

Standard Formaldehyde Source for Chamber Testing of Material Emissions: Model Development, Experimental Evaluation, and Impacts of Environmental Factors

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Abstract

Formaldehyde, which is recognized as a harmful indoor air pollutant for human health, is emitted mainly from urea-formaldehyde resin in wood products. Chamber tests are used to evaluate formaldehyde emission rates from these products. However, there is no available formaldehyde standard reference emission source to assess the performance of chamber testing systems. In this paper, a LIFE (liquid-inner tube diffusion-film-emission) formaldehyde reference is described. The formaldehyde source consists of a polytetrafluoroethylene (PTFE) tube that holds a formaldehyde-water solution with a concentration of 16 g formaldehyde per 100 mL water, with a thin polydimethylsiloxane (PDMS) film cover. Formaldehyde emission parameters for the PDMS film (diffusion coefficient and partition coefficient) were determined experimentally, thereby enabling the prediction of the formaldehyde emissions from the source for use as a reference value in a chamber. Chamber tests were conducted in a 51 L stainless steel ventilated chamber. The impacts of temperature and relative humidity on the emissions were investigated. Results show the LIFE's chamber test results match those predicted by a mass transfer model. As a result, this formaldehyde source may be used to generate a reference concentration in product emission testing chambers, thereby providing a powerful tool to evaluate the performance of the chamber testing systems.

Introduction

Formaldehyde is recognized as a harmful air pollutant for human health (1), which is emitted indoors primarily from resins containing formaldehyde (2) in wood-based materials (3, 4). The World Health Organization (WHO) recommends an indoor formaldehyde limit of 0.1 mg/m³ (0.08 ppm) (5). In order to support the control of formaldehyde emissions

from furniture and building materials, several emission models have been developed (6-12) to describe the emission processes. Also, labeling systems have been established that set testing protocols and the emission criteria (13).

Environmental chambers are commonly employed to measure formaldehyde emission from building materials (14). However, questions exist regarding the performance of environmental chamber testing systems and the errors associated with the measurements of formaldehyde emissions from building materials. Comparisons have been conducted of the performance of the different testing systems for the measurement of formaldehyde emissions from building materials (15-19). Inter-lab variation using European chamber testing methods is found to be 16 % (20).

While the use of an actual building material in laboratory intercomparisons has the advantage of being more realistic, there are also several disadvantages. These disadvantages include the following: (1) the true emission value of a building material is not known, meaning there is no reference value for comparing the results of the laboratory measurements; and (2) some building materials are inhomogeneous, resulting in differences between the emission rates of the samples used by different laboratories.

Paraformaldehyde permeation tubes can be used as a reference formaldehyde source to evaluate the performance of a chamber system (21, 22). However, the depolymerization of paraformaldehyde into monomeric formaldehyde in a chamber environment of 23 °C and 50 % can be slow and unstable. Therefore, the depolymerization usually takes place in a separate heated environment with a temperature higher than room temperature. A carrier gas then transports the depolymerized formaldehyde gas into the target environmental chamber for measurement. Therefore, the resulting chamber concentration is only influenced by the

mass of formaldehyde entering the chamber, and not the chamber environmental conditions (e.g. temperature, humidity).

Previous reference material development efforts have focused on the emission of toluene at a known rate. For example, a polymethyl pentene (PMP) film loaded to equilibrium with toluene has been shown to be a predictable emissions source (23, 24). Other toluene emission source studies include the development of diffusion bottles, such as a reference emitting material (REM) (25, 26) and the liquid-inner tube diffusion-film-emission (LIFE) reference (27, 28). The emission rate of the REM is determined using a micro-balance while the emission rate of LIFE can also be predicted by the mass transfer model. Given the importance of formaldehyde emissions to indoor air, a reference to evaluate the performance of chamber testing systems is needed. In the development of such a reference, five requirements need to be considered: (1) consistent emission rate among different reference samples; (2) an independent method to determine the emission rate of the reference; (3) simple procedures to use the reference and evaluate the chamber system; (4) emission rate dependence on chamber temperature and relative humidity; and (5) stability during shipping and storage.

Methods

Figure 1 is a schematic of the formaldehyde LIFE reference. It is comprised of a 3 mL polytetrafluoroethylene (PTFE) tube that holds approximately 1 mL of a 16 % solution of formaldehyde in water (i.e., formalin, at a concentration of 16 g formaldehyde per 100 mL

water) as the emission source.* A polydimethylsiloxane (PDMS) film of 0.13 mm thickness and 5 mm diameter covers the opening of the tube and controls the emission rate. Aluminum tape is used to hold the film in place. The emission rate of the LIFE reference was designed to generate formaldehyde concentrations of about 0.2 mg/m³, a value that is often reached in indoor formaldehyde tests in Chinese houses or apartments. In addition, the criteria value of the indoor formaldehyde concentration is 0.1 mg/m³ (0.08 ppm) in Chinese standard GB/T 18883-2002 (29). However, the emission rate of the LIFE reference can be modified by changing the thickness or scaling the emission area of the PDMS film, or changing the concentration of the formalin solution. Previous research on the toluene LIFE reference shows that scaling the emission area of the PDMS film is the easiest way to adapt the LIFE reference to different chamber volumes and concentration requirements (28).

Figure 1. Schematic of formaldehyde LIFE reference.

Figure 2. Schematic of LIFE in an environmental chamber.
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To independently predict the emission rate of the LIFE reference in an environmental chamber, a two-component diffusion model was developed. The parameters used in the model and depicted in figure 2 are as follows: (1) $C_{i,j}$, chemical concentration (mol/m³) at location i , with the following values for i : 1 (formaldehyde-water solution), b (tube headspace air), f (film) and a (chamber air); the subscript j is the target chemical, either W (water vapor) or F (formaldehyde); (2) D_j , the diffusion coefficient of each component in the

* Subsequent references to the formaldehyde concentration in the LIFE reference in this paper are expressed as percentages and refer to the g of formaldehyde per mL of water.

film (m^2/s); (3) K_j , the material/air partition coefficient of each component (-); and, (4) Q , airflow rate into and out of the chamber (m^3/s).

There are two diffusion stages for formaldehyde emission from the LIFE tube. One is the diffusion of formaldehyde in the tube headspace, and the other is the diffusion of formaldehyde through the PDMS film on top of the tube. In the mass transfer model of formaldehyde emissions from the LIFE reference, an assumption is made that the diffusion of formaldehyde through the PDMS film is the dominant diffusion stage during the emission process. As a result, the diffusion of formaldehyde in the tube headspace can be neglected. Based on this assumption, the formaldehyde concentration in the LIFE tube headspace is assumed to be homogeneous and can be calculated by Henry's law (30-32):

$$H = \exp(6548.6/T - 13.816) \quad (1)$$

where, H is the Henry's law constant (M/atm), and T is the temperature in the chamber (K).

The equilibrium formaldehyde concentration in the tube headspace can be calculated as:

$$C_{b,F} = \frac{m_{1,F} P_0}{MV_w HRT} \quad (2)$$

where, M is formaldehyde molar mass (g/mol), the V_w is the volume of the solution (L), $m_{1,F}$ is the formaldehyde mass in the solution (g), P_0 is the atmospheric pressure (Pa), and R is the gas constant (J/mol•K). Partition of formaldehyde to the film from the headspace air is described as:

$$C_{f,F} \Big|_{x=0} = K_F \cdot C_{b,F} \quad (3)$$

For each component, j , (j is W for water vapor or F for formaldehyde), the diffusion of mass in the PDMS film can be written as:

$$\frac{\partial C_{f,j}}{\partial t} = D_j \frac{\partial^2 C_{f,j}}{\partial x^2} \quad (4)$$

where, x is the dimension of the film (m) in the direction of the emissions and t is time (s). Assuming the formaldehyde concentration in the chamber's inlet airflow is zero, the mass conservation equation for the formaldehyde in chamber air is written as:

$$V \frac{dC_{a,F}}{dt} = -AD_F \frac{\partial C_{f,F}}{\partial x} \Big|_{x=L} - QC_{a,F} \quad (5)$$

where, V is the volume of the chamber (m^3); A is the emission area of the film (m^2); and L is the thickness of the film (m) If the chamber air is sufficiently well mixed such that the concentration can be represented by a single value, the boundary relation between $C_{a,F}$ and $C_{f,F}$ can be written as:

$$C_{f,F} \Big|_{x=L} = K_F \cdot C_{a,F} \quad (6)$$

The initial formaldehyde concentrations in the film and solution are:

$$C_{f,F} \Big|_{t=0} = 0 \quad (7)$$

$$m_{f,F} \Big|_{t=0} = 0.16 \quad (8)$$

Similar boundary conditions and initial conditions are applicable for the emission of water. However, the emission model can be simplified by assuming the emission rate of water is a constant, which is justified because the change of formaldehyde concentration in the water has a negligible impact on the concentration of water vapor in tube headspace as shown in figure S1 (see supporting information).

The emission profile of the formaldehyde described by equation (4) can be numerically solved by using a finite difference method and the formaldehyde concentration in the chamber described by equation (5) can be predicted if two key parameters, the diffusion coefficient of formaldehyde in the film (D_F) and the film/air partition coefficient (K_F), are known.

Experimental approach

Three steps are involved in defining the emission rate of the formaldehyde LIFE reference: (1) determination of the diffusion coefficient and the partition coefficient; (2) determination of the emission rate of water; and, (3) measurement of the formaldehyde emission rates in a chamber. Steps (1) and (2) are needed for the model prediction of formaldehyde emissions, which are subsequently compared with the chamber testing results in step (3). Table S1 shows the environmental conditions for all of the experiments conducted as part of this study. The LIFE is designed for typical chamber environments of 23 °C and 50 % relative humidity (RH). However, tests were also done at temperatures of 10 °C and 30 °C and with relative humidities of 33 %, 50 % and 70 % at each temperature set point. Environmental condition of 30 °C and 70 % relative humidity is not included due to limitations in the capability of the chamber employed in these tests. These tests enabled

the investigation of the sensitivity of emission rate of the LIFE reference to these environmental conditions.

Figure 3. System to determine D_F and K_F in the film.

To determine the diffusion coefficient and the partition coefficient under step (1), a piece of the PDMS film, 0.13 mm thick and 100 cm² in area, was pre-loaded with formaldehyde in a glass tube until it reached steady state using the system shown in the loading line in figure 3. A paraformaldehyde permeation tube was used as the formaldehyde source at a temperature of 80 °C and with a carrier gas of dry nitrogen at a steady flow rate of 270 ± 5 mL/min. Thus, the formaldehyde concentration from the permeation tube system for film loading is constant. The formaldehyde concentration in the loading tube was monitored by a calibrated Fourier transform infrared absorption (FTIR) to be sure each loading process reached steady state, which took no more than 12 h. The FTIR has a minimum detection limit of 0.01mg/m³ and a measurement uncertainty of 0.02 mg/m³. The loaded PDMS film was then placed in a 100 mL PTFE container with an airflow rate of 100 mL/min. The FTIR was used to monitor the formaldehyde concentration in the container until all of the formaldehyde in the film was emitted and the concentration decreased to zero. The procedure was repeated at each environmental (temperature and relative humidity) set point. The formaldehyde concentration in the film at the beginning of the emission process can be calculated as:

$$C_{F0} = \frac{\int C_{a,F} Q dt}{V_f} \quad (9)$$

where, V_f is the volume of the PDMS film sample (m^3), $C_{a,F}$ and C_{F0} are the chamber formaldehyde concentration during the emission process, and the initial formaldehyde concentration in the PDMS film, respectively (mg/m^3).

D_F and K_F can be determined by fitting the formaldehyde concentration in the chamber during the emission process, as shown in the emitting line in figure 3, to the prediction of a material emission model developed by Little et al. (6). A sequential quadratic programming (SQP) method (33) was used to do a two-parameter regression of the data to the model.

To determine the emission rate of water under step (2), a LIFE tube was filled with pure water. It was weighed every 24 h using an analytical balance, with a measurement uncertainty of 0.01 mg, to record the mass change with time. The test was repeated at each environmental set point listed in Table S1. The water emission rate at each set point can be calculated as:

$$\dot{m}_w = \frac{P_{b,w} - P_{a,w}}{P_{s,w} - P_{a,w}} \frac{dm}{dt} \quad (10)$$

where, \dot{m}_w is the water emission rate ($\mu g/s$), m is the mass of the LIFE tube with pure water (μg), and $P_{s,w}$, $P_{b,w}$ and $P_{a,w}$ are the saturation water vapor pressure, tube headspace water vapor pressure containing the formaldehyde-water solution, and water vapor pressure in the chamber air at each environmental set point (Pa) respectively.

To make the chamber tests under step (3), a 51 L stainless steel ventilated chamber located in an incubator was used. The system used for the chamber testing is shown in figure 4. The uncertainty in the control of the temperature is 0.1 °C and the uncertainty in the control of the relative humidity is 1 %. Formaldehyde free humidified air was connected to

the chamber inlet to maintain a chamber air change rate of 1 h^{-1} . The chamber outlet was connected to the FTIR to analyze the formaldehyde concentration in the air. Before each test, the chamber environmental control system was set at the desired set point as listed in Table S1 and maintained stable for at least one hour. Clean humidified air at a relative humidity set point, which was used as inlet gas to the chamber during the tests, was supplied into the chamber before starting a new test for at least 12 h to make sure that the chamber was formaldehyde free. This initial condition was verified by assuring that the variation of the chamber formaldehyde background concentration was within 0.02 mg/m^3 .

An ampule of 16 % standard formaldehyde solution was opened in a fume hood and 1 mL of the solution was transferred from the ampule to the LIFE tube within five seconds. The cover for the tube was then fastened within five seconds. The loaded formaldehyde LIFE was then placed in the center of the bottom of the chamber. The chamber was closed and sealed within two minutes to minimize the impacts of initial leakage of formaldehyde from the chamber. The formaldehyde concentration in the chamber emitted from LIFE was monitored with the FTIR until it reached steady state, which generally occurred within 24 hours. The measured formaldehyde concentration was then compared with the model predictions.

Figure 4. System for LIFE reference chamber test.

Results and discussion

Table 1. Emission parameters of LIFE.

Measurement of diffusion and partition coefficient. Figure S2 is an example of the formaldehyde concentration during the loading and emitting processes at 23 °C and 50 % relative humidity. Figure S3 shows the curve fit of the emitting processes used to determine the diffusion coefficients of formaldehyde in the PDMS film and the material/air partition coefficient. The resulting value and the standard deviation of D_F is $(1.40 \pm 0.1) \times 10^{-11}$ m²/s, while the value and the standard deviation of K_F is 1000 ± 100 (-). The values of the diffusion and partition coefficients, the water emission rates, and their standard deviations at each environmental set point are listed in Table 1.

Model predictions and chamber tests. Based on the chamber test results, the diffusion coefficient increases but the partition coefficient decreases as the temperature increases. Relative humidity has a negative impact on the diffusion coefficient. However the impact of relative humidity on the partition coefficient is less clear. The chamber results for 24 h at 23 °C and 50 % relative humidity are shown in Figure 5. Three replicate formaldehyde LIFE reference samples (#1, #2, and #3) were made and tested in the chamber to investigate the uniformity of different LIFE samples. The three samples consisted of the same size PTFE tube and PDMS film that was cut from the same roll. The emissions of the references resulted in the formaldehyde concentration in the chamber increasing to 0.25 mg/m³ in 24 h, which is in the range of a typical furniture emission rate. The standard deviation of the formaldehyde concentrations in the chamber at 12 h for the three references samples was 16 %, while the standard deviation of the steady state concentration (20 h to 24 h) of the three references was 5 %. The tests for LIFE #1 were repeated three times to evaluate the repeatability of a single LIFE sample. The resulting average steady-state concentration (20 h

to 24 h) was 0.25 mg/m^3 with a standard deviation of 8 %. However, the deviations of the formaldehyde concentrations during the first 12 hours are larger than at steady state, which is often observed in building material emission tests. This larger deviation might be due to two possible causes. First, about 2 minutes were needed to open the target chamber, put the LIFE reference into the chamber, and seal the chamber. Therefore, fluctuation in the temperature and relative humidity in the chamber are unavoidable at the beginning of the test period. Second, the chamber air was less well mixed at the beginning of the test period. Therefore, the air sampled from the chamber's exhaust would not necessarily represent the formaldehyde concentration in the chamber air. However, once the chamber reached steady-state, all the measured formaldehyde concentrations were within 2 %, which indicates the uniformity of the PDMS film and the repeatability of the experiment.

Figure 6 shows the comparison between the mean value of the chamber formaldehyde concentrations of Figure 5 and that predicted by the model described earlier. The difference in the steady state concentrations between the measurements and predictions is less than 3 %, while the difference is larger than 10 % during the initial 2 h of the chamber tests. More comparisons between the measured steady state formaldehyde chamber concentrations and model predictions are listed in Table 2. The chamber testing results of the formaldehyde concentrations in the chamber match the model predictions within 5 % in most cases. However, the differences between them are larger than 20 % when the chamber environmental set points are 23 °C, 70 % relative humidity and 30 °C, 50 % relative humidity. These larger differences may occur because the proportion integration differentiation controller of the chamber system could not precisely control the temperature and relative humidity at these conditions.

Table 2. Comparisons of the steady state formaldehyde concentrations between chamber testing results and model predictions.
Figure 5. Chamber testing results for 24 h measurement at 23 °C and 50 % relative humidity.
Figure 6. Comparison between chamber testing results and model prediction.

The emitted mass of water and formaldehyde over 24 h of testing are shown in Table S2, which is less than 10 mg at all the environmental conditions. The total amount of emitted mass in 24 h is less than 0.9 % of the total emittable amount. Figure S4 shows the model prediction of the formaldehyde concentration in the chamber over 1000 h at 23 °C and 50 % relative humidity (the green line with the upper x-axis and right y-axis), along with the chamber measurements for 72 h (the blue dots and red line with the lower x-axis and left y-axis). The lifetime of LIFE is longer than 1000 h, which is enough to meet the requirements of the furniture labeling systems, the testing durations of which are normally less than 28 days (13).

Temperature and relative humidity influence. Previous research on wood board emissions show that temperature can greatly affect the formaldehyde diffusion coefficient and the wood/gas partition coefficients, thereby changing the emission rate (34-36). Temperature impacts were also investigated for the LIFE reference. In general, temperature affects the LIFE's emission rate through changes in the Henry's law constant, the formaldehyde concentration in the reference tube headspace, the diffusion coefficient of formaldehyde in the PDMS film and the partition coefficient in the material/gas interference. Since relative humidity plays a less important role compared to temperature, the diffusion

and partition coefficients and the formaldehyde concentration in the chamber from step (1) to (3) at each temperature set point were averaged and are shown in Figure 7 as a summary of the temperature effect on LIFE. Values of the diffusion coefficient and partition coefficient of formaldehyde in the PDMS film and the steady state formaldehyde concentration in the chamber at 23 °C were used as reference values for comparison. The ratio of the emission parameters at 30 °C and 10 °C relative to those at 23 °C reveals the temperature impact. The correlations between emission parameters and temperature can be written as:

$$\frac{D_F|_T}{D_F|_{23^\circ\text{C}}} = 0.20 \exp(0.076T) \quad (11)$$

$$\frac{K_F|_T}{K_F|_{23^\circ\text{C}}} = 5.40 - 1.41 \ln(T) \quad (12)$$

$$\frac{C_{a,F}|_T}{C_{a,F}|_{23^\circ\text{C}}} = 0.17 \exp(0.075T) \quad (13)$$

The fitting accuracies of the correlations between the emission parameters and temperature are characterized by R^2 values, which are 0.97 for the correlation between the diffusion coefficient and temperature, 0.99 for the correlation between the partition coefficient and temperature, and 0.99 for the correlation between the predicted concentration and temperature.

Figure 7. Correlations between emission parameters and temperature.

Since the LIFE formaldehyde reference is placed inside the target chamber, its emission rate is affected by the chamber environment (e.g. temperature, humidity) similar to a typical

building material's emissions. Thus, if the chamber environment (e.g. temperature, humidity) is poorly controlled, the measured emission rate of the LIFE reference would potentially deviate from the reference value.

Chamber testing of formaldehyde emissions from building materials are often done at a temperature of 23 °C. Given a potential temperature fluctuation of ± 0.5 °C in the chamber (14), the corresponding variation of steady state formaldehyde concentration is ± 4 %, which is a key component of the uncertainty associated with the temperature effect in the chamber testing method.

The influence of relative humidity on the LIFE's formaldehyde emission is much less compared to the influence of temperature. In general, relative humidity affects the LIFE's emission rate due to the change in water emission rate, the diffusion coefficient of formaldehyde in the PDMS film and the partition coefficient in the material/gas interference. Figure S5 shows the humidity influence on the diffusion and partition coefficients, water emission rate and the predicted steady state formaldehyde concentration at a temperature of 23 °C. Emission parameters at 50 % relative humidity were used as reference values in this comparison. Given a relative humidity fluctuation of ± 5 % at 23 °C (14), the corresponding variation in the steady state formaldehyde concentration is ± 6 %, which is an indicator of the uncertainty associated with the humidity effect in the chamber testing method.

The LIFE reference is designed to emit formaldehyde at a rate that is typical of a building material for a given product testing procedure. Therefore, the difference between the measured formaldehyde concentration and the predicted reference formaldehyde concentration in the chamber can also be influenced by errors in the testing procedure, e.g., calibration error of the chemical analysis instrument, in chamber air sampling, or in chamber operation.

This study has demonstrated that the formaldehyde LIFE reference meets the requirements stated earlier for a reference emission source: (1) uniform for different LIFE sources; (2) consistency with an independent method to determine the reference emissions; and, (3) able to reveal the controlling accuracy of the temperature and relative humidity in the chamber. In order to use it as a reference to evaluate the performance of chamber testing systems for measuring formaldehyde emissions from building materials, the LIFE tube and the standard formaldehyde-water solution could be shipped to testing laboratories. They could also be provided with the reference steady state formaldehyde concentration under a certain temperature, relative humidity, and airflow rate. The laboratory could then follow defined protocols to load the LIFE reference and test it in a chamber for a specific amount of time, nominally 24 h. The formaldehyde concentration in the chamber should then match the reference value predicted by the model within a prescribed level of agreement. In conclusion, the LIFE reference appears to be a useful reference for the evaluation of the performance of chamber testing system.

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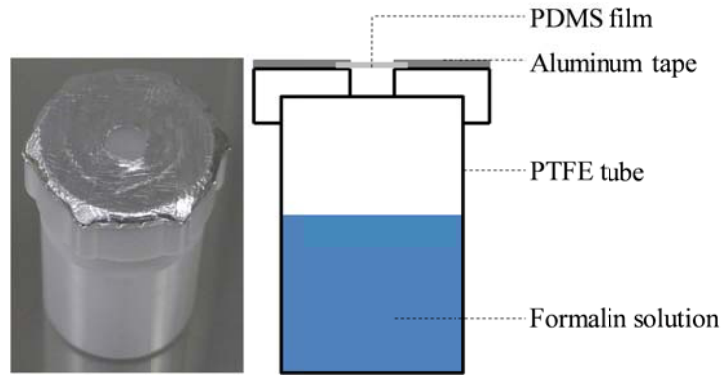


Figure 1. Schematic of formaldehyde LIFE reference.

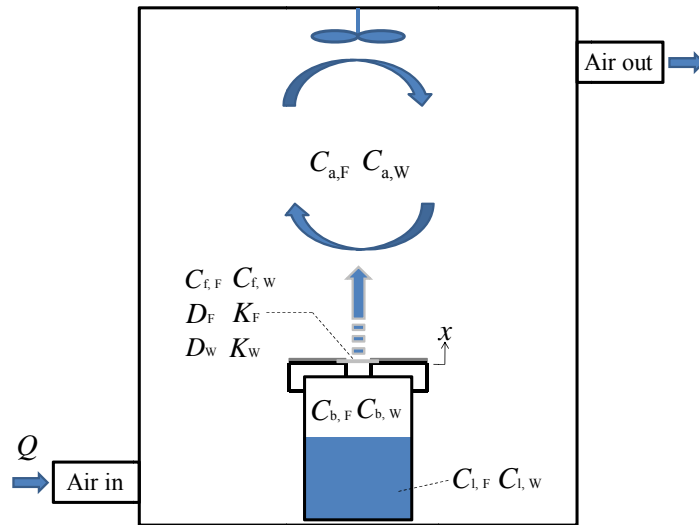


Figure 2. Schematic of LIFE in an environmental chamber.

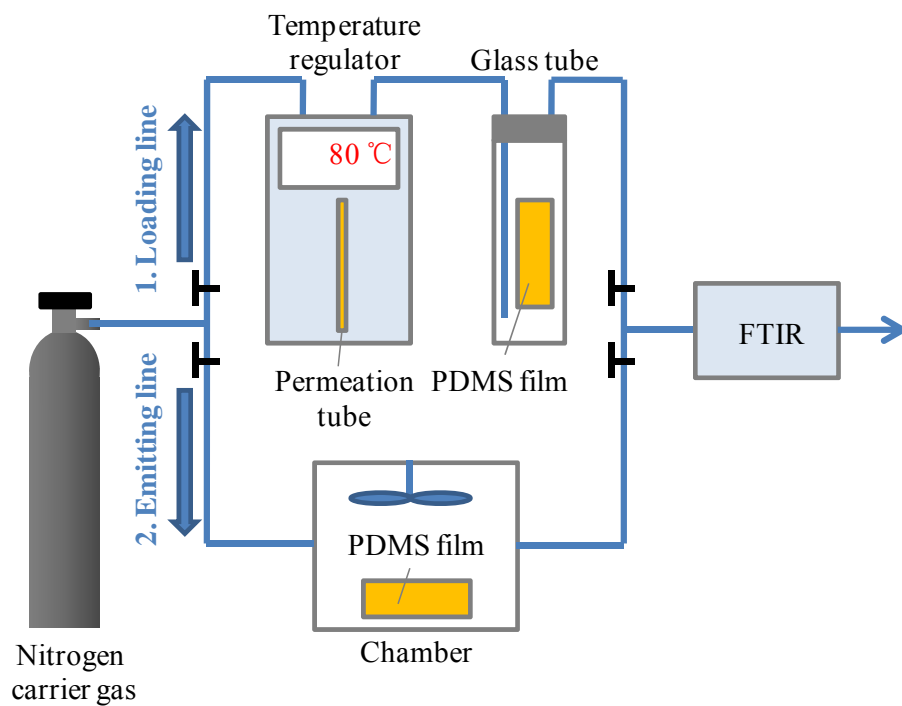


Figure 3. System to determine D_F and K_F in the film.

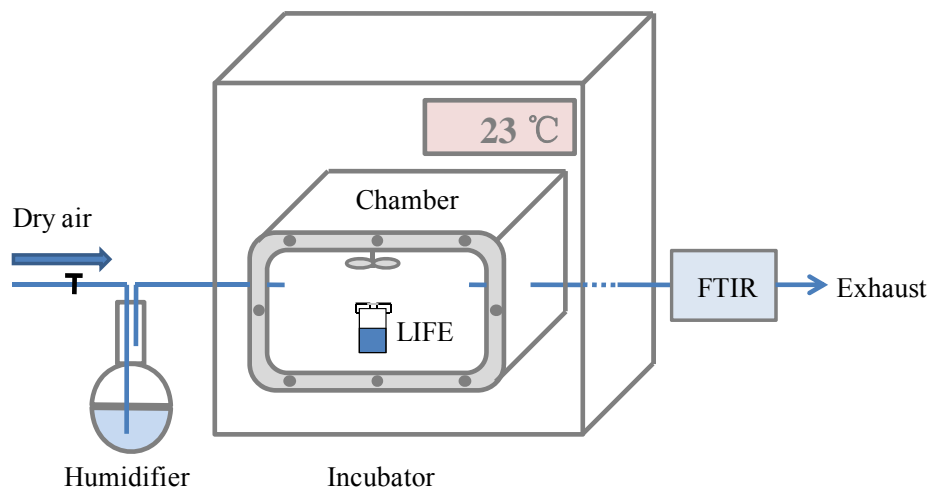


Figure 4. System for LIFE reference chamber test.

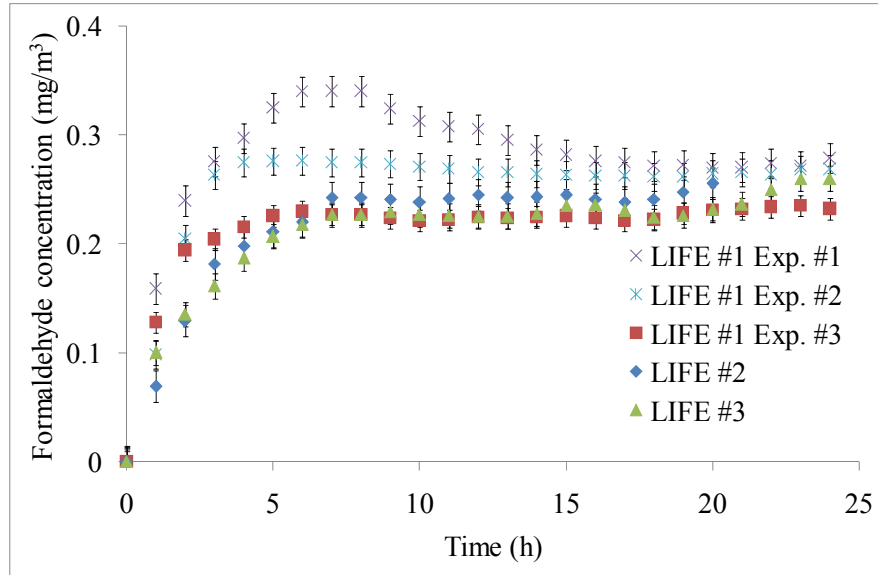


Figure 5. Chamber testing results for 24 h measurement at 23 °C and 50 % relative humidity.

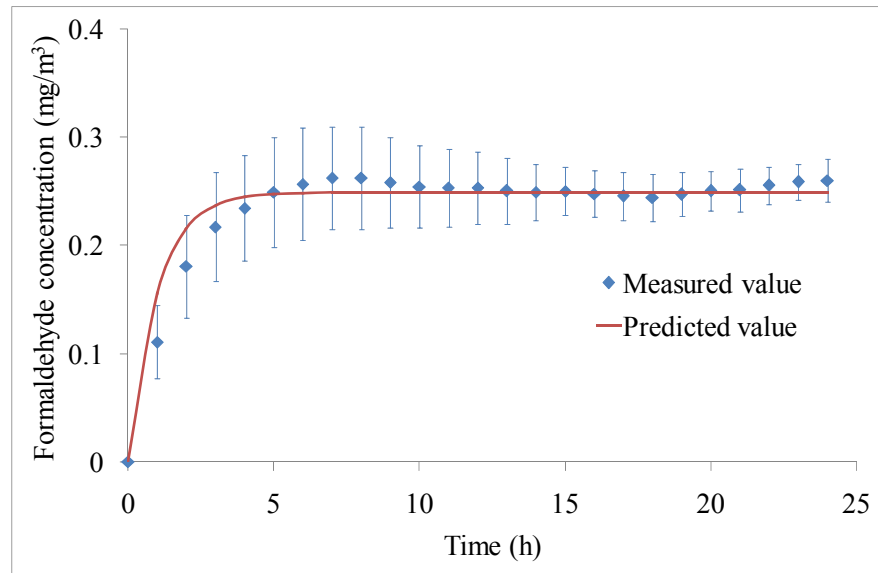


Figure 6. Comparison between chamber testing results and model prediction.

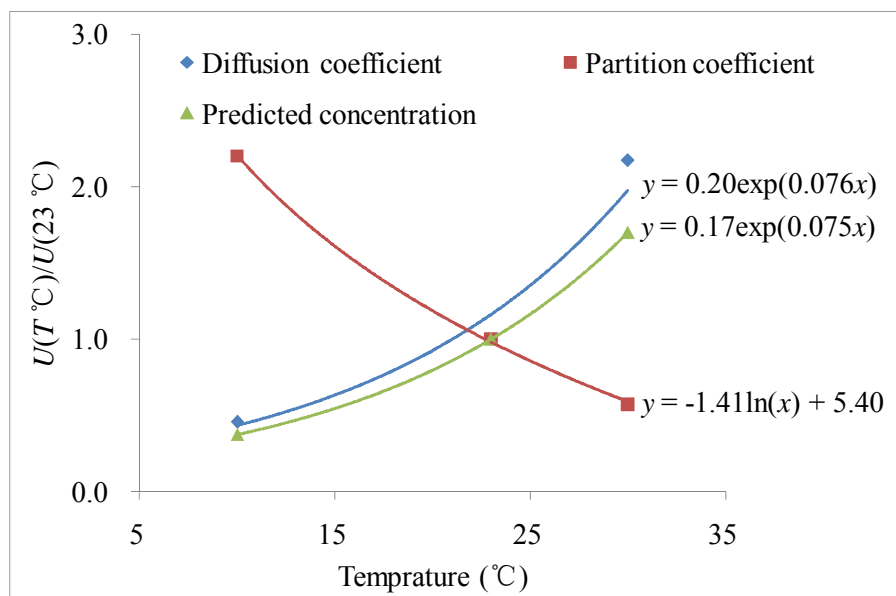


Figure 7. Correlations between emission parameters and temperature.

Table 1. Emission parameters of LIFE.

Environmental condition		D_F (m^2/s)	K_F (-)	\dot{m}_w ($\mu g/s$)
10 °C	33 % RH	$(7.7 \pm 1.1) \times 10^{-12}$	$(2.2 \pm 0.1) \times 10^3$	$(2.4 \pm 0.3) \times 10^{-2}$
	50 % RH	$(7.6 \pm 1.0) \times 10^{-12}$	$(2.2 \pm 0.1) \times 10^3$	$(1.6 \pm 0.2) \times 10^{-2}$
	70 % RH	$(6.0 \pm 1.4) \times 10^{-12}$	$(2.2 \pm 0.1) \times 10^3$	$(0.5 \pm 0.2) \times 10^{-2}$
23 °C	33 % RH	$(1.7 \pm 0.3) \times 10^{-11}$	$(1.0 \pm 0.1) \times 10^3$	$(5.1 \pm 0.3) \times 10^{-2}$
	50 % RH	$(1.4 \pm 0.1) \times 10^{-11}$	$(1.0 \pm 0.1) \times 10^3$	$(3.4 \pm 0.3) \times 10^{-2}$
	70 % RH	$(1.3 \pm 0.4) \times 10^{-11}$	$(1.0 \pm 0.1) \times 10^3$	$(2.1 \pm 0.2) \times 10^{-2}$
30 °C	33 % RH	$(3.5 \pm 0.4) \times 10^{-11}$	$(5.0 \pm 0.2) \times 10^2$	$(9.0 \pm 0.2) \times 10^{-2}$
	50 % RH	$(3.0 \pm 0.2) \times 10^{-11}$	$(5.0 \pm 0.2) \times 10^2$	$(7.5 \pm 0.1) \times 10^{-2}$
	70 % RH	N	N	N

Table 2. Comparisons of the steady state formaldehyde concentrations between chamber testing results and model predictions.

Environmental condition		33 % RH	50 % RH	70 % RH
10 °C	$C_{\text{measured}} \text{ (mg/m}^3\text{)}$	1.2×10^{-1}	1.2×10^{-1}	1.0×10^{-1}
	$C_{\text{predicted}} \text{ (mg/m}^3\text{)}$	1.1×10^{-1}	1.1×10^{-1}	8.9×10^{-2}
	Difference	4 %	3 %	13 %
23 °C	$C_{\text{measured}} \text{ (mg/m}^3\text{)}$	3.7×10^{-1}	2.6×10^{-1}	2.8×10^{-1}
	$C_{\text{predicted}} \text{ (mg/m}^3\text{)}$	3.5×10^{-1}	2.5×10^{-1}	2.3×10^{-1}
	Difference	3 %	2 %	21 %
30 °C	$C_{\text{measured}} \text{ (mg/m}^3\text{)}$	4.6×10^{-1}	5.6×10^{-1}	N
	$C_{\text{predicted}} \text{ (mg/m}^3\text{)}$	5.1×10^{-1}	4.3×10^{-1}	N
	Difference	9 %	30 %	N

Supporting Information

Requirements for choosing an appropriate diffusion film. There are three requirements for choosing an appropriate diffusion film for the formaldehyde LIFE reference: (1) the diffusion resistance of the diffusion film needs to be high enough to prevent the influence of the convective mass transfer in the chamber air on the emission rate; (2) the formaldehyde concentration in the chamber air needs to be able to reach steady state during chamber testing time; and, (3) the ratio of the emission rate of formaldehyde from LIFE to the emission rate of water vapor from LIFE needs to be similar to the formaldehyde concentration in the formaldehyde-water solution. The third requirement leads to the formaldehyde concentration in the formaldehyde-water solution being roughly stable during the chamber testing time. Several different diffusion films were tested to study their emission characteristics and the PDMS film was identified as the one that best meets these three requirements.

Choosing the formaldehyde-water solution. Higher formaldehyde concentrations in the water solution could provide stronger emission sources, but the instability of formaldehyde in the water solution and in the mass transfer process due its tendency to polymerize at high concentration makes higher concentrations less desirable. The 16 % solution of formaldehyde in water (16 g formaldehyde per 100 mL of water) is sufficiently stable and is commercially available. The resulting chamber concentration with this source is at a detectable level and similar to concentrations measured during product testing.

Formaldehyde concentration gradient in the LIFE tube headspace. The simulation of the formaldehyde concentration gradient in the LIFE tube headspace shows that the difference in the formaldehyde concentrations within the headspace at 23 °C and 50 % relative humidity is 4 %, which supports the assumption.

The validity of this assumption can be further established by comparing the formaldehyde diffusion resistances between the LIFE tube headspace and the PDMS film. The formaldehyde diffusion coefficient in the LIFE tube headspace can be calculated using the Chapman-Enskog equation, which yields 1.4×10^{-5} m²/s. The formaldehyde diffusion resistances in the LIFE tube headspace and through the PDMS film at 23 °C and 50 % relative humidity can be calculated by:

$$R_{b,F} = \frac{L_b}{A_b D_{b,F}} \quad (S1)$$

$$R_{f,F} = \frac{L_f}{A_f D_{f,F} K_{f,F}} \quad (S2)$$

where, $R_{b,F}$ and $R_{f,F}$ are the diffusion resistance of formaldehyde in the LIFE tube headspace and through the PDMS film, respectively (s/m³), L_b and L_f are the height of the LIFE tube headspace and the thickness of the PDMS film, respectively (m), A_b and A_f are the area of the headspace opening and the emission area of the PDMS film, respectively (m²), $D_{b,F}$ and $D_{f,F}$ are the diffusion coefficient of formaldehyde in the headspace air and through the PDMS film, respectively (m²/s), and $K_{f,F}$ is the PDMS/air partition coefficient of formaldehyde (-).

The formaldehyde diffusion resistances calculated are 2×10^7 s/m³ in the LIFE tube headspace and 5×10^8 s/m³ through the PDMS film, respectively. The ratio of the formaldehyde diffusion resistance in the LIFE tube headspace to that through the PDMS film is 4 %, which supports the assumption that the diffusion resistance of formaldehyde

through the PDMS film is dominant during the formaldehyde emitting process while the diffusion resistance of formaldehyde in the tube headspace can be neglected. Therefore, the formaldehyde concentration in the LIFE tube headspace can be treated homogeneous and calculated by Henry's law as a simplification of the mass transfer model of LIFE's formaldehyde emission.

Formaldehyde diffusing through the PTFE tube. It is possible for the formaldehyde molecules to diffuse through both the PDMS film and the PTFE tube. However, the thickness of the PDMS film is 0.13 mm while the thickness of the PTFE tube is 3 mm. In order to validate that the diffusion of formaldehyde molecules through the PTFE tube can be neglected, the same formaldehyde-water solution was put into the PTFE tube. A PTFE cover made by the same material as the PTFE tube was used to seal the tube instead of using the PDMS. The same analytical balance with a measurement uncertainty of 0.01 mg was then used to monitor the mass of the PTFE tube containing the formaldehyde-water solution at a temperature of 23 °C for 5 days. No mass decay of the formaldehyde-water solution was observed in this test. Therefore, the diffusion of formaldehyde molecules through the PTFE tube can be neglected.

Influence of formaldehyde vapor on water vapor in LIFE tube headspace. The water vapor pressure in the tube headspace ($P_{b,w}$) can be calculated by Raoult's law, which is related to the water saturation vapor pressure ($P_{s,w}$) and the water molar fraction in the solution ($y_{l,w}$) as:

$$P_{b,w} = y_{l,w} P_{s,w} \quad (S3)$$

The relationships between the formaldehyde concentration in the solution and the water vapor pressure in the tube headspace at temperatures of 10 °C, 23 °C and 30 °C, respectively are shown in figure S1. Initially when the formaldehyde concentration is 16 % (i.e., 16 g of formaldehyde per 100 mL of water) , the water vapor pressure in the tube headspace is 91.2 % of the water saturated vapor pressure under the same temperature. The change in the water vapor pressure in the tube headspace is within ± 5.3 % when the formaldehyde concentration in the solution changes ± 10 % (g of formaldehyde per mL of water) in the range of 6 % (g of formaldehyde per mL of water) to 26 % (g of formaldehyde per mL of water). The influence of formaldehyde concentration in the solution on the water vapor in the tube headspace is therefore negligible. Thus, the emission model can be simplified by assuming the emission rate of water is a constant, which can be measured independently.

Lifetime of formaldehyde LIFE. The formaldehyde vapor pressure in the LIFE tube headspace is 133 Pa while the water vapor pressure is 3810 Pa at 23 °C for the formaldehyde-water solution of 16 % (g of formaldehyde per mL of water). The predicted steady state formaldehyde concentration in the chamber increases slowly because the emission rate of formaldehyde molecules is slower than that of the water molecules at 23 °C and 50 % relative humidity. Simulation shows that the formaldehyde concentration in the chamber increases 4 % from 24 h to 1000 h after the emission starts and the formaldehyde concentration in the formaldehyde-water solution increases from 16 % to 17 % (g of formaldehyde per mL of water) after 1000 h. However during the first 24 hours of the test, the opposite phenomenon is observed in which the emission of formaldehyde molecules are relatively faster than that of the water molecules. There are two reasons for this phenomenon. First, at the beginning of the test, the formaldehyde concentration in the PDMS film is zero,

which enhances the emission of formaldehyde. Second, at the beginning of the test, the formaldehyde concentration in the air in the chamber is zero, which also enhances the emission of formaldehyde until it reaches steady state. Meanwhile, the emission of water vapor is stable during the whole testing period because the relative humidity is controlled at $50 \pm 1 \%$ in the chamber. In general, the initial condition in the PDMS film and in the chamber air enhances the emission of formaldehyde until the system reaches steady state.

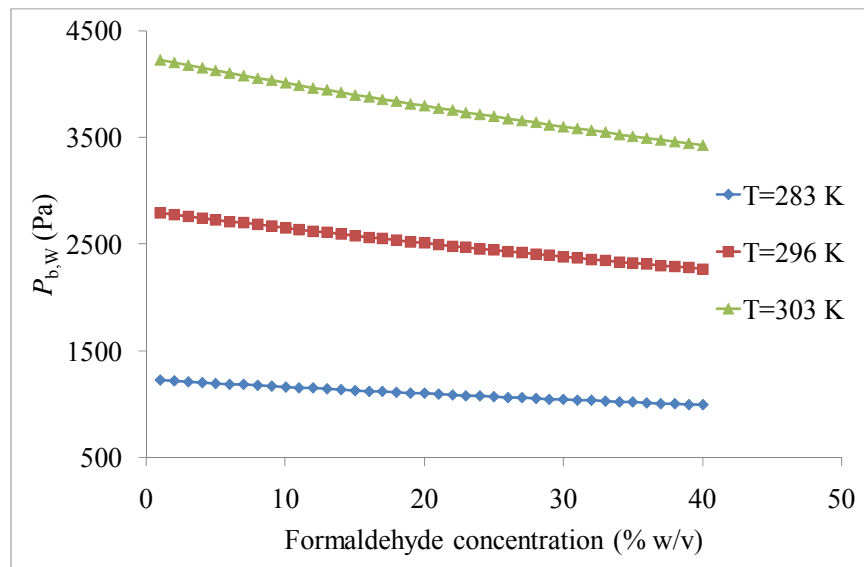


Figure S1. The relationship between the formaldehyde concentration in the solution and the water vapor pressure in the tube headspace.

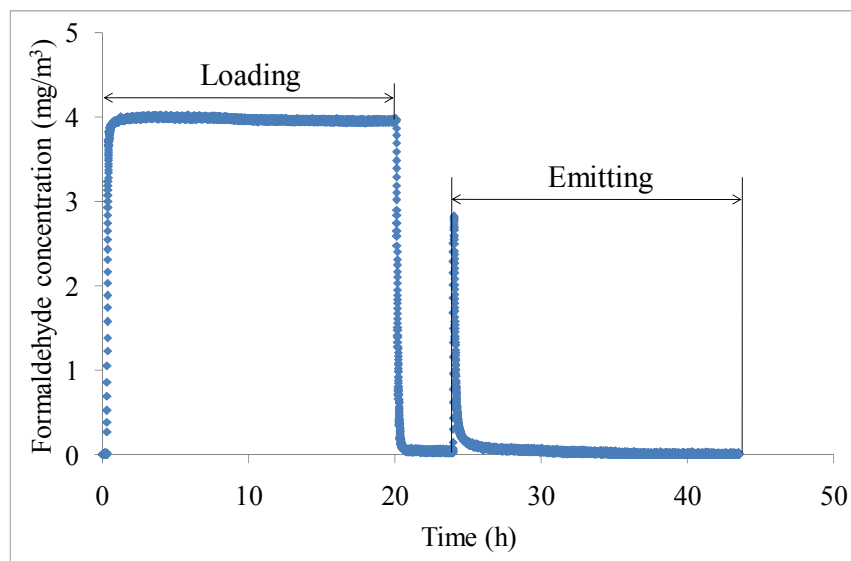


Figure S2. Formaldehyde concentration during loading and emitting processes.

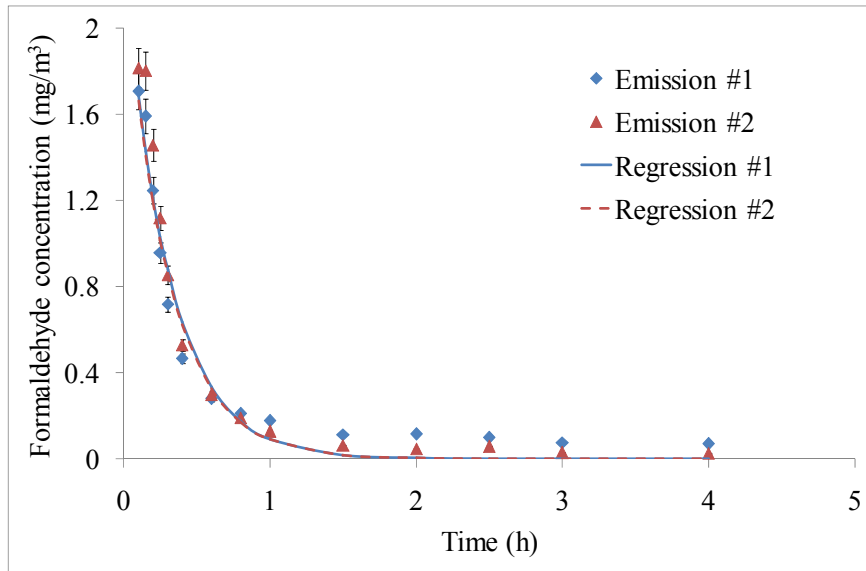


Figure S3. Determination of D_F and K_F at 23 °C and 50 % relative humidity.

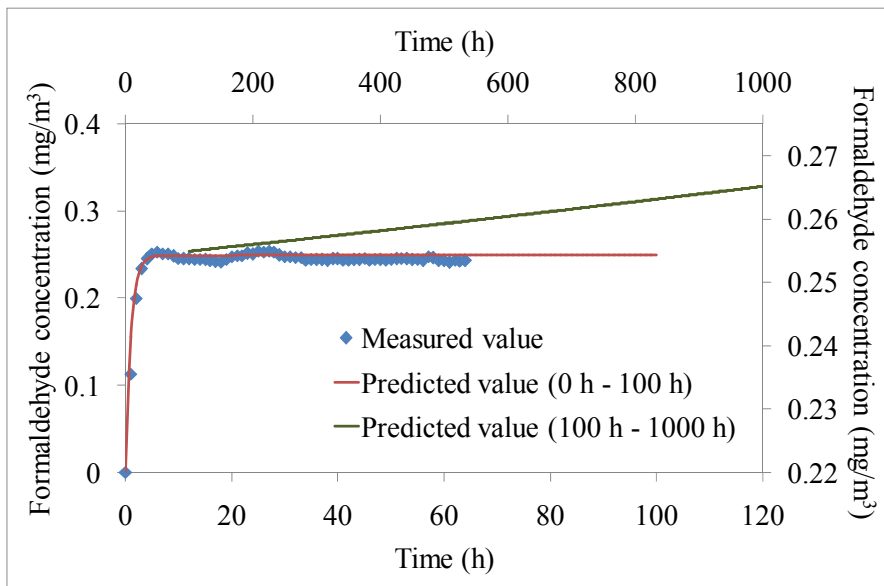


Figure S4. Prediction and measurement of LIFE's long-time emission.

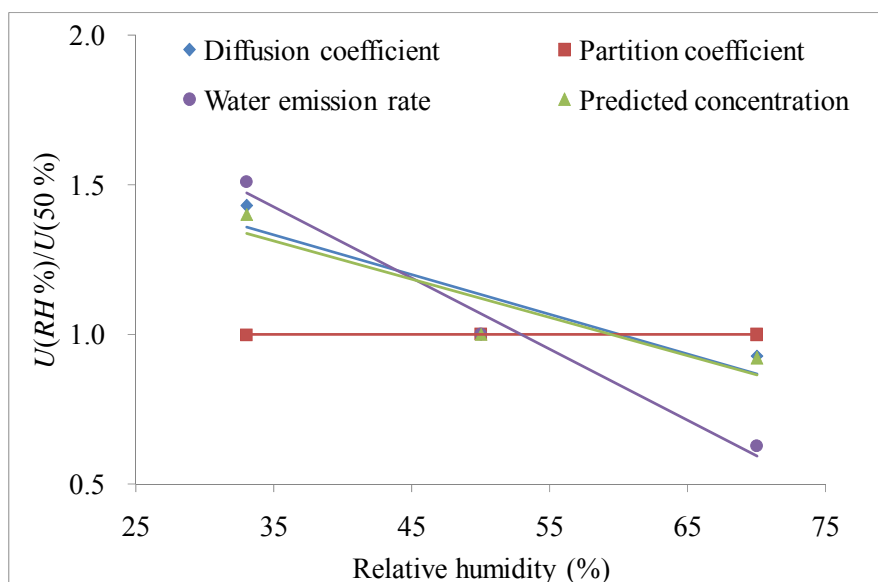


Figure S5. Influence of relative humidity on emission parameters.

Environmental condition		Determine D_F and K_F in the film	Determine the emission rate of water	Chamber test
10 °C	33 % RH	Y	Y	Y
	50 % RH	Y	Y	Y
	70 % RH	Y	Y	Y
23 °C	33 % RH	Y	Y	Y
	50 % RH	Y	Y	Y
	70 % RH	Y	Y	Y
30 °C	33 % RH	Y	Y	Y
	50 % RH	Y	Y	Y
	70 % RH	N	N	N

Table S1. Environmental conditions for all the experiments.

Environmental condition		Emitted mass of formaldehyde in 24 h (mg)	Emitted mass of water in 24 h (mg)
10 °C	33 % RH	0.3	2.1
	50 % RH	0.3	1.4
	70 % RH	0.2	0.4
23 °C	33 % RH	0.8	4.4
	50 % RH	0.6	2.9
	70 % RH	0.5	1.8
30 °C	33 % RH	1.2	7.8
	50 % RH	1.0	6.5
	70 % RH	N	N

Table S2. Emitted mass of formaldehyde and water in 24 h.