

Characteristics of Volatile Organic Compounds Emitted in Building Materials and Their Predictions of Time-dependent Variation

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Abstract

Unlike other countries, Korea uses various kinds of wall-paper as finishing material. Conventional wall-paper consists of paper and vinyl, and petrochemical ink is used for the decoration of the surface. Adhesive is used to paste the wall with the wall-paper, which emit substantial amounts of VOCs and formaldehyde. In this study, VOCs characteristics emitted from specimens made of concrete, mortar, gypsum board and wall-paper were investigated using small chamber method. Moreover, concentration and emission factor of BTEX (Benzene, Toluene, Ethylbenzene, m,p,o-Xylene) and TVOC were investigated, and concentration and emission factor decay were estimated. As a result of the prediction, both time-dependent concentration decay and cumulative concentration can be converted into the logarithmic scale. Furthermore, prediction equations were developed from the experimental results under accurately controlled experimental conditions. Therefore, there may be difference if the estimated equations are directly applied to real buildings. Further research should be done on the generalization of the developed prediction equations.

Keywords: ventilation, emission factor, small chamber, VOCs, TVOC, floor, loading factor

1. INTRODUCTION

Recently, indoor air quality (hereafter IAQ) has become one of the most significant issues for the health of occupants and the comfortable indoor environment. In particular, use of the building materials with high air-tightness has greatly improved the performance on insulation and air-tightness in newly constructed buildings. In addition, applications of various construction methods for energy conservation have also contributed to the enhancement of the insulation and air-tightness performance. However, the IAQ becomes considerably degraded when the residential and indoor pollutants from petrochemical building materials are present. The reason is because these composite materials for buildings tend to emit slowly a substantial amount of hazardous air pollutants (hereafter HAPs) such as volatile organic compounds (hereafter VOCs) over a long period of time.

This research has been motivated by the following two academic and practical reasons. First, previous research on IAQ has focused on the effects of ventilation, particles, CO and CO₂, but not much research has been done about the issue of VOCs. In particular, the research related to the prediction and assessment of indoor concentration decay of VOCs emitted from building materials has been studied recently in Korea. Although the standards of regulating and measuring pollutants in the industrial and outdoor environment have been already established, the scientific methodology for measuring VOCs has not been well established internationally. The reason is partly because of the difficulties in comparing various measurement methods.

Second, Unlike other countries, Korea uses various kinds of wall-paper as finishing material of the wall. Most wall-papers consist of paper and vinyl. Most wall-papers use petrochemical ink for the decoration of the surface. Moreover, wall-papers use adhesive, which is also a significant source of the emission of VOCs and formaldehyde.

Thus, in this paper, we aim at assessing the emission characteristics of the VOCs in building materials. We will use the small chamber method in investigating the question. We then assess emission rates and factors of (1) the VOCs including BTEX (Benzene, Toluene, Ethylbenzene, and m,p,o-xylene) and (2) the total volatile organic compound (hereafter TVOC). We continue to predict the concentration and decrease of the emission factor as a function of time. Our research process is presented in Figure 1.

2. THEORETICAL BACKGROUND

2.1 Indoor concentration of pollutants

If a pollutant is emitted at a regular rate (M [mg/h]) in a room and the room is ventilated at a regular rate (Q [m³/h]) as shown in Figure 2, the average concentration can be expressed as in Equation 1. The model results from the assumption that the rates follow the process of the instantaneous diffusion. Thus, the concentration of pollutants will depend on the source area and ventilation rate as in Equations 8. If we use these equations, we can calculate the emission factors of pollutants in the particular unit area and at the particular unit time. The effects of pollutants on the indoor space can be evaluated using these equations.

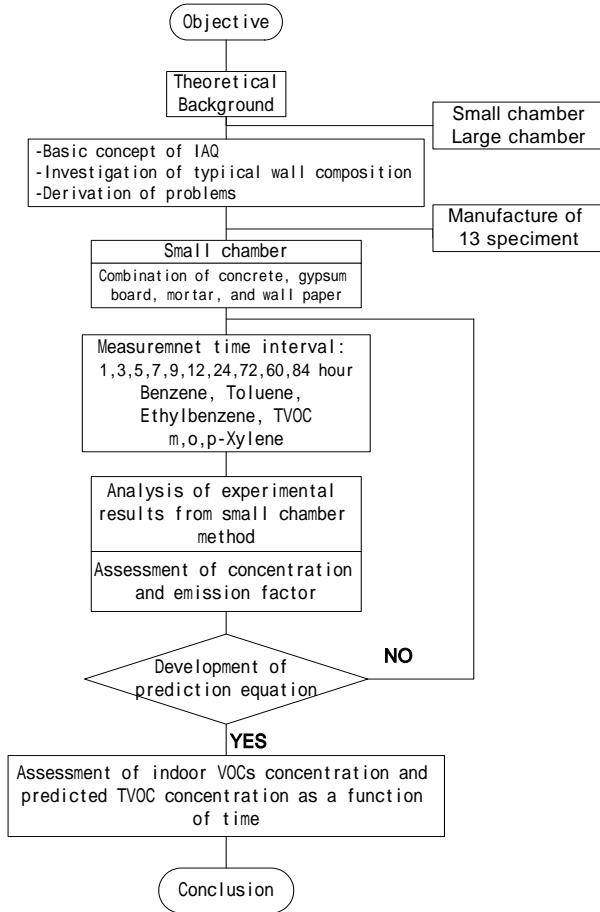


Figure 1. Research process

When the ventilation rates are considered together with the balance of infiltration and ex-filtration, we obtain Equation 1, a mathematical relationship between the emission source and the amount of pollutants removed by the air cleaning system in a time interval of dt .

$$V \frac{dc}{dt} = -Q(c_i - c_s) + M - E \quad (1)$$

When we leave (1) the ventilation rate and the emission rate to be constant and (2) the amount removed to be zero, we obtain Equation 2 in terms of the surface area.

$$V \frac{dc}{dt} = Q(c_i) + AM \quad (2)$$

Dividing both sides of the preceding equation by the room volume of V will result in the following equation.

$$\frac{dc_i}{dt} = \frac{Q}{V}c_i + \frac{A}{V}M \quad \left(\frac{Q}{V} = ACH\right) \quad (3)$$

Arranging both sides of the preceding equation will yield the following equations.

$$\frac{dc_i}{dt} = Nc_i + (L.F)M \quad \left(\frac{A}{V} = L.F\right) \quad (4)$$

$$\frac{dc_i}{Nc_i + (L.F)M} = dt \quad (5)$$

$$\frac{dc_i}{c_i + X} = Ndt \quad \left(X = \frac{(L.F)M}{N}\right) \quad (6)$$

Integrating both sides of the Equation will yield Equation 7.

$$C \approx \frac{(L.F)}{N}M = \frac{A}{V}M = \frac{A}{Q}M = \frac{A}{Q}M \quad (7)$$

Thus, it becomes evident that the indoor concentration of pollutants depends both on the source area and the ventilation rate.

$$C \approx \frac{A}{Q}M \quad (8)$$

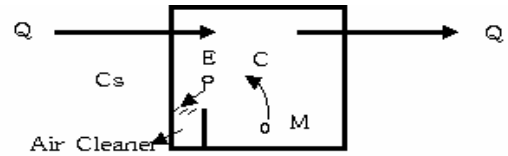


Figure 2. Emission Source of Pollutants in one room model

where,

V : interior volume (m^3)

C_i, C_s : indoor concentration and the concentration of pollutant among the incoming air (mg/m^3)

Q : ventilation rate (m^3/h)

M : emission rate ($\mu g/m^2h$)

E : removed amount of pollutant by air cleaning system ($\mu g/m^2h$)

2.2 Prediction model of VOCs concentration decay¹⁾

The emission factors of the VOCs are the amount of pollutants emitted per unit area and unit time. Equation 9 shows the factors.

$$EF_a = \frac{(C_t - C_{tb,t})Q}{A} = \frac{(C_t - C_{tb,t})NV}{A} \quad (9)$$

$$= (C_t - C_{tb,t})q = (C_t - C_{tb,t})\frac{N}{L}$$

where, EF_a : VOCs Emission Factor per unit area ($\mu g/m^2h$)

C_t : VOCs concentration at time t ($\mu g/m^3$)

$C_{tb,t}$: Travler Blank concentration at time t ($\mu g/m^3$)

A : source area

V : interior volume

N : air exchange rate

q : ventilation rate per unit area

L : Loading Factor

We find in Equation 10 the relationship between the emission factor and the emission rate.

$$ER = A(EF) \quad (10)$$

1) ASTM D 5116 (1997) "Standard Guide for Small-scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/ Products"

where, ER: emission rate [$\mu\text{g}/\text{h}$]
 A: source area [m^2]
 EF: emission factor [$\mu\text{g}/\text{m}^2 \text{ h}$]

Once the chamber concentration data are obtained, the emission factor can be calculated by four methods: (1) direct calculation from individual data points, (2) direct calculation from the time-concentration profile, (3) using an explicit chamber model, and (4) using advanced techniques. Selection of the most suitable method depends on several factors such as the type of source, the data quality, and the sampling frequency.

1) Direct calculation of emission factors by the individual concentration data point

When the emission rate is almost constant and the chamber has reached the steady state, the emission factor can be calculated from a single data point as follows.

$$EF = C_s \frac{N}{L} \quad (11)$$

where, C_s : steady-state chamber concentration [$\mu\text{g}/\text{m}^3$]
 L: loading factor

The estimates by this method can be incorrect when the emission rate is not constant and the chamber is not in the steady state.

2) Direct calculation of emission factors by the time concentration profile.

If we have sufficient data on chamber concentration over a long period of time, we obtain the profile on the time dependent emission factors as in Equation 12.

$$EF(t_i) = \frac{\frac{\Delta C_i}{\Delta t_i} + NC_i}{L} \quad (12)$$

where, $EF(t_i)$: emission factor at time t_i
 C_i : chamber concentration at time t_i
 $\Delta C_i / \Delta t_i$: the slope of the time-concentration curve at time t_i

We can approximate the slope of the equation by using the average of the slopes of the two adjacent intervals.

$$\frac{\Delta C_i}{\Delta t_i} = \frac{\frac{C_i - C_{i-1}}{t_i - t_{i-1}} + \frac{C_{i+1} - C_i}{t_{i+1} - t_i}}{2} \quad (13)$$

Thus, in this equation, the number of emission factor values is (n-1) when the number of data points for concentration is (n+1).

3) Estimation of Emission Factors by the Explicit Chamber Model

When it is possible to approximate the emission patterns by the mathematical expression, we can estimate the emission factors by using non-linear regressions. We fit a

chamber model to the time-concentration data. The following equation of mass balance holds for the constant source with the emission factor of EF .

$$\frac{dC}{dT} = L(EF) - NC \quad (14)$$

Given the initial solutions of $t=0$ and $C=0$, the solution to C will be

$$C = \frac{L(EF)(1 - e^{-Nt})}{N} \quad (15)$$

We can estimate the unknown parameters of EF when fitting Equation 15 to the data of chamber concentration. In the related literature, the source model of the first-order decay is known to be one of the most commonly used empirical models in this type of estimation.

$$EF = (EF_0)e^{-kt} \quad (16)$$

where, EF_0 : initial emission factor [$\mu\text{g}/\text{m}^2 \text{ h}$]

k : first-order decay rate constant

Meanwhile, the corresponding chamber model will be

$$\frac{dC}{dt} = L(EF_0)e^{-kt} - NC \quad (17)$$

This has the following solution under the conditions of $t=0$ and $C=0$.

$$C = \frac{L(EF_0)(e^{-kt} - e^{-Nt})}{(N - k)} \quad (18)$$

An initial estimate for K in Equation 18 is given as

$$k = Ne^{(k-N)t_{\max}} \quad (19)$$

where, t_{\max} : the time of maximum concentration C_{\max}

3. METHODS OF EXPERIMENTS

The experiment was carried out for thirteen specimens that represent the typical composition of walls. We constructed specimens with concrete, gypsum board, mortar, and wall-paper. The size of each specimen was set to be 200mm x 200mm. We also made specimens of concrete, gypsum board and glass panels with liquefied ceramic-paste in order to assess the effect of those materials. We measured the profiles of the VOCs ten times after 1, 3, 5, 7, 9, 12, 72, 120, and 144 hours when investigating their time-concentration profiles. Table 1 reports the details of the constructed specimens. The results of the experiment for each substance (benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene) and the TVOC are measured by the concentration ($\mu\text{g}/\text{m}^3$) and the emission factor [$\mu\text{g}/\text{m}^2 \text{ h}$].

And, the decrease of the time-dependent emission rates is measured by the concentration in the chamber. Figure 3 illustrates the composition of the measure system. In this experiment, we will use the HAQT (Hanyang Air Quality Test) system which is composed of the constant temperature-humidity chamber, the constant temperature chamber, and the measurement chamber. The details of each chamber are explained in Table 2. Photos 1 and 2 respectively show the exterior of the constant temperature chamber, and the constant temperature-humidity chamber.

Table 1. Overview of measured specimens

No.	specimen type (W*H*Dmm)	1st finishing (liquified ceramic 300 μm)	2nd finishing
1	200x200x5, glass panel	O	-
2	200x200, gypsum board	×	-
3	200x200, gypsum board	O	-
4	200x200, gypsum board	O	wall-paper
5	200x200x50, concrete	×	-
6	200x200x50, concrete	O	-
7	200x200x50, concrete	O	wall-paper
8	200x200x50,concrete+mortar	×	wall-paper
9	200x200x50,concrete+mortar	O	-
10	200x200x50,concrete+mortar	O	wall-paper
11	200x200x50,concrete +200x200 gypsum board	×	-
12	200x200x50,concrete +200x200 gypsum board	O	-
13	200x200x50,concrete +200x200 gypsum board	O	liquified bonding agent

Table 2. Overview of HAQT system¹⁾

	constant temp. chamber	constant temp. and humidity chamber	measurement chamber	
size (inner) W×D×H[mm]	1000×1000×1000	500×630×600		
control range	temp. []	-5 ~ 90	-40 ~ 150	
			at 10	15% ~ 85%
			at 30	10% ~ 98%
	RH	-	~ 85	
		at 90	10% ~ 85%	
		at 120	10% ~ 50%	



Photo 1. Constant temp. chamber



Photo 2. Constant temp. and humidity chamber



Photo 3. Measurement chamber

For the measurement of VOCs, air samples were collected for one hour using charcoal tube. For the measurement of formaldehyde, air samples were also collected for one hour using impinger. When implementing the experiments, we set the temperature and humidity of each chamber to be 23°C and 50 %, respectively. Also, the rate of air exchange and the loading factor were respectively set at 0.7/h and 0.1m²/m³.

4. ANALYSIS OF RESULTS

Figure 4 illustrates the time-dependent variation in the concentration of the BTEX and the TVOC of the specimen 11. We find that the concentration does not decrease at a constant rate, but that the rate of the TVOC concentration gradually decreases with time, finally reaching 1000ug/m³. Figures 5 and 6 respectively present time-dependent variations in the concentration of the TVOC for (1) the specimens 6, 7 and 8, and (2) the specimens 9 and 10, respectively. We find in Figure 4 that the concentration for the specimen 8 tends to decrease with time, but that, after three days, the concentration decreases for the specimen 6 and increases for the specimen 7. When we compare the results of the specimens 9 and 10 under the same conditions, we find in Figure 5 that the concentration in the TVOC for the specimen 9 without the attached wall-paper decreases rapidly as time passes. This is interpreted as the effect of the adhesives used in pasting wall-papers.

4.1 Prediction of Decrease in Concentration

Figure 7 presents the prediction results of the decrease in the TVOC concentration for the specimen 7. In this figure, the Y-axis is converted to the natural logarithmic scale.

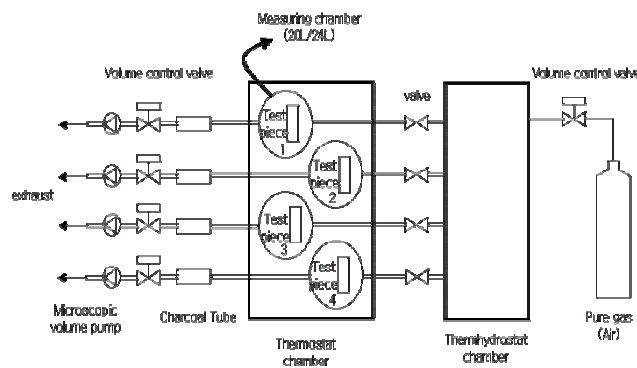


Figure 3. Composition of HAQT System²⁾

2) Lee, Y. J., Kim, H. W., and Sohn, J. Y. (2002) "Performance Test of HAQT (Hanyang Air Quality Test) System for Measuring Volatile Organic Compounds", The 26th Symposium on Human-Environment System

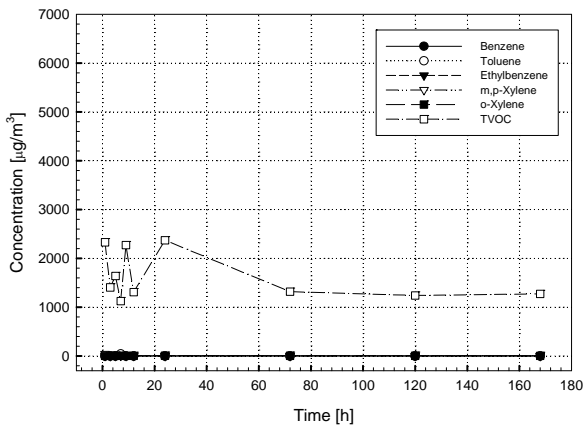


Figure 4. VOCs concentration (specimen 7)

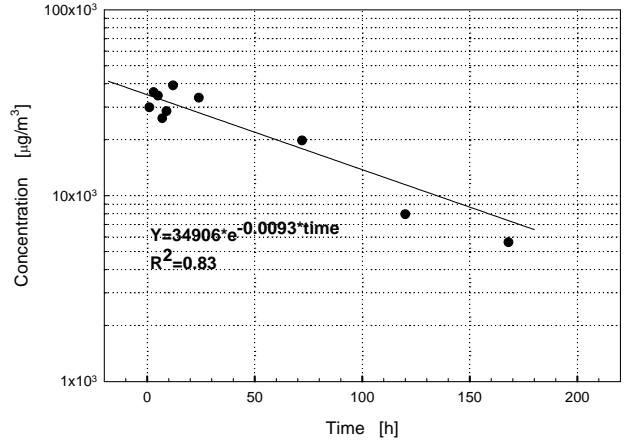


Figure 7. TVOC prediction (specimen 7)

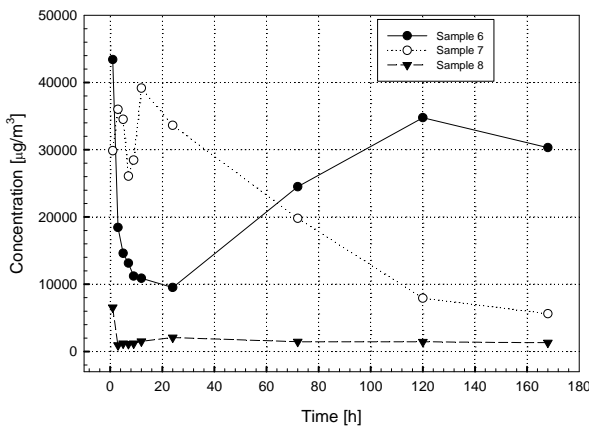


Figure 5. TVOC concentration (specimen 6,7,8)

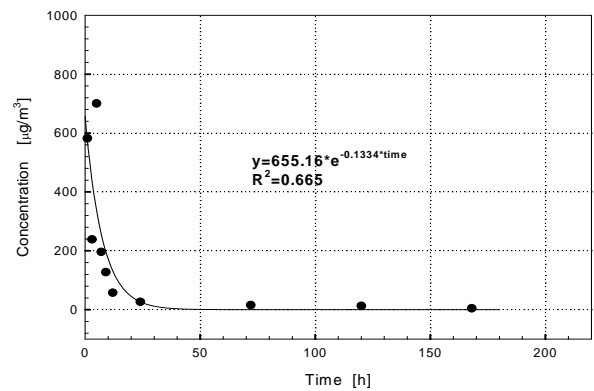


Figure 8. m,p-xylene concentration (specimen 9)

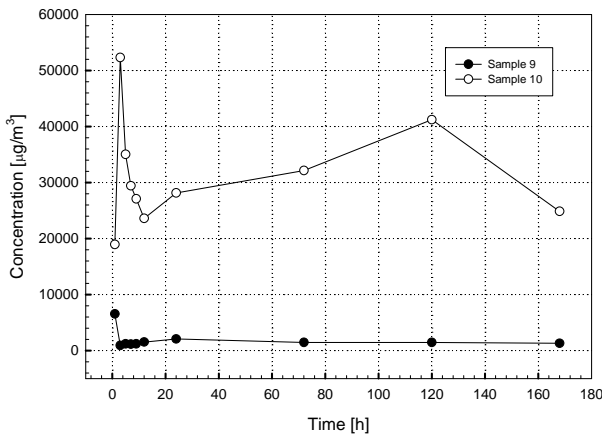


Figure 6. TVOC concentration (specimen 9,10)

It is found that the fitted regression was estimated as $y=34906 * e^{-0.0093 * time}$ with the R^2 of 0.83. This indicates that if we apply the same compositions of walls to the real data, robust prediction results would be obtained. The prediction results of the decrease in m, p-xylene concentration of specimen 9 are shown in Figure 8. The specimen 9 consists of wall-papers with liquefied ceramic attached to concretes. The functional relationship was estimated to be $656.16 * e^{-0.3044 * time}$ with the R^2 of 0.665. In contrast,

Figure 9 illustrates the prediction results of the decrease in ethylbenzene concentration for the same specimen. The regression line was estimated as $534.8 * e^{-0.3044 * time}$ with the R^2 of 0.78. And, the predicted result of the decrease in the emission factors of the VOCs is provided in Figure 10, with the R^2 0.83. We find in this figure that the emission factors decrease abruptly after 100 hours.

4. 2 Prediction of Cumulative Concentration

Figure 11 shows the predicted results of the concentration variations in benzene when the cumulative values of the specimen 7 were used in the analysis. The regression equation was estimated to be $1,274 * (1 - e^{-0.0833 * time})$ with an R^2 of 0.97. Thus, when we apply the same compositions to real buildings, we can predict the decreasing time of the indoor concentration in the case of benzene. Figure 12 provides the prediction results of the concentration in toluene when we carried out the experiment with the same specimen. The estimation result could be expressed as $2,495.17 * (1 - e^{-0.0758 * time})$. And the R^2 was estimated as 0.98, which is a significantly high value. We find in the same figure that the toluene shows much higher concentrations than benzene does, and that its concentration begins to decrease after 60 hours. In addition, it is also found that using the cumulative values of concentration measured by hours is more accurate than using the non-cumulative values. We find in Figure 13 the predicted results of the

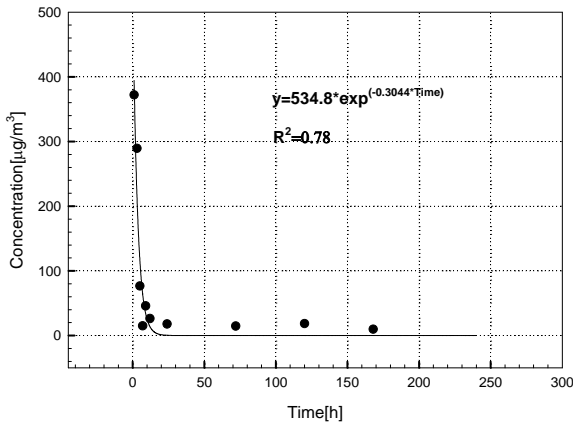


Figure 9. Prediction of ethylbenzene decrease (specimen 9)

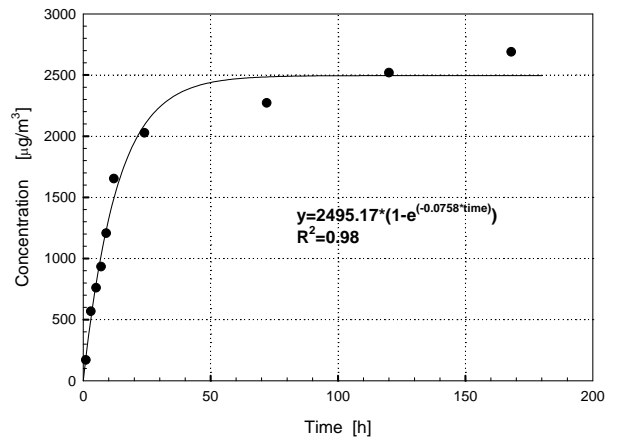


Figure 12. Prediction of toluene cumulative concentration (specimen 7)

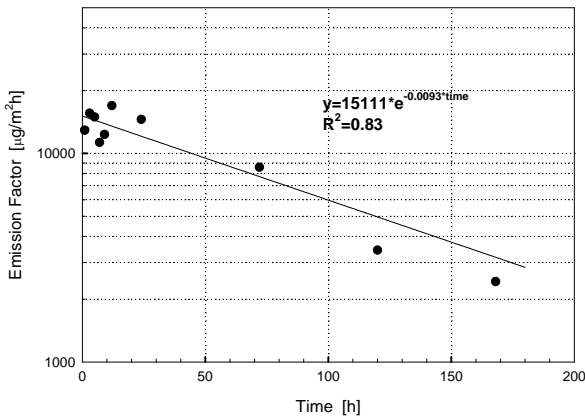


Figure 10. Prediction of emission factor decrease (specimen 7)

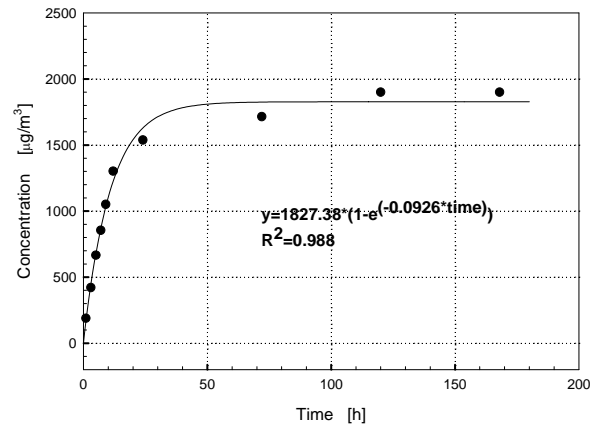


Figure 13. Prediction of ethylbenzene cumulative concentration (specimen 7)

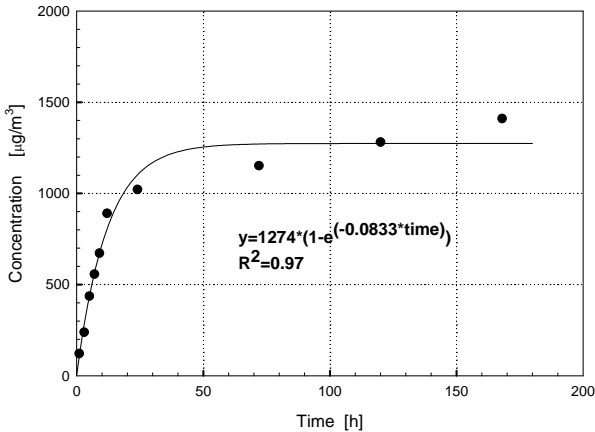


Figure 11. prediction of benzene cumulative concentration (specimen 7)

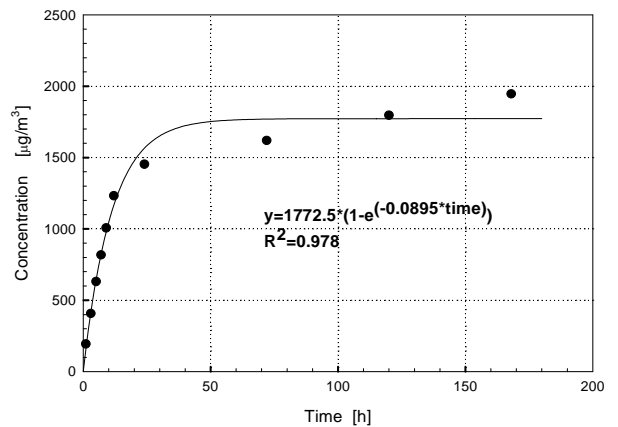


Figure 14. Prediction of m,p-xylene cumulative concentration (specimen 7)

concentration decrease in the case of ethylbenzene. The estimated regression was $1,827 * (1 - e^{-0.0926 * \text{time}})$, with the R^2 being 0.988. The emission rate is estimated in-between the rates of benzene and toluene.

Figure 14 illustrates the predicted results of the m,p-xylene concentration decrease in the specimen 7. We have obtained the regression equation of $1,772.5 * (1 - e^{-0.0895 * \text{time}})$ with an R^2 of 0.978. This indicates that when we predict m,p-xylene concentration decrease, it will be

more accurate to use the hourly-measured cumulative values rather than non-cumulative values. Figure 15 presents the prediction results for the decrease in concentration of o-xylene in the specimen 7. We find in this figure that the emission factor of o-xylene decreases first, and, after 100 hours, it reaches the steady state. The R^2 was 0.987. Thus, if we apply the same compositions to real buildings, we can obtain the highly significant prediction results for o-xylene concentration. In addition, we report in Figure 16

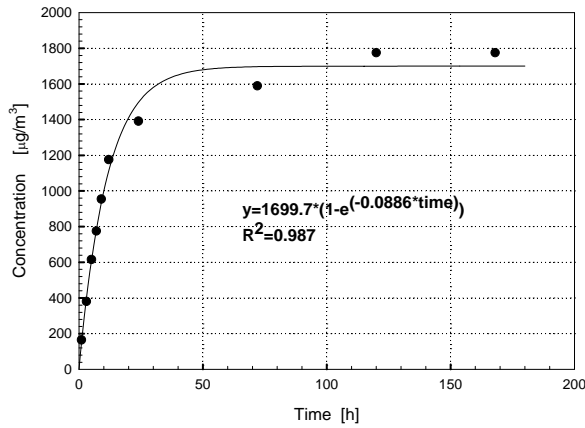


Figure 15. Prediction of o-xylene cumulative concentration (specimen 7)

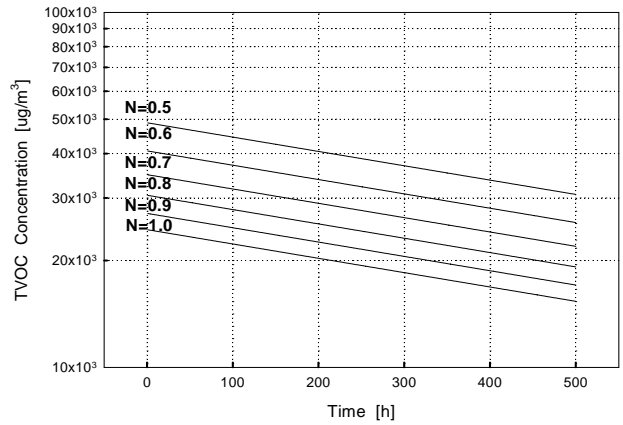


Figure 18. Predicted TVOC concentration under different air exchange rate

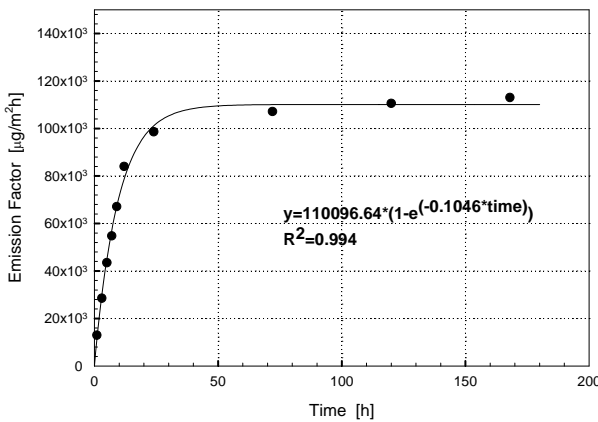


Figure 16. Prediction of cumulative emission factor

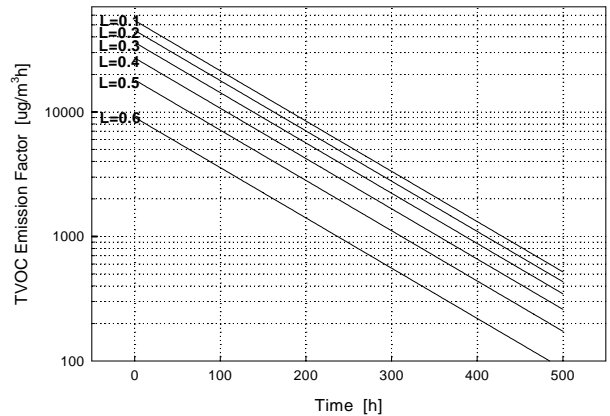


Figure 19. Predicted TVOC emission factor under different loading factor

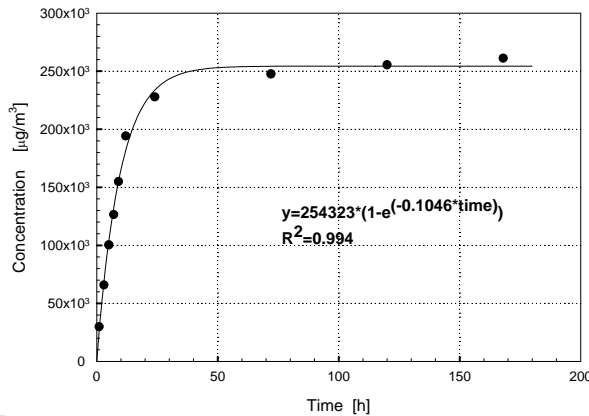


Figure 17. Prediction of TVOC cumulative concentration (specimen 7)

the prediction results of the decrease in emission factors when the cumulative emission factors were used. The R^2 was 0.994, a much higher value than when the non-cumulative values of emission factors were used in the analysis. Thus, it is concluded that more reliable estimates can be obtained when we use the cumulative values of emission factors. We show the prediction results of the decrease in the TVOC concentration as a function of time in Figure 17. The estimated regression is $254,323*(1-e^{-0.1046*time})$ with an R^2 of 0.994. We present the TVOC

concentration under different air exchanges in Figure 18. And, in Figure 19, we present the predicted emission factors of the TVOC under different loading factors.

5. SUMMARY AND CONCLUSION

This study attempted to develop the measurement system with an intention of measuring pollutants which are slowly emitted by the building materials. For this purpose, we constructed specimens with the combination of concrete, gypsum board, mortar, and wall-papers. We then assessed the variation patterns in the VOCs, the TVOC, and the emission factors as a function of time.

The following results were obtained. (1) When we predicted the concentration decrease of the time-dependent TVOC for the specimen 7, the regression equation on a logarithmic scale was $34,906*e^{-0.0093*time}$ with the R^2 of 0.83. (2) When the decrease in the emission factors of VOCs for the specimen 7 was estimated, the prediction equation was estimated as $15,111*e^{-0.0093*time}$ with the R^2 of 0.83. (3) When the concentration decrease of the TVOC for the specimen 7 was estimated, the result could be expressed as $254,323*(1-e^{-0.1046*time})$. (4) When the cumulative values of the emission factors were used in the

estimation process, the predicted results for the decrease in emission factors had an R^2 of 0.994. These preceding results indicate that satisfactory prediction results can be obtained when we apply the same methods to the actual building data.

In this study, prediction methods were considered and developed from the experimental results under accurately controlled experimental conditions. Therefore, there may be difference if the estimated equations are directly applied to real buildings. Further research should be done on the generalization of the developed prediction equations through additional experiments by applying the materials used in this study to real residences.

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