DISTRIBUTION AND EXPOSURE ASSESSMENT THROUGH INHALATION AND DERMAL PATHWAYS TO PHTHALATES IN INDOOR AIR COLLECTED FROM HANOI, VIETNAM

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ABSTRACT

Phthalates (phthalic diesters) is one of endocrine disrupting compound groups which have been recently concerned of the occurrence and harmful effects to human health. In this report, ten common phthalates were analyzed in indoor air collected from hair salons and homes collected from Hanoi, Vietnam. Total concentrations of phthalates in indoor air ranged from 306 to 16000 ng/m³ (mean: 1140 ng/m³). High concentrations of phthalates were measured in indoor air collected from hair salons (mean: 4040 ng/m³). Among the studied phthalates, diethyl phthalate (DEP) was predominant compound and had the highest levels in indoor air. Based on the measured concentrations, the human exposure to phthalates through inhalation and dermal absorption were estimated for various age groups. Overall, the exposure doses decreased with increasing ages.

Keywords: phthalates, indoor air, human exposure, inhalation, dermal.

1. INTRODUCTION

Phthalate di-esters were firstly introduced in 1920s [1]. They are industrial synthetic chemicals that have been widely used to improve the flexibility of plastic materials. So, their occurrence is everywhere in our lives, from personal care products, food wrap films, children’s toys or even in medical equipment. Moreover, diisobutyl phthalate (DiBP) was also used as a light-resistant plasticizer for paints. Globally, over 470 million pounds of phthalates are produced every year. In spite of many significant advantages in industry, phthalates have been called “the silent killers” since their toxicology. Because of widespread usage, phthalates can migrate into human’s bodies and animals through three main ways. These are dietary intake, air inhalation and dermal contact. For phthalates with short alkyl chains (DMP, DEP), monoesters represent the major human metabolite [2]. Otherwise, in case of phthalates with long alkyl chains, including DEHP, diisononyl phthalate (DiNP) and di-isodecyl phthalate (DiDP), the monoesters are further metabolitied via ω-1-oxidation of the aliphatic side chain [3] to transfer to disaccharide to improve ability of dissolving in water [4]. This results in excreting easier. In the
world, there are some regulations for limited use of phthalates in several developed countries. In 2007, REACH (a European Union regulation concerning the Registration, Evaluation, Authorisation and restriction of Chemicals), gave DEHP, DBP and BzBP in section 52, Annex XVII to limit production and usage of these compounds [1]. Up to now in Vietnam, government has just only warned about the danger of these compounds. Recently, the occurrence of phthalates in some cities in Vietnam has been reported [5, 6]. To continue previous studies, this report focuses on phthalate exposure from indoor air samples collected from hair salons and assess the risk for in people in Hanoi, Viet Nam.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

Seven phthalates standard including dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), diisobutyl phthalate (DiBP), di-n-hexyl phthalate (DnHP) and di(2-ethylhexyl) phthalate (DEHP) (purity > 98 %) were purchased from Sigma- Aldrich (MO, USA), benzyl butyl phthalate (BzBP) (purity 99.9 %) was obtained from Supelco (Bellefonte, PA, USA). The corresponding d4-internal standards of above phthalates with purities > 99 % were purchased from Dr. Ehrenstorfer (Germany). Using solvents acetone and n-hexane (purities for GC system), were purchased from Merck KGaA (Darmstadt, Germany) and dichloromethane (purity for GC system) was purchased from Fisher Scientific UK (LE 11 5RG, UK). All standards and internal standards were diluted into n-hexane.

2.2. Sample collection

Tube polyurethane foam (ORBO-1000 PUF inner diameter 2.2 cm and length 7.6 cm) was purchased from Supelco (Bellefonte, PA, USA). Because of ubiquitous occurrence of phthalates, it is necessary to clean the PUF. PUF were cleaned up by extracting with 100 ml mixture of dichloromethane and n-hexane (3:2, volume: volume) in 20 min then repeat the second time with 80 mL this solvent mixture. Quartz filter (Whatman label) (hole size 2.2 μm, diameter 32 mm) was dried at 350 °C for 20 hours then keep at 100 °C until to use. Before and after collecting samples, quartz filter was weighed (exact to 0.01 mg) to find mass of particles in air. PUFs were keep in glass tube (ACE glass, inner diameter 2.2 cm x length 25 cm), quartz filter which was in a container made by Teflon (Supelco, PUF filter cartridge assembly), was kept in the end of glass tube. Indoor air sample was collected from 12 to 24 hours by a low rate pump (LP-7; AP. Buck Inc., Orlando, FL, USA) with flow rate 4 liter/min. Total volume air collected from each place was in a range from 2.88 m³ to 5.76 m³. Air samples (including both PUFs and quartz filter) were kept at -18°C until analysis (≥ 2 weeks).

2.3. Sampling

In vapor phase (kept in two PUFs) spiked 100 ng d4-phthalates (except d4-DEHP 500 ng) into PUFs. Extract the first time with 100 mL mixture of dichloromethane (DCM) and hexane (3:2, v/v), then extract the second time with 80 mL mixture of DCM and n-hexane (3:2, v:v). For each extraction, sample was shaken by Orbital Shaker- SSM1 at 250 rpm for 30 minutes. All of extraction was concentrated to about 7 mL by vacuum rotate concentration then transfer to 15 mL glass tube before concentrating again by N₂ to 1 mL. The final extraction was transferred to GC vial to analyze by GC system. In particle phase (kept in quartz filter): spiked 100 ng d4-
Distribution and exposure assessment through inhalation and dermal Pathways to phthalates…

phthalates (except d$_4$-DEHP 500 ng). After that, sample was extracted by shaking with 5 mL mixture of DCM and hexane (3:2, v:v) for 5 min, repeating two times. All of extraction was transferred to 15 mL glass tube before concentrating to 1 mL by N$_2$ flow to analyze in GC system.

2.4. Instrumental analysis

Seven phthalates were analyzed using a Gas chromatography (GC-7890B) coupling with mass spectroscopy (MS-5977A) (Agilent Technologies). A fused-silica capillary column (DB-5MS from Agilent (5% diphenyl 95% dimethylpolysiloxane); 30 m x 0.25 mm id; 0.25 μm film thickness) was used for separation. Samples (2 μL) were injected in the splitless mode. The temperature of the chamber 80 °C (held 1.0 min) to 180 °C at 12 °C/min (1.0 min), raised up to 230 °C at 6 °C/min followed by increasing continuously to 270 °C at 8 °C/min (2.0 min), then reach to 280 °C at 30 °C/min (held 12.0 min). Ion fragments m/z 163 and m/z 149 were monitored for DMP and others, respectively. Ion fragment m/z 177, m/z 233, m/z 223 and 206, m/z 167 and m/z 279, m/z 297 were used for confirmation of DEP, DiBP, BzBP, DEHP, DnHP, respectively [5, 6]. Ion fragment 167 and m/z 153 to determined d$_4$-DMPP and other internal standards [6, 7, 8].

3. RESULTS AND DISCUSSION

3.1. Phthalates in Particulate and Vapor Phases in Indoor Air

![Figure 1. Mean concentrations of individual phthalate esters found in particulate and vapor phases in indoor air from Hanoi, Viet Nam (n = 18 samples).](image)

The mass of airborne particles in air samples was determined based on the difference in the weight of the quartz fiber filter before and after the collection of samples. In the particulate phase, DEP, DiBP, DBP, DMP, and DEHP were found at high concentrations in all of the samples. DEP was found at the highest mean concentration (1416 ng/m$^3$) in the vapor phase. The total mean concentration of sum of ten phthalates in the particulate phase was 358 ng/m$^3$. The mean concentration of DEP in the vapor phase was 25 ng/m$^3$. The concentration of DEP was 56 times greater in the vapor phase than in the particulate phase. Similarly, the DMP concentration in the vapor phase was 91 ng/m$^3$, which was 91 times greater than that in the particulate phase (1 ng/m$^3$) and DiBP concentration in the vapor phase was 338 ng/m$^3$, which was three times greater than that in the particulate phase (89 ng/m$^3$). Concentrations of other phthalates (i.e., DBP, BzBP, and DEHP) in the vapor and the particulate phases were not significantly different (Fig. 1).
3.2. Pattern of accumulation

The experiments indicate substantial dermal uptake directly from air for phthalates, the measured values for the contribution of the dermal pathway directly from air. Compositions of ten phthalates in indoor air are shown in Fig.2. Sources of indoor phthalates are related to decoration characteristics, life styles and working condition. Contamination levels of phthalates in home and salon hair differ from each other. The total concentration of DEP was highest (1440 ng/m³ approximately 57%), followed by DiBP, DBP, and DEHP. In addition, the concentration of DEP at salons was the highest level (2410 ng/m³), which was 4 times greater than that at home (470 ng/m³). Total concentration of phthalates in the salon was very high (4040 ng/m³), which was 4 times greater than that at home (1130 ng/m³). This can be explained by the fact that salons contain various personal care products, which are significant source of phthalates.

![Figure 2. Composition of ten phthalate diesters in indoor air in from Hanoi, VietNam](image)

However, the concentrations of the DnHP, DPP, BzBP, and DnOP were relatively low. A comparison of total concentration of four phthalates in indoor air among of sampling locations is shown in Fig. 3.

![Figure 3. Concentrations of phthalates (ng/m³; sum of particulate and vapor phase concentrations) in indoor air from Hanoi, Viet Nam.](image)

It was found that in Hangzhou, China, concentration of phthalate is highest (8100 ng/m³). Followed by Germany, Vietnam, USA, and Japan with the corresponding phthalate of 3430, 2960, 640, 420 ng/m³. This may be explained that China’s economic growth, but the environmental protection was limited [7, 8].

3.3. Human Exposure to Phthalates by Way of Inhalation

On the basis of the average inhalation [4], we calculated the inhalation exposure to phthalates by multiplying the measured concentration (ng/m³) with the volume of air inhaled (m³). The average body weights vary with age, infants (< 1 yr): 8 kg-bw, toddlers (1–3 yr): 15
Distribution and exposure assessment through inhalation and dermal Pathways to phthalates …

kg bw, children (3–11 yr): 25 kg bw, teenagers (11–18 yr): 48 kg bw, and adults: 66 kg bw (VietNam, 2008).

Inhalation exposure is calculated by Eq. (1):

\[ DI = \frac{C f}{M} \]  

(1)

where DI is daily inhalation exposure dose (ng/kg bw-day); C is total concentration of phthalates in indoor air (ng/m³); f is inhalation rate (m³/d); M is body weight (kg).

The daily inhalation and body weight of human exposure phthalates was calculated for various age groups (Table 1). The calculated daily inhalation exposure doses of total phthalates for infants, toddlers, children, teenagers, and adults were 1450, 1200, 1000, 720, and 530 ng/kg-bw/d, respectively. These results suggest that phthalate inhalation exposure doses decrease with an increase in age. In which, infants are the highest exposure group (1450 ng/kg-bw/d).

Table 1. Human exposure of phthalates through indoor air inhalation in Hanoi, Viet Nam (ng/kg-bw/d).

<table>
<thead>
<tr>
<th>Age group (years)</th>
<th>Body weight (kg)</th>
<th>Inhalation rates (m³/d)</th>
<th>Concentration (ng/m³)</th>
<th>Daily intake (DI) (ng/kg-bw/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infants</td>
<td>8</td>
<td>4.5</td>
<td>2590</td>
<td>1450</td>
</tr>
<tr>
<td>Toddlers</td>
<td>15</td>
<td>7.0</td>
<td>2590</td>
<td>1200</td>
</tr>
<tr>
<td>Children</td>
<td>25</td>
<td>10.0</td>
<td>2590</td>
<td>1000</td>
</tr>
<tr>
<td>Teenagers</td>
<td>48</td>
<td>13.5</td>
<td>2590</td>
<td>720</td>
</tr>
<tr>
<td>Adults</td>
<td>66</td>
<td>13.5</td>
<td>2590</td>
<td>530</td>
</tr>
</tbody>
</table>

3.4. Human Exposure to Phthalates through Dermal Absorption

Dermal exposure is calculated by Eq. (2) (EPA, 1992):

\[ DE = \frac{C_i \times SA \times ED \times P \times f_{SA}}{BW} \times 10^{-2} \]  

(2)

where DE is dermal exposure dose (ng/kg/d); \( C_i \) is gas-phase concentration of phthalates (ng/m³); ED is exposure duration (h/d); SA is body surface area (m²); \( f_{SA} \) refers to body contact fraction, assuming \( f_{SA} \) of 0.25 in shorts (EPA, 1992); P is overall skin permeability coefficient, 580 cm/h approximately 139 m/d [1]. Based on Eqs. 2, can be estimated for different age groups is shown in Table 2.

Table 2. Human exposure of phthalates by way dermal indoor air in Hanoi, Viet Nam (ng/kg-bw/d).

<table>
<thead>
<tr>
<th>Age group (years)</th>
<th>Body weight (kg)</th>
<th>Body surface area (m²)</th>
<th>Concentration (ng/m³)</th>
<th>( \sum_{DE} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infants</td>
<td>8</td>
<td>0.36</td>
<td>2230</td>
<td>830</td>
</tr>
<tr>
<td>Toddlers</td>
<td>15</td>
<td>0.57</td>
<td>2230</td>
<td>710</td>
</tr>
<tr>
<td>Children</td>
<td>25</td>
<td>0.69</td>
<td>2230</td>
<td>510</td>
</tr>
<tr>
<td>Teenagers</td>
<td>48</td>
<td>1.33</td>
<td>2230</td>
<td>520</td>
</tr>
<tr>
<td>Adults</td>
<td>66</td>
<td>1.84</td>
<td>2230</td>
<td>510</td>
</tr>
</tbody>
</table>

In two tables (1 and 2), the parameters of age, inhalation rate, body weight, exposure duration, and body surface area were taken from US EPA (2011). The dermal absorption exposure of phthalates for infants, toddlers, children, teenagers, and adults were 830, 720, 510, 520.
520, and 510 ng/kg-bw/d, respectively (Table 2). These results suggest that phthalate dermal exposure doses decrease with an increase in age. Similar to the inhalation exposure, infants are the highest exposure group (830 ng/kg-bw/d). Tables (1 and 2) show that, phthalates exposure on people from different age groups different. Intake of infants was the highest by both inhalation and dermal exposure pathway. The daily exposure to phthalates for infants was about 2 times higher than adults for inhalation exposure and 3 times for dermal absorption. That could be explained by the large time children coming in contact with toys.

Table 3. Comparison of human exposure doses to total phthalates through various pathways (ng/kg-bw/d).

<table>
<thead>
<tr>
<th>Exposure pathway</th>
<th>Infants</th>
<th>Toddlers</th>
<th>Children</th>
<th>Teenagers</th>
<th>Adults</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indoor air inhalation</td>
<td>850</td>
<td>420</td>
<td>200</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>Dust ingestion</td>
<td>940</td>
<td>1110</td>
<td>360</td>
<td>220</td>
<td>190</td>
</tr>
<tr>
<td>Indoor air inhalation*</td>
<td>230</td>
<td>190</td>
<td>160</td>
<td>110</td>
<td>80</td>
</tr>
<tr>
<td>Dermal Absorption</td>
<td>140</td>
<td>120</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

The contribution of human exposure to phthalates through indoor air inhalation was compared with other exposure pathways (Table 3). Generally, the estimated exposure dose decreased with increasing of age.

4. CONCLUSION

In this study, ten phthalates were measured in indoor air samples collected from Hanoi, Vietnam. The concentration of phthalates in hair salons were at the highest levels, reflecting significant use of phthalates in personal care products in this micro-environment. The human exposure to phthalates through inhalation and dermal absorption were estimated for various age groups. Infants had the highest exposure doses for both inhalation and dermal contact pathways. Further studies should be implemented to examine phthalates exposure to infants and children since these groups may be at higher risk.

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