The influence of surface sorption and air flow rate on phthalate emissions from vinyl flooring: Measurement and modeling

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HIGHLIGHTS

- A series of controlled chamber tests were conducted to measure phthalate emissions.
- Surface adsorption/absorption were characterized experimentally for phthalates.
- Absorption of phthalates to wood has great influence on phthalate emissions.
- Phthalate concentration was sensitive to chamber air flow rate.
- SVOC emission model was validated for various sorption surfaces and air flow rates.

ARTICLE INFO

ABSTRACT

This study investigated the influences of surface sorption and air flow rate on the emission of phthalates from building materials. Controlled tests were conducted in specially designed stainless steel and wood chambers, and the steady-state concentration in the stainless steel chamber was about 2−3 times higher than that in the wood chamber for di(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate (DINP). The emission rate of phthalates increased in the wood chamber due to the diffusion mass flow through the chamber wall (i.e., surface absorption). The adsorption isotherm of phthalates on the stainless steel surface and the absorption parameters (i.e., diffusion and partition coefficients) of phthalates on the wood surface were determined experimentally, and the values were comparable to those in the literature. The equilibration time scale for phthalates absorbed to the sink reservoir in actual indoor environments was estimated and can be substantial (approximately 80 years), indicating that surface absorption may continuously drive phthalates from their indoor sources to various sinks and thus significantly increase the emission rate of phthalates. The gas-phase concentration of DEHP was measured in two stainless steel chambers operated at flow rates of 300 mL/min and 3000 mL/min, respectively, which were both adjusted to 1000 mL/min after steady state was reached. The gas-phase concentration of DEHP in the chamber was very sensitive to the chamber air flow rate, and higher air flow rates resulted in lower concentration levels. However, the increased emission rate compensated for the dilution in the gas phase and made the DEHP concentration not drop substantially with an increase in the air flow rate. Independently measured or calculated parameters were used to validate a semi-volatile organic compounds (SVOCs) emission model that included absorptive surfaces and for a range of air flow rates, with excellent agreement between the model predictions and the observed chamber concentrations of phthalates.

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1. Introduction

Phthalates have been used as plasticizers to enhance the flexibility of polyvinylchloride (PVC) products. These semi-volatile organic compounds (SVOCs) are found in a wide range of building materials and consumer products (Bornehag et al., 2005), and are present at percent to tens-of-percentage levels (Weschler and

Nazaroff, 2008). Because phthalate additives are not chemically bound to the polymer matrix, slow emission from the products to air or other media usually occurs (Xu et al., 2012). As a result, phthalates are ubiquitous and among the most abundant SVOCs in indoor environments (Bornehag et al., 2005, 2004; Clausen et al., 2012; Rudel and Perovich, 2009). Recent studies suggested that exposure to some phthalates may result in irreversible changes in the development of the human reproductive tract (Heudorf et al., 2007; Jaakkola and Knight, 2008; Latini et al., 2006; Matsumoto et al., 2008; McKee et al., 2004; Ritter and Arbuckle, 2007); increase the risk of asthma, rhinitis, and allergies (Bornehag et al., 2005; Jaakkola et al., 2006, 1999; Kolarik et al., 2008; Øie et al., 1997); and affect endogenous hormones (Rudel and Perovich, 2009).

Understanding of the emission mechanisms of phthalates and their alternatives from various sources is a prerequisite for characterizing their fate and developing suitable approaches to reduce their concentrations in indoor environments. However, very few emission studies have been conducted with low volatile plasticizers as target compounds (Afshari et al., 2004; Clausen et al., 2004, 2012, 2010, 2007; Schossler et al., 2011; Xu et al., 2012), possibly due to the substantial difficulties associated with chamber tests for SVOCs including the long test duration (over months to years), low gas-phase concentration, strong sorption onto surfaces, and ubiquitous contamination in laboratory facilities. Informed by the early chamber studies (Clausen et al., 2004), Xu and Little (2006) developed a fundamental mass-transfer model to predict SVOC emissions from polymeric materials. They showed that emissions of these very low volatility compounds 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. (2012) showed that the emission rate of di(2-ethylhexyl) phthalate (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 (K_s). Liang and Xu (2014) improved the design of the previous emission chamber and developed a novel, rapid method for measuring y_0 for a range of phthalate compounds released from building materials.

In actual indoor environments, there are various interior surfaces such as furniture, ceiling, and walls, many of which are not as impenetrable as stainless steel. Therefore, the simple partition relationship often used for surface adsorption may not be good enough to elucidate the mechanisms governing the process of surface absorption. Liu et al. (2014b) developed an experimental method to estimate the solid-phase diffusion coefficient (D_m) and the material/air partition coefficient (K_{ma}) of polychlorinated biphenyl (PCB) congeners for different sink materials such as glass and concrete. The results can be used to predict the absorption of SVOCs in the materials. However, the researchers also acknowledged that D_m and K_{ma} values obtained were rough estimates, because a single data set was used to fit the two parameters simultaneously, which may result in erroneous values. In addition, because SVOCs sorbed strongly to interior surfaces, surface sorption may also have a great impact on the fate and transport of indoor phthalates. Benning et al. (2013) observed that the total (gas + particle) DEHP concentrations increased by a factor of 3–8 when particles were introduced to a stainless steel chamber. The particles rapidly captured DEHP from the gas phase, substantially enhancing the emission rate of DEHP from the source. To date, no systematic investigations have been conducted to characterize the mechanisms governing absorption of phthalates to interior penetrable surfaces and the influence of surface sorption on emissions of phthalates from building materials.

The effect of increased ventilation on reducing indoor exposure to volatile organic compounds (VOCs) and formaldehyde has been observed in field studies (Hodgson et al., 2004; Zuraimi et al., 2006), but it is difficult to make the same conclusion for SVOCs because they behave quite differently as VOCs whose emissions are generally subject to "internal" control (diffusion within the source material) (Xu and Zhang, 2003). Clausen et al. (2010) measured the emission of DEHP from vinyl flooring at five different flow rates in the Field and Laboratory Emission Cell (FLEC) and found that the emission rate strongly depended on the air change rate (ACH). However, the gas-phase DEHP concentrations in FLEC differed only slightly for the various flow rates and thus were not suitable for use in comparing model prediction and experiment data. Xu et al. (2014) studied the influence of the ACH on indoor concentrations of phthalates and polybrominated diphenyl ethers (PBDEs) in retail stores. The researchers observed that the concentrations of phthalate slightly increased but that of PBDEs decreased significantly when the ACH increased. Liu et al. (2014a) developed a mass balance model incorporating the impacts of ventilation on particle mass concentration, mass transfer, and particle mediation, and found that ventilation affects exposure to SVOCs; but the researchers stated that more experimental studies were needed to further validate the theoretical model.

The aim of this study is to investigate the influence of surface sorption and air flow rate on the emission of phthalates from building materials. The specific objectives are to: (1) conduct controlled tests in specially designed stainless steel and wood chambers, respectively, to examine the effect of surface adsorption/absorption on the emission of phthalates from vinyl flooring; (2) measure the stainless steel/air equilibrium relationship (K_{s_ss}), wood-phase diffusion coefficient (D), and wood/air partition coefficient (K_{s_wd}) for the target phthalates, and characterize the mechanisms governing surface adsorption/absorption of phthalates; (3) measure emission of phthalates in the stainless steel chamber over a range of air flow rates; and (4) more completely validate the SVOC emission model with existence of adsorptive/absorptive surfaces and for a range of air flow rates.

2. Methods and materials

2.1. Chemicals

Standard solutions were used for chemical calibration and identification, in which dimethyl phthalate (DMP), di(2-ethylhexyl) phthalate (DEHP) was obtained from Absolute Standards Inc. and diisononyl phthalate (DINP) from Accustandards, Inc. Standard solutions were used for chemical calibration and identification, including DMP and DEHP (Absolute Standards Inc.), and DINP (Accustandards, Inc.). Tetradeuterium ring labeled DEHP (D4-DEHP) was used as internal standard, and its standard solution was obtained Accustandards, Inc. Hexane, methanol, and dichloromethane (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

Two vinyl flooring samples containing DEHP (23%) and DINP (20%), respectively, were used in this study. The method applied to measure the material-phase concentration of phthalates in vinyl flooring was described in detail in (Liang and Xu, 2014). Each material sample was cut into two 0.45 m × 0.25 m sheets, wrapped in