The Thesis Committee for Chenyang Bi
Certifies that this is the approved version of the following thesis:

The Influence of Temperature on the Fate and Transport of Phthalates in Indoor Environments

APPROVED BY
SUPERVISING COMMITTEE:

Supervisor:

Ying Xu

Atila Novoselac

The Influence of Temperature on the Fate and Transport of Phthalates in Indoor Environments

by

Chenyang Bi, B.E.

Thesis

Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in Engineering

The University of Texas at Austin
May 2014

Acknowledgements

I would like to sincerely thank my committee members: to the chair, Dr. Ying Xu for her wise counsel and direction; to Dr. Atila Novoselac, who gave me support on the use of UTestHouse. I am pleased to acknowledge the support of Yirui Liang who teach me analytical methods and assist my experiments. I extend my gratitude to Shichao Liu for giving me suggestions on the setup of experiments. My heartfelt appreciation also goes out to my girlfriend, Xiaoyue Wang, who kept encouraging me and didn’t mind that I spent most of my time in research without accompanying her. Last but not least, I would also like to thank my parents for supporting me to study at The University of Texas at Austin and thank all the friends who helped and encouraged me in the last two years. Financial support was provided by the National Science Foundation (NSF) (CBET-1150713 and CBET- 1066642).

Abstract

The Influence of Temperature on the Fate and Transport of Phthalates in Indoor Environments

Chenyang Bi, M.S.E.

The University of Texas at Austin, 2014

Supervisor: Ying Xu

Phthalate esters are extensively used as plasticizers in building materials and consumer products, but are associated with serious health concerns. They are ubiquitous indoors, redistributing from their original source to all interior surfaces, including airborne particles, dust, and skin. The main objective of the research is to investigate the influence of temperature on the fate and transport of phthalates in indoor environments. In this study, the concentrations of benzyl butyl phthalate [BBzP] and di-2-ethylhexyl phthalate [DEHP] in indoor air, settled dust, and on different interior surfaces including mirror, glass, plate, cloth and wood were measured periodically in a test house. The measurements were conducted at temperatures of 21 ℃ and 30 ℃, respectively. In addition, sorption kinetics was also monitored at the temperature of 21 ℃. The air concentrations of BBzP and DEHP at 21 ℃ range from 141 ng/m^3 to 210 ng/m^3 and 66 ng/ m^3 to 100 ng/ m^3, respectively. For impervious surfaces such as dish plates, the surface concentrations reached steady-state concentrations in less than 24 hours, to the level between 2 and 8 μg/m^2 for both BBzP and DEHP. In contrast, the time to reach steady state was much longer for porous surfaces such as hardwood (>1 week) and dust (> months). With the temperature increase to 30 ℃, the gas phase concentrations of BBzP and DEHP increased by about five times, and the surface concentrations on various surfaces also increased correspondingly. This investigation suggests that temperature has an important influence on the fate and transport of phthalates in indoor environments.

Table of Contents

List of Tables

List of Figures

Chapter 1: Introduction

Indoor air quality has emerged as a very important topic in recent years. Modern indoor environments contain a vast array of materials and products, many of which emit harmful contaminants (Weschler 2009). Emissions from these sources produce indoor concentrations that are substantially higher than outdoors (Rudel and Perovich 2009). Because people spend 90 percent of their time indoors (Klepeis et al. 2001), indoor exposure is often orders-of-magnitude greater than outdoors. The scale of the problem is vast, with estimated health and productivity gains that could be achieved by improving the indoor environment worth as much as $200 billion per year in the US alone (Fisk 2000). Indeed, the problem is likely to get even worse with the renewed drive for “air-tight” energy-efficient buildings. Among indoor contaminants, semi-volatile organic compounds (SVOCs) are found in a wide range of building materials and consumer products such as vinyl flooring, carpet padding, wall coverings, floor tiles, furniture, and electronics (Bornehag et al. 2005). These SVOCs are used as additives to enhance product performance and are often present in the product at percent to tens-of-percentage levels (Weschler and Nazaroff 2008). However, their indoor occurrence, fate, and transport have not been widely studied as other indoor contaminants, such as volatile organic compounds (VOCs) and inorganic gases, due to the challenges associated with sampling and analysis of SVOCs. With a vapor pressure typically less than 10 Pa, these compounds emit slowly and partition strongly to dust, particles and other interior surfaces, which may result a relatively longer time to transport between sources and sinks.

Among the most abundant SVOCs in indoor environments, phthalates are ubiquitous and have been widely used as plasticizers to enhance the flexibility of polyvinylchloride (PVC) products (Clausen et al. 2012). The global production rate of phthalate plasticizers has increased from 2.5 to 6 million tons/year within a decade (Rudel and Perovich 2009; Schossler et al. 2011; Cadogan and Howick 1996). Bornehag et al. (2005) reported that di (2-ethylhexyl) phthalate (DEHP) accounts for roughly 50% of overall phthalate production. Other phthalates commonly found indoor are n-butyl benzyl phthalate (BBzP), di-n-butyl phthalate (DnBP), diisobutyl phthalate (DIBP) and diethyl phthalate (DEP). Because phthalate additives are not chemically bound to the polymer matrix, they may be emitted slowly from the materials to the air (Xu et al. 2012).

Recent studies suggest that exposure to some phthalates may result in irreversible changes in development of the human reproductive tract (Heudorf et al. 2007; Jaakkola et al. 2008; Latini et al. 2006; Matsumoto et al. 2008; McKee et al. 2004; Ritter et al. 2007); increase the risk of asthma, rhinitis, and allergies (Bornehag et al. 2005; Bornehag et al. 2004; Jaakkola et al. 1999; Kolarik et al. 2008; Øie et al. 1997); and affect endogenous hormones (Rudel and Perovich 2009). Although the negative health impacts caused people’s attention, phthalates are still the most important plasticizer in the market (Schossler et al. 2011). However, following the restrictions on using certain phthalates in toys and child care products (CPSC 2008), phthalates used in PVC products are changing rapidly, with a trend toward using phthalates of higher molecular weight and lower volatility (Schossler et al. 2011; Cadogan and Howick 1996; CPSC 2008; Weschler 2009). Alternative plasticizers, such as diisononyl cyclohexane-1,2-dicarboxylate (DINCH) and di(2-ethylhexyl) adipate(DEHA), are also being used, but because they share chemical structures and properties similar to phthalates, similar emissions and environmental fate and transport may be expected (Schossler et al. 2011).

Phthalates as well as other SVOCs partition strongly to all interior surfaces, including airborne particles, dust, and skin (Weschler and Nazoroff 2008; 2010; 2012). A number of chamber studies have shown that SVOCs may be ad/absorbed by cloth fabrics (Piade et al. 1999; Stapleton et al. 2005; Svennberg and Wadso 2008; Petrick et al. 2010). Nicotine was found to be sorbed strongly to cellulose-containing materials like cotton, rather than polyester (Won et al. 2001). Similarly, a recent study showed that cotton has better water uptake capability than polyester (Svennberg and Wadso 2008). Petrick et al. (2010) reported that high ambient RH can suppress the sorption of nicotine on polyester while the fluctuation of RH doesn't significantly affect the sorption on cotton. In addition to porous materials, recent studies (Diamond et al. 1998; Liu et al. 2003) indicated that most impervious indoor surfaces have been naturally coated with a thin layer of organic film, which may capture SVOCs through adsorption and absorption.

Most field studies that have been conducted recently focused majorly on the air and dust levels of phthalates in indoor environments (Bergh et al. 2011b; Harrad et al. 2006; Kanazawa et al. 2010; Rudel et al. 2010; Thuresson et al. 2012; Vorkamp et al. 2011). In the recent CTEPP study (EPA 2005), concentrations of over 50 target compounds were measured in homes and daycare centers of 260 pre-school children. The two phthalates targeted in the CTEPP study were detected in residential air and house dust, and on a range of interior surfaces and dermal wipe samples. The measured phthalate concentrations were amongst the highest of any of the target

SVOC compounds (including pesticides, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls) and were generally higher on human skin than on all other surfaces (Xu et al. 2009 and 2010a). However, it is unclear how phthalates are redistributed from their original sources to various interior surfaces. Therefore, it is impossible to identify the most important sources of phthalate exposure in the general population. To our knowledge, the fate and transport of phthalates in indoor environments, the sorption kinetics and its equilibrium levels on various interior surfaces have not been investigated in field.

Temperature may have a strong influence on phthalate occurrence in real indoor environments due to the change of chemical vapour pressure, sorption equilibrium, mass transfer coefficient, and emission characteristics. In recent chamber measurements, the mass loss rate of DEHP from PVC increased 500-fold when temperature increased from 20 ℃ to 80 ℃ (Fujii et al. 2003; Ekelund et al. 2010; Clausen et al. 2012). When sunlight shines directly on a surface in a room, the surface temperature can increase significantly and these higher temperatures may increase the emission rate by orders of magnitude, resulting increases of phthalates in air, dust, as well as other interior surfaces. Furthermore, climate change is expected to result in more frequent heat waves and power grid failures during hot summer months due to excessive energy demand for air conditioning. Without air conditioning (AC) for one or two days, the temperature inside houses in the southern US may reach temperatures far above 40 ℃ which could significantly increase the emissions of SVOCs. Additionally, with an increasing desire to save energy there is a trend among many building occupants to turn off AC systems during the unoccupied period of the day causing high indoor temperature. However, no investigations have been conducted to characterize the effect of temperature on the mechanisms governing phthalate fate and transport in indoor environments. There is an urgent need to assess the dynamic concentration changes of phthalates in air, dust, and other interior surfaces due to temperature fluctuation, which represents the essential first step in investigating human exposures to phthalates in indoor environments and developing intervention strategies to limit exposure.

The objectives of this study are to 1) determine the influences of temperature on airborne concentrations of phthalates in a residential test house; 2) measure the partition coefficients of phthalates between air phase and interior surfaces, including dust, window, mirror, dish plate, wood, and cloth at 21 ℃ and 30 ℃, respectively; and 3) investigate the kinetic constraints on the sorptive partitioning.

Chapter 2 Methodology

2.1 Site Description

Field measurements were conducted at the UTest House located at Austin, Texas. As shown in Figure 2.1, the UTest House is a fully instrumented three bedroom/two bath 115 m^2 manufactured home with two independent HVAC systems, automatic eight-port CO_2 tracer gas systems for continuous air exchange measurement, weather stations, and several pressure, heat flux, temperature, velocity, particle, and relative humidity (RH) measurement stations in and around the house. Typical furniture and appliances used in residential homes such as cabinet, tables, oven, and shower curtain were also installed. The floor of the whole house was covered with vinyl flooring which contains approximately 10% (w/w) of BBzP. The experiments were conducted in the living room and the two bedrooms. Temperature, RH, and total suspended particle concentration were monitored in real time.

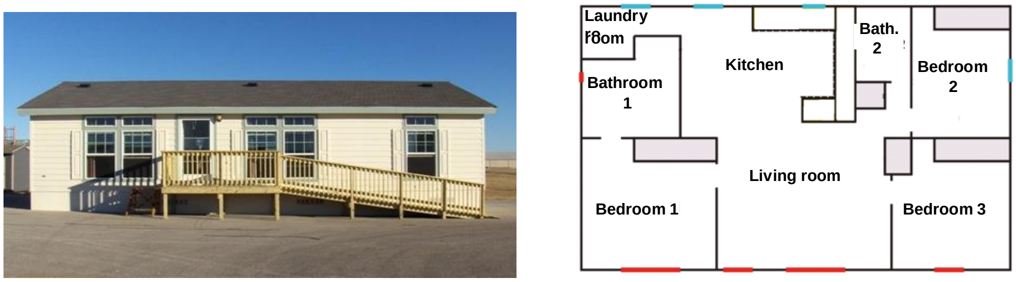

Figure 2.1. Exterior and floor plan of the UTest House.

2.2 Sampling protocol

2.2.1 Air

A low volume pump (A.P.BUCK Manufacturing Inc.) was connected downstream with a polyurethane foam (PUF) cartridge (22 × 100 mm size, 1-section, 76 mm sorbent), and housed with a glass fiber filter (SKC Inc. Cat. No.226-126). Prior to use, the PUF, filter and container were cleaned with hexane by sonication, after which they were dried, wrapped in aluminum foil, sealed in a zip bag, and stored at a temperature below 4 ℃. New glass fiber filter was used in each sampling. To minimize the air sampled relative to the volume of the room and prevent the chance of breakthrough, an air flow rate of 3 L ·min-1 was selected. Duplicate air samples were collected for 48 hours to a total volume of 18 m^3 and a field blank was prepared at each sampling location. The PUF were fortified with the surrogate standard (Dibenzyl phthalate, Diphenyl isophthalate, and Diphenyl phthalate) after sampling but prior to analysis to determine extraction efficiency. After sampling, all sample tubes were stored in a protective casing wrapped in aluminum foil, stored in a refrigerator to maintain a storage temperature below 4 ℃, and analyzed within 2 days of sampling.

2.2.2 Dust

Dust samples were collected using a Eureka vacuum cleaner, modified to collect dust into a 26-60 mm cellulose extraction thimble (Whatman Inc., Cat.No.2800-266). Prior to use, the cellulose thimbles were pre-cleaned by ultra-sonication for 30 minutes and 3 times, and then they were put into the oven to dry for 1h. Because the target analytes are associated with plastic materials, a special crevice tool with a holder for the extraction thimble was constructed of aluminum to avoid contact between dust and any plastic part of the vacuum. The thimble was weighted before and after sampling to obtain the total weight of dust sampled. Additionally, in order to enhance the air flow rate through the thimble, several holes were made at the bottom of the thimble. The mass of dust sampled is generally about 0.2g for 10-15 min vacuum collection. Floor and molding dust were collected separately in the UTest House to examine the potential differences of phthalate concentrations. Cellulose thimbles containing dust were removed and placed in a beaker sealed with aluminum foil. The beaker was then put into a glass jar with a PTFE lid, and stored in a refrigerator to maintain a storage temperature below 4 ℃. Dust samples were typically analyzed within 2 days of sampling.

2.2.3 Interior surfaces

Gauze pads were pre-cleaned before sampling by ultra-sonication for 30 minutes and 3 times, and then they were put into the oven to dry for 1h. Before sampling, the gauze pad (FISHER, 10 x 10 cm – 12 ply; Cat. No.22-415-469) was wetted with 10 mL of hexane. For windows and mirrors, masking tape was used to mark a 30 x 30 cm (0.09 m^2) area. The sample was collected by wiping the designated area of the floor with gloves in one direction, then folding the wipe in half, wiping the surface again in the opposite direction, and finally returning the wipe to the beaker. This process was repeated for an additional two times. The beaker with three gauze pads was put in a glass jar with a PTFE lid. Samples were shipped to the lab in less than ten minutes in a cooler filled with ice and analyzed less than 30 minutes after sampling.

2.3 Chemical Analysis

PUF and gauze pad samples were ultrasonically extracted for 1.5h and then concentrated with rotary evaporation for 20 minutes. A syringeless filter was used to remove the particles in the concentrate. The samples were then transferred to a flask for nitrogen blow down. Nitrogen blow down was done until the final 100 µl was collected into the bottom of the flask. The concentrate was then transferred to the pre-weighted vial and weighed for three times. Using the density of the hexane (in this case 0.672 g/ml), the exact final volume of the concentrate inside the flask was calculated. The detailed procedures for extraction can be found in Appendix A. The method for dust sample extraction was similar, with the exception of reducing the concentrate to a volume of 1mL due to a higher chemical loading.

A GC (Agilent 7890A) coupled to a FID (for phthalate analysis) using a DB-5ht columns was utilized. The system was operated using a 4:1 split injection. The inlet temperature was set at 275 ℃ with a constant column flow set at 1.2 ml/min. The oven temperatures were programmed from 120 ℃ for 2 min, ramp 12 ℃/min for 15 min, hold 3 min, then ramp 20 ℃/min for min, hold 2 min. The detector was set at 320 ℃.

2.4 Quality Control

For air sampling, 10 μl of a 500 μg/ml surrogates (Dibenzyl phthalate, Diphenyl isophthalate and Diphenyl phthalate) was injected before placing the cartridges in the test house. The recovery ratio, on average of 85.3%, which is used to estimate the loss during the whole process is calculated by taking the average of these three surrogates. Wipe removal efficiency were examined using six phthalate standards. A volume of 50 μL of standard solution (200 ng/ μL) was applied to 30 cm x 30 cm glass squares that had been solvent washed and sonicated with ACS grade n-hexane. The spiked solution was applied in small droplets and allowed to completely dry on the glass before experiments were performed. Different dipping solvents were compared to select the one with the best removal efficiency. Detailed procedures and results were shown in Appendix B. For dust, 50 μl of a 500 μg/ml surrogates (Dibenzyl phthalate, Diphenyl isophthalate and Diphenyl phthalate) was injected to the thimble prior to analysis with an average recovery ratio of 91.3%

Chapter 3: RESULTS AND DISCUSSION

3.1 Measurements of phthalates in indoor air

Among six target phthalate compounds, only BBzP and DEHP were detected. Figure 3.1 shows the air concentrations of BBzP and DEHP at different temperatures. At 21 ℃, the gas phase concentrations of BBzP and DEHP ranged from 141 ng/m^3 to 210 ng/m^3 and 66 ng/ m^3 to 100 ng/ m^3, respectively. The results are comparable to previous field studies (Bergh et al., 2011b; Fromme et al., 2004; Kanazawa et al., 2010; Rudel et al., 2010; Otake et al., 2004; Wilson et al., 2001), which show mean concentrations of 20 ng/m^3 to 50 ng/m^3 and 120 ng/m^3 to 600 ng/m^3 for BBzP and DEHP, respectively. The flooring material in the test house containing 10% (w/w) of

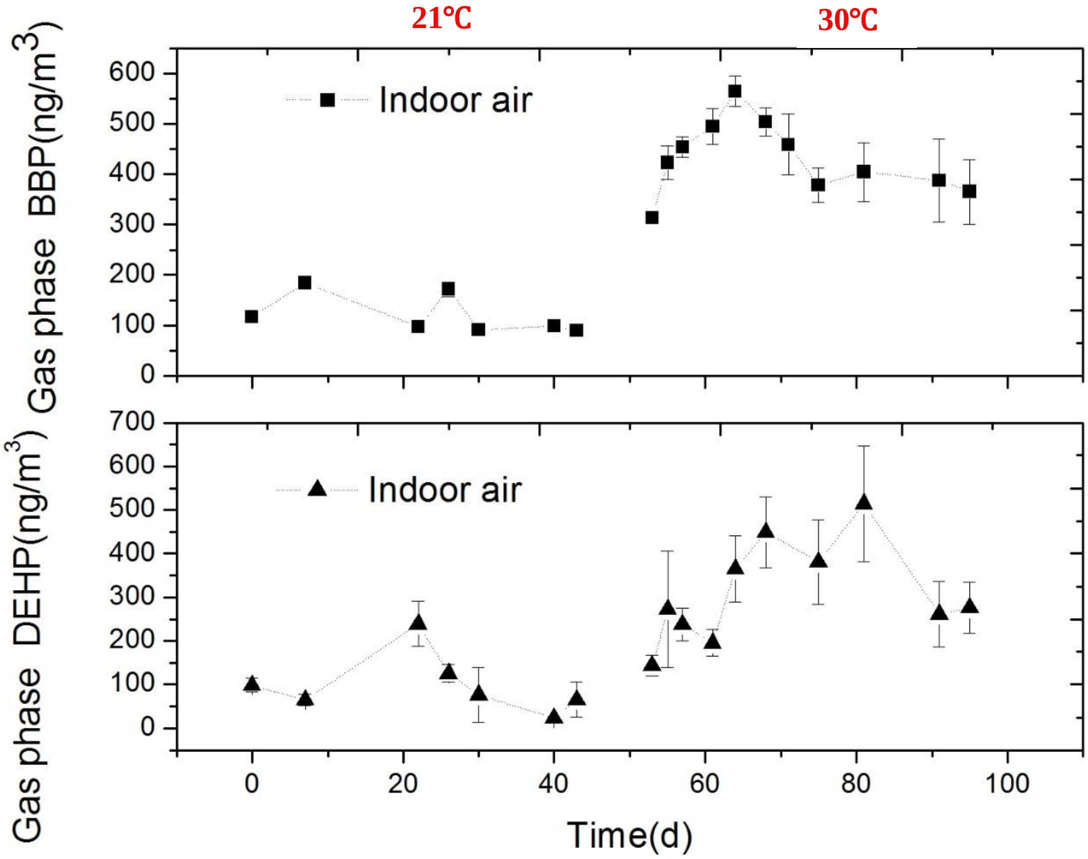

Figure 3.1. Concentrations of BBzP and DEHP in air.

BBzP, which may result in an elevated BBzP concentrations. In contrast, the sources of DEHP in the UTest house may not as many as that in a typical residential house which is possibly associated with the lower DEHP concentrations than other field studies. Because the temperature has been set for 21 ℃ for several months, we assume steady state has been reached. The fluctuation of the phthalates concentrations at steady state may be due to the uncertainties associated with humidity fluctuations, infiltration changes, and human activities. Humidity and infiltration may change with weather, but the impacts of humidity and ventilation rate changes on phthalate levels are still unclear and are not the focus of this study. In addition, even though the house is not occupied, the activities conducted by researchers may influence the steady state concentrations of phthalates.

When temperature was raised to 30 ℃, it took about 12 days for the gas-phase phthalates to reach steady state. Compared with previous chamber studies (Clausen et al. 2005; Xu et al. 2012; Liang and Xu 2014), the time to reach steady state is longer in the test house, where various interior surfaces behaving like sink reservoirs significantly slow down the accumulation of phthalates in air phase. At steady state, the average phthalate levels at 30 ℃ were generally four to five times higher than those at 21 ℃. It indicates that temperature has a great influence on the concentration of phthalates in indoor air which agreed with a previous chamber study (Clausen et al. 2011).

3.2 Measurements of phthalates in dust

As shown in Figure 3.2, the level of BBzP in floor dust (ranging from 2823 to 3518 µg/g) was 17-20 times higher than the non-floor dust (ranging from 140 to 203 µg/g), while little difference was observed for DEHP. Considering that the flooring material installed in the test house only contains BBzP, the findings suggest that dust may capture a significant amount of phthalates from the source by direct contacting with the source. The result is similar as Clausen et al. 2004 found in chamber studies. The levels of phthalates in non-floor dust were comparable to concentrations found in other field campaign measurements in residential homes (Oie et al. 1997; Wilson et al. 2001; Butte et al. 2001; Rudel et al. 2003; Santillo et al. 2003; Bornehag et al. 2005; Langer et al. 2010; Bergh et al. 2011). Compared to air concentrations, the concentrations of phthalates in settled dust were not influenced significantly by temperature in a relatively short

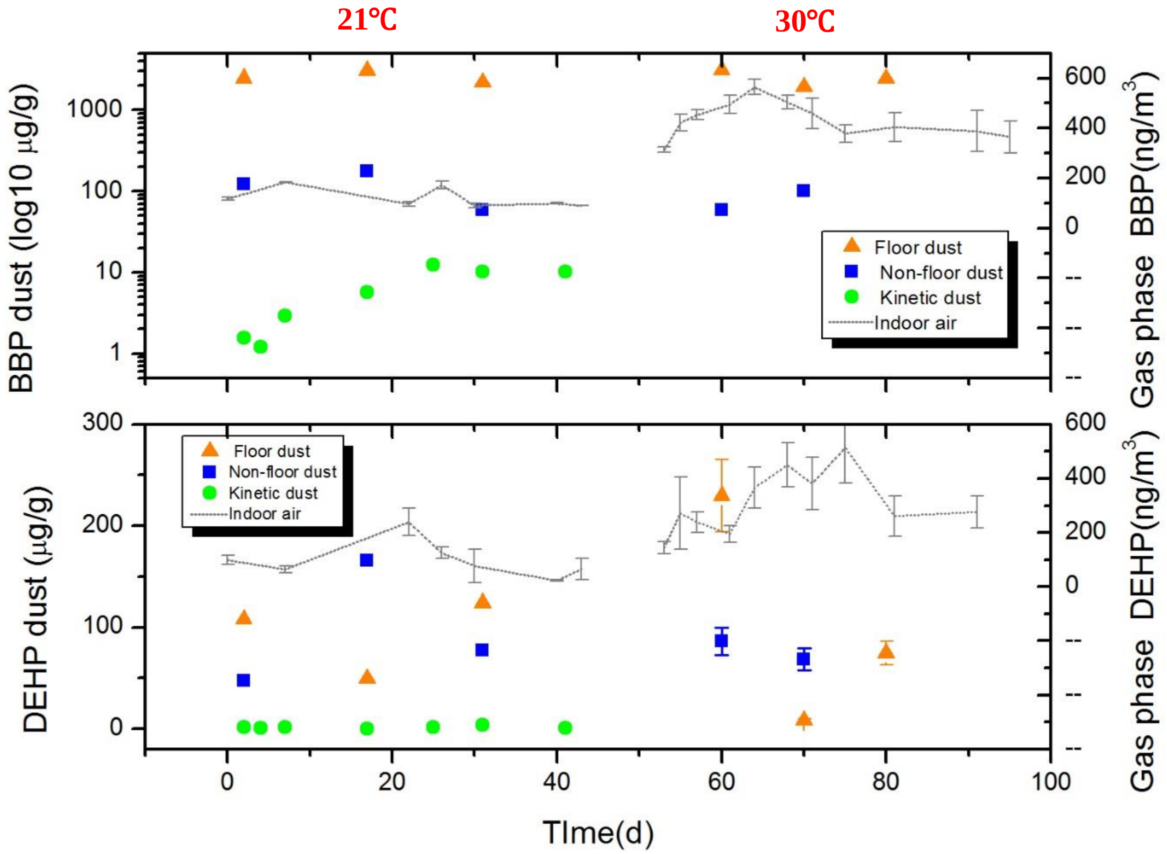

Figure 3.2. Concentrations of BBzP and DEHP in dust.

time period. Because the dust accumulated in the UTestHouse is very limited, only two samples were collected at 30 ℃.

In addition, we monitored the accumulation of phthalates in pre-cleaned dust in this study (shown as the green points in Figure 3.2). The results showed that sorption kinetics was not fast (over months) for BBzP and even slower for DEHP. Due to its high molecular weight, the approach to equilibrium partitioning occurs at a slower rate, and the mass fraction of a SVOC in settled dust may not have sufficient time to equilibrate with its gas phase concentration (Weschler and Nazaroff 2008; Schripp et al. 2010). It may take longer time for phthalates to diffuse deeply into the layer and reach the dust at the bottom.

3.3 Measurements of phthalates on dish plates and mirrors

The concentrations of BBzP and DEHP on impervious surfaces such as dish plates and mirrors were relatively close, as shown in Figure 3.3. The levels are similar as those on food preparation surfaces reported in 34 different homes (Morgan 2004). Diamond et al. (1998) showed evidences that an organic film may develop on impervious surfaces. The consistent concentrations of phthalates on interior surfaces of different homes may indicate a similar partitioning mechanism between gas-phase phthalates and the organic film in indoor environments. Weschler and Nazaroff (2008) further explained the theory and set a model to estimate the equilibrium concentrations and the dynamic nature of the film. Although the level of DEHP slightly increased after the temperature change, the level of BBP was not affected by the temperature. Assuming a linear isotherm of sorption to plates and mirrors, the nearly stable concentrations of both chemicals at different temperatures may be caused by the offset of the reduction in their partition coefficients between surfaces and air, and the increase in their gas phase concentrations. The partition coefficient between surfaces and air (shown in Table 3.1) was calculated by using the average surface concentration divided by the average total airborne concentration. The results were one order of magnitude smaller than other studies (Xu et al. 2009) possibly because instead of the air concentrations, total airborne concentrations were used in the calculation.

Surface	**Partition coefficient (m),21℃**		**Partition coefficient (m),30℃**	
	BBzP	DEHP	BBzP	DEHP
Plate	76.05	286.19	19.60	153.30
Mirror	79.78	288.14	9.93	156.60

Table 3.1. Partition coefficients of BBzP and DEHP between surfaces and air

The results showed that both BBzP and DEHP reached steady-state concentration less than a day, which is much faster than dust. As shown in Figure 3.3, with a first wipe (shown as the first point in Figure 3.3) to clean the mirror surfaces that have not been touched for years, the concentrations of BBzP and DEHP returned to the original level in less than 24 hours. The fast sorption phenomena indicates that the time needed for the organic film to fully develop and for BBzP and DEHP to partition into the organic film is relatively short. An additional test was then conducted at 21 ℃ and found that steady-state concentrations can actually be reached within 24 hours.

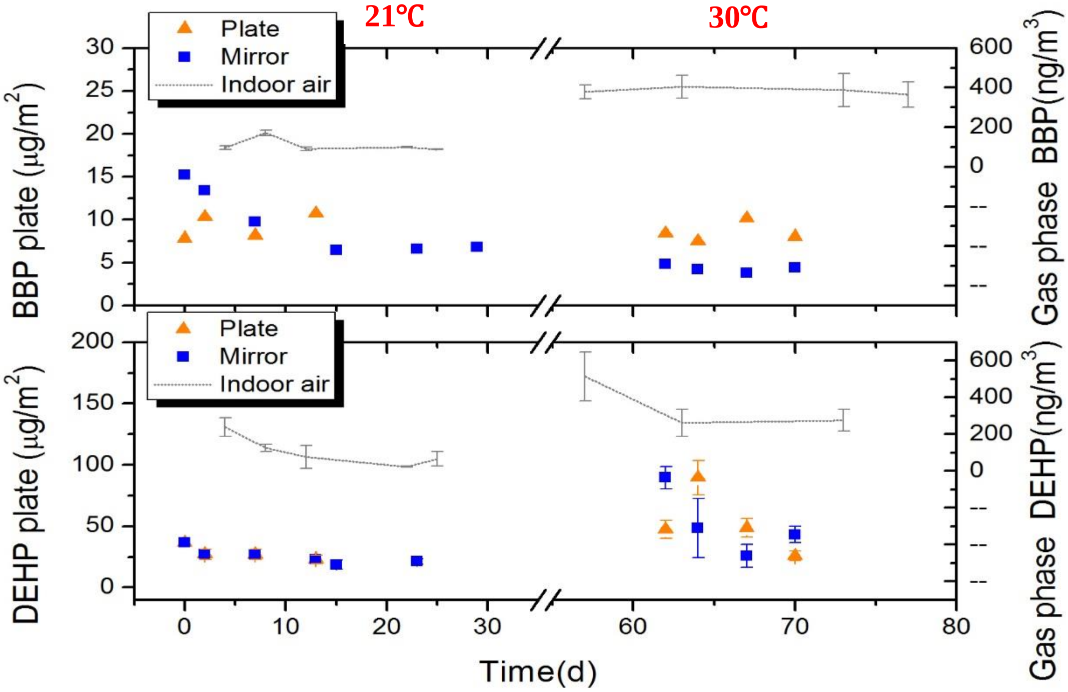

Figure 3.3. Concentrations of BBzP and DEHP on dish plates and mirrors.

3.4 Measurements of phthalates on cotton and polyester

Figure 3.4 shows that the concentrations of BBzP and DEHP in cotton and polyester cloth were relatively close at both 21 ℃ and 30 ℃. The concentrations of phthalates on cloth were seldom reported but the levels of polybrominated diphenyl ethers (PBDEs) were studied on clothes dryer lint by Stapleton et al. (2005). PBDEs levels in their study ranged from 0.1 μg/g to 3 μg/g which were comparable to our study. In contrast to the results of plates and mirrors, temperature increase resulted in six times higher phthalate concentrations in cloth. For porous material, molecular diffusion may be the dominant effect on the accumulation of phthalates. After sorbed onto the surfaces, phthalates will diffuse further into the porous material. Temperature increase may enhance the process by increasing the diffusion coefficient, resulting in concentration changes at different temperatures. Further chamber studies are needed to investigate the effect, because phthalate direct transfer from clothing to skin may play an important role in dermal exposure to phthalates. Compared to the fast sorption onto impervious surfaces, the concentrations of BBzP and DEHP on cloth reached steady-state concentrations in about 12 days.

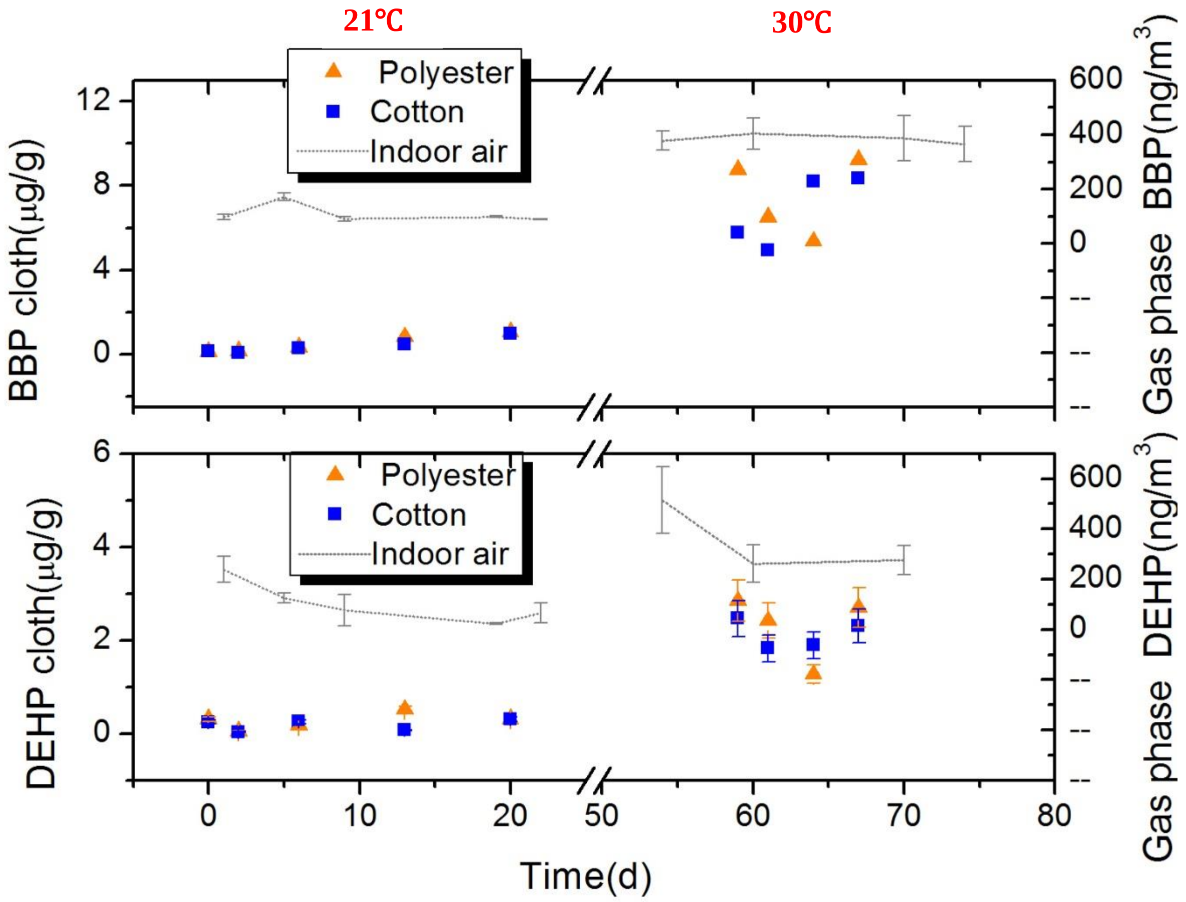

Figure 3.4. Concentrations of BBzP and DEHP on cloth.

3.5 Measurements of phthalates on wood

As shown Figure 3.5, the concentrations of BBzP and DEHP on wood segments increased slowly at 21℃ and have not reached steady state after 20 days. The results suggested that slow diffusion into the wood material happened, which is similar as recent findings in a chamber study (Liang and Xu 2014). Therefore, wood furniture in residential homes may behave like significant sink reservoir to SVOCs and re-emit them as secondary sources when environmental condition changes. The temperature change increased phthalate concentrations in wood to 90 $\mu g/m^2$.

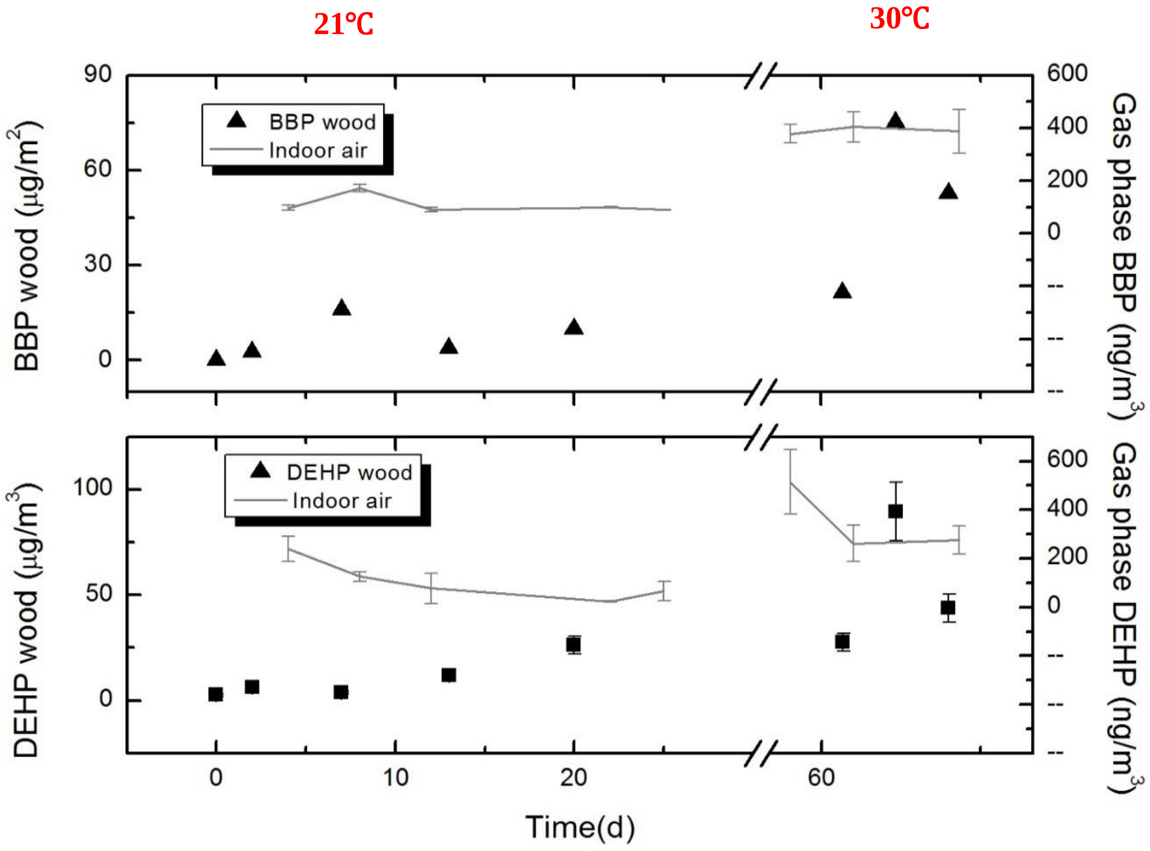

Figure 3.5. Concentrations of BBzP and DEHP on wood segments.

3.6 Estimation of indoor exposure to phthalates

With the measured concentrations on plates, high-end indoor exposure to phthalates can be estimated. The concentration of DEHP ranges from 40 to 100 μg/m^2 on the plates. Assume occupants who eat three meals a day and use 1 to 2 plates each time, which has a surface area of 0.05 m^2. The exposure to DEHP is about 0.12 to 0.6 μg/kg-bw/day. Comparing with the reference dose (RfD) value (20 μg/kg-bw/day) recommended by U.S. EPA, the exposure estimates are far lower. However, the exposure to DEHP for children could increase to the range of 0.4 to 2 μg/kg-bw/day due to their low body weight. The findings are in accordance with those of Guo and Kannan (2011) who measured indoor dust concentrations of phthalates and concluded that children may be more highly exposed than adults. Although this level is only 10 percent of the RfD, the estimates suggest that the plates could be a possible phthalate exposure pathway for toddlers.

There are also other scenarios which may be important for exposure to phthalates. Inadvertent ingestion of house dust is reportedly the largest contributor to SVOC exposure for all life stages. Because young children spend considerable time on the floor, where contaminated particles accumulate, and frequently put their hands and other objects in their mouths, their increased ingestion of dust can lead to a 100-fold higher SVOC exposure than in adults. The case could be even worse if flooring itself is the source of SVOCs, because our results showed that the level of BBP in floor dust (Figure 3.2) is one order of magnitude higher than that in non-floor dust. Additionally, the significant influence of temperature on both polyester and cotton cloth may indicate a higher level of exposure to phthalates through the skin because the skin temperature is higher than the indoor temperature, driving phthalates sorbed to the clothes when people wearing them indoors. Finally, the most recent analysis by the Intergovernmental Panel on Climate Change (IPCC) indicates that, over the last 30 years, the Northern Hemisphere was likely the warmest it has been in the last 1400 years. Indeed, current climate change models predict a 1 ℃ to 3.7 ℃ increase in average surface temperatures by the end of this century, with some models predicting up to a 4.8 ℃ increase. The increased outdoor temperature can result an increase in indoor temperature and thus increase human exposure to phthalates due to the significant influence of temperature to phthalates.

Chapter 4: Conclusions

This study provided evidence that with a 50 percent increase in temperature (from 21℃ to 30℃), the gas phase concentrations of phthalates can increase by a factor of 3 or 4. While the concentrations of phthalates on cloth increased 6 to 8 times with the temperature increase, the concentrations on plates and mirrors were relatively stable. The results may indicate that for impervious surfaces like plates and mirrors, the temperature may reduce the partition coefficient between the surfaces and the air. In contrast, for porous surfaces like cloth, diffusion might be the dominant process where temperature increase enhances the diffusion of phthalates thus increasing the steady-state concentrations of phthalates.

The results of the kinetic study suggest that for impervious surfaces, the concentrations of phthalates reach steady-state fast. In contrast sorption process to dust and cloth is relatively slow and at least 12 days are needed to reach steady-state concentrations.

Further work will focus on the influences of ventilation and humidity on the fate and transport in indoor environments. Remediation strategies to reduce the concentrations of phthalates indoor will also be investigated.

Appendix A: Protocol for Sampling Phthalates Concentrations via PUF, Gauze Pads and Dust extraction

Apparatus

- Sonication system manufactured by Branson 3510
- Volumetric glass flasks
- Nitrile examination gloves from Microflex
- Aluminum foil
- Ice substitute bags manufactured by Coleman
- Rotary Evaporator system manufactured by IKA RV-10
- Syringeless filter device with 0.45 µm PTFE membrane and glass microfiber prefilter and polypropylene housing manufactured by Whatman
- Autovial plunger with ears manufactured by Whatman
- Custom-made glass flask (1.5” D × 5” L)
- Amber glass vials manufactured by National Scientific
- Vial caps with septa by National Scientific
- Vial insert, 250 µl glass with polymer feet manufactured by Agilent
- Nitrogen cylinder (UHP)
- Analytical balance manufactured by Citizen

Chemicals

- 7X Cleaning Solution, MP Bio
- Methanol, assay 99.8%, VWR chemicals
- Hexane, assay ≥99%, Sigma-Aldrich chemicals

- Hexane, ACS grade, VWR chemicals

Glassware clean-up

All glassware was washed with hot water and cleaning solution and rinsed two times with water from the tap. Then, ultrapure water was used to rinse the glassware, followed by rinsing with methanol. Hexane was then used to rinse all the glassware to remove contaminates. All glassware was dried in an 80 ℃ oven for one hour and stored in a clean environment to prevent accumulation of dust and contamination.

Initial amber vial weighing

A vial insert placed inside an amber glass vial and covered with a cap was weighed three times to a precision of 0.01 mg. Each weight was recorded, and an average value was used to determine the weight of the empty vial with cap.

Sonication

PUF. After sampling, the PUF cartridges were returned to its original container and safely stored in a refrigerator at a temperature of ≤4°C. The PUF cartridge was taken to the laboratory and placed in a 150ml volumetric glass beaker. The PUF Cartridge was sonicated with 100 ml of hexane for 30 minutes, and then poured into a 1 liter rotary evaporator glass flask. An ice substitute bag was placed inside the sonicator next to the flask, and aluminum foil was used to cover the flask, to prevent evaporation of the samples. This procedure was repeated 2 additional times.

Gauze pad and thimble. After sampling, the gauze pads and the thimbles were returned to the beaker sealed with aluminum foil and safely stored in a jar with Teflon cap. The jar was shipped to the lab in less than 5 minutes. The beaker was taken out from the jar for sonication in the lab. Other procedures were the same with the PUF cartridges.

Rotary evaporation

The rotary evaporator glass flask was then connected to the rotary evaporation apparatus. The flask was then lowered to a bath of water heated up to 80 ℃ and rotated at a rate of 30 Hz. Rotary evaporation was done until the final 5 ml concentrate were collected in the bottom of the flask.

A syringeless filter device was placed on top of the custom-made glass flask. The concentrate was lightly stirred while still in the 1 liter glass flask to collect any chemicals that might have sorpted to the inner surface of the flask. The concentrate was then transferred using a 10 ml glass pipette to the syringeless filter device.

5 ml of hexane were then poured into the 1 l glass flask, and rotated at a rate of 100 Hz to collect any left-over residuals that might have sorpted to the glass. Then, the hexane was transferred to the syringeless filter device. This procedure was then repeated 3 times.

The concentrate was then pushed from the filter device into the tall glass flask with an autovial plunger with ears. The plunger was removed, and 10 ml were poured into the filter device to collect any chemicals that might have sorpted to the inner surface of the filter device.

Nitrogen blow down

The extract was then placed in an inert atmosphere (such as a fume hood). A nitrogen blow needle was then lowered and submerged into the concentrate. The nitrogen should be very clean, and adjusted to provide a gentle stream. Nitrogen blow down was done until the final 150 µl was collected into the bottom of the flask. In particular, for dust samples, in case the concentrations were too high, final 500 µl was collected into the bottom of the flask. NOTE: This process can take several hours.

The concentrate was then transferred to the empty weighed amber vial using a 100 µl syringe. 60 µl of hexane were poured into the custom-made flask to collect any chemicals that might have sorpted to the inner surface of the flask. Then the hexane was transferred to the amber vial. This procedure was done twice.

Volume determination

The amber vial with the concentrate was then weighed again 3 additional times. Using the density of the hexane (in this case 0.672 g/ml), the exact final volume of the concentrate inside the flask was calculated.

Analysis

A GC (Agilent 7890A) coupled to a FID (for phthalate analysis) using a DB-5ht columns was utilized. The system was operated using a 4:1 split injection. The inlet temperature was set at

275 ℃ with a constant column flow set at 1.2 ml/min. The oven temperatures were programmed from 120 ℃ for 2 min, ramp 12 ℃/min for 15 min, hold 3 min, then ramp 20 ℃/min for min, hold 2 min. The detector was set at 320 ℃.

Appendix B: Quality Assistance/Quality Control

Calibration

6 phthalates are being analyzed in this study, which include:

- Diethyl Phthalate (DEP),
- Dimethyl Phthalate (DMP),
- Di-n-butyl Phthalate (DBP),
- Butyl Benzyl Phthalate (BBP),
- Di(2-ethylhexyl) Phthalate (DEHP),
- Di-n-octyl Phthalate (DoP)

5 different liquid concentrations were prepared per each compound, with the following values (µg/µl): 0.01, 0.02, 0.05, 0.1 and 0.2. Each concentration was injected 3 times into a GC-FID, which gives a response in units of Pico Amperes (pA), and then the values were averaged out. Table B1 shows the current calibration values for the phthalates. Each calibration point showed a small coefficient of variance (≤4%), and the correlation coefficients from signal response to injected amount show a strong relationship ($R^2 \geq 0.995$) from the standards prepared.

Phthalate	**Slope (µg/pA)**	**R^2**
DEP	548.9	0.9998
DMP	497.4	0.9998
DBP	436.9	0.9998
BBP	411.6	0.9999
DEHP	386.0	0.9998
DoP	390.9	0.9998

Table B1. Calibration of phthalates with slope and correlation coefficient.

Recovery Ratio

1. Air

To determine the actual amount of chemicals that transferred from the PUF cartridge to the amber vial, recovery ratios must be determined.

For real samples, 10 µl of a 500 µg/ml surrogates (Dibenzyl phthalate, Diphenyl isophthalate and Diphenyl phthalate) was injected to the PUF prior to sampling in the test house. The recovery ratio which is used to estimate the loss during the whole process is calculated by taking the average of these three surrogates.

Phthalates	Recovery Ratio
Dibenzyl phthalate	82%
Diphenyl isophthalate	89%
Diphenyl phthalate	85%

Table B2. Recovery ratio for surrogate compounds

Preliminary study is conducted to determine the best flow rate and sampling time. The flow rate and sampling time is suitable when the amount of target compounds are above detection limit and no breakthrough is occurred in the PUF. Different combination of flow rate and sampling time is tested and the results are listed in Table.3

Flow rate(L/min)	**Sampling time(h)**	**concentration(ng/m^3)**	
		BBP	DEHP
10.00	24.00	268.430	388.367
10.00	24.00	268.822	441.126
5.00	36.00	402.917	559.712
5.00	36.00	436.566	568.490
5.00	48.00	369.302	377.977
5.00	48.00	425.576	411.555
3.00	36.00	440.253	643.973
3.00	36.00	481.718	802.009
3.00	48.00	501.309	812.082
3.00	48.00	514.337	791.873

Table B3. BBP and DEHP air concentrations with different flow rates and time

2. Surface:

Wipe removal efficiency experiments were performed using six phthalates standards. For removal efficiency determinations, a volume of 50 μL of the 200 ng/ μL standard solution was applied to 30 cm x 30 cm glass squares that had been solvent washed and sonicated with ACS grade n-hexane. The spike solution was applied in small droplets and was allowed to completely dry on the glass before experiments were performed.

Dichloromethane, 2-proponol and hexane were used as dipping solvent to compare the removal efficiency. Each gauze pad was sonicated with hexane three times before test. Blank samples were done to ensure no background phthalates. The glass was then wiped several times, each time with a gauze pad which dipped with 10 mL solvents. The wiping protocol was the same as the preliminary study. The glass was sonicated after the experiment to measure the amount of phthalates left on the glass.

Recovery ratio test is conducted according to the instruction above in the lab. The glass is purchased from the Homedepot. Results are listed in Table.4. After the recovery test in the lab, these three solvent were used in the test house to verify the removal efficiency in the real environment. The results are listed in Table.5.

Wipe Sequence	**Recovery ratio**		
	Hexane	DCM	2-propanol
Two wipes	113.1%	94.9%	108.2%
Three wipes	113.1%	106.9%	108.2%

Table B4. Recovery ratio for BBP with different solvent on glass surface.

Wipe Sequence	**Mass removed from window(µg)**	
	Hexane	2-propanol
1st Wipe	3.015	3.034
2nd wipe	1.950	2.030
3rd wipe	1.457	1.571
4th wipe	<d.l.	<d.l.

Table B5. Mass of BBP removed from window

The results showed 3 wipes is good enough for glass surfaces. Moreover. 2 additional tests (wiped 4 times) were conducted to ensure three wipes are enough to remove all the phthalates on the glass. Both test showed that no phthalates were detected on the 4th wipe.

For the wood surface, five wipes were tried and then analyzed. The amount of phthalates on the 4th and 5th wipes was below detection limit. So three wipes were good for both wood and glass surfaces.

3. Dust

For dust samples, 50 µl of a 500 µg/ml surrogates (Dibenzyl phthalate, Diphenyl isophthalate and Diphenyl phthalate) was injected to the thimble prior to analysis. The recovery ratio was showed in Table 6.

Phthalates	Recovery Ratio
Dibenzyl phthalate	89%
Diphenyl isophthalate	95%
Diphenyl phthalate	90%

Table B6. Recovery ratio for surrogate compounds

References

Bornehag, C. G.; Lundgren, B.; Weschler, C. J.; Sigsgaard, T.; Hagerhed-Engman, L.; Sundell, J., Phthalates in Indoor Dust and Their Association with Building Characteristics. *Environmental Health Perspectives* **2005,** *113*, (10), 1399-1404.

Bornehag, C. G.; Sundell, J.; Weschler, C. J.; Sigsgaard, T.; Lundgren, B.; Hasselgren, M.; Hagerhed-Engman, L., The association between asthma and allergic symptoms in children and phthalates in house dust: A nested case-control study. *Environmental Health Perspectives* **2004,** *112*, (14), 1393-1397.

Butte, W., Hoffmann, W., Hostrup, O., Schmidt, A. and Walker, G. Endocrine disrupting chemicals in house dust: results of a representative monitoring, *Gefahrstoffe Reinhaltung Der Luft,***2001**, 61, 19-23.

Cadogan, D. F.; Howick, C. J., Plasticizers. *Kirk-Othmer Encyclopedia of Chemical Technology* **1996,** *19*, 258-290.

Clausen, P. A.; Liu, Z.; Kofoed-Sorensen, V.; Little, J.; Wolkoff, P., Influence of Temperature on the Emission of Di-(2-ethylhexyl)phthalate (DEHP) from PVC Flooring in the Emission Cell FLEC. *Environmental Science & Technology* **2012,** *46*, (2), 909-915.

Clausen, P. A.; Liu, Z.; Xu, Y.; Kofoed-Sørensen, V.; Little, J. C. Influence of air flow rate on emission of DEHP from vinyl flooring in the emission cell FLEC. *Atmos. Environ.* **2010**, *44*, 2760–2766.

Clausen, P. A. P.; Xu, Y.; Kofoed-Sørensen, V.; Little, J. C.; Wolkoff, P. The influence of humidity on the emission of di-(2-ethylhexyl) phthalate (DEHP) from vinyl flooring in the emission cell "FLEC." *Atmos. Environ.* **2007**, *41*, 3217–3224.

Clausen, P. A.; Hansen, V.; Gunnarsen, L.; Afshari, A.; Wolkoff, P. 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*. **2004**, 38 (9), 2531−2537.

Diamond, M. L.; Gingrich, S. E.; Fertuck, K.; McCarry, B. E.; Stern, G. a.; Billeck, B.; Grift, B.; Brooker, D.; Yager, T. D. Evidence for Organic Film on an Impervious Urban Surface Characterization and Potential Teratogenic Effects. *Environ. Sci. Technol.* **1998**, *34*, 2900–2908.

EPA US EPA Integrated Risk Information System (IRIS). Available at : http://www.epa.gov/iris/. (Dec 10).

Ekelund, M.; Azhdar, B.; Gedde, U. W. Evaporative loss kinetics of di(2-ethylhexyl)phthalate (DEHP) from pristine DEHP and plasticized PVC. *Polym. Degrad. Stab.* **2010**, *95*, 1789–1793.

Fujii, M.; Shinohara, N.; Lim, a; Otake, T.; Kumagai, K.; Yanagisawa, Y. A study on emission of phthalate esters from plastic materials using a passive flux sampler. *Atmos. Environ.* **2003**, *37*, 5495–5504.

Fromme, H., Lahrz, T., Piloty, M., Gebhart, H., Oddoy, A. and Ruden, H. Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany), *Indoor Air*, **2004,** 14, 188-195.

Guo, Y.; Kannan, K., Comparative Assessment of Human Exposure to Phthalate Esters from House Dust in China and the United States. *Environmental Science & Technology* **2011,** *45*, (8), 3788-3794.

Harrad, S., Hazrati, S., Ibarra, C. Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: implications for human exposure. *Environ. Sci. Technol* **2006,** 40, 4633-4638.

Harrad, S., Wijesekera, R., Hunter, S., Halliwell, C., Baker, R. Preliminary assessment of UK human dietary and inhalation exposure to polybrominated diphenyl ethers. *Environ. Sci. Technol* **2004**, 38, 2345-2350.

Hartmann, P.C., Burgi, D., Giger, W. Organophosphate flame retardants and plasticizers in indoor air. *Chemosphere* **2004,** 57, 781-787.

Hazrati, S., Harrad, S. Causes of variability in concentrations of poly- chlorinated biphenyls and polybrominated diphenyl ethers in indoor air. *Environ. Sci. Technol* **2006,** 40, 7584-7589.

Heudorf, U.; Mersch-Sundermann, V.; Angerer, J., Phthalates: Toxicology and exposure. *International Journal of Hygiene and Environmental Health* **2007,** *210*, (5), 623-634.

Intergovernmental Panel of Climate Change (IPCC). Available at : https://www.ipcc.ch/report/ar5/wg1/

Jaakkola, J. J. K.; Knight, T. L., The role of exposure to phthalates from polyvinyl chloride products in the development of asthma and allergies: A systematic review and meta-analysis. *Environmental Health Perspectives* **2008,** *116*, (7), 845-853.

Jaakkola, J. J.; Ieromnimon, A.; Jaakkola, M. S., Interior surface materials and asthma in adults: a population-based incident casecontrol study. *American Journal of Epidemiology* **2006,** *164*, 742-749.

Jaakkola, J. J. K.; Oie, L.; Nafstad, P.; Botten, G., Interior surface materials in the home and the development of bronchial obstruction in young children in oslo, Norway. *American Journal of Public Health* **1999,** *89,* (2), 188-192.

Kanazawa, A., Saito, I., Araki, A., Takeda, M., Ma, M., Saijo, Y., Kishi, R. Association between indoor exposure to semi-volatile organic compounds and building-related symptoms among the occupants of residential dwellings. *Indoor Air* **2010**, 20, 72-84.

Kolarik, B.; Bornehag, C.-G.; Naydenov, K.; Sundell, J.; Stavova, P.; Nielsen, O. F., The concentrations of phthalates in settled dust in Bulgarian homes in relation to building characteristic and cleaning habits in the family. *Atmospheric Environment* **2008,** *42*, 8553–8559.

Latini, G.; Del Vecchio, A.; Massaro, M.; Verrotti, A.; De Felice, C., Phthalate exposure and male infertility. *Toxicology* **2006,** *226,* (2-3), 90-98.

Lai, A. K.; Nazaroff, W. Modeling indoor particle deposition from turbulent flow onto smooth surfaces. *J. Aerosol Sci.* **2000**, *31*, 463–476.

Lai, A. K. Modeling indoor coarse particle deposition onto smooth and rough vertical surfaces. *Atmos. Environ.* **2005**, *39*, 3823–3830.

Lai, A. K.; Nazaroff, W. Modeling indoor particle deposition from turbulent flow onto smooth surfaces. *J. Aerosol Sci.* **2000**, *31*, 463–476.

Langer, S., Weschler, C.J., Fischer, A., Beko, G., Toftum, J. and Clausen, G. Phthalate and PAH concentrations in dust collected from Danish homes and daycare centers, *Atmospheric Environment*, **2010**, 44, 2294-2301.

Leri, A. C.; Anthony, L. N. Formation of organochlorine by-products in bleached laundry. *Chemosphere* **2013**, *90*, 2041–2049.

Liang, Y.; Xu, Y. Improved method for measuring and characterizing phthalate emissions from building materials and its application to exposure assessment. *Environ. Sci. Technol.* **2014**, *48*, 4475–4484.

Liu, Q.-T.; Chen, R.; McCarry, B. E.; Diamond, M. L.; Bahavar, B. Characterization of polar organic compounds in the organic film on indoor and outdoor glass windows. *Environmental science & technology*, **2003**, *37*, 2340–2349.

Matsumoto, M.; Hirata-Koizumi, M.; Ema, M., Potential adverse effects of phthalic acid esters on human health: A review of recent studies on reproduction. *Regulatory Toxicology and Pharmacology* **2008,** *50*, (1), 37-49.

McKee, R. H.; Butala, J. H.; David, R. M.; Gans, G., NTP center for the evaluation of risks to human reproduction reports on phthalates: addressing the data gaps. *Reproductive Toxicology* **2004,** *18*, (1), 1-22.

Øie, L.; Hersoug, L.-G.; Madsen, J. Ø., Residential Exposure to Plasticizers and Its Possible Role in the Pathogenesis of Asthma. *Environmental Health Perspectives* **1997,** *105*, (9), 972-978

Petrick, L.; Destaillats, H.; Zouev, I.; Sabach, S.; Dubowski, Y. Sorption, desorption, and surface oxidative fate of nicotine. *Physical chemistry chemical physics : PCCP*, **2010**, *12*, 10356–10364.

Piade, J. J.; D'Andre, S.; Sanders, E. B. Sorption Phenomena of Nicotine and Ethenylpyridine Vapors on Different Materials in a Test Chamber. *Environ. Sci. Technol.* **1999**, *33*, 2046–2052.

Ritter, L.; Arbuckle, T. E., Can Exposure Characterization Explain Concurrence or Discordance between Toxicology and Epidemiology? *Toxicological sciences* **2007,** *97*, (2), 241-252.

Rudel, R. A.; Perovich, L. J., Endocrine disrupting chemicals in indoor and outdoor air. *Atmospheric Environment* **2009,** *43*, (1), 170-181.

Rudel, R.A., Camann, D.E., Spengler, J.D., Korn, L.R., Brody, J.G. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine- disrupting compounds in indoor air and dust. *Environ. Sci. Technol.* **2003,** 37, 4543-4553.

Santillo, D., Labunska, I., Fairley, M. and Johnston, P. Hazardous chemicals in house dusts as indicators of chemical exposure in the home, *Greenpeace Research Laboratories Technical Note 02/2003 (GRL-TN-02-2003).* 2003.

Schripp, T., Fauck, C., Salthammer, T. Chamber studies on mass-transfer of di(2-ethylhexyl)phthalate (DEHP) and di-n-butylphthalate (DnBP) from emis- sion sources into house dust. *Atmospheric Environment,***2010**, 44, 2840-2845.

Schossler, P.; Schripp, T.; Salthammer, T.; Bahadir, M., Beyond phthalates: Gas phase concentrations and modeled gas/particle distribution of modern plasticizers. *Science of the Total Environment* **2011,** *409*, (19), 4031-4038.

Sherlach, K. S.; Gorka, A. P.; Dantzler, A.; Roepe, P. D. Quantification of perchloroethylene residues in dry-cleaned fabrics. *Environmental toxicology and chemistry / SETAC*, **2011**, *30*, 2481–2487.

Stapleton, H. M.; Dodder, N. G.; Offenberg, J. H.; Schantz, M. M.; Wise, S. A. Polybrominated diphenyl ethers in house dust and clothes dryer lint. *Environ. Sci. Technol.* **2005**, *39*, 925–931.

Svennberg, K.; Wadsö, L. Sorption isotherms for textile fabrics, foams and batting used in the indoor environment. *J. Text. Inst.* **2008**, *99*, 125–132.

U.S. Consumer Production Safety Commission (CPSC). Consumer Product Safety Improvement Act (CPSIA) of 2008. In Bethesda, Maryland, 2008.

Vorkamp, K., Thomsen, M., Frederiksen, M., Pedersen, M., Knudsen, L.E. Pol- ybrominated diphenyl ethers (PBDEs) in the indoor environment and associa- tions with prenatal exposure. *Environ. Int.* **2011**, 37, 1-10.

Weschler, C. J.; Nazaroff, W. W., Semivolatile organic compounds in indoor environments. *Atmospheric Environment* **2008,** *42*, (40), 9018-9040.

Weschler, C. J., Changes in indoor pollutants since the 1950s. *Atmospheric Environment* **2009,** *43*, (1), 153-169.

Wilson, N.K., Chuang, J.C. and Lyu, C. Levels of persistent organic pollutants in several child day care centers, *Journal of Exposure Analysis & Environmental Epidemiology*, **2001**, 11, 449.

Won, D.; Corsi, R. L.; Rynes, M. Sorptive interactions between VOCs and indoor materials. *Indoor Air* **2001**, *11*, 246–256.

Won, D.; Corsi, R. L.; Rynes, M. New Indoor Carpet as an Adsorptive Reservoir for Volatile Organic Compounds. *Environ. Sci. Technol.* **2000**, *34*, 4193–4198.

Xu, Y.; Liu, Z.; Park, J.; Clausen, P. A.; Benning, J. L.; Little, J. C., Measuring and Predicting the Emission Rate of Phthalate Plasticizer from Vinyl Flooring in a Specially-Designed Chamber. *Environmental Science & Technology* **2012,** *46*, (22), 12534-12541.

Xu, Y.; Liang, Y.; Urquidi, J. R.; Siegel, J. a. Phthalates and polybrominated diphenyl ethers in retail stores. *Atmos. Environ.* **2014**, *87*, 53–64.

Zhang, Y.; Luo, X.; Wang, X.; Qian, K.; Zhao, R. Influence of temperature on formaldehyde emission parameters of dry building materials. *Atmos. Environ.* **2007**, *41*, 3203–3216.

Vita

Chenyang Bi was born in Jiujiang, P.R.China in 1991. After completing his work at Jiujiang No.1 middle school, he entered Tongji University in Shanghai, China. He received the degree of Bachelor of Science in Water Supply and Wastewater Engineering from Tongji University in June, 2012. In 2012, he was admitted as a graduate student at The University of Texas at Austin. He was employed as a graduate research assistant in May, 2013 at The University of Texas at Austin.

Permanent email: roadylzl@gmail.com

This thesis was typed by Chenyang Bi.