A Review of Exposure Level and Assessment of Phthalic Acid Esters in Household Dust

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SUMMARY
Phthalic acid esters (PAEs) were a series of endocrine disrupter chemicals, its healthy risk include mutagenesis, carcinogenesis, teratogenicity and reproduction toxicity had aroused widespread attention. There were many studies aimed to the detection and analysis of PAEs metabolite in human blood and urine, besides, a few studies analyzed the indoor PAEs exposure level in household dust. This study reviewed 27 papers in 28 countries and districts with the purpose of summarizing PAEs exposure level in household dust. Result indicated that DEHP had highest concentration among studied PAEs (range from 2.323 to 2353 μg/g), besides, there were difference between the concentration of phthalates in different countries and districts. Furthermore, we found infants and toddlers had higher daily exposure level of PAEs than other people.

INTRODUCTION
Endocrine disrupter chemicals were exogenous chemicals which would interfere with the secretion of organisms. The environment pollution and risk assessment of endocrine disrupter chemicals especially PAEs became a hot topic in the recent year and there were many studies about PAEs (Dhaini and Nassif 2014) (Guo and Kannan 2011) (Lan et al. 2012) (Kamrin 2009). PAEs, a colorless oily viscous liquid, were a series of compound that prepared by phthalic acid and different kinds of fatty alcohol, they were difficult to dissolve in water whereas easy to dissolve in organic solvents. The universal molecular formula of PAEs was showed in figure 1. PAEs were less volatile in normal temperature. Owing to their low-cost, rich variety and high production, PAEs became critical and widespread pollutants.

With the development of economic society and improvement of people’s living standards, material manufacturing had been prosperous, therefore, as a kind of critical auxiliaries in material manufacturing, plasticizer had widely application in manufacture of toy, personal care products, food packaging, electronic or medical equipment. Herein, PAEs had the abundant production and consumption, they could be add into high-molecular polymer to improve plasticity and machinability so that the production could be pliable and had tight connection with people’s life. By the means of heating and volatilizing, PAEs could exist in air, water, wastes, dust and others therefore indoor air quality is very important for human’s health. The usage of PAEs was more than 8.2 million tons all over the world and 1% of usage entered into environment by osmosis (Blount et al. 2000). There were many studies find that PAEs are detected and found in household dust, indoor air. Moreover, a few studies has assessed the health risk of PAEs. Based on the awareness of their risk for human body, the use of PAEs is restricted by legislation in EU, Danmark, America, Japan and other countries or districts. The laws about PAEs usage in EU were indicated in 1999/815/EEC and 2005/84/EC: the content of DEHP, DBP, BBP, DINP, DIDP and DNOP in toys and children products should not exceed 0.1%, and in Danmark, expect laws in EU, laws that the content of other PAEs in toys and products should be not exceed 0.05%. The concentrations of PAEs in household dust can reflect human exposure to some extent (Wang et al. 2012).

Furthermore, many studies about cells and living body indicated that PAEs has mutagenesis, teratogenicity, reproduction toxicity and suspected carcinogenesis (Autian 1973) (Xia et al. 2011) (Kozumbo et al. (1982) (Latini et al. 2006). After the 103 weeks chronic toxicity experiments of rats and mice, Kluwe found that after feeding with food containing DEHP, the prevalence of hepatic carcinoma of experimental subjects were significantly increased (Kluwe et al. 1982). Besides, after sera diagnosis of precocious girls, Xiao found that the DBP, DEHP in sera of precocious girls were higher than in sera of girls who had normal development, the DBP, DEHP in uterus and ovaries had same result as in sera research (Qiao et al. 2007). These experiments can indicated the mutagenesis, teratogenicity, reproduction toxicity and suspected carcinogenesis of PAEs.

People spend more than 80% of whole day indoors, and children even be longer. Indoor environment consist of air, water, wastes, dust and others therefore indoor air quality is very important for human’s health. The usage of PAEs was more than 8.2 million tons all over the world and 1% of usage entered into environment by osmosis (Blount et al. 2000). There were many studies find that PAEs are detected and found in household dust, indoor air. Moreover, a few studies has assessed the health risk of PAEs. Based on the awareness of their risk for human body, the use of PAEs is restricted by legislation in EU, Danmark, America, Japan and other countries or districts. The laws about PAEs usage in EU were indicated in 1999/815/EEC and 2005/84/EC: the content of DEHP, DBP, BBP, DINP, DIDP and DNOP in toys and children products should not exceed 0.1%, and in Danmark, expect laws in EU, laws that the content of other PAEs in toys and products should be not exceed 0.05%. The concentrations of PAEs in household dust can reflect human exposure to some extent (Wang et al. 2012).

Figure 1 The universal molecular formula of PAEs
In present study, the concentrations distribution of PAEs in household dust among 28 countries or districts are reviewed by summarizing 27 papers. The studied common PAEs include DEP, DMP, DBP, DiBP, BBP, DNOP, and DEHP. The health assessment of PAEs were also estimated. This study can provide basic data and scientific basis for related legislation of PAEs.

![Diagram of exposure routes of PAEs to human body](image)

**METHODS**

**Study objects**

By the means of searching in China National Knowledge Infrastructure (CNKI), Web of Science and PubMed (keywords: indoor; dust; PAEs or phthalates), 28 papers meeting the standard were selected finally. The studied PAEs and their physicochemical property were listed in table 1.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full name</th>
<th>Molecular formula</th>
<th>Solubility</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>Dimethyl ortho-phthalate</td>
<td>C₈H₁₀O₄</td>
<td>4200</td>
<td>194.2</td>
</tr>
<tr>
<td>DEP</td>
<td>Diethyl ortho-phthalate</td>
<td>C₁₂H₁₄O₄</td>
<td>1100</td>
<td>222.2</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
<td>C₁₀H₁₂O₄</td>
<td>11.2</td>
<td>278.4</td>
</tr>
<tr>
<td>BBP</td>
<td>Benzyl-α-butyl ortho-phthalate</td>
<td>C₁₃H₁₈O₄</td>
<td>2.7</td>
<td>312.4</td>
</tr>
<tr>
<td>DiBP</td>
<td>Di-iso-butyl ortho-phthalate</td>
<td>C₁₁H₁₂O₄</td>
<td>20.0</td>
<td>278.4</td>
</tr>
<tr>
<td>DNOP</td>
<td>Di-n-octyl ortho-phthalate</td>
<td>C₁₃H₂₁O₄</td>
<td>5×10⁻⁴</td>
<td>390.6</td>
</tr>
<tr>
<td>DEHP</td>
<td>Di-(2-ethylhexyl) Phthalate</td>
<td>C₂₁H₃₂O₄</td>
<td>3×10⁻³</td>
<td>390.6</td>
</tr>
</tbody>
</table>

**Study methods**

Collating paper data according to studied area and studied year. Especially, in order to find the laws between different cities, we divided domestic cities into north cities and south cities. All data treatment were completed by SPSS19.0 (SPSS Ltd. USA), Wilcoxon signed rank test was applied to analyze the difference between two sets of data, p<0.05 means the difference was significant. Weight-based concentrations of sample were also calculated. Furthermore, in order to compare difference between different countries and districts, weight-based concentrations were treated by logarithmics.

**Exposure assessment**

There were two main routes that human exposed to PAEs in household dust: ingestion and dermal absorption (Li, et al. 2016). In our study, the daily exposure dose of PAEs were estimated through application of the exposure/ingestion factors recommended by the EPA for five age groups: infants (<1 year), toddlers (1–5 year), children (6–11 year), teenagers (12–19 year), and adults (>20 year) with different body weight, and dust ingestion rates. Calculation methods were show in equation (2-1, 2-2) (Johnson-Restrepo and Kannan 2009) and the median values of weight-based concentrations of PAEs were applied in calculation.

\[
D_{\text{dust ingestion}} = \frac{C_{\text{PAEs}} \times \text{SIR} \times IEF}{BW} \tag{1}
\]

Where \(C_{\text{PAEs}}\) is PAEs concentrations in dust (ng/m³), SIR is soil ingestion rate (m³/day), IEF is indoor exposure fraction, \(BW\) is body weight (kg).

\[
D_{\text{dermal absorption}} = \frac{C_{\text{PAEs}} \times BSA \times SAS \times AF \times IEF}{BW \times 1000} \tag{2}
\]

Where \(C_{\text{PAEs}}\) is PAEs concentrations in dust (ng/m³), BSA is body surface area (cm²/day), IEF is indoor exposure fraction, \(AF\) is fraction of PAEs absorbed in the skin, \(BW\) is body weight (kg).

**RESULTS AND DISCUSSION**

DEHP has the highest concentration (ranged from 2.323 to 2353μg/g) among studied PAEs, the concentrations of DEHP in most of countries and districts were higher than 100μg/g. In the domestic cities, the concentrations of DEHP were ranged from 200 to 500μg/g, even more than 1000μg/g in Chongqing (Bu et al. 2015) (Bu et al. 2016) and Guangzhou (Lan et al. 2012).

In the developed countries such as Germany (Fromme et al. 2004) (Butte W et al. 2001) (Becker et al. 2002) (Abb et al. 2009) (Fromme et al. 2013), Japan (Kanazawa et al. 2010), Sweden (Bornehag et al. 2005), Kuwait (Gevao et al. 2013), DEHP had higher concentrations than in most domestic cities, herein, Kuwait had the highest concentration of DEHP (2256μg/g). DEHP had the most abundant production and most widespread use, moreover, owing to its large molecular weight, non-volatility, and it was easy to adhere to particles, DEHP was the most common and high concentration PAEs in household dust. Furthermore, the concentration of DBP (ranged from 0.47 to 799μg/g) and DiBP (ranged from 0.392 to 233.8μg/g) in household dust were higher than the concentration of other kinds of PAEs (DEHP was excluded). The concentrations of others studied PAEs were lower than 10μg/g. DEP and DMP had low molecular weight and volatility so that they were not easy to adhere to household dust.

From the data in studied papers, the concentrations of PAEs in household dust of developing countries such as China, Vietnam (Tran T et al. 2016) were higher than them in Japan, German. Using Wilcoxon signed rank test to assess the
difference of weight-based concentrations between foreign countries and domestic countries, results indicated that the difference was statistically significant ($p<0.05$). The reason which account for this phenomenon was that, owing to developed countries had higher levels of economic development, more advanced technology and well-developed industrialization than developing countries, therefore the use of PAEs was more frequent in daily life and industrial development. These facts result in higher concentrations of PAEs than developing countries which had low level of economic and social development. Herein, the concentrations of PAEs in household dust of Vietnam (Tran et al. 2016) were far lower than other countries and districts. Figure 2 indicated the condition of distribution ratio of PAEs in different countries and districts. From the figure, DEHP, DBP, DiBP were also common PAEs in different countries and districts. The distribution ratio of DBP and DiBP in north cities were higher than south cities. Besides, due to different industrial structures, China had significant difference in using PAEs compared with developed countries. The using ratio of BBP in developed countries was higher than China whereas the condition about DiBP was opposite.

Due to different functions of different room such as office room, living room, bedroom, therefore there were different goods in rooms, so that the concentrations of PAEs in different rooms were also significantly different. Besides, the concentrations of PAEs in dust of bedroom or dormitory were lower than them in other studied rooms which had same sample year or studied city. A reasonable explanation for this phenomenon was the single function of sleeping rooms. Different kinds of PAEs had different use not only in industrial production but in daily life (Graham 1973). In office room, DBP had higher concentration than other kinds of PAEs, as a kind of solvent, DBP was mostly used in the production of adhesive and printing ink which were common in office room.

Furthermore, the concentrations of PAEs in Tianjin (Wang 2012) were far lower than them in other similar studies. In the study of Tianjin, the concentrations of PAEs in summer were significantly lower than them in winter ($p<0.05$). PAEs were connected with polyolefins molecules by a hydrogen bonding and van der Waals force, therefore PAEs in plastic products were more volatile and adhered to household dust in summer than in winter.

The data in different year of same city were also analyzed. During 2009 to 2010, the concentrations of PAEs in household dust of Beijing (Shen 2009) (Guo 2011) were decreased with ageing. The concentrations of PAEs in household dust of Guangzhou in 2010 (Guo 2011) were significantly lower than them in 2007 (Lan 2012), and the difference was statistically significant ($p<0.05$). Besides, in the study of Jinan (Guo 2011), the concentrations of all kinds of PAEs in household dust of Jinan were lower than other cities in same studies, and the difference was statistically significant ($p<0.05$). The concentrations of PAEs in Xi’an (Wang et al. 2014), Nanjing (Zhang et al. 2013), Pearl River delta (Kang et al. 2013).
2012) were also applied in calculation of weight-based concentrations in China.

From the data in studied papers, significant difference of the concentrations of PAEs in household dust were found between different countries, and the range of concentrations of PAEs varies greatly. Different climate, level of economic development, the people’s lifestyle were associated with this phenomenon. The weight-based concentrations of PAEs in developed countries were calculated. Compared with data in China, exposure level of different kinds of PAEs in developed countries was higher than in China. Herein, the minimum concentration of DEHP was found in bedroom of Danmark and the maximum was found in Kuwait (Gevao et al. 2013).

The study in Vietnam (Tran et al. 2016) indicated that there were difference in concentrations of household dust-PAEs in different sample sites. DBP and BBP were added to printing ink and adhesive therefore the concentrations of DBP and BBP in office room were higher than in other rooms. Moreover, supermarkets, stores, laboratories had higher the concentrations of PAEs than other rooms. A reasonable explanation was high usage of plastic productions in these sites.

In the same sample site such as daycare, except DEHP, the concentrations of other PAEs in German (Fromme et al. 2013) were lower than them in Danmark (Langer et al. 2010), the concentration of DEHP was higher than values in other foreign studies. The reason for this phenomenon was that, DEHP was wildly applied in production of toys and children products which were common in daycares. Similar result was found in one study aimed to 3 kinds of PAEs (DINP, DiBP, DEHP) in toys and children articles (Earls et al. 2003). The concentrations of DMP, DEP, DBP, BBP and DNOP in household dust in Palermo (Italy) were significantly higher than similar research, the content values were 4-8 times as concentrations of foreign studies (Orecchio et al. 2013).

Table 2 Health assessment of PAEs in different countries and districts among different ages (ng/kg-bw/day)

<table>
<thead>
<tr>
<th>Items</th>
<th>North cities(dust ingestion)</th>
<th>North cities(dermal absorption)</th>
<th>South cities(dust ingestion)</th>
<th>South cities(dermal absorption)</th>
<th>China(dust ingestion)</th>
<th>China(dermal absorption)</th>
<th>Developed countries(dust ingestion)</th>
<th>Developed countries(dermal absorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infants</td>
<td>1.6</td>
<td>2.1</td>
<td>156.1</td>
<td>0.7</td>
<td>1.6</td>
<td>280.2</td>
<td>926.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Toddlers</td>
<td>2.3</td>
<td>2.9</td>
<td>218.9</td>
<td>1.0</td>
<td>2.3</td>
<td>393.1</td>
<td>1299.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Children</td>
<td>0.6</td>
<td>0.8</td>
<td>60.4</td>
<td>0.3</td>
<td>0.6</td>
<td>108.4</td>
<td>358.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Teenager</td>
<td>0.4</td>
<td>0.5</td>
<td>37.5</td>
<td>0.2</td>
<td>0.4</td>
<td>67.4</td>
<td>222.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Adults</td>
<td>0.3</td>
<td>0.4</td>
<td>30.0</td>
<td>0.1</td>
<td>0.3</td>
<td>53.9</td>
<td>178.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>North cities(dust ingestion)</td>
<td>North cities(dermal absorption)</td>
<td>South cities(dust ingestion)</td>
<td>South cities(dermal absorption)</td>
<td>China(dust ingestion)</td>
<td>China(dermal absorption)</td>
<td>Developed countries(dust ingestion)</td>
<td>Developed countries(dermal absorption)</td>
</tr>
<tr>
<td>Infants</td>
<td>2.3</td>
<td>3.9</td>
<td>130.4</td>
<td>2.9</td>
<td>153.6</td>
<td>64.1</td>
<td>2252.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Toddlers</td>
<td>3.2</td>
<td>5.5</td>
<td>182.9</td>
<td>4.1</td>
<td>215.5</td>
<td>89.9</td>
<td>3159.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Children</td>
<td>0.9</td>
<td>1.5</td>
<td>50.5</td>
<td>1.1</td>
<td>59.5</td>
<td>24.8</td>
<td>871.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Teenager</td>
<td>0.6</td>
<td>0.9</td>
<td>31.3</td>
<td>0.7</td>
<td>36.9</td>
<td>15.4</td>
<td>541.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Adults</td>
<td>0.4</td>
<td>0.7</td>
<td>25.1</td>
<td>0.6</td>
<td>29.5</td>
<td>12.3</td>
<td>433.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>North cities(dust ingestion)</td>
<td>North cities(dermal absorption)</td>
<td>South cities(dust ingestion)</td>
<td>South cities(dermal absorption)</td>
<td>China(dust ingestion)</td>
<td>China(dermal absorption)</td>
<td>Developed countries(dust ingestion)</td>
<td>Developed countries(dermal absorption)</td>
</tr>
<tr>
<td>Infants</td>
<td>2.1</td>
<td>3.5</td>
<td>143.1</td>
<td>4.4</td>
<td>118.8</td>
<td>166.2</td>
<td>1941.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Toddlers</td>
<td>2.9</td>
<td>4.9</td>
<td>200.7</td>
<td>6.1</td>
<td>166.7</td>
<td>233.2</td>
<td>2723.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Children</td>
<td>0.8</td>
<td>1.4</td>
<td>55.4</td>
<td>1.7</td>
<td>46.0</td>
<td>64.3</td>
<td>751.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Teenagers</td>
<td>0.5</td>
<td>0.8</td>
<td>34.4</td>
<td>1.0</td>
<td>28.6</td>
<td>40.0</td>
<td>466.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Adults</td>
<td>0.4</td>
<td>0.7</td>
<td>27.5</td>
<td>0.8</td>
<td>22.9</td>
<td>32.0</td>
<td>373.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Compared the concentrations of PAEs in Sweden home in 2001 (Bormhag et al. 2005) and 2008 (Luongo and Ostman 2008), the result was consistent with it in Beijing (Shen 2009) (Guo 2011) and Guangzhou (Guo 2011) (Lan 2012); the concentrations of all kinds of PAEs in 2008 were lower in 2001. On the contrary, there were no significant difference of concentrations of PAEs between Berlin (Fromme et al. 2004) and Harley saller (Abb et al. 2009). Besides, the concentration of PAEs in Danmark bedroom were generally lower than other sample sites (Langer et al. 2010), this result was consistent with domestic cities, reason was mentioned earlier in present study.

The concentrations of PAEs in other developed countries covered Canada (Kubwabo et al. 2013), Bulgarian (Kolarik et al. 2008), American (Rudel et al. 2003), Stockholm (Berghet al. 2011) and France (Mercier et al. 2013) were also applied in calculation of weight-based concentrations in developed countries.
The health assessment (ng/kg-bw/day) of different ages exposed to PAEs was estimated and listed in table 2 in present study. The dust ingestion of PAEs of toddlers was highest among different ages. (toddler > infants > children > teenager > adults). The dust ingestion of PAEs, which was associated with PAEs concentration, in developed countries was higher than in other countries and districts.

The skin was also the main route of human exposure to PAEs, therefore, dermal absorption of PAEs was also estimated. The dermal absorption of PAEs was increased with the decrease of age. Similar with result about dust ingestion and the conclusion could be indicated that people at the younger age were more susceptible to PAEs than the older. According the data in table 2, dust ingestion contributed to significantly higher PAEs exposures than did dermal dust absorption. The tolerable daily intake (TDI) recommend by EFSA and RfD (Reference Dose) of DBP, DiBP, DEHP, DEP, BBP were showed in table 3.

<table>
<thead>
<tr>
<th>PAEs</th>
<th>TDI (μg/kg-bw/day)</th>
<th>RfD (μg/kg-bw/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEP</td>
<td>500</td>
<td>800</td>
</tr>
<tr>
<td>DiBP</td>
<td>10</td>
<td>800</td>
</tr>
<tr>
<td>DBP</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>BBP</td>
<td>500</td>
<td>200</td>
</tr>
<tr>
<td>DEHP</td>
<td>50</td>
<td>20</td>
</tr>
</tbody>
</table>

The tolerable daily intake (TDI) recommend by EFSA and RfD (Reference Dose) of DBP, DiBP, DEHP, DEP, BBP were showed in table 3. Also the calculation values which calculated with median concentrations of PAEs, were below the TDI and RfD, however, we could not ensure that the maximum concentration was also safe for human body. Therefore, the health risk of PAEs couldn’t be ignored.

CONCLUSION

The comprehensive picture about PAEs in household dust among different countries and districts were presented in this study. Herein, the majority of PAEs in dust were DEHP, DBP, DiBP. Due to different climate, lifestyle of people and social economic development level, significant difference of concentrations of PAEs between different countries and districts. The health risk of exposing to PAEs among toddlers and infants were higher than adults.

ACKNOWLEDGEMENT

This work is financially supported by the National Key Research and Development Program of China (2017YFC0702701), National Natural Science Foundation of China (51708347) and the Innovation Program of Shanghai Municipal Education Commission (14ZZ132).

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