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SUMMARY

The objectives of this study were to characterize the changes of VOC material emission profiles over time and develop a method to account for such changes in order to enhance a source identification technique that is based on the measurements of mixed air samples and the emission signatures of individual building materials determined by PTR-MS. Source models, including power-law model, double-exponential decay model and mechanistic diffusion model, were employed to track the change of individual material emission signatures by PTR-MS over a nine-month period. Samples of nine typical building materials were tested individually for nine months and later in combination to obtain actual mixture emissions. VOC emissions from each material were measured in a 50-liter small-scale chamber. Chamber air was sampled by PTR-MS over a 28-day period to determine their emission rate decay characteristics as well as to establish the initial profile of emission signatures unique to individual materials tested.

IMPLICATIONS

This study contains the first known experimental attempt for indoor source identification under laboratory conditions accounting for the effects of VOC emission decay over time. The new technique has the potential to find the sources invisible/hidden behind indoor surfaces when a building with problems of indoor air quality is suspected.

KEYWORDS

Material emission signature; PTR-MS; VOC; Source identification; Long-term emission

INTRODUCTION

One of the recent important research challenges in indoor air pollution is the identification of indoor Volatile Organic Compound (VOC) emission sources to clearly pinpoint the sources of concern in a field condition. In several field studies performed for residential buildings to measure VOC emissions, it was possible to identify several active compounds with great potency to human health and perception, and their chemical measurements were reported. However, it was hard to trace the emission sources of the detected compounds clearly. As an example, Hodgson et al. (2000) identified acetic acid as one of the important compounds, but were not certain about the sources of acetic acid in the studied houses. If there is a VOC related problem in an indoor air environment, different relevant sources can be identified and screened individually by an on-line analytical monitoring device, Proton Transfer Reaction – Mass Spectrometry (PTR-MS), finding the source(s) and eliminating the problem. A study (Han et al., 2010) demonstrated that unique emission patterns appeared to exist for different types of building materials, and these patterns could be established by PTR-MS as emission signatures (ES). With the definition of ESs for different building materials, it is possible to develop a signal processing technique that can help pinpoint the source materials responsible

for certain VOCs of concern in indoor air (Han et al., 2011). Since the relative emission rates of different emitting compounds can change over time, it is necessary to account for such changes in the estimation and prediction of emission signatures at a given later time. It is hypothesized in this study that the change of material emission signatures over a long period of time may be accounted for by using appropriate emission source models. The objectives of this study were to characterize the change of VOC emission profiles for building materials over time, and to develop a methodology to account for such signature changes to improve the source identification method.

MATERIALS and METHODS

Overview. In a previous study, emission signatures were determined for nine individual building materials by small-scale chamber tests with PTR-MS measurements. The signature is the PTR-MS ion mass (m/z, which is a physical quantity denoting the mass-to-charge ratio widely used in the electrodynamics of charged species) spectrum of the air sampled from each material emission test. In this study, emission tests for the nine materials were performed over a nine-month period. Empirical decay models (power-law and double exponential) and a mechanistic diffusion model were examined and used to represent the decay characteristics, and used to project the emission signature at a later time from each initial emission signature. Actual combined emissions from three multi-material mixtures were then sampled and used in combination with the projected signatures to identify the individual emission sources using the two algorithms previously developed based on signal processing principles (Han et al., 2011).

Environmental chamber conditions. A 50-l small-scale environmental chamber (0.5 m × 0.4 m × 0.25 m high) made of electro-polished stainless steel was used with a precise airflow controller and a humidity controller. The chamber was maintained at a constant stable temperature in the range of 19.87-25.99°C (with a small variation of < ±0.02°C during each sampling period) and at a controlled relative humidity of 31±0.3% RH during the 9-month period of the experiment. The background concentrations of individual VOCs in the empty chamber were maintained clean to be less than 1 µg/m³.

Table 1. Flow rates and specimen areas for the PTR-MS experiments.

Material (ID#)	Flow rate – Q_v (l/min) / Specimen area – A (cm²) Q_v/A (l/s/m²)					
	Meas. #1	Meas. #2	Meas. #3	Meas. #4	Meas. #5	Meas. #6
Ceiling (3)	0.50 / 290.7 0.29	1.55 / 290.7 0.89	4.64 / 290.7 2.66			
Wood (9)	0.50 / 265.5 0.31	1.30 / 265.5 0.81	3.85 / 265.5 2.42	1.21 / 265.5 0.76		1.28 / 265.5 0.80
Carpet (7)					1.28 / 240 0.89	
Linoleum (8)	0.50 / 240 0.35	1.28 / 240 0.89	3.83 / 240 2.66	1.21 / 240 0.84	1.28 / 240 0.89	1.28 / 240 0.89
PVC (2)						
Polyolefine (1)						
Gypsum (4)	0.50 / 416 0.20	1.03 / 416 0.41	3.08 / 416 1.23			
Paint 1 (5)	0.50 / 402 0.21	0.99 / 402 0.41	2.97 / 402 1.23			
Paint 2 (6)	0.50 / 490.2 0.17	1.21 / 490.2 0.41	3.63 / 490.2 1.23	1.21 / 490.2 0.41		

* Meas. stands for 'Measurement'.
* Measurements #1-3: from single material tests.
* Measurements #4-6: from material mixture tests with the selected materials put in the chamber together.

Test specimens. Nine typical building materials were investigated including carpet, ceiling material, gypsum board, linoleum, paint 1 (water-based acrylic), paint 2 (with linseed oil), polyolefine, PVC and wood. Specimens were cut and prepared according to the sizes specified

in **Table 1**. The prepared specimens were placed vertically, parallel with the airflow in the chamber. The range of area-specific ventilation rates was set by adjusting the airflow to the chamber while keeping the size of specimen unchanged.

PTR-MS setting. A PTR-MS device (*Ionicon Analytik high-sensitivity model with a detection limit as low as 1 pptv, Austria*) was operated at the standard conditions (Drift tube pressure: 2.20±1.9e-5 *mbar*, PC: 355 *mbar*, FC: 7.0 STP *cc/min*, U SO: 85 *V*, U S: 120 *V*, Drift tube voltage: 600 *V* and Source: 6.0 *mA*). Lindinger et al. (1998) describes the detailed explanations on the device and its principle. The normalized product ion count rate (*ncps*) was used to quantify the concentration levels of target VOCs.

Test procedure. The nine building materials were previously studied at three different area-specific ventilation rates (Measurements #1, #2 and #3) to establish an initial ES library by PTR-MS specific to each individual material. After one year of the experiment for the establishment of the initial ES library, long-term emission experiments using the same nine materials sealed and preserved in a well conditioned storage space have been performed for nine months. Three multi-material mixture emission measurements were collected (Measurements #4-#8) after the long-term experiments to obtain combined emission signatures and to assess the effects of the long-term ES change consideration on the source identification performance of the developed algorithms. Three source models – a power-law decay model (Zhu et al., 1999), a double-exponential model (Brown, 1999) and a mechanistic diffusion model (Little et al., 1994) were applied to the collected long-term measurements for estimating and predicting the long-term VOC emissions and the corresponding material ESs at a given later period. The corresponding source identification performance was assessed by using three performance indices – norm error expectation, score and success rate as follows (The detailed definitions can be found in Han et al., 2011):

$$Err \equiv E\left\{\left\|\vec{\alpha}_{est} - \vec{\alpha}_{true}\right\|_2\right\}, \quad Score \equiv E\{scr(N)\}, \quad SR \equiv \left(N - N_{fail}\right) \times 100 / N \qquad (1)$$

where *Err* is the expected value of the 2-norm of the difference between the estimated value of signal intensity factor vector (α) and the true one, *N* is the total number of random samples for source identification trial for each case, N_{fail} indicates the number of material identification failures that occurred during the trial, *Score* is the expected value of success score (*scr*), and *SR* represents the success rate in source material identification defined in percentage.

For each measurement, the mass spectra for the background emission signal from the empty chamber and for the sample emission signal with each prepared specimen inside the chamber were measured all after three volumetric air changes from the start of ventilation to allow concentrations in the chamber to reach over 95% of the quasi-steady state level. PTR-MS was set to scan from *m/z* = 21 to *m/z* = 250 once every 12 s with an ion mass resolution interval of 50 ms. The total sampling period was 10 min (600 s) with 50 ion mass spectra collected for each dataset. During each measurement, another set of duplicate mass spectra was scanned to verify the collected data.

RESULTS

Long-term ES estimations/predictions by using source models
Can the long-term emission signatures at a later period of time be estimated by using some information on the initial material emission signatures?
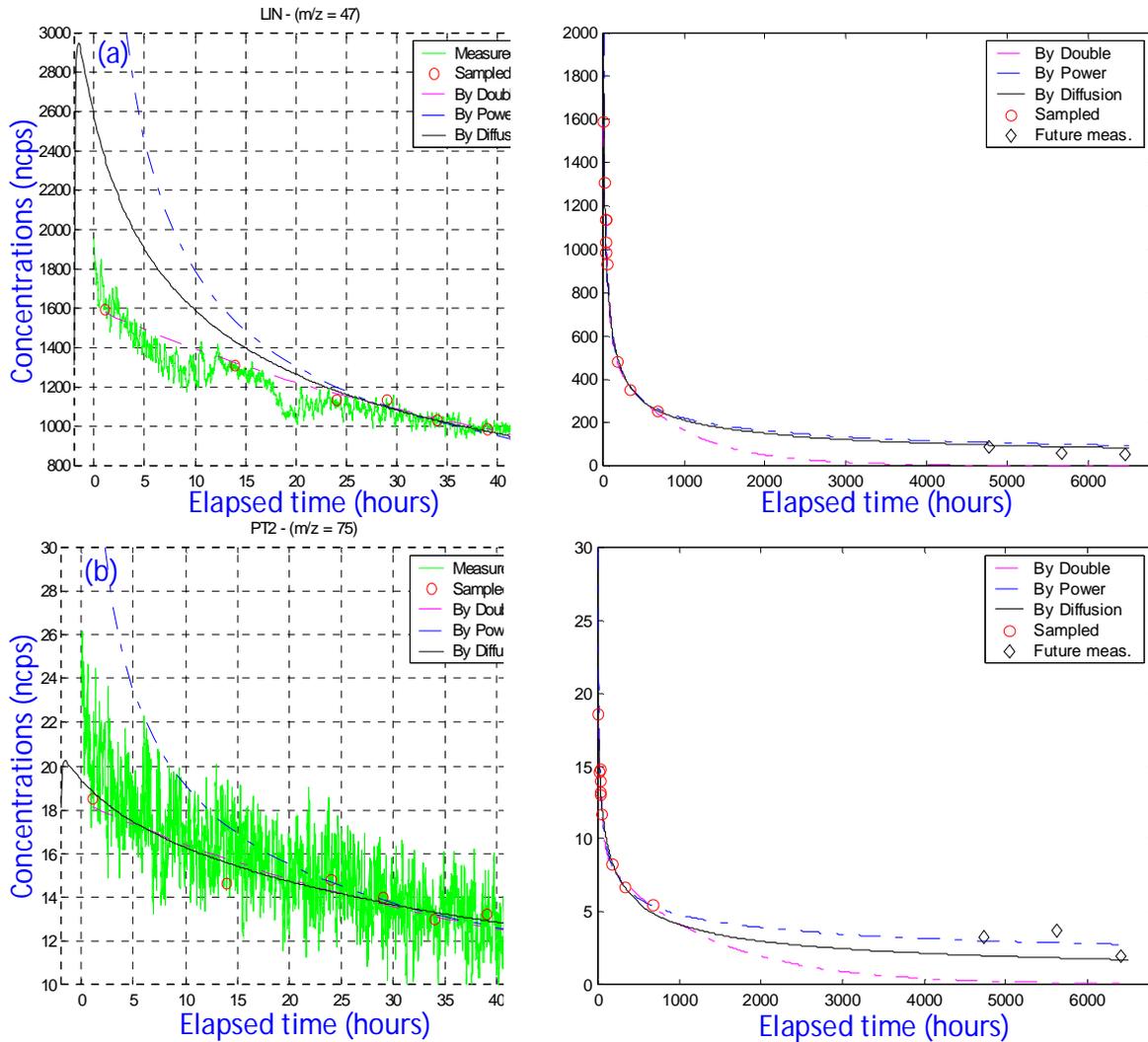
Figure 1. Prediction of the long-term emissions at 7, 8 & 9 months by source models with short-term measurements (≤ Day 28). (a) Ethanol (m/z=47) from Linoleum. (b) Propanoic acid (with a small portion of ethanol, m/z=75) from Paint 2.

The present study investigated the feasibility of the estimation and prediction of long-term emission signatures by using collected measurements and source models. Two materials – Linoleum and Paint 2 were selected and studied in this aspect, and their results were presented here as an example because these two materials are representative of two characteristic material types distinct by a steady (or slow) emission decay and a fast emission decay over time, respectively. The measurements at t_{meas} = [1, 14, 24, 29, 34, 39, 44 hours, Day 7, Day 14, and Day 28] were sampled and utilized for this examination. The source models, double-exponential, power-law decay models and Little's mechanistic diffusion model, were applied to get the optimal fitting line for each case in terms of least squared error between the estimated concentrations and the measured ones, by using ***Powell*** search algorithm (Powell, 1964) customized via Matlab, and the fitting results were used for predicting the long-term emission concentrations at 7, 8 and 9 months. The ES estimation is also possible using the full measurements collected for the period of 9 months, but the results were not presented here due to the limited available pages. For the fitting with the power-law model, only the measurements after 24 hours were used due to the apparent internal-diffusion controlled emissions observed after this hour (Refer to the NRC report, Zhu et al., 1999). **Figure 1**

demonstrates the prediction performance of the diffusion source model, comparing this approach with the two empirical source models. Except for outliers, the mean percentage of prediction error at the target months with the double-exponential model was < 15% for Linoleum (> 0.59 of R^2, Note: R^2 is calculated for all the points presented, which are the sampled measurements and the future measurements) and < 19.1% for Paint 2 (> 0.91 of R^2) when applied to all ES composing compounds of each material, whereas that with the power-law was < 3.3% for Linoleum (> 0.93 of R^2) and < 4.1% for Paint 2 (> 0.86 of R^2) as well. The absolute magnitude of this prediction error was calculated in percentage with regard to the concentration level at 24 hours in the profile of each case. Long-term ESs can also be predicted at a certain given time by utilizing the source models. **Figure 2** exemplifies the approach for emission signature predictions and the performance result using a source model for Linoleum at the 9-month period. The figure implies that with some information on the measured profile of material emission signatures over an early stage, the long-term change of ESs for a given material at a specific elapsed time can be effectively predicted and may be used for enhancing the performance of source identification. The prediction performance of long-term ESs was 3.16% for Linoleum and 6.87% for Paint 2 in terms of error variance when the power-law decay model was utilized to predict them at the 9-month period (Note: The percentage value here represents the error variance between the estimated emission signature and the measured one for a target material at a given time. The smaller the values, the better the ES prediction performance).
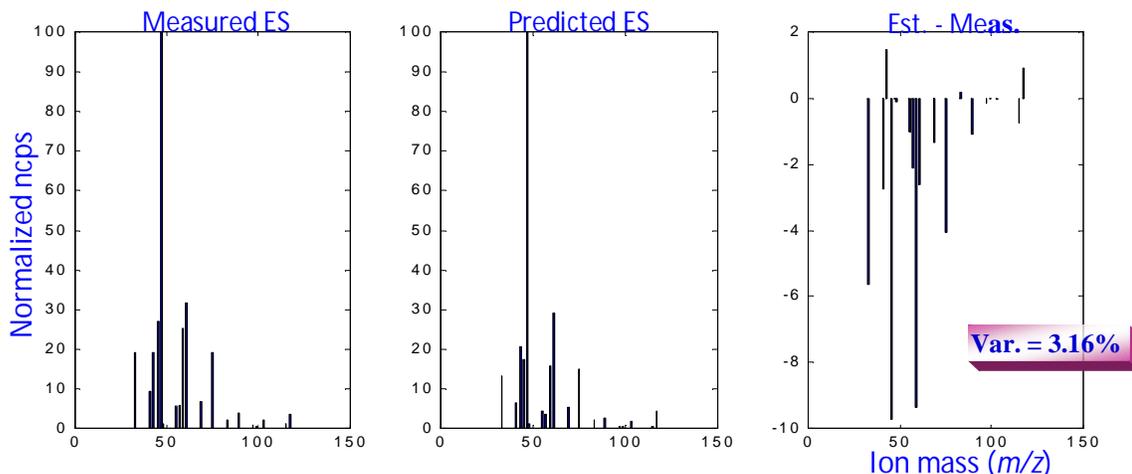

Figure 2. Prediction of emission signatures exemplified by Linoleum at 9 months via Power.

Reconstructed library of ES (with the power-law decay model at the 9-month period)
After predicting the long-term ESs for a given set of material mixtures used, the dataset of ESs can be re-established, and used in effectively separating and identifying emission signatures for improving the source identification performance over long-term emissions.

ES separation/identification performance with the long-term ES change consideration
The source ID enhancement with the long-term consideration is summarized in **Table 2**.

Table 2. Comparison of source ID performance by the ES predictions for various cases.

Ground truths	ID_{est1} à α_{est1}[a]	ID_{est2} à α_{est2}[a]	Err1[b]	Err2[b]	Score1	Score2	SR1	SR2
[6 8 9] w/ INIT	[**6** 7 **8 9**] à [**0.20**$_2$ 0.17$_7$ **0.05**$_6$ **0.09**$_9$]	[**6** 7 **8 9**] à [**0.06**$_7$ 0.15$_4$ **0.19**$_4$ **0.32**$_3$]	0.42	0.26	25.20	23.00	28.00	26.00
[6 8 9] w/ LT à [0.12 0.39 0.49]	[3 **6**] à [0.04$_0$ **0.38**$_4$]	[3 **6 8 9**] à [0.05$_1$ **0.17**$_1$ **0.20**$_0$ **0.26**$_8$]	0.40	0.28	27.20	66.00	30.00	**76.00**
[7 8] w/ INIT	[6 **7 8**] à [1.09$_1$ **0.53**$_5$ 2.57$_7$]	[6 **7 8**] à [0.63$_0$ **0.48**$_1$ 2.84$_9$]	0.95	0.76	45.00	44.60	50.00	50.00
[7 8] w/ LT à [0.51 2.60]	[3 **7 8**] à [0.18$_3$ **0.34**$_3$ 3.00$_2$]	[3 **7 8**] à [0.16$_3$ **0.46**$_0$ 2.80$_2$]	0.61	0.38	86.00	83.60	**96.00**	**96.00**
[8 9] w/ INIT	[3 6 **8 9**] à [0.05$_7$ 0.57$_4$	[6 7 **8 9**] à [0.70$_4$ 0.13$_2$	1.37	1.28	73.00	66.60	88.00	88.00

[8 9] w/ LT à [2.50 4.25]	2.03_5 3.09_4] [1 3 **8 9**] à [0.05_8 0.26_1 2.87_5 3.79_1]	2.35_6 3.08_1] [3 **8 9**] à [0.29_9 2.43_1 3.66_1]	0.63	0.72	72.00	74.20	**88.00**	**88.00**

[a] To exemplify the form of the results from the two algorithms, these estimation results (material ID set and the corresponding signal intensity factor vector) were presented in the table, obtained when applying the algorithms to the representative (i.e. by averaging the measured 50 samples) emission signature measured for each given material mixture. However, the three performance indices were calculated using the 50 measured samples for each mixture, following the definitions shown in Equation (1). [b] 1: of Algorithm 1, 2: of Algorithm 2. * w/ INIT: with initial emission signatures; w/ LT: with the consideration of long-term emissions.

DISCUSSION

The power-law model was simple and efficiently fast, and seemed to properly represent the physical decay characteristics of long-term VOC emissions. The mechanistic diffusion model showed a better initial response than the power-law and a similar performance to the double-exponential. This model well represented the up-and-down characteristic concentration profile at an early emission stage as illustrated in **Figure 1**. Its long-term emission predictions at 7, 8 and 9 months were good and for some cases, better than the power-law. As found in the double-exponential case, its fitting process was hard and time-consuming (due to partial differential equations), and even infeasible with bad-conditioned initial parameter guesses. The good prediction property of this diffusion model for the entire emission period was very encouraging because the model parameters could also be measured using procedures completely independent of the chamber studies and their measurements, or obtained from the comparison with expected values, where possible (Little et al., 1994). Because of this attractive property, emission measurements shorter even than 28 days might be used to predict long-term material ESs for a longer period of VOC emissions. The proper prediction of the long-term ESs using source models seemed to improve the separation/identification performance as demonstrated in **Table 2**. However, for very consistent ESs over a long-term period (i.e. Case [8 9]), the predictions made no marked difference in source identification.

CONCLUSIONS

It was feasible to use the emission decay models to account for the effects of emission decay on the material's emission signatures. The adjusted emission signature could be used to successfully identify the individual emission sources based on the air sample from spaces where multiple emission sources existed. The source identification technique has the potential to pinpoint emission sources that may be invisible or hidden from the visual inspection (even) by experts when a building with air quality problems is concerned.

ACKNOWLEDGEMENT

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