAD if needed. The smaller sections will be placed in separate µ-CTE chambers at a temperature of 60 ºC and a flow of 350 mL/min. An integrated DNPH sample will be collected for a minimum of 5 hours to determine the residual formaldehyde on or in the film.

Table 3-5. Proposed Sampling Schedule for Small Chamber Tests

Elapsed Time (Hrs)	Primary Sample	Duplicate Sample	Sample Volume (L)[a]
-1 – Background	X	X	35
0.1 (6 min)	X		3.5
0.3 (18 min)	X		3.5
0.5 (30 min)	X	X	3.5
0.7 (42 min)	X		3.5
1	X		3.5
2	X	X	7
4	X		7
6	X		7
8	X	X	7
10	X		7
24	X		21
28	X		21
32	X	X	21
48	X		42
72	X		60
96	X	X	60
Total number of primary samples	16		
Duplicates	6		
Field blanks	3		
Field controls (when needed)	3		
Total number of samples per test	28		

[a] Samples will be collected at 350 mL/min

The specific procedures for the small chamber tests are listed below:

1. Clean three chambers as detailed in MOP 801(L:\Lab\NRML_Public\APPCD MOPs and Facility Manuals\APPCD MOPS and Facility manuals\800-Small Chamber\Appendix B - Operating Procedures).

2. Set up chamber to specified parameters: fan blowing upward and placed to the rear of the chamber, 0% RH, 1 ACH, and 25 °C.

3. Flush for at least 24 hours - collect single DNPH sampling cartridge background for 2 hours at 350 mL/min.

4. Analyze sample, if results show elevated formaldehyde area response above 4.5, re-clean chamber.

5. Repeat steps 2-4.

6. Clean the film holder using the same process detailed in MOP 801 at least one day prior to the beginning of the test. Place the empty holder in each of the small chambers (Figure 3.3).
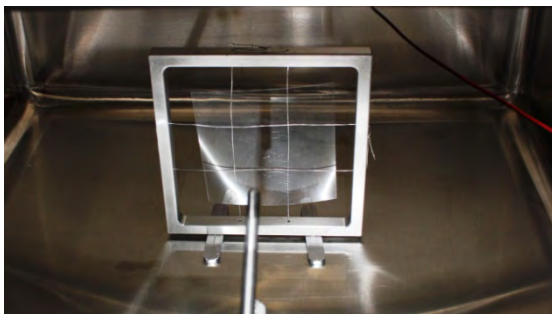
Figure 3-3. Film Frame with Film in Chamber

7. Reseal chamber and flush under set parameters for a minimum of 16 hours-collect duplicate DNPH sampling cartridge background for two hours at 350 mL/min.

8. After the background samples are removed, open the chamber and remove the film holder.

9. Remove the test film from freezer. Let the film equilibrate to room temperature approximately 5 min before placing it in the holder. Make sure that the films are from the same batch and insert the film into the film holder for each chamber (Figure 3.3).

10. Place the holder with the film in the chamber (Figure 3.3).

11. Reseal chamber and begin sampling as outlined in Table 3.5.

12. After test is complete remove the film from the chamber.

13. Photograph on a grid surface (Figure 3-4) for determination of surface area using Auto CAD (SOP 6016) if needed.
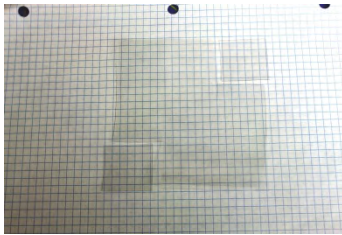
Figure 3-4. Reference Material Film after SCh Test

14. Cut two sections from the film to be placed in the μ-CTE chambers at a temperature of 60 ºC and a flow of 350 mL/min.

15. Collect an integrated DNPH sample for a minimum of 5 hours to determine the residual formaldehyde on or in the film.

16. Wrap remaining film in three layers of aluminum foil, place in a plastic zip bag and place in the freezer in E383.

17. The chamber will be completely disassembled, cleaned (MOP 801) and readied for the next test starting with step 1.

3.2.3.1.2 Packaging Test

One small chamber test, SES-SCH#-F6-W(0) will be conducted to investigate the effectiveness of the packaging. This test will continue for least a two weeks and may be extended depending on the data that is collected. The sampling schedule can be adjusted to incur no weekend sampling for this test.

1.   Prepare small chamber as described in steps 1-8 above.

2. As soon as films are received, remove one film from the shipping cooler, photograph and remove any extra packaging such as plastic bags.

3. Place the aluminum foil wrapped film on to the film stand (Figure 3-3) and place in the chamber.

4. Seal the chamber and begin sampling according to the sample schedule in Table 3-6.

Table 3-6. Sample Schedule for DNPH for the Package Evaluation Test

Elapsed Time (Hrs)	Primary Sample	Duplicate Sample	Sample Volume (L)[a]
-1 – Background	X	X	35
Day 1	X		100
Day 3	X	X	100
Day 5	X		100
Day 8	X		100
Day 10	X		100
Day 12	X		100
Day 16	X	X	100
Total number of primary samples	8		
Duplicates	2		
Field blanks	2		
Field controls (when needed)	3		
Total number of samples per test	15		

[a] Samples will be collected at 350 mL/min

3.2.3.2 C_0 µ-CTE Procedure

On the same day that the film tests start, a 3.5 cm x 3.5 cm film from the same batch will be extracted thermally using the µ-CTE to determine C_0. The following section details the procedure for determining C_0.

1. For the C_0, clean two micro-chambers and set test parameters to 60 ºC and the pressure to approximately 48 psi (300 -450 mL/min)

2. Flush the system with clean dry air from the small chamber clean air system for at least 24 hours, then collect backgrounds from each chamber for 5 hours

3. Extract and analyze samples. If the results show elevated formaldehyde area response above 4.5, re-clean chamber.

4. Repeat steps 6-8

5. Once the background passes, continue to flush with the system air until time for the test to begin

6. On the day the small chamber test starts, remove one of the 3.5 cm x 3.5 cm films from the freezer. Make sure that it is from the same batch as the films being used with the small chamber tests.

7. Immediately place the film in the film slicer (Figure 3-4) and divide film in half

Figure 3-5. Film Slicer

8. Put a DNPH cartridge on the lid of each of two chambers that have been prepared for testing

9. Place each half of the divided film into one of the µ-CTE chambers, seal the lid and record the time

10. Collect the chamber effluent onto a DNPH cartridge for 5 hours

11. Remove the DNPH cartridge and replace with a second DNPH cartridge to collect overnight

12. Remove DNPH cartridge, extract and analyze samples

13. Clean chambers

3.2.4 Task 4: Evaluation of Formaldehyde Emission Rates from the Reference Material at Varying RH

The performance of this task will depend on the available funding and resources. For this task one chamber test at 0% RH, one test at 70% RH and a set of duplicate chamber tests at 50% RH are proposed. Details of this task are TBD. The sampling schedule for these tests will follow the schedule outlined in Table 3.5.

3.2.5 Task 5: Interlaboratory Comparison

Once the details of packing, shipping and chamber testing have been establish, EPA has proposed a small interlaboratory comparison for the process with at least one other laboratory. The details of this task are currently under discussion.

3.2.6 Test and Sample Identification

In order to differentiate individual tests, each test will have a unique identification. The nomenclature of the conditioning phase of the test will be as follows:

[SES]-[Chamber #]-[Film Test #]-[Week #]-[Type of Test]-[Elapsed Time]-[Replicate]

where:
SES = Standard Emissions Source
Chamber = (MCH = µCTE (#1-6), SCH = small chamber (#1-8), HTC = high temperature chamber, LE = liquid extraction)
Film Test # = F1 - TBD
Week Number = W(#)
Type of Test = [C_0 Eval, Packaging, Shelf life (W0 –W10), Interlaboratory comparison (IC)]
Type or Elapsed Time (BKG = chamber background, Elapsed Time = #hr),
Replicate ID = A, B.

A typical sample name would be:

SES- SCH1–F10-W0-Bkg (-24hr) A

3.3 **DNPH Sampling Method**

All air samples will be collected on DNPH-treated silica gel for analysis of formaldehyde by Agilent 1200 HPLC. This analysis is a standardized method used extensively in the source characterization laboratory [3].

The commercially available cartridges (Waters Sep-Pak DNPH Silica Gel Cartridge, Waters Associates, Milford, PA) contain 350 mg of a 55- to 105-µm chromatographic-grade silica gel coated with DNPH. Samples will be collected on the cartridges by drawing air from the sampling line located within 0.3 m of the source using mass flow controllers and vacuum pumps at a sampling rate of 100 to 300 mL/min. The sampling rate flow rate will be set with the mass flow controller and then measured with a Gilibrator. After collection, DNPH cartridge samples will be capped, placed back in their original air-tight re-sealable relabeled pouch and stored in the freezer located in E378A before solvent extraction. DNPH cartridges will be extracted with 5 mL of acetonitrile (HPLC grade) before analysis and must be extracted within 2 weeks of collection. Sample information will be recorded on labels affixed to the pouch in which samples are stored, in the Excel notebook, and in the laboratory logbook. Details of the sampling and analysis procedure are given in MOPs 812, 826 and 827 of the small chamber MOPs (L:\Lab\NRML_Public\APPCD MOPs and Facility Manuals\APPCD MOPS and Facility manuals\800-Small Chamber).

4. QA/QC

Work on this project will be performed following the general guidelines for QA/QC described in the *Facility Manual for the Small Chamber Laboratory* (August 2003) and the *Facility Manual for the Large Indoor Air Quality Environmental Test Chamber* (2006). Section 6 (Quality Assurance/Quality Control) of this approved QAPP details the Data Quality Indicator goals that are to be followed for this study. Any deviations will be noted in the report.

4.1 Data Reporting

Data from all tests will be reported in electronic files. Reported data will include the concentration of target carbonyls at each sampling time, operating parameters of tests, and results for analyses of QC samples. Written and verbal communications with Virginia Tech will be prepared by the WAM/PI, Xiaoyu Liu, for this project. Table 4-1 details the data reporting requirements associated with these tests.

Table 4-1. Data Reporting Requirements

Measurement Parameters	Unit
Carbonyl Concentrations	$\mu g/m^3$
Inorganic Gases Concentrations	ppb
Temperature	°C
Pressure	Pa
Relative Humidity	%
Air Exchange Rate	h^{-1}
Air Flow	mL/min
Mass	g

5. References
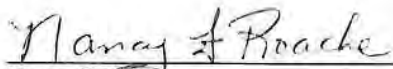
[1]   S. 1660 (111th): Formaldehyde Standard for Composite Wood Products Act
      (FSCWA) *http://www.govtrack.us/congress/bill.xpd?bill=s111-1660* , Site last
      accessed May 16, 2012.

[2]   Little , John, Quality Assurance Project Plan, *Developing a Reference Material for
      Formaldehyde Emissions Testing (ver. 2);* Department of Civil and Environmental
      Engineering, Virginia Tech, Blacksburg, VA.

[3]   EPA method IP-6A, *Determination of Formaldehyde and Other Aldehydes in
      Indoor Air Using a Solid Adsorbent Cartridge*, U. S. Environmental Protection
      Agency

U.S. EPA Office of Research and Development
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division

Standard Operating Procedure 880

Test Procedure for Formaldehyde Reference Material Testing Using Small Chamber

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Revision Record

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	June 27, 2012	EPA QA	QA comments for - QLOG No. A-16211 / QTRAK 11037, QA Category IV - "acceptable with minor revisions"
1	June 28, 2012	Nancy Roache	Revised to reflect comments from QA office

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APPENDIX A: Chain of Custody Form
APPENDIX B: See Attached Excel File

1. **TITLE**

Test Procedure for Formaldehyde Reference Material Small Chamber Testing

2. **PURPOSE AND SCOPE**

This SOP provides a written, repeatable procedure for the set up, sampling, analysis and data reduction of the small chamber testing for the Formaldehyde Reference Material.

The scope of this project is to collaborate with Virginia Polytechnic Institute and State University (Virginia Tech or VT) researchers to test the emission characteristics of the polymer film that will be developed as a carrier for a formaldehyde reference material whose emissions can be predicted by a fundamental emission model. Small environmental chambers will be used to determine the emission rate of formaldehyde from a polycarbonate film that has been dosed with formaldehyde gas.

3. **SUMMARY OF METHOD**

Tests to evaluate the emission rate of formaldehyde from a polycarbonate film will be conducted in small environmental chambers operated at specified environmental conditions. The source for the chamber tests will be a product that has been developed by Virginia Tech as a proposed reference material for evaluating the uncertainties of small chamber testing for formaldehyde. The reference material will be sealed in the chamber and a series of timed air samples collected from the chamber effluent onto 2,4-dinitrophenylhydrazine (DNPH) cartridges. DNPH cartridges will be extracted and analyzed by high performance liquid chromatography (HPLC) and the data reported to the EPA Principal Investigator (PI).

4. **DEFINITIONS**

- Small environmental chamber - 53-liter electropolished stainless steel chambers that meet the specifications in ASTM Standard Guide D5116-10 — Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products (ASTM, 2010)

- DNPH Cartridge - silica gel cartridge coated with 2,4-dinitrophenylhydrazine (DNPH)

- Sampling Pump System- consists of vacuum pump connected by a valve system to 4 mass flow controllers (MFC) whose output is controlled by a mass controller box (CB). The four pump lines are designated as pump 1 (P1), pump 2 (P2), pump 3 (P3), and pump 4 (P4).

- Practical Quantification Limit (PQL) (MOP 826) is defined as the lowest standard on the calibration curve if the following conditions are met:
    - PQL peak is identifiable with a precision of 15% and accuracy of 15%
    - PQL response is at least 5 times that of the IDL.

- DI Water – Deionized water.

- Reference Material – A polymer film designed as a carrier for formaldehyde.

- Film Holder - 150 mm x 150 mm aluminum holder with wire cross hairs to hold film and feet to stand upright (provided by VT)

5. HEALTH AND SAFETY

Good laboratory practice will be followed including all safety procedures outlined in the "Chemical Hygiene Plan" revised in February 2012.

6. INTERFERENCES

The presence of moisture creates the potential for formaldehyde to polymerize, therefore it is recommended that the films should be handled and stored in environments with relative humidities lower than 20%.

7. RELATED DOCUMENTS

- MOP 802 - Operation of Small Emissions Chambers during Testing (under revision 2012)

- MOP 803 - Operation of the Opto Display Software Data Acquisition System (DAS) in the Small Chamber Laboratory (under revision 2012)

- MOP 806 - Operation of the Clean Air System for the Small Chamber Laboratory (under revision 2012)

- MOP 808 - Determination of Small Chamber Formaldehyde Emission using DNPH-Coated Silica Gel Cartridges

- MOP 811 - Collecting Air Samples Using Sorbent Tubes

- MOP 812 - Collection and Extraction of Air Samples on DNPH-Silica Gel Cartridges

- MOP 826 - High Pressure Liquid Chromatography (HPLC) Analytical Procedures

- MOP 871 - Glassware Cleaning Procedures for Small Chamber Lab

8. EQUIPMENT AND SUPPLIES

Below is a list of equipment associated with the small chamber laboratory that is used for this procedure.

- Small environmental chamber system (Table 1)

Table 1. Small Environmental Chamber System Components

Component	Manufacturer	Model #	Manufacturer's Location
Clean Air System			
Pressure Regulator	Wilkerson	B18-03-FK00	Richland, MI
Compressed Air Dryer	Hankison	SSRD10-300	Ocala, FL
Carbon Trap	Supelco	24565	Bellafonte, PA
Moisture Trap	Supelco	23992	Bellafonte, PA
Pure Air Generator	Aadco	737-11A	Cleves, OH
Pressure Regulator	Norgren	B736-2AK-API-RMG	Littleton, CO
Mass Flow Controllers (8)	Teledyne	HFC-E-202	Hampton, VA
Constant Temperature Bath	Blue M	MR 3240C-1	Blue Island, IL
1000mL Round Bottom Flask (4)	Prism Glass	PRG-5795-03	Raleigh, NC
Midget Impinger Bubbler (4)	Prism Glass	PRG-5030-23	Raleigh, NC
Chamber System			
Incubator	So-Low	C-SCN4-52-8	Cincinnati, OH
Inlet RH Probes (4)	Vaisala	HMT333	Helsinki, Finland
Internal RH Probes (4)	Vaisala	HMT335	Helsinki, Finland
Thermocouples (4)	Pyromation	E-Type	Fort Wayne, IN
DAS System			
Opto Control System	Opto 22	B3000	Temecula, CA
Electrical Control Box	Carotek, Inc	AT-607983	Mathews, NC
Opto Operation Computer	Dell	Optiplex 745	Round Rock, Tx

- Sampling Vacuum System (Table 2)

Table 2. Sampling System Components

Component	Manufacturer	Model #	Manufacturer's Location
Vacuum Pump	Welch	2565B-50	Skokie, Il
Mass Flow Controllers (4)	Coastal Instruments	FC-260	Burgaw, NC
Mass Flow Control Box	Porter Instrument Co.	CM4	Hatfield, PA
Gilibrator	Sensidyne	800286	Clearwater, FL
Flexible PFA (Perfluoroalkoxy) Tubing	Fisher Scientific	----	----
Flexible Silicone Tubing	Fisher Scientific	----	----
3-Port Glass Sampling Manifold	Prism Research Glass	----	Raleigh, NC

- DNPH-Silica Gel Cartridge (Waters Sep-Pak®) – Short Body, 55-105μm
  http://www.waters.com/waters/partDetail.htm?partNumber=WAT037500&locale=en_US

- Extraction Supplies

  o Acetonitrile, HPLC Grade (Fisher Scientific)

  o 5 ¾" Glass Pasteur Pipettes (Fisher Scientific)

  o 5 mL Glass Syringe (Fisher Scientific)

  o 5 mL Class A volumetric flasks (Fisher Scientific)

- Film Holder – provided by Virginia Tech

9. PROCEDURE

The following procedure is specifically for the small chamber tests associated with the
Formaldehyde Reference Material. Chamber preparation, setup, and empty chamber background
checks should be completed before the arrival of the test films.

9.1 Chamber Cleaning

1. Wash chambers, faceplate, and chamber O-ring thoroughly in the sink with detergent (Liquinox
   or Sparkleen) and hot water.

2. Follow with three rinses of warm water and then three rinses of DI water. Dry chambers and
   faceplate with Kimwipes (Fisher Scientific).

3. Diffusers and sampling manifolds are cleaned in a similar manner and then placed in the oven at 125 °C. Fans are cleaned with isopropanol wipes then baked at 125 °C for 10 minutes then wiped again with an isopropanol wipe and dried with a Kimwipe. Nitrile gloves should be worn while cleaning the chambers.

9.2 Chamber Reassembly

1. Reassemble the chamber with the small-hole diffuser on the inlet air side of the chamber cover and the large-hole diffuser on the outlet side of the cover.

2. If a mixing fan is desired for the chamber test, install a 40mm brushless DC cooling fan by snaking two wires through the inlet diffuser holes on the inside of the chamber and connecting them to the fan wires. Test the fan before sealing to ensure proper wiring.

3. The fan is suspended in the back center of the chamber by attaching thin steel wire diagonally from the end of each diffuser creating an "X" between the inlet and outlet diffuser manifolds. The fan is attached at the center of the "X" with about 1½" of small steel wire.

4. The fan is operated at the 12 volt setting on an AC/DC converter that rotates the fan at 6500 rpm ±10% and a nominal air speed at the surface of 7.7CFM ± 10%.

9.3 Chamber Preparation for Testing

Experimental conditions for the reference material testing are shown in Table 3. The chambers should be set to the test parameters and operated with the film holder in place at least 16 hours prior to collection of a chamber background sample.

Table 3. Experimental Conditions for Small Chamber Reference Material Tests

Parameter	Value
Temperature (in chamber) [a], °C	25 ± 0.5
Relative humidity(inlet air) [b], %RH	50 ± 5 or otherwise determined
Air flow [c], m^3/h	0.053 ± 5%
Air exchange rate, h-^{1}	1 ± 0.05
Test materials	VT Reference material
Loading factor [d], m^{-1}	0.397 ± 0.02
Substrate surface area [e], m^2	0.021 ± 0.001 or otherwise determined
Test period [f], days	4 or longer

[a] As measured by a Pyromation E-Type thermocouple (calibrated annually by EPA Metrology Laboratory).

[b] As measured by a Viasala model HMT333 Humidity Transmitter with HUMICAP180 humidity sensor (calibrated annually by EPA Metrology Laboratory).

[c] Air input to the 53 liter chamber as measured by a Gilibrator.

[d] Loading factor (m^{-1}) = surface area of the substrate (m^2)/ volume of the chamber, (m^3).

[e] Information provided by Virginia Tech or measured with NIST calibrated calipers.

[f] Testing period is a nominal value that can be extended or stopped at anytime during the test.

The specific procedures for the small chamber tests are listed below:

1. At least 4 days before film arrival, clean chambers as detailed above.

2. Set up chambers to specified parameters: mixing fan blowing up and placed to the rear of the chamber.

3. Flush for at least 16 hours - collect single DNPH background for 2 hours at 350 mL/min to validate cleanliness of chamber.

4. Analyze the samples, if the results show an elevated formaldehyde area response above the PQL response, repeat steps 1-4.

5. At least one day before the film test is to be conducted, clean the film holder using the same procedure as used for the chamber parts and place a holder without the film in each of the small chambers

6. Reseal chamber and flush under test parameters for a minimum of 16 hours- collect duplicate DNPH backgrounds for 2 hours at 350 mL/min.

7. Analyze the samples, if the results show an elevated formaldehyde area response above the PQL response then re-clean holder and repeat steps 5-7.

8. Remove and analyze the background samples. The chambers are ready for testing.

9.4 Reference Materials

The reference materials to be tested on this project have been developed and prepared by Virginia Tech. The samples will be overnight shipped from VT.

The date and time the film is removed from the loading vessel is considered as time zero. Each film that is supplied will be numbered with the loading date and time as well as the position in the loading vessel. A chain of custody will be delivered with each sample batch (Appendix A). The gas-phase formaldehyde concentration and the polymerized formaldehyde concentration will also be included on the COC. Films from each loading batch are considered equal; however, the films from different loading batches may vary slightly. The films will be removed from the loading vessel and immediately packaged for shipping by Virginia Tech then overnight shipped to Testing Laboratory.

Upon receipt of the films from VT, the packaged films will be removed from the cooler documented as to their ID, temperature upon receipt (if provided), and size. The chain of custody (COC) form received with the samples will be dated, initialed and placed with the samples.
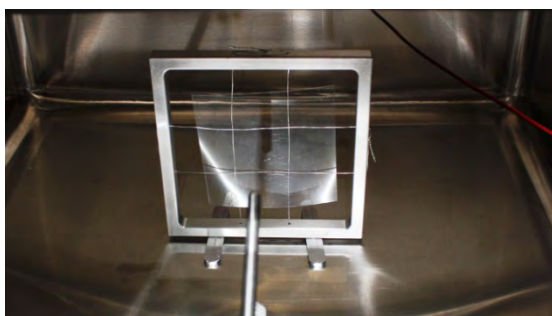
Figure 1. Film Holder with Film in Chamber

1. Remove the test film from its packaging. Make sure that the films have been individually wrapped (no piggy-back films). If multiple films are in the package select another package.

2. Open the chamber and remove the film holder

3. Place the film in the holder (Figure 1) and place the holder back in the chamber.

4. Reseal chamber, record time (time zero for the start of the test) and begin sampling as outlined in Table 4.

5. After the test is complete remove the film from the chamber and wrap with 3 layers of aluminum foil, label and place in freezer until results are reviewed.

Table 4 outlines the proposed sampling schedule for the small chamber tests evaluating the shelf life of the films. Single samples will be collected at 350 mL/min from one port of the 3-port glass manifold. Duplicate samples will be collected at 350 ml/min from 2-ports of the 3-port glass manifold (MOP812). The elapsed time is calculated using the time zero start time of the test and the midpoint of the sampling duration. The sampling duration and vacuum flow rate through the sample media determine the volume. The volume of sample air to be collected is determined by the calibration range of the instrument being used to analyze the extracted samples. A large enough volume must be collected to at least provide a target analyte concentration above PQL. An optimum sample volume would give the recovery of the target analyte concentration in the mid-level of the calibration. With DNPH extracts if the target analyte is above the highest calibration standard concentration the solution can be diluted to the acceptable range.

Table 4. Sampling Schedule for Small Chamber Tests

Elapsed Time (Hrs)[a]	Primary Sample	Duplicate Sample
-1 – Background	X	X
0.1 (6 min)	X	
0.3 (18 min)	X	
0.5 (30 min)	X	X
0.7 (42 min)	X	
1	X	
2	X	X
4	X	
6	X	
8	X	X
10	X	
24	X	
28	X	
32	X	X
48	X	
72	X	
96	X	X
Total number of primary samples	16	
Duplicates	6	
Field blanks	3	
Field controls (when needed)	3	
Total number of samples per test	28	

[a] Sampling time in hours from start of chamber test to midpoint of sample duration

9.5 DNPH Sample Extraction and Analysis

All DNPH sample cartridges will be extracted and analyzed using established methods: MOP 812 - Collection and Extraction of Air Samples on DNPH-Silica Gel Cartridges and MOP 826 - High Pressure Liquid Chromatography (HPLC) Analytical Procedures. Any deviation from these methods will be reported in the final report.

10. Reporting Data

Data from all tests will be reported in electronic files. An Excel notebook (Appendix B) will be sent to the tester for data reporting. Reported data will include the concentration of target carbonyls at each sampling time, operating parameters of tests, and results for analyses of QC samples. Written and verbal communications will be with Dr. Xiaoyu Liu (EPA PI). Table 5 details the data reporting requirements associated with these tests

Table 5. Data Reporting Requirements

Measurement Parameters	Unit
Formaldehyde concentrations	$\mu g/m^3$ and ppb
Volume	liters
Temperature	°C
Relative Humidity	%
Air Exchange Rate	h^{-1}
Air Flow	mL/min
Elapsed time	hour
Test duration	hours

APPENDIX A

Chain of Custody Form

CHAIN OF CUSTODY FORM

Page _1__ of ___

COC #

Sent from:				
	Contact & Company Name: A	Telephone: E		
	Address: B	Fax: F		
	City, State, Zip C	E-mail Address: G	**FILM SIZE**	
	Project Name/Location (City, State): D	Project #: H		

Item #	Film ID	Film removed from loading vessel				Monomer HCHO conc	Polymerized HCHO conc	10 cm x 10 cm	3.5 cm x 3.5 cm				REMARKS
		Date	Time	Batch #	Position #	g/m^3	g/m^2						
1	XXXXXX-XX-XXXXX	3/27/2012	10:00	1	6	192.00	0.0034	X					

Temperature upon receipt º C =_____   Measured by: Device_____;

Manufacturer_____;Model#_____

		Relinquished By	Received By	Relinquished By	Received By
		Printed Name:	Printed Name:	Printed Name:	Printed Name:
		Signature:	Signature:	Signature:	Signature:
		Firm:	Firm:	Firm:	Firm:
		Date/Time:	Date/Time:	Date/Time:	Date/Time:

APPENDIX B

Electronic Notebook Data File

(See attached excel file)

Test Summary

Input required information in blue cells

Project/Test Name: Interlaboratory Comparison of Formaldehyde Reference Material Emissions using Small Environmental Chambers

Purpose: Measure formaldehyde concentrations in a small chamber containing formaldehyde reference material (film) provided by Virginia Tech under 50% RH, 1 ACH, 25C

Methods/Instruments: Small Chamber Data Acquisition System, DNPH-HPLC

Test Period:

Report date 12/14/2011

At the end of testing summarize the chamber conditions below for each chamber

Test Conditions:

Chamber ID				Test Plan Proposed
Start Time (Chamber Closed after Film in)				
Test End Time				
Test Duration, Hr				48
Chamber Volume, L				53
	Average	STD	%RSD	
ACH (/h) by Inlet Air Flow				1
Chamber Inlet %RH				50
Chamber %RH				50
Chamber Temperature, °C				23
Fan				

Chamber ID				Test Plan Proposed
Start Time (Chamber Closed after Film in)				
Test End Time				
Test Duration, Hr				48
Chamber Volume, L				53
	Average	STD	%RSD	
ACH (/h) by Inlet Air Flow				1
Chamber Inlet %RH				50
Chamber %RH				50
Chamber Temperature, °C				23
Fan				

Test Material Conditions:
Date and time received
Monomer Formaldehyde concentration, g/m3
Polymer Formaldehyde Concentration, g/m2
Test material condition upon receipt

Narrative

Description of Test procedure and problems encountered

Chamber Preparation

Input required information in blue cells				
Parameter	**Setpoint Value**	**Actual Value**	**Uncertainty**	**Measurement Instrument**
Temperature (°C)	25			
Relative Humidity (%)	50			
Chamber Airflow Rate (m^3/h)	0.053			
Chamber Mixing Fan	yes/no			
Chamber Volume (m^3)	Input value			
Chamber Conditioned at Setpoints Empty Chamber (h)	at least 16 h			
Chamber Conditioned at Setpoints EC with Frame (h)	at least 16 h			
Chamber Background Concentration of Formaldehyde (µg/m^3)	< 2			

Sample Preparation

Input required information in blue cells

Date =

Film ID =

| Action	Approximate Action Duration	Comments
1. Remove film shipping package		
2. Record date and sample number (be sure to save spreadsheet with sample number in name)		
3. Wait 5 minutes to allow film package to reach room temperature		
4. Unwrap Sample (wear nylon or similar gloves).		
5. Using tweezers, place reference material in sample holder (refer to photo below). If possible, do this procedure with sample holder inside chamber.		
6. Seal chamber - This is time zero for the test.		
7. Sample loading complete		

Picture of Poly film in Film Frame in Chamber
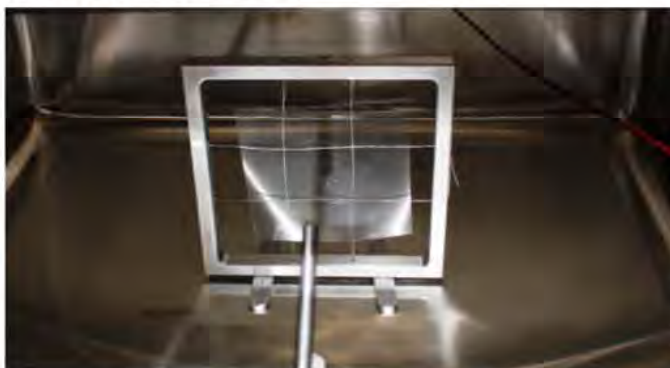
Photo of Film Frame with film in EPA small chamber.

If possible, please place holder in chamber where airflow is the same on either side of the sample.

For example, in this picture the holder is parallel to the main airflow streamlines of the mixing fan, which is blowing upward.

Chamber Air Sampling Information

Input required information in blue cells

Input these values

Start date:
Start time:

Conversion Factor
0.000694444

Spreadsheet to enter sampling data following schedule above.

Sample Description	Sampling Media	Vial(s) Tube ID	Sample Date	Start Time	End Time	Sample Time (midpoint)	Elapsed Time	Average Sample Flow (mL/min)	Sample Flow Standard Deviation (mL/min)	Sample Volume (collected L)	Sample Duration (min)	Comments
						#DIV/0!	#DIV/0!			0.00	0.0	Empty Chamber Background
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	
						#DIV/0!	#DIV/0!			0.00	0.0	

LC Calibration

Input required information in blue cells

Calibration Information

Formaldehyde Conc. (ug/mL)	RF RF

Calibration Values	RT (min)	RF
Average		
Std. Deviation		
%RSD		

Concentrations of Formaldehyde Measured during Test

Input required information in blue cells

Reporting Format:	nnn	In calibration
	nnn	Estimated value above quantification limit (bold italics)
	~~nnn~~	Estimated value below quantification limit (bold strikethrough)
	<u>nnn</u>	Estimated value below detection limit (bold underlined)

Sample ID	Description	Elapsed Time (h)	Sample Volume (L)	Formaldehyde Concentration (ug/m3)	Formaldehyde Concentration (ppb)

Formaldehyde Emission (ppb)

Elapsed Time (h)