Occurrence, human exposure and dynamics of phthalates in ACMV indoor environments : method development and field studies

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**OCCURRENCE, HUMAN EXPOSURE AND DYNAMICS OF
PHTHALATES IN ACMV INDOOR ENVIRONMENTS:
METHOD DEVELOPMENT AND FIELD STUDIES**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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METHOD DEVELOPMENT AND FIELD STUDIES**

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Abstract

Phthalates are a group of common indoor semi-volatile organic compounds (SVOCs) that can concurrently exist in gas-phase, airborne particle-phase and settled dust phases, due to their special physicochemical properties. Human exposure to phthalates in indoor environments has raised public concerns owing to the identified associations between phthalates and a number of adverse human health effects.

This study first develops sampling and analytical methods for field studies of airborne phthalates. Based on the methods, the study investigates occurrence of typical phthalates in indoor air of air-conditioned environments and assesses the impacts of air-conditioning and mechanical ventilation (ACMV) system on indoor phthalate concentrations. The study further examines phthalate concentration differences in indoor air and in personal air. More importantly, the study investigates the impacts of human induced particle resuspension and generation on airborne phthalates concentrations. Meanwhile, it evaluates gas/particle partitioning of selected phthalates when there are different levels of particle concentrations in real indoor environments.

In the development of sampling and extraction method, works mainly focus on testing homemade two-bed sorbent tubes with silanized glass wool and Tenax TA as sorbents for airborne phthalate sampling. The sorbent tubes can sample airborne phthalate at low air flow rate for shorter sampling times, improve detection limits of low-volatile phthalates, and are compatible with thermal desorption (TD) method. The development of analytical method tests the extraction efficiency of the tubes. The extraction procedures and parameters are optimized. Important issues including carry-over, recovery, repeatability and linearity are considered.

The study investigates occurrence of five typical phthalates in 24 ACMV indoor environments that are covered with different flooring materials. The results show that

bis(2-ethylhexyl) phthalate (DEHP) has higher airborne concentrations in the involved indoor environments when compared with the literature data. There is also evidence that the rooms covered by polyvinyl chloride have apparently higher DEHP concentrations than those covered by carpets. The calculated whole room emission rates suggest that there are strong source strengths of DEHP and DBP (di-n-butyl phthalate) in the indoor environments.

The study evaluates the impacts of operations of the ACMV system on indoor concentrations of DEHP and DBP in a typical office. The results indicate that indoor DEHP and DBP concentrations accumulate when the ACMV system is off, but decrease continuously to certain quasi-stable levels when the ACMV system is on. The evidence demonstrates that the ACMV system does have certain level of impacts on the indoor concentrations of the both high-volatile and low-volatile SVOCs.

The study compares personally sampled phthalates with the corresponding phthalates in the bulk indoor air in three rooms. The results show that there is no detectable difference between the personal concentrations and the environmental concentrations. The explanation may be that the sedentary subjects' activities are not strong enough to resuspend settled particles, which carry significantly higher phthalate concentrations.

This study conducts intentional particle resuspension and generation in well-controlled real rooms to understand the impacts of human activities on airborne phthalate concentrations as well as their gas/particle partitioning variations. The results suggest that increased airborne particle concentration due to both particle resuspension and generation can result in obvious increases in airborne concentrations of phthalates with low volatilities. The increases are because of either resuspension of phthalates bound to settled dust or partitioning of gas-phase phthalates to the airborne particles. The findings also demonstrate that the gas fractions of the low-volatile phthalates decrease when the airborne particle concentrations increase.

List of publications

Chen A., Gall E. T., Chang, V. W.-C.. Indoor and outdoor particles in tropical classrooms with different ventilation modes. *Atmospheric Environment*, submitted.

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Chen, A., Cao, Q., Chang, V. W.-C.. Occurrence of airborne phthalates in different air-conditioned buildings in Singapore. 13th International Conference on Indoor Air Quality and Climate.

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Chen, A., Cao, Q., Zhou, J., Nazaroff, W. W., Yang, B., Chang, V. W.-C.. Indoor/outdoor particle relationships in an air-conditioned room during and after the 2013 haze in Singapore. 13th International Conference on Indoor Air Quality and Climate.

Chen, A., Chang, V. W.-C.. Human health and thermal comfort of office workers in Singapore. *Building and Environment*, Volume 58, 2012, P 172-178

Chen, A., Chang, V. W.-C.. Indoor air quality and sick building syndrome in offices a university in Singapore. 12th International Conference on Indoor Air Quality and Climate, Volume 2, 2011, P 1570-1571.

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List of important symbols

A	Room area (m^2)
C_i	Indoor airborne pollutant concentration (ng/m^3)
C_o	Outdoor airborne pollutant concentration (ng/m^3)
K_{part}	Gas/particle partitioning coefficient ($\text{mg}/\mu\text{g}$)
λ	Air exchange rate (h^{-1})
S	Whole room emission rates of pollutants ($\mu\text{g m}^{-2} \text{h}^{-1}$)

List of abbreviations

ACMV	Air conditioning and mechanical ventilation system
ACH	Air exchange rate (h^{-1})
BBzP	Benzyl butyl phthalate
CLIMPAQ	Chamber for laboratory investigation, pollution and air quality
DBP	Di-n-butyl phthalate
DEHP	Bis (2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DiBP	Diisobutyl phthalate
DMP	Dimethyl phthalate
DNOP	Di-n-octyl phthalate
DOP	Dioctyl phthalate
FLEC	Field and laboratory emission cell
GC/ECD	Gas chromatography/electron capture detector
GC/FID	Gas chromatography/flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
GW	Glass wool
HPLC	High performance liquid chromatography
HPLC-ESI-MS	High performance liquid chromatography-electrospray tandem mass spectrometry

LIST OF ABBREVIATIONS

HVAC	Heating, ventilation and air conditioning
HVS	High volume sampling
ID	Internal diameter
LOD	Limit of detection
LVS	Low volume sampling
MAE	Microwave-assisted extraction
MAPD	Matrix solid phase extraction
MDL	Method detection limit
OPC	Optical particle counter
OPS	Optical particle sizer
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
PLE	Pressurized liquid extraction
PM	Particulate matter
PTFE	Polytetrafluoroethylene
PUF	Polyurethane foam
PVC	Polyvinyl chloride
RH	Relative humidity
RSD	Relative standard deviation
SER	Specific emission rate
SF ₆	Sulfur hexafluoride

LIST OF ABBREVIATIONS

SHWE	Subcritical hot water extraction
SMPS	Scanning mobility particle sizer
SPME	Solid phase microextraction
SPE	Solid phase extraction
SVOCs	Semi-volatile organic compounds
TD	Thermal desorption
VOCs	Volatile organic compounds

Chapter 1. Introduction

1.1. Problem statement

Phthalate esters are widely used as plasticizers to soften and increase the feasibility of polyvinyl chloride (PVC) plastics, they generally account for a large fraction of the plastics. The phthalates can easily leach into surrounding environment because they are not chemically bound to the polymers. They are therefore abundant in indoor environments decorated with considerable quantity of plastics. Phthalates are classified as semi-volatile organic compounds (SVOCs), which have vapor pressures between 10^{-14} and 10^{-4} atm (10^{-9} to 10 Pa) (Weschler and Nazaroff 2008) or boiling points between 240-260°C and 380-400°C (Clausen and Kofoed-Sørensen 2009). In the indoor environment, due to their special physicochemical properties, the phthalates can concurrently exist in air, airborne particle, settled dust, or on surfaces (Weschler and Nazaroff 2008, Weschler and Nazaroff 2010, Xu and Zhang 2011). The coexistence of phthalates in different phases can complicate human exposure assessment in indoor environments because of the diverse exposure pathways such as inhalation, dermal exposure, dust digestion, and so on. Among the pathways, inhalation and dermal exposure, which are of more importance for the general indoor occupants, are closely correlated with airborne phthalate concentrations (gas and particle phases).

Exposure to phthalates is associated with a number of adverse human health effects, which include damages in respiratory tract, reproductive and so on. Human exposure to phthalates via inhalation and dermal exposure may account for a significant fraction of the total exposure since people spend more than 85% of their time in indoor (Gall et al. 2015). Moreover, evidence show that indoor phthalate concentrations are generally one magnitude higher than the corresponding outdoor concentrations (Rudel and Perovich

2009). It is therefore desirable to advance our knowledge on occurrence, human exposures, influential factors and variations on concentrations of phthalates in typical indoor environments. The literature can see an increasing volume of studies on indoor phthalates. However, more scientific efforts are needed to develop more reliable and efficient methods, to quantify occurrence, source strength and human exposure of indoor phthalates, and to understand the impacts of building services and human activities on indoor phthalate concentrations.

Currently, novel sampling and extraction methods are needed to overcome some of the coherent limitations of the conventional sampling and extraction methods. High volume air sampling coupled with solvent extraction followed by gas chromatography/mass spectrometry analysis (GC/MS) is the conventional sampling, extraction and analysis methods for indoor phthalate studies. But the application of the method is limited by several shortcomings. The sampling process is time-consuming, and generally needs vacuum pumps with high noise level. The long time period needed restricts its application to quantifying short-term variations on concentrations. The high noise from high volume vacuum pump also impedes its applications to indoor environments with occupants. Furthermore, the samples are vulnerable to contamination from surrounding environments and solvent used during the extraction process. The solvent extraction method needs large amount of target compounds but only one thousand or even less of the phthalates' mass will be injected into the GC/MS for quantification; therefore the corresponding detection limit will be poor. Low air volume sampling coupled with thermal desorption followed by GC/MS (TD-GC/MS) can be an alternative of the traditional method. There were already trials using the TD-GC/MS method to quantify indoor phthalates. However, more work is needed to validate the applicability of the method, and protocols based on the method should be developed.

It is important to understand the occurrences, source strengths, and human exposure of airborne phthalates in typical indoor environments. Airborne phthalates play important roles in phthalates' transport from their host materials to the bulk air and human

exposure via inhalation and dermal exposure. Most of the previous studies focus on occurrence of phthalates in residential buildings with few of them were conducted in workplaces (Butte 2009, Kim et al. 2013). In the previous studies, measurement of the specific emission rates (SERs) of the phthalates majorly depended on specifically designed chambers/cells, in which there are well-defined and controlled environmental conditions (Wensing et al. 2005). However, straightforward applicability of the SERs to real buildings needs further verifications as there is only a small volume of literature to prove such validities. Moreover, it is still an open question if we are sampling the accurate concentrations of pollutants to which the occupants are exposing in the indoor air. There are some studies in the residential indoor environments finding that human expose to higher SVOC concentrations than those sampled in the indoor air (Allen et al. 2007, Adibi et al. 2008). But the finding is still inconclusive and more evidence are desirable to explore the scientific truths. It is also important to understand how the air conditioning and mechanical ventilation (ACMV) system influences indoor concentrations of typical phthalates. The ACMV system supplies outdoor air into the indoor environment, which dilutes the concentrations of various pollutants. The dilution effect can eliminate accumulation of airborne phthalates emitted from their host materials. The filtration system can reduce the airborne phthalate concentrations when it captures the particles and absorbs the gases.

The airborne phthalates exist in both gas and particle phase in the indoor air but we have limited knowledge on the impacts of human activity induced particle dynamics on indoor airborne phthalates and their gas/particle partitioning. Previous studies on the impacts are either theoretical predictions/simulations (Xu and Little 2006, Weschler and Nazaroff 2008, Weschler et al. 2008, Liu et al. 2010, Liu et al. 2012, Hu et al. 2013) or chamber studies with extremely high particle concentrations (Benning et al. 2013). However, there is still lacking real field study results on such impacts, which may be majorly due to the limitations of the conventional sampling and extraction methods. The improved TD-GC/MS method developed in the thesis will enable us to evaluate

the impacts of indoor particle dynamics on airborne phthalate and their gas/particle partitioning in real environments.

1.2. Objectives

The objectives of the PhD work are to:

- i. Develop thermal desorption–gas chromatography/mass spectrometry (TD-GC/MS) method for sampling and analysis of indoor airborne phthalates, including selection of optimal adsorbents and design of the sorbent tube, determination of the optimal sampling protocols and optimization of the desorption parameters.
- ii. Understand the occurrence, source strengths and human exposure of airborne phthalates in typical ACMV buildings.
- iii. Evaluate the impacts of ACMV operation on the indoor airborne concentrations of typical indoor phthalates.
- iii. Understand impacts of settled dust resuspension and new particle generation on airborne concentrations and gas/particle partitions of phthalates in real indoor environments.

1.3. Dissertation overview

This dissertation includes six chapters; the technical framework illustrating relationships between works in different chapters is shown in Figure 1-1. Chapter 1 and 2 are introduction and literature review. Chapter 6 is the conclusion and recommendations.

Chapter 3 develops and validates an improved two-bed sorbent tube containing glass wool and Tenax TA that is compatible with the thermal desorption (TD) method. It also includes comparisons of performances between the two-bed sorbent tube and the conventional one-bed Tenax TA tub. With the improved sorbent tube, the method

detection limit of DEHP is highly improved and the potential of contamination is reduced.

Chapter 4 investigates occurrence of airborne phthalates in 24 ACMV buildings, calculates the whole building emission rates, evaluates the impact of ACMV system on indoor concentration of phthalates, and compares differences between personal air phthalates and indoor air phthalates.

Chapter 5 investigates the impacts of settled dust resuspension and particle generation by mosquito coil burning on indoor airborne phthalate in indoor environments with different phthalate sources. It also includes investigations on the gas/particle partitions of phthalates under conditions with different levels of airborne particles.

Figure 1–1. The technical framework illustrating the relationships between works in different chapters.

Chapter 2. Literature review

2.1. -Production, application and sources of phthalates

2.1.1. Production

Phthalate esters have been introduced to the industry since the 1920s, to overcome the excessive volatility and undesirable odor of camphor (Graham 1973). Globally, the total consumption of phthalate is estimated to be more than 3.5 million metric tons per year and DEHP accounts for roughly 50% of the market share (Cadogan and Howick 2000). DBP and BBzP have a relatively smaller market but still quite large, with the annual production of each of them exceeds 100,000 metric tons (Cadogan and Howick 2000). DEHP is the dominant plasticizer, with roughly 95% of its production used in polyvinyl chloride (PVC), where it typically constitutes 30% of PVC by weight (Cadogan and Howick 2000). The consumptions of DEHP in the U.S. and Europe have been declining, being replaced mainly by higher molecular weight phthalates, with the concurrent concerns on DEHP's human health effects. Europe now consumes about 1/5 of global phthalate production, with DEHP representing about 15% of the plasticizer sales, compared to nearly 40% a decade ago (Morse 2011).

2.1.2. Application

The major field of application for phthalates is the use as general purpose plasticizers in polymers, primarily in PVC, roofings, wall coverings, cables, sealants, coatings, paints, clothing, packaging materials, toys, lacquers and adhesives (Wittassek et al. 2007). The applications of individual phthalates are summarized in Table 2-1.

2.1.3. Indoor Sources

Products containing phthalates are widely used in indoor environments. Therefore, phthalates are ubiquitously detected in indoor environments. Since phthalates are not chemically bound to the polymers, they can slowly leach into the surrounded air or dissolved upon contact with liquids or fats. For example, 20 m² of PVC flooring may contain 20kg of a plasticizer, the phthalate can emit continuously throughout the time that the host material is in the indoor environment give the large quantities and low emission rate (Weschler and Nazaroff 2008).

Table 2–1. The major applications of individual phthalates.

Acronym	Full Name	Main Applications
DEHP	Di-ethyl-hexyl-phthalate	Perfumes, flexible PVC products (shower curtains, garden hoses, diapers, food containers, plastic film for food packaging, bloodbags, catheters, gloves, and other medical equipment (such as tubes for fluids, etc.).
BBzP	Benzyl butyl Phthalate	Perfumes, hair sprays, adhesives and glues, automotive products, vinyl floor coverings
DBP	Di-n-butyl phthalate	Plastics such as PVC, adhesives, printing inks, sealants, grouting agents used in construction, additive to perfumes, deodorants, hair sprays, nail polish, and insecticides
DiBP	Di-isobutyl phthalate	Nitro cellulose plastic, nail polish, explosive material, lacquer Similar application and properties as DBP: used as a substitute, e.g. in PVC, paints, printing inks and adhesives
DMP	Dimethyl phthalate	Lacquers, plastics, safety glasses, rubber coating agents, molding powders, insect repellants, and pesticides, etc. (http://www.epa.gov/ttnatw01/hlthef/dimet-ph.html)
DEP	Diethyl phthalate	Cellulose ester plastic films and sheets (photographic, blister packaging, and tape application); molded and extruded articles; cosmetic formulations; adhesives, plasticizers, surface lubricants, etc. (http://www.atsdr.cdc.gov/toxprofiles/tp73-c4.pdf).

Once released into the indoor environment, the less volatile phthalates bond primarily to either settled dust or airborne particles; while the more volatile phthalates majorly exist in gas phase. In the indoor environments, products containing phthalates include plasticizers, solvents, adhesives, and fixing fragrances. The general indoor phthalates can come from personal care products and cosmetics, flexible PVC, PVC flooring, wall covering, electrical cable insulation, casing and circuit boards, etc. (Bonvallot et al. 2010). Indoor surfaces such as walls, ceiling, floors, TV sets, and computers are the major places from which the indoor phthalates are emitted (Saito et al. 2007).

There are less studies aiming to quantify the indoor sources strengths of individual phthalates from different indoor facilities or surfaces, which are mainly based on environment-controlled chambers. Katsumata et al. (2008) report that the emission rates of DBP from notebook computer for idle and operating statuses are 100 and 650 $\text{ng h}^{-1} \text{unit}^{-1}$, respectively.

2.2. Human health risk of phthalates

Phthalates can bio-accumulate in humans but do not bio-magnify because human can efficiently metabolize and excrete phthalate (Shea 2003). Phthalates are thought to be safe for humans but concerns have been raising recently by studies finding that phthalates may cause cancers, endocrine disruption, and reproductive and developmental toxicity (Shea 2003, Hauser and Calafat 2005, Heudorf et al. 2007, Latini et al. 2010). There are also studies reveal that exposure to phthalate in indoor environment may cause respiratory diseases to children, such as asthma and allergy (Shea 2003, Bornehag et al. 2004, Sathyanarayana 2008, Fuentes-Leonarte et al. 2009, Choi et al. 2010, Hsu et al. 2012). Bonvallot et al. (2010) found that the phthalates in dust impose top-ranked health risks to residential occupants among the normally detected indoor semi-volatile organic compounds. The potential exposure sources and health effects for major phthalates are tabulated in Table 2-2.

2.3. Physicochemical properties of phthalates

Phthalates are diakyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid, the general structure of phthalates is shown in Figure 2-1. They are usually clear liquids in pure form; some of them are with faint sweet odors and some with faint yellow color. They are formed when methanol, ethanol or other alcohols react with the carboxyl groups on the benzene ring of phthalic acids. Phthalates are hydrophilic in nature and vary in structure and composition, generally, the molecular weights of phthalates range from 194 to 396 with low melting points range from -4.6°C to 5.5°C.

Table 2–2. Potential exposure sources and health effects of major phthalates.

Acronym	Potential sources of exposure	Potential health effects
DEP	Personal care products (e.g. fragrances), coatings (e.g. pharmaceuticals), dyes, insecticides	Reduced growth rate, food consumption and increased organ weights
DBP	Cellulose acetate plastics, personal care products (e.g. nail polish, cosmetics), lacquers, varnishes, coatings (e.g. pharmaceuticals)	Hepatic and renal effects, developmental and reproductive effects, reduced fetal weight, cryptorchidism, hypospadias, reduced anogenital distance in males.
BBzP	Vinyl flooring, adhesives and sealants, car-care products, toys, food packaging, synthetic leather, industrial solvents, personal care products	Testicular toxicity, cryptorchidism, reduced anogenital distance, teratogenic, modulates steroid hormone levels
DEHP	PVC plastics used in household products (e.g. toys, floor tiles and furniture upholstery, wall coverings), food packaging, blood storage bags and medical devices	Hepatocellular carcinoma, testicular toxicity, anovulation, teratogenic at high doses, affects fetal growth, reduced growth and birth, potential relation with asthma and allergies in Children.

Part of the information in this table is cited from (Hauser and Calafat 2005).

Figure 2–1. The general chemical structure of phthalates (R and R' are general placeholders, are alkenyl and aryl groups).

The general physical and chemical properties of selected phthalate esters are shown in Table 2-3 and 2-4, respectively.

Table 2–3. Physical properties of selected phthalate esters.

Compound	Acronym	CAS #	M.W.	M.F.	B.P. °C	M.P. °C	D, kg/m ³	W.S., mg/L
Dimethyl phthalate	DMP	131-11-3	194.2	C ₁₀ H ₁₀ O ₄	283	5.5	1.19	4,200 at 20 °C
Diethyl phthalate	DEP	84-66-2	222.2	C ₁₂ H ₁₄ O ₄	298	-40.5	1.12	1,00 at 25 °C
Diisobutyl Phthalate	DiBP	84-69-5	278.4	C ₁₆ H ₂₂ O ₄	320	-35	1.064	13 at 25°C
Di-n-butyl Phthalate	DBP	84-74-2	278.4	C ₁₆ H ₂₂ O ₄	340	-35	1.05	13 at 25°C
Benzyl butyl Phthalate	BBzP	85-68-7	312.4	C ₁₉ H ₂₂ O ₄	370	-35	1.0	2.7
Bis-(2-ethylhexyl) Phthalate	DEHP	117-81-7	390.6	C ₂₄ H ₃₈ O ₄	385	-50	0.9732	0.003

Abbre.- Abbreviation; M.W.- Molecular Weight; M.F.- Molecular Formula; B.P.-Boiling Point; M.P.-Melting Point; D- Density; W.S.- Water Solubility.

With boiling points between 230 to 486 °C, phthalates are classified as semi-volatile organic compounds (SVOCs), so they have the similar characteristics as other indoor

SVOC pollutants such as partitioning between gas-phase, particle phase, dust phase, persistent in the indoor environment, etc.

Table 2–4. Chemical properties of selected phthalate esters ¹.

Compound	ACL	log Ps	log H	log C _{w-sat}	log K _{ow}	log K _{oa}	Chemical Structure
DMP	1	-6.46	4.99	-3.22	1.61	6.39
DEP	2	-6.83	4.41	-4.17	2.41	7.21
DiBP	4	-8.3	4.16	-5.88	4.11	9.66
DBP	4	-8.0	3.5	-4.6	4.6	9.5
BBzP	4,6 ^a	-10	4.8	-5.2	4.9	11.2
DEHP	8	-11.5	3.6	-7.9	7.7	12.7

ACL- Alkyl Chain Length; a-Aromatic Ring; log =log₁₀; Ps = saturation vapor pressure (atm); H= Henry's law constant (M atm⁻¹); C_{w-sat}= water solubility (M); K_{ow} = octanol-water partition coefficient (-); K_{oa}= octanol-air partition coefficient (-); 1-Calculated by SPARC Online Calculator.

2.4. Sampling and analysis of airborne phthalates

The sampling and analysis of airborne phthalates are among the most challenging parts in the indoor phthalate studies. These parts include field air sampling, extraction and instrumental quantification in the laboratory. In each of the above steps, there are different options having different characteristics and being suitable for different cases. Therefore we shall first have a full picture on the characteristics of different methods, based on which, we can choose the optimal methods for the particular target pollutants or cases. The sampling, extraction (cleanup and pre-concentration) and analytical

procedure are shown in Figure 2. The general used sampling, extraction (cleanup) and analytical methods for phthalates in air are summarized in Table 2-5.

Figure 2–2. The sampling, extraction (cleanup & preconcentration) and analytical procedure for indoor phthalate study (Krol et al. 2011).

Table 2–5. Sampling, extraction and analytical methods for phthalates in air.

Target Pollutants	Sampling Method	Extraction Method	Instrumental Analysis	Recovery Rate (%)	RSD (%)	LOD (MDL)	Ref.
6 phthalates	1L/min for 8h; glass tube with 2g XAD-2 and 37mm glass fiber filter.	Ultrasonic extraction.	GC-FID	P: 91-115; G: 97-109	N.A.	11-26pg	Pei et al. (2013)
7 phthalates	330ml/min for 24h; stainless tubes with PDMS/Tenax TA.	Thermal desorption;	GC/MS	95-125	<20%	2-229pg/m ³	Lazarov et al. (2013)
9 phthalates	100ml/min for 15mins, stainless tubes with Tenax TA	Thermal desorption;	GC/MS	--	0.1-16	3-3300ng/m ³	Aragón et al. (2013)
3 phthalates	72m ³ air; glass fiber filters.	Ultrasonic extraction followed by SPE.	HPLC	88-105	3.8-9.2	10-60ng	Wang, et al, 2012
12 phthalates	830L/min for 24 h; on PM10 quartz filter.	Pressurized liquid extraction.	GC/MS	90-110	0.5-6.5	40-200pg/m ³	Aragon, et al, 2012
6 phthalates	40L/min for 24 h; PM10 sampled by quartz fiber filters.	Ultrasonic extraction and cleaned by SPE.	GC/MS	65-116	--	--	Salapasidou, et al, 2012
6 phthalates	1L/min for 24h; SPE cartridge.	SPE elution	GC/MS/MS	>95	0.5-1.6	10-30pg	Bergh, et al, 2010
11 phthalates	70 L/min for 24h; parallel 160mm URG cartridge containing an impact equipped inlet followed by a 25mm quartz fiber filter and a 3g bed of XAD-2.	Soxhlet extraction	GC/MS	--	<30	--	Rudel et al, 2010
7 phthalates	4L/min flow rate; 26 mm quartz fiber filter and cartridge with XAD-2 and PUF.	Soxhlet extraction	GC/MS	85-104	1.4-2.5	1-5µg	Hines, et al, 2010
7 phthalates	200ml/min for 48 h; 10 mm SPE disk.	Ultrasonic extraction	GC/MS	--	--	0.8-65ng/m ³	Kanazawa, et al , 2010

P-particle-phase, G-gas phase.

Table 2-5 (continuous). Sampling, extraction and analytical methods for phthalates in sir.

Target Pollutants	Sampling Method	Extraction Method	Instrumental Analysis	Recovery Rate (%)	RSD (%)	LOD (MDL)	Ref.
2 phthalates	80 ml/min for 60-90min; glass tube with 300mg Tenax TA.	Thermal desorption	GC/MS	--	--	--	Choi, et al, 2010
6 phthalates	500L/min for 12h; GFF coupled with PUF.	Soxhlet extraction	GC/MS	80-98	1-6	0.4-1.3pg/m ³	Wang et al. (2009)
5 phthalates	4 L/min for 48 h; QFF and PUF cartridge.	Soxhlet extraction	GC/MS	--	--	--	Adibi et al. (2008)
6 phthalates	500-2000m ³ air; PUF/XAD-2 cartridge along with GFF.	Soxhlet extraction	GC/MS	80-140	2-16	0.2-17 pg/m ³	Xie et al. (2007)
4 phthalates	40 L/min with QFF.	Ultrasonic extraction	HPLC-ESI-MS	45-49'	--	0.04-0.2ng/m ³	Rakkestad, et al, 2007
6 phthalates	40L/min for 280h; XAD-2 coupled with GFF.	Volatilization-condensation extraction of GFF FOR 12 h; sohlext extraction for XAD-2 for 3 days.	GC-ECD	--	--	25-75 pg/m ³	Teil, et al, 2006
6 phthalates	500 mL/min for 30 min; thermal desorption tube with 100 mg polydimethylsiloxane (PDMS) particles.	Thermal desorption	GC/MS	86-102	2.3-9.2	In the order of 10 pg.	Tienpont, et al, 2000
5 phthalates	1 L/min for 3 days; glass tubes containing charcoal granules.	Ultrasonic extraction	GC/MS	68-102	5.6-9.6	2.5-5 pg	Otake, et al, 2004;
9 phthalates	5 L/min for 7h; on PUF by gas sampler GS-312	Accelerated solvent extraction	GC/MS	--	--	10 ng/m ³	Fromme, et al, 2004
2 phthalates	4 L/min for 48 h; URG sampler with XAD-2, PUF and GFF.	Soxhlet extraction and ultrasonic extraction; SPE cleanup.	GC/MS	--	--	40pg/m ³	Wilson, et al, 2003

2.4.1. Sampling methods

Air samples are mainly collected either by active air sampling or by passive air sampling techniques. The active air sampling technique uses an air sampling pump (high volume or low volume) to pull air through a tube containing solid sorbent(s) or a filter, on which the target pollutants are adsorbed. The technique is widely used for air sampling of volatile and semi-volatile organic compounds, including alkanes, carboxylic acids, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), phthalates, and musk fragrances. For a particular group of target pollutants, there are needs to perform optimizations on the adsorbents, sampling flow rate, sampling duration, etc. There are numerous types of solid adsorbents and no one adsorbent can capture all types of air pollutants. The optimization on adsorbent mainly includes checking repeatability/reproducibility, breakthrough, and recovery rates. The sampling flow rate would affect the breakthrough of the adsorbent chosen and the sampling duration needed to fulfill the detection limits in the instrumental quantification. The sampling duration would partially affect the target pollutants collected on the adsorbent. Therefore, these two parameters shall also be optimized before practical field air sampling.

The active air sampling comprises of high volume (HVS) and low volume (LVS) air samplings. As shown in table 2-5, most of the studies for atmospheric phthalates employ the HVS technique. The HVS generally operates with high flow rate and long sampling duration. The total air volume sampled ranges from 220 to 2700m³ and the sampling time ranges from 12 h to 7 days depending on the types of target pollutants. In general, the sampling flow rate is around 40-500L/min and the sampling duration is around 24 h in purpose of sampling enough amount of target pollutants and avoiding clogging up of filters (Yusà et al. 2009). A HVS sampler is generally comprised of a high volume air pump, a cartridge with solid adsorbents and filter holder with glass fiber or quartz fiber filter. The conventional solid adsorbents for gaseous pollutant

sampling can be XAD resin, polyurethane foam (PUF) or a combination of XAD and PUF (Xie and Ebinghaus 2008).

There are a number of benefits associated with the HVS technique, including well-defined sampling rates, lower detection limits, short sampling duration, effective enrichment and ease of calibration. However, the applicability of the HVS method to indoor air sampling is limited. The HVS technique bears losses from breakthrough and degradation because of long term sampling duration. In addition, application of HVS to gas-particle partitioning study might lead to some biases such as blow on and blow off (Yusà et al. 2009). Most importantly, the high sampling rates ($0.2\text{-}1\text{ m}^3/\text{min}$) along with 8-24 h sampling duration can easily exceed the room volume, and cause underestimation of the indoor pollutant concentration. In addition, the HVS devices are normally with big size and higher noise level, which would disturb the occupants' general life. Consequently, the HVS technique is rarely employed for air sampling in occupied indoor environments.

The LVS technique with a flow rate range of 1-10L/min, is normally applicable to indoor phthalate sampling, (Wilson et al. 2001, Wilson et al. 2003, Fromme et al. 2004, Adibi et al. 2008, Hines et al. 2010, Bergh et al. 2011, Bergh et al. 2011, Pei et al. 2013). The LVS sampler generally has a similar configuration with a HVS sampler, but the sampling flow rate is much smaller and noise level is lower. The size of the device is also much smaller, which occupies less indoor space during the sampling. Along with the low noise level, it causes much less disturbance to occupants. However, if coupled with solvent extraction, the LVS method requires largely extended sampling time to collect sufficient quantity of pollutants in either resins or filters. Normally the sampling campaign would last for 8 h to 24 h; there is also study lasting for 3 days.

LVS sampling time can be much shorter (30min-2h) if coupled with thermal desorption (TD) technique. This is because that the TD method can achieve much better limits of detections than the traditional solvent extraction methods (Tienpont et al. 2000, Choi et al. 2010, Aragón et al. 2013, Lazarov et al. 2013). The advantages of TD method over

solvent extraction method will be discussed in the following section. Tenax TA, which is a type of porous organic polymer, is commonly used for indoor phthalate sampling as seen in Table 2-5. Though the TD method based on Tenax TA for volatile organic compounds (VOCs) sampling is well developed and validated, its reliability for SVOC sampling is still open. It is because that the Tenax TA has moderate surface area, limited thermal stability and potential chemical degradation (Ras et al. 2009). The moderate surface area and limited thermal stability may combine together to cause severe residue issue inside the sorbent tube. The chemical degradation may create ghost peaks that challenge the quantification process. Novel adsorbents like polydimethylsiloxane (PDMS) particles have also been tested for the phthalate sampling (Tienpont et al. 2000, Lazarov et al. 2013), but large-scale application is rare. Currently, the TD method can only collect total airborne phthalate, lacking the capacity to separate particle phase phthalate from their gaseous counterparts. It is important to develop a method that is not only compatible with TD method but can separate particle and gaseous phthalates in the indoor environments.

There are other methods for sampling semi-volatile organic compounds in air, including diffusion denuder and passive sampling (solid phase microextraction (SPME), semi-permeable membrane device, PUF disk) (Bartkow et al. 2005, Xie and Ebinghaus 2008, Yusà et al. 2009, Cecinato et al. 2012, Tuduri et al. 2012). But the applicability of these methods is largely restricted by the long sampling time needed, which is usually 60 days to several months.

Methods combined LVS with TD method can generally only collect total airborne phthalates, lacking the capacity to separate gas phase and particle-phase from each other. This is because that the conventionally adopted absorbents for particle-phase SVOCs either cannot tolerate the high temperature during the thermal extraction process or have high surface area that can result in significant positive artifacts. Methods that are not only compatible with the TD method but also can separate particle and gaseous phthalates in the indoor environments are desirable.

Table 2–6. Pros and cons of the major solvent extraction methods.

Technique	Pros	Cons
Soxhlet extraction	<ul style="list-style-type: none"> ▪ High extraction efficiency ▪ Can handle large mass of samples ▪ Pre-filtration not needed ▪ Not matrix dependent ▪ Unattended operation ▪ Cost-effective 	<ul style="list-style-type: none"> ▪ Long extraction time needed ▪ Large amount of solvent (300-500ml) ▪ Manual post-evaporation and cleaning required ▪ Less potential of automation
Sonication	<ul style="list-style-type: none"> ▪ Time-efficient (30-60min) ▪ Capable of handling large amount of sample ▪ Not matrix dependent ▪ Cost-effective 	<ul style="list-style-type: none"> ▪ Large amount of solvent (300-500ml) ▪ Laborious ▪ Manual post-evaporation and cleaning required ▪ Modifier added
Supercritical fluid extraction (SFE)	<ul style="list-style-type: none"> ▪ Time-efficient (30-60min) ▪ Supercritical fluid is safe ▪ High selectivity ▪ Small amount of solvent (5-10ml) ▪ Pre-filtration not needed ▪ No solvent exposure ▪ Automated 	<ul style="list-style-type: none"> ▪ Limited sample mass (<10g) ▪ Matrix dependent ▪ Modifier added ▪ High cost ▪ Clean-up step needed ▪ Not useful to extract ionic and polar compounds
Microwave-assisted extraction (Maertens et al.)	<ul style="list-style-type: none"> ▪ Time efficient (20-30min) ▪ Small amount of solvent (30ml) ▪ Controllable ▪ Stirring possible ▪ Higher temperature\ ▪ No drying agents needed 	<ul style="list-style-type: none"> ▪ Post-filtration required ▪ Polar solvent needed ▪ Post-cleaning needed ▪ Moderate cost
Pressurized solvent extraction (PLE)	<ul style="list-style-type: none"> ▪ Time efficient (~15min) ▪ Small amount of solvent ▪ Large mass of sample (up to 100g) ▪ No filtration needed ▪ Automated ▪ Possible to integrate with clean-up 	<ul style="list-style-type: none"> ▪ High initial cost ▪ Matrix dependent
Ultrasonic extraction	<ul style="list-style-type: none"> ▪ Time-efficient ▪ Cost-efficient ▪ Useful for thermo labile compounds 	<ul style="list-style-type: none"> ▪ Post-filtration required ▪ Large amount of solvent

2.4.2. Extraction methods

After the sampling process, the pollutants trapped in the adsorbents shall be extracted by either gas or liquid for further instrumental analysis. The purposes of sample extraction are: to isolate the analytes from the adsorbents, to improve the analytes' chromatographic behaviors and to increase the analytes' detection limits (Koning et al. 2009). There are a variety of extraction methods for environmental sample extraction, which can be sub-classified into either solvent extraction or solvent-less extraction. The solvent extraction methods include Soxhlet extraction, pressurized liquid extraction (PLE), subcritical hot-water extraction (SHWE), microwave-assisted extraction (MAE), ultrasonic extraction, supercritical fluid extraction (SFE), matrix solid-phase dispersion (MAPD) and so on. The readers can refer to the review by Koning et al. (2009) for more details in terms of the characteristics, operational procedures and applications of individual methods. The pros and cons of the major solvent extraction methods are summarized in Table 2-6.

The most frequently adopted solvent extraction method for airborne phthalate studies is Soxhlet extraction (Wilson et al. 2001, Wilson et al. 2003, Teil et al. 2006, Xie et al. 2007, Adibi et al. 2008, Wang et al. 2008, Hines et al. 2010, Rudel et al. 2010, Wang et al. 2012) and ultrasonic extraction (Otake et al. 2004, Rakkestad et al. 2007, Kanazawa et al. 2010, Salapasidou et al. 2011, Wang et al. 2012, Pei et al. 2013) as seen in Table 2-6. The wide application of the two traditional solvent extraction methods is because of their well-developed protocols and low costs. There are also studies that adopted pressurized liquid extraction (PLE) method (Fromme et al. 2004, Aragón et al. 2012), but this method needs much higher initial investments. Eluting of SPE directly after the air sampling using the cartridge is also used as a simple extraction method (Bergh et al. 2010, Bergh et al. 2011, Bergh et al. 2011); however, the SPE cartridge cannot work properly under high flow rate. The flow rates have to be low enough to guarantee no breakthrough, which prolongs the sampling time. Recently, the application of TD method to air-phase SVOC studies is increasing, given its obvious advantages over the traditional solvent extraction methods.

The TD method includes two desorption stages to achieve a necessary step of focusing. The first stage is the primary desorption process and the second stage is the secondary desorption stage. As illustrated in Figure 2-3, in the primary desorption process, the oxygen and water in the sorbent tube are purged out first by dry carrier gas at ambient temperature; then the tube is heated up to a higher temperature (normally 300-400°C). The analytes are carried out of the tube by the carrier gas, then trapped by a cold trap at a subzero temperature, in which the analytes are concentrated before the GC injection. These traps are usually quartz tubes that are filled with a sorbent or a mixture of them, and their common dimensions are 10 cm length and 2-3 mm ID (Ras et al. 2009). In the secondary desorption, the cold trap is heated up and the analytes are transferred into the GC column in split or splitless mode by the carrier gas. The purpose of the two-stage process is to create a rapid process which can avoid the broad initial band in the capillary GC column and drastically reduced resolution caused by direct TD injection (Ras et al. 2009).

TD method provides an excellent alternative to the solvent extraction methods. Comparing with the traditional solvent extraction methods, the TD method has advantages as follows (Urbanowicz et al. 2011):

- Typically 1,000 times better sensitivity and less quantity of sample needed;
- Simple sample preparation and lower probability of contamination;
- No interferences from solvent;
- Time and labor saving;
- Better recovery (with desorption efficiency >90%);
- Environmental friendly (without solvent disposal) and cost effectiveness;
- No solvent choice issue and solvent peak;
- Automation.

Among the above advantages, it is worthwhile to highlight the special advantages of TD method for airborne phthalate study. First of all, the TD method reduces the potential of environmental contamination to the lowest level. Phthalates are a group of

pollutants that are ubiquitous in the indoor environments and even solvents. Therefore, there is much higher risk of contamination from the surrounding environment and solvent used if the solvent extraction method is used. Secondly, the TD method needs less quantity of sample compared with the solvent extraction methods. The solvent extraction methods need more quantity of sample to offset the low sensitivity; much longer sampling duration is normally needed for collecting sufficient quantity of samples. In this case, it is challenging to study the short-term indoor phthalate variations. The higher sensitivity of the TD method offers the opportunity of studying short-term indoor phthalate variations, given the less sample needed.

Figure 2–3. A simple schematic of the TD processes. (a) primary desorption; (b) secondary desorption (Ras et al. 2009).

However, the TD method does not without its limitations, which may cause bias or even failure if there is poor optimization before field monitoring. There is no adsorbent that is compatible with all types of pollutants, special adsorbent should be chosen according to target analytes in consideration of breakthrough, thermal degradation, incomplete desorption and so on. Moreover, the potential of carry-over, transfer loss, molecular rearrangement, fragmentation or breakdown of more thermally labile analytes at higher extraction temperature and matrix may complicate the application of the TD method (Urbanowicz et al. 2011). Therefore, the adsorbent and cold trap for the special target analytes should be carefully chosen; the TD temperature program should

be optimized accordingly; the potential transfer loss should be quantified. Well-developed protocols is still lacking though the TD method has been increasingly applied to airborne phthalate study. More work on this technique is still needed.

2.4.3. Instrumental analysis

As seen in table 2-5, GC/MS is the most frequently employed instrument to quantify phthalates after extracting from their matrices. There are also studies used other instruments such as HPLC (Rakkestad et al. 2007, Wang et al. 2012), GC/ECD (Teil et al. 2006), GC/FID (Pei et al. 2013), as well as GC/MS/MS (Bergh et al. 2010, Bergh et al. 2011, Bergh et al. 2011, Bergh et al. 2012). Among these instruments, GC/MS/MS has the best sensitivity, followed by GC/MS, while the left instruments have worse sensitivities (Krol et al. 2011). The GC/MS generally meets the sensitivity requirement for indoor phthalate analysis, that why it is most widely adopted in this research area. The GC/MS can usually achieve detection limits of 1-100pg depending on the individual phthalate and method detection limits in the sub-ppb level, depending on the sampling time and air volume sampled. Given the phthalate concentrations in indoor environments are normally between 10ng/m³ and 100ng/m³, the detection limits obtained by the GC/MS are able to quantify the phthalates safely.

2.5. Indoor occurrences of phthalates

2.5.1. Occurrence of phthalates in indoor air

In studies about indoor and outdoor occurrence of phthalates, the usually chosen target compounds are DMP, DEP, DiBP, DBP, BBzP and DEHP. The reported indoor and outdoor occurrences of the six major phthalates in air are summarized in Table 2-7. Given the ubiquitous application of plastic materials in indoor environment, the indoor sources of phthalates are abundant; hence the phthalates are frequently detected in indoor environments, with concentration levels about 1 to 1,000 times higher than the outdoor concentration levels. The total indoor concentration levels of the six major phthalates are: DMP: 5-1,500ng/m³; DEP: 10-2300ng/m³; DiBP: 13-1,700ng/m³; DBP:

30-11,000ng/m³; BBzP: 10-4,000ng/m³; and DEHP: 20-4,000ng/m³. The total outdoor concentration levels of the six major phthalates are: DMP: <LOD -400ng/m³; DEP: 0.1-1,380 ng/m³; DiBP: 100-200ng/m³; DBP: 0.4-1,200ng/m³; BBzP: 0.04-70ng/m³; and DEHP: 4-800ng/m³. In the indoor environments, the highest phthalate concentrations are found in newly decorated homes in China (Pei et al. 2013), the authors report that indoor concentration levels of the five major phthalates (DMP, DEP, DBP, BBzP, DEHP) are all between 1,000-4,000ng/m³, especially for DBP, BBzP and DEHP, whose concentration levels are above 2,000ng/m³. These findings indicate that large amount of materials containing phthalates are used in indoor environments, and these materials act as indoor sources of phthalates. In addition, the indoor phthalate concentration levels in developed countries (U.S.A., Germany, Japan, Belgium, Sweden, etc.) are comparable with each other, which are generally between 100-1,000ng/m³, indicating the similar application of plastic materials in indoor environments in these countries.

In indoor air, SVOCs can concurrently exist in gas and particle phases. Especially for less volatile compounds, such as DEHP and BBzP, they majorly exist in the particle-phase. Understanding gas/particle partitioning of indoor airborne phthalates is important since the partitioning affects their emission, transport and human exposure essentially. There are studies that try to quantify the distributions of airborne phthalates in difference environments. For example, Wang et al. (2014) measure the gas-phase and particle-phase concentrations of phthalates in homes and offices in Xi'an, China. Xie et al. (2007) sample phthalate concentrations in the two phases in the Arctic air and Teil et al. (2006) did the sampling in the ambient air of Paris, France. All these studies depended on the HVS methods using QFF for the particle-phase compounds and PUF and XAD-2 for the gas-phase compounds. Currently, this method is the most frequently adopted one to separate gas-phase and particle-phase SVOCs though it bears several limitations such as positive and negative artifacts (Yusà et al. 2009). To our best knowledge, there has not been any LVS based method to separate gas-phase and

particle-phase SVOCs at the flow rate of 100ml/min to 1L/min. There are research needs to develop such as LVS based method to meet the scientific requirements.

Human exposure and gas/particle partitioning of SVOCs depend heavily on the size distribution of airborne particles (Cao et al. 2012, Rauert et al. 2014). But there are few studies about size distribution of particle-phase phthalates in the literature. Zhang et al. (2014) sample the phthalate concentrations in PM₁₀ and PM_{2.5} in 13 homes during both summer and winter in Tianjin, China. Rakkestad et al. (2007) also measured phthalate concentrations in the PM₁₀ and PM_{2.5} in different indoor air. But the two studies have different findings, indicating that it is necessary to have more studies on this topic.

Emission of phthalates from their host materials is also an important topic but there are few related studies in real buildings. The previous studies on this topic majorly depend on chamber studies (Wensing et al. 2005). Wensing et al. (2005) and Rauert et al. (2014) review the experimental methods used to determine specific emission rates of building materials, equipment, etc. in chamber studies. A detailed discussion on this will be present in Section 2.6. The only study that tried to measure the whole building emission rates of phthalates is the one by Xu et al. (2014) in retail stores.

CHAPTER 2. Literature review

Table 2–7. Occurrence of phthalates in air (ng/m³).

Locations	Sites	DMP	DEP	DiBP	DBP	BBzP	DEHP	Ref.
Austin, USA.	Retail stores	150 (8-810)	150 (7-440)	--	230 (48-1,430)	50 (2-100)	130 (10-440)	Xu et al. (2014)
Xi'an, China	Homes & offices	G: 510 (0-2,460); P: 100 (0-1,750)	--	G: 1,000 (0-6,170); P: 1,620 (0-7,970)	G: 590 (0-2,150); P: 1,060 (0-4,920)	--	G: 470 (50-1,860); P: 1,040 (90-4,160)	Wang et al. (2014)
Tianjing, China	13 homes	PM ₁₀ : 9 (0.3-47.5); PM _{2.5} : 3 (0.2-25.3)	PM ₁₀ : 1.5 (0.1-7.5); PM _{2.5} : 0.8 (0.1-4.5)	--	PM ₁₀ : 318 (7-1,466); PM _{2.5} : 30.5 (0.2-25.3)	PM ₁₀ : 0.63 (0.01-8.03); PM _{2.5} : 0.32 (0.01-4.79)	PM ₁₀ : 92 (3-305); PM _{2.5} : 44 (1-180)	Zhang et al. (2014)
3 states in Germany	63 daycare centers	163 (10-1431)	208 (72-781)	516 (95-2613)	283 (49-1276)	5-215	276 (25-889)	Fromme et al. (2013)
Nanjing, China	Homes	G: 1299; P: 156	G: 1829; P: 461.2	--	G: 872.6; P: 1066	G: 2068; P: 1907	G: 1116; P: 1322	Pei et al. (2013)
Flanders, Belgium	Outdoor	15-454	4-1380	--	18-1190	0.4-21	58-681	Lazarov et al. (2013)
Nanjing, China	9 sites	P: 10.5	--	--	P: 62	--	P: 33	Wang et al. (2012)
Tarragona, Belgium	Outdoor	--	1.93	167	--	0.08	8.67	Aragón et al. (2000)
Thessaloniki, Greece	Outdoor	--	--	--	0.43-3.36	0.04-0.98	4.63-45	Salapasidou et al. (2011)
Stockholm, Sweden	Homes, daycares, workplaces.	Home: 18; Daycare: 6.2; Work: 4.6.	Home: 1598; Daycare: 1246; Work: 667.	Home: 296; Daycare: 239; Work: 310.	Home: 925; Daycare: 682; Work: 599.	Home: 28; Daycare: 19; Work: 16.	Home: 208; Daycare: 267; Work: 118.	Bergh et al. (2011)
Stockholm, Sweden	Workplace	27	320	430	270	21	230	Bergh et al. (2010)
California, U.S.A.	Homes	--	330 (110-2500)	130 (17-1700)	140 (28-11000)	38(6.8-80)	130 (68-200)	Rudel et al. (2010)

a – the unit of the concentration is pg/m³; G- gas-phase concentration; P- particle phase concentration.

Table 2–7 (Continuous). Occurrence of phthalates in air (ng/m³).

Locations	Sites	DMP	DEP	DiBP	DBP	BBzP	DEHP	Ref
Tokyo, Japan	Homes	47.9 (12-191)	61 (22-203)	75(13-321)	200 (80-740)	nd (nd-27)	147 (12-600)	Kanazawa et al. (2010)
Sweden	Homes	--	--	--	--	380 (10-4550)	1310 (20-4046)	Choi et al. (2010)
New York, U.S.A.	Homes	--	Pe: 2150 (1920-2410); I: 1660 (1380-2000)	Pe: 500 (440-570); I: 450 (380-530)	Pe: 450 (410-510); I: 380 (330-450)	Pe: 50 (40-60); I: 30 (20-40)	Pe: 180 (160-210); I: 90 (80-100)	Adibi et al. (2008)
Arctic ^a	Outdoor	G: 74 (46-223) P:3 (1-8)	G: 320 (205-895); P: 18 (5-41)	G: 137 (96-549); P: 59 (20-74)	G: 273 (158-432); P: 143 (75-189)	G: 40 (17-68); P: 30 (18-56)	G:215 (75-460); P: 589 (264-735)	Xie et al. (2007)
Oslo, Norway	Indoor	--	--	--	PM ₁₀ : 75 (51-93) PM _{2.5} : 74 (42-99)	PM ₁₀ : 10 (3-27) PM _{2.5} : 11 (0-31)	PM ₁₀ : 12 (3-29) PM _{2.5} : 12 (1-22)	Rakkestad et al. (2007)
Paris, France	Outdoor	G: 5 (0.1-21); P: 0.1 (---0.3)	G: 8.7 (2-25); P: 0.4 (0.1-0.9)	--	G: 17 (3-59); P: 2 (0.6-5)	G: 4 (0.5-12); P: 0.3 (0.1-0.5)	G: 12 (3-26); P: 5 (2.4-10)	Teil et al. (2006)
Ghent, Belgium	Car park	<LOQ-25	<LOQ-252	<LOQ-1027	<LOQ-946	<LOQ-48	<LOQ-1046	Tienpont et al. (2000)
Tokyo, Japan	Homes	--	100 (10-610)	--	390 (10-6180)	(Rudel and Perovich 2009)10 (1-110)	110 (1-3130)	Otake et al. (2004)
Berlin, Germany	Homes	436	643	--	1083	18	156	Fromme et al. (2004)
Berlin, Germany	Kindergarten	331	353	--	1188	<LOD	458	Fromme et al. (2004)
North Carolina, USA	Child daycare centers	--	--	--	I: 488 (222-786); O: 74(24-110)	I: 144 (128-151); O: 133 (102-192)	--	Wilson et al. (2003)
North Carolina, USA	Homes	--	--	--	I: 288 (190-451); O: 31(1-85)	I: 143 (50-267); O: 127 (1-474)	--	Wilson et al. (2003)

G-gas-phase concentration; P- particle phase concentration; I- indoor air concentration; Pe-personal air concentration; O-outdoor air concentration.

Table 2–8. Concentrations of phthalates in indoor dust (µg/g).

Location	Sites	DMP	DEP	DiBP	DBP	BBzP	DEHP	DnOP	Ref
Xi'an, China	Homes & offices	5.7 (0-68.8)	--	901 (0-7,228)	448 (4-4,357)	--	799 (67-3,475)	--	Wang et al. (2014)
Canada	Homes	0.12 (0-22)	2.0 (0-193)	5.2 (0-69)	16.8 (0-1392)	42.3 (0.6-977)	462 (36-3,836)	--	Kubwabo et al. (2013)
Seoul, South Korea	50 nursery schools	3.1±1.9	24.6	--	66.9±50.1	60.7±35.9	3950±2760	--	Kim et al. (2013)
3 states in Germany	63 daycare centers	0.7 (0.1-11)	3.4 (0.4-111)	39 (7-339)	30 (2-266)	21 (1-348)	1973 (99-10,086)	--	Fromme et al. (2013)
Palermo, Italy	13 homes	15	31	--	799	99	304	41	Orecchio et al. (2013)
Guangzhou, China	20 homes	8.09 (0.1-39.5)	8.3 (2.3-22.8)	9.9 (2.8-25.8)	17.9 (2.6-46.6)	8.22 (0.08-44.3)	690 (285-1070)	8.4 (2.4-21.8)	Wang et al. (2013)
Hongkong, China	20 homes	0.40 (0.1-2.2)	1.4 (0.5-4.6)	1.0 (0.1-3.8)	6.0 (0.3-17.4)	14.6 (0.6-81.9)	641 (96.8-2190)	5.0 (0.3-13.5)	Wang et al. (2013)
Greece	20 homes	--	5	25	--	54	335	35	Papadopoulos et al. (2013)
Kuwait	21 homes	0.01 (0-0.1)	1.5 (0.1-16)	--	51 (8.3-160)	6.4 (0-160)	1700 (380-7800)	14 (0-1300)	Gevao et al. (2013)
Nanjing, China	215 homes	0.4 (0-24)	0.9 (0-34)	--	52 (0-2150)	3 (0-39)	462 (1-9950)	2 (0-40)	Zhang et al. (2013)
China	20 offices	1.3 (0.2-3.7)	1.7 (0.5-7)	32 (13-79)	69 (27-138)	15 (2-175)	721 (82-1490)	9 (1-69)	Kang et al. (2012)
China	4 schools	0.3 (0.1-25)	1.7 (1.3-2.8)	57 (16.5-79)	52 (42-74)	10 (4.6-32.8)	819 (372-952)	8.6 (2.5-16.7)	Kang et al. (2012)
China	5 shopping malls	1.5 (0.8-6.4)	2.3 (1.3-35.6)	30.9 (19.1-50.8)	82.4 (59-135)	24.2 (11-284)	958 (909-1050)	17 (8.7-66.2)	Kang et al. (2012)
China	16 hospitals	0.4 (0.1-3.4)	1 (0.3-1.8)	24.7 (5.1-113)	51.8 (18-89)	10.6 (4.9-328)	707 (165-1020)	5.7 (2-33.5)	Kang et al. (2012)
China	23 homes	0.05 (0-0.55)	1.5 (0-13.8)	34 (0.6-401)	77 (3.1-878)	4.6 (0-157)	1190 (175-8680)	7.6 (1.1-160)	Kang et al. (2012)

Table 2–8 (Continuous). Concentrations of phthalates in indoor dust (µg/g).

Locations	Sites	DMP	DEP	DiBP	DBP	BBzP	DEHP	DnOP	Ref
Guangzhou, China	15 offices	1.8 (1.2-3.1)	1.7 (0.4-6.8)	57.6 (18.9-165)	77.6 (34.4-210)	1.6 (0-4.1)	1429 (706-2837)	8.1 (3.6-27.8)	Lan et al. (2012)
Guangzhou, China	10 living rooms	2.2 (1.2-4.5)	1.8 (0.8-4.7)	37.5 (22.3-65.1)	44.5 (27.2-73.2)	1.5 (0.5-3.4)	1039 (627-1506)	4.8 (2.5-6.4)	Lan et al. (2012)
Guangzhou, China	10 bedrooms	0.9 (0.1-1.8)	0.9 (0.05-1.8)	26.6 (6.3-43.9)	34.4 (11-58)	0.8 (0-2.2)	376 (100-627)	2 (0.3-3.3)	Lan et al. (2012)
Sweden	NIST 2585 dust	1.0±0.03	6.7±0.34	6.0±0.26	31±1.1	93±1.9	570±11	17±0.92	Bergh et al. (2012)
China	75 homes	1.2 (nd-8.2)	0.4 (nd-45.5)	17.2 (2.6-299)	20.1 (1.5-1160)	0.2 (nd-12)	228 (9.9-8400)	0.2 (nd-45.7)	Guo and Kannan (2011)
Albany, USA	33 homes	0.08 (nd-3.3)	2 (0.7-11.8)	3.8 (0.7-34.4)	13.1 (4.5-94.5)	21.1 (3.6-393)	304 (37.2-9650)	0.4 (nd-14.1)	Guo and Kannan (2011)
Fyn, Denmark	500 bedrooms	--	3.1±8.8	16.6±6.3	8.1±7.2	4.2±4.0	220±2.4	--	Langer et al. (2011)
Fyn, Denmark	151 daycare centers	--	1.9±2.6	18.1±3.1	30±4.6	16.4±3.4	540±1.9	--	Langer et al. (2011)
France	Homes	6.9	1.5	119	55	28	505	81	Bonvallot et al. (2010)
Halle/Saale, Germany	30 homes	--	--	--	87.4	15.2	604	--	Abb et al. (2009)
Sofia/Burgas, Bulgaria	177 homes	260 (280)	350 (340)	--	7860 (9930)	320 (340)	960 (1050)	250 (300)	Kolarik et al. (2008)
Sweden	390 homes	--	31 (nd-2425)	97 (nd-3810)	150 (nd-5446)	319 (nd-45549)	770 (nd-40459)	--	Bornehag et al. (2005)
Berlin, Germany	59 homes	10.8 (1.5)	44.6 (6.1)	--	55.6 (47)	86.1 (29.7)	775.5 (703.4)	--	Fromme et al. (2004)
Cape Cod, USA	60 homes	--	5 (nd-111)	1.91 (nd-39.1)	20.1 (nd-252)	45.4 (3.9-1310)	340 (16.7-7700)	--	Rudel et al. (2003)

2.5.2. Occurrence of phthalates in indoor dust

Dust is one of the most important sinks and reservoirs for indoor phthalates. The phthalates emitted from their host materials can migrate into the indoor settled dust by different mechanisms. The mechanisms mainly include gas/dust partitioning (Weschler and Nazaroff 2010), settlement of suspended particles (Liu et al. 2010), direct contact (Schrapp et al. 2010). Previous studies demonstrate that the analysis of house dust could give a credible indication on the indoor contamination, their sources as well as assessment of human exposure (Lioy et al. 2002, Bonvallot et al. 2010, Gevao et al. 2013). There is also direct evidence that links dust phase concentration of several phthalates with human exposure and health symptoms. For example, Langer et al. (2013) report that dust phase concentrations of DEP, DBP, DiBP and BBzP in children's bedrooms and daycare centers significantly correlate with the concentrations of these phthalates' metabolites in the children's urine. Dust-phase BBzP is associated with allergic or asthmatic children (Bornehag et al. 2004, Hsu et al. 2012). DEHP is also associated with asthma (Bornehag et al. 2004), and higher levels of DBP may result in childhood allergic and respiratory morbidity (Hsu et al. 2012).

There are a number of studies carried out in different countries/regions to detect the abundance of phthalates in indoor dust, majorly of residential buildings. Table 2-8 summarizes the reported phthalate concentrations in the literature. DMP, DEP, DiBP, DBP, BBzP, DEHP and DiOP are the phthalates that most of the previous studies reported in indoor dust. The median dust-phase concentrations for DMP, DEP, DiBP, BBzP, DEHP and DiOP are normally within the range of 0.5-10 μ g/g, 1.0-50 μ g/g, 10-50 μ g/g, 20-250 μ g/g, 10-50 μ g/g, 200-2000 μ g/g, and 2-10 μ g/g, respectively. The values suggest that the dust-phase concentrations vary within some reasonable ranges, although they change in different buildings (Hwang et al. 2008).

There are studies that try to evaluate impacts of factors such as building materials, cleaning habits, polishing detergent, etc. on the dust-phase concentrations of phthalates. Dust-phase concentrations of DEHP are correlated with the amount of PVC floorings,

wall materials, building age, polishing agents and frequency of dusting (Bornehag et al. 2005, Kolarik et al. 2008, Kim et al. 2013). Those of BBzP are associated with PVC flooring, wall materials, self-reported, frequency of dusting, and polishing agents (Bornehag et al. 2005, Kolarik et al. 2008). Dust phase concentration of DnOP is likely to be higher in homes with low frequencies of dusting and the use of polish (Kolarik et al. 2008). Moreover, Kim et al. (2013) report that DINP shows a critical relationship with the number of children in the institution and the agency operating the nursery school. Specifically for the correlations between dust-phase phthalate concentrations and building materials, Kolarik et al. (2008) do not find differences on dust-phase phthalate concentrations in homes with PVC or linoleum floorings and those with wood floorings. But Abb et al. (2009) report that reduced carpet and plastic materials result in decrease of phthalates in dust in an apartment. Moreover, plastic materials are stronger phthalate sources than carpet but the percentage of plastic materials is harder to identify than carpet. Building age, flooring material, dampness and use of humidifier are also the factors that might affect total dust phase phthalates. These findings will be helpful in developing strategies to control indoor phthalate sources as well as to reduce human exposure.

There are also studies that try to correlate dust-phase phthalate concentrations with the airborne concentrations. However, findings from different studies are inconsistent with each. For example, Fromme et al. (2004) report that no statistically significant correlation can be found between indoor air and dust concentration of phthalates. Bergh et al. (2011) also find the correlation between indoor air and dust concentrations of phthalates is weak. But in another study, Fromme et al. (2013) observe significant correlations between air and dust phases for some phthalates. Theoretical analysis based on thermodynamic properties of the SVOCs and the matrices have shown there are some predictable correlations between gas phase, particle phase and dust phase of phthalates (Weschler and Nazaroff 2008, Weschler and Nazaroff 2010), but more experimental evidence is desirable to confirm the correlations in different matrices in indoor environments.

Most of the above cited studies take settled dust as passive indicator of indoor phthalate pollution. But the settled dust can still re-enter the indoor air by different human activities and re-contaminant the air since it is abundant with various pollutants. For example, Ferro et al. (2004) report that human activities such as folding blankets, folding clothes, dry dusting, making a bed, dancing on a rug, dancing on a wood floor, vacuuming, and walking around and sitting on upholstered furniture could result in substantial increase of particles. Chen and Hildemann (2009) find that higher human activity levels result in elevated concentrations of particles, protein, endotoxin and (1-3)-beta-D-glucan. The coarser fractions of particle mass and bioaerosols are more strongly correlated with human activity levels. In addition, human activities can also resuspend endotoxin, dust mite allergen, and cat and dog dander (Raja et al. 2010). Furthermore, Martuzevicius et al. (2011) report that resuspension of street dust may act as a source of airborne particle-bound PAHs. However, to our best knowledge, there is no study that tries to take indoor settled dust as potential pollutant source and assess the impacts of human activities induced settled dust resuspension on airborne concentrations of SVOCs, such as phthalates. It is also important to assess the potential impacts on human exposure to airborne SVOCs when the settled-dust-phase SVOCs are resuspended.

2.6. Chamber Studies

Environmental test chambers and cells are important tools to study emission of VOCs and SVOCs from their host materials under well-controlled environments. A detailed discussion about characteristics and applications of typical chambers and cells can be found in the review by (Salthammer 2009). For phthalate emission studies, there are three types of such chambers and cells: the Chamber for Laboratory Investigation, Pollution and Air Quality (Climpaq), the Field and Laboratory Emission Cells (FLEC) and the stainless steel thermal desorption test chamber designed by Katsumata et al. (2008).

Table 2–9. Measured steady-state air concentrations and specific emission rates (SERs) from different building materials in test chambers and cells.

Phthalate	Material	V (m ³)	ACH (h ⁻¹)	T (°C)	Air Con. (µg/m ³)	SER (µg m ⁻² h ⁻¹)	Reference
DEHP	PVC flooring	--	--	25	0.1	--	Wensing et al. (2005)
	PVC flooring	--	--	60	5.2	--	Wensing et al. (2005)
	Wallcovering	1	1	23	<0.35	--	Wensing et al. (2005)
	Wallcovering	1	1	40	2.0	--	Wensing et al. (2005)
	Wallcovering	1	1	23	0.94	--	Uhde et al. (2001)
	PVC skirting	0.051	10-12	22	1.2	--	Afshari et al. (2004)
	Polyolefin flooring	0.051	10-12	22	0.2	--	Afshari et al. (2004)
	PVC flooring	0.051	9.8-11	22	1.0	1.4	Clausen et al. (2004)
	Insulator	0.00039	9.5	28	--	3.0	Katsumata et al. (2008)
	Insulator	0.00039	9.5	40	--	16.0	Katsumata et al. (2008)
	PVC flooring	0.00039	9.5	28	--	26	Katsumata et al. (2008)
	PVC flooring	0.00039	9.5	40	--	73	Katsumata et al. (2008)
	Curtain	0.00039	9.5	28	--	4	Katsumata et al. (2008)
	Curtain	0.00039	9.5	40	--	43	Katsumata et al. (2008)
	Imitation Leathers	0.00039	9.5	28	--	5, 9, 42	Katsumata et al. (2008)
	PVC flooring	0.00035	771	23	0.9	--	Clausen et al. (2012)
	PVC flooring	0.00035	771	35	10	--	Clausen et al. (2012)
	PVC flooring	0.00035	771	47	38	--	Clausen et al. (2012)
	PVC flooring	0.00035	771	55	91	--	Clausen et al. (2012)
	PVC flooring	0.00035	771	61	198	--	Clausen et al. (2012)
	PVC flooring	0.00035	771	22	0.8-0.9	--	Xu et al. (2012)
DBP	PVC flooring	1	1	23	3.0	--	Wensing et al. (2005)
	PVC flooring	1	1	23	5.1	--	Uhde et al. (2001)
	Curtain	0.00039	9.5	40		3	Katsumata et al. (2008)
	Imitation Leather	0.00039	9.5	28		13	Katsumata et al. (2008)

Among the phthalates, DEHP and DBP are the ones that are more frequently studied in chamber studies. Table 2-9 lists the measured steady-state air concentrations and specific emission rates (SERs) of selected building materials from chamber/cell studies. The data suggests that temperature is the most important factor that affects the steady-state concentration of DEHP, and an increase of air temperature from 23 to 35°C would result in 10 times higher airborne DEHP concentration and the increase is mainly in the

gas phase (Clausen et al. 2012). DEHP is also strongly dependent on the surface flow rate of the material and its sorption of cell surfaces is lower under high flow rate (Clausen et al. 2010). Other factors, such as chamber characteristics, RH, material types, have marginal effects on the air concentrations (Afshari et al. 2004, Clausen et al. 2007); and PVC flooring area and chamber surface area only affect the time needed to reach steady state (Xu et al. 2012). For DBP, there are few studies on its air concentration and SERs from different building materials.

There are also other findings based on chamber/cell studies. For example, Clausen et al. (2004) find that gas-phase mass transfer limits the DEHP emission rate and external concentration gradient above the PVC surface created by dust layer increased the DEHP emission rate. Schripp et al. (2010) find that mass transfer of DEHP via gas phase to dust is significantly lower but the effect of direct contact is substantial. And the uptake rate is associated with initial chemical concentrations in the materials.

Benning et al. (2013) test impacts of airborne particle on DEHP emission rate in a chamber. The authors find that increasing particle concentration from $100\mu\text{g}/\text{m}^3$ to $245\mu\text{g}/\text{m}^3$ result in 3-8-fold increases in total airborne phthalate concentrations and the DEHP emission rate is significantly enhanced.

The chamber/cells provide well-controlled environments for testing emissions from various building materials. However, current studies majorly focus on the emission of DEHP from PVC floorings. More studies about emission of different phthalates from different building materials as well as related transport and exposure are desirable. It is also important to verify the applicability of the SER values from chamber/cell studies to real built environments.

2.7. Modeling

There are also modeling/simulation works on phthalate emission (mainly DEHP from PVC flooring) as well as its gas/particle partitioning, which are majorly based on mass transfer theory and mass balance model. The basic governing equations for transport of

indoor phthalates and their interaction with PM and surfaces have been given by the mass balance equation given by Xu and Little (2006):

$$\frac{dy(t)}{dt}V = Qy_{in}(t) - A_i \frac{dq(t)}{dt} - V \frac{dq_p(t)}{dt} + A_s \dot{m}(t) - Qy(t) - Qq_p(t) \quad (2-1)$$

$$q_p = K_p y(t) TSP \quad (2-2)$$

$$q = K_s y(t)^n \quad (2-3)$$

Where $y(t)$ is the gas-phase SVOC concentration in the well-mixed indoor air (ng/m^3), t is the time (h), V is the volume of the indoor environment (m^3), Q is the ventilation rate of the indoor environment (m^3/h), $y_{in}(t)$ is the SVOC from outdoor air, A_i is the indoor surface area (m^2), $q(t)$ is the SVOC concentration in the surface (ng/m^2), $q_p(t)$ is the particle-phase SVOC concentration (ng/m^3), A_s is the surface area of the host material (m^2), $\dot{m}(t)$ is the emission rate of the SVOC ($\text{ng}/(\text{m}^2 \text{ h})$), K_p is the particle/air partition coefficient (unitless), TSP is the total suspended particle concentration ($\mu\text{g}/\text{m}^3$), and K_s and n are the Freundlich isotherm parameters (unitless). In the literature, studies majorly focus on understanding of emission of SVOCs from their host materials and the impacts of particle on the SVOC emission and transport.

Xu and Little (2006) find that emissions of SVOCs of low volatility are subject to partitioning into the gas phase, the convective mass-transfer coefficient, and adsorption to interior surfaces, which are “external forces”. Their model predicts that DEHP emission rate increases when the gas-phase concentration is high and partitioning to airborne particle is strong.

Weschler and Nazaroff (2008) study SVOC equilibrium partitioning and persistence between indoor air, particle and surfaces based on the corresponding physical and chemical properties. The authors evaluate the conditions needed to reach equilibrium in indoor environments and the time scale needed for SVOC uptake in indoor sportive compartments accordingly. Then the authors discuss the indoor fate of SVOCs from

their sources and sinks to air based on mass-balance concept. They find that many SVOCs persist in the indoor environments for hundreds of hours to years even though the host sources are removed out given the ventilation is the only removal mechanism.

Xu et al. (2009) develop a two-room model to predict the DEHP emission rate from PVC flooring and the evolving gas-phase and adsorbed surface concentrations. The predicted steady state DEHP concentration is 150 ng/m³ and both rooms need long time to reach steady state. In addition, increased ventilation rate is found to increase the DEHP emission rate and increased total suspended particle concentration results in considerably decrease in gas phase concentration.

Xu et al. (2010) predict human exposure via inhalation, dermal absorption, and oral digestion based on a three-compartment model (main house, kitchen, bathroom) in a residential building. The sensitivity analysis indicates that the DEHP emission rate and associated human exposure are substantially affected by the source characteristics, external mass-transfer coefficient and ventilation rates.

Liu et al. (2010) investigate the influence of particles on the accumulation of DEHP in indoor environments based on a mass-balance model. The results show that particle dynamic affects airborne DEHP concentration significantly and approximately 39% of particle-phase DEHP exists in particles of 0-5 μ m. The authors also evaluate the influences of particle deposition, particle emission from cooking, outdoor particle penetration and particle resuspension on airborne DEHP concentrations. They declare that particle deposition and cooking exhibit significantly impacts on airborne DEHP while the effects of particle penetration and resuspension are unimportant.

Liu et al. (2012) study impacts of particles on DEHP transport in indoor environments and find that DEHP transport is significantly enhanced in presence of particles. The flux can be increased 5 folds over the transport compared with the absence of particles and particles >2 μ m could not influence the flux significantly. It is concluded that particle could result in an increase of human exposure by 4-10 folds.

Hu et al. (2013) investigate the influence of particles on indoor DEHP emissions. They claimed that for particles with diameter of micron or larger, the DEHP could not reach equilibrium under elevated ventilation rate; therefore the influence of particles on DEHP emissions is insignificant. However, within a certain range, elevated ventilation rate would reduce the particle-phase DEHP concentration. And particles with diameters in the order of nanometer largely shorten the time needed to reach gas/particle partitioning equilibrium and finally increase particle-phase concentration.

Liu et al. (2013) review the SVOC emission models, summarize the governing equations as well as the estimation methods of key model parameters. The authors point out that more chamber studies to determine required model parameters and verify model results are needed.

2.8. Short summary

The extensive use of building materials containing large amount of phthalates and the potential health risks related to phthalate exposure have facilitated researches on this group of compounds in the indoor environments. There have been efforts to advance our knowledge on their occurrence in different indoor environments, their transport from the host materials to different matrices, and the human exposure pathways. However, there are still needs to improve the sampling and analysis method for studying short-term variation of indoor phthalate concentrations and for eliminating the frequently happened contaminations during the extraction step. Although there are a lot of studies about occurrence of indoor phthalates in different countries/regions, less is known about the occurrence in Singapore, especially in air-conditioned and mechanically ventilated buildings. Moreover, our knowledge on the phthalate emission rates in real buildings and human exposure is still lacking. Previous studies verify that the settled dust is important reservoir of phthalates, especially for less volatile phthalates such as DEHP. Inversely, the settled dust can act as pollutant source given the presence of forces that can resuspend them such as human activities. The real indoor environment is more dynamic than it is assumed in most epidemiological studies.

Therefore, it is worthwhile to understand how resuspension of settled dust would affect airborne phthalate concentrations in indoor environments.

Chapter 3. Development and validation of sampling and analysis for selected indoor phthalate quantification using thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS).

3.1 Introduction

Sampling and analysis of airborne phthalates (both gas and particle phases) are important for advancing our understanding on human exposures and their indoor transports. Indoor occupants can expose to indoor phthalate via inhalation, dermal exposure and dust ingestion (Weschler and Nazaroff 2012). Among these pathways, inhalation and dermal exposure link closely with gas-and particle-phase phthalates in the indoor air. In addition to the concerns from human exposure, sampling and quantification of airborne phthalate are important issues from the perspectives of understanding indoor transport and fate of phthalates. Previous studies demonstrate that gas phase phthalates can be a medium for the transport of phthalates from the host materials to surfaces (e.g. particles, walls, furniture, and human skin) (Xu et al. 2009, Xu et al. 2010). Therefore, it is of importance to develop and validate methods that can sample and quantify the indoor airborne phthalates rationally.

It is challenging to sample and analyze indoor airborne phthalates. The conventional processes and methods adopted majorly include high volume air sampling, solvent extraction/cleanup, and the GC/MS analysis with liquid injection. Application of the conventional methods is generally restricted by the potential contaminations in the extraction/cleaning up process, poor detection limits, time-and-labor intensity (Urbanowicz et al. 2011). Small volume air sampling followed by thermal desorption (TD) extraction and GC/MS analysis has been applied to indoor airborne phthalate

sampling and analysis in some previous studies (Tienpont et al. 2000, Choi et al. 2010, Lazarov et al. 2013). As discussed in Section 2.4, the TD method owns a number of advantages over the conventional solvent extraction methods such as better detection limits, less potential of environmental contamination, time-and labor-savings as well as better recovery (Urbanowicz et al. 2011). Upon this, short-time sampling (30 min to 4 hours) with small sampling airflow rates (100-500 ml/min) is applicable. It is capable to quantify short-term variations on indoor airborne phthalate concentrations in timescales of hours or less.

Tenax TA is the adsorbent that is commonly used in both indoor and outdoor airborne phthalate studies when the TD method is used (Clausen and Wolkoff 1997, Uhde et al. 2001, Steele and Hardy 2009, Aragón et al. 2013, Xu et al. 2014). It is a type of porous organic polymer, with surface area of 35m²/g, weak strength and a maximum temperature of 350°C (Dettmer and Engewald 2002). Tenax TA is only applicable for adsorption/desorption of SVOCs with boiling points lower than 350°C due to its moderate surface area, limited thermal stability and potential degradation under high temperature (Aragón et al. 2013). There would be considerable carry-overs for some of the phthalates, such as DBP, BBzP and DEHP, which have boiling points around or above 350°C, even under optimized conditions (Aragón et al. 2013). Our experimental results also show that low volatile phthalates such as DEHP can form significant residues in the Tenax TA tubes. Especially after tens of rounds of adsorption/desorption, the carry-over issue would be so influential that can exacerbate the detection limits considerably. It needs long-time (up to hours) to condition the Tenax TA tubes to eliminate the residues. Generally, it is necessary to condition and check each individual tube before each round of adsorption/desorption. This process is time-consuming and makes handling with large numbers of samples (up to hundreds of samples) troublesome. In addition, our experiences suggest that the blank values for the DEHP in Tenax TA vary in wide ranges, even after hours of conditioning. The variations on blank values make it difficult to accurately quantify DEHP blank concentration even though there are rational QA/AC measures.

There are studies testing novel absorbents and approaches to replace the single-bed tube with Tenax TA for airborne phthalate sampling. For example, Tienpont et al. (2000) use 5% polydimethylsiloxane (PDMS) coated on an inert support. The authors test the performance of the adsorbent and report that it has high sensitivity, accuracy, repeatability as well as strongly reduced risk of contamination. Lazarov et al. (2013) adopt two-bed tubes with PDMS particles and Tenax TA for airborne SVOC samplings in Belgian urban environments. Performance tests show that the tube has valid limits of detections, linearity and repeatability for various compounds. However, the preparation of PDMS foams/particles is costly, complicated and challenging, which limit its application in large-scale.

The study in the chapter aims to develop and validate improved two-bed thermal desorption tubes containing salinized glass wool and Tenax TA for airborne phthalate sampling. The homemade two-bed sorbent tube is applicable to sampling of phthalates with a wide range of volatilities, from the most volatile DMP to the much less volatile DEHP. The content includes design of the tube and the related performance tests.

3.2 The experimental section

3.2.1 Chemicals and reagents

The standard mixture (M-8061A-PAK, 1mg/mL of each compound in hexane) includes dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), Benzyl butyl phthalate (BBzP), Bis(2-ethylhexyl) phthalate (DEHP) was purchased from Accustandard (New Haven, U.S.A.). The salinized glass wool (estimated surface area of $0.7\text{m}^2/\text{g}$) was purchased from Sigma-Aldrich (Singapore). The Tenax TA adsorbent (40/60 mesh, surface area of $35\text{m}^2/\text{g}$) was purchased from Markes International (Llantrisant, U.K.). Hexane and methanol at GC grade were both purchased from Fisher Scientific (Singapore City, Singapore). All standards and solvents were used as received and the Nitrogen used for standard spiking with purity of 99.9995% was from Air Liquids Inc. (Singapore).

3.2.2 Sorbent Tubes

Stainless steel (SS) tubes with dimensions of 89mm×6.4mm (O.D.) (Markes International, Llantrisant, U.K.) were used in the study. The SS tubes with a single bed of Tenax TA (200mg) were first tested to check its applicability to airborne phthalate sampling. But after the observation of the residue issues of DEHP in the single-bed Tenax TA tubes, a two-bed sorbent tube was designed with 100mg salinized glass in the first bed and 100mg Tenax TA in the second bed. The glass wool in the first bed is designed to collect less volatile phthalates such as DEHP and BBzP; while the Tenax TA was used to collect more volatile phthalates of DMP, DEP and DBP. A diagram of the configuration of the two-bed sorbent tube is shown in Figure 3-1.

Figure 3–1. Configuration of the GW/Tenax TA sorbent tube.

There are several steps in packing and testing of the GW/Tenax TA tubes. First, the empty SS tubes and packing tools were ultrasonically pre-cleaned in methanol for 3 times, 20mins per time. Second, the first stainless steel gauge was installed and weighted glass wool was packed into the tube. The glass wool was pressed slightly using a TubeMate grip (Markes International, U.K.), the backpressure was measured by a personal air sampling pump (Gilair plus, Sensidyne Inc., Florida, U.S.A.) and the

length of bed was measured by a rule. Third, the weighted Tenax TA was packed into the tube followed with a small piece of glass wool to hold the Tenax TA. Finally, the backpressure of the whole tube was measured after installing the stainless steel gauge as well as the gauge retaining spring. Basic parameters as well as their repeatability of the packed tubes are given in Table 3-1.

Freshly packed tubes were first conditioned at 320°C for 2 hours followed by 335°C for 30mins. After conditioning, blanks of the tubes were quantified by the TD-GC/MS to guarantee their clearness. The conditioned tubes were capped by long-term storage caps fitted with combined PTFE ferrules (6mm I.D.) and stored at room temperature prior to use.

Table 3–1. Physical parameters of the GW/Tenax TA sampling tubes (n=9).

Parameter	Quantity (n=7)	Repeatability (% , n=7)
Weight of GW (mg)	101.7	0.93
Bed Length of GW (mm)	18.3	3.85
Back pressure (mm H ₂ O)	7.5	3.00
Weight of Tenax TA (mg)	101.3	1.32
Total back pressure (mmH ₂ O)	13.2	3.54

3.2.3 Instrumentation and parameters

A TD-100 thermal desorber (Markes International, Llantrisant, U.K.) was used to desorb the analytes retained by the adsorbents. Bates et al. (2008) have described the principle of the two-stage thermal desorption. Briefly, in the primary desorption stage, the SS tube is heated and pressurized in an oven, the retained analytes are purged out of the tubes with helium as carrier gas; in the meanwhile, the analytes are retained by a cold trap (general purposes, Markes international) at a low temperature (normally -10 to 0°C). In the secondary desorption stage, the cold trap is rapidly heated up to a high temperature (normally 280-350 °C) and the analytes are purged out of the cold trap by the carrier gas. The analytes are then introduced into the GC column for separation via a heated and deactivated fused-silica transfer line. In the current study, TD parameters

of the TD system are determined by considering the limits of the TD system, the upmost temperature of the adsorbent and the potential residue of DEHP and BBzP inside the tubes. The parameters adopted are tabulated in Table 3-2.

Table 3–2. The TD parameters adopted in the desorption processes.

Compounds	Primary desorption	Secondary desorption
Phthalates	Time: 30 min	Time: 10 min
	Temperature: 335°C	Cold trap temperature: 370°C
	Tube flow rate: 50ml/min	Split flow rate: 1.5ml/min
	Split flow rate: 50ml/min	Transfer line: 220°C
	Cold trap temperature: 0°C	Transfer line flow rate: 1.5ml/min

For most of the thermal desorption parameters in the primary desorption stage, they are set to be the upmost limits that either the desorber or the sorbents can work sustainably. For desorption time, we found a time longer than 30min does not help to enhance the MS responses. For the desorption temperature, 335°C is chosen in consideration of desorbing the less volatile phthalates to the largest extent and it is the maximum temperature that the Tenax TA can tolerate in long-time period. The flow rate going through the tube and the cold trap is set to 50ml is because that it is the maximum value the cold trap can have. The cold trap temperature of 0°C is found to be able to trap the desorbed compounds efficiently and avoid formation of ice (Aragón et al. 2013). In the secondary desorption, the desorption temperature of the cold trap is set to be 370°C although Lazarov et al. (2013) find that a temperature of 400°C could result in higher intensity of MS responses for compounds with lower boiling points. This is because the maximum temperature of cold trap used in the present study is 375°C (general purpose hydrophobic, C4/5-C26, for TD-100 thermal Desorber). The desorption time is set to be 10 min according to Lazarov et al. (2013).

An Agilent GC 7890A gas chromatography coupled with an Agilent MS 5975C mass spectrometry was employed to quantify the analytes. The temperature program of the GC oven is: 60°C hold for 2 min, then ramps to 240 °C and hold for 10mins at a rate of 20 °C/min, finally the temperature ramps to 280 °C at a rate of 20 °C/min and hold for

5mins. The flow rate of the carrier gas (helium) was 1.5ml/min. The GC column used for separation was DB-5MS (30m×0.25mm×0.25μm) (Agilent Technology Inc., Singapore). The MS worked in a positive chemical ionization model with methane as reagent gas at a flow rate of 1ml/min. The target analytes were detected and quantified by selective ion monitoring (SIM), with the precursor ions and retention times as listed in Table 3-3.

Table 3–3. Target compounds with quantifier ions, qualifier ions (with their percent abundances in brackets) and the time windows used for the SIM detection.

NO.	Compound	Quantifier ion	Qualifiers ions	R. T. (min)
1	DMP	163.0	77.1, 194.0	9.395
2	DEP	149.0	177.1, 150.0	10.264
3	DBP	149.0	150.0, 223.1	12.284
4	BBzP	149.0	91.0, 206.1, 150.0	15.365
5	DEHP	149.0	167.0, 150.0, 279.1	18.056

3.2.4 Performance tests of the GW/Tenax TA tubes

Testing of the performance of the GW/Tenax TA tubes majorly includes: particle retention efficiencies of the GW bed, phthalate absorption efficiencies of the GW bed, blank checking, method recovery rates, carry-over of the tubes and the TD system, repeatability and reproducibility, and detection limits and linearity. Among these, the purpose of the particle filtration and phthalate retention of the GW bed is to evaluate the fraction of both gas-phase and particle-phase phthalates that can be captured by the GW bed. This is because that the major assumption under the study is that the GW bed will absorb/desorb the less volatile phthalates efficiently, while the Tenax TA bed can absorb/desorb the more volatile ones efficiently.

Particle retention efficiencies of the GW bed. The GW bed's particle retention efficiencies were tested by connecting a particle sizer in the downstream of tubes with GW bed only. The TSI optical particle sizers (OPS, Mode 330, 16 channels, TSI Inc.,

Minnesota, U.S.A.) were used to test the retention efficiency of particles of 0.3-10 μm . The TSI Nanoscan nanoparticle sizers (SMPS, Mode 3910, 13 channels, TSI Inc., Minnesota, U.S.A.) were used to measure the retention efficiencies of particles of 10 - 420 nm (0.01-0.42 μm). The particle number concentrations recorded by the particle sizers connected to the tubes were compared to those recorded by reference sizers without the tubes. The flow rate of the OPS is 1000 mL/min and that of the SMPS is 750 mL/min, both of which are higher than the air sampling flow rate of 300 mL min⁻¹. We used outdoor particles as the test particles, which can reasonably guarantee validity of the test results because of its similarity with indoor particles in both concentrations and size-distributions.

Phthalate breakthrough ratios of the GW bed. Two microliter of liquid standard mixture with concentration of 10 ng μl^{-1} for each compound was manually spiked into a primary tube with GW bed only, which was followed by a pre-cleaned secondary tube with 200 mg Tenax TA. The tubes were purged by nitrogen at two flow rates (200ml min⁻¹ and 400ml min⁻¹) and for two durations (2 hour and 4 hours), respectively. The primary tube and the secondary tube were connected by an inert metal connector, which is considered to be free of phthalate emission. Teflon tube was used as nitrogen pipeline to eliminate the contamination. Both tubes were analyzed immediately after spiking under optimized TD conditions. The adsorption efficiency of the GW bed for a specific phthalates was calculated by dividing the MS responses from the secondary tubes with the total MS responses from both the first and secondary tubes. The results were reported as phthalate breakthrough through the glass wool bed under different flow rates and purge times.

Blank checking. There are two rounds of blank checking activities. In the first round, newly packed sorbents were analyzed after conditionings. In the second round, pre-cleaned GW/Tenax TA tubes (n=8) and Tenax TA tubes (n=8) were simultaneously used for phthalate sampling in a environmental lab environment with whole poly vinyl floorings. The tubes were first analyzed twice under optimized TD and GC/MS conditions. Then each tubes was analyzed for a third time to check for the blank. This

method was to mimic real conditions when the tubes were used in practical environmental sampling. Chromatograms from the two types of tubes were screened and compared to evaluate the blanks.

Carry-over of the tubes and the TD system. Carry-over experiments were conducted to check the residues in both sorbent tubes and TD system. We conducted four times of desorption (the 1st desorption, the 2nd desorption, the 3rd desorption, and the 4th desorption) for each of the tube, which was spiked with 20 ng of mixture standard. The 1st desorption and 2nd desorption directly desorb the same loaded tube to desorb the absorbed target analytes. The 3rd desorption is to desorb a clean empty SS tube with purpose of checking the residues inside the TD system. The 4th desorption is to re-desorb the load tube that has been desorbed for two times, to check the remaining residues inside it. We analyzed eight replicates in the carry-over test experiment.

Method recovery rates. Two concentration levels of 2 ng and 20 ng standards were spiked into the sorbent tube. The tube was purged by different volume of air (0.018 m³, 0.036 m³ and 0.054 m³) at a flow rate of 300 mL min⁻¹, so the corresponding purge times are 1 h, 2 h and 3 h, respectively. The tube was then analyzed under the optimized conditions and quantified based on the calibration curves established (Wu and Chang 2012). The MS responses of these tubes were compared with those from tubes that were purging for 5 min at a flow rate of 300 mL min⁻¹ after spiking of liquid standards. The recovery rates are reported as percentages and considered to be valid if they are within the range of 65 – 135%.

Repeatability and Accuracy. Repeatability was evaluated at two concentration levels for the phthalates (2 ng and 20 ng). Eight replicates at each concentration level were analyzed in the same day and the relatively standard deviations (RSD) were calculated. The calibration method was based on external standard at six concentration levels. The accuracy of the method was evaluated at concentration levels of 2 ng and 20 ng by analyzing the results of repeatability experiment with a student's t-test ($p < 0.01$).

Linearity. Calibration curves for individual phthalate were developed based on six concentration levels: 2 ng, 4 ng, 8 ng, 10 ng, 20 ng and 40 ng. One microliter of liquid standard in hexane was spiked into the tubes using a standard Agilent GC syringe (10 μ l) via a calibration solution loading rig (CSLRTM, Markes International, Llantrisant, U.K.). After the standard spiking, the tubes were purged by nitrogen (99.9995 %) at a flow rate of 300 mL min⁻¹ for 5 min. The liquid vaporizes along with the carrier gas inside the rig; the analytes are retained by the adsorbents while the hexane is purged out of the tubes. The loaded tubes are desorbed and analyzed immediately after the spiking process.

Detection Limits. As all the compounds are detectable in the blank sorbent tubes, the MDLs were determined by the sum of the mean concentrations detected in the blank sorbent tubes (n=8) and three times of the standard deviations. The MDLs were converted to a concentration basis by dividing with air volume sampled by the personal sampling pump in the real environmental sampling.

3.2.5 QA/QC

Before packing adsorbents into the SS tubes, the tubes and tools were washed by methanol for three times under ultrasonic (30 mins per time). After washing, the tubes and tools were naturally dried in a clean fume hood. Then they were packed on methanol rinsed aluminum foil to avoid contamination by the phthalates in the air. After package, the Tenax TA tubes were firstly conditioned at 320°C for 2.5hrs, and secondly conditioned at 335°C for 30mins. After conditioning, the tubes were capped by brass long-term storage caps with teflon ferrule in room temperature. Before each sampling, the tubes were conditioned if they had been stored for more than one week. After the conditioning, blanks of at least 3 of the tubes would be checking.

Teflon tube was used to connect the calibration solution-loading rig with the nitrogen cylinder to avoid potential contaminations from plastic tubes. In standard spiking, at least one blank was conducted to check the contamination levels from the rig. In the beginning of each analytical round, an empty SS tube was analyzed twice to eliminate

the potential carry-overs inside the TD pipelines; at the end of the round, the empty tube was analyzed for another time to check the residual of analytes inside the TD system.

3.3 Results and discussion

3.3.1 Particle retention tests

Figure 3–2. Particle retention efficiencies of the glass wool beds with different back pressures.

The particle retention efficiencies of different GW beds, which have different back pressures, are shown in Figure 3-2. For the beds with back pressures higher than 7.3mmH₂O, the retention efficiencies of particles smaller than 160nm were all more than 85%. For the ones with back pressures larger than 4.6mmH₂O, the retention efficiencies for particles larger than 0.3μm were all more than 85%. We have to highlight that for the particle retention efficiency tests, the air flow rate of the SMPS is 0.7L/min and that of OPS was 1L/min, both of which are considerably higher than the sampling flow rate, which is 300ml/min. It is expectable that the relatively lower sampling flow rate in the practical air sampling process will enhance the particle retention efficiencies for all particle sizes. The findings here imply that the GW beds with backpressure higher than 7.3 mmH₂O is able to absorb more than 85% percent of

the phthalates that bond to particles. Therefore, for less volatile phthalates such as DEHP, which favors particle phase, will be retained in the GW bed after sampling by the GW/Tenax TA tube.

Figure 3–3. Breakthrough ratios of the five selected phthalates in GW bed at different flow rates and with different purging times.

3.3.2 Phthalates breakthrough tests

The work further tests the breakthrough ratios of the five selected phthalates in the GW bed at different flow rates and with different purging times, the results are shown in Figure 3-3. For DMP and DEP, which are more volatile phthalates and exist majorly in gas phase in the real indoor environment, >50% of their mass will pass through the GW bed, which means the GW bed cannot absorb these two phthalates efficiently. For DBP, under all conditions, the breakthrough ratios are between 20% and 30%. For DEHP and BBzP, the breakthrough ratios are approximately 15% for the first three conditions, but prolonged purging time at higher flow rate (400ml/min for 4h) appears to result in higher breakthrough ratios for both phthalates. However, readers should bear in mind that the phthalates spiked on the GW bed are more likely in gas phase due to evaporation of the solvent after spiking. The findings suggest that the GW bed adsorb gas-phase BBzP and DEHP efficiently but its applicability for DMP, DEP and DBP is limited.

3.3.3 Blank checking and carry-over

Figure 3–4. Total ion chromatogram (TIC) of a GW/Tenax TA tube and a Tenax TA tube.

The typical MS responses from analysis of a used sorbent tube are illustrated by Figure 3-4. The blank value of DEHP in the Tenax TA tube is approximately eight times higher than that in the GW/Tenax TA tube, and the blanks for other phthalates are either comparable or higher. The elevated blank concentrations in the Tenax TA tubes suggest that the adopted desorption parameters cannot efficiently desorb DEHP from the single-bed Tenax TA tube although the parameters have been in the upper limits of either the adsorbent or the equipment. The elevated blank concentrations would severely exacerbate the detection limits and may also result in considerable bias in the practical application. In contrast, there are significantly decreased blank levels in the GW/Tenax TA tube, especially for DEHP, which are among the most challenging compounds in the indoor phthalate studies. The largely decreased blank levels are expectable because the strength of the glass wool is much weaker, it can absorb the majority of the low volatile phthalates during the sampling process, and can release them much easier during the desorption process. We further checked the blank issue by testing spiked GW/Tenax tubes with different rounds of desorption. From figure 5a and 5b, we can see that for all phthalates, after two rounds of desorption (1st desorption and

2nd desorption), the residue (4th desorption) inside the tube accounts for approximately 10% of the mass spiked into the tube. The results suggest that the analytes can be efficiently desorbed after two rounds of desorption and also indicate that the blank level would not affect the experimental results significantly.

Figure 3–5. Thermal desorption efficiencies of the phthalates for GW/Tenax TA tube spiked with 20ng of standard mixture in the first to fourth thermal desorption cycles. a. mass abundance; b. percentage distributions.

Another issue is about the carry-over effect of the TD system itself. We found that the carry-over of the TD system (includes the cold trap, the transfer line, etc.) cannot be overlooked since the level is so high that it has high probability to bias the MS responses from the following tubes. Figure 3-5b shows the residues inside the TD system (3rd desorption results) can account for 10-17% of the total spiked mass in the tube, even though desorption parameters have been optimized. It is understandable given the lower temperature of the transfer line and the flow rate of the cold trap in the

secondary desorption stage. The upper temperature of the transfer line is 220°C, which is much lower than both the tube temperature in the primary desorption stage and the coldtrap temperature in the secondary desorption stage. The desorbed phthalates can re-absorb by the transfer line when transport from the tube to the cold trap. The lower desorption flow rate in the secondary desorption stage, which is 1.5ml/min to 15ml/min depending on different split ratios, also limits the desorption efficiency of the cold trap.

A simple approach to fix the carry-over issue is to desorb the loaded sorbent tubes for a third time under the optimized conditions. With this approach, the carry-over inside both the TD system and the sorbent tubes can reduce to be approximately 10% of the total mass spiked into the tube (Figure 3-5). Future users should bear in mind this issue because carry-over inside the TD system after desorption of tubes with extremely high mass concentrations of less volatile phthalates can result in severe contamination to the subsequently analysis of other tubes. Lazarov et al. (2013) also propose to measure a blank tube after each real sample to eliminate the influence of the carry-over.

Figure 3–6. Average method recoveries (n=3) of phthalates using GW/Tenax TA tubes at spiking levels of 2ng (a) and 20ng (b) followed by sampling of 0.018, 0.036 and 0.054m³ air; error bars are standard deviations.

3.3.4 Method recovery rates

The phthalate recovery rates of the GW/Tenax TA tubes are shown in Figure 3-6. The recovery rates are studied by spiking different concentrations of liquid standards to pre-cleaned tubes (2ng and 20ng triplicates in each concentration level) with different purging volumes of air (0.018m³, 0.036m³, and 0.054m³ at purging flow rate of 300ml/min). The recovery rates for all the five phthalates are between 90% and 130%, indicating less breakthrough and contamination in these two concentrations levels for all compounds.

3.3.5 Repeatability and accuracy

Table 3–4. Repeatability of the GW/Tenax TA tubes expressed in relative standard deviations (%) at spiked levels of 2ng and 20ng (n=8).

Compounds	2ng			20ng		
	RSD (%)	<i>t</i> -test	<i>p</i>	RSD (%)	<i>t</i> -test	<i>p</i>
DMP	8.7	1.665	0.140	8.7	1.700	0.133
DEP	8.0	1.336	0.223	9.3	2.810	0.026
DBP	14.8	1.137	0.293	17.8	2.125	0.071
BBzP	7.6	1.428	0.196	12.9	1.857	0.106
DEHP	10.6	2.300	0.055	11.5	1.445	0.192

The repeatability of the GW/Tenax TA tubes at spiked levels of 2ng and 20ng (n=8) is shown in Table 3-4. At the concentration level of 2ng, the relative standard deviations (RSD, %) are between 8.0% and 10.6%; while at the concentration level of 20ng, the RSDs are between 8.7% and 17.8%. The RSDs indicating that the GW/Tenax TA tubes have good reliability.

For the accuracy, Table 3-4 shows that at the concentration levels of both 2ng and 20ng, the average value of eight replicates are not different from the reference concentration levels at a confident level of 95% for all compounds. The results suggest

that the GW/Tenax TA tubes can guarantee reasonable accuracy in this concentration range.

3.3.6 Detection limits and linearity

For the GW/Tenax TA tubes, the method detection limits (MDLs) for the five phthalates are between 10.6 and 110.7ng/m³. For the Tenax TA tubes, the MDLs are between 14.3 and 855.37ng/m³. In the GW/Tenax TA tubes, the blank concentrations of both DMP and DEP are lower than the detection limits while those of the left four phthalates are higher than the detection limits. In the Tenax TA tubes, only DMP is undetectable in the blank tubes. It is important to highlight here that the blank tubes analyzed for determining MDLs are used ones other than the newly packed ones. The reason for using the used tubes for MDLs is that the authors found that the carry-over effect inside the used tubes is much higher than the blank values in the newly packed tubes. The accumulated residues inside the used tubes can deteriorate the detection limits considerably and result in severe contaminations. Therefore, it is more reasonable to determine the MDLS based on used tubes.

As shown in table 3-5, use of the GW/Tenax TA tubes can highly improve the MDLs of DEHP, which normally has the highest indoor concentrations and is more challenging in the process of analysis given its low volatility. Before the analysis, the used tubes are conditioned for 1 hour at conditions of 335°C and 100ml/min, which is to mimic the true analysis and conditioning processes of real loaded samples. The results show that the MDL of DEHP obtained by the Tenax TA tubes is approximately eight times higher than that achieved by the GW/Tenax TA tubes. More importantly, the MDL of DEHP obtained by the Tenax TA tubes is more likely to exceed the DEHP concentrations in normally indoor environments; while that achieved by the GW/Tenax TA tubes is safely below the normal indoor DEHP concentrations. The improved MDL of DEHP can effectively avoid contaminations from residues inside the tubes and highlights the advantages of the GW/Tenax TA tubes over the conventional Tenax TA tube.

The linearity was determined in the range of 500pg-20ng. As indicated in Table 3-5, the six point calibration curves of all phthalates show good linearity with correlation coefficients between 0.9948 and 0.9996, which are all higher than criteria of 0.990.

Table 3–5. MDL and linearity of method using GW/Tenax TA tubes.

Compounds	MDL (ng/m ³)		Linearity, R ²
	GW/Tenax TA tube	Tenax TA tube	
DMP	10.6	24.5	0.9996
DEP	17.3	40.0	0.9995
DBP	82.3	47.2	0.9990
BBzP	12.8	14.3	0.9948
DEHP	110.7	855.3	0.9993

3.4 Short Summary

This chapter presents development and validation of an improved sorbent tube that can be compatible with the low volume air sampling and thermal desorption methods. The GW bed in upstream of the conventional Tenax TA bed can efficiently sorb both gas and particle-phases of the less volatile phthalates such as DEHP and BBzP. Performance tests validate the applicability of the improved two-bed sorbent tube for airborne phthalate sampling. In application of the sorbent tube and TD method to indoor airborne phthalate sampling and extraction, the carry-over of the TD system requires special attention, especially when the target compound's concentration in the real environment is high. The sorbent tube is simple and inexpensive. It has the potential to apply to study of other indoor airborne SVOCs, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), Polybrominated diphenyl ethers (PBDEs) and so on.

Chapter 4. Occurrence, emission and human exposure of airborne phthalates in ACMV buildings

4.1. Introduction

Phthalates are among the most frequently detected semi-volatile organic compounds (SVOCs) in indoor environments. It is important to understand occupants' phthalate exposure levels in indoor environments. This is because that: 1. there are well recognized human health risks associated with phthalate exposures; 2. people spend large fractions of times indoors; and 3. the assessment of human exposure to indoor phthalates are challenging since they exist in various phases due to their complicated physicochemical properties. Indoor phthalates migrate from the host materials and redistribute in indoor air and surfaces (including particles, dusts, human skins, as well as building surfaces) (Xu and Zhang 2011). Indoor occupants therefore can expose the phthalates via different pathways such as inhalation, dermal exposure, dust digestion, or even dietary.

Studying of airborne phthalates is of importance in understating emission, transport and control of the compounds in the indoor environments. There are at least three reasons: i. airborne phthalate are closely correlated with human exposure pathways of inhalation and dermal exposure; ii. gas phase is one of the major mediums for phthalate to transport from their host materials to indoor surfaces; iii. devices for controlling airborne phthalate concentrations, such the HVAC system and air purifiers, mainly affect the indoor airborne phthalate concentrations. With these reasons, large-scale survey on airborne phthalate concentration in different types of indoor environments is valuable for human exposure assessment, air quality evaluation and control measure developments.

There are few studies on occurrences of phthalates in commercial and public buildings such as office and institutional buildings, although there have been many studies in residential buildings (Butte 2009, Wang et al. 2010, Bergh et al. 2011, Wang et al. 2014). It would be difficult to comprehensively assess the related human exposure if we lack phthalate occurrence data from commercial and public buildings. It is also worthwhile to understand the impacts of air conditioning and mechanical ventilation (ACMV) system operation on the indoor airborne phthalate concentrations as pointed out by Xu and Zhang (2011) and Parthasarathy et al. (2012). In the process of ACMV operation, it is associated with heat and mass transfer and phase change, which inevitably affects fates of the phthalates carrying by the air that is conditioned by the ACMV system. However, evidence of such impacts from real indoor environments is still lacking, which makes our knowledge on this topic unclear.

In the literature, there is limited data on indoor phthalate emission rate in real indoor environments although it is an indicator of the rate of the phthalate migrating from their host materials into the bulk air. Contemporarily, studies on the phthalate emission rates are mainly based on chamber/cell studies (Katsumata et al. 2008). To our best knowledge, only one study is on the phthalate emission rates in the real indoor environment (Xu et al. 2014). Simple comparisons between the chamber study results and environmental monitoring results suggest that the emission rates different considerably with each other. More efforts are needed to advance our knowledge on this topic with limited volume of literature in real environments.

Furthermore, from the perspective of human exposure to phthalates, it is still unclear if we are measuring the same quantity of phthalates as people are exposing when we conduct indoor phthalate sampling. Most of the studies on indoor occurrence of phthalates are performed to sample or monitor the phthalate concentration levels in the bulk indoor air or dust. But some studies report that the personal exposure may be noticeably higher than the background concentrations (Allen et al. 2007, Adibi et al. 2008). The main reason may be the personal cloud effect. The increased particles surrounding human body may also result in elevated SVOC concentrations as the

SVOCs can partition to the particles, especially for the low-volatility phthalates such as DEHP and BBzP. Therefore, indoor occupants may also have higher phthalate exposure than the background concentrations as the phthalate are also a group of typical indoor SVOCs. To our best knowledge, there is no such investigation on this topic in offices. It is therefore worthwhile to conduct such studies to answer if there is any difference between personal air concentrations and bulk air concentrations of phthalate in the normal indoor environments.

Our knowledge on indoor emission and transport as well as the impacts from related building service equipment is still lacking; and the gap between indoor phthalate concentrations and human exposed phthalate concentrations is still unfilled. More studies on the occurrence of phthalates in non-residential buildings are promising to better understand emission, transport, control as well as human exposure of indoor phthalates. The objectives of the current study are: 1. quantification of indoor airborne phthalate concentrations in ACMV public buildings; 2. quantification of indoor phthalate emission rates during ACMV on in public buildings; 3. understanding of the interactions of ACMV system with indoor airborne phthalates; and 4. understanding of the differences between measured indoor concentrations and personal exposed phthalate concentrations in ACMV indoor environments.

4.2. Experimental section

4.2.1. Characteristics of the monitored indoor environments

The field study of indoor occurrence of airborne phthalates engaged ten staff offices, four tutorial rooms, two lecture theatres and eight library areas. The major characteristics of the engaged indoor environments are tabulated in Table 4-1, which include the surface areas, flooring materials, ACMV modes, sampling times, etc. All of the indoor environments were equipped with ACMV systems and the major ventilation mode is mechanical ventilation during the sampling times. The investigation focus on indoor environments furnished with two different flooring materials: carpet and PVC

floorings. In the eight library areas, due to the large area, measurement of the ACHs are very challenging so there are no ACH values for them in the table.

Table 4–1. Basic information of the indoor environments investigated.

Room #	Function	Flooring Material	Area (m ²)	ACH (h ⁻¹)	Height (m)
1	Staff office	PVC flooring	150	1.3	3
2	Staff office	PVC flooring	150	1.4	3
3	Staff office	PVC flooring	150	1.5	3
4	Staff office	PVC flooring	150	2.4	3
5	Staff office	PVC flooring	150	2.7	3
6	Staff office	Plywood tiles	75	2.2	3
7	Staff office	PVC flooring	150	2.3	3
8	Staff office	PVC flooring	150	1.4	3
9	Staff office	PVC flooring	300	3.8	3
10	Staff office	PVC flooring	150	2.4	3
11	Library	Carpet	n.a	n.a	n.a
12	Library	Carpet	n.a	n.a	n.a
13	Library	Carpet	n.a	n.a	n.a
14	Library	Carpet	n.a	n.a	n.a
15	Library	Carpet	750	n.a	3
16	Library	Carpet	750	n.a	3
17	Library	Carpet	750	n.a	3
18	Library	Carpet	750	n.a	3
19	Tutorial room	Plywood tiles	75	1.2	2.4
20	Tutorial room	Plywood tiles	75	1.3	2.4
21	Tutorial room	PVC flooring	60	0.7	2.4
22	Tutorial room	PVC flooring	60	0.6	2.4
23	Lecture theatre	Carpet	200	2.5	3.5
24	Lecture theatre	Carpet	200	3	3.5

Another typical ACMV office was used to study impacts of the ACMV system on the indoor airborne phthalate concentrations. The office is furnished with PVC flooring, plywood cubicles and cabinets, typical office chairs made of high-density foam and nylon swivel. In addition to these major indoor phthalate sources, there are some minor

indoor sources such personal computers and electrical cables. In that specific room, the ACMV system was on during 7:30am and 6:30pm and it was off in the left time of a day. Indoor environmental conditions and ACH of the room are quite stable given the unchanged ACMV operation mode and yearly uniform outdoor climate in the tropical region. Moreover, there were fewer interventions inside since it is a research student office and the most frequently observed human activity is walking.

4.2.2. Phthalate sampling and environmental monitoring

In the occurrence study, total airborne phthalate concentrations (both gas-phase and particle phase) were sampled by the GW/Tenax TA tubes as designed and validated in Chapter 3. In each sampling site, there were paralleled samples collected by personal sampling pumps (Gilair Plus, Sensidyne Inc., Florida, U.S. A.) at a flow rate of 300ml/min for 3 hours. There were two blanks paralleled with the samples. Both sample and blank tubes were preconditioned at 335°C with a helium flow rate of 100ml/min for 30min by a thermal desorber (TD-100, Markes International Limited, Llantrisant, U.K.). The sampling was conducted 1.2m above the floor in representative sites. In each indoor environment, the sampling was performed between 2 pm-5pm of a workday, when the indoor environment was stable and the indoor airborne phthalate concentrations reached reasonably steady state.

For the study about impacts of the ACMV system on the indoor airborne phthalates, continuous sampling at an interval of 3 hours was conducted in the staff office for 48 hours. In every 3 hours, two paralleled samples along with two blanks were collected during that time period. The sampling pump, flow rate and time were identical with those in the phthalate occurrence study. The sampling site was in the center of the room and away from ceiling diffusers to avoid disturbance of supplied air.

In the personal exposure study, indoor air temperature, relative humidity (RH) and particulate matter (PM) concentrations were monitored simultaneously during the sampling time. The indoor air temperature and RH were recorded by CM-0018 CO2 meters (CO2Meter, Florida, U.S.A.). The size-resolved indoor PM of 0.3-25µm and

ultrafine PM of 11.5-365 nm were monitored by the TSI Optical Particle Sizer 3330 (TSI Inc., Minnesota, U.S.A) and the TSI Nanoscan SMPS Nanoparticle Sizer 3910 (TSI Inc., Minnesota, U.S.A). The monitors were placed as close as possible to the sampling tubes at a height of about 1.2m above the floor during the monitoring period but potential disturbance from the particle sizers was carefully avoided.

In 16 out of the 24 engaged indoor environments as listed in Table 4-1, ACHs were measured by the tracer gas method using either Sulfur Hexafluoride (SF6) or Carbon Dioxide (CO2) as tracer gas. The ACHs were calculated based on the recorded tracer gas concentrations following the tracer gas decay method developed by Sherman (1990). The tracer gas concentrations were recorded by either a SF6 analyzer (InfraRan Specific Vapor Analyzer, Wilks Enterprise Inc., Connecticut, U.S.A.) or a CO2 meter (CM-0018 CO2 meter, CO2Meter, Florida, U.S.A.) at a time interval of 30 s.

4.2.3. Indoor phthalate emission rates calculation

In 16 of the above-mentioned indoor environments (except for the eight library areas), in which ACH values were measured, the indoor phthalate emission rates were calculated based on measured airborne phthalate concentrations, ACHs and assumptions that there was equilibrium at the time when the sampling was conducted and the rooms were well-mixed. Wu et al. (2011) define the concept of whole building emission rates S ($\mu\text{g m}^{-2} \text{h}^{-1}$) as the apparent source strength for the combined mix of individual indoor sources by assuming steady-state, well-mixed box model, incorporating outdoor concentrations, building ventilation rates, and building volumes. The whole building emission rates are calculated by the below steady state mass balance equation:

$$S = \frac{\lambda(C_i - C_o)}{A} \quad (4-1)$$

Where λ is the air exchange rate, C_i is the measured total indoor airborne phthalate concentration, C_o is the outdoor airborne phthalate concentration and A is the surface

area of the studies indoor environment. In the present calculation, given the much lower outdoor phthalate concentration, which is generally one magnitude lower than indoor concentrations, C_o is assumed to be equal to zero. Since the indoor sampling of airborne phthalate was in the afternoon of a day (generally between 2pm-5pm), when the indoor airborne phthalate concentrations reached steady-states after approximately 6 hours of mechanical ventilation, the model is applicable to our present study.

4.2.4. Personal exposure monitoring

Airborne phthalate concentrations in human inhalation zone were sampled in three indoor environments. The first one is a staff office, with typical office cubicles, tables, chairs and floor fully covered by PVC floorings. The second one is a student activity center, with tables, chairs, sofas, and the floor fully carpeted. The third one is the carpeted study zone in a library, with computers on top of plywood tables. The detailed sampling protocols were as below: paralleled samples along with two blanks were taken in the inhalation zone of the human subjects. Concurrently, airborne PM concentrations of 11.5nm-25 μ m in the inhalation zone were also sampled by OPSs and SMPSs. The inlets of the sampling tubes, OPSs and SMPSs were approximately 3cm away from the noses of the subjects. The whole sampling lasted for 3 hours and during this time period; the subjects were requested to conduct normal office activities such as typing and reading. The subject may leave for short rests but the total maximum duration was less than 10 mins. At the same time, environmental background phthalate concentrations were sampled at sites that were approximately 2 m away from the human subjects. The sites were normally in the center of the room and interventions from the diffusers and indoor occupants were avoided. The sampling time and methods for the background and personal sampling were identical with those used in the occurrence study.

It is worthwhile to highlight that during the personal and environmental sampling period, the ACMV system run in its normal mode. The environmental sampling point was 1.2 m above the floor while the height of the personal sampling point was

determined by the height of the sedentary human subjects. Generally, the human subjects sit in cubicles where the microenvironments were less influenced by the diffusers in the ceiling and the neighboring occupants. The human subjects dressed normal clothing ensembles in the hot and humid climate and there was no obvious PM and phthalate sources nearby the tested subjects.

4.3. Results and discussions

4.3.1. Indoor occurrence of airborne phthalates

Figure 4–1. Indoor phthalate concentrations and percentage distributions in the investigated rooms.

Indoor airborne concentrations and percentage distribution of the five selected phthalates are illustrated in figure 4-1. Total airborne phthalate concentrations range from 500ng/m³ to 1600ng/m³ (figure 4-1(a)). DMP, DBP and DEHP are detected in all of the investigated indoor environments, and DEP is detected in 22 out of the 24 investigated indoor environments. BBzP is the one with the lowest detection frequency, which was detected in 13 indoor offices. The concentration levels of DMP, DEP, DBP, BBzP and DEHP are 5 to 48ng/m³, <LOD to 68ng/m³, 160 to 1110ng/m³, <LOD to 123ng/m³, and 265 to 900ng/m³, respectively. Among these compounds, DEHP and DBP are the dominant phthalates, the averaged contribution of DEHP to total airborne phthalates is 59% and that of DBP is 33% (figure 4-1(b)). The findings here are

consistent with those reported in the literature data (summarized in Table 2-6, Chapter 2) that DEHP and DBP are the dominant contributors of airborne phthalates.

Figure 4–2. Comparisons between airborne phthalate concentrations detected in the present study and the reported values in the literature.

The detected phthalate concentrations in the present study are compared with those reported in the literature in Figure 4-2. The reported values presented in the figure are the medians of the reported median values from different studies in the literature. It can be seen that for DMP, DEP, BBzP, the concentrations detected in the present study are all significantly lower than their corresponding median concentrations of the literature data at a 95% confidence level. For DMP, the lower indoor concentrations could be attributed to operation of the mechanical ventilation, which keeps on removing the chemical from the indoor environment, though there may be strong indoor sources (Xu and Zhang 2011, Parthasarathy et al. 2012). For DEP, the low indoor concentrations found in the present study are mainly the results of absence of indoor sources. For DBP, the detected concentrations in the present study are approximately 200ng/m³ lower than the corresponding median value of the literature data. In the investigated ACMV buildings, which had controlled ventilations, the concentrations detected here suggest

that there are constant and strong indoor DBP sources. For BBzP, the concentrations in the current study are not different significantly with the median values in the literature. For DEHP, the concentrations detected in our study are statistically comparable with the medians values reported in the literature. With the wide use of PVC floorings and other unidentified sources, it is rational to observe high DEHP concentrations in the involved indoor environments.

Figure 4–3. Concentrations of the selected phthalates in indoor environments with carpet and PVC floorings.

Comparisons of concentrations of the selected phthalates in indoor environments covered with carpet and PVC floorings are displayed in Figure 4-3. In the environments with PVC floorings, the median DEHP concentration is approximately 250ng/m³ higher than the median in carpeted indoor environments. The difference suggests that PVC flooring is stronger indoor source of DEHP than carpet. However, for each of the remaining phthalates, their median airborne concentrations are comparable in these two types of indoor environments. The comparable concentrations for these phthalates in these two types of indoor environments can be attributable to two different mechanisms: one is the absence of strong indoor sources; the other one is the effects of ACMV systems. But it is difficult to figure out which is the dominant factor based on the data in the current study. More studies are desirable to understand the occasions when either

of these mechanisms dominates. In both types of indoor environments, DEHP and DBP are the top two compounds that contribute to the total indoor airborne phthalates. The findings are different from the observations reported by Xu et al. (2014), that the biggest contributors varied from site to site.

4.3.2. Indoor phthalate source strengths

The whole building emission rates of the five selected phthalates from 16 out of the 24 investigated indoor environments are shown in Figure 4-4. Basic information of the 16 indoor environments are tabulated in Table 4-1 and the emission rates are calculated when the ACMV systems are on. The whole building emission rates are $3.60 \pm 1.88 \mu\text{g m}^{-2} \text{ h}^{-1}$, $0.26 \pm 0.37 \mu\text{g m}^{-2} \text{ h}^{-1}$, $1.39 \pm 0.58 \mu\text{g m}^{-2} \text{ h}^{-1}$, $0.14 \pm 0.09 \mu\text{g m}^{-2} \text{ h}^{-1}$, and $0.16 \pm 0.13 \mu\text{g m}^{-2} \text{ h}^{-1}$ for DEHP, BBzP, DBP, DEP and DMP, respectively. Here the data suggests that for the indoor environments, there are strong indoor sources for DEHP and DBP, which are compatible with the normally detected high indoor concentrations of these two phthalates. The findings here also suggest that controlling indoor sources of DEHP and DBP is the major task to reduce indoor phthalate concentrations.

The whole building emission rates of DMP, DEP and BBzP in the present study are comparable with the values reported by Xu et al. (2014). In retail stores, Xu et al. (2014) detect whole building emission rates of $0.25 \pm 0.42 \mu\text{g m}^{-2} \text{ h}^{-1}$, $0.25 \pm 0.18 \mu\text{g m}^{-2} \text{ h}^{-1}$, and $0.08 \pm 0.06 \mu\text{g m}^{-2} \text{ h}^{-1}$ for DMP, DEP and BBzP, respectively. However, we detect higher whole building emission rates DBP when compare with those reported by Xu et al. (2014). In their study, the whole building emission rate of DBP is $0.38 \pm 0.60 \mu\text{g m}^{-2} \text{ h}^{-1}$. Our median emission rate is also higher than the DBP emission rates (0.16 and $0.43 \mu\text{g h}^{-1} \text{ m}^{-2}$ at 20°C) from one type of PVC samples in chamber study conducted by Fujii et al. (2003). But our emission rates are in the same magnitude with those reported by other studies.

Figure 4–4. Whole building emission rates of the five selected phthalates.

For DEHP, the reported emission rates vary in a wide range and our value fall safely inside that range. Our median emission rate is one magnitude higher than the whole building emission rate in retail stores ($0.21 \pm 0.22 \mu\text{g m}^{-2} \text{h}^{-1}$) reported by Xu et al. (2014), which maybe because of the wide use of the PVC flooring in the investigated indoor environment in our study. The chamber study results reported by Fujii et al. (2003) show that three types of PVC flooring samples have emission rates of $0.79\text{--}5.0 \mu\text{g m}^{-2} \text{h}^{-1}$ at 20°C can partially support this hypothesis, though they found the other type of PVC flooring sample have ~ 10 times higher emission rates. In another chamber study, Katsumata et al. (2008) report an emission rate of $26.0 \mu\text{g m}^{-2} \text{h}^{-1}$ at 28°C . Fujii et al. (2003) explain that the variations on phthalate emission rates are attributable to boundary layer thickness and the temperature. In the study by Xu et al. (2012), the authors report the emission rates of the PVC flooring fall into the range of $0.14\text{--}0.18 \mu\text{g m}^{-2} \text{h}^{-1}$ after steady state is reached in chamber environment. Hu et al. (2013) simulate the DEHP emission rates from PVC flooring in FLEC, finding the emission rates of $1.0\text{--}10.0 \mu\text{g m}^{-2} \text{h}^{-1}$, which depend heavily on the surface flow rates of the PVC flooring. In chamber studies, Clausen et al. (2004) find that the major DEHP emission rates from PVC flooring are between 1.0 and $1.8 \mu\text{g m}^{-2} \text{h}^{-1}$. It is easy to understand the

variations on DEHP emission rates in different studies since the involved indoor environments or chosen PVC floorings are different considerably.

There is limited literature volume that tries to understand the emission rates of phthalates in real indoor environments, which makes assessment and control of indoor phthalates challenging. It is desirable to have more well-designed indoor investigations, with well-controlled temperature, precisely measured ventilation rates, detailed building material inventory, etc., to evaluate the emission rates of the phthalates, especially of DBP and DEHP in different types of real indoor environments.

4.3.3. Impacts of the ACMV system on airborne phthalate concentrations

Figure 4–5. Time-resolved DEHP and DBP concentrations in a typical ACMV office.

Time-resolved DEHP and DBP concentrations in a typical ACMV office in a typical workday are displayed in Figure 4-5. In the office, the ACMV system is turned on at 6:30am and off at 6:30pm. Indoor total airborne concentrations of DBP drop continuously during the time period when the ACMV system is on. But for DEHP, the airborne concentration keeps dropping in the first seven hours but begins increasing at around 13:30 pm in the afternoon. When the ACMV system is off, concentrations of both phthalates increase continuously and hit the highest levels just before the ACMV system is turned on. However, concentrations of these two compounds have different

profiles even though they share similar trend when the ACMV system is on and off. For DBP, the operation of the ACMV system results in quick decrease in the airborne concentration and the concentrations keep declining until about 15:00 pm. For DEHP, operation of the ACMV system results in decrease of the concentration in the first 7 hours; however, the concentration arrives at a quasi-steady state approximately after 13:00 pm.

Looking at the time-resolved concentration of both compounds when the ACMV system is off, with reasonably low ACH (0.2h^{-1}), the indoor sources strength of DEHP is stronger than those for DBP. The total airborne DEHP concentration reaches the highest level at 6am but the level is not likely the maximum since operation of the ACMV system reduces the concentration quickly. For DBP, the total airborne concentration hit the maximum level at about 4 am, which is about 10 hours after the ACMV system is off. The results here demonstrate that the operation of the ACMV system can significantly influence indoor concentrations of SVOCs with both high and low volatilities. The findings here support the hypothesis presented by Xu and Zhang (2011) claiming that the ventilation system can play important roles in controlling indoor SVOC concentrations.

The indoor source strengths and ACMV system removal efficiencies of these two phthalates in the room are computable based on the mass balance model of equation 4-1. The assumptions include: 1. the ACH is steady when the ACMV system is on; 2: the indoor source strengths of the compounds are steady during both the ACMV system is on and off; 3: the indoor airborne concentrations reach steady-states between 15:00-18:00pm; 4: the indoor concentrations of the compounds reach equilibrium state between different matrices, such as air, airborne particles, indoor settled dusts, indoor surfaces as well as surfaces of the ACMV system components; 5: the concentration and physicochemical characteristics of indoor particles are steady. In the ACMV offices, the indoor particle concentrations are generally low ($\sim 10\mu\text{g}/\text{m}^3$) and with fewer variations. Therefore, it is rational to assume that the removal efficiency of DEHP via particle filtration is relatively weak. In the special indoor environment, the computed

source strengths of DBP and DEHP are $0.54\mu\text{g m}^{-2} \text{ h}^{-1}$ and $2.10\mu\text{g m}^{-2} \text{ h}^{-1}$, respectively. More investigations are desirable to more deeply understand the role of the ACMV system playing in controlling indoor SVOC concentrations, especially its impacts on airborne particles bound low volatile SVOCs.

4.3.4. Personal sampling versus environmental sampling of phthalates

This work further compares personally sampled airborne phthalate concentrations and environmentally sampled airborne phthalate concentrations in an office (Site 1), a student activity center (Site 2) and the study zone in a library (Site 3), respectively (Figure 4-6a, 6b and 6c). In the figures, we exclude BBzP data since in all the indoor environments, the BBzP concentrations are close to the detection limit, which makes comparisons between results from these two sampling approaches hard. In addition, in Site 3, the comparisons do not include DEP, since the DEP concentrations in the room are also very close to the detection limit of the method. Therefore, the comparisons are mainly with respect to DEHP, DBP and DMP, which have concentrations much higher than their detection limits.

In Site 1, the mean concentration of the DEHP by personal sampling is 190ng/m^3 higher than that by environmental sampling (1379ng/m^3 vs. 1189ng/m^3) but the difference is statistically insignificant. For DBP, DMP and DEP, the differences between values detected by these two approaches are statistically insignificant (162ng/m^3 vs. 167ng/m^3 , 22ng/m^3 vs. 19ng/m^3 , and 65ng/m^3 vs. 65ng/m^3 , respectively). In both sites 2 and 3, the personally sampled concentrations and environmentally sampled concentration are comparable with each other for all phthalates.

Figure 4–6. Personal exposure concentrations versus environmental airborne concentrations in three indoor environments. a. in an office; b. in a student activity center; c. in a library.

The findings here are inconsistent with findings from studies comparing personal air and environmental air concentrations of phthalates and PBDEs. In the study by Adibi et al. (2008), the geometric mean concentration of the phthalates are higher in the personal air than in indoor air. Allen et al. (2007) report that total personal air concentrations are 469 pg/m³ for non-209 BDEs and 174 pg/m³ for BDE 209. The concentrations are both significantly higher than bedroom and main living room concentrations ($p \leq 0.01$). The authors further explained that the differences are majorly due to the personal cloud effect. In the current study, the explanation for the insignificant differences between personally sampled and environmental sampled phthalate concentrations may be that the effect of particle resuspension by human activities is not strong enough to influence the personal air concentrations of phthalates. During the sampling time period, the subjects sit sedentarily and were much less active than the occupants in residential buildings. Their light activity levels as well as the dilution/filtration effects from the ACMV system may not be able to create significantly higher particle concentrations around the sedentary subjects and consequently cannot increase the airborne phthalate concentrations in the subjects' breathe zones.

To our knowledge, there are only two studies that try to assess the differences from personally sampled SVOC concentrations and the environmentally sampled SVOC concentrations in indoor environments (Allen et al. 2007, Adibi et al. 2008). There is need to have more studies in this topic to further confirm if there is any differences between these two type of concentrations. Otherwise, it will be difficult to assess human exposure to indoor SVOC accurately given the truth that most of the current studies only focus on environmental sampling.

4.4. Short summary

This chapter presents environmental monitoring results conducted in real ACMV indoor environments. The contents include four parts: the occurrences of total airborne phthalates, the whole building emission rates of different phthalates, the impacts of

ACMV system on indoor concentration levels of phthalates with different volatilities, and the comparisons between personally sampled and environmentally sampled phthalate concentrations.

In the involved indoor environments, DEHP and DBP are the top two phthalates that contribute to the total airborne phthalate concentrations. For DEHP and BBzP, the median concentrations are comparable with the corresponding median concentrations reported in the literature; while for the remaining three phthalates, the median concentrations in the present study are significantly lower than their corresponding concentrations reported in the literature. In the offices covered by PVC floorings, there are higher levels of DEHP than those with carpet. But for other compounds, the differences on airborne concentrations are statistically insignificant. The results imply that PVC flooring is the major indoor source of DEHP but it is necessary to further identify indoor sources of other phthalates, especially of DBP.

DEHP and DBP have much stronger indoor source strengths than other phthalates in the current study. The source strengths of these two phthalates are also higher than the values detected by other studies, which is majorly due to the wide use of PVC floorings. For other phthalates, the indoor sources strengths are comparable with the values in the literature. Therefore, controlling of indoor sources of DEHP and DBP is the major measure to reduce human exposure to phthalates in indoor environments. It is also desirable to build up source inventories of phthalates in typical indoor environments.

When the ACMV is on, indoor airborne concentrations of both DBP and DEHP decreased and reach quasi-steady states after several hours but the times are different. When the ACMV is off, those of both compounds increase continuously. The indoor source strength and air exchange rate are the main factor governing the removal efficiency of the ACMV system for both compounds. The findings also demonstrate that operation of the ACMV system can apparently affect the indoor airborne phthalate concentrations.

Comparisons between personally sampled concentrations and environmentally sampled concentrations of phthalates show that there is no detectable difference in terms of these two types of concentrations. The explanations may be the sedentary subjects' activities are not strong enough to resuspend settled dust, which can carry higher phthalate concentrations around the subjects. However, more studies are still desirable to confirm the findings here.

The findings in this chapter suggest that indoor phthalate study shall focus on DEHP and DBP in the local context. It is important to have more studies focusing on indoor source strengths of DEHP and DBP in true indoor environments. More information on impacts of the ACMV system on emission, transport and human exposure of indoor phthalates are desirable. We also need more experimental data on human exposure to indoor phthalates via different pathways.

Chapter 5. Correlation between particle resuspension and generation and indoor airborne phthalate concentrations

5.1. Introduction

Human exposure to phthalate raises many public concerns given its association with a variety of human health risks (Hauser and Calafat 2005). Indoor environment is one of the most important occasions in which people may expose to phthalates via dietary, inhalation, and dermal exposure or even dust digestion (Xu and Little 2006, Weschler and Nazaroff 2012). Moreover, people stay approximately 85% of their time in their houses and workplaces daily (Gall et al. 2015) and indoor phthalate concentration levels are generally more than one magnitude higher than those in the outdoor environments (Rudel and Perovich 2009, Salapasidou et al. 2011, Aragón et al. 2012). It is therefore important to understand the indoor phthalate concentrations as well as the variations induced by human activities.

Phthalates can concurrently exist in gas, airborne particle, settled dust and surfaces in indoor environments. There were many studies aiming at understanding occurrences of indoor phthalates in different phases as summarized in table 2-6 and 2-7 in chapter 2. Most of the studies were conducted based on an assumption that the sampled concentrations can reflect the real phthalate concentrations to which the indoor occupants expose in normal days (Butte 2009, Kim et al. 2013). But the assumption may be biased as the real indoor environment is more dynamic due to a variety of internal and external factors such as human activities. Human activities such as walking, dancing, cooking, may resuspend or generate large quantities of particles, which can accordingly change airborne concentrations of phthalates as well as their distributions in different phases. Human activity induced dynamics of indoor airborne phthalates is

an important research topic as they affect human exposure via dermal exposure and inhalation.

Increased indoor suspended particle concentrations has been found to lead to significantly elevated airborne phthalate concentrations, specifically for less volatile compounds such as DEHP (Xu and Little 2006, Weschler and Nazaroff 2008, Liu et al. 2010, Liu et al. 2012, Benning et al. 2013, Hu et al. 2013). But these studies were mainly based on either theoretical predictions upon a number of assumptions or chamber studies with well-controlled environments. Findings from both study methods would be subjected to a variety of limitations due to their departure from the real indoor environment. Studies carried out in real indoor environments therefore are needed.

Experiments reported in this chapter were carried out in a test building with rooms covered by either PVC flooring or carpets. Indoor conditions were well controlled and the effects of other environmental conditions were well eliminated. The experiments comprise of two parts: in the first part, settled dusts were intentionally resuspended; in the second part, elevated particle concentrations were generated by burning mosquito coils. At the same times, airborne particle concentrations were monitored and airborne phthalate concentrations were sampled. The purposes of the studies are: 1. To understand how the settled dust resuspension would affect the airborne concentration of phthalates with different volatilities; 2. To understand how the particle generation would affect the airborne concentration of phthalates with different volatilities; 3. To understand the impacts of variations on airborne particles on the gas/particle partitioning of the airborne phthalates in the real indoor environments.

5.2. Experimental section

5.2.1 The test rooms

The testing rooms were located in an office at the Nanyang Technological University (NTU) in Singapore. It is a staff office and is more than 5 years old. Before conducting

the experiments, the office had been unoccupied for more than 18 months. During that time period, the office was never cleaned but the air conditioning and mechanical ventilation (ACMV) system was operated in a normal mode (on: 7:30am-6:30pm; off: 6:30pm-7:30am of the next day). The whole area of the office is 300m² and the height is 3 m, so the volume of the office is approximately 900 m³. The whole office is divided into different staff rooms and staff rooms as shown in Figure 5-1.

Figure 5–1. Simple diagram of the rooms and the whole rooms where the experiments were conducted. Room A was carpeted, Room B and C were covered by the same type of polyvinyl chloride flooring. There were intentional particle resuspension activities and mosquito coil burning activities in Room A and B; while there was no either activities in Room C (the control). The height of the office is 3 m.

Experiments were conducted in Room A, B and C as shown in Figure 5-1. Room A, B and C are three small staff offices inside an big staff office, which is served by an individual air-conditioning and mechanical ventilation system. Room A is a small meeting room with an area of 20 m², and the floor is covered by carpet. Both Room B and C are staff offices with areas of 19 m², and with floors covered by PVC flooring.

Room A is furnished with four wall cabinets made of plywood, one round table (6m²) made of the same materials and 12 office chairs mainly made of ultrahigh density foam and polyester upholstery. Room B and Room C are both furnished by plywood tables and five office chairs. During the experiments, settled dust resuspension and generation were deliberately performed in Room A and B, while there was no intervention in Room C, which was taken as a reference environment. The doors and windows of the three rooms were all closed their normal statuses. The experiments were conducted when the ACMV system was off. When the experiments were carried out in workdays, the time was generally between 20:00–23:00; when the experiments were in weekends, the time was between 10:00–13:00 or 13:00–16:00. During these time periods, the measured air exchange rates in each room were about 0.2–0.3 h⁻¹.

5.2.2 Phthalate sampling and particle monitoring

Figure 5–2. A simple diagram showing connection of the filter holder, the GW/Tenax TA tube and the personal sampling pump for the indoor phthalate sampling.

Both total airborne phthalates and total airborne particles were sampled by the methods developed in Chapter 3. Briefly, the total airborne phthalates were sampled by the GW/Tenax TA tubes and the gas-phase phthalates were sampled by the identical tubes

but with PTPE filters (25mm) on top of the tubes as shown in Figure 5-2, which worked to remove the particle-phase phthalates from the airstream. The particle-phase phthalate concentrations were then calculated by deducting the gas-phase concentrations from the total airborne phthalate concentrations (Benning et al. 2013). Duplicate samples along with duplicated blanks were collected in each room in each experiment. The sampling time was 3 hours and the airflow rate was 300ml/min. The loaded tubes were capped by copper storage caps and were desorbed by a Thermal Desorber (TD) and quantified by a gas chromatography/mass spectrometry (GC/MS) within 24 hours. More details with respect to the sampling and analysis methods could be found in Chapter 3.

The airborne particle concentrations in the size range of 0.3-25 μm were monitored by handheld airborne particle counters (OPC mode: Handheld 3016 IAQ, Lighthouse Worldwide Solutions, California, U.S.A.). In each room, two OPCs run in parallel in the same height as the sampling tubes and the potential disturbance were avoided. The air temperature and relative humidity (RH) in each room were also recorded by the OPCs. The OPCs were collocated before the experiments to generate adjustment factor for particles in each channel based on the mean readings of all the OPCs for each channel. Based on the monitored particle count number concentrations (counts/m^3), airborne particle surface area concentrations ($\mu\text{m}^2/\text{cm}^3$) were calculated by assuming the particles are in spherical shapes. Airborne particle mass concentrations ($\mu\text{g}/\text{m}^3$) were computed by assuming a particle density of $2000 \text{ kg}/\text{m}^3$ for all the size channels (Weschler and Nazaroff 2010).

ACH in each room was measured by the tracer gas method using sulfur hexafluoride (SF_6) as tracer gas. The tracer gas concentrations were recorded by a SF_6 analyzer (InfraRan Specific Vapor Analyzer, Wilks Enterprise Inc., Connecticut, U.S.A.) at a time interval of 30 s. The ACHs were calculated based on the recorded tracer gas concentrations following the tracer gas decay method developed by Sherman (1990).

5.2.3 The experimental procedure

Before each round of the experiments, the door of each room was opened to make the room air to mix with the bulk air in the whole office. The mixing time was generally more than 21 hours in the weekdays and 4 hours in the weekends, respectively. With the prolonged the mixing time, the initial particle and phthalate concentrations in the three rooms were assumed to be identical. For the settled dust resuspension experiments, after setup of the sampling devices and OPCs, settled dust was re-suspended by a new broom with cloth head. The broom was a commercially available product purchased from a local supermarket. In the experiments, we used the new broom to mimic dry cleaning of the floors (without water) but intentionally adjusted the cleaning vigor to create different indoor particle concentrations. The intentional particle resuspension activity was performed once per hour (about 3 min per event) to sustain high particle concentrations in the intervened rooms. In the intervened rooms, there were no other external disturbances or interventions except for the intentional settled dust resuspension. For the particle generation experiments, mosquito coils were burnt inside the room during the whole experiment. The mosquito coils were placed about 2 m away the sampling tubes and OPCs and an electric fan was on in each room to mix the generated particles. Researcher did not enter each room after the mosquito coils were lighted and the sampling and monitoring were started, to minimize the influence from other human activities.

5.3. Results and discussion

5.3.1 Indoor environmental conditions

The average temperature and RH in the three rooms when there were intentional particle resuspension activities or mosquito coil burnings in Room A and B are depicted in Figure 5-3. In the particle resuspension experiments, the indoor air temperatures and RH were 26.0 ± 1.5 °C and 79.3 ± 4.2 % in Room A, 25.7 ± 1.0 °C and 82.1 ± 4.1 % in Room B, and 25.8 ± 1.0 °C and 78.7 ± 5.2 % in Room C. In the

mosquito coil burning experiments, the indoor air temperatures and RH were 26.6 ± 1.0 °C and 78.2 ± 3.9 % in Room A, 26.5 ± 0.7 °C and 80.1 ± 3.6 % in Room B, and 25.9 ± 0.7 °C and 79.0 ± 4.8 % in Room C. One-way ANOVA test results suggest that there were no significant differences between either temperatures or RH values in the three rooms with all p values > 0.01 . Therefore, the impacts of either temperature or RH on the sampled airborne phthalate concentrations can be considered to be similar in all the rooms.

Figure 5–3. Summary of indoor temperature and relative humidity values in the three rooms during the experiments. The p values denote one-way ANOVA test results. The error bars refer to standard deviations. a. Indoor temperatures when there were intentional particleresuspension activities in Room A ($n=13$) and Room B ($n=11$); b. Indoor RH when there were intentional particle resuspension activities in Room A ($n=13$) and Room B ($n=11$); c. Indoor temperatures when there were intentional particle generation activities in Room A ($n=3$) and Room B ($n=3$); d. Indoor RH when there were intentional particle generation activities in Room A ($n=3$) and Room B ($n=3$).

The average particle mass and surface area concentrations in the three rooms when there were intentional particle resuspension activities in Room A and Room B are illustrated in Figure 5-4. The one-way ANOVA test results suggest that the particle resuspension activities significantly enhance the mass and surface area concentrations of particles with diameters $>1.0 \mu\text{m}$ (p values < 0.01). Figure 5-5 shows the average particle mass and surface area concentrations in the three rooms when mosquito coil burning (intentional particle generation) took place in Room A and Room B. The results suggest that the particle generation activities significantly enhanced the concentrations of particles with diameters $< 1.0 \mu\text{m}$, and their influence on particles with diameters of $> 2.5 \mu\text{m}$ is insignificant ($p > 0.01$). Similar prior studies on particles released by mosquito coil burning reported that most of the particles were in the size range of $0.01\text{--}0.3 \mu\text{m}$ (Liu et al. 2003) within the ultrafine and accumulation modes, which were not measured in the current study due to the limitations of the instrument.

Figure 5-4. Size-resolved airborne particle mass and surface area concentrations in the three rooms when there were intentional particle resuspension activities in Room A ($n=13$) and Room B ($n=11$). There was no intervention in Room C ($n=13$). The p values denote one-way ANOVA test results; the error bars refer to standard deviations. a. Airborne particle mass concentrations; b. Airborne particle surface area concentrations.

Figure 5–5. Size–resolved airborne particle mass and surface area concentrations in the three rooms when there were mosquito coil burnings in Room A (n=3) and Room B (n=3). There was no intervention in Room C (n=3). The p values denote one–way ANOVA test results; the error bars refer to standard deviations. a. Airborne particle mass concentrations; b. Airborne particle surface area concentrations.

5.3.2 Particle resuspension and total airborne phthalate concentrations

Total airborne concentrations of the selected five phthalates in the three rooms in the settled dust resuspension experiments are illustrated in Figure 5-6. For DMP, which is the most volatile phthalate among the selected compounds and mainly exists in gas phase, the influence of settled dust resuspension on its total airborne concentrations was weak by comparing the concentrations in Room A and B with those in Room C. Moreover, the differences on DMP concentrations among the three rooms also suggest that indoor DMP source strength were different from each other.

For DEP and DBP, there are no differences between total airborne concentration in the rooms as settled dust resuspension happened in both Room A and Room B when comparing with Room C. There are two reasons for these findings. The first one is that the two phthalates mainly exist in gas phase; their capacities of partitioning on airborne particle are limited even though the airborne particle concentrations are elevated. The

second on is that for the two phthalates, they are not likely to exist in settled dust; therefore, the total airborne concentrations would not increase considerably given the lower mass associated with resuspended settled dust. The equations 1-5 and table 1c in the review paper by Weschler and Nazaroff (2010) could well support the explanations here.

Figure 5–6. Airborne phthalate (gas-phase+particle-phase) concentrations and particle surface area concentrations in the three rooms when there were intentional particle resuspension activities in Room A (n=13) and Room B (n=11). There was no such intervention in Room C (n=13). The p values denote one-way ANOVA test results. The error bars refer to standard deviations across all the indicated number of replicates. a. airborne phthalate concentrations; b. airborne particle surface area concentrations.

For BBzP, much higher concentrations were detected in Room B than in Room C; while the concentrations in Room A were comparable with Room C. The elevated BBzP concentrations in Room B were because of the resuspension of the BBzP that bound to the settled dust. Along with the resuspension of the settled dusts, the BBzP bound to the dusts were also resuspended. The BBzP migrated into the air and therefore

resulted in the much higher airborne concentrations. The elevated BBzP concentrations in Room B are not likely the results of strong gas/particle partitioning happened during the experiments. The dust resuspension activities majorly resuspended particles of 2.5-25 μ m and a much longer time a much long time is needed for the phthalates to reach gas/particle partitioning equilibrium. For particles in this size range, a rough calculation indicated that long time scales from 6-576h are needed for the BBzP to reach gas/particle partitioning equilibrium (Weschler and Nazaroff 2008). During an experiment time of 3 h, the BBzP was not able to reach gas/particle partitioning even without considering the effects of particle deposition and removal by ventilation.

The comparable BBzP concentrations in Rooms A and C implies that there was no BBzP source and the BBzP concentrations in the settled dust phase was low or minor in the carpeted Room A. Without BBzP emission, the gas-phase BBzP would not be supplemented after it was adsorbed by the elevated airborne particles and consequently the total airborne BBzP concentrations would not increase significantly. The low or minor BBzP concentrations in settled dust phase are easy to understand since the transport of particles larger than 2.5 μ m inside the office was limited. Indoor particles larger than 2.5 μ m are generally removed by the ACMV filtration system and the inter-room transport of these particles is minor. In addition, inter-room transport of settled dust is less likely to happen as absence of occupants. In view of this, the settled dusts and particles larger than 2.5 μ m containing BBzP in the areas covering PVC floorings have fewer chances to migrate to the carpeted flooring (Room A). Therefore, it is rational to observe marginal increase of airborne BBzP concentration in Room A, though there were settled dust resuspension.

For DEHP, in both Room A and Room B, there were much higher total airborne concentrations when the settled dusts were resuspended, which were averagely five times higher than those in Room C. Similar with the elevated airborne BBzP concentrations in Room B, the findings in terms of airborne DEHP concentrations imply that the increased airborne DEHP are attributable to the DEHP bound to the resuspended settled dust, which also indicates that there were indoor sources of DEHP

in both Room A and B. Theoretically, with a low volatility, the airborne DEHP would majorly exist in particle-phase (>95%) and be abundant in settled dust. A calculation based on the model given by Weschler and Nazaroff (2008) found that the time scales needed for resuspended airborne particles of 2.5-25 μ m range from 200–18225h. Therefore, the elevated airborne DEHP concentrations are not likely the results for gas/particle partitioning when the airborne particle concentrations were elevated.

The above findings indicate that for phthalates with lower volatility such as DEHP and DBP, elevated airborne particles triggered by settled dust resuspension can significantly increase the total airborne concentrations. The elevated airborne phthalate concentrations when settled dusts were resuspended were because of the resuspension of less volatile phthalates that were bound to the settled dust. The mechanism is quite different from that reported by previous studies that the elevated airborne phthalate concentrations were because of the prompted gas/particle partitioning and increased net flow from the host materials. However, when it comes to more volatile phthalates such as DMP, DEP and DBP, which have less fractions of mass in airborne particles and settled dust, settled dust resuspension would affect the total airborne concentrations marginally.

5.3.3 Correlation between airborne particle and phthalate concentrations

Correlations between indoor particle concentrations and total airborne concentrations of DEHP in Room A and Room B when the settled dusts were resuspended are shown in Figure 5-7. It is clear that the total airborne DEHP concentrations have significant linear correlations with indoor particle concentrations ($R^2 > 0.85$, $p < 0.001$). The findings here are consistent with theoretical analysis that indoor airborne phthalate majorly exists in particle phase. For example, in a typical indoor environment with particle concentration of 20 μ g/m³ and organic fraction of 0.4, approximately 97% of the airborne DEHP exists in particle phase (Weschler and Nazaroff 2008). The fraction of airborne DEHP in particle phase is expectable to increase when the particle

concentration is enhanced based on the equation shown by Weschler and Nazaroff (2008).

Figure 5–7. Linear correlations between airborne (gas-phase+particle-phase) particle concentrations and airborne DEHP concentrations in Room A and Room B. There were intentional particle resuspension activities in both rooms. Each data point of phthalate concentration denotes one of the trials. Each particle mass concentration is the average value over the three-hour experimental period in each trial.

A quick calculation suggests that when the airborne particle concentration increases to $300\mu\text{g}/\text{m}^3$ and with a long enough timescale, more than 99.7% of the airborne DEHP will partition to the airborne particles. However, readers should be careful that the theory presented by Weschler and Nazaroff (2008) rested on two assumptions that: 1. The airborne particles initially contain no the specific SVOC and 2. The timescale is large enough for the SVOCs to reach gas/particle partitioning equilibrium. But in the real environment, neither condition would happen given the ubiquitous of DEHP and particle dynamics ruled by different mechanisms. By Weschler and Nazaroff (2008)’s theory, timescales ranging from tens to thousands of hours are needed for the DEHP to

reach gas/particle equilibrium for particles ranged from 1.0–25 μm . The timescales are much higher than the timescales for particle deposition under low ACH, which range from 0.35 to 1.32 h for particles of 1.0–25 μm (Thatcher and Layton 1995). Considering an ACH value of 0.2–0.4 h^{-1} , the residence time of the resuspended particles in the indoor environments would be less than 1h, which means that they cannot get enough time to reach gas/particle partition equilibrium.

The short residence and the good correlations imply that the enhanced airborne DEHP concentrations are because of the resuspension of DEHP that is bound to the settled dust in the rooms. In other words, the DEHP bound to the settled dust was resuspended concurrently when the settled dusts were resuspended due to human activities. The resuspended DEHP migrates into the air along with the resuspended particles and but still exist in the particle phase. However, the total airborne DEHP concentrations increased significantly.

Quick calculations suggest that the DEHP concentrations in the resuspended particles were 2640 $\mu\text{g/g}$ and 2720 $\mu\text{g/g}$ in Room A and Room B, respectively. The calculated DEHP concentrations in resuspended particles are consistent with the median level of the reported values but are in line with the reported maximum DEHP concentrations in settled dusts summarized in Table 2-7 in Chapter 2. The consistency between the calculated concentrations and reported values partially substantiates the hypothesis that the airborne DEHP mainly comes from the resuspended settled dust when they are resuspended. The calculated values are reasonably valid since the indoor environment involved has not been occupied for more than one and a half years. During that time of period, there were no cleaning or human intervention, the DEHP in settled dust accumulated by both gas-dust mass transfer and direct contact with the host materials. This would be quite different from the scenarios in homes or occupied offices where the literature data came from, in which the floorings were supposedly to be cleaned much more frequently.

Figure 5–8. Linear correlations between airborne particle concentration and airborne BBzP concentration in Room A (n=13) and Room B (n=11). There were intentional particle resuspension activities in the room. Each data point of phthalate concentration denotes one of replicates. Each particle mass concentration is the average value over the three-hour experimental period in each replicate. We consider the data point marked by green circle as an outlier.

The statistically significant correlation between indoor particle concentrations and airborne BBzP concentrations in both Room A and B when the settled dusts were resuspended is shown in Figure 5-8. A quick calculation suggests that the particle-phase BBzP concentrations are $26\mu\text{g/g}$ and $460\mu\text{g/g}$ in Room A and B, respectively. The findings are consistent with dust-phase BBzP concentrations reported in the literature (summarized in Table 2-7, Chapter 2). Along with the good linear correlation between the particle concentrations and total airborne BBzP concentrations, the findings imply that the particle-phase BBzP dominates the airborne BBzP concentrations when settled dust resuspension happens. This is very different from the theoretical result indicating that half of the total airborne phthalates would exist in gas-phase. It is also reasonable to hypothesize that the BBzP in settled dust may be mainly

from abrasion of the host materials given the low airborne BBzP concentrations in Rooms A and C. However, more efforts are needed to advance our knowledge on this topic.

Figure 5-9. Analysis of correlations between total suspended particles and airborne DBP concentrations in Room A (n=13) and Room B (n=11). There were intentional particle resuspension activities in both rooms. Each data point of phthalate concentration denotes one of the trials. Each particle mass concentration is the average value over the three-hour experimental period in each trial. There are no significant linear correlations between TSP and airborne DBP concentrations in either room.

Linear regression analysis results about correlations between airborne particle concentrations and total airborne DBP concentrations in Room A and B are illustrated in Figure 5-9, respectively. The results suggest that there is no correlation between the two. This regression results are consistent with the findings shown in Figure 5-6 and highlight that the DBP mainly exist in gas phase other than in particle and settled dust phase as predicted by theoretical analysis.

The linear regression analysis of correlations between particle concentrations and total airborne phthalate concentrations suggest that for phthalates with low volatility, they mainly exist in particle and settled dust phases. When the settled dusts are resuspended by human activities, the phthalates bound to the settled dusts would be resuspended simultaneously and result in elevated airborne concentrations. However, the process is different from the mass transfer and thermodynamic processes proposed by previous studies (Xu and Little 2006, Liu et al. 2010, Liu et al. 2012, Hu et al. 2013, Liu et al. 2013). For phthalates with higher volatility such as DBP, the influences of airborne particle on their total airborne concentrations would be insignificant since they mainly exist in gas phase.

5.3.4 Impacts of particle generation on airborne phthalates

The phthalates concentrations in the three rooms when mosquito coils were burnt in Room A and B are displayed in Figure 5-10. The indoor particle surface area concentrations increased from $\sim 100 \mu\text{m}^2/\text{cm}^3$ to about $1000 \mu\text{m}^2/\text{cm}^3$ when the mosquito coils were burnt, and the particles were mainly smaller than $1.0 \mu\text{m}$. Moreover, the initially released fine particles were supposed to be free of phthalates. For DMP, DEP and DBP, the increase of fine particles did not result in obvious increased total airborne phthalate concentrations in both of the rooms with intervention. The findings indicate that the three phthalates mainly exist in gas-phase and the enhanced particle concentrations have limited impacts on the total airborne concentrations. The findings here are consistent with those in Section 5.3.1.

When it comes to BBzP, the increased submicron particles resulted in similar trend as shown in Figure 5-6 that the airborne concentrations increased significantly in Room B (approximately 20 folds) while the concentration in Room A were negligibly affected. But the mechanisms for the increase of airborne BBzP concentrations are different significantly for the two particle enhancement modes. As discussed in section 5.3.1, the increased airborne BBzP concentrations during settled dust resuspension are mainly attributed to the resuspension of BBzP bound to the settled dust. When the submicron

particles are generated by mosquito coils burning, the airborne BBzP can reach gas/particle partitioning equilibrium upon the much shorter timescales needed for submicron particles (0.13–1.03 h for particles of 0.3–1.0 μm and much shorter time for particles with smaller diameters). The submicron particles absorb the gas phase BBzP quickly and result in much lower gas-phase concentrations. With lower gas-phase concentrations, the external force that controls the BBzP emission from its host materials is strengthened. Therefore, the BBzP emission rates are enhanced and therefore result in much higher total airborne BBzP concentrations as observed. Moreover, comparison between the airborne BBzP concentrations in Room A and Room B with mosquito coil burnings also further confirms the lacking of BBzP sources in the former room, which indicates that the carpet used in the room does not emit BBzP.

Figure 5–10. Airborne phthalate (gas-phase+particle-phase) concentrations and particle surface area concentrations in the three rooms when there were mosquito coil burnings in Room A (n=3) and Room B (n=3). There was no such intervention in Room C (n=3). The p values denote one-way ANOVA test results. The error bars refer to standard deviations across all the indicated number of replicates. a. airborne phthalate concentrations; b. particle surface area concentrations.

For DEHP, the enhanced concentrations of submicron particles also resulted in two to three times increases in total airborne DEHP concentrations in both Room A and B. The mechanism that governs the enhancement of airborne DEHP is actually the same with that for BBzP, which has been discussed in the above paragraph. However, there are two points that need further highlighting. The first one is that the increases of airborne DEHP concentrations in the two rooms are weaker than those for BBzP. This is because that DEHP needs much longer time for gas/particle partition equilibrium even for submicron particles. For example, the timescales needed are 4-33 hours for particles of 0.3–1.0 μm , which suggests that DEHP is less likely to reach gas/particle partition equilibrium during the time-period of 3 hours of the experiments. The second point is that the airborne DEHP concentrations in Room A were about $100\text{ng}/\text{m}^3$ higher than that in Room B. The observation may suggest that the DEHP source strength is stronger in Room A than in Room B given the identical ACH and mosquito burning.

5.3.5 Gas-phase fractions of the phthalates

Figure 5–11. Gas-phase fractions of the airborne individual phthalates and particle surface area concentrations in the three rooms when there were intentional particle resuspension activities in Room A ($n=13$) and Room B ($n=11$). There was no such intervention in Room C ($n=13$). The p values denote one-way ANOVA test results. The

error bars refer to standard deviations across all the indicated number of replicates.

The gas-phase fractions of total airborne concentrations of the five selected phthalates in all the three rooms when there were particle resuspension in Room A and B are shown in Figure 5-11. When there were increased particle concentrations, the gas phase fractions of DMP, DEP and DBP, which are more volatile phthalates and supposed to majorly exist in gas phase, were comparable with the three rooms.

The findings are consistent with the previous findings illustrated in Figure 5-6, and further confirm that the particle concentrations have limited influence on their gas phase concentrations. However, when it comes to DEHP and BBzP, which are less volatile phthalates and should have large fractions existing in particle phase, increased particle concentrations result in pronounced decreases in gas phase concentrations in both Room A and B. There are two explanations for the decrease in gas fractions of DEHP and BBzP. The first one is that particle-phase phthalates increase as the settled dust bound compounds entered the air by resuspension. The increased particle phase phthalates results in lower gas fractions of these two phthalates. The other reason is that the gas-phase phthalates are absorbed by the resuspended particles in the air, which results in lower gas phase of the phthalates. Actually, the gas fractions of the two phthalates were less than 2.5% when the particle concentrations were elevated.

5.4. Short summary

In this chapter, experimental evidence shows that both elevated particle concentrations from settled dust resuspension and mosquito coil burnings result in increased airborne concentrations for less volatile phthalates such as DEHP and BBzP. But the mechanisms that result in the airborne phthalate concentration increases are different. For settled dust resuspension induced particle concentration elevations, the increase of airborne DEHP and BBzP concentration are attributed to the resuspension of settled dust bound compounds. For mosquito coil burning induced particle concentration

elevations, the increase of airborne DEHP and BBzP concentration are attributed to transport of the two compounds from their gas phase to the particle phase and the enhanced emission rates. For more volatile phthalates such as DMP, DEP and DMP, the influences of elevated particle concentrations induced by either measure are limited, which are consistent with the theoretical predictions.

There are statistically significant linear relationships between airborne DEHP and BBzP concentrations and particle concentration when the settled dusts are resuspended. The consistency between calculated particle-phase DEHP and BBzP concentrations and the corresponding measured dust-phase concentrations further suggests that human activities induced particle resuspension can lead to considerable elevation on the airborne concentrations of phthalates with low volatilities. The elevated airborne phthalate concentrations can further result in increasing human exposure to the SVOCs by inhalation and dermal exposure. More studies on the magnitude of increase on human exposure therefore are desirable.

The evidence also shows that the raised indoor airborne particle concentrations can reduce the gas-phase fractions of low volatile SVOCs, but increase the total airborne concentrations. The reduced gas-phase concentrations can facilitate the SVOCs' emissions from their host materials and the increased total airborne concentrations can exacerbate human exposure to these SVOCs. More field studies in real indoor environments are needed to advance our knowledge on these two topics.

Chapter 6. Conclusions and recommendations

6.1. Conclusions

This study develops an improved two-bed sorbent tube for indoor airborne phthalate study and tests its compatibility with the TD-GC/MS method. The study further investigates indoor occurrence, emission rates, and influential factors of phthalates in typical ACMV buildings. It also evaluates the differences between personally sampled and environmental sampled phthalate concentrations. Lastly, it examines the impacts of human activity induced particle resuspension and generation on airborne phthalate concentrations in a typical indoor environment.

The homemade two-bed sorbent tube with GW and Tenax TA as adsorbents is applicable to sampling indoor airborne phthalates with a wide range of volatilities. The GW bed can absorb both gas-phase and particle-phase of the low volatile phthalates efficiently; while the Tenax TA bed can capture the high volatile phthalates without obvious breakthrough. The tube is compatible with the two-stage thermal desorption method well. It can overcome the residue issue associated with the conventional single-bed Tenax TA tube. It also considerably improves the detection limit of DEHP, which has the lowest volatility among the target compounds and render the biggest challenge in the process of quantification.

DEHP and DBP are the two phthalates that have the highest indoor concentrations as well as detection frequencies in the investigated indoor environments in the current study. The application of PVC floorings can result in obviously elevated indoor airborne DEHP concentration when compared with carpeted rooms. But the differences in flooring materials have marginal impacts on indoor airborne concentrations of other

phthalates. In the investigated indoor environments, DEHP and DBP have the highest whole room emission rates but the calculated emission rates are difficult to be consistent with the specific emission rates from chamber/cell based studies.

The operation of ACMV system does work to dilute and filtrate indoor airborne concentrations of phthalates with both high and low volatilities, which suggests that the ACMV system can be an important measure to reduce human exposure to indoor phthalates. The ACMV system can also play important roles in indoor phthalate removal. The study does not find significant differences between the personally sampled and environmental sampled airborne phthalate concentrations. The explanation may be that the ACMV system dilutes and filters the particles surrounding the subjects, and consequently decreases the phthalate concentrations around the human bodies. In addition, the sedentary subjects have light activity levels, which may not be able to resuspend the settled dust significantly.

Both human activity induced particle resuspension and generation can result considerable increases in indoor airborne concentrations of phthalates with low volatilities such as DEHP and BBzP. When settled particles are resuspended, the low volatile phthalates that bound to the particles are also resuspended simultaneously, which consequently cause increase in the corresponding airborne concentrations. When submicron particles are generated by mosquito burning in the indoor environments, the gas-phase phthalates with low volatilities can partition to the generated particles quickly and result in elevated airborne phthalate concentrations. The study also shows that when the airborne particle concentrations increase, the gas fractions of the low volatile SVOCs would decrease significantly, which suggests that the raised airborne particle surfaces can adsorb more phthalates and consequently promote the partitioning of phthalates from their gas phase to the particle phase.

In indoor environments, occupants can expose to airborne phthalates via inhalation, dermal exposure or dust ingestion. Indoor phthalate exposure may account for a significant fraction of human total exposure, especially when indoor phthalate

concentrations are high. Therefore it is important to understand human phthalate exposure as well as the methods to control indoor phthalate concentrations in all phases. Till now, to my best knowledge, there are no any standards about sampling, occurrence and control of phthalates in indoor environments. The sampling and analytical method developed in the dissertation may provide some preliminary bases for standards of sampling and quantification of indoor airborne phthalates based on TD-GC/MS. The findings about occurrence, transport and human exposure of phthalate in ACMV buildings may provide some data bases for further standards that aim to assess and control human phthalate exposure in indoor environments. The findings about impacts of indoor particle dynamics on airborne phthalates highlight the importance of considering human activity patterns when assess their phthalate exposures; this is an aspect that shall be considered in a further standard about human phthalate exposure and the relevant ways to reduce human exposure.

6.2. Recommendations

In the sampling process, the method developed in the current study cannot separate phthalates in the gas and particle phases effectively. The study uses a telfon filter in upstream of the sorbent tube to filter out the particle-phase but biases may come from positive sampling artifacts due to adsorption of gas-phase phthalates in the filter. More depressingly, it is very challenging to quantify the positive sampling artifacts on the filter. Therefore, researchers shall try to develop new approaches to quantify the positive sampling artifacts on the filters, or develop novel methods to separate phthalates in the two phases more accurately.

In the extraction process, the most challenging issue is the carry-over effects of low volatile phthalates in the TD system. It calls for new materials that can be applicable to the TD system to eliminate the carry-over effect, which can consequently simplify the extraction process and improve the MDLs.

There have been few studies on indoor phthalates in Singapore. It is worthwhile to conduct large-scale field studies in residences, commercial buildings, schools, child care centers, to develop a database on occurrence of phthalates in the indoor environments. The database shall include information on indoor phthalate concentrations in gas phase, particle phase, settled dust as well as indoor surfaces. In addition, the database shall investigate the roles played by different influential factors such as the building materials, the ACMV systems, cleaning habits and so on. Based on the database, we can assess human exposure to phthalates indoors via different pathways. Moreover, we can also develop approaches and measures to control indoor phthalate concentrations and reduce human exposure indoors.

Human activity induced particle resuspension and generation increase total airborne phthalate concentration indoors. But less is known about how particle resuspension and generation would affect the human exposure to airborne phthalates. It is important to understand the exposure levels increased when the airborne phthalate concentrations are elevated due to these mechanisms. We also need more environmental information on the gas/particle partitioning activities as well as the related emissions when there are elevated particle concentrations indoors.

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