Building and Environment 95 (2016) 283–290

Contents lists available at ScienceDirect

Building and Environment

journal homepage: www.elsevier.com/locate/buildenv

Characterizing the equilibrium relationship between DEHP in PVC flooring and air using a closed-chamber SPME method

Cong Liu, Yinping Zhang*

Department of Building Science, Tsinghua University, Beijing, China

A R T I C L E I N F O

Article history:
Received 23 July 2015
Received in revised form
26 September 2015
Accepted 29 September 2015
Available online 3 October 2015

Keywords:
Indoor air quality (IAQ)
Emission
Mass transfer
Semivolatile organic compound (SVOC)
Persistent organic pollutants (POPs)

A B S T R A C T

The di-(2-ethylhexyl) phthalate (DEHP) concentration in the air immediately adjacent to a polyvinyl chloride (PVC) flooring surface, y_0 ($\mu g/m^3$), has been identified as one of the critical parameters governing the emission process and consequent exposure. At room temperature and below, the relationship between y_0 and the vapor pressure of pure DEHP (P_{sat}) is still unclear. Few studies have been conducted to examine the influence of the mass fraction of DEHP in PVC on the relationship. In this study a new closed-chamber solid phase microextraction (SPME) method is developed to characterize ratio of y_0 to P_{sat} at 23 °C. This method avoids the artifact from wall-loss of sampling lines and of the thermal desorption system, in contrast to ventilated-chamber methods. Results show that at 23 °C y_0 is significantly lower than the vapor pressure of pure DEHP. When the mass fraction of DEHP in PVC flooring increases from 13% to 23%, y_0/P_{sat} is increased by 7.2%, similar to what is reported in the literature. The sorption capacity of SPME stainless steel (SS) rods differs by up to 104%, although they are all made of SS. Based on error analysis, strategies are recommended to improve the precision and time efficiency. The method developed here should work for other SVOC-polymer systems.

1. Introduction

Phthalate esters have been used as plasticizers to enhance the flexibility of polyvinylchloride (PVC) products [1]. The estimated worldwide production of phthalates is approximately 5 million tons/year [2], of which a significant part is consumed in China [3]. Di-(2-ethylhexyl) phthalate (DEHP) accounts for 50% of the global market share for phthalates, at least 95% of which is added to PVC products [4]. The huge amount of consumption makes DEHP the most important congener of the phthalate group. Because DEHP is not chemically bound to the PVC matrix, emission from the products to the air usually occurs. Due to its low volatility, DEHP tends to be distributed among many media such as airborne particles [5], surfaces of indoor items [6] and food [1]. This distribution may result in oral, dermal and inhalation [7] exposure, with most from food [8,9]. Several adverse health effects such as reproductive toxicity [10,11], endocrine disorder [12,13], asthma [14,15] and allergies [16,17] have been associated with exposure to DEHP and other phthalates.

Emissions of volatile organic compounds (VOCs) out of wood-based materials are generally subject to “internal” control (diffusion within the source material) [18–20], with three parameters of the source material that govern the emission process: C_0, the initial concentration in a source material, $\mu g/m^3$; D, diffusion coefficient in a source material, m^2/s; K, partition coefficient between a source material and air, dimensionless. Xu et al. [21] extended the emission model of VOCs to examine emissions of DEHP. They conducted a sensitivity analysis on D within a range of 10^{-5}–10^{-16} m^2/s, finding that D has no influence on either gas-phase concentration or the emission rate. This finding indicates that emission of DEHP is subject to “external” control (partitioning from the source material into the gas phase, convective mass-transfer, and sorption onto interior surfaces including airborne particles), confirmed by the following study [22]. This also means that D is not important in predicting emissions of DEHP, and the emission process can be described by the lumped parameter method. Later, it was found that only 0.003% of the total mass of DEHP in PVC flooring was emitted after 1 year [23], indicating that the DEHP concentration in PVC flooring can be regarded as constant for a long period. Instead of the three key parameters for VOCs (C_0, D and K), for DEHP, only one parameter, y_0 ($\mu g/m^3$) = C_0/K, representing the DEHP concentration in the air immediately adjacent to a material surface, has

---

* Corresponding author.
E-mail address: zhangyp@tsinghua.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.buildenv.2015.09.028

been identified as the critical emission characteristic parameter governing the emission process [19,24]. Fig. 1 illustrates that y_0 initiates the transport of and the consequent exposure to DEHP.

Efforts have been made to determine and characterize y_0. Researchers have developed models [21,25–27] for emission of DEHP out of PVC flooring in ventilated chambers [28,29]. y_0 has been obtained by fitting the models to the measured DEHP concentration in the air of the ventilated chambers such as the Chamber for Laboratory Investigations of Materials, Pollution, and Air Quality (CLIMPAQ) [30], the Field and Laboratory Emission Cell (FLEC) [30] and a sandwich-like chamber [22]. The influence of environmental factors such as humidity and temperature on y_0 was examined. For example, it was found that humidity in the range of 10%–70% has no influence on the emission of DEHP out of vinyl flooring [31], indicating that y_0 is independent of humidity. Clausen et al. [32] found a significant influence of temperature on y_0 by running emission tests in a FLEC between 23 °C and 61 °C. They also concluded that y_0 is equal to the vapor pressure of pure DEHP (P_{sat}) (Fig. 4 and the relevant text in the paper by Clausen et al.). Although this might be persuasive at temperatures no lower than 32 °C, a significant difference can be found between these two parameters at 23 °C in Fig. 4 of the paper by Clausen et al.: $y_0 = 0.95\ \mu g/m^3$ while $P_{sat} = 2.4\ \mu g/m^3$. And it should also be noted that the determination of vapor pressure for low volatility compounds such as DEHP is subject to significant uncertainty [33]. The large scale of the y-axis of this figure (up to 200 $\mu g/m^3$) makes the significant difference between these two parameters less visible. It indicates a ratio of 0.40 of y_0 to P_{sat} at 23 °C. But this ratio of y_0 to P_{sat} at 23 °C is subject to errors, due to the assumption that the gas-phase concentration at steady state ($C_{g,steady}$) in FLEC is treated as equal to y_0. This assumption stands only for equilibrium state. Based on the mass balance principle, the gas-phase concentration at steady state is:

$$C_{g,steady} = \frac{h_m A}{h_m A + Q} y_0 \tag{1}$$

where h_m (m/s) is the convective mass transfer coefficient at the source surface, A (m^2) is the surface area, Q (m^3/s) is the ventilation rate. If y_0 is treated as equal to $C_{g,steady}$, the value of y_0, and the consequent ratio of y_0/P_{sat}, is expected to be underestimated. The extent of the underestimation depends on the ratio of h_mA to Q. Liang and Xu [34] developed an improved method to study y_0 and P_{sat} for several vinyl floorings at 25 °C, finding that y_0 is indeed lower than P_{sat}, and becomes insensitive to high mass fractions of DEHP. This observation is highly interesting, but data for this aspect is still scarce, necessitating more work.

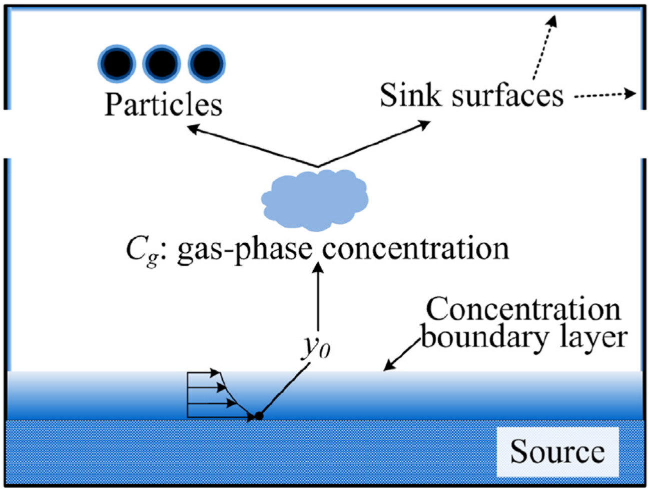

Fig. 1. Schematic of y_0 initiating the transport of and the consequent exposure to DEHP.

In addition, all of the experimental work to characterize y_0 reported in the literature use ventilated chamber methods. For such methods, an air supply system (including clean air cylinders and tubes), a mass flow controlling system (mass flow controllers) and a sampling system (including tubes, sorbent tubes and pumps) are usually necessary. An automated thermal desorption (ATD) unit is needed to desorb the sorbent tube for gas chromatograph (GC) analysis. Wall loss of SVOCs onto the sampling tubes and transfer lines in ATD in such methods could significantly impact the reliability of the measurement results [22]. In addition, a significant number of instruments (e.g., mass flow controllers, sorbent tubes, ATD, pumps) and materials (e.g., tubes and clean air) are required for such experimental work. Therefore a less costly and simpler method is desired.

Subsequently, the objectives of this study are to: 1) develop a closed-chamber method with solid-phase microextraction (SPME) to examine the relationship between y_0 and P_{sat} at 23 °C, 2) examine the influence of mass fraction of DEHP in PVC on y_0, and 3) optimize the performance of SPME in the new method in relation to speed and precision. The method is expected to be free from wall-loss artifacts and less costly and simpler, in contrast to a ventilated-chamber method. The results of the characteristics of y_0 are useful to predict DEHP emissions and to assess consequent exposure. The method developed here should work for other SVOC-polymer systems.

2. Materials and methods

2.1. Chemicals

DEHP (>98.0%) was bought in the market, which is produced by Tokyo Chemical Industry Co. Ltd. DEHP was put into a vial to create an atmosphere with an air concentration of P_{sat}.

2.2. Vinyl flooring

5-mm thick homogeneous polyvinyl chloride (PVC) floorings were used in this study. Some of the PVC flooring from randomly chosen positions was cut into small pieces of about 2 mm × 2 mm × 5 mm. These were put into the headspace vial to sample DEHP at the concentration of y_0.

The DEHP content in the PVC was measured. A sample of approximately 0.5 g of the flooring was cut out of the PVC at randomly chosen positions. The sample and two blanks were Soxhlet extracted with dichloromethane at 70 °C for 6 h, followed by rotary evaporation. Then the volumes of the extracts were adjusted to 25 ml by adding dichloromethane. A 1 µl aliquot of the 25 ml of extracts was injected into a GC–MS system for analysis. The residuals of the extracted sample were re-extracted one more time to check for any remaining DEHP. A known amount of DEHP was added to one of the blanks to determine recovery.

2.3. Headspace vial

4 ml glass vials (4.5 cm height, 1.0 cm diameter) were used in this experiment. Some were filled with small pieces of PVC flooring, and the others with pure liquid DEHP. These vials were filled to roughly the same height, leaving a space with a height of about 1.0 cm as the headspace. The cap of the vial is soft so as to be puncturable by the SPME needle.