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보건학박사 학위논문

**Evaluation of Phthalate Concentrations in Settled  
Dust from Nursery Schools and Related Factors**

어린이 보육시설에서의 먼지 내 프탈레이트  
농도와 관련 요인

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## **ABSTRACT**

# **Evaluation of Phthalate Concentrations in Settled Dust from Nursery Schools and Related Factors**

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Phthalates have reproductive and developmental effects and are endocrine disruptors. Phthalates have been used commercially in a variety of consumer products and industrial goods. Because plasticizers tend to leach, migrate, or evaporate from polyvinyl chloride (PVC)-containing products for thermodynamic reasons, they are considered ubiquitous global contaminants. Exposure to phthalates in the general population is widespread and widely

variable. Children may be more pharmacodynamically sensitive to the adverse effects of phthalates than adults. Unfortunately, phthalate exposure levels are higher in children than adults. In addition to phthalate exposure through food or inhalation, the ingestion of contaminated indoor dust is another principal exposure route. Indoor dust can therefore be used as a tool to assess human exposure to contaminants. Children are exposed to dust contaminated with phthalates not only in their homes but also in nursery schools, where they spend most of their time. The main objectives of this study were to evaluate the mass fractions of phthalates in indoor dust samples from nursery school classrooms and to identify the most important sources.

In the first study, dust samples were collected from 64 classrooms located in 50 nursery schools, and various consumer products and building materials were analyzed using a portable X-ray fluorescence (XRF) analyzer to determine whether they contained PVC. For materials proven to contain PVC, the areas or weights were measured and related to the phthalate concentration. Eight phthalates were analyzed in sampled dust using a gas chromatograph/mass-selective detector: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), Di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP), di-isononyl phthalate (DINP), and di-isodecyl phthalate (DIDP). Of these, DEHP was the

most abundant phthalate, with a geometric mean concentration of 3,170  $\mu\text{g/g}$  dust, which was significantly correlated with the area of flooring verified to contain PVC. DINP, which has not been widely-reported in other studies, was the second-most abundant phthalate, with a geometric mean concentration of 688  $\mu\text{g/g}$ , which was influenced by the number of children in the institution and the agency operating the nursery school. It was concluded that the use of PVC-verified building materials and the building management characteristics were significant factors affecting the mass fractions of phthalates in indoor dust.

In the second study, we examined 3,180 consumer products to determine whether they contain PVC and evaluate their correlation with the mass fraction of phthalates in indoor dust to identify the major sources of each phthalate. A portable XRF analyzer was used to determine whether products contained PVC, and the levels of the eight phthalates in indoor dust were analyzed using GC/MS. It was confirmed that 1,067 consumer products (33.6%) contained PVC materials. The weights of toy blocks, articles used for role playing, and gymnastic apparatuses were significant factors affecting the DBP concentration. Interior materials used in the construction of the building accounted for 83.2% of the total area of PVC-verified products, and the area of PVC floors was significantly correlated with the mass fraction of DEHP.

The mass fraction of DINP in dust was related to the weights of toys, teaching aids, doors and musical instruments, such as pianos. It was found that many PVC consumer products are used in nursery schools, and their usage increased the phthalate concentration of indoor dust.

In addition to the evaluation of phthalate concentrations in indoor dust and the associated source determination, two sampling methods (sampling dust using a modified vacuum cleaner and collection of dust from the bag of the regularly used vacuum cleaner) for indoor dust were compared. The correlations and agreements between the results using the two sampling methods were moderate for DBP but poor to moderate for DEHP. The spatial variability was small for DBP and DEHP in indoor dust samples collected from separate classrooms of a nursery school. The repeatability of the two sampling methods was good for DBP and DEHP. However, the correlation and agreement between the results obtained using the two sampling methods and the repeatability were poor for DINP, with a high level of room-to-room variability. If the area cleaned was recorded, then the phthalate content of the dust in the bag of a regularly used vacuum cleaner could be used to estimate phthalate exposure. The physico-chemical properties of phthalates must be considered when designing phthalate exposure assessment studies, because the mass fractions of phthalates in dust (especially long-chain phthalates such

as DINP) obtained from different sampling methods, sites, and periods might differ based on the type of phthalate.

This is the study to investigate the quantitative relationship between the mass fractions of phthalates in dust and the use of PVC-verified materials, especially for regularly used consumer products and building materials in nursery schools. Considering the developmental toxic risk of phthalates and the vulnerability of children, exposure to children is a main public health concern. Phthalate levels in indoor dust were associated with the use of PVC products, including building materials and consumer products. Various PVC products were found to be used in nursery schools. Although the ingestion of food contaminated with phthalates is regarded as a major exposure route for the general population, the contamination of indoor dust with phthalates can result in elevated phthalate exposure. Therefore, to reduce phthalate exposure in children, it is necessary to reduce or eliminate the use of PVC products.

**Key words: phthalates, PVC, children, nursery school, indoor dust, vacuum cleaner**

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## **CHAPTER 1.**

# **INTRODUCTION**

## 1.1. BACKGROUND

**Plastics and plasticizers.** Plastics are inexpensive, lightweight, strong, durable, and corrosion-resistant materials, with high thermal and electrical insulation properties. Plastics are ubiquitous in modern life, but it is evident that our current approach to their production, use and disposal are not sustainable and create concerns for wildlife and human health.<sup>1</sup>

Polyvinyl chloride (PVC) was produced on an industrial scale at the end of the 1920s, after which mass production of plastics began in the 1940s. After World War II, the use of PVC increased rapidly, and PVC production has since grown worldwide at a rate of more than 4% per year over an extensive period. In terms of volume, it is currently the second most abundant plastic produced worldwide.<sup>2</sup> Due to its continuous growth for over 50 years, global production of PVC reached 288 million tonnes in 2012.<sup>3</sup>

To obtain the desired properties of PVC, it is sometimes mixed with large amounts of plasticizers. The amount of additives in a PVC formulation is determined by the properties required and ranges from 15–60% by weight. Globally, approximately six million tonnes of plasticizer are consumed every year.<sup>4</sup> At present, some 300 plasticizers are manufactured, at least 100 of

which are of commercial importance. Phthalates have commonly been used as a primary plasticizer component, because they increase flexibility, workability, and distensibility.<sup>5</sup>

**Characteristics of phthalates.** The demand for phthalates in the market increased dramatically after it was found they could replace the more expensive plasticizer, camphor.<sup>6</sup> Phthalates have widespread and extremely diverse applications. The largest market for phthalates is as plasticizing agents for PVC. They have properties that decrease the interactive forces between adjacent polymer chains and lower the glass transition temperature, which promotes chain mobility and thus material flexibility. Phthalate plasticizers can account for up to 40% of the final product in which they are used, and the content ratio determines the degree of flexibility.<sup>7</sup> Phthalates have been commercially used in a variety of consumer products and industrial goods. Table 1-1 shows examples of the main PVC consumer products that incorporate phthalates.

Table 1-1. Physical properties of phthalates and their main uses

Phthalates		Physical properties		Uses
Full name	Abbreviation	MW	VP <sup>a</sup>	
Di-ethyl-phthalate <sup>8</sup>	DEP	222.3	$2.0 \times 10^{-3b}$	Solvent, fixative for cosmetic products, plasticizer for packaging materials
Butyl benzyl phthalate <sup>9</sup>	BBP	312.35	$6 \times 10^{-7}$	Vinyl tile, food conveyor belts, carpet tile, artificial leather, tarps, automotive trim, weather stripping, traffic cones, vinyl gloves, adhesives
Di-n-butyl phthalate <sup>10</sup>	DBP	278.35	$2.7 \times 10^{-5}$	Coalescing aid in latex adhesives, plasticizer in cellulose plastics, solvent for dyes
Di(2-ethylhexyl)phthalate <sup>11</sup>	DEHP	390.62	$1.0 \times 10^{-7}$	Building products(flooring and pavements, roof coverings, wallpaper, polymeric coatings, tubes and containers, wire and cable insulation), car products (vinyl upholstery, car seats, underbody coating, trim), clothing (footwear, raincoats), food packaging, children's products (toys, crib bumpers), medical devices
Di-n-hexyl-phthalate <sup>12</sup>	DnHP	334.4	$5.0 \times 10^{-6}$	Automobile parts(air filters, battery covers), dip-molded products(tool handles, dishwasher baskets), flooring, canvas tarps, notebook covers,

Di-n-octyl-phthalate <sup>13</sup>	DnOP	390.54	$1.0 \times 10^{-7}$	<p>traffic cones, toys, vinyl gloves, weather stripping, flea collars, shoes, conveyor belts</p> <p>No known commercial uses for pure DnOP, DnOP constitutes about 20 % of C6-10 phthalate substance, such phthalates are used in PVC products, such as carpet tile, toys, vinyl gloves, etc., food applications(seam cements, bottle cap liners, conveyor belts)</p> <p>Film and sheet(stationary and wood veneer, pool liner), flooring(tiles, sheets), artificial leather, coated fabrics(tarps, conveyor belts), Dip coating/slush molded(gloves, toys, traffic cones), tubing and profiles(profiles, garden hoses), wire and cables, shoes, under-body coating, sealants(carpet backing)</p>
Di-isononyl phthalate <sup>14</sup>	DINP	419	-	<p>Film and sheet(Skins-unsupported, pool lining), artificial leather, coated fabrics, dip coating/slush molded(toys, traffic cones, gloves), tubings, wire and cables, automobile under-body coating, shoes, carpet backing</p>
Di-isodecyl phthalate <sup>15</sup>	DIDP	447	-	<p>Film and sheet(Skins-unsupported, pool lining), artificial leather, coated fabrics, dip coating/slush molded(toys, traffic cones, gloves), tubings, wire and cables, automobile under-body coating, shoes, carpet backing</p>

Abbreviations: MW, molecular weight; VP, vapor pressure.

<sup>a</sup>Unit for vapor pressure: mm Hg at 25°C <sup>b</sup>Unit for vapor pressure: mm Hg at 20°C

**Health effects of phthalates.** Public concerns have been raised due to the accumulated evidence associating reproductive and developmental effects with phthalate exposure.<sup>16, 17</sup> Additionally, it is clear that phthalate exposure leads to behavioral changes in human populations. Although, the effects of phthalates on brain development have been not investigated fully, it is apparent that phthalate exposure adversely affects many aspects of neurodevelopment in animals, particularly rodents.<sup>18</sup>

Phthalate exposure is regarded as one of the risk factors for atopic diseases in children as well as adults. There has been a sharp increase in global morbidity and mortality associated with asthma over the last 40 years, particularly in children.<sup>19</sup> Exposure to environmental contaminants such as phthalates is one of the many possible explanations for this increase. There is some evidence supporting the relationship between phthalate exposure and allergic diseases, including respiratory conditions. Some studies have suggested a relationship between the use of PVC products and the incidence of asthma. DEHP is the most frequently targeted phthalate by epidemiological studies of allergic diseases. Additionally, BBP was found to be associated with rhinitis and eczema in children.<sup>20-25</sup>

**Methods used for phthalate exposure assessment.** Exposure to phthalates can occur through ingestion, inhalation or dermal absorption from a variety of sources, such as food, water, air, dust, and the use of consumer and personal-care products containing phthalates.<sup>26</sup> Phthalate exposure assessments can be performed by human biomonitoring, through measurements of primary or secondary metabolites. Alternatively, phthalate levels can be measured in environmental media, food, and consumer products. Studies have evaluated phthalate concentrations in air, dust, diet, and biospecimens to estimate human exposure to these chemicals and to determine the critical exposure routes.

Environmental contamination by phthalates contributes to the levels found in food, water, and indoor dust.<sup>27</sup> In addition to food and the workplace, indoor air and dust are significant exposure sources for the general population, especially children.

Indoor dust contains long-term accumulations of semivolatile organic compounds and particle-bound matter, and it has been regarded as an indoor-pollution archive.<sup>28</sup> Analyses of compounds in indoor dust provide measurements of indoor contamination, and the results can be used to determine the possibility of significant exposure via one or more routes into the body.<sup>29, 30</sup> For example, Langer et al.<sup>31</sup> showed that the mass fractions of phthalates in dust collected from children's bedrooms and daycare centers

were significantly correlated with the concentration of phthalate metabolites, with the exception of DEHP.

The phthalate concentrations in dust could be used to estimate a resident's personal exposure. Øie et al.<sup>32</sup> reported a mean of 960 µg total phthalates/g dust in 38 homes in Norway, and estimated the mean adult inhalation exposure to DEHP from this source to be 0.76 µg/day. Additionally, it was estimated that the ingestion of dust containing 640 µg DEHP/g dust would yield a dose of 64 µg/day.

The contamination of indoor dust with phthalates can result in an elevated phthalate concentration in airborne particulate. The concentration of semi-volatile organic compounds (SVOCs), including phthalates, in airborne particles tends to correlate with the concentration in dust.<sup>33</sup> Otake et al.<sup>34</sup> analyzed phthalate levels in the indoor air of 27 houses in Tokyo and reported median concentrations of 0.10, 0.39, 0.01, and 0.11 µg/m<sup>3</sup> for DEP, DBP, BBP, and DEHP, respectively. For an adult weighing 64 kg and breathing in 22 m<sup>3</sup>/day, the maximum inhalation exposure can be approximately 30% of the dietary intake, or 20% of the total intake, of DBP. These comparisons indicate the possible significance of the contribution of phthalate esters in indoor air to

the total exposure. Inhalation or ingestion of contaminated dust will result in larger exposures.

Indoor dust has been used as a tool to assess human exposure to indoor contaminants. In addition to collecting dust directly from the floor using a standard vacuum cleaner, such as a high-volume small-surface sampler (HVS3),<sup>35-37</sup> investigators typically sample residential dust by collecting the subjects' vacuum cleaner dust bags<sup>38-40</sup> or using a brush or broom.<sup>39,41</sup> In some studies, dust has been sampled using modified vacuum cleaners equipped with a thimble or membrane filter.<sup>42-45</sup>

Each sampling method has advantages and disadvantages as summarized in Table 1-2. Dust sampling by a researcher is regarded as an effective method for evaluating indoor contaminants, because it provides a standard dust loading value, compared with dust collection from a regularly used household vacuum cleaner. However, simply collecting a dust bag is more cost effective and easier.

Table 1-2. Comparison of advantages and disadvantages of dust sampling methods

Dust sampling method	Advantages	Disadvantages
Dust sampling by researcher with modified vacuum cleaner	<ul style="list-style-type: none"> <li>- Dust loading: specific to one room and short period of time</li> <li>- Collected dust is immediately removed from air stream</li> </ul>	<ul style="list-style-type: none"> <li>- Expensive</li> <li>- Labor intensive</li> </ul>
Collection of dust bag from regularly used vacuum cleaner	<ul style="list-style-type: none"> <li>- Non invasive</li> <li>- Cost-effective</li> <li>- Easy to use</li> </ul>	<ul style="list-style-type: none"> <li>- Dust concentration: several rooms over periods of months or years</li> <li>- Different design and practice</li> <li>- Repeated aeration</li> <li>- Contamination from itself</li> </ul>

A universal, gold-standard method for sampling contaminants in indoor dust has not been developed.<sup>46</sup> Further studies are needed to develop standardized protocols for exposure characterization.

**The phthalate body burden of the general population.** For thermodynamic reasons, plasticizers tend to migrate to the surface of a product,<sup>47</sup> and are therefore constantly released into the environment by direct release, migration, evaporation, leaching, and abrasion.<sup>26</sup> Therefore, consumer products containing PVC can be sources of phthalate exposure through direct contact and use or through environmental contamination following abrasion and incorporation into indoor dust.<sup>27</sup>

Phthalates are considered ubiquitous global contaminants, and it is likely that their exposure is unavoidable for the majority of people. Phthalate exposure in the general population is widespread and extremely variable. Some studies have indicated that phthalate exposure is both higher and more common than previously suspected. The levels of phthalate metabolites detected in urine samples indicated that the test subjects were exposed to phthalate esters on a daily basis.

Table 1-3 shows evidence that the general population is exposed ubiquitously to phthalates. The articles cited were retrieved from a systematic

search of two electronic databases (ScienceDirect and Web of Science). The search strategy included a combination of keywords such as “phthalate” and “exposure” among the titles, abstracts, and keywords of articles. The references used were restricted to peer-reviewed articles investigating the phthalate exposure level of the general population. Table 1-3 shows the levels of phthalate exposure reported in various countries. In the U.S., the urinary monoester phthalate metabolites were detected in 2,540 samples collected from participants of the National Health and Nutrition Examination Survey, with a geometric mean of 3.1  $\mu\text{g/g}$  creatinine (DEHP metabolite). This was comparable to the concentrations reported from Germany. The median concentration in the German population ranged from 4.3 to 9.2  $\mu\text{g/g}$  creatinine. In some other countries, the urine concentrations of DEHP metabolites in the population were even higher. For example, the median concentrations of the DEHP metabolite in urine samples from Taiwan, Poland, and Korea were 17.3, 15.1, and 13.2  $\mu\text{g/g}$  creatinine, respectively. Although, there were no significant differences in the phthalate metabolite urine concentrations between males and females, it was apparent that the body burden from phthalate exposure was higher in children than in adults.

Table 1-3. Phthalate exposure levels in the general population

Reference	Country	N	Main results	DEHP metabolite, GM(SD) <sup>a</sup>	Media
Blount BC, et al. (2000) <sup>48</sup>	USA	289	Highest level of metabolites reflecting exposure to diethyl phthalate, dibutyl phthalate, and benzyl butyl phthalate were detected	3.0	Urine
			Women of reproductive age (20-40 years) were found to have significantly higher levels of monobutyl phthalate than other age groups	-	
Koch HM, et al. (2003) <sup>49</sup>	German	85	10 concentrations exceeded tolerable daily intake(TDI) value for DEHP	9.2 <sup>c</sup>	Urine
			26 subjects had values higher than the reference dose(RfD) for DEHP	40.2 <sup>c</sup>	
Silva MJ, et al., (2004) <sup>50</sup>	USA	2,540	Widespread exposure in the United States to phthalates	3.1	Urine
			Children had significantly higher levels of phthalate metabolites compared to adults and adolescents	-	
Fromme H, et al. (2007) <sup>51</sup>	German	50	Phthalate metabolite levels did not consistently differ by sex or age.	4.3(male)/4.3(female) <sup>c</sup>	Urine
			Day-to-day variation and within-subject variation were substantial	18.3(male)/18.5(female) <sup>c</sup>	

Wittassek M, et al. (2007) <sup>52</sup>	German	634	Ubiquitous exposure of the German population to all five phthalates throughout the last 20 years The trends observed in phthalate exposure may be associated with a change in production and usage pattern.	7.3 <sup>c</sup> 21.0 <sup>c</sup>	Urine
Becker, K., et al. (2009) <sup>53</sup>	German	600	14% of the subjects daily DnBP intakes above the TDI value All metabolites could be detected in nearly all urine samples All children showed three to five fold higher urine concentrations than adults	6.4 <sup>c</sup> 47.9 <sup>c</sup>	Urine
Yayoi Suzuki, et al. (2009) <sup>54</sup>	Japan	50	Phthalate ester metabolites had high detection rates in 50 subjects Results reflected longer-term exposure to the corresponding diesters of subjects	4.6 (3.32) 12.9 (1.98)	Urine
Guo Y, et al. (2011) <sup>55</sup>	Seven Asian countries	262	Total phthalate metabolite concentration: India, China, Vietnam, Japan, Korea, Malaysia The estimated exposure doses to DEHP in Kuwait were above the RfD recommended by the EPA.	3.0(China)/4.0 (Korea) 7.7(China)/5.7 (Korea)	Urine
Lin S, et al. (2011) <sup>56</sup>	Taiwan	100	Total urinary phthalate metabolite concentration was found to be higher in children(398.6 $\mu\text{g/l}$ for DEHP metabolite) than pregnant women(205.2 $\mu\text{g/l}$ ) Metabolites in urine are mainly from DEHP	17.3(woman)/27.5(2-years) 36.3(woman)/140.4(2-years)	Urine, cord serum, breast milk

Casas L, et al. (2011) <sup>57</sup>	Spain	120/30	Urinary concentrations of all phthalate metabolites were higher in the children than in the pregnant women up to 4 times according to kind of phthalates	4.4(woman)/6.2(2-years) <sup>b,c</sup> 17.3(woman)/57.4(2-years) <sup>b,c</sup>	Urine
Jurewicz J, et al. (2013)	Poland	269	Urinary phthalate metabolites levels were significantly associated with a decrease in sperm motility and testosterone level and an increase sperm DNA damage and sperm aneuploidy	15.1(3.0) 19.5(2.6)	Urine, semen
Langer S, et al. (2014) <sup>31</sup>	Denmark	441	The median concentrations of the phthalate metabolites in urine children in this study tended to be similar to those reported in other studies The mass fractions of phthalates in dust significantly correlated with the concentrations of phthalates' metabolites except for DEHP	4.6(2.4) <sup>b</sup> 32.4(24.4) <sup>b</sup>	Urine, dust
Kim S, et al. (2014) <sup>58</sup>	Korea	39	The level of MiBP and MnBP in urine among Korean children were 8 and 3 times greater than those reported for US children Consumption of dairy products or meat, and use of a plastic material were significantly associated with the DEHP metabolites or MnBP levels	13.2 <sup>c</sup> 79.1 <sup>c</sup>	Urine

Abbreviation: GM, geometric mean, SD, Standard deviation. <sup>a</sup>All values are for geometric means unless stated otherwise( $\mu\text{g/g}$  creatinine), the values of the line above is for concentration of MEHP(mono-(2-ethylhexyl)phthalate) and the values of the next line is for the concentration of 5OH-MEHP(mono-(2-ethyl-5-hydroxyhexyl)phthalate), <sup>b</sup>Values not adjusted with creatinine concentration( $\text{ng}/\text{m}\ell$ ), <sup>c</sup>Values for medians

Generally, the ingestion of food contaminated with phthalates is regarded as a major exposure route for the general population.<sup>26, 27, 59</sup> Contamination of food can occur during processing, handling, transportation, packaging, and storage. Other sources of phthalate exposure are reported to be related to the use of personal-care and cosmetic products and consumer products such as clothing and vinyl gloves.<sup>27</sup> For example, it has been reported that for long-chain phthalates, such as DEHP and DINP, food seems to be the dominant exposure route in adults, but for short-chain phthalates, such as DBP, DiBP, and BBP, sources other than food have equal importance.<sup>60</sup>

The degradation of consumer products can contaminate indoor dust and provide a significant source of phthalates. However, only a few studies have investigated phthalate sources in indoor dust. One epidemiological study demonstrated that PVC flooring in homes was associated with bronchial obstruction and inferred that the plasticizers used in PVC synthesis are the agents responsible for disease.<sup>61</sup> Other studies have shown that the use of products such as PVC flooring is strongly associated with phthalate concentrations in dust, although these are not the only sources of phthalates.<sup>43,</sup>

62, 63

**Phthalate exposure in children.** As outlined in the ‘Faroes Statement’ on the effects of environmental chemical exposure on human health and development, children’s health is especially important in conjunction with developmental toxicity risks. In addition to the hazardous material exposure dose in the child, prenatal and early postnatal exposure is a critical factor in developmental toxicity.<sup>64</sup> The phthalate exposure level in children was reported to be even higher than in adults. For example, in infants and toddlers, it is estimated that the total intake of DEHP might be approximately two to three times higher than that of an adult as a result of exposure to products that contain DEHP.<sup>59</sup> Studies have also revealed that children have significantly higher (~ 2-4-fold) levels of phthalate metabolites compared with adolescents and adults.<sup>50, 53, 56, 57</sup>

Children are considered to be at higher risk of phthalate exposure, because pharmacokinetic differences between children and adults may result in greater absorption of phthalates, greater conversion of phthalates to their metabolites, and reduced excretion of metabolites in children.<sup>65</sup> Children may be more pharmacodynamically sensitive to the adverse effects of phthalates than adults. Additionally, because the blood-testis barrier forms just before puberty in humans, its permeability is higher in children.<sup>66</sup> Therefore, children are considered to have an increased risk for the adverse effects of phthalates.

**Phthalate exposure in nursery schools.** Most studies on phthalate exposure have considered the health risks in children, and most data, especially that on the mass fractions of phthalates in dust, have been collected in homes.<sup>21, 32</sup>

While economic activity in most countries has increased markedly in recent decades, the time for parenting has subsequently become limited and attitudes towards childcare have been altered.<sup>67</sup> Employment opportunities for mothers have created a demand for early education as part of childcare, and the number of children enrolled in pre-primary schools has increased dramatically. This trend has also extended to the children of non-employed mothers.<sup>68</sup> When not at home, children now spend most of their time in nurseries. However, few studies have investigated the mass fractions of phthalates in dust present in nursery schools.<sup>36, 37, 45</sup> The few studies that have been conducted focused on certain types of phthalates, and attempts to determine the sources of phthalates in the nursery have not been successful.

Therefore, it would be valuable to evaluate the levels of phthalate contamination in nurseries to assess the possibility of phthalate exposure in children. If the sources of phthalates in the indoor environment can be

determined, this would greatly assist the development of an environmental management strategy.

## **1.2. OBJECTIVES**

The overall objectives of this study were to evaluate the mass fractions of phthalates in dust samples from nursery school classrooms and to identify their sources. Therefore, the specific objectives of this study were as follows:

- 1) To evaluate phthalate levels in nursery schools and to determine the key factors influencing phthalate concentrations by focusing on the characteristics of the building.
- 2) To investigate the level of usage of PVC products, as possible phthalate sources, in nursery schools and to identify the key sources of phthalates according to the types of consumer products used regularly in nursery schools.
- 3) To compare the effectiveness of two sampling methods (sampling dust using a modified vacuum cleaner and dust collection from the bag of the regularly used vacuum cleaner), for the assessment of phthalates in indoor dust.

Fig 1-1 shows the experimental design. There are many factors that affect the mass fractions of phthalates in indoor dust, including the types and concentrations of phthalates in PVC products, the age of the product, frequency of use, maintenance and housekeeping practices, and the building characteristics. It would be impractical to investigate all of these factors within a single investigation. However, it was possible to confirm the number of PVC materials in use and how the buildings were utilized and maintained. Considering these limitations, we investigated the key factors affecting the phthalate concentration in indoor dust.

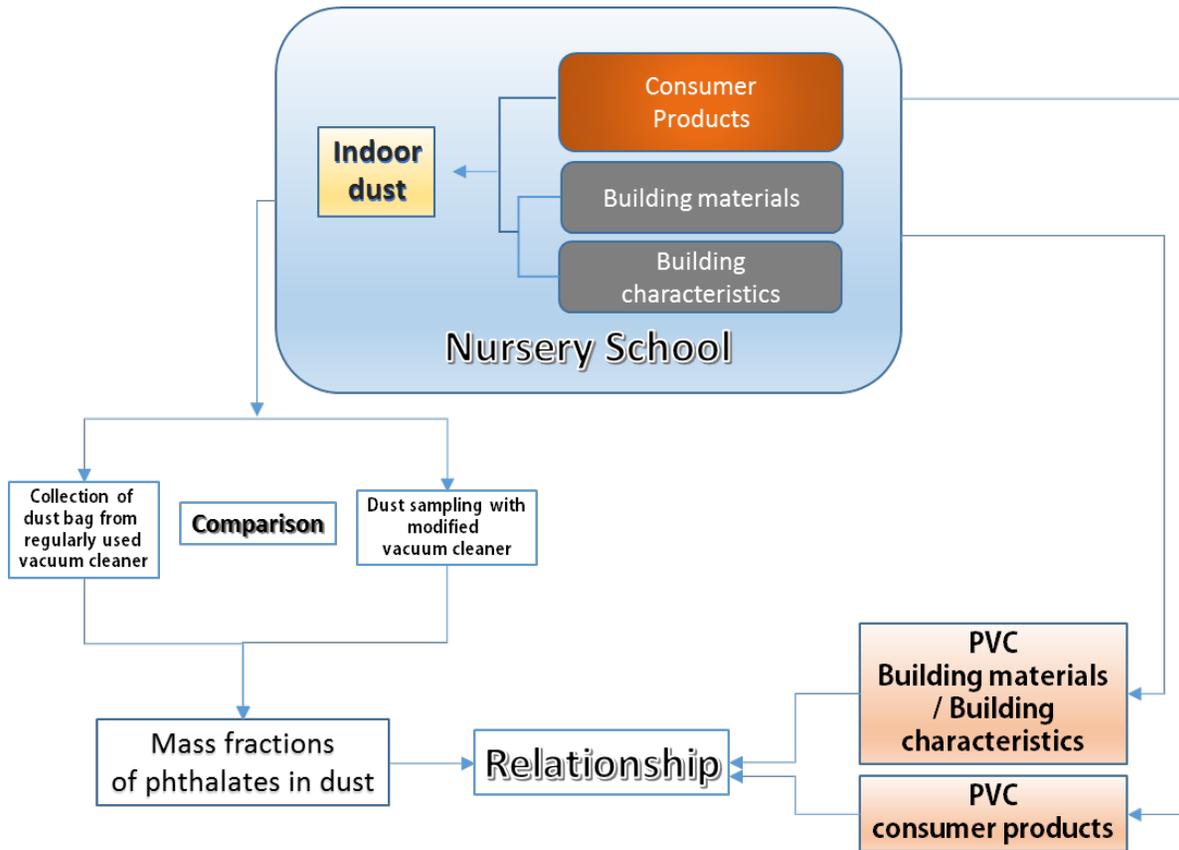


Figure 1-1. The experimental design.

## REFERENCES

1. Thompson, R. C.; Moore, C. J.; vom Saal, F. S., et al. Plastics, the environment and human health: current consensus and future trends. *Philosophical Transactions of the Royal Society B: Biological Sciences* **2009**, *364* (1526), 2153-2166.
2. Braun, D. Poly(vinyl chloride) on the way from the 19th century to the 21st century. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (3), 578-586.
3. Plastics Europe Plastics - the Facts 2013. <http://www.plasticseurope.org/> (14 April),
4. Plasticisers Information Center Plasticisers. <http://www.plasticisers.org> (12 March),
5. Cadogan, D. F.; Howick, C. J., Plasticizers. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000; Vol. 27, pp 509-618.
6. Lorz, P. M.; Towae, F. K.; Enke, W., et al., Phthalic Acid and Derivatives. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000; Vol. 27, pp 131-180.

7. Ambrogi, V.; Carfagna, C.; Pannico, M., et al., *Phthalates*. NOVA Science Publisher, Inc.: New York, 2012; p 211-224.
8. Kamrin, M. A.; Mayor, G. H. Diethyl Phthalate: A Perspective. *J. Clin. Pharmacol.* **1991**, *31* (5), 484-489.
9. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of butyl benzyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 453-487.
10. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-butyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 489-527.
11. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di(2-ethylhexyl) phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 529-653.
12. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-hexyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 709-719.

13. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-octyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 721-734.
14. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-isononyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 679-708.
15. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-isodecyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 655-678.
16. Fisher, J. S. Environmental anti-androgens and male reproductive health: focus on phthalates and testicular dysgenesis syndrome. *Reproduction* **2004**, *127* (3), 305-315.
17. Swan, S. H.; Main, K. M.; Liu, F., et al. Decrease in anogenital distance among male infants with prenatal phthalate exposure. *Environ. Health Perspect.* **2005**, *113* (8), 1056-1061.
18. Smith, C. A.; Holahan, M. R., *Phthalates*. NOVA Science Publisher, Inc.: New York, 2012; p 179-195.

19. Braman, S. S. THE global burden of asthma\*. *CHEST Journal* **2006**, *130* (1\_suppl), 4S-12S.
20. Jaakkola, J. J. K.; Verkasalo, P. K.; Jaakkola, N. Plastic Wall Materials in the Home and Respiratory Health in Young Children. *Am. J. Public Health* **2000**, *90* (5), 797-799.
21. Bornehag, C. G.; Sundell, J.; Weschler, C. J., et al. The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. *Environ. Health Perspect.* **2004**, *112* (14), 1393-1397.
22. Deutsche, T.; Reiter, R.; Butte, W., et al. A controlled challenge study on di (2-ethylhexyl) phthalate (DEHP) in house dust and the immune response in human nasal mucosa of allergic subjects. *Environ. Health Perspect.* **2008**, *116* (11), 1487-1493.
23. Kolarik, B.; Naydenov, K.; Larsson, M., et al. The association between phthalates in dust and allergic diseases among Bulgarian children. *Environ. Health Perspect.* **2008**, *116* (1), 98-103.
24. Jaakkola, J.; Knight, T. L. The role of exposure to phthalates from polyvinyl chloride products in the development of asthma and allergies: a systematic review and metaanalysis. *Environ. Health Perspect.* **2008**, *116* (7), 845-53.

25. Bornehag, C. G.; Nanberg, E. Phthalate exposure and asthma in children. *Int. J. Androl.* **2010**, *33* (2), 333-345.
26. Wittassek, M.; Koch, H. M.; Angerer, J., et al. Assessing exposure to phthalates – The human biomonitoring approach. *Molecular Nutrition & Food Research* **2011**, *55* (1), 7-31.
27. Schettler, T. Human exposure to phthalates via consumer products. *Int. J. Androl.* **2006**, *29* (1), 134-139.
28. Cizdziel, J. V.; Hodge, V. F. Attics as archives for house infiltrating pollutants: Trace elements and pesticides in attic dust and soil from southern Nevada and Utah. *Microchem. J.* **2000**, *64* (1), 85-92.
29. Butte, W.; Heinzow, B. Pollutants in house dust as indicators of indoor contamination. *Rev. Environ. Con. and Tox.* **2002**, *175*, 1-46.
30. Liroy, P. J.; Freeman, N. C.; Millette, J. R. Dust: a metric for use in residential and building exposure assessment and source characterization. *Environ. Health Perspect.* **2002**, *110* (10), 969.
31. Langer, S.; Bekö, G.; Weschler, C. J., et al. Phthalate metabolites in urine samples from Danish children and correlations with phthalates in dust samples from their homes and daycare centers. *Int. J. Hyg. Environ. Health* **2014**, *217* (1), 78-87.

32. Øie, L.; Hersoug, L. G.; Madsen, J. Ø. Residential exposure to plasticizers and its possible role in the pathogenesis of asthma. *Environ. Health Perspect.* **1997**, *105* (9), 972-978.
33. Weschler, C. J.; Salthammer, T.; Fromme, H. Partitioning of phthalates among the gas phase, airborne particles and settled dust in indoor environments. *Atmos. Environ.* **2008**, *42* (7), 1449-1460.
34. Otake, T.; Yoshinaga, J.; Yanagisawa, Y. Exposure to phthalate esters from indoor environment. *J. Exposure Anal. Environ. Epidemiol.* **2004**, *14* (7), 524-528.
35. Axel Clausen, P.; Lindeberg Bille, R. L.; Nilsson, T., et al. Simultaneous extraction of di(2-ethylhexyl) phthalate and nonionic surfactants from house dust: Concentrations in floor dust from 15 Danish schools. *J. Chromatogr. A* **2003**, *986* (2), 179-190.
36. Wilson, N. K.; Chuang, J. C.; Lyu, C., et al. Aggregate exposures of nine preschool children to persistent organic pollutants at day care and at home. *J. Exposure Anal. Environ. Epidemiol.* **2003**, *13* (3), 187-202.
37. Morgan, M. K.; Sheldon, L.; Croghan, C. *A pilot study of children's total exposure to persistent pesticides and other persistent organic pollutants (CTEPP)*; Washington, DC, 2004.

38. Becker, K.; Seiwert, M.; Angerer, J., et al. DEHP metabolites in urine of children and DEHP in house dust. *Int. J. Hyg. Environ. Health* **2004**, *207* (5), 409-417.
39. Guo, Y.; Kannan, K. Comparative Assessment of Human Exposure to Phthalate Esters from House Dust in China and the United States. *Environ. Sci. Technol.* **2011**, *45* (8), 3788-3794.
40. Gevao, B.; Al-Ghadban, A. N.; Bahloul, M., et al. Phthalates in indoor dust in Kuwait: Implications for non-dietary human exposure. *Indoor Air* **2013**, *23* (2), 126-133.
41. Huang, Y.; Chen, L.; Peng, X., et al. PBDEs in indoor dust in South-Central China: Characteristics and implications. *Chemosphere* **2010**, *78* (2), 169-174.
42. Rudel, R. A.; Camann, D. E.; Spengler, J. D., et al. Phthalates, Alkylphenols, Pesticides, Polybrominated Diphenyl Ethers, and Other Endocrine-Disrupting Compounds in Indoor Air and Dust. *Environ. Sci. Technol.* **2003**, *37* (20), 4543-4553.
43. Bornehag, C. G.; Lundgren, B.; Weschler, C. J., et al. Phthalates in indoor dust and their association with building characteristics. *Environ. Health Perspect.* **2005**, *113* (10), 1399-1404.

44. Kolarik, B.; Bornehag, C. G.; Naydenov, K., et al. The concentrations of phthalates in settled dust in Bulgarian homes in relation to building characteristic and cleaning habits in the family. *Atmos. Environ.* **2008**, *42* (37), 8553-8559.
45. Langer, S.; Weschler, C. J.; Fischer, A., et al. Phthalate and PAH concentrations in dust collected from Danish homes and daycare centers. *Atmos. Environ.* **2010**, *44* (19), 2294-2301.
46. Whitehead, T.; Metayer, C.; Buffler, P., et al. Estimating exposures to indoor contaminants using residential dust. *J. Expo. Sci. Environ. Epidemiol.* **2011**, *21* (6), 549-564.
47. Navarro, R.; Pérez Perrino, M.; Gómez Tardajos, M., et al. Phthalate plasticizers covalently bound to PVC: plasticization with suppressed migration. *Macromolecules* **2010**, *43* (5), 2377-2381.
48. Blount, B. C.; Silva, M. J.; Caudill, S. P., et al. Levels of seven urinary phthalate metabolites in a human reference population. *Environ. Health Perspect.* **2000**, *108* (10), 979.
49. Koch, H. M.; Drexler, H.; Angerer, J. An estimation of the daily intake of di(2-ethylhexyl)phthalate (DEHP) and other phthalates in the general population. *Int. J. Hyg. Environ. Health* **2003**, *206* (2), 77-83.

50. Silva, M. J.; Barr, D. B.; Reidy, J. A., et al. Urinary levels of seven phthalate metabolites in the U.S. population from the National Health and Nutrition Examination Survey (NHANES) 1999-2000. *Environ. Health Perspect.* **2004**, *112* (3), 331-8.
51. Fromme, H.; Bolte, G.; Koch, H. M., et al. Occurrence and daily variation of phthalate metabolites in the urine of an adult population. *Int. J. Hyg. Environ. Health* **2007**, *210* (1), 21-33.
52. Wittassek, M.; Wiesmuller, G. A.; Koch, H. M., et al. Internal phthalate exposure over the last two decades--a retrospective human biomonitoring study. *Int. J. Hyg. Environ. Health* **2007**, *210* (3-4), 319-33.
53. Becker, K.; Güen, T.; Seiwert, M., et al. GerES IV: Phthalate metabolites and bisphenol A in urine of German children. *Int. J. Hyg. Environ. Health* **2009**, *212* (6), 685-692.
54. Suzuki, Y.; Niwa, M.; Yoshinaga, J., et al. Exposure assessment of phthalate esters in Japanese pregnant women by using urinary metabolite analysis. *Environ. Health and Preve. Med.* **2009**, *14* (3), 180-187.
55. Guo, Y.; Alomirah, H.; Cho, H. S., et al. Occurrence of phthalate metabolites in human urine from several Asian countries. *Environ. Sci. Technol.* **2011**, *45* (7), 3138-44.

56. Lin, S.; Ku, H. Y.; Su, P. H., et al. Phthalate exposure in pregnant women and their children in central Taiwan. *Chemosphere* **2011**, *82* (7), 947-55.
57. Casas, L.; Fernández, M. F.; Llop, S., et al. Urinary concentrations of phthalates and phenols in a population of Spanish pregnant women and children. *Environ. Int.* **2011**, *37* (5), 858-866.
58. Kim, S.; Kang, S.; Lee, G., et al. Urinary phthalate metabolites among elementary school children of Korea: Sources, risks, and their association with oxidative stress marker. *Sci. Total Environ.* **2014**, *472* (0), 49-55.
59. Meek, M. E.; Chan, P. K. L. Bis(2-ethylhexyl)phthalate: Evaluation of risks to health from environmental exposure in Canada. *J. Environ. Sci. Health, Part C* **1994**, *12* (2), 179-194.
60. Koch, H. M.; Müller, J.; Wittassek, M., et al. Influence of Alimentary Abstinence on Body Burden to Phthalates. *Epidemiology* **2006**, *17* (6), S300.
61. Jaakkola, J. J.; Øie, L.; Nafstad, P., et al. Interior surface materials in the home and the development of bronchial obstruction in young children in Oslo, Norway. *Am. J. Public Health* **1999**, *89* (2), 188-192.
62. Zhang, Q.; Lu, X. M.; Zhang, X. L., et al. Levels of phthalate esters in settled house dust from urban dwellings with young children in Nanjing, China. *Atmos. Environ.* **2013**, *69*, 258-264.

63. Carlstedt, F.; Jönsson, B. A. G.; Bornehag, C. G. PVC flooring is related to human uptake of phthalates in infants. *Indoor Air* **2013**, *23* (1), 32-39.
64. Grandjean, P.; Bellinger, D.; Bergman, Å., et al. The Faroes statement: human health effects of developmental exposure to chemicals in our environment. *Basic Clin. Pharmacol. Toxicol.* **2008**, *102* (2), 73-75.
65. Food, U.; Administration, D. Safety assessment of Di-(2-ethylhexyl) phthalate (DEHP) released from PVC medical devices. *Center for Devices and Radiological Health* **2001**.
66. Latini, G.; De Felice, C.; Verrotti, A. Plasticizers, infant nutrition and reproductive health. *Reprod. Toxicol.* **2004**, *19* (1), 27-33.
67. Mindlin, M.; Jenkins, R.; Law, C. Essay: Maternal employment and indicators of child health: a systematic review in pre-school children in OECD countries. *J. Epidemiol. Community Health* **2009**, *63* (5), 340-350.
68. Bianchi, S. Maternal employment and time with children: Dramatic change or surprising continuity? *Demography* **2000**, *37* (4), 401-414.

## **CHAPTER 2.**

### **Phthalate levels in nursery schools and related factors**

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# Phthalate levels in nursery schools and related factors

**ABSTRACT.** Phthalate esters, which are known endocrine disruptors, are ubiquitously present throughout indoor environments. Leaching from building materials may be a major source of phthalate esters. In this study, we evaluated phthalate ester concentrations in dust samples from 64 classrooms located in 50 nursery schools and explored the critical factors affecting phthalate concentrations, especially with regard to building materials. Dust was sampled by a modified vacuuming method, and building materials were assessed using a portable X-ray fluorescence (XRF) analyzer to determine whether they contained polyvinyl chloride. Di-n-butyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), and di-isononyl phthalate (DINP) were the most frequently detected phthalates. Of these, DEHP was the most abundant phthalate, with a geometric mean of 3,170  $\mu\text{g/g}$  dust, and concentrations were significantly correlated with the area of polyvinyl chloride (PVC)-verified flooring. DINP, which has not been well-reported in other studies, was the second-most abundant phthalate, with a geometric mean of 688  $\mu\text{g/g}$  dust, and showed a critical relationship with the number of children in the institution and the

agency operating the nursery school. This is the first study to verify the sources of phthalates with an XRF analyzer and to evaluate the relationship between phthalate concentrations and PVC-verified materials.

## **INTRODUCTION**

Polyvinyl chloride (PVC) was produced on an industrial scale at the end of the 1920s. After World War II, the use of PVC exploded, and PVC production has since grown worldwide at a rate of more than 4% per year for many years. It is presently the second highest plastic product produced, by volume.<sup>1</sup>

To obtain the desired properties, PVC is sometimes mixed with large amounts of plasticizers. The amount of additives in a PVC formulation is determined by the required properties, and ranges between 15–60% by weight. For thermodynamic reasons, plasticizers tend to leach into the environment.<sup>2</sup> Phthalates have commonly been used as a primary plasticizer component because they increase flexibility, workability, or distensibility.<sup>3</sup>

The demand for phthalates in the market increased dramatically after it was found that they could replace the more expensive plasticizer camphor.<sup>4</sup> Phthalates have been commercially used in a variety of consumer products and industrial goods. For example, di-n-butyl phthalate (DBP) is used mainly as a

coalescing aid in latex adhesives. DBP is also used as a plasticizer in cellulose plastics and as a solvent for dyes.<sup>5</sup> The largest use of butyl benzyl phthalate (BBP) is in vinyl tile. BBP is also employed as a plasticizer in PVC, which is used to manufacture food conveyor belts, carpet tile, artificial leather, tarps, etc.<sup>6</sup> Di(2-ethylhexyl) phthalate (DEHP) is one of the most common phthalates and is used mainly in buildings, cars, and children's products, as well as food packaging and medical devices.<sup>7</sup> Di-isononyl phthalate (DINP) is largely used in flooring, wire, cables, toys, etc.<sup>8</sup> In contrast to the aforementioned phthalates, there are no known commercial uses for pure di-n-octyl phthalate (DnOP), although it constitutes ~20% of all C6–10 phthalate substances.<sup>9</sup>

Researchers have conducted various studies to assess the relationship between exposure to phthalates and their health effects. Many studies have revealed an association between phthalate exposure and reproductive and developmental effects.<sup>10, 11</sup> More recently, phthalate exposure has been regarded as one of the risk factors for atopic diseases in children.<sup>12, 13</sup> In some studies, indoor dust was shown to be significantly contaminated with phthalates, and phthalate concentrations were associated with building characteristics such as the year of construction and the presence of PVC flooring or wall material.<sup>14, 15</sup>

As outlined in the ‘Faroes Statement’ on the human health effects of developmental exposure to environmental chemicals, children’s health is especially important in conjunction with developmental toxicity risks. In addition to the dose of the hazardous material, prenatal and early postnatal exposure is a critical factor in developmental toxicity.<sup>16</sup> It is now well known that phthalates are endocrine disruptors. Most studies of phthalate exposure have addressed health risks in children, and most data, especially for the mass fraction of phthalates in dust, have been collected in homes.<sup>17, 18</sup>

Nursery schools are one of the places where children spend the most time, apart from their homes. However, few studies have evaluated the mass fraction of phthalates in dust at nursery schools.<sup>19-21</sup> Moreover, it is noteworthy that these few studies focused on certain types of phthalates, and unfortunately, the attempts to determine the sources of phthalates in the nursery school environments were not sufficient.

The aims of the present study were to evaluate phthalate contamination levels in nursery schools and to explore the critical factors related to phthalate concentrations, focusing especially on building characteristics.

## **METHODS**

**Building selection.** The buildings to be studied were selected as part of an intensive environmental management project for nursery schools sponsored by the Seoul Medical Center. From March to October 2012, 50 public or private nursery schools, including daycare centers and kindergartens located in 25 autonomous districts in Seoul, volunteered for this project. Each facility cares for 40–222 children (average = 136) ~1–7 years in age.

**Building investigation.** A checklist was developed for investigating building characteristics, and questionnaires were completed by the respective nursery school teachers. The list of items included the year of construction, timing of building occupation, timing of renovations, recent purchase of furniture, ventilation method, number of cleanings per week, and number of times per week that surfaces were wiped with a damp cloth. Ventilation types were classified as local air conditioning and natural ventilation systems. The frequencies of wiping with damp cloth was divided into two groups on the basis of 4 times per month.

**Dust sampling.** Indoor dust has been used as a medium for assessing human exposure to indoor contaminants through inhalation, inadvertent ingestion, or direct absorption through the skin.<sup>22</sup> The method for dust sampling was modified from Rudel et al.<sup>23</sup> Dust was collected on a cellulose extraction thimble (external diameter, 28 mm; internal diameter, 26 mm; length, 100 mm;

Advantec MFS, Inc., Tokyo, Japan) mounted on a vacuum cleaner. In each of the 50 nursery schools, two classrooms were recommended by the director of the nursery school as representative of the school. Dust was vacuumed by slowly and lightly drawing the crevice tool just above the surfaces of upholstery, windowsills, household appliances, furniture, etc. The crevice tool and other parts of the vacuum cleaner were composed of phthalate-free materials. Sampled dust was removed from the cellulose thimble and placed in a pre-cleaned glass vial with a Teflon-lined lid. To prevent cross-contamination, all of the equipment was cleaned between samples using a series of ultrasonic cleaning, several washes with distilled water, and hot-air drying.

The samples were kept in a cooler and shipped to the laboratory on the same day. After delivery, the samples were stored at -20°C until analyzed. Large debris was physically extracted, and dust was sieved to < 100-µm particle size and weighed.

**Chemical analysis.** Eight phthalates were analyzed: dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, BBP, DEHP, DNOP, DINP, and diisodecyl phthalate (DIDP).

Dust sample extraction and analysis was modified from Becker et al.<sup>24</sup> and Bornehag et al.<sup>18</sup> Each 30-mg dust sample was extracted, in a pre-cleaned, 20-

mL glass vial, by ultrasonification for 1 h, using 10 mL of cyclohexane containing anthracene and chrysene d-12 as internal standards. An aliquot from each vial was injected into a gas chromatograph/mass-selective detector (GC/MSD; HP 6890 plus/HP 6973 MSD; USA) and analyzed using the selected ion monitoring mode. A blank was analyzed with every 10 samples. Additionally, blanks ( $n = 7$ ) spiked with each phthalate were prepared and analyzed along with samples to determine recovery efficiency. The recovery efficiency ranged from 96.3 to 137.0%, and the relative standard deviation (RSD) was between 2.1 and 18.0% according to the type of phthalate (see supplementary Table S1). The instrumental detection limit (IDL) was calculated as three times the standard deviation of seven replicate measurements of the lowest standard. The method detection limits (MDLs) were calculated by the IDLs, the volume of extracts, and sample weights. The MDLs for DMP, DEP, DBP, BBP, DEHP, DNOP, DINP, and DIDP were 4.1, 4.9, 5.3, 10.6, 13.0, 7.7, 154.5, and 202.3  $\mu\text{g/g}$  dust, respectively. Concentrations below the MDL were set to  $1/\sqrt{2}$  MDL for subsequent calculations because most of the geometric standard deviations of detected phthalates were below 2.0.<sup>25</sup>

**PVC verification of surface materials.** To verify the PVC materials as a phthalate source, we used a portable X-ray fluorescence unit (XRF; Olympus

INNOV-X Delta/Standard; USA), which applies a nondestructive method to detect elements with atomic numbers up to 92. All building materials, interior materials, and furniture, including flooring, wall paper, windowsills, molding, curtains, blinds, and furniture upholstery, were examined to determine whether they contained PVC. Three separate measurements of 40 s were performed for each item, covering the entire target area. According to manufacturers' specifications, materials can be verified as PVC products when the chlorine concentration is >50,000 ppm. For materials verified as PVC products, the area was measured for analysis as an independent factor for phthalate concentration.

**Statistical analysis.** Most distributions of the detected phthalate concentrations were right skewed, and the logarithmically transformed data were evaluated graphically using probability plots (Figure 2-1). In the case of BBP, its detection rate was only 25.0%, so it was excluded from the statistical analysis because it would result in biased estimates.<sup>25</sup> Phthalate concentrations are reported as geometric means, arithmetic means, and medians according to their type. Pearson's correlation was performed to assess correlations within log-transformed phthalate concentrations. Univariate linear regression was performed to assess relationships between the log-transformed phthalate concentrations and related factors. The most important variables in a

univariate analysis, those with  $p$ -values  $< 0.05$ , were entered into a multivariate analysis. The factors included were areas verified as PVC, construction period of the building, number of children in the institution, age of children, and the agency operating the nursery school. A multiple linear regression model was used with the backward elimination method. For the final models, differences were considered significant at  $p < 0.05$ . Model diagnostics were carried out with plots of residuals against predicted values and the standardized normal probability plots. Results of diagnostics indicated that the model assumptions were robust for the dataset. All analyses were performed using SPSS 20.0 (IBM, Armonk, NY), and graphs were drafted with SigmaPlot 8.0 (SPSS, San Jose, California, USA).

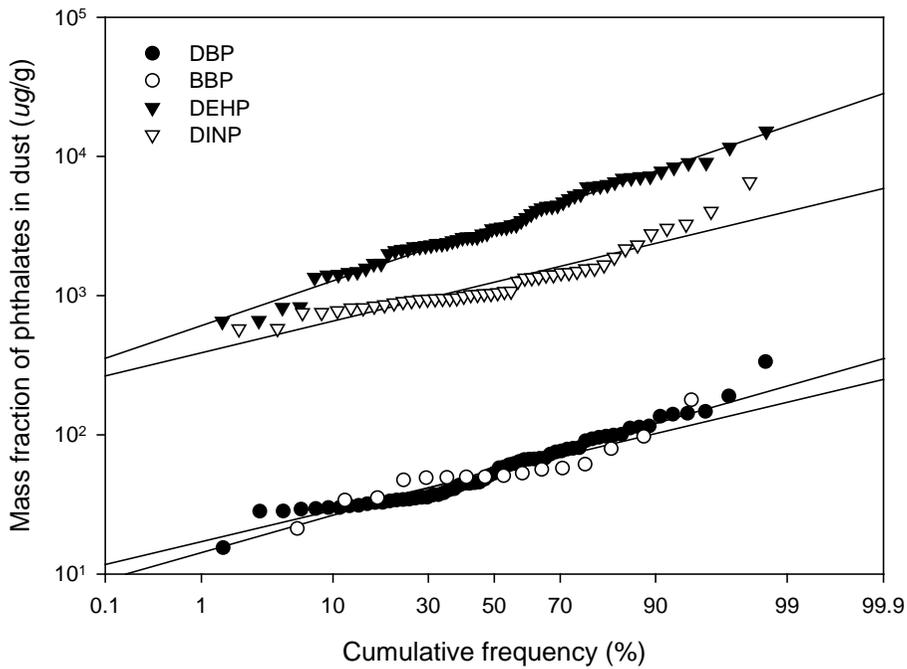


Figure 2-1. Concentration distribution of phthalates.

## RESULTS

The general characteristics of the nursery schools and classrooms are summarized in Table 2-1. Of the 100 targeted classrooms, dust samples sufficient for analysis were collected in 64 classrooms at 50 nursery schools; one classroom was surveyed at 36 nursery schools, and two classrooms were surveyed at 14 nursery schools. According to the teachers, nearly all the rooms

were cleaned at least once a day; thus, it was difficult for the professional inspectors to collect sufficient dust for analysis. The numbers and ages of children cared for by the institution, building history, frequency of cleaning, ventilation type, and PVC-verified area did not differ among management entities. The exception was the use of an air cleaner; nursery schools managed by a private entity tended to use air cleaners more often than did public institutions.

Table 2-1. General characteristics of inspected buildings

Characteristic	Public			Private			Total	
	N	Mean ± SD	Min-Max	N	Mean ± SD	Min-Max	N	Mean ± SD
Number of children								
In institution <sup>a</sup>	32	137±37.8	40-222	18	134±35.8	84-205	50	136±36.7
In classroom <sup>b</sup>	40	29±11.9	7-66	24	29±12.3	9-51	64	29±12.0
Age of children	40	5.4±0.9	3.5-7	24	5.4±1.0	3.5-7	64	5.4±0.9
Building history (years) <sup>c</sup>								
Construction period	38	14.4±7.9	2-29	22	19.3±12.3	3-44	60 <sup>d</sup>	16.2±9.9
Institution opening period	38	17.3±9.0	1-31	22	17.6±12.0	3-44	60 <sup>d</sup>	17.5±10.1
Recent renovation period	29	1.2±1.0	0-4	17	3.1±3.6	0-12	46 <sup>e</sup>	1.9±2.5
Ventilation type (%)								

Characteristic	Public			Private			Total
Natural ventilation	25(62.5)			18(75.0)			43(67.2)
Air conditioning	15(37.5)			6(25.0)			21(32.8)
Use of air cleaner (%)							
No	28(70.0)			23(95.8)			51(79.7)
Yes	12(30.0)			1(4.2)			13(20.3)
Frequency of cleaning							
Vacuuuming (/day)	40	1.1±0.4	1-2	23	1.1±0.3	1-2	63 <sup>f</sup> 1.1±0.3
Wiping with damp cloth (/mon)	37	3.8±4.6	0.2-30	23	5.0±8.1	0.2-30	60 <sup>g</sup> 4.3±6.1

Abbreviations: SD, standard deviation; Min, minimum; Max, maximum.

<sup>a</sup>Total number of children cared for by respective institutions. <sup>b</sup>Number of children in the classroom where phthalate measurements were performed. <sup>c</sup>Each period was counted backward from the time when the building was inspected. Construction period: number of years since the building was constructed. Institution opening period: number of years since the institution was first opened. Recent renovation period: number of years since the recent renovation. <sup>d</sup>Four directors or assistant directors did not report the exact year. <sup>e</sup>Eighteen classrooms were not renovated until recently. <sup>f</sup>Researchers could not obtain the exact frequency of cleaning for one classroom. <sup>g</sup>Researchers could not obtain the exact frequency of wiping with a damp cloth for four classrooms.

The concentrations of eight types of phthalates identified in the dust from 64 classrooms, at 50 nursery schools, are listed in Table 2-2. DBP, DEHP, and DINP were the most frequently identified phthalates. DMP, DEP, and DIDP were detected in only 1–3 dust samples, and DNOP was not detected in any dust samples. DEHP had the highest detection rate as well as the highest

concentration, with a geometric mean of 3,170  $\mu\text{g/g}$  dust, followed by DINP, with a geometric mean of 688  $\mu\text{g/g}$  dust. DBP was moderately correlated with DEHP, with a Pearson's correlation coefficient of 0.607 ( $p < 0.01$ ).

Table 2-2. Detection rates and concentrations ( $\mu\text{g/g}$  dust) of phthalates in dust

Phthalate	Detection rate	GM (GSD)	Mean $\pm$ SD	Median	95th percentile
	N (%)				
DBP	63(98.4)	54.5(1.9)	66.9 $\pm$ 50.1	52.0	146
DEHP	64(100.0)	3,170(2.0)	3,950 $\pm$ 2,760	3,030	9,030
DINP	46(71.9)	688(3.2)	1,090 $\pm$ 1,070	946	3,200

Abbreviations: GM, geometric mean; GSD, geometric standard deviation; SD, standard deviation. Phthalates having less than 50 % of detection rate were excluded from this tables: DMP, DEP, BBP, DNOP, and DIDP

**PVC-verified area.** Building materials, interior materials, and furniture upholstery located in each classroom were assessed for PVC using a portable XRF analyzer, and the relevant surface areas of materials verified as PVC were measured (Table 2-3). Three frequently detected phthalates were tested to determine relationships with PVC-verified areas.

Table 2-3. PVC-verified areas related to logarithmically transformed DEHP concentrations ( $\mu\text{g/g}$  dust) in dust in univariate analysis

Surface area(m <sup>2</sup> )	Public		Private		Total	DEHP			
	N(n <sup>a</sup> )	Mean $\pm$ SD	N(n <sup>a</sup> )	Mean $\pm$ SD	N	Mean $\pm$ SD	$\beta$	(SE)	<i>p</i> -value
Total area	40	68.7 $\pm$ 33.9	24	82.4 $\pm$ 38.6	64	73.8 $\pm$ 36.1	0.144	(0.001)	0.256
PVC area <sup>b</sup>									
Flooring	(37)	53.4 $\pm$ 39.2	(24)	70.4 $\pm$ 41.4		59.7 $\pm$ 40.6	0.324	(0.001)	0.009
Wallpaper	(3)	2.3 $\pm$ 10.1	(6)	9.3 $\pm$ 19.6		4.9 $\pm$ 14.6	0.081	(0.003)	0.527
Furniture upholstery <sup>c</sup>	(31)	8.9 $\pm$ 19.6	(23)	6.3 $\pm$ 7.9		7.9 $\pm$ 16.2	-0.110	(0.002)	0.385
Etc. <sup>d</sup>	(14)	3.6 $\pm$ 5.9	(8)	3.8 $\pm$ 8.3		3.7 $\pm$ 6.8	-0.262	(0.005)	0.037

Abbreviation: SD, standard deviation; SE, standard error.

<sup>a</sup>Number of classrooms in which PVC was detected <sup>b</sup>PVC area was measured after being verified by portable XRF determination. <sup>c</sup>Furniture included sofas, bookshelves, tables, and other. <sup>d</sup>Etc. represents interior materials such as curtains, blinds, and window frames.

Only the log-transformed DEHP concentrations showed a weak positive relationship with PVC flooring ( $r^2 = 0.105$ ,  $p < 0.01$ ) as well as a weak negative correlation with interior materials such as curtains, blinds, and window frames ( $r^2 = 0.068$ ,  $p < 0.037$ ).

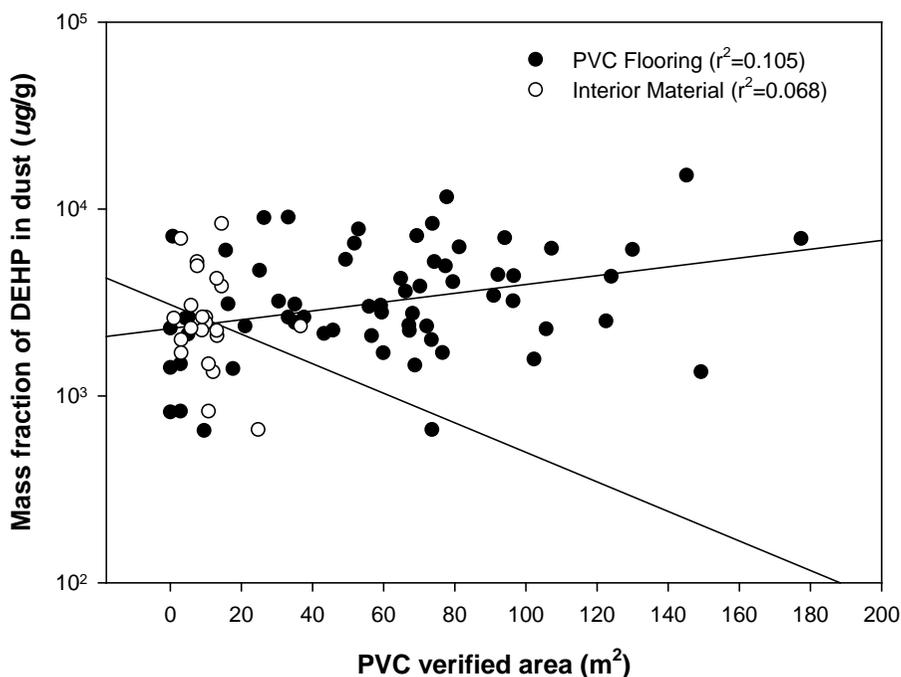


Figure 2-2. Scatterplot of mass fraction of DEHP in dust ( $\mu\text{g/g}$ ) against the corresponding PVC-verified flooring and PVC-verified interior materials.

**Building characteristics.** Table 2-4 summarizes the correlations among the three most frequently detected phthalates and the building characteristics. Of DBP, DEHP, and DINP, only DEHP was significantly correlated with the construction period of the building ( $p = 0.010$ ). There was no difference in phthalate concentrations among patterns of space utilization except for DINP with respect to the number ( $p = 0.004$ ) and age of children ( $p = 0.020$ ) in the institution.

Table 2-4. Building characteristics related to the logarithmically transformed mass fraction of phthalates in dust ( $\mu\text{g/g}$  dust) in univariate analysis

Characteristic	DBP			DEHP			DINP		
	N	$\beta$ (SE)	<i>p</i> -value	$\beta$ (SE)	<i>p</i> -value	$\beta$ (SE)	<i>p</i> -value		
Building history (years) <sup>a</sup>									
Construction period	60 <sup>b</sup>	0.169 (0.004)	0.196	0.331 (0.004)	0.010	0.089 (0.007)	0.496		
Institution opening period	60 <sup>b</sup>	0.051 (0.004)	0.698	0.234 (0.004)	0.072	0.198 (0.007)	0.130		
Recent renovation period	46 <sup>c</sup>	0.237 (0.019)	0.112	0.279 (0.019)	0.060	-0.193 (0.029)	0.198		
Utilization of space									
Children in institution ( <i>n</i> )	64	0.074 (0.001)	0.559	-0.108 (0.001)	0.394	0.357 (0.002)	0.004		
Children in classroom ( <i>n</i> )	64	-0.037 (0.003)	0.769	0.093 (0.003)	0.465	0.088 (0.005)	0.489		

Characteristic		DBP		DEHP		DINP	
Age of children <sup>d</sup>	64	0.045 (0.045)	0.723	-0.042 (0.040)	0.743	0.289 (0.065)	0.020
Space density <sup>e</sup>	64	0.163 (0.004)	0.198	0.121 (0.005)	0.339	0.151 (0.008)	0.235

Abbreviations: SE, standard error. <sup>a</sup>Each period was counted backward from the time when the building was inspected. Construction period: number of years since the building was constructed. Institution opening period: number of years since the institution was first opened. Recent renovation period: number of years since the recent renovation. <sup>b</sup>Four directors or assistant directors did not report the exact year. <sup>c</sup>Eighteen classrooms were not renovated until recently. <sup>d</sup>Age of children refers to the average age of children in the respective classroom. <sup>e</sup>Space density was calculated by dividing classroom area by the number of children.

**Indoor maintenance.** Table 2-5 shows the relationships between the concentrations of phthalates and indoor maintenance practices. Most nursery schools were cleaned very frequently, and some institutions operated an air conditioner or air cleaner in the classrooms. The majority of phthalate concentrations did not differ among the variables, except for significantly higher DBP concentrations in dust sampled from naturally ventilated rooms ( $p = 0.010$ ) compared with dust collected from air conditioned rooms. Cleaning performance in the classroom was not associated with a meaningful difference in any phthalate concentrations.

Table 2-5. Indoor maintenance practices related to the logarithmically transformed mass fraction of phthalates in dust ( $\mu\text{g/g}$  dust) in univariate analysis

Variable	Phthalate concentration, $\mu\text{g/g}$ dust											
	DBP				DEHP				DINP			
	N	GM (GSD)	$\beta$ (SE)	<i>p</i> -value	N	GM (GSD)	$\beta$ (SE)	<i>p</i> -value	N	GM (GSD)	$\beta$ (SE)	<i>p</i> -value
Operating body												
Reference: Public	40	49.8 (2.0)			40	2,950 (1.9)			40	843 (2.7)		
Private	24	63.3 (1.8)	0.181 (0.072)	0.152	24	3,580 (2.0)	0.138 (0.076)	0.275	24	435 (3.8)	-0.278 (0.126)	0.026
Indoor maintenance												
Ventilation												
Reference: Air conditioner	21	40.5 (2.1)			21	2,750 (2.1)			21	707 (3.1)		
Natural	43	63.0 (1.7)	0.321 (0.072)	0.010	43	3,400 (1.9)	0.146 (0.078)	0.248	43	635 (3.3)	-0.044 (0.135)	0.732
Use of air cleaner												
Reference: No	51	54.6 (2.0)			51	3,180 (2.0)			51	725 (3.0)		

Variable	Phthalate concentration, $\mu\text{g/g}$ dust											
	DBP				DEHP				DINP			
	N	GM (GSD)	$\beta$ (SE)	<i>p</i> -value	N	GM (GSD)	$\beta$ (SE)	<i>p</i> -value	N	GM (GSD)	$\beta$ (SE)	<i>p</i> -value
Yes	13	53.9 (1.7)	-0.008 (0.088)	0.952	13	3,120 (2.1)	-0.011 (0.092)	0.931	13	451 (4.0)	-0.165 (0.156)	0.192
Cleaning with a vacuum cleaner <sup>a</sup>												
Reference: Once a day	55	54.8 (1.9)			54	3,160 (1.9)			54	632 (3.3)		
Twice a day	8	55.2 (1.9)	0.003 (0.108)	0.979	8	2,950 (2.3)	-0.034 (0.112)	0.793	8	994 (2.6)	0.131 (0.191)	0.307
Wiping with a damp cloth <sup>b</sup>												
Reference: <4 times/month	27	49.9 (2.0)			27	3,010 (2.1)			27	508 (2.8)		
$\geq 4$ times/month	33	57.8 (1.9)	0.113 (0.074)	0.390	33	3,270 (1.9)	0.060 (0.077)	0.651	33	794 (3.6)	0.190 (0.132)	0.147

Abbreviations: GM, geometric mean; GSD, geometric standard deviation; SE, standard error.

<sup>a</sup>One teacher did not respond regarding the frequency of cleaning with a vacuum cleaner. <sup>b</sup>Four teachers did not respond regarding the frequency of wiping with a damp cloth.

**Multiple linear regression analysis.** The parameters confirmed to be significantly associated with concentrations of phthalates, including PVC flooring area, construction period of the building, number of children in the institution, agency operating the nursery school, and the age of children, were used in a multiple linear regression analysis (Table 2-6). PVC flooring area and construction period were significant factors affecting DEHP concentration, but only PVC flooring area remained in the final regression model. Number and age of children in the institution, as well as the operating agency, were significantly correlated with DINP concentration, but the age of children was removed from the final regression model.

Table 2-6. Multiple linear regression modeling of phthalate concentrations in dust samples

Dependent variables	$\beta$ (SE)	<i>p</i> -value	Modelling Result
DEHP concentration			
Intercept	3.254 (0.078)	< 0.01	N=60
PVC flooring area	0.267 (0.001)	0.038	<i>p</i> = 0.004
Construction period	0.252 (0.004)	0.051	R <sup>2</sup> =0.175
DINP concentration			
Intercept	1.755 (0.371)	< 0.001	N=64

Dependent variables	$\beta$ (SE)	<i>p</i> -value	Modelling Result
Number of children in institution	0.276 (0.002)	0.023	<i>p</i> = 0.001
Operating body <sup>a</sup>	-0.247 (0.118)	0.034	R <sup>2</sup> =0.227
Age of Children	0.205 (0.064)	0.089	

Abbreviations: SE, standard error.

<sup>a</sup>Public institution is the reference.

## DISCUSSION

In this study, we evaluated the mass fraction of phthalates in 64 classrooms at 50 nursery schools and explored the main factors influencing phthalate levels. Compared with other spaces in different countries, the classrooms in the present study were highly contaminated with phthalates, especially DEHP (Table 2-7). DEHP was the most abundant phthalate and was linked with PVC flooring and the construction period of building. Unlike in other studies, whether the flooring was PVC was verified using a portable XRF analyzer; thus, it was possible to quantitatively confirm the relationship between areas of PVC-verified flooring and phthalate concentrations. In addition, DINP has not been well reported in previous studies but was evaluated here as a relatively abundant phthalate significantly related to the number of children in the institution and the operating agency. In contrast, the detection rate of BBP

reported in this study was three to four times lower compared with that in other studies.<sup>14, 15, 21, 26-29</sup> According to the Korean government documents,<sup>30</sup> plasticizers produced about 650,000 tons of phthalates in Korea in 2004, of which 64% was DEHP. They reported that small amounts of DBP were produced; however, BBP was not produced in Korea in 2008. Although we do not know the volume imported and the quantity used, these circumstances may be reflected in the low detection rate of BBP.

Table 2-7. Concentrations of phthalates in dust ( $\mu\text{g/g}$ ) as reported in relevant studies

Reference	Country	Sampling site	N	DBP	BBP	DEHP	DINP	Sampling Method
Øie et al. (1997)	Norway	Homes	38	100 <sup>a</sup>	110 <sup>a</sup>	640 <sup>a</sup>	-	Vacuuming
Clausen et al. (2003) <sup>31</sup>	Denmark	School	15			3,214 <sup>a</sup>		Vacuuming
Rudel et al. (2003) <sup>26</sup>	USA: MA	Homes	119	20.1	45.4	340		Vacuuming
Wilson et al. (2003)	USA: NC	Homes	9	1.2 <sup>a</sup>	5.9 <sup>a</sup>	-	-	Vacuuming
Wilson et al. (2003)	USA: NC	Daycare centers	4	1.9 <sup>a</sup>	3.7 <sup>a</sup>	-	-	Vacuuming
Morgan et al. (2004)	USA: OH	Homes	127	5.2	17	-	-	Vacuuming
Morgan et al. (2004)	USA: OH	Daycare centers	16	15	29	-	-	Vacuuming
Morgan et al. (2004)	USA: NC	Homes	129	5.6	17	-	-	Vacuuming
Morgan et al. (2004)	USA: NC	Daycare centers	13	14	58	-	-	Vacuuming
Becker et al. (2004)	Germany	Home	252	-	-	515	-	Collecting bag <sup>b</sup>
Bornehag et al. (2005)	Sweden	Homes	346	150	135	770	639	Vacuuming
Deutschle et al. (2008)	Germany	Homes	42	49.2 <sup>a</sup>	34.0 <sup>a</sup>	410 <sup>a</sup>	-	Collecting bag <sup>b</sup>
Kolarik et al. (2008)	Bulgaria	Homes	177	9,930	340	1,050	-	Vacuuming
Langer et al. (2010)	Denmark	Homes	497	15	3.7	210	-	Vacuuming

Reference	Country	Sampling site	N	DBP	BBP	DEHP	DINP	Sampling Method
Langer et al. (2010)	Denmark	Daycare centers	151	38	17	500	-	Vacuuming
Guo and Kannan(2011) <sup>27</sup>	China	Homes	75	20.1	0.2	228	-	Sweeping
Guo and Kannan(2011)	USA:NY	Homes	33	13.1	21.1	304	-	Collecting bag <sup>b</sup>
Gevao et al. (2013)	Kuwait	Homes	21	45	8.6	2,256	-	Collecting bag <sup>b</sup>
Zhang et al. (2013)	China	Homes	215	23.7	1.6	183	-	Collecting bag <sup>b</sup>
This study	Korea	Daycare centers	64	52.0	50.4	3,030	946	Vacuuming
				66.9 <sup>a</sup>	60.7 <sup>a</sup>	3,950 <sup>a</sup>	1,090 <sup>a</sup>	

All values are medians unless stated otherwise. <sup>a</sup>Mean concentration. <sup>b</sup>The dust bag was collected from the vacuum cleaner in regular use at the target area.

The concentrations of phthalates in this study were somewhat higher than those in previous studies. DEHP has been reported as the most frequently detected phthalate species and the predominant compound in dust, making up ~69–92% of the total amount of phthalates.<sup>17, 28</sup> Nevertheless, the concentration of DEHP measured in the present study was much higher than that in any other study. This difference could be reasonably explained by the housing culture in Korea, where most indoor spaces tend to be covered with a floor pad, which is highly likely to be made from PVC containing phthalates. Moreover, as explained by Bornehag et al.,<sup>15</sup> the sampling method by which dust is vacuumed directly from the surfaces of building materials, such as windowsills, moldings, and furniture upholstery can also result in higher concentrations of some kinds of phthalates. Specifically, in this study, the mass fraction of phthalates in dust may have been higher because we sampled dust on household appliances, such as ceiling fans, local air conditioners, personal computers, televisions, etc. But the influence of this on the outcome is expected to be low because we checked all materials of household appliances with a portable XRF analyzer during sampling. The results indicated that only two of 94 (2.1 %; data not shown) household appliances were verified as products made of PVC materials.

Although many studies have evaluated the mass fraction of phthalates in dust, only a few have revealed the critical sources of phthalates. One epidemiological study showed that PVC flooring in homes was associated with bronchial obstruction, and the author inferred that the plasticizers used in the synthesis of PVC could be the source of the chemical causing the related disease.<sup>32</sup> Another study showed that PVC products such as PVC flooring had a strong association with concentrations of BBP and DEHP, although these are not the only sources of phthalates.<sup>15</sup> In contrast, some studies found no significant relationship between PVC flooring and the concentrations of phthalates or metabolites of phthalate.<sup>14, 24</sup> Recent investigations of the contribution made by PVC flooring to phthalate concentrations reported a positive correlation.<sup>29, 33</sup> All of the studies, positive or negative, only qualitatively assessed the PVC content of interior materials using questionnaires<sup>14, 24, 33</sup> or a check by trained inspectors.<sup>14, 15, 29, 32</sup> As in other studies, we found that only DEHP was significantly correlated with PVC flooring. However, unlike other studies, we not only verified the PVC materials using a portable XRF analyzer but also measured the surface areas of PVC-verified materials, making it possible to quantitatively analyze the significance of the relationships. As demonstrated by Kolarik et al.<sup>14</sup>, the classification of flooring types has been so arbitrary that PVC verification by

observers has resulted in confusion. Therefore, the statistically confirmed relationship in the current study, based on quantitative methodology, is a more accurate and rigorous result than those of previous studies.

In addition to the area of PVC flooring, DEHP was significantly correlated with the construction period, as observed in another study.<sup>15</sup> PVC flooring in older buildings is likely to contain more phthalates compared with more recent flooring materials. In fact, the dominant plasticizer used in PVC flooring has been DEHP. As concerns regarding the potential health effects of DEHP have increased, other plasticizers (e.g., DINP) have been substituted for DEHP.<sup>34</sup> Such changes in phthalate use may have been reflected in the results of this study.

PVC interior materials such as curtains, blinds, and window frames were negatively correlated with DEHP concentrations. There have been only a few analyses establishing a connection between interior materials and phthalate levels. In the Finnish study, lower respiratory tract symptoms were associated with the presence of plastic wall materials, and the chemicals emitted from the materials were presumed to be causing the symptoms.<sup>35</sup> In the present study, only twenty two buildings had PVC interior materials, and the areas were relatively small compared with the flooring areas (mean areas: 3.7 vs. 59.7 m<sup>2</sup>).

Consequently, more detailed research is needed to accurately assess the relationship between interior materials and phthalate concentrations.

Unlike DEHP, DINP has not been thoroughly investigated in previous studies. Although data for assessing the human health effects of DINP exposure are scant, studies in laboratory animals have revealed that DINP has conceptus developmental toxicity.<sup>8</sup> As the present study has revealed, DINP is a relatively abundant phthalate. Similar to the results of this study, Abb et al.<sup>36</sup> reported that the mass fraction of DINP was the second highest phthalate in indoor dust, behind DEHP. These results are due to the fact that DEHP has been replaced by DINP as a result of government regulations, and thus the use of these two phthalates has displayed opposing trends in Western Europe since 1998.<sup>36</sup> However, unlike DEHP, which was correlated with building characteristics such as PVC flooring, the mass fraction of DINP was related to occupants' characteristics, such as the number of children in the institution and the operating agency; this means that there are other sources of DINP. While DINP was used in the production of flooring, it was also widely used in the toy, construction, and general consumer product markets.<sup>8</sup> For example, DINP was mainly used in various products such as tubings, wires, cables, shoes, sealants, toys, etc.<sup>8</sup> The fact that DINP has been a major plasticizer used in children's toys<sup>37</sup> supports the finding that DINP exposure in infants,

toddlers, and children was much higher than exposure in adults.<sup>38</sup> Therefore, one may infer that those consumer products are the main sources of the mass fraction of DINP in dust. Accordingly, the relationship between the mass fraction of DINP in dust and the agency operating the nursery school may reflect a trend in product purchase, as environmentally friendly products that contain lower amounts of phthalates or that are phthalate free tend to be more expensive. More detailed research on the PVC verification of regularly used consumer products is needed.

Of the phthalates detected in this study, only DINP was related with occupants' characteristics, such as the number of children in the institution. Children's activity likely increases with an increase in the number of children. This increase in activity may increase the abrasion of phthalate-containing surfaces, leading to higher concentrations of phthalates in indoor dust. For example, Webster et al.<sup>39</sup> reported that BDE 209, a nonvolatile compound at room temperature, was transferred to dust via physical processes such as abrasion or weathering. Although the physical properties of each compound are somewhat different, we assumed that, to some extent, the mass fraction of DINP, one of the high-molecular-weight phthalates, may have been the result of physical breakdown. DINP contamination of indoor dust, especially where children spend time, warrants more research.

DINP is the predominant plasticizer currently being used, and the exposure of children to DINP through children's products is a public concern.<sup>8</sup> Infants and toddlers have a much higher exposure to DINP compared with all other consumer groups due to exposure routes unique to their age group.<sup>38</sup> Although DINP has been recognized as an important contaminant to which children are exposed, relatively few data have been published on childhood exposures. Given the presence of DINP in the indoor environment, the routes of exposure for children<sup>33, 38</sup>, and the known toxicity of DINP, a more thorough investigation of DINP is needed.

DBP concentrations differed depending on the ventilation method used. In the present study, we did not measure ventilation rates, but we classified ventilation systems as local air conditioning and natural ventilation systems; none of the nursery schools used a mechanical ventilation system. When children were in the classroom, they engaged in diverse activities including learning, playing, exercising, and even taking naps. In classrooms that were naturally ventilated, windows were opened frequently when occupants felt the indoor air was too warm. The nursery schools equipped with air conditioners had either wall mounted or floor-type air conditioners that circulated internal air only and did not introduce outdoor air. When an air conditioner was operated in a classroom, most of the windows were likely to be closed to

conserve energy. Therefore, classrooms with air conditioners had a lower ventilation rate than did classrooms with natural ventilation through open windows. In practice, opening windows and doors was associated with a higher air exchange rate.<sup>40</sup>

DBP levels were significantly lower in classrooms where an air conditioner was operated. The concentration of DBP in air may be more influenced by ventilation rate than other phthalates are due to the relatively high volatility of DBP. However, it is unclear whether the ventilation rate has an influence on the mass fraction of DBP in dust. It is possible that, in classrooms utilizing natural ventilation, more of the DBP emitted from sources is sorbed to dust as a result of its high volatility.

This study, which determined the mass fraction of phthalates and quantitatively confirmed the critical factors affecting phthalate concentrations, has some limitations. First, more powerful variables are needed to fit the model. In the final multiple regression models, the respective correlation coefficients (i.e.,  $r^2$  values) were very low, which means that the model does not explain much of the variation in the mass fractions of phthalates. Therefore, phthalate-containing sources other than those related to building materials and occupants are needed to explain the variation in the mass fractions of phthalates found in dust. Phthalates are mainly used in PVC products, but they

are also found in a variety of consumer products, such as personal care products.<sup>38</sup> Thus, PVC verification of regularly used consumer products in their respective environments is worth careful consideration. Moreover, expanding the scope of the investigation to non-PVC products such as personal care products should also be considered.

Second, we did not measure certain meaningful factors such as ventilation rates and temperature. If we had measured such factors, we could have better explained the distribution of phthalates in dust according to their physico-chemical properties and characteristics of the microenvironment.

In addition to data from nursery schools, measuring the concentrations of phthalates in dust at children's homes would have allowed us to estimate daily exposure to phthalates. For example, Bekö et al.<sup>41</sup> and Langer et al.<sup>42</sup> collected dust samples both from children's homes and from the daycare center. They estimated airborne concentrations of phthalates using mass fractions of phthalates in the dust from the two major living spaces, which allowed for the estimation of daily phthalate exposure. The microenvironment of home might be different from that of the nursery school. Measuring phthalate concentrations in all major living spaces would provide a more accurate estimation of total phthalate exposure of occupants.

Although phthalate concentrations in indoor dust reflect the possibility of exposure, the present study did not address exposure or health effects. However, the results from this study would be beneficial in designing a study to investigate the relationship between exposure to phthalates and adverse health effects such as atopic diseases, which have been intensively studied.<sup>12, 13, 18</sup> Furthermore, the portable XRF analyzer used in this study can be used in future studies as a non-destructive and cost-effective screening tool for identifying sources of phthalates.

## REFERENCES

1. Braun, D. Poly(vinyl chloride) on the way from the 19th century to the 21st century. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (3), 578-586.
2. Navarro, R.; Pérez Perrino, M.; Gómez Tardajos, M., et al. Phthalate plasticizers covalently bound to PVC: plasticization with suppressed migration. *Macromolecules* **2010**, *43* (5), 2377-2381.
3. Cadogan, D. F.; Howick, C. J., Plasticizers. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000; Vol. 27, pp 509-618.

4. Lorz, P. M.; Towae, F. K.; Enke, W., et al., Phthalic Acid and Derivatives. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000; Vol. 27, pp 131-180.
5. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-butyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 489-527.
6. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of butyl benzyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 453-487.
7. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di(2-ethylhexyl) phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 529-653.
8. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-isononyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 679-708.

9. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-octyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 721-734.
10. Fisher, J. S. Environmental anti-androgens and male reproductive health: focus on phthalates and testicular dysgenesis syndrome. *Reproduction* **2004**, *127* (3), 305-315.
11. Swan, S. H.; Main, K. M.; Liu, F., et al. Decrease in anogenital distance among male infants with prenatal phthalate exposure. *Environ. Health Perspect.* **2005**, *113* (8), 1056-1061.
12. Kolarik, B.; Naydenov, K.; Larsson, M., et al. The association between phthalates in dust and allergic diseases among Bulgarian children. *Environ. Health Perspect.* **2008**, *116* (1), 98-103.
13. Bornehag, C. G.; Nanberg, E. Phthalate exposure and asthma in children. *Int. J. Androl.* **2010**, *33* (2), 333-345.
14. Kolarik, B.; Bornehag, C. G.; Naydenov, K., et al. The concentrations of phthalates in settled dust in Bulgarian homes in relation to building characteristic and cleaning habits in the family. *Atmos. Environ.* **2008**, *42* (37), 8553-8559.

15. Bornehag, C. G.; Lundgren, B.; Weschler, C. J., et al. Phthalates in indoor dust and their association with building characteristics. *Environ. Health Perspect.* **2005**, *113* (10), 1399-1404.
16. Grandjean, P.; Bellinger, D.; Bergman, Å., et al. The Faroes statement: human health effects of developmental exposure to chemicals in our environment. *Basic Clin. Pharmacol. Toxicol.* **2008**, *102* (2), 73-75.
17. Øie, L.; Hersoug, L. G.; Madsen, J. Ø. Residential exposure to plasticizers and its possible role in the pathogenesis of asthma. *Environ. Health Perspect.* **1997**, *105* (9), 972-978.
18. Bornehag, C. G.; Sundell, J.; Weschler, C. J., et al. The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. *Environ. Health Perspect.* **2004**, *112* (14), 1393-1397.
19. Wilson, N. K.; Chuang, J. C.; Lyu, C., et al. Aggregate exposures of nine preschool children to persistent organic pollutants at day care and at home. *J. Exposure Anal. Environ. Epidemiol.* **2003**, *13* (3), 187-202.
20. Morgan, M. K.; Sheldon, L.; Croghan, C. *A pilot study of children's total exposure to persistent pesticides and other persistent organic pollutants (CTEPP)*; Washington, DC, 2004.

21. Langer, S.; Weschler, C. J.; Fischer, A., et al. Phthalate and PAH concentrations in dust collected from Danish homes and daycare centers. *Atmos. Environ.* **2010**, *44* (19), 2294-2301.
22. Whitehead, T.; Metayer, C.; Buffler, P., et al. Estimating exposures to indoor contaminants using residential dust. *J. Exposure Sci. Environ. Epidemiol.* **2011**, *21* (6), 549-564.
23. Rudel, R. A.; Brody, J. G.; Spengler, J. D., et al. Identification of Selected Hormonally Active Agents and Animal Mammary Carcinogens in Commercial and Residential Air and Dust Samples. *J. Air Waste Manage. Assoc.* **2001**, *51* (4), 499-513.
24. Becker, K.; Seiwert, M.; Angerer, J., et al. DEHP metabolites in urine of children and DEHP in house dust. *Int. J. Hyg. Environ. Health* **2004**, *207* (5), 409-417.
25. Hornung, R. W.; Reed, L. D. Estimation of average concentration in the presence of nondetectable values. *Appl. Occup. Environ. Hyg.* **1990**, *5* (1), 46-51.
26. Rudel, R. A.; Camann, D. E.; Spengler, J. D., et al. Phthalates, Alkylphenols, Pesticides, Polybrominated Diphenyl Ethers, and Other Endocrine-Disrupting Compounds in Indoor Air and Dust. *Environ. Sci. Technol.* **2003**, *37* (20), 4543-4553.

27. Guo, Y.; Kannan, K. Comparative Assessment of Human Exposure to Phthalate Esters from House Dust in China and the United States. *Environ. Sci. Technol.* **2011**, *45* (8), 3788-3794.
28. Gevao, B.; Al-Ghadban, A. N.; Bahloul, M., et al. Phthalates in indoor dust in Kuwait: Implications for non-dietary human exposure. *Indoor Air* **2013**, *23* (2), 126-133.
29. Zhang, Q.; Lu, X. M.; Zhang, X. L., et al. Levels of phthalate esters in settled house dust from urban dwellings with young children in Nanjing, China. *Atmos. Environ.* **2013**, *69*, 258-264.
30. Pilju, P.; Jisung, K.; Minsung, K., et al. *Research on the implementation state of voluntary agreement on the restriction of phthalates use*; Ministry of Environment: Seoul, 2009.
31. Axel Clausen, P.; Lindeberg Bille, R. L.; Nilsson, T., et al. Simultaneous extraction of di(2-ethylhexyl) phthalate and nonionic surfactants from house dust: Concentrations in floor dust from 15 Danish schools. *J. Chromatogr. A* **2003**, *986* (2), 179-190.
32. Jaakkola, J. J.; Øie, L.; Nafstad, P., et al. Interior surface materials in the home and the development of bronchial obstruction in young children in Oslo, Norway. *Am. J. Public Health* **1999**, *89* (2), 188-192.

33. Carlstedt, F.; Jönsson, B. A. G.; Bornehag, C. G. PVC flooring is related to human uptake of phthalates in infants. *Indoor Air* **2013**, *23* (1), 32-39.
34. Weschler, C. J. Changes in indoor pollutants since the 1950s. *Atmos. Environ.* **2009**, *43* (1), 153-169.
35. Jaakkola, J. J. K.; Verkasalo, P. K.; Jaakkola, N. Plastic Wall Materials in the Home and Respiratory Health in Young Children. *Am. J. Public Health* **2000**, *90* (5), 797-799.
36. Abb, M.; Heinrich, T.; Sorkau, E., et al. Phthalates in house dust. *Environ. Int.* **2009**, *35* (6), 965-970.
37. Bogen, K.; Boekelheide, K.; Cunningham, M., et al., Report to the US consumer product safety commission by the chronic hazard advisory panel on diisononyl phthalate. In Bethesda: 2001.
38. Wormuth, M.; Scheringer, M.; Vollenweider, M., et al. What Are the Sources of Exposure to Eight Frequently Used Phthalic Acid Esters in Europeans? *Risk Anal.* **2006**, *26* (3), 803-824.
39. Webster, T. F.; Harrad, S.; Millette, J. R., et al. Identifying Transfer Mechanisms and Sources of Decabromodiphenyl Ether (BDE 209) in Indoor Environments Using Environmental Forensic Microscopy. *Environ. Sci. Technol.* **2009**, *43* (9), 3067-3072.

40. Bekö, G.; Toftum, J.; Clausen, G. Modeling ventilation rates in bedrooms based on building characteristics and occupant behavior. *Build. Environ.* **2011**, *46* (11), 2230-2237.
41. Bekö, G.; Weschler, C. J.; Langer, S., et al. Children's Phthalate Intakes and Resultant Cumulative Exposures Estimated from Urine Compared with Estimates from Dust Ingestion, Inhalation and Dermal Absorption in Their Homes and Daycare Centers. *PloS one* **2013**, *8* (4), e62442.
42. Langer, S.; Bekö, G.; Weschler, C. J., et al. Phthalate metabolites in urine samples from Danish children and correlations with phthalates in dust samples from their homes and daycare centers. *Int. J. Hyg. Environ. Health* **2013**, (0).

## **CHAPTER 3.**

### **PVC-verified consumer products and the mass fractions of phthalates in dust from nursery schools**

# PVC-verified consumer products and the mass fractions of phthalates in dust from nursery schools

**ABSTRACT.** Because phthalate esters have been incorporated into polyvinyl chloride (PVC) products, consumer products containing PVC may be a major source of phthalates in the indoor environment. In this study, we measured the mass fractions of phthalates in dust from 64 classrooms located in 50 nursery schools and evaluated whether the use of PVC-verified products affected phthalate concentrations. Dust was sampled using a modified vacuuming method, and consumer products used regularly in the nursery schools were analyzed using a portable X-ray fluorescence (XRF) analyzer to determine whether they contained PVC. Of the 3,180 consumer products examined, 1,067 (33.6%) were verified to contain PVC. Interior materials used in the construction of the building accounted for 83.2% of the total area of PVC-verified products and were significantly related to the mass fraction of di(2-ethylhexyl) phthalate (DEHP). Toys and teaching aids were the heaviest consumer products and comprised approximately half the total weight of PVC-

verified products. The use of these PVC toys and teaching aids was correlated with di-isononyl phthalate (DINP) concentration, but the statistical significance was weak. The weight of toy blocks, items used for role-playing, and gymnastic apparatuses were significant factors affecting the Di-n-butyl phthalate (DBP) concentration. This is the first study to prove that PVC-verified consumer products used regularly in nursery schools are a source of phthalates.

## **INTRODUCTION**

Because of its stability and flexibility, PVC has been used extensively in commercial applications. To obtain these properties, plasticizers are incorporated into the PVC products. Of the various available plasticizers, phthalates are the most commonly used worldwide, because they increase the desired properties of flexibility, workability, or distensibility.<sup>1</sup> Globally, approximately six million tonnes of plasticizer are consumed every year.<sup>2</sup>

Phthalates have been used commercially in a variety of consumer products and industrial goods. For example, they have been used as latex adhesives, plasticizers in plastics, solvents for dyes, in vinyl tiles, food conveyor belts, artificial leathers, building materials, car materials, wires, cables, food

packaging materials, medical devices, and in products used by children.<sup>3-7</sup> For thermodynamic reasons, plasticizers tend to leach, migrate, or evaporate from PVC-containing products into the environment.<sup>8</sup> Therefore, consumer products containing PVC can be sources of phthalate exposure through direct contact and use or through environmental contamination following abrasion and incorporation into indoor dust.<sup>9</sup> Phthalate exposure in the general population is widespread and extremely variable. Some studies have indicated that phthalate exposure is both higher and more common than suspected previously.<sup>10</sup> The levels of phthalate metabolites detected in urine samples have indicated that the test subjects were exposed to phthalate esters on a daily basis.<sup>11</sup>

Public concerns have been raised due to the accumulation of evidence associating reproductive and developmental effects with phthalate exposure.<sup>12,</sup><sup>13</sup> More recently, phthalate exposure was shown to be a risk factor for atopic diseases in children and adults.<sup>14-16</sup> Consumer exposure is indirectly connected to the use of plasticized products in the household, which can contaminate residences.<sup>17</sup> Data regarding phthalate exposure is essential for human risk assessment, especially among potentially susceptible populations. Identification of the sources of phthalates is also important for estimating the level of exposure and developing a prevention strategy.

The first objective of this study was to determine how many PVC products are used in nursery schools where children spend most of their time when not at home. We then correlated the mass fractions of different phthalates to the key consumer product sources regularly used in nursery schools.

## METHODS

**Building selection.** The buildings used for evaluation were selected as part of an extensive environmental management project for nursery schools sponsored by the Seoul Medical Center. From March to October 2012, 50 public or private nursery schools, including day-care centers and kindergartens, located in 25 autonomous districts in Seoul, volunteered for the project. Each facility cares for 40–222 children (average = 136) aged ~1–7 years.

**Dust sampling.** Indoor dust has been used as a medium for assessing human exposure to indoor contaminants.<sup>18</sup> We collected dust directly from the floor of the classrooms using a direct dust sampling method modified from Rudel et al.<sup>19</sup> Rudel et al. utilized a modified vacuum cleaner to sample dust using a thimble (19 × 90 mm), whereas we collected dust using a cellulose extraction thimble (external diameter = 28 mm; internal diameter = 26 mm; length = 100 mm; Advantec MFS, Inc., Tokyo, Japan) mounted on a ready-made vacuum

cleaner (VC-PU521, Samsung Electronics, Korea). The dust was vacuumed up slowly and lightly using the vacuum cleaner's crevice tool held immediately above upholstery, windowsills, household appliances, furniture, and other surfaces. For further details on dust sampling using a modified vacuum cleaner, see Kim et al.<sup>20</sup> The samples were kept in a cooler and shipped to the laboratory the same day. After delivery, the samples were stored at -20°C prior to analysis. Large debris was removed physically, and the dust was sieved to collect particles < 100 µm and weighed.

**Chemical analysis.** The following eight phthalates were analyzed: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP), and di-isodecyl phthalate (DIDP).

The dust sample extraction and analysis methods were modified from those of Becker et al.<sup>21</sup> and Bornehag et al.<sup>22</sup> Each 30-mg dust sample was extracted in a pre-cleaned 20-mL glass vial via ultrasonification for 1 h using 10 mL cyclohexane together with anthracene and chrysene d-12 as internal standards. An aliquot from each vial was injected into a gas chromatograph/mass-selective detector (GC/MSD; HP 6890 plus/HP 6973 MSD; USA) and analyzed using the selected ion monitoring mode. The limits of detection for

DMP, DEP, DBP, BBP, DEHP, DNOP, DINP, and DIDP were 4.2, 4.9, 3.9, 8.5, 13.0, 7.7, 82.7, and 202.3  $\mu\text{g/g}$  dust, respectively. For concentrations below the method detection limit (MDL), we used  $1/(2^{1/2})$  MDL for subsequent calculations, since most of the geometric standard deviations detected in the phthalates were below 2.0.<sup>23</sup> Our analytical method has been reported in detail previously.<sup>20</sup>

**PVC verification of products.** To verify PVC materials as phthalate sources, we used a portable X-ray fluorescence unit (XRF; Olympus INNOV-X Delta/Standard; USA), which uses a nondestructive method to detect elements with atomic numbers up to 92. In each classroom, all building materials, interior materials, furniture, household appliances, stationery, toys and teaching aids, musical instruments and physical education aids, and articles for public use including bags, tableware, and indoor shoes, were examined to determine whether they contained PVC. Three separate 40-s measurements were performed for each item, covering the entire target area. According to the manufacturers' specifications, a material can be verified as a PVC product if the chlorine concentration is  $>50,000$  ppm. For materials verified as PVC products, the areas or weights were measured and related to the phthalate concentration. Furniture, household appliances, and interior materials were measured in terms of area, whereas stationery, toys and

teaching aids, and articles for public use were measured in terms of weight. For musical instruments and physical education aids, each item was measured in terms of area or weight according to its shape (Table 3-1).

Table 3-1. Classification system used to define the classroom items

Category	Division	Item	Dimension
Furniture	Sofa	Sofa	Area
	General furniture	Furniture	Area
	Molding	Molding	Area
Household appliances	Household appliances	Desk, chair, bookshelf, drawer, table, locker, sink	Area
Articles for public use	Bags	Bag for nursery school, bag for lunch box, shoe pouch,	Weight
	Tableware	Spoon holder, lid of lunch box, cup, water bottle	Weight
	Indoor shoes	Indoor shoe	Weight
Interior materials	Doors	Door, window frame	Area
	Floors	Floor, mat for floor, carpet	Area
	Walls	Wallpaper, curtain, blind	Area
Stationery	Art stationery	Clay, paint, crayon, etc.	Weight
	Writing implements	Pen, scissor, glue, board, ruler, pencil case, etc.	Weight
Toys and teaching aids	Toys etc.	Basket for toys, items not classified elsewhere	Weight
	Blocks	Lego block, other toy block, puzzle, characters for letter teaching, pieces of counting game, etc.	Weight

Category	Division	Item	Dimension
Musical instruments physical education aids	Models and dolls	Models mimicking animal, vegetable, food, dinosaur, and others. Dolls	Weight
	Housekeeping play sets	Dish, pot, toy sink, knife, fork, spoon, etc.	Weight
	Articles for role playing	shoes, handbags, bags, and adult wallets, clothing used for special jobs (firefighting garments, doctor and police uniforms, etc.)	Weight
	Musical instruments	Maracas, tambourine, castanets, microphone, xylophone, piano	Area / weight
	Mats and cushions	Mats and cushions for shock prevention	Area
	Gymnastic apparatus	Ball, seesaw, slide, car, jump rope, hula hoop, etc.	Area / weight

**Statistical analysis.** The number of PVC-verified products in use was counted, and the results were reported as a percentage of the total. The distributions of the area or weight of PVC-verified products in the classrooms were skewed to the right. Logarithmically transformed data were evaluated graphically using probability plots, with the exception of the areas of furniture, floor, and walls, and most of these distributions were also right skewed. Logarithmically transformed data were used for statistical analysis. The detection rate of BBP was only 25.0% and was therefore excluded from the statistical analysis.<sup>23</sup> Univariate linear regression was performed to assess the relationships between log-transformed phthalate concentrations and related factors. Only data from classrooms containing PVC-verified consumer products were used in the linear regression analysis. All analyses were performed using SPSS 20.0 (IBM, Armonk, NY, USA).

## **RESULTS**

**Mass fractions of phthalates.** Sufficient dust samples for analysis were collected from 64 classrooms among 50 nursery schools. DBP, DEHP, and DINP were the most frequently identified phthalates. DMP, DEP, and DIDP were detected in only 1–3 dust samples, and DNOP was not detected in any.

DEHP had the highest detection rate as well as the highest concentration, with a geometric mean of 3,170  $\mu\text{g/g}$  dust (GSD, 2.0), followed by DINP, which had a geometric mean of 688  $\mu\text{g/g}$  dust (GSD, 3.2). The general characteristics of the nursery schools and their classrooms and the phthalate mass fractions are detailed in Tables 2-1 and 2-2.

**PVC-verified consumer products.** All of the consumer products in each classroom were examined to determine whether they contained PVC using a portable X-ray fluorescence unit. The consumer products were classified into seven categories according to their purpose: furniture, household appliances, articles for public use, interior materials, stationery, toys and teaching aids, and apparatuses used in musical and physical education. Of the 3,180 consumer products examined, 1,067 (33.6%) were verified to contain PVC (Figure 3-1). The articles for public use (e.g., bags, tableware, and indoor shoes) category showed the highest percentage (54.1%) of PVC products, followed by interior materials (51.1%). The presence of PVC products was verified in the bottoms of all indoor shoes. Half of all sofas, floor materials, moldings, mats and cushions, bags, models and dolls, and doors were verified to contain PVC.

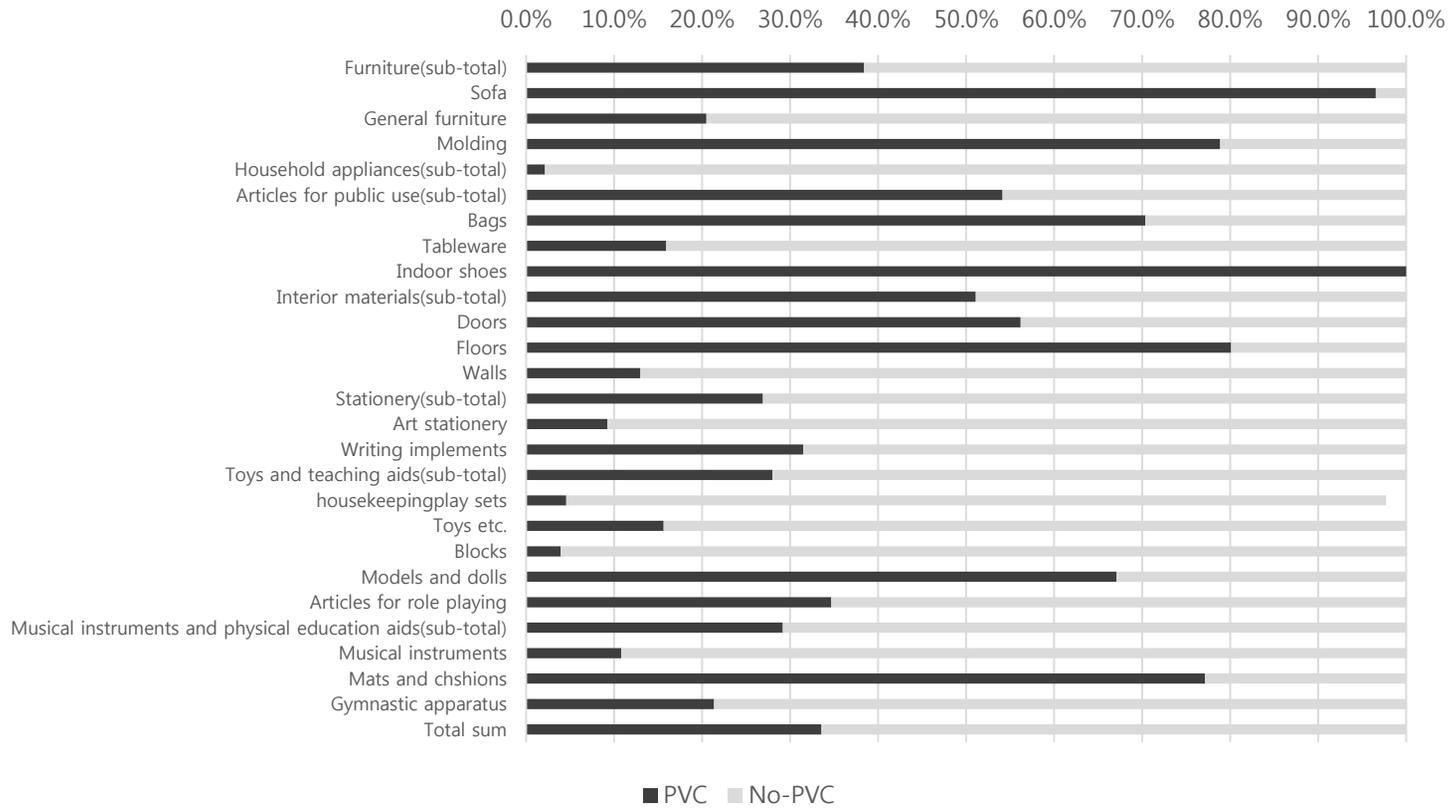


Figure 3-1. Percentage composition of PVC in consumer products.

**Area or weight of PVC-verified consumer products.** The number of PVC-verified consumer products and their areas or weights are shown in Table 3-2. Of the items measured by area, the floor, followed by the walls, was the most extensive PVC-verified product. Therefore, materials used in internal construction constituted 83.2% of the total area of PVC-verified products. Models and dolls accounted for a large proportion (35.2%) of the total weight of PVC-verified products. Toys and teaching aids were the heaviest PVC-verified products and accounted for approximately half of the total weight.

Table 3-2. Area or weight of PVC-verified consumer products

Products category	Area		Weight	
	N (%)	m <sup>2</sup> (%)	N (%)	g (%)
Furniture	222 (42.4)	612.6 (11.1)		
Sofa	28 (5.4)	80.4 (1.5)		
General furniture	83 (15.9)	418.6 (7.6)		
Molding	111 (21.2)	113.6 (2.1)		
Household appliances	2 (0.4)	7.4 (0.1)		
Household appliances	2 (0.4)	7.4 (0.1)		
Public articles			71 (13.4)	28,159.6 (8.4)
Bags			56 (10.5)	25,427.6 (7.6)
Tableware			7 (1.3)	686.0 (0.2)
Indoor shoes			8 (1.5)	2,046.0 (0.6)
Interior materials	230 (44.0)	4,587.7 (83.2)		
Doors	66 (27.7)	204.8 (3.7)		
Floors	145 (12.6)	3,859.6 (70.0)		
Walls	19 (3.6)	523.2 (9.5)		
Stationery			85 (16.0)	127,899.0 (38.3)
Art stationery			6 (1.1)	23,576.0 (7.1)

Products category	Area		Weight	
	N (%)	m <sup>2</sup> (%)	N (%)	g (%)
Writing implements			79 (14.9)	104,323.0 (31.2)
Toys and teaching aids			353 (66.5)	163,849.6 (49.1)
Toys etc.			10 (1.9)	4,776.0 (1.4)
Blocks			17 (3.2)	9,518.0 (2.9)
Models and dolls			202 (38.0)	117,675.6 (35.2)
Housekeeping play sets			5 (0.9)	1,946.0 (0.6)
Articles for role playing			119 (22.4)	29,934.0 (9.0)
Instruments for music and physical education	69 (13.2)	309.2 (5.6)	22 (4.1)	14,040.0 (4.2)
Musical instruments	11 (2.1)	43.1 (0.8)	4 (0.8)	5,412.0 (1.6)
Mats and cushions	54 (10.3)	133.8 (2.4)		
Gymnastic apparatus	4 (0.8)	132.3 (2.4)	18 (3.4)	8,628.0 (2.6)
Total	523	5,516.9	531	333,948.2

**PVC-verified products and phthalate concentrations** The PVC-verified product areas or weights were used for linear regression as the independent variables, and the phthalate mass fractions in dust were used as the dependent variables (Table 3-3). The weights of toy blocks, articles used in role playing, and gymnastic apparatuses were significant factors affecting the DBP concentration. The total area of the PVC products was significantly related to the mass fraction of DEHP in dust from classrooms. This might have been due to the large area of the PVC-verified flooring materials. The total weight of the toys and teaching aids was correlated with the DINP concentration, but the statistical significance of this correlation was weak. The area of doors and the area of musical instruments affected the DINP concentrations significantly.

Table 3-3. The relationship between PVC-verified products and the logarithmically transformed phthalate mass fraction in dust ( $\mu\text{g/g}$  dust) following univariate analysis

PVC-verified products <sup>a</sup>	DBP			DEHP			DINP		
	N	$\beta$ (SE)	<i>p</i> -value	$\beta$ (SE)	<i>p</i> -value	$\beta$ (SE)	<i>p</i> -value		
Furniture(area, m <sup>2</sup> )	55	0.058 (0.075)	0.676	-0.146 (0.078)	0.289	-0.163 (0.139)	0.234		
General furniture	39	0.044 (0.007)	0.790	-0.101 (0.007)	0.541	0.038 (0.013)	0.817		
Sofa	20	0.034 (0.131)	0.888	-0.019 (0.139)	0.937	-0.196 (0.250)	0.407		
Molding	36	0.069 (0.066)	0.691	-0.072 (0.093)	0.677	-0.053 (0.167)	0.760		
Interior materials(area, m <sup>2</sup> )	64	0.183 (0.001)	0.147	0.341 (0.001)	0.006	-0.069 (0.001)	0.586		
Floor	64	0.085 (0.001)	0.502	0.336 (0.001)	0.007	0.080 (0.002)	0.530		
Walls	12	0.444 (0.002)	0.148	0.421 (0.002)	0.173	-0.352 (0.005)	0.262		
Door	35	0.090 (0.105)	0.606	0.106 (0.103)	0.544	0.361 (0.169)	0.033		
Stationery(weight, g)	44	-0.050 (0.073)	0.749	-0.185 (0.079)	0.228	0.086 (0.130)	0.578		
Writing implements	44	-0.047 0.074	0.764	-0.187 (0.080)	0.224	0.082 (0.132)	0.597		
Toys and teaching aids(weight, g)	59	0.099 (0.102)	0.456	-0.016 (0.109)	0.905	0.246 (0.183)	0.060		

PVC-verified products <sup>a</sup>	DBP			DEHP			DINP		
	N	$\beta$ (SE)	<i>p</i> -value	$\beta$ (SE)	<i>p</i> -value	$\beta$ (SE)	<i>p</i> -value		
Blocks	11	0.603 (0.094)	0.049	-0.014 (0.161)	0.968	0.122 (0.320)	0.722		
Articles for role playing	42	0.314 (0.104)	0.043	0.214 (0.112)	0.174	0.253 (0.185)	0.106		
Models and dolls	59	-0.022 (0.092)	0.867	-0.053 (0.098)	0.693	0.165 (0.166)	0.211		
Etc.	8	-0.289 (0.116)	0.488	-0.221 (0.105)	0.598	-0.250 (0.220)	0.551		
Instruments for music and physical education (weight, g)	14	0.430 (0.182)	0.125	0.126 (0.206)	0.667	0.011 (0.315)	0.969		
Gymnastic apparatus	11	0.605 (0.216)	0.049	0.106 (0.259)	0.757	0.063 (0.357)	0.853		
Instruments for music and physical education (area, m <sup>2</sup> )	29	-0.196 (0.102)	0.308	-0.207 (0.101)	0.280	-0.112 (0.164)	0.564		
Musical instruments	10	-0.063 (0.196)	0.864	0.326 (0.430)	0.358	0.648 (0.482)	0.043		
Mats and cushions	27	-0.099 (0.119)	0.624	-0.093 (0.117)	0.645	-0.044 (0.188)	0.829		
Total weight (weight, g)	61	-0.065 (0.081)	0.620	-0.111 (0.087)	0.394	0.094 (0.148)	0.469		
Total area (area, m <sup>2</sup> )	64	0.177 (0.001)	0.161	0.302 (0.001)	0.015	-0.104 (0.001)	0.412		

Abbreviations: SE, standard error.

<sup>a</sup>All variables were log transformed except for, area of furniture, floor, and walls.

## DISCUSSION

In this study, we evaluated most of the consumer products present in classrooms to determine whether they contained PVC for the purpose of identifying the sources of phthalates. We collected and analyzed indoor dust samples for phthalates to determine the correlation between the areas or weights of PVC-verified products and the phthalate mass fractions in dust from each classroom. The results showed that 33.6% of the consumer products contained PVC. The concentrations of DBP and DEHP correlated with the weight of toys and teaching aids and with the area of the interior materials, respectively. The mass fraction of DINP was significantly correlated with the area of doors and the area of musical instruments.

This is the first study to use an experimental instrument to verify the presence of PVC in consumer products regularly used in nursery schools, where children spend most of their time outside of the home. Although some previous studies have assessed the PVC content of materials, they have used qualitative data obtained through the use of questionnaires<sup>21, 24, 25</sup> or through assessments by trained inspectors.<sup>24, 26-28</sup> A further advantage of this study is that the measured weights or areas of the PVC-verified products provided a quantitative statistical tool to increase the robustness of regression analysis,

since no arbitrary judgments were required by the researchers or study participants.<sup>24</sup>

PVC production has increased globally over a long period at a rate of more than 4% per year, and its production volume is currently the second largest of any plastic in the world.<sup>29</sup> Although, there have been several studies that identified phthalates in toys and personal care products,<sup>30, 31</sup> no study has determined empirically how many consumer products containing PVC are actually used in real living spaces. Additionally, no studies have examined the relationship between the quantity of PVC-verified consumer products and the mass fractions of phthalates in dust sampled from the indoor environment.

DBP is one of the most commonly used plasticizers and is known to affect the reproductive and developmental processes of organisms through various routes of exposure.<sup>3, 32, 33</sup> DBP is used as a coalescing aid in latex adhesives, as a plasticizer in cellulose plastics, and as a solvent for dyes.<sup>3</sup> Because DBP is not bound to the final product, it can be released into the environment during the use of these products. In this study, the mass fraction of DBP was significantly correlated with the weights of toy blocks, articles used in role playing, and gymnastic apparatuses. Toy blocks used in building games and alphabet-learning materials were verified to contain PVC. Articles used in role playing that were verified for PVC included shoes, handbags, bags, and adult

wallets. Most gymnastic apparatuses, measured in terms of weight, included balls used for playing sports. Such products were confirmed to affect the mass fraction of DBP in dust.

DEHP, used as a plasticizer for PVC in the manufacture of various consumer products, is produced in high volumes. Important uses of DEHP include building products (flooring, wallpaper, polymeric coatings, wire and cable insulation), car products, clothing, food packaging, children's products, and medical devices.<sup>5</sup> As revealed in this study and its predecessor, the mass fraction of DEHP was significantly correlated with the area of materials used in internal construction, such as flooring, and also with the total area of PVC-verified products. Some studies have shown that certain PVC products, such as flooring, have a strong association with total DEHP concentrations in an environment, even though there may be other sources of phthalates present.<sup>25-</sup>  
<sup>27</sup> Considering the main use of DEHP, these results were expected.

DINP is a general-purpose plasticizer with a broad range of applications and is used in flexible PVC. It is widely used in the toy, construction, and general consumer product markets.<sup>6</sup> DINP was the phthalate most frequently found in toys, and it tended to be present in the highest concentrations.<sup>30, 34</sup> For example, DINP was found in 64% of 42 plastic products intended for teething, or with a high potential for mouth contact in children, and its concentration ranged

from 3.9 to 44%.<sup>35</sup> These consumer products could therefore be the main sources of DINP in dust. In this study, the mass fraction of DINP in dust showed a correlation, albeit not statistically significant, with the weight of toys and teaching aids.

Other consumer products that significantly influenced the DINP concentration included doors and musical instruments, e.g. pianos. DINP use in films and sheets of consumer products has been reported.<sup>6</sup> Most of the doors examined were covered with plastic; therefore, such products might contribute to the DINP presence in indoor dust.

This study has certain limitations. First, we did not differentiate the physical properties of PVC products, i.e., whether they were soft or hard. It is possible that the softer the product, the greater the amount of phthalate present. Examining whether consumer products contain PVC is considered a suitable methodology for identifying significant factors that affect the mass fractions of phthalates. However, it was difficult to determine an obvious borderline distinguishing between soft and hard PVC products.

Second, in some cases, it was difficult to determine the most appropriate dimension to use to measure the quantity of PVC-verified products. For example, weight was considered to be appropriate for moldings; however,

since they were incorporated into building materials, the surface of the moldings was measured in terms of area. Products with a complex structure presented another problem, as it was difficult to measure their exact area. An approximate area was estimated based on the more simplified structures within the product.

Third, no statistical analysis was undertaken on consumer products classified as articles for public use. In most cases, they were kept in public areas and not located in the classroom, and children took them home after school. Some items, such as lunch boxes, are used at certain times of the day only; thus, they were not considered to be associated with the classroom. Although they were not present in the classroom, their use could still affect the mass fractions of the phthalates present.

Fourth, not all of the consumer products were checked for PVC. For example, we could not examine all of the cables (e.g., electrical or internet cables) in the classroom. Some cases were verified to contain PVC, but most were in inaccessible locations. Although it was possible to verify that the cables contained PVC, it was not possible to measure their area or weight.

Although this study had certain limitations, it revealed the extent of use of PVC-containing consumer products in nursery schools. This is the first study to quantitatively determine the sources of phthalates in the indoor environment.

The results will enable a better understanding of the relationship among the sources of different phthalates and the possibility of phthalate exposure to children in the areas they spend most of their time.

## REFERENCES

1. Cadogan, D. F.; Howick, C. J., Plasticizers. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000; Vol. 27, pp 509-618.
2. Plasticisers Information Center Plasticisers. <http://www.plasticisers.org> (12 March),
3. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-butyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 489-527.
4. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of butyl benzyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 453-487.

5. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di(2-ethylhexyl) phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 529-653.
6. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-isononyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 679-708.
7. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-octyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 721-734.
8. Navarro, R.; Pérez Perrino, M.; Gómez Tardajos, M., et al. Phthalate plasticizers covalently bound to PVC: plasticization with suppressed migration. *Macromolecules* **2010**, *43* (5), 2377-2381.
9. Schettler, T. Human exposure to phthalates via consumer products. *Int. J. Androl.* **2006**, *29* (1), 134-139.
10. Blount, B. C.; Silva, M. J.; Caudill, S. P., et al. Levels of seven urinary phthalate metabolites in a human reference population. *Environ. Health Perspect.* **2000**, *108* (10), 979.

11. Suzuki, Y.; Niwa, M.; Yoshinaga, J., et al. Exposure assessment of phthalate esters in Japanese pregnant women by using urinary metabolite analysis. *Environ. Health Preve. Med.* **2009**, *14* (3), 180-187.
12. Fisher, J. S. Environmental anti-androgens and male reproductive health: focus on phthalates and testicular dysgenesis syndrome. *Reproduction* **2004**, *127* (3), 305-315.
13. Swan, S. H.; Main, K. M.; Liu, F., et al. Decrease in anogenital distance among male infants with prenatal phthalate exposure. *Environ. Health Perspect.* **2005**, *113* (8), 1056-1061.
14. Kolarik, B.; Naydenov, K.; Larsson, M., et al. The association between phthalates in dust and allergic diseases among Bulgarian children. *Environ. Health Perspect.* **2008**, *116* (1), 98-103.
15. Bornehag, C. G.; Nanberg, E. Phthalate exposure and asthma in children. *Int. J. Androl.* **2010**, *33* (2), 333-345.
16. Jaakkola, J.; Knight, T. L. The role of exposure to phthalates from polyvinyl chloride products in the development of asthma and allergies: a systematic review and metaanalysis. *Environ. Health Perspect.* **2008**, *116* (7), 845-53.

17. Wormuth, M.; Scheringer, M.; Vollenweider, M., et al. What Are the Sources of Exposure to Eight Frequently Used Phthalic Acid Esters in Europeans? *Risk Anal.* **2006**, *26* (3), 803-824.
18. Whitehead, T.; Metayer, C.; Buffler, P., et al. Estimating exposures to indoor contaminants using residential dust. *J. Expo. Sci. Environ. Epidemiol.* **2011**, *21* (6), 549-564.
19. Rudel, R. A.; Brody, J. G.; Spengler, J. D., et al. Identification of Selected Hormonally Active Agents and Animal Mammary Carcinogens in Commercial and Residential Air and Dust Samples. *J. Air Waste Manage. Assoc.* **2001**, *51* (4), 499-513.
20. Kim, W.; Choi, I.; Jung, Y., et al. Phthalate Levels in Nursery Schools and Related Factors. *Environ. Sci. Technol.* **2013**, *47* (21), 12459-12468.
21. Becker, K.; Seiwert, M.; Angerer, J., et al. DEHP metabolites in urine of children and DEHP in house dust. *Int. J. Hyg. Environ. Health* **2004**, *207* (5), 409-417.
22. Bornehag, C. G.; Sundell, J.; Weschler, C. J., et al. The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. *Environ. Health Perspect.* **2004**, *112* (14), 1393-1397.

23. Hornung, R. W.; Reed, L. D. Estimation of average concentration in the presence of nondetectable values. *Appl. Occup. Environ. Hyg.* **1990**, *5* (1), 46-51.
24. Kolarik, B.; Bornehag, C. G.; Naydenov, K., et al. The concentrations of phthalates in settled dust in Bulgarian homes in relation to building characteristic and cleaning habits in the family. *Atmos. Environ.* **2008**, *42* (37), 8553-8559.
25. Carlstedt, F.; Jönsson, B. A. G.; Bornehag, C. G. PVC flooring is related to human uptake of phthalates in infants. *Indoor Air* **2013**, *23* (1), 32-39.
26. Bornehag, C. G.; Lundgren, B.; Weschler, C. J., et al. Phthalates in indoor dust and their association with building characteristics. *Environ. Health Perspect.* **2005**, *113* (10), 1399-1404.
27. Zhang, Q.; Lu, X. M.; Zhang, X. L., et al. Levels of phthalate esters in settled house dust from urban dwellings with young children in Nanjing, China. *Atmos. Environ.* **2013**, *69*, 258-264.
28. Jaakkola, J. J.; Øie, L.; Nafstad, P., et al. Interior surface materials in the home and the development of bronchial obstruction in young children in Oslo, Norway. *Am. J. Public Health* **1999**, *89* (2), 188-192.

29. Braun, D. Poly(vinyl chloride) on the way from the 19th century to the 21st century. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (3), 578-586.
30. Stringer, R.; Labunska, I.; Santillo, D., et al. Concentrations of phthalate esters and identification of other additives in PVC children's toys. *Environ. Sci. & Pollut. Res.* **2000**, *7* (1), 27-36.
31. Koniecki, D.; Wang, R.; Moody, R. P., et al. Phthalates in cosmetic and personal care products: Concentrations and possible dermal exposure. *Environ. Res.* **2011**, *111* (3), 329-336.
32. Zhang, Y.; Jiang, X.; Chen, B. Reproductive and developmental toxicity in F1 Sprague–Dawley male rats exposed to di-n-butyl phthalate in utero and during lactation and determination of its NOAEL. *Reprod. Toxicol.* **2004**, *18* (5), 669-676.
33. Jiang, J.; Ma, L.; Yuan, L., et al. Study on developmental abnormalities in hypospadiac male rats induced by maternal exposure to di-n-butyl phthalate (DBP). *Toxicology* **2007**, *232* (3), 286-293.
34. Bogen, K.; Boekelheide, K.; Cunningham, M., et al., Report to the US consumer product safety commission by the chronic hazard advisory panel on diisononyl phthalate. In Bethesda: 2001.

35. Gill, U. S.; Lalonde, P. J.; Chantal, P. D., et al. Analysis of diisononyl phthalate in PVC consumer products used by children. *Int. J. Consum. and Prod. Safety* **1999**, 6 (4), 223-234.

## **CHAPTER 4.**

**A comparison of the mass fractions of phthalates in dust from a household vacuum cleaner and a modified vacuum cleaner**

# A comparison of the mass fractions of phthalates in dust from a household vacuum cleaner and a modified vacuum cleaner

**ABSTRACT.** Phthalates are considered primary indoor contaminants. In this study, we compared the correlations between the mass fractions of phthalates in dust from two representative sampling methods: collecting dust with a modified vacuum cleaner and collecting from a household vacuum cleaner dust bag. The two sampling methods were applied in 50 nursery schools, and 31 pairs of dust samples were collected from the same classrooms using the two methods. The concordance rates for the phthalate detected were over 70%. The di-n-butyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) concentrations were 2- to 5.7-fold higher in dust from the household vacuum cleaner, but these differences disappeared upon adjusting the data based on the sampled and cleaned areas. The correlation and agreement using the two sampling methods were moderate for DBP ( $r = 0.430-0.563$ , intraclass coefficient (ICC) =  $0.579-0.565$ ) but poor to moderate for DEHP ( $r = -0.021-$

0.376, ICC = -0.041-0.408). The agreement between DBP and DEHP in dust from separate classrooms in a school was moderate to good. And the repeatability of sampling method for DBP and DEHP was good. But for diisononyl phthalate (DINP), the correlation and agreement between sampling methods, room-to-room variability, and repeatability were poor.

## **INTRODUCTION**

Polyvinyl chloride (PVC) is one of the most commonly used plastics in daily life. To generate desired properties, PVC is mixed with multiple types of plasticizers. Phthalates have been used as key plasticizer components because they increase flexibility, workability, or distensibility<sup>1</sup>, and they have been used commercially in various consumer products and industrial goods, such as vinyl tile, film, artificial leather, flooring, conveyor belts, toys, latex adhesives, canvas tarps, vinyl gloves, electrical cables, and hoses.<sup>2-8</sup>

Contrary to their commercial merits, phthalates are known hazardous materials that threaten public health. Due to thermodynamics, plasticizers tend to migrate to the surface of an object, which eventually produces environmental contamination.<sup>9</sup> Researchers have revealed an association between phthalate exposure and reproductive and developmental effects.<sup>10-14</sup>

Recently, researchers have begun to regard phthalates as a significant risk factor for atopic diseases in children.<sup>15-18</sup>

To estimate human exposure to these chemicals and determine their critical exposure routes, researchers have evaluated their concentrations in air, dust, diet, and biospecimens. Among such media, indoor dust has been used to assess human exposure to indoor contaminants; however, a universal, gold-standard method for sampling contaminants in indoor dust has not been developed.<sup>19</sup> Effective methodologies for measuring expected contaminants in air have been developed, but until the early 1990s, few methods were available to assess exposure through dermal contact and oral ingestion. For example, in 1988, the United States Environmental Protection Agency (EPA) designed and tested a high-volume surface sampler to collect indoor dust and semi-volatile organics in indoor dust,<sup>20</sup> and the following year, the method was confirmed as generally satisfactory.<sup>21</sup> Methodologies that use a high-volume small-surface sampler (HVS3) were expanded to study exposure to polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), and these methodologies were determined to be suitable for quantitative collection in indoor dust.<sup>22</sup>

In addition to collecting dust directly from the floor using a standard vacuum cleaner, such as HVS3,<sup>23-25</sup> investigators typically sample residential dust by

collecting the subjects' vacuum cleaner dust bags<sup>26-28</sup> or using a brush or broom.<sup>27, 29</sup> In certain studies, dust was sampled using modified vacuum cleaners equipped with a thimble or membrane filter.<sup>30-33</sup> In contrast to the HVS3, which primarily collects floor dust, such modified vacuum cleaners collect dust above the floor level from upholstery, windowsills, household appliances, and shelf surfaces. The aforementioned methods for sampling dust indoors have advantages and disadvantages. For example, collecting dust bags from a household vacuum cleaner is easy and cost effective compared with other methods, but the disadvantages include repeated aeration, contamination from the dust bag, and different user cleaning practices. The HVS3 and modified vacuum cleaner methods are labor intensive but have been evaluated for their potential to provide more accurate and specific information, such as dust loading.<sup>34</sup> Additionally, the modified vacuum cleaner method is relatively inexpensive.

Many scientists have studied indoor dust using methods to evaluate the concentrations of indoor contaminants, such as pesticides, PAHs, PCBs, and polybrominated diphenyl ether (PBDE), and the results of various methods have been compared.<sup>34-37</sup> However, no study has compared the suitability of such methods for assessing phthalates in indoor dust.

The aim of the present study was to compare the effectiveness of two sampling methods, the use of a modified vacuum cleaner and the collection of dust from a regularly used vacuum cleaner bag, for the assessment of phthalates in indoor dust.

## METHODS

**Building selection.** The buildings studied were selected as part of an intensive environmental management project for nursery schools sponsored by the Seoul Medical Center. From March to October 2012, 50 public or private nursery schools volunteered for this project, including daycare centers and kindergartens located in 25 autonomous districts in Seoul. Each facility cares for 40-222 children (average = 136) ~1-7 years in age.

**Dust sampling.** For each of the 50 nursery schools, the nursery school director recommended two classrooms to represent the school. In this study, we simultaneously used two sampling methods for a single classroom. One method was direct indoor dust sampling using a modified vacuum cleaner, and the other method was the collection of the dust bag from the vacuum cleaner regularly used in the target classroom. The direct dust sampling method was modified from Rudel et al.<sup>38</sup> Rudel et al. modified the vacuum cleaner to equip

the thimble (19 x 90 mm), whereas we collected dust on a cellulose extraction thimble (external diameter, 28 mm; internal diameter, 26 mm; length, 100 mm; Advantec MFS, Inc., Tokyo, Japan) mounted on a ready-made vacuum cleaner. The dust was vacuumed slowly and lightly using the crevice tool immediately above the upholstery, windowsills, household appliances, and furniture, among other surfaces. For further details on sampling dust using a modified vacuum cleaner, see Kim et al.<sup>39</sup> The area where researchers collected dust using the modified vacuum cleaner was measured. Then, the researchers interviewed the teachers to identify an area cleaned using a household vacuum cleaner and measured the corresponding area.

In addition to direct dust sampling using a modified vacuum cleaner, researchers collected vacuum cleaner dust bags regularly used in the respective classrooms. Generally, teachers individually used the vacuum cleaners to clean the classroom and maintain their space and surrounding spaces. The dust samples were removed from the vacuum cleaner dust bag and then transferred to a prepared clean bag composed of polyethylene.

The samples were stored in a cooler and shipped to the laboratory on the same day. After delivery, the samples were stored at  $-20^{\circ}\text{C}$  until analysis. The

large debris was physically extracted, and the dust was sieved to a <100  $\mu\text{m}$  particle size and weighed.

To test the repeatability of each method, we sampled dust and collected dust bags of regularly used vacuum cleaners in 6 classrooms over periods of 18-19 months between 2012 and 2014. Additionally, we collected dust bags again in the same classrooms about 2 weeks later from the time of last collection of dust bags. Teachers were interviewed and confirmed that there had been no changes to contribute the phthalate concentrations in dust from each classrooms.

**Chemical analysis.** Eight phthalates were analyzed: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP), and di-isodecyl phthalate (DIDP).

The dust sample extraction and analysis methods were modified from Becker et al.<sup>26</sup> and Bornehag et al.<sup>40</sup> Each 30 mg dust sample was extracted in a pre-cleaned 20 mL glass vial through ultrasonification for 1 h using 10 mL of cyclohexane with anthracene and chrysene d-12 as internal standards. An aliquot from each vial was injected into a gas chromatograph/mass-selective detector (GC/MSD; HP 6890 plus/HP 6973 MSD; USA) and analyzed using

the selected ion monitoring mode. The limits of detection for DMP, DEP, DBP, BBP, DEHP, DNOP, DINP, and DIDP were 4.2, 4.9, 3.9, 8.5, 13.0, 7.7, 82.7, and 202.3  $\mu\text{g/g}$  dust, respectively. For concentrations below the method detection limit (MDL), we used  $1/(2^{1/2})$  MDL for subsequent calculations because most of the geometric standard deviations in the phthalates detected were below 2.0.<sup>41</sup> Our analysis method has been detailed previously.<sup>39</sup>

**Statistical analysis.** Most of the detected phthalate concentration distributions were right skewed, and the logarithmically transformed data were graphically evaluated using probability plots. For BBP, the detection rate was only 25.0-41.1%; therefore, BBP was excluded from the statistical analysis because it would generate biased estimates.<sup>41</sup> Phthalate concentrations have been reported as a geometric mean and median based on the type of phthalate. To determine the differences between the mass fractions of phthalates in dust using the two sampling methods, a paired t-test was used. Pearson's correlation was used to assess the correlations between the log-transformed phthalate concentrations and the phthalate concentrations using the two sampling methods. An intraclass correlation coefficient (ICC) was used to determine the level of agreement between the phthalate concentrations using the two sampling methods from each classroom with a two-way random model. Further, the ICCs for phthalate concentration in dust from separate classrooms

in a nursery school by the same sampling method were assessed using a one-way random model. Additionally, the repeatability of each method was tested using ICCs with a two-way mixed model to elucidate consistency in phthalate concentrations between sampling times.

The data were analyzed using SPSS 21.0 (IBM, Armonk, NY), and the graphs were generated using SigmaPlot 8.0 (SPSS, San Jose, California, USA) and an Excel spreadsheet (Microsoft® Excel® 2013; Microsoft Corp., Redmond, WA).

## **RESULTS**

One hundred classrooms in 50 nursery schools were investigated, and interviews were conducted by trained researchers. We collected 64 dust samples using a modified vacuum cleaner and 73 dust bag samples from household vacuum cleaners. In 31 classrooms, we collected paired dust samples using both methods. In addition, we collected 14 pairs of dust samples with the modified vacuum cleaner and 29 pairs of dust samples from the regularly used household vacuum cleaner dust bags in separate classrooms in a nursery school.

## **Detection rate and concentration.**

As explained in the methods section, we sampled indoor dust using two methodologies in each classroom. Although 100 samples using the two methods was the original target, we only collected 64 indoor dust samples using a modified vacuum cleaner and 73 samples from the dust bags of regularly used vacuum cleaners. According to the teachers interviewed, nearly all of the classrooms were cleaned at least once a day; thus, it was difficult for the professional inspectors to collect sufficient quantities of dust for analysis.

The concentrations of the eight types of phthalates identified in the dust collected using the two sampling methods are listed in Table 4-1. DBP, DEHP, and DINP were the most frequently identified phthalates, irrespective of the sampling method. DMP, DEP, DNOP, and DIDP were not detected in dust collected from the vacuum cleaner in regular use and were identified only in 1-3 dust samples collected with the modified sampling method. For both methods, DEHP had the highest detection rate, a 100% detection rate for both methods, and the highest concentration, with a geometric mean of 3,170  $\mu\text{g/g}$  dust for the modified method and 5,560  $\mu\text{g/g}$  dust for the dust bag collection method. DINP showed the second highest concentration and detection rate, with a geometric mean of 1,250  $\mu\text{g/g}$  dust for the modified vacuum cleaner method and 2,700  $\mu\text{g/g}$  dust for the dust bag collection method.

Table 4-1. Phthalate detection rates and concentrations ( $\mu\text{g/g}$  dust) in dust sampled using different methods

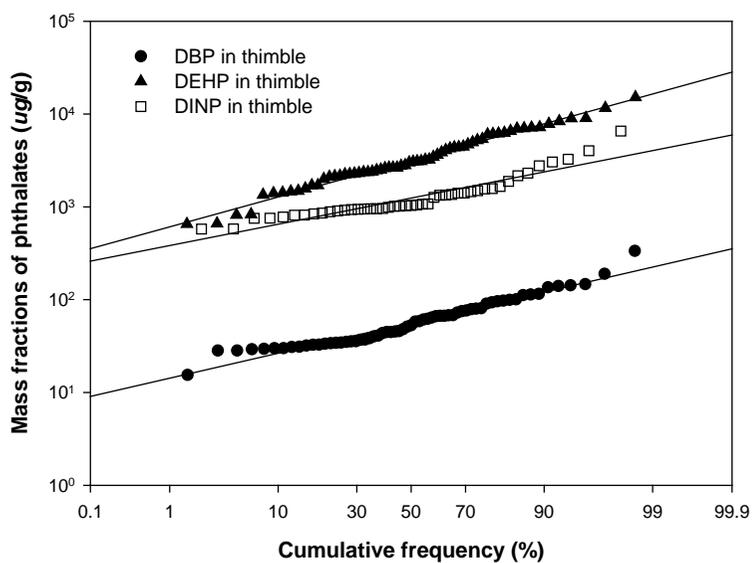
Phthalate	Modified vacuum cleaner					Regularly used vacuum cleaner				
	Detection rate, N <sup>a</sup> (%)	GM(GSD)	Median	Min	Max	Detection rate, N <sup>a</sup> (%)	GM(GSD)	Median	Min	Max
DBP	63(98.4)	56.6(1.8)	53.0	<6.9	336	73(100.0)	93.3(2.9)	63.1	30.2	2,630
DEHP	64(100.0)	3,170(2.0)	3,030	654	15,160	73(100.0)	5,560(2.0)	4,820	1,560	26,200
DINP	46(71.9)	1,250(1.6)	1,040	<322	6,560	71(97.3)	2,700(2.8)	2,360	<155	25,400

Abbreviations: GM, geometric mean; GSD, geometric standard deviation; Min, minimum; Max, maximum.

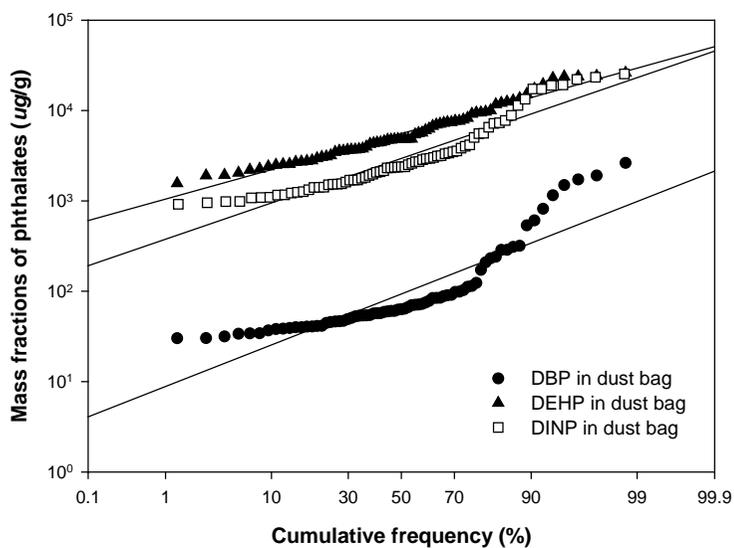
<sup>a</sup>Number of phthalates detected.

Phthalates having less than 50 % of detection rate were excluded from this tables: DMP, DEP, BBP, DNOP, and DIDP

DBP was moderately correlated with DEHP and yielded a Pearson's correlation coefficient of 0.607 ( $p < 0.01$ ) using the modified vacuum cleaner method; DBP was also correlated with DEHP and DINP and yielded coefficients of 0.632 ( $p < 0.01$ ) and 0.366 ( $p < 0.01$ ), respectively, using the regularly used vacuum cleaner dust bag method. Generally, the phthalate concentrations were much higher when the dust samples were collected from the household vacuum cleaners (Figure 4-1).



(a) Dust from the modified vacuum cleaner



(b) Dust from regularly used vacuum cleaner

Figure 4-1. Phthalate concentration distribution.

**Concordance rate.**

Of the 64 indoor dust samples from the modified vacuum cleaner and the 73 dust samples collected from the regularly used vacuum cleaner, 31 dust sample pairs were collected from the same classrooms. The detection rates and concentrations of the phthalates analyzed for the same sites are summarized in Table 4-2. Generally, the concordance rate was high and ranged from 70 to 100%. DBP and DEHP were detected in each pair of samples from the same site. The DINP detection rate in dust from the regularly used vacuum cleaner was somewhat higher than for the dust collected from a modified vacuum cleaner, at 96.8% versus 74.2%, respectively.

Table 4-2. Phthalate detection rates and concentrations ( $\mu\text{g/g}$  dust) for dust sample pairs from the same sites using different methods

Phthalate	Modified vacuum cleaner					Regularly used vacuum cleaner					Concordance rate
	Detection rate N <sup>a</sup> (%)	GM(GSD)	Median	Min	Max	Detection rate N <sup>a</sup> (%)	GM(GSD)	Median	Min	Max	N (%)
DBP*	31(100.0)	55.4(1.9)	44.7	15.5	336	31(100.0)	111(3.2)	84.0	30.2	1,910	31(100.0)
DEHP*	31(100.0)	2,990(2.2)	2,520	654	15,200	31(100.0)	6,320(2.0)	5,690	1,560	26,200	31(100.0)
DINP*	23(74.2)	638(3.1)	936	<322	3,260	30(96.8)	3,660(3.3)	2,950	<155	23,400	22(71.0)

Abbreviations: GM, geometric mean; GSD, geometric standard deviation; Min, minimum; Max, maximum.

<sup>a</sup>Number of phthalates detected.

Phthalates having less than 50 % of detection rate were excluded from this tables: DMP, DEP, BBP, DNOP, and DIDP

\* $p$ -value < 0.001 for paired t-test.

### **Sampling method comparison.**

Tables 4-2 and 4-3 summarize the phthalate concentration differences using the different sampling methods for the three most frequently detected phthalates, and the differences were adjusted based on the total area covered by each sampling method.

We observed significant differences between the log-transformed concentrations for each of the three types of phthalates based on the sampling methods (Table 4-2). The phthalate concentrations were higher in dust from the regularly used vacuum cleaner. For example, in these samples, the concentration difference was approximately double for DEHP and 5.7-fold for DINP.

In contrast to the results from directly comparing each phthalate concentration, when the results were adjusted based on the total area, the log-transformed ratio did not differ significantly, except for the DINP data (Table 4-3). In fact, dust was collected from a much wider area with the regularly used vacuum cleaner compared with the researcher-sampled area using a modified vacuum cleaner.

Table 4-3. A comparison of phthalate concentrations in dust from the different sampling methods adjusted based on area

Variable	Modified vacuum cleaner		Regularly used vacuum cleaner		Difference	
	N <sup>a</sup>	GM(GSD)	N <sup>a</sup>	GM(GSD)	N	<i>p</i> -value <sup>b</sup>
DBP/Total area( $\mu\text{g/g/m}^2$ )	31	0.8(2.4)	29	0.6(3.0)	29	0.148
DEHP/Total area( $\mu\text{g/g/m}^2$ )	31	43.6(2.7)	29	34.4(2.2)	29	0.264
DINP/Total area( $\mu\text{g/g/m}^2$ )	23	9.3(3.7)	29	22.2(3.3)	29	0.005
Total area <sup>c</sup> (m <sup>2</sup> )	31	79.2(41.6)	29 <sup>d</sup>	196(101.7)	29	< 0.001

Abbreviations: GM, geometric mean; GSD, geometric standard deviation.

<sup>a</sup>Number of phthalates detected. <sup>b</sup>Paired t-test *p*-value. <sup>c</sup>Area where the above-floor dust was sampled by researchers in each classroom or where the teachers cleaned with the regularly used vacuum cleaner. The data are normally distributed, and the arithmetic means and standard deviations were calculated. <sup>d</sup>Two directors or assistant directors did not report the exact area.

Figure 4-2 shows scatterplots for the mass fractions of phthalates in the dust sampled using the different methods. Unlike DINP, DBP and DEHP yielded moderate to low correlations between the concentrations using the two sampling methods. However, when the phthalate concentration was adjusted for the total area vacuumed, the statistical significance for DEHP ( $r = -0.021$ ,  $p = 0.914$ ) disappeared.

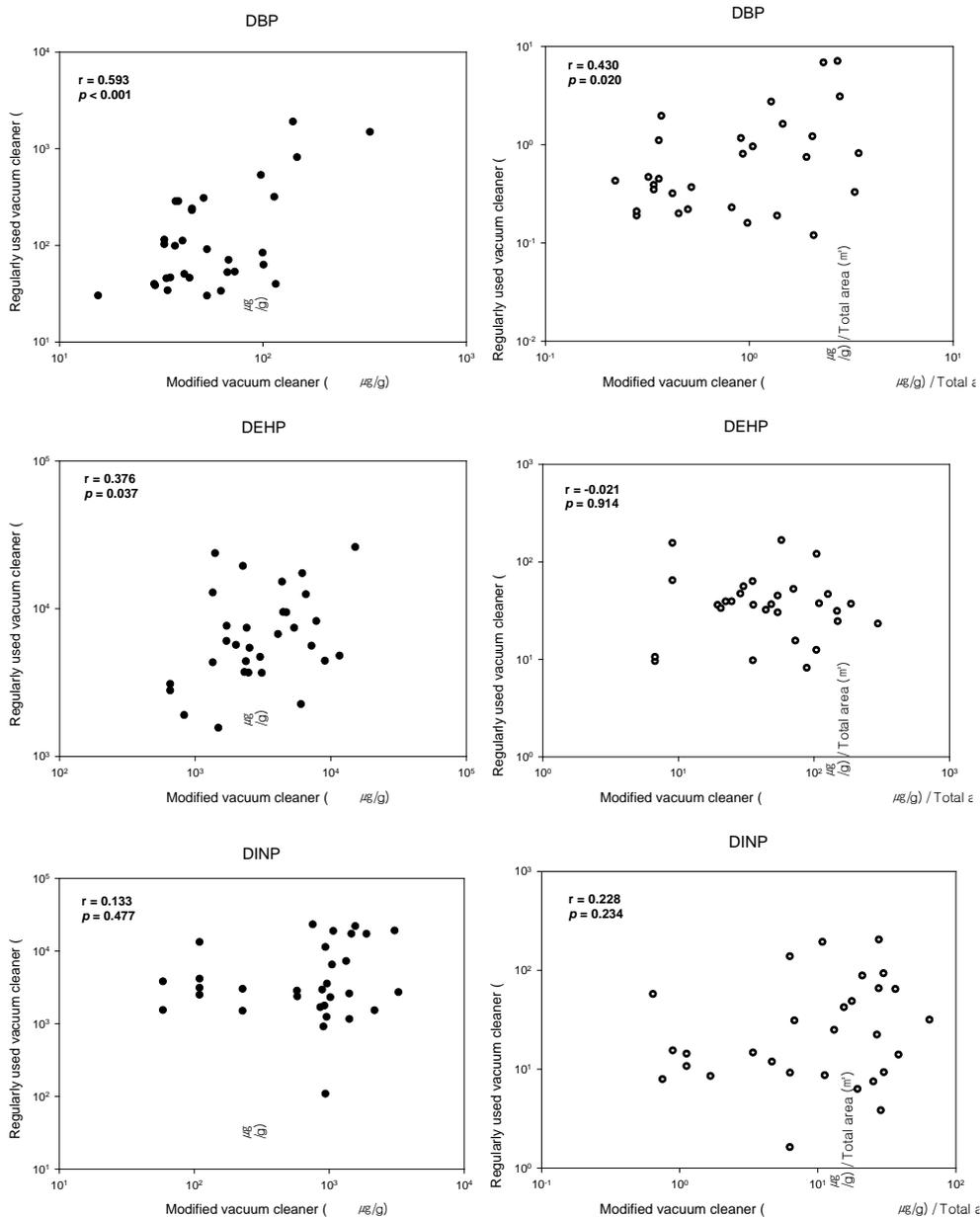


Figure 4-2. Correlations between the phthalate concentrations in dust from the modified vacuum cleaner and regularly used vacuum cleaner.

The ICCs from the sampling methods used to measure the phthalate concentrations in dust are summarized in Table 4-4. For the DBP and DEHP mass fractions, the agreement between the concentrations from the two sampling methods was fair to moderate, but the ICC for DINP was poor.

Table 4-4. Sampling dust inter-method reliability for phthalate concentration measurements

Variable	N <sup>a</sup>	ICC	95% CI
DBP( $\mu\text{g/g}$ )	31	0.565	0.032 - 0.799
DBP/Total area( $\mu\text{g/g/m}^2$ )	29	0.579	0.128 - 0.800
DEHP( $\mu\text{g/g}$ )	31	0.408	-0.150 - 0.708
DEHP/Total area( $\mu\text{g/g/m}^2$ )	29	-0.041	-1.193 - 0.509
DINP( $\mu\text{g/g}$ )	31	0.118	-0.223 - 0.442
DINP/Total area( $\mu\text{g/g/m}^2$ )	29	0.312	-0.263 - 0.651

Abbreviations: ICC, intraclass correlation; CI, confidence interval.

<sup>a</sup>Number of phthalates detected. <sup>b</sup>Two directors or assistant directors did not report the exact area.

### **Room-to-room variability.**

In 14 nursery schools, researchers collected a pair of dust samples from two distinct classrooms with the modified vacuum cleaner. For dust collected from

the regularly used vacuum cleaner, 29 sample pairs were collected from each nursery school.

Figure 4-3 shows the distributions of the differences between the phthalate concentrations in dust collected using the same sampling method from separate classrooms in the same nursery school. The DINP concentration differences in dust collected from the regularly used vacuum cleaners were sufficiently large to exceed the lower concentrations of both samples in more than half of the paired samples; samples showing this difference accounted for 10-52% depending on the sampling methods and type of phthalate.

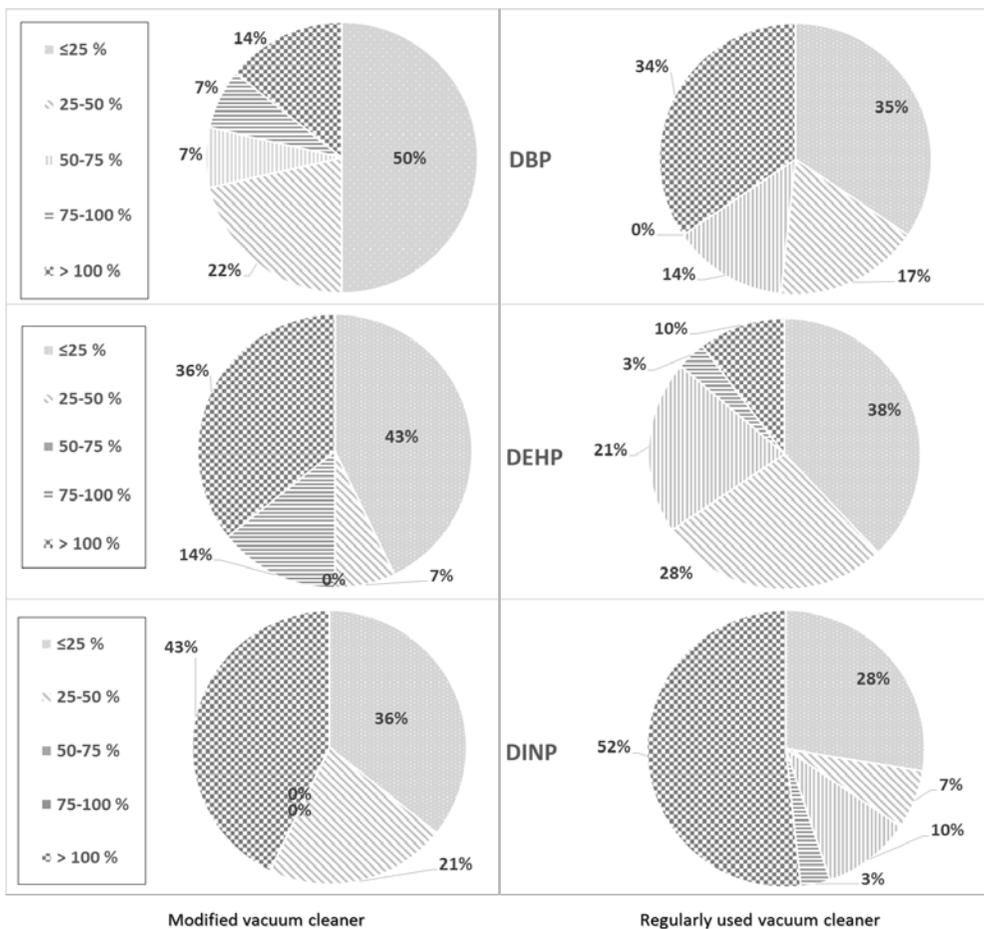


Figure 4-3. Phthalate concentration difference distributions in dust collected using the same sampling method.

The categories in the box represent the proportion of phthalate concentration differences in the paired dust samples compared with the lower concentration. The pie chart represents the percentages of paired samples classified in respective categories.

The ICCs for DBP and DEHP were moderate to high, but the DINP ICC was not (Table 4-5). The DBP and DEHP concentrations in dust collected from separate classrooms in the same nursery school showed significantly close agreement, especially for the sampling method in which dust was collected from the regularly used vacuum cleaner. Even where the concentrations were adjusted using the area included by the vacuum cleaner, the trends did not change.

Table 4-5. Correlation between the paired phthalate concentrations in dust collected using the same sampling method

Variables	Modified vacuum cleaner <sup>a</sup>				Regularly used vacuum cleaner <sup>b</sup>			
	N	ICC	95%	CI	N	ICC	95%	CI
DBP ( $\mu\text{g/g}$ )	14	0.739	0.215	0.915	29	0.912	0.814	0.959
DBP / Total area ( $\mu\text{g/g/m}^2$ )	14	0.614	-0.162	0.875	26	0.922	0.828	0.965
DEHP ( $\mu\text{g/g}$ )	14	0.215	-1.365	0.745	29	0.883	0.752	0.945
DEHP / Total area ( $\mu\text{g/g/m}^2$ )	14	0.487	-0.546	0.833	26	0.843	0.653	0.929
DINP ( $\mu\text{g/g}$ )	14	0.499	-0.509	0.837	29	0.280	-0.518	0.661
DINP / Total area ( $\mu\text{g/g/m}^2$ )	14	0.287	-1.146	0.769	26	0.467	-0.175	0.760

<sup>a</sup>The phthalate concentrations and concentrations adjusted for the area cleaned were normally distributed. <sup>b</sup>The phthalate concentrations and concentrations adjusted for the area cleaned were log-normally distributed.

### Repeatability.

Dust was sampled in six classrooms using a modified vacuum cleaner, and the dust bags from regular vacuum cleaners were collected twice over a period of 18-19 months in the same classrooms. Approximately 2 weeks after the second sampling day, the dust bags were collected again from the same classrooms. In one classroom, the final dust bag could not be collected due to a mechanical failure of the vacuum cleaner.

Most of the phthalate mass fractions were distributed normally. As shown in Figure 4-4, the phthalate concentrations in dust measured using the two sampling methods were relatively well matched for DBP and DEHP, but this was not true for DINP.

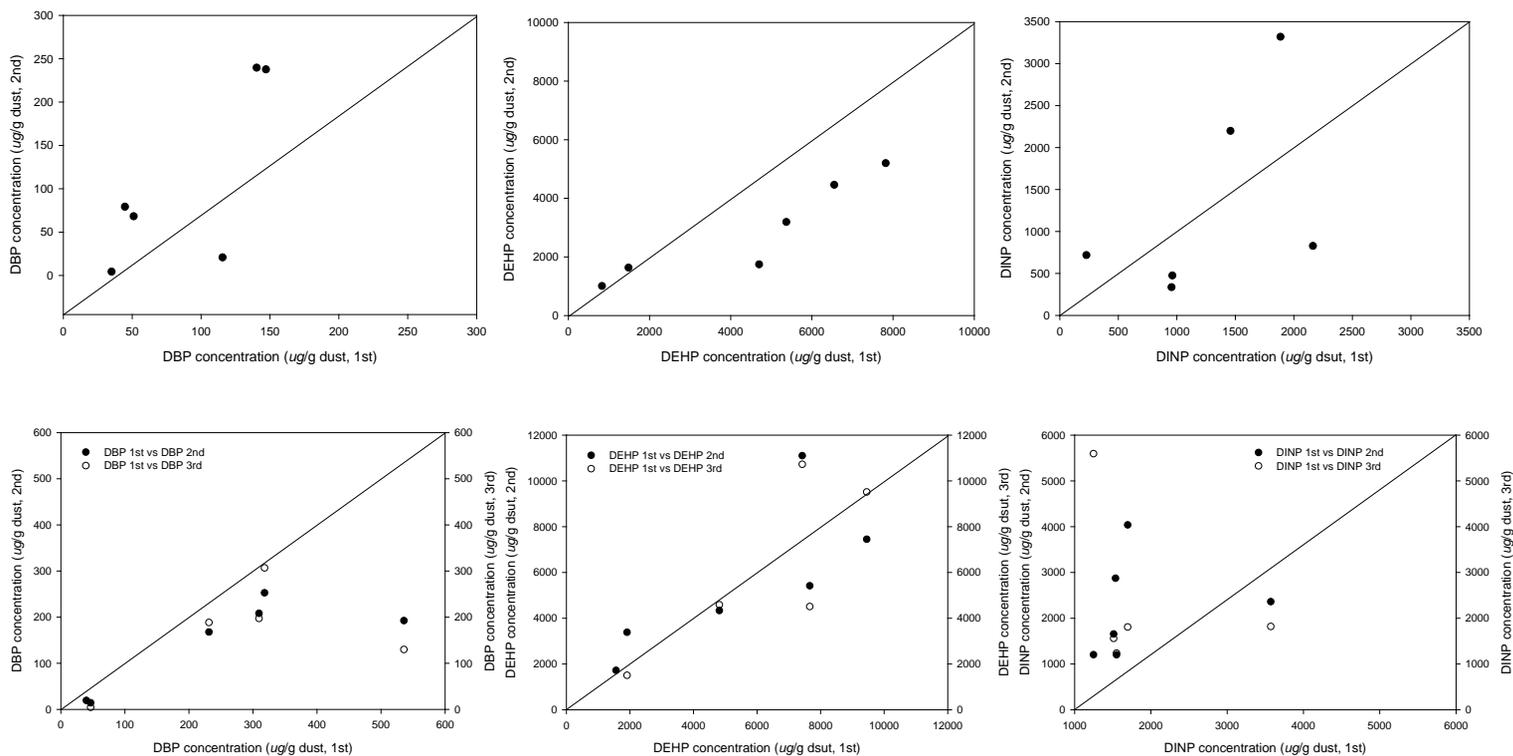


Figure 4-4. The relationship between phthalate concentrations in dust sampled using two different sampling methods. The top and bottom row figures show the results following sampling by a researcher and dust collection from a regular vacuum cleaner, respectively.

The ICCs for DBP and DEHP in dust sampled repeatedly from the two sampling method were high, but the ICC for DINP was not (Table 4-6).

Table 4-6. Consistency of phthalate concentrations between sampling times

Variables	Modified vacuum cleaner <sup>a</sup>				Regularly used vacuum cleaner <sup>b</sup>			
	N	ICC	95%	CI	N	ICC	95%	CI
DBP ( $\mu\text{g/g}$ )	6	0.750	-0.282	0.932	5	0.773	-0.149	0.975
DEHP ( $\mu\text{g/g}$ )	6	0.899	0.280	0.986	5	0.919	0.592	0.991
DINP ( $\mu\text{g/g}$ )	6	-0.005	-6.180	0.859	5	0.019	-3.957	0.891

<sup>a</sup>Dust sampling repeated twice. <sup>b</sup>Dust bag collection repeated three times. Phthalate concentrations were normally distributed.

## DISCUSSION

In this study, we compared the sensitivities of two sampling methods used to evaluate the mass fractions of phthalates in dust and determined the correlations between the phthalate concentrations in dust; the methods included indoor dust directly sampled by researchers using a modified vacuum cleaner and dust collected from regularly used vacuum cleaner bags at nursery schools. Generally, the mass fractions of phthalates in dust from the regularly used vacuum cleaners were much higher (approximately 2- to 5.3-fold) compared with the dust collected using the modified vacuum cleaner, but these differences disappeared when the values were adjusted based on the area

sampled. Further, the concordance rate was over 70% for each type of phthalate; however, the dust bag collection method yielded a slightly more sensitive detection rate for DINP than the modified vacuum cleaner, at 96.8% and 74.2%, respectively. For the DBP and DEHP mass fractions, the concentration correlations and agreement from the two sampling methods were fair to moderate ( $r = 0.376-0.593$ ,  $ICC = 0.408-0.579$ ), but the DINP coefficient was poor. Compared with the DBP and DEHP concentrations using the same sampling method in dust from distinct classrooms in a nursery school, the ICC was 0.487-0.922; however, the DINP concentrations varied with the room.

As noted above, no study has compared the phthalate concentrations in dust from different sampling methods; however, as summarized in Table 4-7, a few studies have compared different sampling methods to evaluate other indoor contaminants. Colt et al.<sup>34, 35</sup> showed that using HVS3 or collecting dust bags from a regularly used household vacuum cleaner did not yield different results; such findings are in contrast to the results reported by Allen et al.<sup>37</sup> and Björklund et al.,<sup>36</sup> wherein the PBDE concentrations in dust collected by the researchers were higher than from a home vacuum cleaner bag.

Table 4-7. A comparison of different methods to assess indoor dust contaminants

Author (year)	Methods	Target contaminants	Primary results
Colt et al. (1998)	HVS3 Dust bag <sup>a</sup>	Pesticide, PAHs, PCB	No clear difference between the results obtained by two sampling methods
Allen et al. (2008)	Thimble + Vacuum cleaner Dust bag <sup>a</sup>	PBDEs	Concentration: Researcher-collected dust > home vacuum bag Correlation: poor to moderate
Colt et al. (2008)	HVS3 Dust bag <sup>a</sup>	Pesticide, PAHs, PCB	No significant difference between the results from the two sampling methods
Björklund et al. (2012)	Cellulose filter + Vacuum cleaner Dust bag <sup>a</sup>	PBDE, Hexabromocyclododecane (HBCD)	Concentration: PBDE: Researcher-collected dust > home vacuum bag dust; HBCD: Researcher-collected dust < home vacuum bag dust Correlation: significant correlation for $\Sigma$ OctaBDE and $\Sigma$ DecaBDE but not for $\Sigma$ PentaBDE and HBCD BDE-47 in vacuum cleaner bag dust and a breast milk sample

<sup>a</sup>The dust bag was from the regularly used household vacuum cleaner.

However, this study's results are unique because the phthalate concentration differences from the different methods are statistically significant where only concentration was used, but the significance disappeared when it was adjusted based on the area sampled, except for the DINP data. This finding can be explained by the results reported by Allen et al.,<sup>37</sup> which indicate that the dust mass collected is proportional to the surface area sampled. In fact, the area cleaned by the household vacuum cleaner was much larger than the area sampled using the modified vacuum cleaner, which may account for the different mass fractions of phthalates in dust.

Additionally, the phthalate concentration in dust from the regularly used vacuum cleaner was much higher than in dust collected using the modified vacuum cleaner. However, this trend was reversed when the concentration was adjusted based on the area; there were no significant differences except for the DINP concentrations. In fact, the dust from the two different sampling methods differed in origin; the dust from the regularly used vacuum cleaner is floor-level dust, whereas the dust from the modified vacuum cleaner is above-floor-settled dust. As explained by Bornehag et al.,<sup>31</sup> the surface from which the dust is collected can also influence the resulting phthalate concentrations. For example, Clausen et al.<sup>42</sup> presented results that indicated that DEHP was directly transferred from PVC flooring to the dust that contacted the PVC

flooring, which acted as a sorption media. Generally, in Korea, the housing layout includes a floor pad that covers most indoor spaces and is typically manufactured using PVC with phthalates. Therefore, it is reasonable to speculate that the mass fraction of phthalates in dust from a regularly used vacuum cleaner may be higher than dust from a modified vacuum cleaner. However, when the concentration was adjusted based on the sample area, the findings were in contrast to this speculation. DINP did not produce such trends; the DINP concentration difference between the two dust sampling methods was significant regardless of whether the results were adjusted based on the area sampled. Additionally, the concentration was much higher in dust from the regularly used vacuum cleaner. This difference likely resulted from the aeration effect due to the frequent use of the household vacuum cleaner because DINP, which is a high-molecular-weight phthalate, is considered to be relatively unchanged by aeration compared with DBP and DEHP.

In previous studies that compared indoor dust sampling methods, the concentration correlations between the results from each method were evaluated using statistical indices such as Spearman's rank correlation coefficients or Pearson's correlation coefficients. For example, Colt et al.<sup>34, 35</sup> reported moderate to high Spearman rank correlation coefficients for most compounds. Allen et al.<sup>37</sup> and Björklund et al.<sup>36</sup> showed a statistically

significant correlation between two sampling methods based on the type of contaminant. In the present study, we also evaluated the correlation using both the Pearson correlation coefficient and ICC. The Pearson correlation coefficient only measures the association between variables, but the ICC indicates agreement between variables.<sup>43</sup> Furthermore, the ICC can be used for an interchangeable dataset to compare room-to-room variability, as in the present study. The results from this study show a fair to moderate correlation and agreement between the concentrations using the two sampling methods for DBP and DEHP. However, the DINP mass fraction correlation and agreement in dust sampled using the different methods was poor; the basis for this low to moderate correlation is unclear. In contrast to DBP and DEHP, the DINP mass fraction in dust may be influenced by indoor materials specific to a microenvironment that is distinct from building characteristics such as flooring. In fact, in our previous study, we showed that the DEHP mass fraction in dust was significantly correlated with the PVC-verified flooring.<sup>39</sup> Additionally, the area cleaned with the regularly used vacuum cleaner was much wider than the restricted classroom area where the researchers collected dust, and it included such diverse areas as a living room, corridor, and warehouse; thus, the potential phthalate sources may differ and may have resulted in the observed low to moderate correlation and agreement. Therefore,

it is unreasonable to conclude that the two sampling methods provide equal assessments for the mass fractions of phthalates in indoor dust.

To evaluate the suitability of sampling methods for indoor contaminant measurements, spatial variability is another factor that should be considered. For example, researchers have shown that PBDE and PCB congener concentrations in dust from separate rooms in a home were significantly different,<sup>37, 44, 45</sup> these researchers concluded that this difference resulted from the different microenvironments in the room. Even in-room spatial variability has been observed, and the distance from a substantial HBCD or PBDE source was identified as critical to the concentration distribution.<sup>45-47</sup>

In this study, we evaluated the agreements between the phthalate concentrations in dust using the same sampling method from distinct classrooms in a nursery school; we also assessed phthalate concentrations using ICC statistical indices. The results show that the agreement for DBP in dust using the two sampling methods and DEHP from the dust in regularly used vacuum cleaners was almost perfect. However, the agreement for DEHP in dust from a modified vacuum cleaner and DINP in dust using the two sampling methods was only fair. The rationale underlying the opposite ICC for DEHP in dust based on the sampling method was unclear. For DINP, the fair ICC may result from the different phthalate sources in the different rooms;

notably, DINP is widely used in toys, construction materials, and general consumer products.<sup>4</sup> Therefore, we conclude that the data varied with the rooms in a building, especially for DINP, and the mass fraction agreements for DBP and DEHP in dust from separate rooms in a nursery school were acceptable.

Additionally, we tested the repeatability of each sampling method whether they could consistently reflect the mass fractions of phthalates in repeatedly sampled dust at same classrooms. The DBP and DEHP concentrations in dust collected from different sampling period showed significantly close agreement, irrespective of dust sampling method. But in the case of DINP, there was no consistency between the concentrations from the repeatedly sampled dust. As identified in the previous Chapter 2 and 3, the DBP concentration was affected by the consumer products such as toy blocks, articles for role playing, and balls for playing. And the mass fraction of DEHP in dust was revealed to be strongly related with the PVC flooring. But, apart from the effects owing to the presences of toys and teaching aids in the spaces, DINP concentration was correlated with the utilization of space such as number of children and operating body of the nursery schools. Of the related factors, number of children in nursery school might be fluctuated with the time. Therefore, such differences of principal factors affecting respective phthalate concentration

might have effects on the distinction of results depending on the sampling period.

In another aspect of the results, the consistency of phthalate concentration in dust means that if PVC products were not eliminated in the indoor environment, then mass fractions of phthalates in dust would not be reduced. Therefore, inhabitants' phthalate exposure level would be maintained.

Although this study is unique and showed the suitability and correlation between two sampling methods for indoor dust based on phthalate concentrations and area-adjusted concentrations, it has certain limitations. First, we did not include other sampling methods, such as HVS3, which has been widely used in the studies to measure indoor contaminants. If we had used another method to sample indoor dust through HVS3, then we could have compared the advantages and disadvantages for the three primary sampling methods. However, such a trial may be difficult due to the rigid cleaning practices in nursery schools. Second, we could not determine the most suitable sampling method for measuring the mass fractions of phthalates. The mass fractions of phthalates in dust could be used to estimate exposure, and biomarkers indicate exposure to specific agents. If we had information on the concentration of biomarkers generated from phthalate exposure, we could

compare the two methods and determine which method more accurately estimates the potential exposure to phthalates.

Nevertheless, based on the results from this study, we can present certain useful ideas for epidemiological studies on inhabitants' phthalate exposure. Dust sampling by researchers is regarded as an effective method for evaluating indoor contaminants because it presents a standard dust loading value compared with dust collected from a regularly used household vacuum cleaner. However, because the area-adjusted phthalate concentrations from the two sampling methods did not differ and the consistency and repeatability of each sampling method is sufficiently good, collecting dust from a household vacuum cleaner is likely suitable if the researcher identifies the area cleaned by the user. In reality, household vacuum cleaners are used in various areas, such as rooms, living rooms, corridors, and warehouses. Thus, if information on the cleaned area with regularly used vacuum cleaner is available, then the results could be used to carefully determine the estimated phthalate exposure. Additionally, the physico-chemical properties of phthalates must be considered in designing phthalate exposure assessment studies because mass fractions of phthalates in dust, especially for DINP, from different sampling methods, sampling sites, and sampling period might differ based on the type of phthalate.

## REFERENCES

1. Cadogan, D. F.; Howick, C. J., Plasticizers. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000; Vol. 27, pp 509-618.
2. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-octyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 721-734.
3. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-hexyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 709-719.
4. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-isononyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 679-708.

5. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-isodecyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 655-678.
6. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di(2-ethylhexyl) phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 529-653.
7. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-n-butyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 489-527.
8. Kavlock, R.; Boekelheide, K.; Chapin, R., et al. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of butyl benzyl phthalate. *Reprod. Toxicol.* **2002**, *16* (5), 453-487.
9. Navarro, R.; Pérez Perrino, M.; Gómez Tardajos, M., et al. Phthalate plasticizers covalently bound to PVC: plasticization with suppressed migration. *Macromolecules* **2010**, *43* (5), 2377-2381.

10. Wilson, V. S.; Lambright, C.; Furr, J., et al. Phthalate ester-induced gubernacular lesions are associated with reduced insl3 gene expression in the fetal rat testis. *Toxicol. Lett.* **2004**, *146* (3), 207-215.
11. Akingbemi, B. T.; Youker, R. T.; Sottas, C. M., et al. Modulation of Rat Leydig Cell Steroidogenic Function by Di(2-Ethylhexyl)Phthalate. *Biol. Reprod.* **2001**, *65* (4), 1252-1259.
12. Fisher, J. S. Environmental anti-androgens and male reproductive health: focus on phthalates and testicular dysgenesis syndrome. *Reproduction* **2004**, *127* (3), 305-315.
13. Liu, K.; Lehmann, K. P.; Sar, M., et al. Gene Expression Profiling Following In Utero Exposure to Phthalate Esters Reveals New Gene Targets in the Etiology of Testicular Dysgenesis. *Biol. Reprod.* **2005**, *73* (1), 180-192.
14. Swan, S. H.; Main, K. M.; Liu, F., et al. Decrease in anogenital distance among male infants with prenatal phthalate exposure. *Environ. Health Perspect.* **2005**, *113* (8), 1056-1061.
15. Bornehag, C. G.; Nanberg, E. Phthalate exposure and asthma in children. *Int. J. Androl.* **2010**, *33* (2), 333-345.
16. Deutsche, T.; Reiter, R.; Butte, W., et al. A controlled challenge study on di (2-ethylhexyl) phthalate (DEHP) in house dust and the immune response in

- human nasal mucosa of allergic subjects. *Environ. Health Perspect.* **2008**, *116* (11), 1487-1493.
17. Kolarik, B.; Naydenov, K.; Larsson, M., et al. The association between phthalates in dust and allergic diseases among Bulgarian children. *Environ. Health Perspect.* **2008**, *116* (1), 98-103.
  18. Villberg, K.; Mussalo-Rauhamaa, H.; Haahtela, T., et al. Prevalence of Plastic Additives in Indoor Air related to Newly Diagnosed Asthma. *Indoor Built Environ.* **2008**, *17* (5), 455-459.
  19. Whitehead, T.; Metayer, C.; Buffler, P., et al. Estimating exposures to indoor contaminants using residential dust. *J. Expo. Sci. Environ. Epidemiol.* **2011**, *21* (6), 549-564.
  20. Roberts, J. W.; Ruby, M. G. *Development of a High Volume Surface Sampler for Pesticides in Floor Dust*; 1988.
  21. Budd, W. T.; Robert, J. W.; Ruby, M. G. *Field Evaluation of a High Volume Surface Sampler for Pesticides in Floor Dust*; 1990.
  22. Chuang, J. C.; Gordon, S. M.; Roberts, J. W., et al. *Evaluation of HVS3 Sampler for Sampling Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls*; 1994.

23. Axel Clausen, P.; Lindeberg Bille, R. L.; Nilsson, T., et al. Simultaneous extraction of di(2-ethylhexyl) phthalate and nonionic surfactants from house dust: Concentrations in floor dust from 15 Danish schools. *J. Chromatogr. A* **2003**, *986* (2), 179-190.
24. Wilson, N. K.; Chuang, J. C.; Lyu, C., et al. Aggregate exposures of nine preschool children to persistent organic pollutants at day care and at home. *J. Exposure Anal. Environ. Epidemiol.* **2003**, *13* (3), 187-202.
25. Morgan, M. K.; Sheldon, L.; Croghan, C. *A pilot study of children's total exposure to persistent pesticides and other persistent organic pollutants (CTEPP)*; Washington, DC, 2004.
26. Becker, K.; Seiwert, M.; Angerer, J., et al. DEHP metabolites in urine of children and DEHP in house dust. *Int. J. Hyg. Environ. Health* **2004**, *207* (5), 409-417.
27. Guo, Y.; Kannan, K. Comparative Assessment of Human Exposure to Phthalate Esters from House Dust in China and the United States. *Environ. Sci. Technol.* **2011**, *45* (8), 3788-3794.
28. Gevao, B.; Al-Ghadban, A. N.; Bahloul, M., et al. Phthalates in indoor dust in Kuwait: Implications for non-dietary human exposure. *Indoor Air* **2013**, *23* (2), 126-133.

29. Huang, Y.; Chen, L.; Peng, X., et al. PBDEs in indoor dust in South-Central China: Characteristics and implications. *Chemosphere* **2010**, *78* (2), 169-174.
30. Rudel, R. A.; Camann, D. E.; Spengler, J. D., et al. Phthalates, Alkylphenols, Pesticides, Polybrominated Diphenyl Ethers, and Other Endocrine-Disrupting Compounds in Indoor Air and Dust. *Environ. Sci. Technol.* **2003**, *37* (20), 4543-4553.
31. Bornehag, C. G.; Lundgren, B.; Weschler, C. J., et al. Phthalates in indoor dust and their association with building characteristics. *Environ. Health Perspect.* **2005**, *113* (10), 1399-1404.
32. Kolarik, B.; Bornehag, C. G.; Naydenov, K., et al. The concentrations of phthalates in settled dust in Bulgarian homes in relation to building characteristic and cleaning habits in the family. *Atmos. Environ.* **2008**, *42* (37), 8553-8559.
33. Langer, S.; Weschler, C. J.; Fischer, A., et al. Phthalate and PAH concentrations in dust collected from Danish homes and daycare centers. *Atmos. Environ.* **2010**, *44* (19), 2294-2301.
34. Colt, J. S.; Zahm, S. H.; Camann, D. E., et al. Comparison of Pesticides and Other Compounds in Carpet Dust Samples Collected from Used Vacuum Cleaner Bags and from a High-Volume Surface Sampler. *Environ. Health Perspect.* **1998**, *106* (11), 721-724.

35. Colt, J. S.; Gunier, R. B.; Metayer, C., et al. Household vacuum cleaners vs. the high-volume surface sampler for collection of carpet dust samples in epidemiologic studies of children. *Environ. Health* **2008**, *7*:6.
36. Björklund, J. A.; Sellström, U.; de Wit, C. A., et al. Comparisons of polybrominated diphenyl ether and hexabromocyclododecane concentrations in dust collected with two sampling methods and matched breast milk samples. *Indoor Air* **2012**, *22* (4), 279-288.
37. Allen, J. G.; McClean, M. D.; Stapleton, H. M., et al. Critical factors in assessing exposure to PBDEs via house dust. *Environ. Int.* **2008**, *34* (8), 1085-1091.
38. Rudel, R. A.; Brody, J. G.; Spengler, J. D., et al. Identification of Selected Hormonally Active Agents and Animal Mammary Carcinogens in Commercial and Residential Air and Dust Samples. *J. Air Waste Manage. Assoc.* **2001**, *51* (4), 499-513.
39. Kim, W.; Choi, I.; Jung, Y., et al. Phthalate Levels in Nursery Schools and Related Factors. *Environ. Sci. Technol.* **2013**, *47* (21), 12459-12468.
40. Bornehag, C. G.; Sundell, J.; Weschler, C. J., et al. The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. *Environ. Health Perspect.* **2004**, *112* (14), 1393-1397.

41. Hornung, R. W.; Reed, L. D. Estimation of average concentration in the presence of nondetectable values. *Appl. Occup. Environ. Hyg.* **1990**, *5* (1), 46-51.
42. Clausen, P. A.; Hansen, V.; Gunnarsen, L., et al. Emission of Di-2-ethylhexyl Phthalate from PVC Flooring into Air and Uptake in Dust: Emission and Sorption Experiments in FLEC and CLIMPAQ. *Environ. Sci. Technol.* **2004**, *38* (9), 2531-2537.
43. Müller, R.; Büttner, P. A critical discussion of intraclass correlation coefficients. *Stat. Med.* **1994**, *13* (23-24), 2465-2476.
44. Hazrati, S.; Harrad, S. Causes of variability in concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in indoor air. *Environ. Sci. Technol.* **2006**, *40* (24), 7584-7589.
45. Muenhor, D.; Harrad, S. Within-room and within-building temporal and spatial variations in concentrations of polybrominated diphenyl ethers (PBDEs) in indoor dust. *Environ. Int.* **2012**, *47*, 23-27.
46. Stuart, H.; Ibarra, C.; Abdallah, M. A.-E., et al. Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: Causes of variability and implications for human exposure. *Environ. Int.* **2008**, *34* (8), 1170-1175.

47. Harrad, S.; Abdallah, M. A.-E.; Covaci, A. Causes of variability in concentrations and diastereomer patterns of hexabromocyclododecanes in indoor dust. *Environ. Int.* **2009**, *35* (3), 573-579.

## **CHAPTER 5.**

### **SUMMARY AND CONCLUSIONS**

Phthalates are well-known endocrine disruptors, regarded as one of the risk factors for atopic diseases in children. When not at home, children now spend most of their time in a nursery environment. The main objective of this study was to evaluate the mass fractions of phthalates in dust samples from nursery school classrooms and to identify the key sources.

Dust samples were collected from 64 classrooms of 50 nursery schools, and the consumer products used regularly in these areas, including the building materials, were analyzed using a portable XRF analyzer to determine whether they contained PVC. For the materials confirmed to contain PVC, the areas or weights were measured and related to the phthalate concentration. Eight phthalates were analyzed in dust samples using a gas chromatograph/mass-selective detector: DMP, DEP, DBP, BBP, DEHP, DnOP, DINP, and DIDP

DEHP was the most abundant phthalate, with a geometric mean concentration of 3,170  $\mu\text{g/g}$  dust, which was significantly correlated with the area of flooring containing PVC. DINP, which has not been widely-reported in other studies, was the second-most abundant phthalate, with a geometric mean concentration of 688  $\mu\text{g/g}$  dust, influenced by the number of children in the institution and the agency operating the nursery school.

Because phthalates have been incorporated into PVC during production,

consumer products containing PVC may be a major source of phthalates. In this study, we examined 3,180 consumer products to verify whether they contained PVC. It was found that 1,067 consumer products (33.6%) were made of PVC material. Interior materials used in the construction of the building accounted for 83.2% of the total area of PVC-verified products, and the PVC floor was correlated significantly with the mass fraction of DEHP. The mass fraction of DINP in dust showed relationships with the weights of toys and teaching aids, doors, and musical instruments, such as pianos. The weights of blocks for toys, articles for role playing, and gymnastic apparatuses were significant factors affecting the DBP concentration.

In addition to the evaluation of phthalate concentrations in indoor dust and the associated source determination, two indoor dust sampling methods (dust sampling using a modified vacuum cleaner and collection of dust from the bag of the regularly used vacuum cleaner) were compared. The correlations and agreements of the results between the two sampling methods were moderate for DBP, but poor to moderate for DEHP. The spatial variability was small for DBP and DEHP in indoor dust sampled from separate classrooms in a nursery school. The repeatability of the two sampling methods was good for DBP and DEHP. However, the correlations and agreements of the results obtained between the two sampling methods and the repeatability were poor for DINP, with a high level of

room-to-room variability. If the area cleaned was recorded, the phthalate content of the dust in the bag of a regularly used vacuum cleaner could be used to estimate phthalate exposure. The physico-chemical properties of phthalates must be considered when designing phthalate exposure assessment studies, because the mass fractions of phthalates in dust (especially long-chain phthalates such as DINP) obtained from different sampling methods, sites, and periods might differ based on the type of phthalate.

This is the study to investigate the quantitative relationship between the mass fractions of phthalates in dust and the use of PVC-verified materials, especially for regularly used consumer products and building materials in nursery schools. Considering the developmental toxicity risk of phthalates and the vulnerability of children, exposure in children is a major public health concern. Phthalate levels in indoor dust were associated with the use of PVC products, including building materials and consumer products. It was found that various PVC products were used in nursery schools. Although the ingestion of foods contaminated with phthalates is regarded as a major exposure route for the general population, the contamination of indoor dust with phthalates can result in elevated phthalate exposure. Therefore, to reduce phthalate exposure in children, it is necessary to reduce or eliminate the use of PVC products.

## 초록

### 어린이 보육시설에서의 먼지 내 프탈레이트 농도와

### 관련 요인

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프탈레이트는 생식독성과 발달독성을 갖고 있으며 환경호르몬으로 잘 알려진 물질이다. 프탈레이트는 소비제품과 공업제품 등에 매우 다양하게 사용되어왔으며 특히 polyvinyl chloride (PVC) 제품에서 가소제로 사용되어 왔다. 그러나 열역학적인 이유로 인해 제품으로부터 쉽게 빠져 나와 주변 환경을 오염시키는 특징을 갖고 있다. 일반인구에 대한 노출은 매우 광범위하고 그 수준이 다양하다. 어린이들은 프탈레이트 노출에 대해 약리역학적으로 어른들에 비해 훨씬 취약하다고 알려져 있으나 불행히도 노출 수준이 성인에 비해 높다. 프탈레이트에 대한 노출의 주요 경로는 음식을 통한 섭취라고 알려져 있지만 프탈레이트로 오염된

먼지의 흡입이나 섭취 역시 주요한 노출경로로 파악되고 있다. 따라서 실내 먼지의 평가는 환경오염물질에 대한 인간의 노출을 예측하는 데 있어 유용하게 활용될 수 있다. 어린이들은 집에서뿐만 아니라 그 다음으로 많은 시간을 보내는 보육시설 등에서도 프탈레이트로 오염된 먼지에 노출될 가능성이 있다. 본 연구의 목적은 어린이 보육 시설 내 먼지에서의 프탈레이트 농도를 평가하고 그것에 영향을 미치는 주요한 요인들을 찾아내는 것이다.

첫 번째 연구에서는 50 개의 보육시설 내 64 개의 교실에서 먼지를 채취하였고 X-ray fluorescence (XRF) analyzer 를 이용해서 건축 내장재와 가구와 같은 건축 구성물 등을 중심으로 PVC 여부를 확인하였다. PVC 로 확인된 제품은 면적이나 무게로 측정하여 먼지 내 프탈레이트 농도와의 상관성을 평가하였다. Gas chromatograph/mass-selective detector (GC/MS)를 이용해 먼지 내에서 8 가지 종류의 프탈레이트를 분석하였다: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), Di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP), di-isononyl phthalate (DINP), and di-isodecyl phthalate (DIDP). DEHP 는 기하평균 3,170  $\mu\text{g/g dust}$  의 농도로써 프탈레이트 중 가장 높은 수준이 확인되었으며 PVC 바닥재 면적과

통계적으로 유의한 관계가 있음을 보여주었다. 다른 연구에서 잘 보고되지 않은 DINP 의 경우, 기하평균 688  $\mu\text{g/g dust}$  의 농도로써 DEHP 의 뒤를 이어 높은 농도가 확인되었으며 보육시설 내의 어린이의 수 그리고 운영주체의 구분에 따라 먼지 내 농도가 영향을 받고 있었다. 이처럼 PVC 건축자재의 사용이나 건물의 운영이 보육시설 내 프탈레이트의 농도에 영향을 미치고 있음을 확인하였다.

두 번째 연구에서는 보육시설 내에서 사용되고 있는 3,180 개의 소비제품들을 대상으로 PVC 여부를 확인하고 그것이 먼지 내 프탈레이트의 농도에 어떻게 영향을 미치는지를 평가하였다. 첫 번째 연구에서와 마찬가지로 XRF analyzer 를 이용해 소비제품의 PVC 여부를 확인하였고 GC/MS 를 이용해 먼지 내 프탈레이트의 농도를 분석하였다. 평가 결과, 1,067 (33.6 %)개의 소비제품들이 PVC 재질의 제품들로 확인되었다. 장난감 블록, 역할놀이 용품들, 그리고 공과 같은 체육용품들의 무게가 DBP 의 농도에 영향을 미치는 요인으로 파악되었다. 건물 내장재는 PVC 로 확인된 제품의 전체 면적 중 83.2 %를 차지하고 있었고 PVC 바닥재의 면적은

DEHP 의 농도와 유의한 상관성을 보여주었다. 먼지 중 DINP 의 농도는 PVC 로 확인된 장난감이나 교구들의 무게 그리고 문이나 피아노 같은 것들의 면적과 유의한 상관성이 있었다. 이처럼 어린이 보육시설 내에 PVC 제품들이 많이 사용되고 있고 이들이 먼지의 프탈레이트 오염에 영향을 미치고 있음이 확인되었다.

실내 먼지에서의 프탈레이트 농도와 그것에 영향을 미치는 유효한 요인을 평가하는 것 이외에, 유해물질 분석을 위한 실내 먼지를 샘플링하는 두 가지 방법(변형된 진공청소기를 이용하여 연구자가 직접 먼지를 샘플링하는 방법과 기존에 사용중인 진공청소기의 먼지 주머니를 수거하여 먼지를 취하는 방법)의 효과를 비교해 보았다. 두 방법에 의해 샘플링된 먼지 내 프탈레이트의 농도 간 상관성과 일치도는 DBP 의 경우 적절하였으며 DEHP 의 경우 일부 부족하거나 적절한 수준이었다. 동일 보육 시설 내 두 곳의 교실에서 샘플링된 먼지 중 프탈레이트의 농도를 비교한 결과 각 방법에 의한 결과는 DBP 와 DEHP 의 경우 공간적 변이가 적었다. 또한 각 방법에 의한 반복 테스트 결과에서도 DBP 와 DEHP 의 경우 일치도가 높았다. 그러나

DINP 의 경우 두 방법간 상관성이나 일치도가 낮을 뿐만 아니라 공간적 변이도 높았으며 재연성 역시 좋지 않았다. 따라서 기존의 진공청소기를 이용하더라도 청소기가 사용된 면적에 대한 정확한 정보를 얻을 수 있다면 dust loading 과 같은 결과를 얻어낼 수 있어 프탈레이트 노출을 예측하는 데 쉽고 유용한 샘플링 방법으로 활용할 수 있을 것으로 판단된다. 다만, 노출 평가를 위한 연구 설계에 있어 어떤 샘플링 방법을 채택하더라도 프탈레이트의 물리화학적 특징이 잘 고려되어야 한다. 왜냐하면 프탈레이트의 종류에 따라서 (DINP 와 같이 긴 사슬을 갖고 있는 프탈레이트의 경우) 샘플링 방법, 위치, 그리고 시기에 따라서 먼지 내 농도가 달라질 수 있기 때문이다.

본 연구는 보육 시설에 사용된 건축자재와 소비제품을 중심으로 PVC 여부를 확인하고 그것이 시설 내 먼지 중 프탈레이트의 농도와 어떤 관련이 있는지를 정량적으로 평가한 연구이다. 프탈레이트가 갖고 있는 발달독성과 노출로 인한 건강영향의 측면에서 어린이들의 취약성을 고려할 때, 어린이들의 프탈레이트 노출은 보건학적으로 중요한 의미를 갖는다고 하겠다. 본 연구의

결과, 보육 시설에서 다양한 PVC 제품이 사용되고 있음이 확인되었고 실내 먼지 중 프탈레이트 농도는 PVC 소재의 건축자재나 소비제품의 사용과 관련이 있었다. 비록 프탈레이트로 오염된 음식을 섭취하는 것이 일반인구에게 프탈레이트에 대한 주요한 노출경로이지만 그것으로 오염된 실내 먼지는 프탈레이트의 노출 수준을 더욱 높일 수 있다. 따라서 어린이들의 프탈레이트 노출 수준을 낮추기 위해서는 PVC 제품의 사용을 줄이거나 차단하는 것이 필요하다.

주요어: 프탈레이트, PVC, 어린이, 보육시설, 실내 먼지, 진공청소기

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