



## Measuring chemical emissions from wet products—Development of a new measurement technique

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### ABSTRACT

A new approach for estimating chemical emissions from wet products has been developed. The concept of such approach is that emission rates can be estimated from the amount of target chemicals in the product as a function of evaporation time. Samples were placed under a laboratory fume hood under controlled conditions (surface air velocity and temperature). Weight losses of the product were monitored and residuals at different time intervals were chemically analyzed. Emission factors of the target chemicals were then calculated based on the weight losses and residual levels of the chemicals. To demonstrate the applicability of this approach, two wet products with very different physical characteristics, one liquid and one paste-like viscous fluid, were chosen. Emissions of two principle chemicals in the products, decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) were measured. The influences of initial sample weight, surface air velocity, and temperature were investigated. The calculated emission profiles were compared with those obtained from the chamber method. The described approach could be used as an alternative screening method for emission tests of wet products, especially for compounds with low vapour pressure when sink effect poses serious challenge in traditional chamber-based emission tests.

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### 1. Introduction

There has been a growing concern about the quality of indoor environment, which has been associated with adverse health effects that have significant socio-economic impacts. Emissions of chemicals from consumer products, and building materials, are important contributors to such chemicals in air [1–5]. Understanding the emission behaviour of chemicals from products is critical for predicting the concentration and occupant's exposure to these chemicals, and for the design of better mechanical ventilation systems. Studies have shown that concentrations of many airborne chemicals are higher in indoor air than in outdoor air, which means that they have strong indoor-related sources [6,7]. Major sources of these compounds include consumer products such as cosmetics, perfumes and deodorants.

In general, the product emission rate is controlled partly by internal diffusion as a result of concentration gradient and partly by surface emissions through convection or evaporation due to interaction of the material surface with adjacent air [4,5,8]. Emission from wet products is characterized by its initially high but fast

decay profiles [9]. Air temperature, relative humidity and surface air velocity have a pronounced impact on the product emission rate. Environmental chambers in which these parameters can be controlled are therefore commonly used as the standard procedure in product emission testing [1,4,8].

One of the challenges facing chamber-based emission tests is the sink effect, which refers to the phenomenon in which chemicals emitted from the products are adsorbed on the inner surface of the chamber and its sampling system [10,11]. The severity of the sink effect increases as the vapour pressure of the target chemical decreases [12]. Therefore, the sink effect poses particular challenge for measuring emissions of chemicals with low vapour pressure such as di-(2-ethylhexyl) phthalate [13] and nicotine [14]. Quantitative loss of decabromodiphenylether (BDE-209) to the interior surfaces of the chamber system was also observed [2]. The sink effect has so far proven to be one of the major issues in estimating an accurate product/material emission profile [15].

Efforts have been made to minimize the sink effect in chamber-based emission tests by either reducing the interior surface area [16,17] or developing predictive tools compensating for the sink effect [10,18]. The objective of this study is to illustrate a new concept for an alternative approach to the chamber-based method. The uniqueness of the proposed method is based on measuring (1) the product weight losses over a period of time, and (2) chemi-

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cal residual levels in the product over that period. Although many researchers have used electronic balance to measure the overall emissions, none has developed a method for the individual chemical emissions [19]. In this study, both product weight loss and chemical residual analysis are determined in order to estimate emissions of individual chemicals from two wet products without the use of a chamber, hence eliminating the errors caused by the sink effect.

## 2. Experimental

### 2.1. Samples, standards and reagents

Two wet products, one diaper cream and one pump-bottled fragrance were obtained from retail stores in Canada [5]. Decamethylcyclotrisiloxane (D5) and dodecamethylcyclotrisiloxane (D6) were obtained from Sigma–Aldrich Canada Ltd. (Oakville, ON, Canada) and Fluorochem Ltd. (Derbyshire, UK), respectively. Hexane and methylene chloride were obtained from OmniSolv (EM Science, Gibbstown, NJ). All standard solutions were prepared in either hexane (for the residual analysis of chemicals in products) or methylene chloride (for the analysis of ORBO-43/XAD-2 tubes collected from the field and laboratory emission cell (FLEC) tests).

### 2.2. Apparatus

The weight losses of the two test products were monitored using an electronic balance (Denver APX-323, readability = 0.001 g, Fisher Scientific, Ottawa, ON, Canada), with a data recorder. Aluminum weighing dishes (52 mm in diameter, resulting in an evaporation surface area ( $A$ ) of 21.2 cm<sup>2</sup>) (VWR, Mississauga, ON, Canada) were used as the substrate, on which the products were placed. The surface air velocity above the sample surface in the laboratory fume hood was monitored by a TSI 9880 surface air velocity meter (Shoreview, MN, USA). The room temperature and relative humidity were monitored by a Cole-Parmer 37950-10 thermo-hygrometer (Fisher Scientific). A temperature-controlled heating pad (VWR 575 digital hotplate stirrer, Mississauga, ON, Canada) was used to heat the weighing dishes when desired.

### 2.3. Measuring weight loss over time and sample preparation for residual analysis

The balance and the aluminum dishes were placed at the constant height in the fume hood and with the same distance from the sash (Fig. 1) to achieve the same surface air velocity during the experiments. Earlier work showed that the surface air velocity and turbulent intensity have significant impact on the emission rate [4,8]. The height of the sash was adjusted to achieve desired surface air velocity. To mimic the indoor air condition, experiments were

also carried out by placing sample dishes on a laboratory bench, outside the laboratory fume hood.

The diaper cream (0.5 g) was applied on the aluminum dish using a spatula and spread it to the entire surface of the dish using a flat bottom of a clean 2-mL GC vial. As per the spray, because it was impractical and difficult to control the spray action during sample loading, the spray head of the bottled fragrance was therefore removed and the liquid (0.4 g) was transferred to the aluminum dish with a Pasteur pipette to form a thin film by gently swirling the dish. Attention was paid to apply similar amount of the products to each replicate sample dish. The sample-loaded dishes were set to the stand with starting time recorded.

One of the sample dishes was placed on the electronic balance and its weight loss over time was monitored: it was measured every 30 seconds and the average values of every 4 minutes were calculated and recorded. Each sample had several replicates for chemical analysis. For diaper cream product, a small aliquot (about 0.1 g) of the diaper cream in the replicates, aluminum dishes that were not on the balance, was taken at respective evaporation times using a spatula and placed in a 15-mL vial for residual analysis.

For the fragrance, due to difficulties in sampling aliquot from the sample dishes, residual levels of the target chemicals at different evaporation times were measured using a different procedure. Same amount of the fragrance (0.3 g) was added to two groups of 15-mL vials. One group of vials was evaporated under a breeze of nitrogen flow of 1000 mL min<sup>-1</sup> above the liquid at a flow rate of, mimicking slow evaporation. The other group of vials was under a flow rate of 2000 mL min<sup>-1</sup> to achieve a higher evaporation rate where visible waves and splashes of the liquid surface were observable. The vials were capped after various evaporation times for residual analysis.

### 2.4. Residual analysis

The general extraction procedure of D5 and D6 from the products was described elsewhere [5]. Briefly, 4 mL of hexane was added to the 15-mL sample vial. After mechanical shaking and centrifugation, the upper clear layer was collected and properly diluted for the gas chromatograph–mass spectrometry (GC–MS) analysis.

GC–MS analysis was carried out using Agilent 6890 N coupled with 5973 MSD (Agilent Technologies, Palo Alto, CA, USA) [5]. D5 and D6 were separated using a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5MS column (J&W Scientific, Folsom, CA, USA). The GC injection port temperature was set at 280 °C; GC oven temperature was set at 45 °C for 5 min, increased to 210 °C at 15 °C min<sup>-1</sup>, further to 270 °C at 8 °C min<sup>-1</sup>, and to 310 °C at 30 °C min<sup>-1</sup>, and kept at 310 °C for 25 min. The MS was operated in full scan mode. The ions used for quantifying D5 and D6 were  $m/z$  355 and  $m/z$  341, respectively. The qualification of the target chemicals was based on the related mass spectrum of each chemical extracted from the chromatograms.

### 2.5. Chamber test

A field and laboratory emission cell (FLEC) (FL-0001/FL-0150, Chematec, Denmark) was used for emission tests. Test sample was applied to the bottom of the aluminum weighing dish and placed inside the FLEC. The temperature and relative humidity of the incoming nitrogen gas were controlled at 24.0 ± 0.2 °C and 50 ± 1% RH. The flow rate (FR) of the FLEC was 540 mL min<sup>-1</sup> and 740 mL min<sup>-1</sup> for diaper cream and fragrance, respectively. ORBO-43/XAD-2 tubes (Sigma–Aldrich) were used to capture the target chemicals (D5 and D6) in the outlet air of the FLEC. Methylene chloride was used to elute these chemicals for GC–MS analysis. Emission factor (EF, mg m<sup>-2</sup> h<sup>-1</sup>) of target chemicals was then esti-

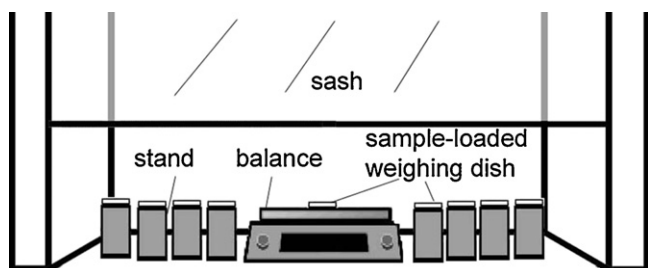


Fig. 1. Experimental setting: balance and sample dishes are placed inside a fume hood.

mated from the concentrations of target chemicals in the chamber air ( $C$ ,  $\text{mg m}^{-3}$ ) using  $\text{EF} = C \times \text{flow rate} / \text{evaporation surface area}$ .

### 3. Results and discussions

#### 3.1. Concept of non-chamber test method

Fig. 1 illustrates the experimental set-up for placing multiple dishes in the fume hood. The airflow through the opening of the fume hood window was controlled by the position of the sash. All sample dishes in the fume hood are placed parallel to the fume hood window and at the same height and distance from the sash in order to obtain similar evaporation condition among all sample dishes. They therefore, can be considered replicate samples in the experiment. One of the sample dishes was placed on an electronic balance while others on the stands.

The weight losses of the product in the weighing dish were monitored in real time using an electronic balance, while the residual levels of target chemicals in other aluminum dishes were periodically analyzed. The loss of the target chemicals, equivalent to the amount of chemicals emitted from the product, at various evaporation times can be determined if the remaining weight of the product and the residual levels of the target chemicals in the remaining sample at various evaporation times are known. This can be achieved by analyzing the residual levels of the target chemicals in the replicate samples that are arranged under the same experimental conditions at different evaporation times from the sample dishes whose weight are monitored. The residual levels of the target chemicals at different sampling times can then be applied to the weight loss curve to calculate the remaining amount of the target chemicals in the test product over time. Thus, at any given time  $t$ , the weight of a target chemical in the remaining product ( $W_t$ ) can be calculated using,

$$W_t = P_t C_t \quad (1)$$

where  $P_t$  is the weight of the remaining product that is obtained from the weight loss curve and  $C_t$  is the concentration of the target chemical in the product at time  $t$ . Once the  $W_t$  is known, emission profiles can be generated by plotting the emission rate ( $W_{t1} - W_{t2}$ ) as a function of time. Since the evaporation is dependent on the surface area ( $A$ ) available for the evaporation, the emission factor (EF) is used to characterize the emissions (Eq. (2)).

$$\text{EF}(\text{mg m}^{-2} \text{h}^{-1}) = \frac{W_{t1} - W_{t2}}{(t_2 - t_1)A} \quad (2)$$

#### 3.2. Method performance

Fume hood provides an easy way to control the surface air velocity for evaporation by adjusting the fume hood sash. The surface air velocity above the samples was relatively stable during the product evaporation period. Even at a relatively high surface air velocity of  $0.75 \text{ m s}^{-1}$  the relative standard deviation of the air velocity was only about 3% (Fig. 2). The measurements of low surface air velocity on the experiments that were conducted on the lab bench rather than those in the hood were limited by the sensitivity of the air velocity meter which has a detection limit of  $0.03 \text{ m s}^{-1}$ . Therefore, the measured air velocity in the bench experiments was less than  $0.03 \text{ m s}^{-1}$ . While the laboratory temperature was well controlled by the building heating, ventilation and air conditioning system with a standard deviation (s.d.) of  $0.2^\circ\text{C}$ , the day-to-day variation of relative humidity in the laboratory could not be controlled. As demonstrated in Fig. 2, not only were the values of the RH in the room very different in the consecutive two days, but also drifted upwards during the second day probably due to sudden changes in the outdoor air condition.

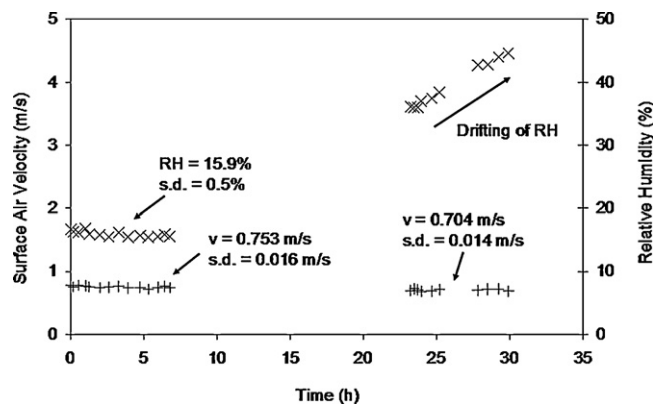


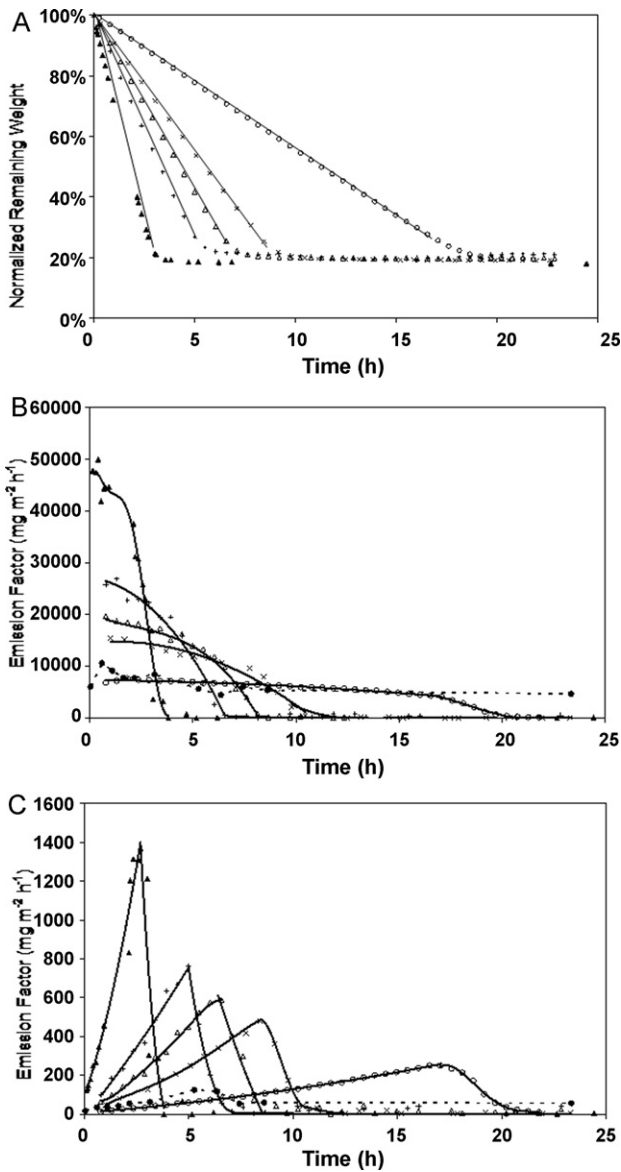
Fig. 2. Air velocity and relative humidity in a fume hood monitored over 30 h. Room temperature was  $23.7 \pm 0.3^\circ\text{C}$ . (+) surface air velocity; (x) relative humidity (%).

Since the surface air velocity may create a slight pressure and impact the balance reading, the performance of the electronic balance used in the study was investigated. Compared to the situation of zero air velocity, the highest air flow of  $0.75 \text{ m s}^{-1}$  used in this study resulted in a mean reading of  $0.009 \text{ g}$  (s.d. =  $0.003 \text{ g}$ ) over a period of 24 h. Since in each experiment, the balance was always tared (for the resetting of zero reading) prior to the sample loading, this reading due to air pressure can be corrected. However, the variation of the balance reading would limit the detection of small changes of product weight during the weight loss measurements. In this case, a detection limit of the weight loss measurement of  $0.009 \text{ g}$  was estimated based on 3 times the standard deviation (s.d. =  $0.003 \text{ g}$ ) of the balance reading. The detection limit however, can be further improved by employing a more sensitive and stable electronic balance to detect small changes in the weight loss of the product [20].

#### 3.3. Product weight loss profile

Figs. 3A and 4A describe the weight loss curves of the fragrance and diaper cream under different experimental conditions of temperature ( $24\text{--}32^\circ\text{C}$ ) and surface air velocity ( $0.03\text{--}0.75 \text{ m s}^{-1}$ ). The remaining weights were normalized to eliminate the small differences in sample loadings among the test products. It is clear that a higher temperature or a higher air velocity resulted in a higher weight loss rate. The profiles of the two products behaved quite differently. The product weight loss curve of the fragrance decreased first linearly over time and then leveled off at about 20% remaining weight (Fig. 3A). A non-linear decrease was observed in the weight loss of diaper cream (Fig. 4A). The former product is mostly liquid and weight loss profile resembled that reported for the pure liquid mixture [19]. The diaper cream is a thick semi-solid mixture. The evaporation of components in the sample is a more complicated process: it is not only controlled by the external environment such as temperature and surface air velocity, but also governed by the internal diffusion rates of the volatile components during evaporation, and the interaction between the volatile components and the substrate [4,6,8].

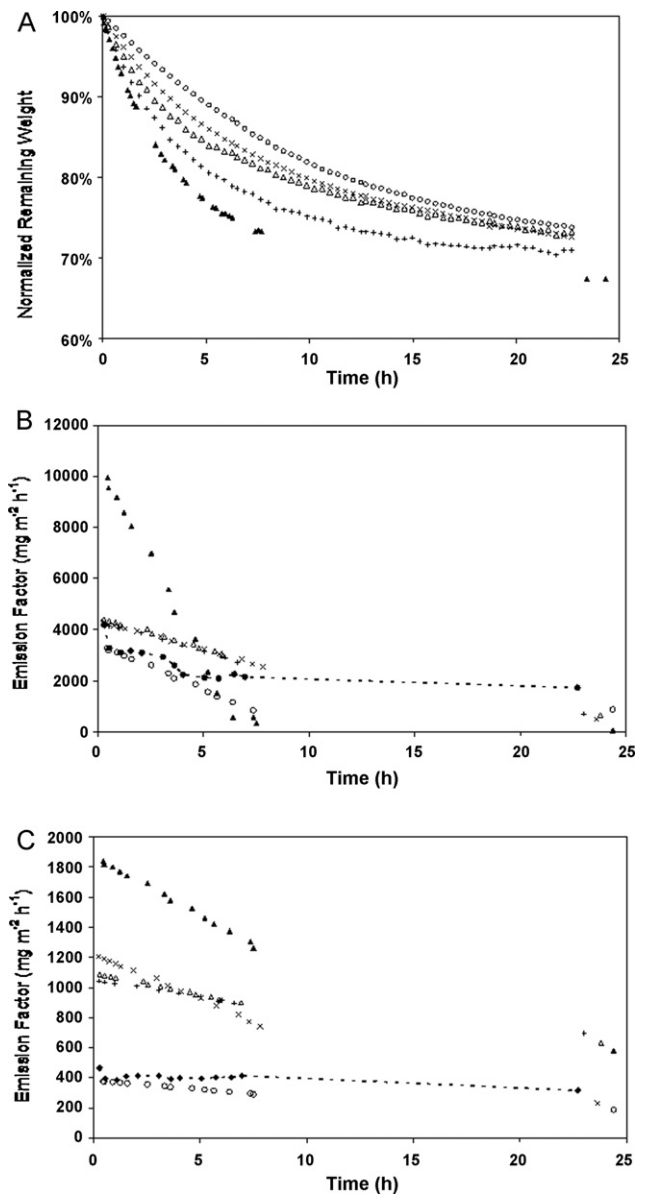
The weight loss profile determined by the balance method was reproducible. Fig. 5 shows that two diaper cream samples evaporated in two different days provided almost identical weight loss profiles over a 24-h period under the same air velocity ( $0.75 \text{ m s}^{-1}$ ) and initial amount of  $0.532 \text{ g}$ . However, the initial amount that applied to the aluminum dish could influence the product weight loss profile. The normalized weight losses showed clear differences among the initial weights of  $0.677 \text{ g}$ ,  $0.532 \text{ g}$  and  $0.522 \text{ g}$  measured under the same condition (Fig. 6). For example, a difference of 2.8% in percentage weight loss between samples with initial weight of



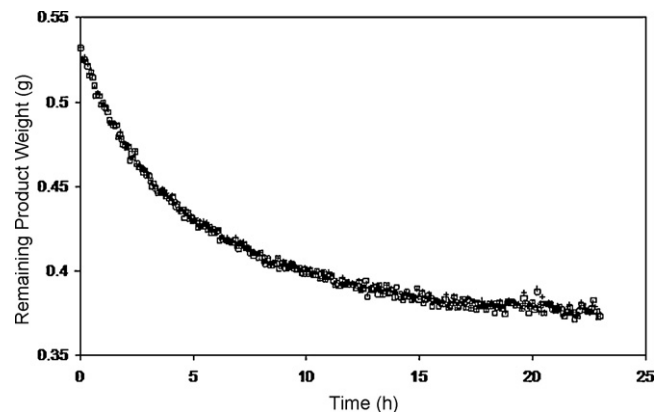
**Fig. 3.** Emission test results of fragrance under various temperature ( $t$ ) and surface air velocity ( $v$ ) conditions. (A) Normalized weight loss curve; (B) emission factors of D5; (C) emissions of D6. ( $\blacktriangle$ )  $v=0.03\text{ m s}^{-1}$ ,  $t=32.0^\circ\text{C}$ ; ( $+$ )  $v=0.75\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; ( $\triangle$ )  $v=0.55\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; ( $\times$ )  $v=0.35\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; ( $\circ$ )  $v=0.03\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; and ( $\bullet$ ) FLEC test,  $v=0.02\text{ m s}^{-1}$ ,  $t=24^\circ\text{C}$ .

0.677 g and 0.522 g was observed at 2 h, it grew to 5.7% at 4 h, 7.3% at 8 h and 8.8% at 16 h. It is understandable that for the same surface area, a larger quantity takes longer than a smaller quantity to reach the same percentage of weight loss. It seems that the weight loss decay rate is smaller for samples with larger quantity due to some internal diffusive mechanisms. The initial evaporation rate however, is controlled by the surface area not the applied amount. As shown in the inserted figure, the regression for the first hour had linear weight loss curves and the decay constants were very similar among the samples with three different initial weight.

It is therefore critical to have same initial amount applied to the replicate dishes for the test. The sample loading ( $\text{g cm}^{-2}$ ) in this study was chosen considering the following two factors. The amount should be close to the reported user patterns so that to have the weight loss profile relevant to the real situation [21,22], and should be in the range for easy handling and good reproducibility. In this study, the initial sample weight was kept close to 0.5 g for the diaper cream and 0.4 g for the fragrance.



**Fig. 4.** Emission test results of diaper cream under various temperature ( $t$ ) and surface air velocity ( $v$ ) conditions. (A) Normalized weight loss curve; (B) emission factors of D5; (C) emissions of D6. ( $\blacktriangle$ )  $v=0.03\text{ m s}^{-1}$ ,  $t=32.0^\circ\text{C}$ ; ( $+$ )  $v=0.75\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; ( $\triangle$ )  $v=0.55\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; ( $\times$ )  $v=0.35\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; ( $\circ$ )  $v=0.03\text{ m s}^{-1}$ ,  $t=23.7^\circ\text{C}$ ; and ( $\bullet$ ) FLEC test,  $v=0.02\text{ m s}^{-1}$ ,  $t=24^\circ\text{C}$ .



**Fig. 5.** Comparison of diaper cream weight loss with same initial weight of 0.532 g conducted at two different times.  $t=23.7^\circ\text{C}$ ,  $v=0.75\text{ m s}^{-1}$ . ( $+$ ) Sunny days; and ( $\square$ ) Rainy days.

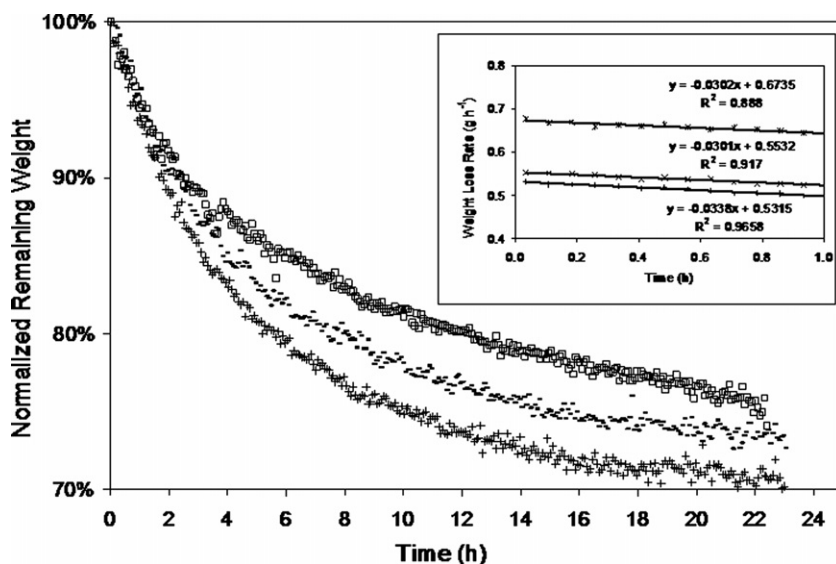


Fig. 6. Influence of the initial weight on weight loss of the diaper cream.  $t=23.7^{\circ}\text{C}$ ,  $v=0.75\text{ m s}^{-1}$ ; (+) 0.532 g; (-) 0.552 g; and (□) 0.677 g. Insert: linear weight loss in the first 60 min at a rate of 0.03.

### 3.4. Residual analysis

Residual analysis of target chemicals in the remaining sample is another critical aspect for the accurate determination of chemical emission profiles. For the diaper cream, this could be achieved by scooping a small quantity out of the product in the replicate aluminum dishes at various evaporation times and determining the concentrations of the target chemicals by GC–MS.

Because of the difficulties in sampling liquid in the dish, residual analysis of the liquid fragrance had to be conducted using a different approach. Assuming internal diffusion of a chemical in a liquid is fast enough and the concentration in the liquid is therefore in equilibrium state at any given time during the evaporation, the residual levels of the chemicals in the remaining product is solely depended on the percentage of liquid evaporated. Hence, the concentrations of the target chemicals (D5 and D6) were determined separately under two nitrogen flow rates. Both flow rates produced similar results, the residual levels of D5 and D6 was independent from the nitrogen flow rate and was dependent on the percentage of liquid evaporated. The measured concentrations as a function of percentage of product evaporated were then used to calculate the remaining target chemicals using the product weight loss profile described in Fig. 3A.

### 3.5. Chemical emission over time from different products: the fume hood method

The emission factors (EF,  $\text{mg m}^{-2}\text{ h}^{-1}$ ) of the two target chemicals (D5 and D6) from two products determined by the above mentioned fume hood method are presented in Figs. 3B and C, and 4B and C for fragrance and diaper cream, respectively. The boiling points and the vapor pressures (at  $25^{\circ}\text{C}$ ) of D5 and D6 are 23 Pa and 4 Pa, respectively. D5 emission factors were higher than that of D6, consistent with the volatilities of the chemicals.

Similar to the weight loss profile, both temperature and surface air velocity had an impact on the emission factors of the target chemicals. When the temperature increased from  $24^{\circ}\text{C}$  (room temperature) to  $32^{\circ}\text{C}$  (skin temperature) for the emission tests of diaper cream, the emission factors increased by about three times (from about  $3000\text{ mg m}^{-2}\text{ h}^{-1}$  to  $10,000\text{ mg m}^{-2}\text{ h}^{-1}$ ) for D5 and more than four times (from  $400\text{ mg m}^{-2}\text{ h}^{-1}$  to  $1900\text{ mg m}^{-2}\text{ h}^{-1}$ )

for D6, respectively. A positive relationship between emission factors of D5 and temperature could also be observed for fragrance where the emission factor increased 5 times when the temperature changed from  $24^{\circ}\text{C}$  to  $32^{\circ}\text{C}$ .

The emission factor of D6 for fragrance increased over time to a maximal value before decreasing. The time of the maximal emission factor corresponded well with the time when the linear decrease of product ceased and the weight loss curve leveled off (Fig. 3A). Since the initial concentration of D6 in the fragrance was very small at about 2% compared to 60% of D5, the initially evaporated product contained largely D5 and other more volatile components. As the evaporation progressed, D6 became progressively concentrated resulting in increased emission factors to a maximal value.

A further comparison of the emission profiles of the two products reveals that in the high surface air velocity ranging of  $0.35\text{--}0.75\text{ m s}^{-1}$ , surface air velocity had little impact on the emission factors of D5 and D6 for the diaper cream. A difference in emission factors can only be seen when this high surface air velocity was compared to the one near the instrument detection limit of  $0.03\text{ m s}^{-1}$  (Fig. 4B for D5 and C for D6). For fragrance however, emission factors changed significantly in this high surface air velocity range (Fig. 3B for D5 and C for D6). The different emission behaviours of the two products indicates that internal diffusion in the diaper cream sample was probably one of the limiting factors in determining the emission rate at high air velocity, while the internal diffusion plays negligible role in the emission rate of chemicals from liquid samples. Internal diffusion, however, did not have significant role in the evaporation of overall components in the product, as the product weight loss profiles were different at the high air velocity range (Fig. 4A).

### 3.6. Comparison to emission profiles generated by FLEC

The emission factors of D5 and D6 resulting from FLEC tests are also shown in Figs. 3 and 4 for the two products. The emission factors of D5 and D6 measured in FLEC tests were in the same range as those determined by weight loss tests that were conducted at low air velocity ( $0.03\text{ m s}^{-1}$ ), especially at the early period of the emission times. Considering the uncertainties and limitations of both experimental settings as stated below, the emission factors between the two methods were comparable. First, the air velocity value inside FLEC is difficult to characterize [23,24]. So there was

a great uncertainty in the actual surface air velocity in FLEC tests. The determination of low surface air velocity above the laboratory bench in a typical indoor environment was also difficult to achieve as such low air velocity is already in the range of the detection limit ( $0.03 \text{ m s}^{-1}$ ) of the air velocity meter used in the study. The uncertainty of the air velocity might be the major contributor to the differences between the emission factor values of the two methods. Second, compared to the fume hood method, the decrease of emission factors during the late period of the experiment in the FLEC tests (dash lines in Figs. 3B and C, and 4B and C) was much smaller (slower decay). This might be due to the reemitting of the chemicals from reversible absorption of the chemicals on the inner surface of the FLEC system during emission tests, a phenomenon called sink effect. de Bortoli et al. estimated in a European wide inter-laboratory comparison study that, when other errors in chamber operation were eliminated, the loss of chemicals in FLEC chambers, due to sink effect, was likely to be about 40% for dodecane (b.p. =  $216.2^\circ\text{C}$ ), and 65% for TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) (b.p. =  $281^\circ\text{C}$ ) [25]. Since boiling point of D5 and D6 is  $211^\circ\text{C}$  and  $245^\circ\text{C}$ , respectively, the degree of sink effect D5 and D6 in our FLEC was likely similar. In the fume hood method, such reemitting phenomenon, which is caused by the sink effect does not occur. The absence of the sink effect could mean more robust emission results.

#### 4. Conclusions

This study has demonstrated an experimental design aiming at estimating the emission factors of chemicals from test products by determining the weight loss and the remaining amount of the chemicals in the product over time. Two very different types of wet products were tested. They represented liquid and semi-liquid samples respectively. As a result, two different approaches have been taken for the residual analyses: measurement of concentrations of chemicals in replicate sample dishes in one case and determination of the concentrations as a function of percentage of evaporation of the product independently in the other case. Both techniques produced emission factors that were relatively comparable to those determined by a chamber-based (FLEC) method.

Although the degree of sink effect in the FLEC tests was not estimated in this study, emission factors of D5 and D6 determined at 24 h were higher in FLEC than those in the balance method. This might indicate additional emissions from the secondary source due to sink effect in FLEC tests and/or due to variations of air velocity between these approaches. Due to the design of the experiment, the balance method developed here eliminates the sink effect that is associated with emission chambers and provides more information about the air movement over the sample. In this non-chamber test method, emissions were estimated by the remaining chemical in the sample, instead of from the chamber air concentration. Therefore, the loss of chemicals to the surface of the testing facility did not impact the determination of emission factors in the fume hood method. This could be particularly important for estimating emission factors of chemicals that may have strong sink effects using traditional chamber tests.

Meanwhile, the developed balance method conducted in a fume hood is also flexible in setting up the experimental conditions. For example, the temperature-controlled heating pad heats the samples while maintaining the surrounding environment at room temperature. Such experimental setting can mimic the temperature of the skin on which the personal care products were applied, which may be useful for dermal exposure assessment [5].

This paper represents a proof of concept, as the first attempt to use non-chamber methods to estimate products emission factors. The study focused on emissions of chemicals from wet products. More studies are needed to further improve, validate and cali-

brate the method. For example, a more sensitive microbalance with a better detection limit might dramatically increase the method detection sensitivity to the small weight changes in products during the tests allowing potential application of this method in the emission measurement of chemicals with lower vapour pressure such as semi-volatile organic compounds like polycyclic aromatic hydrocarbons and phthalic acid diesters. Unlike environmental test chambers, control of humidity in a room was proven to be difficult. Although the emissions of lipophilic compounds such as D5 and D6 are less prone to the change of humidity, emissions of some other chemicals, particularly the polar ones could be influenced by relative humidity [1,26]. A better control of relative humidity within a room will certainly improve the method performance. This methodology however, with further improvements, could provide an alternative way to measure emission profiles of wet products for the benefits of eliminating sink effects of the chamber tests,

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#### References

- [1] F. Haghighat, L. de Bellis, Material emission rates: literature review, and impact of indoor air temperature and relative humidity, *Build. Environ.* 33 (1998) 261–277.
- [2] S. Kemmlin, O. Hahn, O. Jann, Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials, *Atmos. Environ.* 37 (2003) 5485–5493.
- [3] Y. Xu, J.C. Little, Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles, *Environ. Sci. Technol.* 40 (2006) 456–461.
- [4] Y. Zhang, F. Haghighat, The impact of surface air movement on material emissions, *Build. Environ.* 32 (1998) 551–556.
- [5] R. Wang, R.P. Moody, D. Koniecki, J. Zhu, Low molecular weight cyclic volatile methylsiloxanes in cosmetic products sold in Canada: implication for dermal exposure, *Environ. Int.* 35 (2009) 900–904.
- [6] J. Zhu, R. Newhook, L. Marro, C.C. Chan, Selected volatile organic compounds in residential air in the city of Ottawa, Canada, *Environ. Sci. Technol.* 39 (2005) 3964–3971.
- [7] B.H. Wilford, T. Harner, J. Zhu, M. Shoeib, K.C. Jones, Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: implications for sources and exposure, *Environ. Sci. Technol.* 38 (2004) 5312–5318.
- [8] F. Haghighat, Y. Zhang, Modeling of emission of volatile organic compounds from building materials emission of gas phase mass transfer coefficient, *Build. Environ.* 34 (1999) 377–389.
- [9] J. Zhu, J.S. Zhang, C.Y. Shaw, Chemical composition analysis and its application in estimation of voc emission rates from hydrocarbon solvent-based indoor materials, *Chemosphere* 39 (1998) 2535–2547.
- [10] C.S. Lee, F. Haghighat, W. Ghaly, Conjugate mass transfer modeling for voc source and sink behavior of porous building materials: when to apply it? *Build. Phys.* 30 (2006) 91–112.
- [11] B.A. Tichenor, Overview of source sink characterization methods, in: B.A. Tichenor (Ed.), *Characterizing Sources of Indoor Air Pollution and Related Sink Effects*, ASTM STP, 1287, American Society for Testing and Materials, West Conshohocken, PA, 1996.
- [12] T. Salthammer, Emissions of volatile organic compounds from products and materials in indoor environments *The Handbook of Environmental Chemistry*, Part F, vol. 4, Springer-Verlag, Berlin, Heidelberg, 2004, pp. 37–71.
- [13] E. Uhde, M. Bednarek, F. Fuhrmann, T. Salthammer, Phthalic esters in the indoor environment – test chamber studies on PVC-coated wall coverings, *Indoor Air* 11 (2001) 150–155.
- [14] M. Vanlooy, V. Lee, L. Gundel, J. Daisey, R. Sextro, W. Nazaroff, Dynamic behavior of semivolatile organic compounds in indoor air. 1: nicotine in a stainless steel chamber, *Environ. Sci. Technol.* 31 (1997) 2554–2561.
- [15] E. Uhde, T. Salthammer, Influence of molecular parameters on the sink effect in test chambers, *Indoor Air* 16 (2006) 158–165.
- [16] P.A. Clausen, V. Hansen, L. Gunnarsen, A. Afshari, P. Wolkoff, Emission of di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ, *Environ. Sci. Technol.* 38 (2004) 2531–2537.

- [17] T. Schripp, B. Nachtwey, J. Toelke, T. Salthammer, E. Uhde, M. Wensing, M. Bahadir, A microscale device for measuring emissions from materials for indoor use, *Anal. Bioanal. Chem.* 387 (2007) 1907–1919.
- [18] H. Huang, F. Haghghat, Modeling of volatile organic compounds emission from dry building materials, *Build. Environ.* 37 (2003) 1349–1360.
- [19] J.S. Zhang, G. Nong, C.Y. Shaw, J.M. Wang, Measurements of volatile organic compound (VOC) emissions from wood stains by using an electronic balance, *ASHRAE Trans.* 105 (1999) 279–288.
- [20] D. Kumar, J.C. Little, Single-layer model to predict the source/sink behavior of diffusion-controlled building materials, *Environ. Sci. Technol.* 37 (2003) 3821–3827.
- [21] H.J. Bremmer, L.L.C.H. de Prud'homme, J.G.M. van Engelen, Personal care product and personal care products, Fact Sheet RIVM report 320104001/2006.
- [22] L. Loretz, A. Api, L. Barraj, J. Burdick, D.A. Davis, W. Dressler, E. Gilberti, G. Jarrett, S. Mann, Y.H.L. Pan, T. Re, K. Renskers, C. Scrafford, S. Vater, Exposure data for personal care products: hairspray, spray perfume, liquid foundation, shampoo, body wash, and solid antiperspirant, *Food Chem. Toxicol.* 44 (2006) 2008–2018.
- [23] E. Uhde, A. Borgschulte, T. Salthammer, Characterization of the field and laboratory emission cell – FLEC: flow field and air velocities, *Atmos. Environ.* 32 (1998) 773–781.
- [24] L.Z. Zhang, J.L. Niu, Laminar fluid flow and mass transfer in a standard field and laboratory emission cell, *Int. J. Heat Mass Trans.* 23 (2003) 91–100.
- [25] M. de Bortoli, S. Kephelopoulos, S. Kirchner, H. Schauenburg, H. Vissers, State-of-the-art in the measurement of volatile organic compounds emitted from building products: results of European interlaboratory comparison, *Indoor Air* 9 (1999) 103–116.
- [26] H. Huang, F. Haghghat, P. Blondeau, VOC adsorption on material: influence of gas phase concentration, relative humidity and VOC type, *Indoor Air* 16 (2006) 236–247.