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Large-scale chamber investigation and simulation of phthalate emissions from vinyl flooring

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ABSTRACT

This study investigated phthalate emissions from vinyl flooring in a large-scale chamber. Vinyl flooring materials were examined for their phthalates content; one with high contents of diisononyl phthalate (DINP) and di(2-ethylhexyl) phthalate (DEHP) was selected for emissions testing in a small chamber at two different temperatures. Using the same type of vinyl flooring, large-scale chamber experiments were then conducted in three testing phases. In the first phase, the gas-phase concentrations of DINP and DEHP in the large chamber at 36 °C were about three times lower than those in the small chamber under the same temperature, which is consistent with its lower area/volume ratio. In the second phase, when a large air mixing fan inside the chamber was replaced with a small fan, the gas-phase concentrations of DINP and DEHP in the large chamber were reduced slightly, due to the decease of mass transfer coefficient and emission rate. During the last phase, when the temperature of the chamber was reduced to 25 °C, phthalate concentrations dropped instantly and steeply due to the significantly reduced emissions. However, they did not decrease as quickly thereafter because of desorption of phthalates from the internal surfaces of the large chamber. A fundamental mechanistic model was developed to interpret the experimental results in the large chamber based on the emission characteristics obtained in the small chamber measurements. Reasonable agreement was obtained between the model calculation and experimental data. Further model simulations show that temperature and air mixing above the source material have important effects on the fate of phthalates, while the impact of air change rate (ACH) is not significant.

1. Introduction

Phthalates have been used as plasticizers to enhance the flexibility of polyvinyl chloride (PVC) products. These semi-volatile organic compounds (SVOCs) can be found in a wide range of building materials and consumer products including vinyl flooring, wall coverings, carpet padding, ceiling and floor tiles, furniture, and electronics [1]. They are abundant in source materials and usually are present at percent to tens-of-percentage levels [2]. Because phthalate additives are not chemically bound to the polymer matrix, emissions from source products usually occur [3]; as a result, phthalates are ubiquitous in indoor environments [1,4–6] and present in humans [7,8]. Exposure to phthalates and their metabolites may result in a number of adverse health effects [9]. Detailed information on health effects can be found in recent studies [9–20]. Collectively, these studies show that exposure to phthalates can cause irreversible changes in the development of the reproductive tract, especially in males. Effects such as increases in prenatal mortality, reduced growth and birth weight, and skeletal, visceral and external malformations, are also associated with exposure to phthalates.

Phthalates are dominant in the current market of plasticizers [21]. In the last decade, the global production of phthalates has increased from 3.5 to 6.0 million tons/yr [6,22]. Recently, the U.S. Consumer Product Safety Improvement Act was enacted to restrict the use of phthalates in toys and child care articles [23]. As a result, phthalates used in polymeric products are changing rapidly, with a shift from low to high molecular phthalates [24]. In addition, alternative plasticizers, such as di(2-ethylhexyl) terephthalate

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(DEHT) and diisononyl cyclohexane-1,2-dicarboxylate (DINCH) have emerged very recently. Given that these alternatives share properties similar to those of phthalates, similar emissions, environmental fate and transport, and human exposure are expected [21].

It is important to understand the mechanisms by which phthalates are emitted and transported in indoor environments, because it is the essential first step for investigating subsequent exposure and health effects and for developing strategies to limit the exposure. However, very few emission studies have targeted on these low volatility plasticizers [3,4,21,25–28], possibly due to the substantial difficulties associated with chamber tests for SVOCs, including the long duration of tests (months to years), the low gas-phase concentrations in test chambers, strong sorption onto surfaces, and ubiquitous contamination in laboratory facilities. Clausen et al. [28] measured emissions of di(2-ethylhexyl) phthalate (DEHP) from vinyl flooring for about 500 days in both the Field and Laboratory Emission Cell (FLEC) and Chamber for Laboratory Investigations of Materials, Pollution, and Air Quality (CLIMPAQ). Based on the measurements, Xu and Little [29] developed a fundamental mass-transfer model to predict SVOC emissions from polymeric materials. They showed that emissions of these compounds that have very low volatility are subject to "external" control (partitioning from the material into the gas phase, the gas-phase mass–transfer coefficient, and strong sorption onto interior surfaces, including airborne particles). Using data collected in a specially-designed stainless steel chamber, Xu et al. [3] showed that the emission rate of DEHP from vinyl flooring can be predicted based on a priori knowledge of y_0, the gas-phase concentration of DEHP in equilibrium with the material phase, the material to air and air to stainless steel surface mass transfer coefficients (h_m), and the stainless steel/air equilibrium relationship. Liang and Xu [30] recently improved the design of the previous small chamber and developed a novel, rapid method to measure y_0 for a range of phthalate compounds released from building materials. The mechanisms that govern emissions of phthalates from polymeric materials were also elucidated further by their small-chamber study.

The emission rate measured in a small-scale emission chamber can be quite different from those associated with the same material in a real indoor environment, because the emissions of SVOCs such as phthalates are controlled by external gas-phase resistance and exterior sinks [29]. However, the SVOC emission model [29] is based on mass-transfer mechanisms with model parameters that have clear physical meaning. Therefore, it can predict emissions for various conditions if the requisite model parameters are known. Xu et al. [31,32] extended the chamber-based model to a fate and transport model to predict human exposure to DEHP emitted from vinyl flooring in a realistic residential environment and conducted sensitivity and uncertainty analyses. Based on the research, Liu et al. [33] further investigated the influence of aerosol particles on the accumulation of indoor airborne DEHP with consideration of a variable particle concentration. Although the predicted phthalate concentrations in indoor air were consistent in orders of magnitude with data in literature, application of these transport models without validation of measurements may result in high uncertainty. Therefore, validation of the mechanisms governing the fate and transport of phthalates via large-scale chamber experiments or field measurements has become a high research priority.

Environmental conditions (e.g., temperature and air flow rate) may have important impacts on the fate and transport of indoor phthalates. Temperature increases may significantly increase phthalate emission from sources and desorption from interior sink surfaces due to the increase in chemical vapor pressure. Fujii et al. [34] studied the emission of phthalates from plastic materials using a passive flux sampler. They found that the maximum emissions of DEHP increased 100-fold when the temperature increased from 20 to 80 °C. Clausen et al. [4] measured emissions of DEHP from PVC flooring in the FLEC at different temperatures. They observed that the steady-state concentrations of DEHP increased considerably as temperature increased, while adsorption to the chamber walls decreased greatly as temperature increases. Liang and Xu [35] measured emissions of phthalates and phthalate alternatives from vinyl flooring and crib mattress covers in a specially-designed small chamber at four different temperatures between 25 and 55 °C and obtained y_0 values using the method they developed [30]. They found that the ratio of phthalate material-phase concentration to y_0 was exponentially proportional to the reciprocal of temperature. In addition, an increase in ventilation to reduce indoor exposure to SVOCs may not be as effective as for volatile organic compounds (VOCs) whose emissions are generally subject to "internal" control (diffusion within the source material) [36]. For SVOCs, the emission rate may increase greatly with an increase of air flow rate due to the enhanced mass transfer above the surface of the emission source. As a result, recent small-chamber studies have found that, although the increased flow rate of fresh air reduced the residence time of air and introduced more dilution, the enhanced emission compensated for the decrease in the gas phase, and thus the gas-phase concentration of SVOCs did not drop substantially with increasing air flow rates [25,37]. However, current studies were mostly carried out in small-scale experimental chambers, and there are no comprehensive and systematic investigations on the influence of environmental conditions on the fate and transport of indoor phthalates that have been conducted in large-scale chambers, which are more representative of indoor environments than small chambers.

The main aim of this study is to investigate the fate of phthalates emitted from vinyl flooring in large-scale chambers. The specific objectives are to: (1) conduct small-chamber tests to characterize phthalate emissions from vinyl flooring and obtain the dominant emission parameter (y_0); (2) conduct controlled tests in a room-sized chamber to measure phthalate emissions from the same type of vinyl flooring at different environmental conditions (i.e., temperature and air velocity); and (3) extend the SVOC emission model to simulate phthalate concentrations in the large chamber, based on the y_0 obtained in small-chamber measurements, and investigate the effect of environmental condition changes on the fate and transport of phthalates.

2. Methods and materials

2.1. Chemicals

Standard solutions were used for chemical calibration and identification, in which butyl benzyl phthalate (BBP) and di(2-ethylhexyl) phthalate (DEHP) were obtained from Absolute Standards Inc., di(2-ethylhexyl) isophthalate (iso-DEHP) from SPEX CertiPrep, and diisononyl phthalate (DINP) from Accustandards, Inc. Tetradeuterium ring labeled DEHP (D_4-DEHP) was used as internal standard, and its standard solution was obtained Accustandards, Inc. Hexane, methanol, sodium sulfate, and dichloromethane (DCM) (Sigma–Aldrich Co. LLC., anhydrous, >99%) were used as solvent in extraction and cleaning without further purification. The solvents were regularly analyzed to monitor potential phthalate contamination.

2.2. Test materials

Six types of vinyl floorings were purchased in the United States, and the contents of phthalates in each sample were