Phthalates in indoor air and dust from Hanoi, Vietnam: distriution and human exposure

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Astract

Phthalates are a group of chemicals used as plasticizer additives in hundreds of products. Therefore, they were found in many different environmental and human matrices such as water, soil, sludge, air, dust, lood, and urine. This paper presents the determination method, occurrence and distriution of phthalates in indoor dust and indoor air samples collected in Hanoi, Vietnam. The optimal method has met the requirement to accurately identify phthalates in environmental samples. The highest concentrations of phthalates were measured in indoor dust samples and air collected at hair salons. The correlation of phthalates concentrations etween indoor air and dust collected at hair salons were also higher than that in other micro-environments. Among the studied phthalates, di (2-ethylhexyl) phthalate (DEHP) was found at the highest concentrations in oth of dust and air samples. The exposure doses to phthalates through inhalation were ten times higher than other pathways such as dust ingestion. In general, the risk of human exposure doses to phthalates decreases with increasing ages.

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1 Introduction

Phthalates or phthalate esters are esters of phthalic acid known as plasticizers. They are added to plastics to increase their flexiility, transparency, duraility, and longevity. Recent studies show that phthalates are added to plastic and cosmetic products up to few percent in weight[1-4]. The widespread use of phthalates facilitates to their appearance and distriution in most of environments such as water, air, dust, sewage, and food[5-10]. Phthalates were also found in iological samples such as lood and urine in the form of their metaolites[11,12]. Further, several earlier researches have shown the changes in child ehaviors relate to the high concentration of phthalate metaolites in their lood and urine[13-15]. Additionally, laoratory studies have shown that phthalates are endocrine disrupting compounds[16,17]. Di (2-ethylhexyl) phthalate (DEHP) is a compound that dramatically changes the genital hormones of rats, specially, DEHP delays puerty, suppresses testosterone production, and inhiits reproductive tract development in male Sprague-Dawley and Long-Evans rats[18].

In Vietnam, several studies were performed y our group shown the wide occurrence and distriution of endocrine disruptor including phthalates in environment and food samples[19,20]. However, the understandings aout the environmental occurrence and consequent health effects of phthalates in human are still limited. Hence, this current study provides new insights on exposure to phthalates in indoor environments in Hanoi, Vietnam.

2 Material and methods

2.1 Chemicals

Acetone and *n*-hexane were purchased from Merck KGaA (Darmstadt, Germany), dichloromethane (analytical reagent grade) was purchased from Fisher Scientific (Leicestershire, UK). Ten standard compounds including Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dipropyl phthalate (DPP), Di*iso*utyl phthalate (DiP), Diutyl phthalate (DP), Dihexyl

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phthalate (DnHP), Dicyclohexyl phthalate (DCHP), Di-(2-ethylhexyl) phthalate (DEHP) and Di-*n*-octyl phthalate (DnOP) with their purities ≥ 98% were purchased from Sigma-Aldrich (St. Louis, MO, USA) and enzyl utyl phthalate (zP) with purity 99.9% was purchased from Supelco (ellefonte, PA, USA). Seven d_4 (deuterated) surrogate standards which are d_4-DMP, d_4-DEP, d_4-DPP, d_4-DiP, d_4-DnHP, d_4-zP, and d_4-DEHP with purity of > 99% corresponding with aove standard compounds were purchased from Dr. Ehrenstorfer GmH (Wesel, Germany). Standards and surrogate standards were dissolved in *n*-hexane.

2.2 Sample collection

Seventy five indoor air samples were collected y using two polyurethane foam plugs (ORO-1000 PUF 2.2cm I.D. and 7.6cm length, Supelco, ellefonte, PA, U.S.A.) and quartz filter (Whatman, 2.2µm pore diameter and 32mm I.D.) comined with a low speed pump (LP-7; A.P. uck Inc., Orlando, FL, U.S.A.). Samples were collected during 12 to 24h with a flow rate of 4L/min (sample volume: 2.88-5.76m^3). Samples were divided into categories such as homes, cars, kindergartens, laoratories, offices, and hair salons.

Thirty two indoor dust samples were collected y a vacuum cleaner or y sweeping the floor with a rush directly. Dust samples were divided into homes, pulish places, laoratories, and offices. Dust samples were sieved through a 150µm sieve and homogenized. Samples were stored in glass jars at 4^{o}C in dark until analysis.

2.3 Sample preparation

The sample preparation was similar to that descried earlier[10,20] with minor modifications. Prior to analysis, samples (oth PUFs and filters) were spiked with 500 ng each of d_4-laeled surrogate standards. Two PUF plugs were extracted y shaking in an orital shaker (Stuart, Japan) with dichloromethane (DCM) and *n*-hexane (3:2, v:v) for 30 min. The extraction was performed twice, with 100 mL solvent mixture for the first extraction and 80 mL for the second. The extracts were concentrated in a rotary evaporator (IKA RV 05, Staufen, Germany) at 40^{o}C to approximately 5mL. And then the solution was transferred into a 12-mL glass tue and concentrated y a gentle stream of nitrogen to exactly 1mL and transferred into a GC vial. The particulate fraction was extracted y shaking the quartz fier filter with a 5 mL mixture of DCM and *n*-hexane (3:2, v:v) each time for 5 min, which was repeated three times. Finally, the extract was concentrated under a gentle stream of nitrogen to exactly 1 mL and transferred into a GC vial.

Fifty nanograms of d_4-phthalates (except for d_4-DEHP, for which 250 ng was spiked) were spiked onto 300–350 milligrams of dust samples, as internal standards. The spiked dust samples were equilirated for 30 min at room temperature. Dust samples were extracted three times y shaking in an orital shaker (Eerach Corp., Ann Aror, MI, USA) with a 4 mL mixture of dichloromethane (DCM) and *n*-hexane (3:2, v:v) for 10 min each time. After shaking, samples were centrifuged at 2000*g* for 5min (Eppendorf Centrifuge 5804, Hamurg, Germany), and the supernatant was transferred into a 15mL glass tue. The extracts were concentrated to 1mL under a gentle stream of nitrogen, filtered through a regenerated cellulose memrane filter (Phenex^{TM}, pore size: 0.2µm), and then transferred into a GC vial for the analysis.

2.4 Instrumental analysis

An Agilent Technologies 7890 gas chromatograph (GC) interfaced with a 5977A mass spectrometer (MS) was used for the analysis of phthalates. Chromatographic separation of phthalates was achieved y a D-5MS capillary column. Further details of the analysis are provided in the Supporting Information and elsewhere [2,3,7,10,20].

Tale 1 Ion fragments, method quantification limits (MQL) of phthalates

Compounds	Ion fragments (*m/z*)		MQL		
	Quantification	Confirmation	Gas phase (ng/m^3)	Particulate phase (µg/g)	Dust (ng/g)
DMP	163	177	0.2	3.0	8.0
DEP	149	-	0.1	1.5	4.0
DPP	149	-	0.1	1.5	4.0
DiP	149	233	0.1	1.5	4.0
DP	149	233	0.1	1.5	4.0
zP	149	223; 206	0.15	2.0	6.0
DnHP	149	279	0.2	3.0	8.0
DCHP	149	167	0.3	4.5	1.1. 12.0
DEHP	149	167; 279	0.1	1.5	6.0
DnOP	279	-	0.3	4.5	1.2. 12.0
d4-DMP	167	-	-	-	-

d_4-DEP, d_4-DPP, d_4-DiP, d_4-DnHP, d_4-zP, d_4-DEHP	153	-	-	-	-

2.5 Quality assurance and quality control

Phthalates contamination in laoratory materials including solvents used in extraction, have een studied in our laoratory [2,3,10,20]. A challenge in the analysis of low levels of phthalates is ackground contamination in laoratory materials. Procedural lanks were analyzed with every atch of samples. Trace levels of phthalates were found in procedural lanks, therefore all reported concentrations in indoor air samples were sutracted from the mean value found in procedural lanks.

Five hundred nanograms each of native and surrogate standards (d_4-phthalates) was spiked into a lank PUF, quartz fier filter, dust and passed through the entire analytical procedure. The method detection limit (MDL) and the method quantification limit (MQL) were determined from an average volume of air collected (4.46 m^3), average weight of airorne particles collected (0.35mg) for air samples and average weight of dust (300 mg) for dust samples. The MQL values are shown in Tale 1. Recoveries of surrogate standards in lank procedures ranged from 82.5 to 115% (RSD: 1.0-3.5 %) for gas phase, particulate phase, and dust.

3 Result and discussion

3.1 Phthalates in indoor air

In this study, phthalates in indoor air were collected and measured in two phases: gas phase and particulate phase. The sum concentrations of ten phthalates in gas phase ranged from 62.4 to 14,800 ng/m^3 (mean: 964 and median: 487). Meanwhile, the sum concentrations of phthalates in particulate phase ranged from 95.2 to 13,500 µg/g (mean: 4,190 and median: 3,640). The highest concentrations of phthalates were found in oth of gas and particulate phases of indoor air from hair salons. The total concentration of phthalates in indoor air (particulate plus gas phase) ranged from 112 to 16,000ng/m^3 (mean: 1,250 and median: 795). The distriution of phthalates in indoor air collected from various micro-environments is shown in Figure 1. The highest total concentration of phthalates was found in indoor air collected from hair salons. These results suggest that phthalates are commonly used in health care products and up to several percent in weight[2,3].

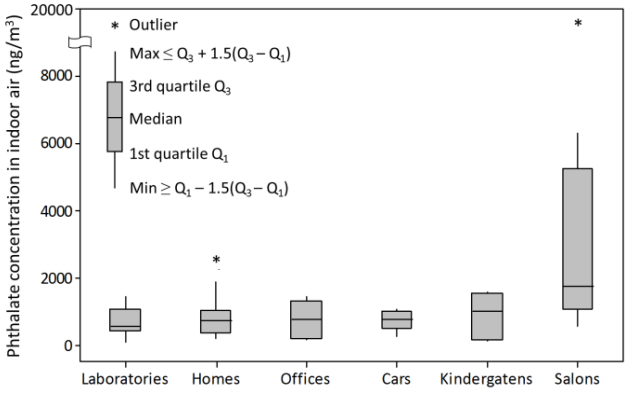

Fig 1 Concentrations of phthalates in indoor air collected from Hanoi, Vietnam

In general, the concentrations of phthalates found in indoor air collected from Hanoi, Vietnam are not much different from previous studies in other places (Figure 2). The results in this study are lower than that in the studies in India and Japan and similar to that of indoor air from China, European coutries and the United States [6,8,9,10].

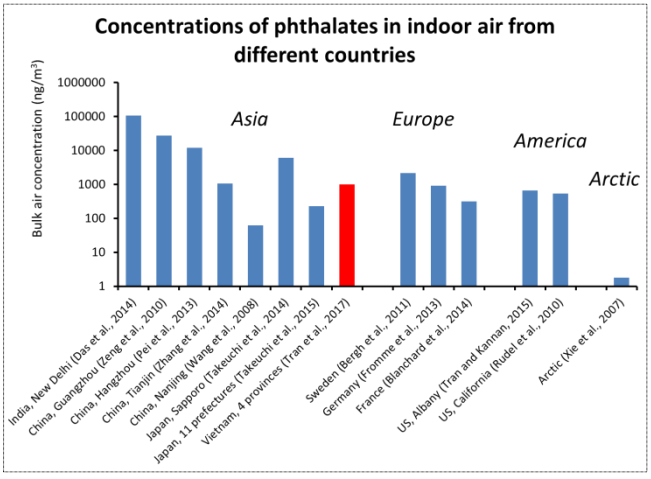

Fig 2 Comparison of phthalate concentrations in indoor air

3.2 Phthalate in indoor dust

All 10 phthalates were detected in dust samples with relatively high levels. The mean and the median concentrations of total phthalate content are 35,000 and 32,000ng/g (Figure 3). Total mean concentration of phthalates found in dust collected from homes was the highest level (46,000ng/g), followed y offices (43,000ng/g), laoratories (28,000ng/g), and pulic places (23,000ng/g). Phthalate content in dust samples from this study is much lower than that of some other countries such as Italy, the United States and China with average values of 128,000; 396,000; and 295,000ng/g, respectively [11]. However, the existence of a high content of dust phthalates indicates the risk

of dispersing these sustances into the environment through the use, sale, disposal of phthalate-containing materials and products.

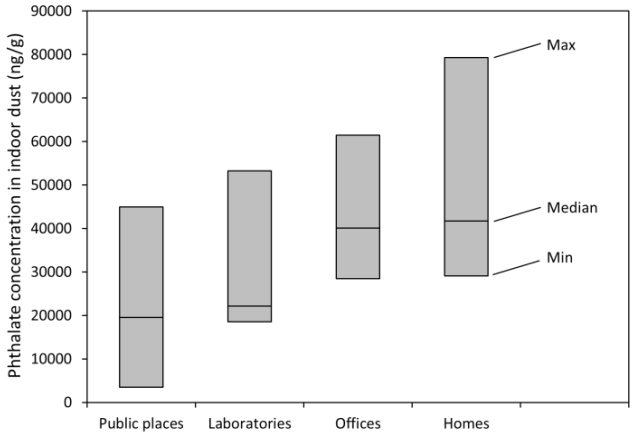

Fig 3 Concentrations of phthalates in indoor dust collected from Hanoi, Vietnam

Among the studied phthalates, DEHP accounted for the highest level, up to 60%, followed y DP (15%). The distriution of phthalates in the total content does not provide a specific rule for each type of activity. However, it helped to identify the main contaminant, DEHP, which is consistent with many studies. The DEHP content in dust samples collected in German nurseries has an average value of 888,000ng/g, accounting for 70%[14]. DEHP was also measured at the highest concentration in indoor dust samples collected from other countries such as Canada, France, China and the United States[9,11,21]. The high percentage of DEHP can e explained y the advantages of suitale physicochemical properties and low cost, leading to its superior production compared to other phthalates, with an estimated 3 million tons of DEHP has een produced every year worldwide[22].

3.3 Human exposure doses to phthalates through inhalation and dust ingestion

In this study, the human exposure doses to phthalates through inhalation and dust ingestion were estimated y Eq. 1 and Eq. 2:

$ED_{air} = (C_{air} \times f_{inhalation})/M(1)$

$ED_{dust} = (C_{dust} \times f_{ingestion})/M(2)$

Where, ED_{air} and ED_{dust} are respectively exposure doses through inhalation and dust ingestion (ng/kg-w/h). C_{air} (ng/m^3) and C_{dust} (ng/g) are concentrations of phthalates in indoor air and indoor dust. $f_{inhalation}$ is the average inhalation rate (0.188m^3/h for infants, 0.292m^3/h for toddlers, 0.417m^3/h for children, 0.563m^3/h teenagers and adults [1]. $f_{ingestion}$ is dust ingestion rate (0.00125 g/h for infants and 0.0025 g/h for other age groups [U.S.EPA, 2008]. M is the average ody weights (w) for Vietnamese: infants (6–12 months): 8 kg, toddlers (1–5yrs): 15 kg, children (6–11yrs): 25 kg, teenagers (12–18yrs): 48 kg, and adults (≥19yrs): 66kg [23].

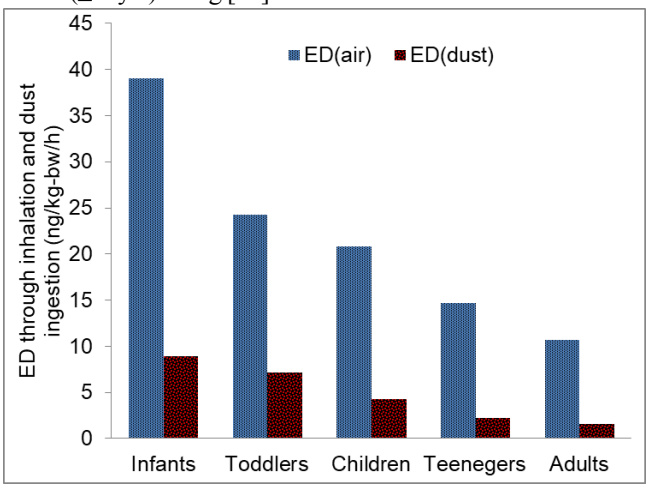

Fig 4 Human exposure doses to phthalates through inhalation and dust ingestion

The results in Figure 4 show that the levels of exposure doses in oth pathways inhalation and dust ingestion gradually decrease from children to adults. Although the high concentrations of phthalates were measured in indoor dust, however the exposure dose to phthalates through air inhalation is aout ten times higher than that of ingesting dust. These results explain that the exposure doses also denpend on the rates of inhalation and dust ingestion. It is worth noting that the risk of exposure to polutted chemicals through inhalation is more difficult to avoid than other exposure pathways. Meanwhile, chemical exposure through food consuming, water drinking and dust ingesting can e limited y our changing living haits. In general, the effective prevention of the human exposure to endocrine disruptors is the usage them in a controlled manner.

4 Conclusions

This study has provided new insights into the occurrence of endocrine disruptive compounds in indoor environments in Hanoi, Vietnam. The study shows the widespread distriution of phthalates in indoor air and dust in different micro-environments with corresponding concentration ranged from 112 to 16,000 ng/m^3 and from 3,440 to 79,300 ng/g, respectively. The risk of phthalate exposure through air inhalation and dust ingestion is also estimated in this study for different age groups. Generally, the inhalation is the major source of exposure dose to phthalates than the dust ingestion in the indoor environment.

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Phthalate trong không khí và bụi trong nhà tại Hà Nội, Việt Nam: sự phân ố và phơi nhiễm

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Tóm tắt Phthalate là nhóm hợp chất được sử dụng rộng rãi với vai trò phụ gia nhựa và chiếm tới vài phần trăm về khối lượng trong các sản phẩm. Vì vậy, chúng được tìm thấy trong nhiều loại mẫu môi trường và sinh vật khác nhau như nước, đất, ùn, không khí, ụi, máu và nước tiểu người. áo cáo này giới thiệu về phương pháp xác định và sự phân ố của phthalate trong mẫu không khí và ụi trong nhà thu tại Hà Nội, Việt Nam. Phương pháp tối ưu đã đáp ứng được yêu cầu của việc phân tích định lượng phthalate trong mẫu môi trường. Trong số các vi môi trường nghiên cứu, nồng độ cao nhất của phthalate đo được cao nhất trong mẫu ụi và không khí trong nhà thu tại các cơ sở làm tóc. Mức độ tương quan về nồng độ của phthalate trong mẫu ụi và không khí thu tại hiệu làm tóc cũng cao hơn so với các môi trường khác. Trong số các phthalate nghiên cứu, (2-ethylhexyl) phthalate (DEHP) được tìm thấy với nồng độ cao nhất trong cả mẫu ụi và không khí trong nhà. Liều lượng phơi nhiễm phthalate thông qua hít thở cao hơn mười lần so với liều phơi nhiễm qua con đường ăn nuốt ụi. Nhìn chung, rủi ro phơi nhiễm phthalate thông qua cả hai con đường hít thở không khí và ăn nuốt ụi đều giảm dần theo chiều tăng của nhóm lứa tuổi.

Từ khóa phthalate, không khí trong nhà, ụi trong nhà, phơi nhiễm, Việt Nam.