Passive flux sampler for measurement of formaldehyde emission rates

4 AUTHORS, INCLUDING:

Naohide Shinohara
National Institute of Advanced Industr…
43 PUBLICATIONS **500** CITATIONS

SEE PROFILE

Minoru Fujii
National Institute for Environmental S…
74 PUBLICATIONS **679** CITATIONS

SEE PROFILE

Akihiro Yamasaki
Seikei University
196 PUBLICATIONS **1,776** CITATIONS

SEE PROFILE

Passive flux sampler for measurement of formaldehyde emission rates

Naohide Shinohara[a,*], Minoru Fujii[b], Akihiro Yamasaki[c], Yukio Yanagisawa[d]

[a]*Research Center for Chemical Risk Management (CRM), National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba-Shi, Ibaraki 305-8506, Japan*
[b]*Research Center for Material Cycles and Waste Management, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba-Shi, Ibaraki 305-8506, Japan*
[c]*Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba-Shi, Ibaraki 305-8506, Japan*
[d]*Institute of Environmental Studies, Graduate School of Frontier Sciences, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Abstract

A new passive flux sampler (PFS) was developed to measure emission rates of formaldehyde and to determine emission sources in indoor environments. The sampler consisted of a glass Petri dish containing a 2,4-dinitrophenyl hydrazine (DNPH)-impregnated sheet. At the start of sampling, the PFS was placed with the open face of the dish on each of the indoor materials under investigation, such as flooring, walls, doors, closets, desks, beds, etc. Formaldehyde emitted from a source material diffused through the inside of the PFS and was adsorbed onto the DNPH sheet. The formaldehyde emission rates could be determined from the quantities adsorbed. The lower determination limits were 9.2 and 2.3 $\mu g\,m^{-2}\,h^{-1}$ for 2- and 8-h sampling periods. The recovery rate and the precision of the PFS were 82.9% and 8.26%, respectively. The emission rates measured by PFS were in good agreement with the emission rates measured by the chamber method ($R^2 = 0.963$). This shows that it is possible to take measurements of the formaldehyde emission rates from sources in a room and to compare them. In addition, the sampler can be used to elucidate the emission characteristics of a source by carrying out emission measurements with different air-layer thicknesses inside the PFS and at different temperatures. The dependency of the emission rate on the thickness of the air layer inside the PFS indicated whether the internal mass transfer inside the source material or the diffusion in the gas-phase boundary layer controlled the formaldehyde emission rate from a material. In addition, as a pilot study, the formaldehyde emission rates were measured, and the largest emission source of formaldehyde could be identified from among several suspected materials in a model house by using the PFS.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Flux; Emission source; Formaldehyde; Boundary layer; Rate-limiting process; Passive sampler

1. Introduction

Recently, buildings are being constructed to be more tightly sealed off from the external

---

*Corresponding author. Tel.: +81 29 861 8030; fax: +81 29 861 8415.

E-mail address: n-shinohara@aist.go.jp (N. Shinohara).

atmosphere, and the use of new types of building materials has caused air pollution problems inside many houses in Japan. Many people are suffering from sick building syndrome (SBS) and from multiple chemical sensitivity (MCS). Formaldehyde emitted from adhesives, bleach, fungicides, etc., has been reported to be one of the chemical substances responsible for causing SBS and MCS symptoms, e.g., eye irritation, respiratory tract irritation, dizziness, fatigue and neurotoxicity (Kim et al., 2002; Paustenbach et al., 1997; Shinohara et al., 2004). Indoor concentrations of formaldehyde in Japanese houses have been reported at 39.9 ± 33 (Amagai et al., 2000) and $78.9 \pm 22 \, \mu g \, m^{-3}$ (Shinohara et al., 1999) in summer, and 58.6 ± 20 (Shinohara et al., 1999) and $17.6 \pm 1.8 \, \mu g \, m^{-3}$ (Sakai et al., 2004) in winter. The guidelines set by the Japanese Ministry of Health, Labour and Welfare (MHLW) and by the World Health Organization (WHO) for formaldehyde in indoor air are $100 \, \mu g \, m^{-3}$ (0.08 ppm) based on levels that have been shown to cause nose and throat irritation in humans (MHLW, 2000; WHO, 1999). The reference concentration of formaldehyde in the atmosphere was recommended to be 0.01 ppm based on carcinogenic effects (Naya and Nakanishi, 2005). In Japan, plywood and particle board are classified into four categories depending on their formaldehyde emission rates as measured by emission chamber or desiccator methods, and the areas in which these materials can be used in house construction are limited by their classification and by the ventilation capacity of the house (MLIT, 2002).

Although it would be desirable to remove the primary emission sources of formaldehyde, it is difficult to determine which sources significantly affect the indoor air quality because there are several possible sources in indoor environments, such as flooring, doors, closets, desks, beds, etc. Emission chambers (IHCP, 1999; ASTM, 1996, 1997; JISC, 2003; Tichenor, 1989), the desiccator method (JISC, 2001), and field and laboratory emission cells (FLEC) (Wolkoff et al., 1991; Uhde et al., 1998; Risholm-Sundman, 1999) have been used to measure the emission rates of chemical compounds from building materials. The emission rates from sample materials, however, cannot be measured in a real room by using the chamber or desiccator methods. Thus, the emission sources cannot be identified in a real room by using these methods. Although FLECs can be used in both the field and the laboratory, they are unsuitable for multipoint field sampling because of size, weight, and cost considerations.

In this study, a new passive flux sampler (PFS) was developed which is easy to use to measure emission rates of formaldehyde and which can be used in standard methods for measuring such emission rates. Primary emission sources of formaldehyde could be easily identified using the sampler. In addition, pilot studies suggest that the PFS can be used for the determination of emission characteristics of formaldehyde sources.

2. Methods

2.1. PFS design

The PFS is shown in Fig. 1. A glass Petri dish (inner diameter: 36 mm, depth: 10 or 28 mm) was used as the frame of the PFS. At the start of sampling, a 2,4-dinitrophenylhydrazine (DNPH)-coated glass filter (OLBO 827, Supelco Co., USA) (referred to below as a "DNPH sheet") was placed on the bottom of the Petri dish as an adsorbent.

2.2. Sampling procedure

At the start of sampling, a DNPH sheet was placed at the bottom of the Petri dish. The PFS was then placed with the open face facing each of the materials to be tested, such as flooring, walls, ceilings, doors, closets, desks, beds, etc. Formaldehyde emitted from a material diffused through the inside of the PFS and was adsorbed onto the DNPH sheet. After a 2–24-h sampling period, the sheet was
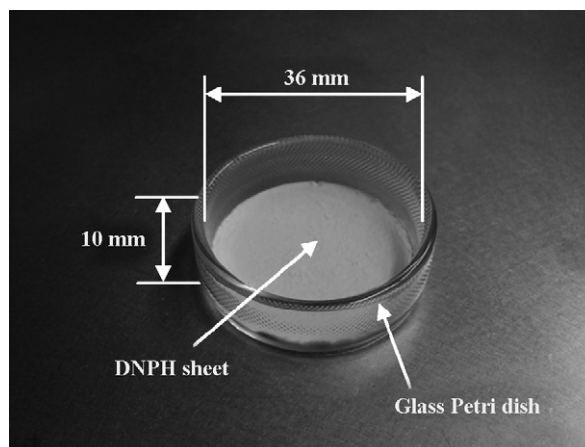

Fig. 1. Photograph of passive flux sampler (PFS).

removed from the Petri dish and was individually stored in a zip-sealed Mylar package at 4 °C until analysis. The objective of using the PFSs was to identify the primary emission sources (e.g., building materials and furniture), which emit chemicals over long periods in the indoor environment and cause adverse health effects. To measure the emissions from materials in which emissions decrease rapidly (in many cases, these emission sources can be identified without measurement) using the PFS, sampling periods must be shorter; such measurements were not made in this study because the emissions from the most suspected materials in the indoor environment would not obviously decrease over just one or two weeks, except if the materials were new.

2.3. Theoretical explanation of PFS

2.3.1. Emission from the source to indoor air

Chemicals in emission sources, such as flooring, walls, ceilings, doors, closets, desks, and beds,

migrate: (i) from the inside of the material to the surface of the material; (ii) from the material phase to the air phase at the interface; and (iii) from the air phase at the interface to the indoor bulk air in the gas-phase boundary layer by molecular diffusion. Fig. 2 is a schematic representation of the emission of chemicals from the source to indoor air. In a steady state, internal mass transfer inside the source material is equal to the flux of the diffusion in the gas-phase boundary layer. Thus, the emission flux (emission rate) from the source material is limited by the rate-determining process, which has the slowest transfer rate.

Mass transfer inside the source material (Little et al., 1994) can be described by

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C(x)}{\partial x^2}, \tag{1}$$

where C_m (g m^{-3}) is the concentration of the chemical in the source material, D_m (m^2 s^{-1}) is the apparent diffusion coefficient in the source material,
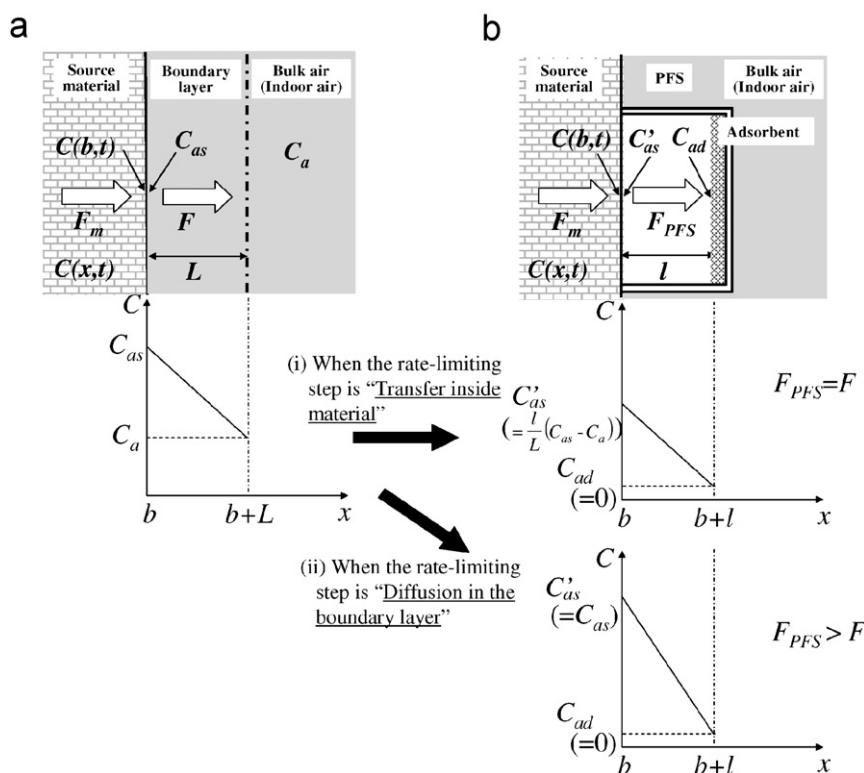

Fig. 2. Schematic representation of formaldehyde transfer in the boundary layer (a) and the PFS (b). C_i is the hypothetical concentration of formaldehyde inside the material, C_0 is the concentration of formaldehyde in the air just above the material surface, C_a is the concentration of formaldehyde in the indoor air, C_{ad} is the concentration of formaldehyde in the air just above the adsorbent, L is the thickness of the boundary layer and l is the thicknesses of the air layers in the PFSs.

t (s) is time, and x (m) is the coordinate in the material.

The equilibrium relationship between the concentrations in the air phase and material phase can be expressed by the linear isotherm (Little et al., 1994)

$$C|_{x=b} = KC_{as}, \qquad (2)$$

where $C|_{x=b}$ (g m^{-3}) is the concentration of the chemical at the surface of the source material, K (dimensionless) is the material/air partition coefficient, and C_{as} (g m^{-3}) is the gas-phase concentration of the chemical at the surface of the source material.

The molecular diffusion in the gas-phase boundary layer, which was often called "convective mass transfer" in the previous studies (Dunn, 1987; Clausen et al., 1991; Little et al., 1994; Huang and Haghighat, 2002), can be described as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \qquad (3)$$

where C (g m^{-3}) is the concentration of the chemical in the gas-phase boundary layer and D $(\text{m}^2\,\text{s}^{-1})$ is the molecular diffusion coefficient. Thus, the emission flux from the source material surface to the indoor bulk air can be obtained by the following equation (Fick's Law):

$$F = -D \frac{dC}{dx} = -D \frac{C_a - C_{as}}{L}, \qquad (4)$$

where F $(\text{g m}^{-2}\,\text{s}^{-1})$ is the emission flux (emission rate), C_a (g m^{-3}) is the concentration of the chemical in the indoor air, and L (m) is the thickness of the gas-phase boundary layer. In a previous study, the thickness of the gas-phase boundary layer L in an indoor environment was reported to have been between 10 and 30 mm (Zhang et al., 1995). The gas diffusion coefficient of formaldehyde in air is $1.58 \times 10^{-5}\,\text{m}^2\,\text{s}^{-1}$, calculated by Hirschefelder's equation (Hirschfelder et al., 1954).

2.3.2. Emission from the source inside the PFS

In the indoor environment, chemicals diffuse through the surface gas-phase (boundary layer) from the source material to bulk air, whereas inside the PFS, chemicals diffuse from the source material to the adsorbent (Fig. 2). The emission flux (emission rate) in the PFS from the surface of the source material to the adsorbent, F_{PFS} $(\text{kg m}^{-2}\,\text{s}^{-1})$, is given by

$$F_{PFS} = -D \frac{dC}{dx} = -D \frac{C_{ad} - C'_{as}}{l}, \qquad (5)$$

where l (m) is the thickness of the air layer inside the PFS, C_{ad} (g m^{-3}) is the gas-phase concentration equilibrium at the adsorbent, and C'_{as} (g m^{-3}) is the gas-phase concentration at the surface of source material. Since we can assume C_{ad} to be zero due to the strength of the adsorption, F_{PFS} is expressed as

$$F_{PFS} = D \frac{C'_{as}}{l}. \qquad (6)$$

The thicknesses of the air layer inside the PFS must be set close to the thicknesses of the gas-phase boundary layer in indoor environments that have been reported, that is, between 10 and 30 mm (Bruce et al., 1993; Zhang et al., 1995).

Fig. 2(a) shows the emission from the source material to bulk air in a steady state in an indoor environment or chamber. When the PFS measurement is started on a material, the gas-phase concentration on the bulk air side of the boundary layer, C_a, changes suddenly to the gas-phase concentration equilibrium at the adsorbent, C_{ad} $(=0)$ (Fig. 2(b)). If the emission is limited by transfer inside the material, the diffusion at the gas-phase boundary layer does not affect the emission flux and the gas-phase concentration on the source material decreases (Fig. 2(b)–(i)). Thus, when the rate-limiting step is transfer inside the material, F_{PFS} obtained by the PFS is equal to the emission flux F in the indoor environment or chamber:

$$F = F_{PFS}. \qquad (7)$$

On the other hand, if the emission is limited by diffusion in the gas-phase boundary layer, the gas-phase concentration on the source material does not change $(C_{as} = C'_{as})$ (Fig. 2(b)–(ii)). Hence, when the rate-limiting step is diffusion in the gas-phase boundary layer, the emission rate in the indoor environment or chamber can be calculated from Eq. (8) derived from Eqs. (4) and (6):

$$F = \frac{F_{PFS} l - DC_a}{L}. \qquad (8)$$

In the cases of both rate-limiting steps, the time to change the gas-phase concentration on the source material or flux is approximately 10 s, calculated from $t = L^2/D$. Thus, the change in time can be ignored because it is much shorter than the sampling period.

2.4. Analysis

Formaldehyde was captured as its DNPH derivative (DNPH-formaldehyde) on the adsorbent. DNPH-formaldehyde was extracted from the adsorption filter with 5 mL of acetonitrile (HPLC grade, Wako Pure Chemicals Co. Ltd., Japan) by ultrasonication. The ultrasonic bath used in this study was W-113 MK-2 (Honda Electronics Co., Japan) and sonication was continued for 30 min at 24 kHz. The extracted DNPH-formaldehyde was analyzed by high performance liquid chromatography (HPLC; HP1100, Hewlett Packard, USA) with a photodiode array detector at a wavelength of 365 nm. The mobile phase was a 65% acetonitrile and 35% water mixture with a flow rate of 1 mL min^{-1}. Twenty microliters of the analyte was injected onto an XDB-C18 packed column (ZORBAX Eclipse; length 250 mm, inner diameter 4.6 mm; particle size 5 µm), which was maintained at 35 °C. The DNPH-formaldehyde standard used in this study was purchased from Supelco Co., Ltd., USA (4M-7177 Formaldehyde-DNPH 100 µg mL^{-1} in acetonitrile).

2.5. Lower detection limit, determination limit, and upper limit

The lower limit of detection was defined as the concentration giving a signal-to-noise ratio equal to three. To investigate the lower limits of determination, the standard deviations of the measured concentrations in blank filters were examined ($N = 5$). The lower determination limit was defined as ten times the standard deviation of the mean amount found in the blank. If formaldehyde was not detected, the lower determination limit was defined as the lowest concentration of the analyte at which the calibration curve became nonlinear. The upper limit was estimated by using the impregnated amount of DNPH in the DNPH sheet.

2.6. Recovery efficiency and precision

To determine the recovery efficiency, aliquots of 100 µL of a methanol solution of formaldehyde (7.40 µg/aliquot) were spiked onto five filters with a microsyringe. The Petri dishes were then covered with tight-fitting glass plates for 60 min to remove the solvent. To evaluate the precision of the method, the formaldehyde emission flux emitted from a commercially available plywood, classed as F$_{C0}$

according to Japanese Agricultural Standards (JAS), was sampled five times at the same point for 2 h (changing samplers every 2 h). To identify and measure any point-to-point variability in the plywood sample, side-by-side samplings were also carried out at five points on the same plywood sheet for 2 h.

2.7. Time-variation of emission rates from a plywood board measured by PFS

To check the sampling time dependency of the emission rates measurement by the PFS, the emission rates of formaldehyde from a plywood board were measured at different sampling periods. Sampling periods were set at 0.5, 1, 2, 4, 8.5, 16, and 24 h, and the thickness of the air layer inside the PFS was set at 10 mm. The samplings were continuously conducted at the same point over 56 h. The plywood had been placed in a controlled clean chamber at 20 °C for 24 h before sampling.

2.8. Comparison with chamber method

To confirm the measurement by PFS, the emission rates of formaldehyde from plywood were measured by the chamber method and the PFS method. The chamber experiment was conducted in a 20-L chamber (ADPAC-A2; ADTEC Co., Japan) according to Japanese Industrial Standard JIS A1901 (JISC, 2003). The flow rate, temperature and relative humidity of the fresh air introduced into the chamber were 167 mL min^{-1}, 28 °C, and 50%, respectively. The surface area of the plywood was 0.000962 m^2. PFS experiments were conducted at three points on the plywood, which was the same sample as in the chamber test, using the PFS with an air-layer thickness of 10 mm for 2 h at 28 °C immediately after the chamber test.

2.9. Applications and pilot study

2.9.1. Dependency on thickness of the air layer inside the PFS on emissions from plywood board

It is necessary to clarify whether the emissions are primarily limited by the migration from inside a material or the diffusion in the gas-phase boundary layer in order to measure the emission rates accurately. Dependency on the thickness of the air layer inside the PFS on emissions from a plywood board could yield information about the

emission-limiting step. The emission rate of formaldehyde from a plywood board was measured to elucidate how the thickness of the gas-phase boundary layer affected the emission. The thicknesses of the air layer inside the PFS were set at 3, 5, 8, 10, 13, 15, 20, 25, and 28 mm, with a sampling period of 2 h. The plywood had been placed in a controlled clean chamber for 24 h before sampling.

2.9.2. Temperature dependency of emission from a plywood board

To evaluate the temperature dependency of the emission rate, the formaldehyde emission from the plywood was measured at 20, 50, and 80 °C for 2-h periods. The thickness of the air layer inside the PFS was set at 10 and 28 mm for these tests. The plywood had been placed in a controlled clean chamber for 24 h before sampling.

2.9.3. Indoor environment

The formaldehyde emission rate was measured at several points in a Japanese-style room and in a bedroom of a model house in Kyoto, Japan, in the winter of 2002. In the pilot study, the thickness of the air layer inside the PFS was set at 10 mm and the sampling duration was 8 h. All the windows and doors were opened for 30 min to purge the air before the emission flux sampling was conducted. Subsequently, the measurement was carried out with heating (23.0 °C) and without heating (10.5 °C) in the bedroom.

3. Results and discussion

3.1. Lower detection limit, determination limit, and upper limit

The lower detection limit for formaldehyde was 7.56×10^{-3} μg for a single filter. The amounts of formaldehyde in the blank filters were below the detection limit. The lower determination limit, estimated from the concentration at which the calibration curve became nonlinear, was 1.88×10^{-2} μg for a single filter. Hence, the detection limits for formaldehyde emission flux were calculated to be 3.71 and 0.928 μg m^{-2} h^{-1} for 2- and 8-h sampling periods, respectively, and the determination limits of the formaldehyde emission flux were calculated to be 9.2 and 2.3 μg m^{-2} h^{-1} for 2- and 8-h sampling periods, respectively. The upper limit for the PFS was the captured amount

when the gas-phase concentration on the absorbent could not be assumed to be zero. Assuming that instant reactive adsorption on the surface layer of the adsorbent was maintained until 1% (0.02 mg) of the impregnated DNPH (2 mg) in the DNPH sheet was consumed, the upper limit was 3 μg of formaldehyde for a single filter. Thus, the upper limits of the formaldehyde emission flux were calculated as 1500 and 370 μg m^{-2} h^{-1} for 2- and 8-h sampling periods, respectively. Since plywood and particle board are classified into four categories in Japan depending on their formaldehyde emission rates (<5, 5–20, 20–120 and >120 μg m^{-2} h^{-1}) measured by emission chamber or desiccator methods (MLIT, 2002), the determinable range of PFS is sufficient for measurements in indoor environments.

3.2. Recovery test and precision

The mean recovery rate was 82.9% and the precision was 8.26%. These results show that the PFS was efficient in measuring the emission rates of formaldehyde from any material in an indoor environment. Point-to-point variability of the emission rates in a sample was, however, larger (26.3%) than the sampling precision. The reason for the larger variability might be due to the heterogeneity of the scale and distribution of pores inside the plywood. Thus, emission rates must be sampled simultaneously at several points to estimate an average emission from each emitting material in an indoor environment.
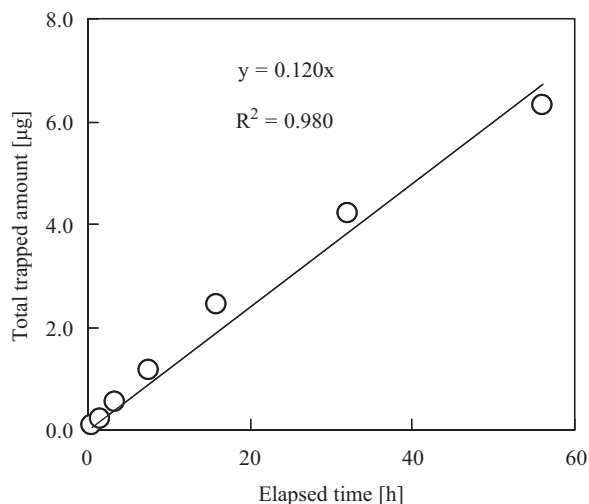

Fig. 3. Time variation of emission rates measured by PFS.

3.3. Time variation of emission rates from a plywood board measured by PFS

The trapped amounts were proportional to the sampling periods (Fig. 3; $R^2 = 0.980$). It was confirmed that the emission flux was constant during the 2- and 8-h periods used in this study for the sampling. The emission flux did not change until at least 16 h after the start of PFS sampling. Thus, the determinable range can be widened by changing the sampling period depending on the presumed emission rates.

3.4. Comparison with chamber method

The emission rate F was calculated by Eq. (7) assuming that the rate-limiting step was migration inside the material because the thickness of the air layer inside the PFS was 1 cm. The emission rates obtained by the PFS method were proportional to the emission rates measured by the chamber method (Fig. 4 (open circles); $R^2 = 0.963$). This indicates that it is possible to perform the comparison of the formaldehyde emission rates for any of the sources in a room. The slope of the regression line shows that the emission rates measured by PFS were about 25% larger than the emission rates measured by the chamber method. One reason might be point-to-point variability (11–21% ($N = 3$)) of the emission

rates from plywood. Another reason might be the assumption about the rate-limiting step for some plywoods. If the rate-limiting step was diffusion in the gas-phase boundary layer, the emission rate calculated by Eq. (8) would be smaller than that under the assumption of the material being limiting (Fig. 4 (gray diamonds)).

3.5. Applications and pilot study

3.5.1. Dependency on thickness of the air layer inside the PFS on emission from a plywood board

The formaldehyde emission rate at air-layer thicknesses inside the PFS of 3 and 28 mm were 150 and 48.2 μg m^{-2} h^{-1}, respectively. The dependency on thickness of the air layer inside the PFS of the formaldehyde emission rate from the plywood board is shown in Fig. 5. The formaldehyde emission flux was inversely proportional to the thickness of the air layer inside the PFS when it was 15 mm or greater than 15 mm. When the thickness of the air layer inside the PFS was less than 10 mm, the dependency of emission rates on the thickness of the air layer inside the PFS became small and was nearly constant regardless of the thickness of the gas-phase boundary layer. This indicated that the rate-limiting step of the formaldehyde emission from the plywood was the diffusion in the gas-phase boundary layer when the gas-phase boundary
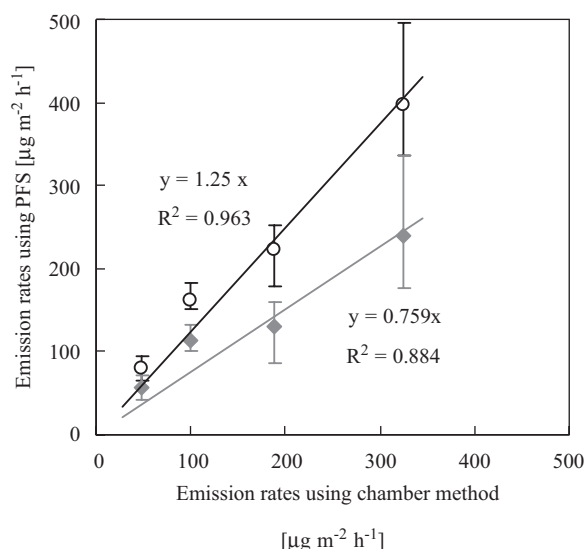

Fig. 4. Correlation of emission rates measured using the chamber method and the PFS under the assumption of two rate-limiting steps: transfer inside the material (open circles) and diffusion in the boundary layer (gray diamonds).
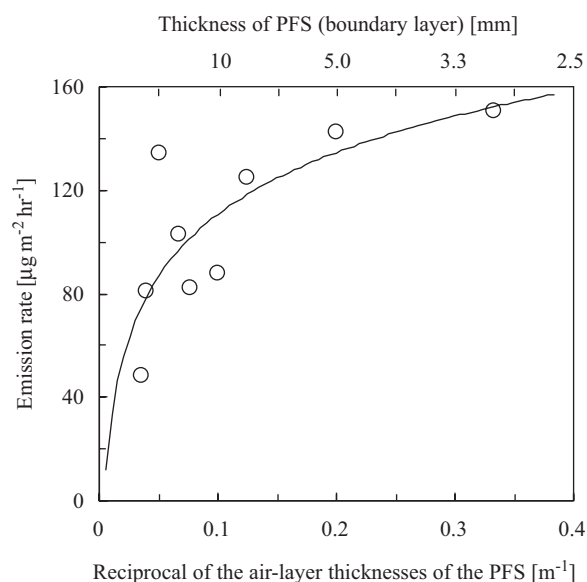

Fig. 5. Emission rate versus the reciprocal of the air-layer thicknesses of the PFS.
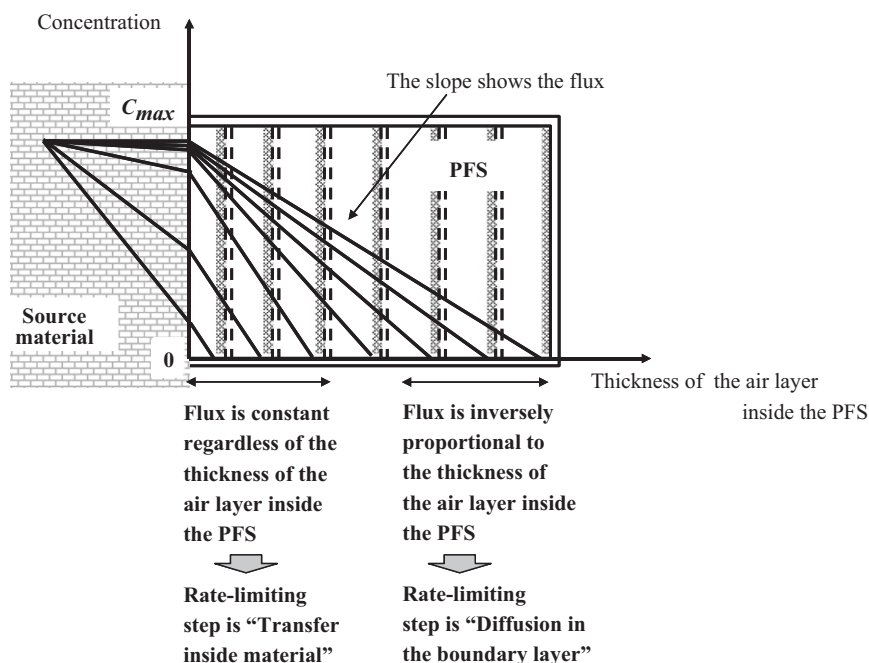
Fig. 6. Schematic diagram showing the dependence on air-layer thickness of PFS of the emission flux.

layer was over 15 mm in thickness because the emission rates depended on Fick's law. It was also implied that the plywood surface concentration C_{as} was almost constant when the gas-phase boundary layer was over 15 mm in thickness. When the gas-phase boundary layer was less than 10 mm in thickness, the internal mass transfer inside the material mainly limited the emission rates of formaldehyde (Fig. 6).

The rate-limiting step for formaldehyde emission from the plywood tested in this study changed within a range of air-layer thicknesses inside the PFS of 10–15 mm. The thickness of the gas-phase boundary layer depends on a number of factors, such as the speed of indoor air movement, which was reported to be 53–150 mm s^{-1} in previous papers (Matthews et al., 1989; Hart and Int-Hout, 1980; Schiller and Arens, 1988), the texture of the surface, the shape of the room, and the location of the site within the room. Thus, it is necessary that each specific relevant speed and the thickness of each gas-phase boundary layer be determined by simulation, e.g., by computational fluid dynamics (CFD) simulation. In previous studies, the thickness of the gas-phase boundary layer was measured as 14–16 mm when the speed of indoor air movement was 80 mm s^{-1} at 15 mm above the floor (Bruce et al., 1993) and was measured as 10–30 mm in four

ventilated rooms when the speed of indoor air movement was 50–120 mm s^{-1} at 20 mm above the surface (Zhang et al., 1995).

It is possible to determine whether the emission of chemical compounds depends on internal mass transfer, on diffusion in the gas-phase boundary layer, or on mixed diffusion and to estimate the emission flux in an actual environment, by doing the following. First, emission flux is measured at two or more air layer thicknesses of the PFS that are outside of the thicknesses of the common boundary layer, such as at 5 and 30 mm. Next, the emission rates F_{PFS} obtained by the PFS method are plotted against the inverse of the thickness of the air layer inside the PFS. If the emission flux is found to be proportional to the reciprocal of the thicknesses of the diffusion boundaries, it is suggested that the emission depends upon diffusion though the gas-phase boundary layer and the emission rates F can be calculated by Eq. (8). If the line between the two plots does not go through the origin and the emission rates seem constant, the emission flux depends on internal mass transfer (diffusion, reaction, absorption, or desorption) inside the materials and the emission rates F can be calculated by Eq. (7). If the line between the two plots does not go thorough the origin and has a slope, the emission rate depends on the intermediate transition-state

between the two processes, such as the plywood in the present study and the emission rates F can be calculated by Eqs. (7) and (8).

3.5.2. Temperature dependency of emission from a plywood board

The emission flux increased exponentially with temperature for the PFSs with both air-layer thicknesses. The emission rates were 48.2 µg m^{-2} h^{-1} at 10 °C, 9.63×10^2 µg m^{-2} h^{-1} at 50 °C, and 3.00×10^5 µg m^{-2} h^{-1} at 80 °C when the thickness of the air layer inside the PFS was 28 mm. The apparent activation energy was determined by the Arrhenius equation:

$$\ln k = \ln k' - \frac{E}{RT}, \tag{9}$$

where k (kg m^{-2} s^{-1}) is the rate constant, k' (dimensionless) is the frequency factor, E (kJ mol^{-1}) is the apparent activation energy, R (kJ mol^{-1} K^{-1}) is the gas constant and T (K) is the temperature. When the vertical axis is $\ln k$ and the horizontal axis is $1/T$, the slope of the graph represents the value of $-E/R$ (Fig. 7). Arrhenius plots exhibited good linearity for the PFSs with both 10- and 28-mm air-layer thicknesses, and no significant differences were observed. These plots show the temperature dependency of the surface equilibrium concentration of plywood. Thus, it is suggested that a similar mechanism dominated both the maximum internal transfer inside the material and the surface equili-
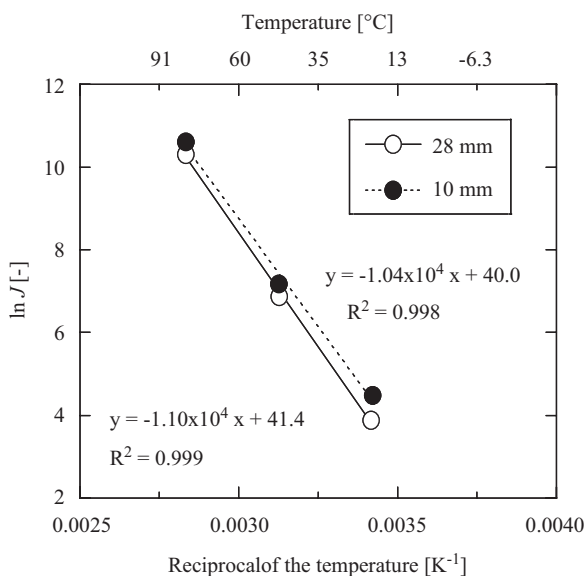

Fig. 7. Arrhenius plot for formaldehyde emitted from plywood.

brium concentration of plywood. The apparent activation energy, calculated from the slope of the Arrhenius plot, was 91.3 kJ mol^{-1} (thicknesses of PFS: 10 mm) and 87.3 kJ mol^{-1} (thicknesses of PFS: 28 mm). In the previous study, the activation energies were reported as 3.65 kJ mol^{-1} for molecular diffusion (10–30 °C), 23.0 kJ mol^{-1} for evaporation of formaldehyde (Kagakukougakukai, 1999), and 93.5 kJ mol^{-1} for decomposition of paraformaldehyde (Takaya and Minato, 1997). Compared to these data, the apparent activation energy of formaldehyde emission flux from plywood in the present study was close to that for decomposition of paraformaldehyde. Other mechanisms which have similar apparent activation energy, however, may have contributed to the internal transfer in the material and the surface equilibrium concentration.

3.5.3. Indoor environment

The emission rate in the indoor environment was obtained by using PFS under the assumption that the emissions were limited by transfer in the materials. The results for the formaldehyde emission rates in a model house are shown in Table 1. The formaldehyde emission rates from the source materials in the Japanese-style room were between 3.93 and 10.2 µg m^{-2} h^{-1}. The formaldehyde emission rates from the source materials in the bedroom were trace (<2.30 µg m^{-2}) to 8.27 µg m^{-2} h^{-1} at 10.5 °C and were 7.77–11.3 µg m^{-2} h^{-1} at 23.0 °C. The relative standard deviation (RSD) of triplicate values measured for the wall and the ceiling were 11.3% and 24.7%, respectively.

The indoor concentration C_a (g m^{-3}) in the steady state is given by

$$C_a = \frac{\sum F_j A_j}{VN}, \tag{10}$$

where F_j (g m^{-2} s^{-1}) is the emission rate from material j, A_j (m^2) is the area of material j, V (m^3) is the room volume, and N (s^{-1}) is the ventilation rate. Hence, the contribution ratio of each material to the indoor concentration can be expressed as

$$CR_k = \frac{F_k A_k}{\sum F_j A_j} \times 100, \tag{11}$$

where CR_k (%) is the contribution ratio of material k. CR values of some materials, from which emission rates were under the determination limit, were calculated with an emission rate of one-half the lower determination limit (1.15 µg m^{-2} h^{-1}). In the Japanese-style room the clay wall contributed 35%

Table 1
Emission flux, area, and CR value of each material

Room	Material	Flux ($\mu g\,m^{-2}\,h^{-1}$)	Area (m^2)	CR value (%)
Japanese-style room (13.6 °C)	Clay wall	8.37	19	35
	Tatami mat	8.59	13	25
	Sliding screen	10.2	9.9	23
	Ceiling	4.11	13	12
	Pillar	7.50	1.6	2.6
	Cross piece	8.00	0.7	1.3
	Wood floor	3.93	0.7	0.65
	Sliding edge	4.00	0.6	0.58
Bedroom (10.5 °C)	Wall	2.52	28	45
	Ceiling	2.56	20	33
	Flooring	t.r. (<2.30)	20	15[a]
	Desk	t.r. (<2.30)	5.5	4.0[a]
	Door	t.r. (<2.30)	2.0	1.5[a]
	Closet	t.r. (<2.30)	2.0	1.5[a]
	Chair	8.27	0.14	0.71
Bedroom (23.0 °C)	Wall	11.8	29	48
	Flooring	10.8	20	30
	Ceiling	7.77	20	22

t.r.: trace, CR: contribution ratio.
[a] CR values were calculated with an emission flux of 1/2 the lower determination limit (1.15 $\mu g\,m^{-2}\,h^{-1}$).

to the indoor formaldehyde concentration. In the bedroom, the contribution ratios of the wall at 10.5 and 23.0 °C were 45% and 48%, respectively. If these emission sources were removed, the indoor formaldehyde concentration would be substantially decreased. The emission flux variances for the same material were significantly less than those among different building materials. Thus, it was confirmed that the largest emission source could be determined among several suspected materials in a room by this method.

4. Conclusion

A PFS was developed to determine the emission rates of formaldehyde from building materials and other materials found indoors. The lower and upper determination limits, the recovery rate, and the precision assured PFSs of sufficient quality for measuring formaldehyde emission rates from indoor materials. The emission rates obtained using the PFS were in good agreement with the emission rates measured by the chamber method ($R^2 = 0.963$). This indicates that it is possible to perform comparisons of the formaldehyde emission rates of any sources in a room. When the emission was limited by transfer inside a material, the measured flux was equal to the indoor emission rate, whereas the indoor emission

rates could be calculated with the gas-phase concentration at the surface of the material and indoor concentration when the emission was limited by the diffusion in the gas-phase boundary layer. The rate-limiting step of emission could be obtained by the emission flux measurement with different thicknesses of the air layer inside the PFS. In a pilot study, the PFS was used to measure the formaldehyde emission flux and to determine the primary emission source of formaldehyde from among several suspected materials in a model house.

Acknowledgments

References

Amagai, T., Ohura, T., Sugiyama, T., Fusaya, M., Matsumura, H., 2000. A survey of indoor and outdoor air pollution by aldehydes in summer in Fuji, Shizuoka. Journal of Society of Indoor Environment, Japan 3 (1), 35–43.
ASTM (American Society for testing and materials), 1996. E1333-96, standard test method for determining

formaldehyde concentrations in air and emission rates from wood products using a large chamber.

ASTM (American Society for testing and materials), 1997. D5116-97, standard guide for small-scale environmental chamber determinations of organic emissions from indoor materials/products.

Bruce, A.T., Zhishi, G., Leslie, E.S., 1993. Fundamental mass transfer model for indoor air emission from surface coatings. Indoor Air 3, 263–268.

Clausen, P.A., Wolkoff, P., Holst, E., Nielse, P.A., 1991. Long-term emission of volatile organic compounds from water-borne paint—methods of comparison. Indoor Air 4, 562–576.

Dunn, J.E., 1987. Models and statistical-methods for gaseous emission testing of finite sources in well-mixed chambers. Atmospheric Environment 21 (2), 425–430.

Hart, G.H., Int-Hout, D., 1980. The performance of a continuous linear air diffuser in the perimeter zone of an office environment. ASHRAE Transactions 86 (2), 107–124.

Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., 1954. Molecular Theory of Gases and Liquids. Wiley, New York, p. 539.

Huang, H., Haghighat, F., 2002. Modelling of volatile organic compounds emission from dry building materials. Building and Environment 37 (12), 1349–1360.

IHCP (Institute for health and consumer protection), 1999. ENV717-1, WOOD-BASED PANELS. Determination of formaldehyde release, formaldehyde emission by the chamber method.

JISC (Japanese Industrial Standards Committee), 2001. JIS A1460, building boards determination of formaldehyde emission—desiccator method, Tokyo.

JISC (Japanese Industrial Standards Committee), 2003. JIS A1901, small chamber method—determination of the emission of volatile organic compounds and aldehydes for building products. Tokyo.

Kim, W.J., Terada, N., Nomura, T., Takahashi, R., Lee, S.D., Park, J.H., Konno, A., 2002. Effect of formaldehyde on the expression of adhesion molecules in nasal microvascular endothelial cells: the role of formaldehyde in the pathogenesis of sick building syndrome. Clinical and Experimental Allergy 32 (2), 287–295.

Little, J.C., Hodgson, A.T., Gadgil, A.J., 1994. Modeling emissions of volatile organic compounds from new carpets. Atmospheric Environment 28 (2), 227–234.

Matthews, T.G., Thompson, C.V., Wilson, D.L., Hawthorne, A.R., 1989. Air velocities inside domestic environments: an important parameter in the study of indoor air quality and climate. Environment International 15, 545–550.

MHLW (Ministry of Health, Labour and Welfare, Japan), 2000. Interim Report of Panel on sick house (indoor air pollution) problem, Environmental Health Bureau, Planning Division. Tokyo.

MLIT (Ministry of Land, Infrastructure and Transport, Japan), 2002. Notice no. 1113 of the Ministry of Land, Infrastructure and Transport, Japan, Tokyo.

Naya, M., Nakanishi, J., 2005. Risk assessment of formaldehyde for the general population in Japan. Regulatory Toxicology and Pharmacology 43 (3), 232–248.

Paustenbach, D., Alarie, Y., Kulle, T., Schachter, N., Smith, R., Swenberg, J., Witschi, H., Horowitz, S.B., 1997. A recommended occupational exposure limit for formaldehyde based on irritation. Journal of Toxicology and Environmental Health 50 (3), 217–263.

Risholm-Sundman, M., 1999. Determination of formaldehyde emission with field and laboratory emission cell (FLEC)–recovery and correlation to the chamber method. Indoor Air 9, 268–272.

Sakai, K., Norback, D., Mi, Y.H., Shibata, E., Kamijima, M., Yamada, T., Takeuchi, Y., 2004. A comparison of indoor air pollutants in Japan and Sweden: formaldehyde, nitrogen dioxide, and chlorinated volatile organic compounds. Environmental Research 94 (1), 75–85.

Schiller, G.H., Arens, E.A., 1988. Thermal comfort in office building. ASHRAE Journal 39, 26–32.

Shinohara, N., Yanagisawa, Y., Nakai, S., Takagi, Y., Nishioka, Y., Vallarino, J., Spengler, J., Kawai, R., Maeda, M., Ikeda, K., 1999. Measurement of indoor air in Hokkaido: aldehydes tracing study. Journal of Society of Indoor Environment, Japan 2 (1), 84–85.

Shinohara, N., Mizukoshi, A., Yanagisawa, Y., 2004. Identification of responsible volatile chemicals that induce hypersensitive reactions to multiple chemical sensitivity patients. Journal of Exposure Analysis and Environmental Epidemiology 14 (1), 84–91.

Takaya, Y., Minato, K., 1997. Mechanism of formaldehyde emission from wood substances and reducing effect by ammonia treatment. Mokuzai Gakkaishi 43 (5), 427–433.

The Society of Chemical Engineers, Japan, 1999. Kagakukougakubinran, 6th ed., Maruzen, Japan, pp. 17–46.

Tichenor, B.A., 1989. Indoor air sources; using small environmental test chambers to characterize organic emissions from indoor materials and products. EPA-600 8-89-074.

Uhde, E., Borgschulte, A., Salthammer, T., 1998. Characterization of the field and laboratory emission cell—FLEC: flow field and air velocities. Atmospheric Environment 32 (4), 773–781.

WHO (World Health Organization), 1999. Air Quality Guidelines for Europe, WHO Regional Publications European Series, Regional Office for Europe, Copenhagen.

Wolkoff, P., Clausen, P.A., Nielsen, P.A., Gustafsson, H., Jonsson, B., Rasmusen, E., 1991. Field and laboratory emission cell: FLEC. Healthy buildings '91, ASHRAE, pp. 160–165.

Zhang, J.S., Shaw, C.Y., Nguyen, L.C., MacDonald, R.A., Kerr, G., 1995. Field measurements of boundary-layer flows in ventilated rooms. ASHRAE Transactions: Research 101 (2), 116–124.