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Phthalate Esters on Hands of Office Workers: Estimating the Influence of Touching Surfaces

Wei Shi,[†] Jing Guo,[†] Yubin Zhou,[†] Dongyang Deng,[†] Zhihua Han,[†] Xiaowei Zhang,[*,†] Hongxia Yu,[*,†] and John P. Giesy[†,‡,§,∥]

[†]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, People's Republic of China

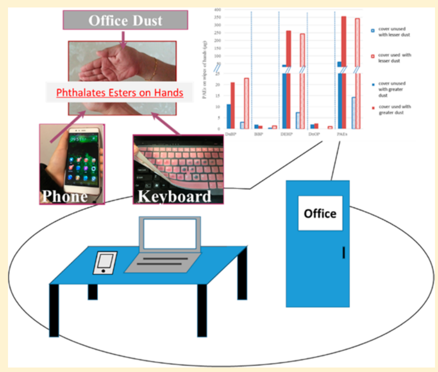
[‡]Department of Veterinary Biomedical Sciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5B3, Canada

[§]Department of Zoology and Center for Integrative Toxicology, Michigan State University, East Lansing, Michigan 48824, United States

[∥]Department of Biology & Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong, Kowloon, Hong Kong SAR, China

Supporting Information

ABSTRACT: Phthalate esters (PAEs) are known to be transferred to hands by contact with surfaces, however, little is known about the associations between masses on hand wipes and the frequency or duration of touching surfaces, especially surfaces in office environments. Relationships between PAEs on hands and multiple surfaces in offices were investigated. Wipes of hands, computers, and mobile phones as well as dust on furniture were collected from 55 offices in China. Positive associations were found between masses of di-2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DnBP), benzyl butyl phthalate (BBP), and di-*n*-octyl phthalate (DnOP) on wipes of hands and wipes of keyboards of computers. When workers used keyboards with polymer covers (dust covers), masses of these lipophilic PAEs on hands were significantly correlated with masses on keyboards rather than dust on furniture. For workers who used keyboards without polymer covers, masses on hands were related to masses in dust on furniture. Use of polymer covers containing PAEs and less washing of hands could increase the extent of exposure via hand to body of office workers, which could further result in as much as 10-fold greater hazard. Thus, more hand washing and less use of polymer products containing PAEs were recommended for office workers to reduce exposure.



INTRODUCTION

Phthalate esters (PAEs) are used as plasticizers to enhance the flexibility of a variety of household and building materials, including cables, wires, silicone films, screen guards, vinyl flooring, and polyvinyl chloride (PVC) tubing.[1] Phthalate esters, including di-2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DnBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), benzyl butyl phthalate (BBP), and di-*n*-octyl phthalate (DnOP) (Table S1),[2,3] are not chemically bound within products and can be slowly emitted into indoor environments. In a study that analyzed 89 organic chemicals in 120 homes, PAEs were some of the most abundant indoor pollutants.[4]

Recently, indoor exposure of humans to PAEs on skin and especially on hands has been shown to be non-negligible.[5,6] Phthalate esters that are transferred to hands by contact with surfaces and direct air-to-skin transport can represent a significant proportion of total accumulation.[6] Besides direct absorption through skin, PAEs on hands can result in inadvertent ingestion, by biting of nails, sucking of digits, or eating of finger foods.[7,8]

Because previous studies of PAEs have focused on residential exposure, little is known about exposure in offices, although studies have shown greater concentrations of PAEs in dust from offices than in dust from apartments.[9] Phthalate esters that tended to be strongly adsorbed to indoor surfaces, such as protectors of computer screens, keyboards, furniture, floor, and desks, are commonly touched by hands of office workers.[10] Whether and how touching surfaces in offices can increase penetration through hands and further increase the health risk is unknown.

It was hypothesized that PAEs in office furniture might result in exposure of office workers through touching surfaces. The main objectives of this study were to examine relationships between PAEs on hands of people and on probable touched

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surfaces in offices by determining amounts of PAEs on surfaces in offices, including computers, mobile phones, and dust on furniture. Another objective was to improve our understanding of the role of behaviors of workers, including the use of polymer covers and habits of hand washing, in these relationships and also the hazards of exposure via hand to body.

■ MATERIALS AND METHODS

Collection of Samples. Samples were collected from April to June 2014. Participants for this study consisted of 55 adults who worked at least 20 h a week in an office and were healthy nonsmokers in the cities of Huaian (n = 12), Zhenjiang (n = 31), and Nanjing (n = 12) in east China. Offices were located in 10 different buildings, and only one person per office participated in the study. Questionnaires were also completed at the time samples were collected (see the study design in the Supporting Information). Within-individual variability was estimated by collecting samples in triplicate from four participants. Samples of dust were collected from each participant's office, including dust on desks, chairs, bookcases, and personal accessible furniture, using a standardized protocol that used a mini-vacuum cleaner.

To avoid contamination of hands from sources other than the offices, participants were asked to wash their hands before entering the office. Samples of PAEs on hands were collected by use of wipes applied at close of business. A 7.6 cm × 7.6 cm sterile gauze pad precleaned with dichloromethane and acetone was immersed in 3.0 mL of isopropyl alcohol (Tedia Co. Ltd., Fairfield, OH) and then used to wipe the palm and back of the hand from wrist to fingertips, including sides. Wipes of computer keyboards and mobile phones were collected from participants in their office after collection of wipe samples of hands and at least 1 day after the last time the computer, phone, or furniture was cleaned.

To confirm sources of PAEs, wipes of keyboards were further collected from 12 computers in six offices. In each office, there were two keyboards, one with a polymer cover and one without a polymer cover. Polymer keyboard covers are removable polymer plastic sheets that are placed on keyboards and left in place while typing. Keyboards and polymer covers were cleaned with isopropyl alcohol in the morning and were kept in offices without disruption for 5 days. More information about the collection of samples is given in the Supporting Information.

Preparation of Samples and Quantification of PAEs. PAEs in samples were extracted using accelerated solvent extraction (ASE). PAEs were quantified using a Thermo (San Jose, CA) TSQ Quantum Discovery triple-quadrupole mass spectrometer in multiple-reaction monitoring (MRM) mode. More detailed information about instrumental analysis, procedural blanks, and other QA/QC procedures is given in the Supporting Information and Tables S1 and S2.

Assessment of Cumulative Hazard. The concept of relative cumulative hazard quotient (HQ), developed previously, was employed to incorporate cumulative exposure into the assessment.[11] The daily intake (DI) of PAEs through exposure on hands was divided by tolerable daily intake values for each PAE (TDI_i value), and the HQs for individual PAEs (HQ-PAE_i) were summed to obtain total hazard quotients (HQs), including BBP, DBP, DEP, and DEHP.

$$\mathrm{HQs} = \sum_{i=1}^{n} \text{HQ-PAE}_i = \sum_{i=1}^{n} \frac{\mathrm{DI}_i(\mu\text{g/kg of body weight/day})}{\mathrm{TDI}_i(\mu\text{g/kg of body weight/day})} \quad (1)$$

where DI_i is the daily intake (exposure through hand) of individual PAEs and n is the number of PAEs considered. DI_i is the sum of exposure through hand-to-mouth contact (micrograms per kilogram of body weight per day) and absorption through the dermis of the hand (micrograms per kilogram of body weight per day) (more detail is given in the Supporting Information and Table S3).

Data Analysis. We used Spearman correlations (SPSS statistics software package, version 17.0) to determine associations between continuous variables while minimizing the influence of outliers. To minimize effects of skewed data and outliers, we created categorical variables from surfaces and hand wipe data. Two-level variables (lesser and greater) were created using the median as a cut point (detail in the Supporting Information).

■ RESULTS AND DISCUSSION

Phthalate Esters on Wipes of Hands. Phthalate esters were detected in all wipes of surfaces of hands (Table S4). As expected, DEHP was the predominant compound, followed by DnBP and DnOP. This pattern for skin wipes is consistent with the pattern observed in serum of people from China for DEHP, DnBP, and DnOP, although no study has previously reported masses of DnOP on wipes of hands.[12,13] Few studies have examined phthalates on wipes of hands (Table S5). Generally, DEHP and DnBP are among the most widely detectable PAEs on wipes of hands in Korea, Beijing, and also east China detected in this study.[14,15] DEP was not detected on wipes of hands of Koreans, while a frequency of detection of <20% was observed in the study of people in Beijing, which is approximately the same as the frequency of 52% observed in our study. This might be due to its greater vapor pressure, which results in a greater partition coefficient.[16]

Phthalate Esters from Surfaces in Offices. PAEs could be detected on surfaces of furniture, keyboards, and phones, which on the basis of the results of questionnaires, were the most touched surfaces (Table S4). DnBP, BBP, DEHP, and DnOP had a greater detection frequency for all types of surface samples. DEHP was the most predominant compound, with geometric means (GMs) of 148, 83.6, and 10.2 μg for dust, keyboards, and phones, respectively. For all PAEs, masses on keyboards were 3–8-fold greater than those on phones, which might be due to the large area of keyboards, and limited variation indicated similar sources for PAEs on keyboards and phones. Distributions of masses and normalized concentrations of PAEs measured on wipe samples had similar variability (Figure S1), and masses, not concentrations, on wipes of hands and surfaces of computer keyboards and phones were used in the following studies. Concentrations and masses of PAEs in repeated samplings of dust and wipes over a 3 month period are mostly consistent (see repeated measurements in the Supporting Information and Figure S2).

Associations of PAEs on Hand Wipes with Indoor Surfaces. Total masses of PAEs on wipes of hands were positively correlated with masses on wipes of surfaces of computer keyboards, with a Spearman correlation coefficient (R) of 0.59 [p < 0.001 (Figure S3)]. Among the six PAEs,

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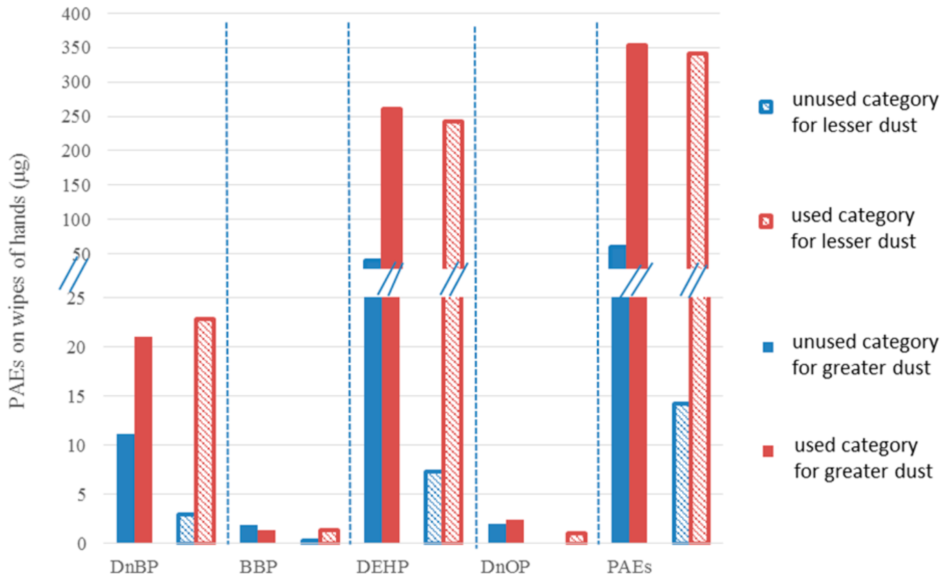

Figure 1. Geometric means (GMs) of masses of phthalate esters on wipes of hands by the amount of dust in the office and polymer cover using categories (n = 39). Greater masses were found in the less dust/used category than in the more dust/unused category ($p < 0.05$).

masses of DEHP and DnBP on wipes of keyboards and hands were most correlated, with Spearman correlation coefficients (R) of 0.58 ($p < 0.001$) and 0.47 ($p < 0.001$), respectively (see Figures S4 and S5). Results of linear regression showed that DEHP and DnBP on surfaces of computer keyboards were a significant predictor of PAEs on hands [$p < 0.001$ (Table S6)]. Masses of DEP and DMP on wipes of computer keyboards were not associated with masses on hands. This indicated that the behavior of congeners with shorter alkyl side chains, such as DEP and DMP, in the indoor environment might differ from that of longer chain congeners.[17] Results of previous studies have indicated that shorter chain PAEs are more hydrophilic; thus, they might be less likely to stick to surfaces of hands, especially for longer periods of time.[18]

Total masses of PAEs on wipes of hands were weakly correlated with concentrations in office dust and wipes of surfaces of phones. Similar results were obtained for other individual phthalates. Previous studies have also shown weak associations between masses of penta-BDE, BDE-183, or BDE-209 in office dust and masses on hands.[19−21]

Predictors of Masses of PAEs in Wipes of Hands. Masses of total PAEs were further categorized according to the number of times hands were washed during the work day. Participants who washed their hands fewer than four times per day had on average masses of Σphthalate esters on their hands ∼10-fold greater than the masses of those who washed more frequently. Similar situations were observed for masses of DnBP, BBP, DEHP, and DnOP on less frequently washed hands, which were 3-, 7-, 16-, and 7-fold greater than masses on hands that were washed more frequently (Table S6).

According to the questionnaire, participants who washed their hands fewer than four times per day were further divided into two categories according to whether they used a polymer keyboard cover (Table S6). Masses of the sum of PAEs on wipes of hands of those who used polymer covers (n = 24) were approximately 14-fold greater than masses on hands of individuals who did not use polymer covers on keyboards (n = 15), although concentrations in dust from offices for the two categories were similar. Similar trends were observed for DEHP and DnBP on wipes of hands, which were 4- and 18-fold greater, respectively. Masses of DEHP and DnBP on polymer keyboard covers were significantly correlated with masses on hands of those who used polymer covers (for DEHP, r = 0.88 and $p < 0.001$; for DnBP, r = 0.66 and $p < 0.001$), and the correlations were stronger than those for the person who did not use polymer covers on keyboards (for DEHP, R = 0.57 and $p < 0.001$; for DnBP, R = 0.38 and $p < 0.001$). For persons who used polymer covers, the greater masses of PAEs on their hands were likely caused by direct contact with polymer covers during working hours.

Participants in offices with lower concentrations of ΣPAEs, DnBP, BBP, DEHP, and DnOP (with ΣPAEs being lower than median masses) in dust who used polymer covers (n = 10) had masses of PAEs on wipes of their hands significantly ($p < 0.01$) greater than those of people who worked in offices with greater concentrations (with ΣPAEs being greater than median masses) in dust but did not use polymer covers [n = 14 (Figure 1)]. For those who did not use polymer covers, participants in offices with higher concentrations of PAEs in dust had significantly ($p < 0.01$) greater masses of PAEs on wipes of their hands. This result indicated that for workers who did not use polymer covers on their keyboards, redistributions of PAEs in office environments influenced masses on hands and concentrations in dust on furniture were correlated with masses on hands. Masses on hands of workers who used polymer covers on their keyboards were less related to concentrations in office dust and more related to masses on polymer covers, which seems to be the source of the PAEs on hands.

Influence on Hazards of Exposure via Hand to Body. Estimated HQs of total exposure via hands during working were 0.03 (50th percentile of masses) and 0.8 (95th percentile of masses), which were less than 1.0, but by a small margin of safety (1.0/0.8 = 1.3) (Table 1). The mean cumulative HQ for participants who washed their hands fewer than four times was twice the amount for those who washed more than four times per day. Among the participants who washed their hands fewer than four times per day, the HQ for people who used keyboard polymer covers was 0.18 and is as much as 10-fold greater than that for people who did not use polymer keyboard covers.

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Table 1. Hazard Quotients (HQs) for Lipophilic Phthalate Esters (PAEs) through Hand to Body Exposures among Different Categories

	individual TDI_i [μg (kg of body weight)$^{-1}$ day^{-1}]	total absorption through hands		more frequent hand washers		less frequent hand washers		not using a keyboard dust cover		using a keyboard dust cover	
		50th percentile HQ	95th percentile HQ	50th percentile HQ	95th percentile HQ	50th percentile HQ	95th percentile HQ	50th percentile HQ	95th percentile HQ	50th percentile HQ	95th percentile HQ
DnBP	10	1.71×10^{-2}	5.84×10^{-2}	2.31×10^{-2}	2.31×10^{-2}	2.38×10^{-2}	7.59×10^{-2}	1.30×10^{-2}	3.00×10^{-2}	3.72×10^{-2}	9.01×10^{-2}
BBP	200	7.91×10^{-5}	6.46×10^{-4}	8.55×10^{-5}	8.55×10^{-5}	1.17×10^{-4}	1.25×10^{-3}	1.16×10^{-4}	2.72×10^{-4}	1.13×10^{-4}	1.14×10^{-3}
DEHP	50	9.09×10^{-3}	7.82×10^{-1}	1.10×10^{-2}	1.10×10^{-2}	2.99×10^{-2}	1.05	6.98×10^{-3}	2.54×10^{-2}	1.44×10^{-1}	1.06
DnOP	370	2.72×10^{-5}	5.80×10^{-4}	7.12×10^{-5}	7.12×10^{-5}	6.13×10^{-5}	5.64×10^{-4}	1.13×10^{-5}	1.67×10^{-4}	7.09×10^{-5}	6.57×10^{-4}
sum		2.63×10^{-2}	8.42×10^{-1}	3.42×10^{-2}	3.42×10^{-2}	5.38×10^{-2}	1.13	2.01×10^{-2}	5.58×10^{-2}	1.82×10^{-1}	1.15

Among multiple surfaces in offices, exposure to PAEs through hands is likely affected by exposure to PAEs on surfaces of computer keyboards, especially when keyboard polymer covers are used. Washing of hands and not using polymer keyboard covers could reduce the mass and related hazard of exposure of office workers to PAEs via hands. Today, polymer products, including polymer keyboard covers and protective films for phone/pad screens, that contain PAEs are widely used and act as the most common touchable surface according to our questionnaire survey, with total contact being as much as 10 h per day. These polymer products contain PAEs as supplements or impurities. Significant migration of PAE from some polymer packaging of foods or oil has been investigated previously. However, to the best of our knowledge, little information is available from which to evaluate migration of PAEs from polymer surfaces to hands. Because direct contact with these may be an underappreciated source of exposure of humans, more attention should be paid to the additive compositions of polymer products in general.[22,23]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00458.

Supporting experimental section, results section with a detailed description, Tables S1−S6, and Figures S1−S5 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhangxw@nju.edu.cn. Telephone: 86 25 89680623. Fax: 86 25 89680623.

*E-mail: yuhx@nju.edu.cn.

Notes

The authors declare no competing financial interest.

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[†]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, People's Republic of China

[§]Department of Veterinary Biomedical Sciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5B3, Canada

[‖]Department of Zoology, and Center for Integrative Toxicology, Michigan State University, East Lansing, MI 48824, USA

[#]Department of Biology & Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong, Kowloon, Hong Kong SAR, China

Experimental Section

Chemicals and materials.

Phthalate esters (PAEs) including di-2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DnBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), benzyl butyl phthalate (BBP) and di-n-octyl phthalate (DnOP) were purchased from Labor Dr. Ehrenstorfer-Schäfers (Augsburg, Germany), with a purity of >99% (Table S1). Corresponding deuterated internal standards including DnBP-d4 and DEHP-d4 were purchased from AccuStandard Inc. (New Haven, CT), with a purity of >99%.

Study design.

Offices were located in ten different buildings, and only one person was allowed to participate per office. Participants consisted of 30 females and 25 males that ranged from 22 to 50 years old with a median age of 37 years. Collection of dust from wipes of surfaces of computers, mobile phones and hands as well as administration of the questionnaire were done at the same time. All participants gave their informed consent and filled out a short questionnaire with questions regarding age, sex, occupation, the most probable surfaces touched; frequency/hours for touching various surfaces. Some related habits including washing of hands, cleaning of surfaces of computers and phones and use of polymer covers on computer keyboards; Materials of which computer keyboards, phone screens and other furniture were made. Protocols were approved by the School of the Environment of Nanjing University Institutional Review board. Participants were excluded if they had washed their hands within the previous 60 min prior to collection of wipes of hands. Samples were collected from participants in their offices during the afternoon. Samples were stored at -20 °C until analysis. Within-individual variability was estimated by collecting samples in triplicate from four participants.

Surface samples were collected from each participant's office, including dust on desks, chairs, bookcases and personal accessible furniture by use of a standardized protocol that used a mini vacuum cleaner. Each office was vacuumed for approximately 10 min. To prevent cross-contamination, equipment used for collection of dust and processing was cleaned between samplings with a solution of 10% methanol (Tedia Co. Ltd, Fairfield, OH, USA), and hot water. Homogenized samples were placed in amber glass jars that was combusted at 450 °C for 4 hour, then pre-cleaned with dichloromethane (Tedia Co. Ltd, Fairfield, OH, USA), and acetone (Tedia Co. Ltd, Fairfield, OH, USA).

Samples of PAEs on hands were collected by use of wipes applied at close of business. One wipe was used per hand and the two wipes collected per individual were gathered in a pre-cleaned amber glass jar and further extracted and analyzed together, providing one measurement per participant.

Concentrations of PAEs on wipes were normalized to surface area of the hand by use of the protocol described in the U.S. EPA Exposure Factors Handbook [1] (Equations S1 and S2).

$$\text{Hand surface area (HSA)} = a \times \text{Body surface area (BSA)} \quad \text{(S1)}$$

$$\text{Body surface area (BSA)} = b \times \text{mass}^c \times \text{height}^d \quad \text{(S2)}$$

Where: HSA, BSA, weight and height are reported in units of cm^2, cm^2, kg and cm, respectively. The variables *a*, *b*, c and *d* represent specific constants as 2.5%, 71.84, 0.425 and 0.725, respectively [2].

A 7.6 cm×7.6 cm sterile gauze pad that had been pre-cleaned with dichloromethane and acetone was immersed in 3 mL isopropyl alcohol. One wipe was used for the surface of the keyboard and another for the mouse, and the two wipes collected per computer were combined in a pre-cleaned amber glass jar. One wipe was used for the front surface of the mobile phone and another for the back, and the two wipes were combined in a pre-cleaned amber glass jar.

As a very limited investigation of temporal variability in concentrations of PAEs, within-individual variability was estimated by collecting samples including coincident dust and wipes of hands, computers and mobile phones in triplicate from four participants (three samples per participant performed in April, May and June). The participants who were included were one man from Nanjing, one man from Huaian and two women from Zhenjiang.

Quantification of PAEs.

Two grams of each sample of dust or gauze pad were extracted three times with dichloromethane: acetone (1:1, v/v). One aliquot of each sample extract was concentrated to 2 mL, and passed through a 10 g florisil (60-100 mesh size; Sigma Chemical Co., St. Louis, MO, USA) column, which had been pre-rinsed with dichloromethane and acetone. The column was eluted with 100 mL dichloromethane followed by 100 mL dichloromethane and acetone (1:1, v/v). Elutes were then concentrated and reconstituted in 0.1 mL dichloromethane for quantification.

Phthalate esters (PAEs) were quantified using a Thermo TSQ Quantum Discovery triple-quadrupole mass spectrometer (San Jose, CA, USA) in multiple-reaction monitoring (MRM) mode [3]. Helium was used as carrier gas with flow rate of 1.0 mL/min. A pulsed, split-less injector was used for injecting 1.5 µL of extract into GC-MSMS equipped with a DB-5MS capillary column (0.25 mm × 30 m, 0.25 µm, J&K Scientific, USA) for analyzing phthalate esters. Temperature of the inlet was set as 250 °C. The initial oven temperature was set as 80 °C, held at 80 °C for 2 min, heated to 180 °C at 15 °C/min, held at 180 °C for 15 min, then heated to 300 °C at 15 °C/min, and held at 300 °C for 5 min. The mass spectrometer was operated in negative ion chemical ionization mode, and the source and transfer line temperature was set at 180 °C and 280 °C, respectively.

QA/QC.

To minimize background contamination, samples or extracts did not come into contact with PAEs or other polyvinyl chloride (PVC) materials during collection or preparation of samples. Coefficients of determination (r^2) of calibration curves for all target analytes were greater than

0.99.

Method blanks of the chromatograph as direct injections of dichloromethane were made to check the presence of PAEs in the chromatographic system. None of the target compounds were present in chromatograms. Procedural blanks for dust (n=3) were conducted in the laboratory by vacuuming sodium sulfate powder (a surrogate for dust) from a clean aluminum foil surface. Procedural blank for wipe sample (n=3) were collected by soaking a gauze pad in isopropyl alcohol and placing it directly into the glass vial in laboratory. Limits of quantification (LOQ) for dust and wipe samples were determined as ten times the standard deviation of the appropriate procedural blanks (Table S2).

Dust field blanks in offices (n = 10) were conducted by vacuuming sodium sulfate powder (a surrogate for dust) from a clean aluminum foil surface. Field blank wipe sample were collected with each hand wipe, computer and mobile phone by soaking a gauze pad in isopropyl alcohol and placing it directly into the glass vial. Target analytes in field blanks were less than their corresponding LOQs. Final concentrations of compounds were the concentrations in samples corrected by subtracting concentrations in field blanks.

Recoveries were determined by spiking each target compounds into sodium sulfate powder and soaked gauze pad for dust and wipe samples, respectively. The matrix spike recovery tests were conducted by spiking each target compounds into dust and wipe samples from Huaian, Nanjing and Zhenjiang, respectively. The spiked levels for PAEs were 1μg. Three replicates were conducted for QA/QC. The procedural recoveries and matrix spike recoveries of the tested compounds were listed in Table S2.

Internal standards DnBP-d4 (CAS 93952-11-5) and DEHP-d4 (CAS 93951-87-2) were added to the solutions before analysis for quantification. During sample analysis, quality control samples were consisted of duplicate samples, calibration check standards and solvent blanks. Duplicate samples were used to assure precision and accuracy of each batch of samples, and deviations of duplicate samples were less than 20%. Calibration check standards were run after every ten sample to check the instrument. If the calibration check standards were out of ± 20% of its theoretical value based on the calibration curve, a new calibration curve was prepared. Solvent blanks were run prior to every ten sample to check the instrumental background.

Assessment of exposure to PAEs.

Exposure from hand-to-mouth contact has been determined previously (Equation S3) [4]:

$$EDhm = TM \times TE \times A \times F \quad (S3)$$

Where: EDhm is exposure through hand-to-mouth contact (μg/kg bm/day), TM is total PAEs mass present on the hands (μg/kg bm/day), TE is transfer efficiency, A is the proportion of the hand area contacted in each event, and F is frequency of contact over a 24-hour period. Estimated hand-to-mouth contact frequency (F) is variable, depending upon the method used [5].

Absorption of PAEs through the dermis of the hand was estimated with the exposure calculation developed by Weschler and Nazaroff (Equation S4) [6,15].

$$J = k_{p\_l} \times C_l \times HSA \quad \text{(S4)}$$

Where: J is transdermal flux of PAEs (μg/kg bm/day) through dermal absorption of hand, k_{p_l} is permeability coefficient that describes transport of PAEs dissolved in skin-surface lipids through the stratum corneum/viable epidermis composite (m/hour), and C_l is concentration of PAE in skin-surface lipids (μg/m^3) [7]. In this study it was assumed that there were 1.3×10^{-6} m^3 skin surface lipids per m^2 skin for adults [8]. Here k_{p_l} could be obtained by equation S5.

$$k_{p\_l} = k_{p\_w} / K_{lw} \quad \text{(S5)}$$

Where: k_{p_w} is permeability coefficient through the stratum corneum/viable epidermis composite of PAE when the species concentration is measured in water in contact with skin (m/hour) and K_{lw} is coefficient of equilibrium partitioning for PAE between skin-surface lipids and water. The physical-chemical properties of common indoor PAEs were listed in supporting information (see SI, Table S3).

Data analyses

Masses of total PAEs were further categorized according to number of times hands were washed or use of polymer covers during work. Masses of PAEs on hands of participants who washed their hands less than four times (median time) were compared to those who washed more than four times per day. Participants who washed their hands less than four times per day were further divided into two categories according to the using of keyboard polymer covers. Concentrations of ΣPAEs in office dust were also categorized, with ΣPAEs less than median masses as the lower category and ΣPAEs greater than median masses as the greater category.

Final concentrations/masses of compounds in dust were that the concentrations/masses in samples subtracted mean concentrations/masses in field blanks, and wipes were corrected by subtracting each individual's paired wipe field blank measurement. Concentrations less than the limit of quantification (LOQ) were substituted with half of the LOQ. The coefficient of variation (CV) was used in the present study to measure the variability of a series of numbers independently of the unit of measurement (Equation S6).

$$\text{Coefficient of variation (CV)} = \text{Standard Division (SD)/Mean (M)} \quad \text{(S6)}$$

Results Section

Masses and concentrations of phthalate esters

DnBP, BBP, DEHP and DnOP were the most abundant phthalates on wipes of hands. DEHP and DnBP were detected in all samples from hands. BBP and DnOP were detected somewhat less frequently as 95% and 96%, respectively. DMP and DEP had the least frequencies of detection, which were less than 55%. Masses of DnBP, BBP, DnOP and DEHP on wipes of hands were inter-correlated. Normalized concentrations of the sum of PAEs were correlated with masses on hands. Concentrations of PAEs normalized to HSA ranged from 1 to 9417 ng/cm^2 with a median value of 151 ng/cm^2. Concentrations of the predominant compound DEHP ranged from 0.2 to 9304 ng/cm^2. Distributions of loadings and normalized concentrations of PAEs measured in wipes of hands had similar variability (Figure 1). For all the PAEs, concentrations of PAEs normalized to HSA were significantly correlated with the mass on wipes of hands (r =0.99, p < 0.001). Normalizing to HSA did not reduce variability in the measurements. Variability in masses of PEAs is not attributed to HAS which differs little among adults, and is likely a result of behavior or exposure differences. As the most abundant PAEs, the normalized concentrations of DEHP measured on wipes of hands from Nanjing (n=18) and Huaian (n=19) were slightly greater than those from Zhenjiang (n=18), which is in accordance with the levels on wipes of skin in Beijing, China but a bit greater than the level on hand wipes of children in Korea. Normalized concentrations of DnBP on wipes of hands of office workers detected in present study were less than concentrations on wipes of hand detected in Beijing and Korea [9, 10].

For dust samples, concentrations of DEHP were 30 to 60-fold greater than those of DnOP and BBP, and were 1000-fold greater than concentrations of other PAEs analyzed. Concentration of DnBP was a bit lower than those from Stockholm and the Pearl River Delta of China, while concentrations of DEHP were much greater than those reported previously. The reason might be that dust in the present study was collected from surfaces of furniture while most previous studies focused on floor dust, which indicated that when using indoor dust as an exposure assessment, it is very important to note where samples were collected. DEHP and DnBP were also the most abundant PAEs in office dusts in the study of Pearl River Delta, China and Stockholm[11, 12]. Concentrations of DEHP and DnBP measured in office dust in Nanjing were more than 2-fold greater than those from Nantong and Zhenjiang.

Repeated measurements.

Concentrations and masses of PAEs in repeated samplings of dust and wipes over a three month period are mostly consistent (Figure S2). Concentrations of PAEs in dust were relatively consistent. Masses of phthalate esters on hands and computers were more variable with the coefficient of variation (CV) ranging from 18% to 32% and 23% to 57%, respectively (Information on the equation for CV is provided in SI). These observations suggest that furniture dust might have more consistent masses of PAEs. Masses on wipes of hands and computers might depend on behavior or time since last cleaning event. Friedman test showed that there were not significant differences between ΣPAEs, DnBP, and DEHP levels on hand, keyboard and furniture surface at different sampling times which indicated the reasonably representative of levels which did not vary substantially during the period. However, wipes of phone had variable masses, with the CV ranging from 61% to 98%. The surface of phone is more often cleaned or scratched, and this might be the factor in the variability observed. Moreover, the phone likely experiences multiple environments and is placed in pockets and purses where it could sorb or desorb PAEs. However, this investigation was limited to four individuals and three replicates and more studies are needed to fully examine temporal variability.

Washing of hands.

Both variable, frequency of washing hands and masses on wipes of computer were included to determine relationships between masses of PAEs on wipes of computer keyboards and hand and how often participants washed their hands. For the less frequent hand washing category (who washed their hands fewer than four times per day), greater PAEs occurred on hands when greater PAEs (who washed their hands greater than four times per day) is detected in office dust. However, for the frequent washing category, the mass of PAEs on hands are similar for both groups having greater and lesser concentrations of PAEs in office dust. This is in accordance with previous studies which indicated the notable removal efficiency of PAEs by hand washing. Similar result was also found by Watkins et al., which indicated a significant difference in the mass of penta-BDE in the hand wipes of high frequency hand washers versus low frequency hand washers[13].

Exposure to PAEs via hands.

The U.S. EPA's reference doses (RfDs) of daily intake for DEHP, DnBP, DEP and BBP are 20, 100, 800 and 200 μg/kg bm/day, respectively [14]. Exposures via hand to body observed in this study exceeded the RfDs of DEHP for 16% of participants. Tolerable daily intakes were 50 μg//kg bm/day for DEHP as previously reported [15, 16]. Among the 55 participants, intake of DEHP was greater than the TDI_i for only two participants. Intake of none of the other PAEs by any of the participants exceeded the TDI_i through hand to body during working time. Median, daily exposure via hand to mouth of these PAEs was more than 100-fold less than the TDI_i value for each respective PAE.

Further verification was done by comparing amounts of PAEs in furniture dust, on wipes of keyboard without polymer cover and wipes of polymer covers. The results showed that masses pf PAEs on wipes of polymer covers were significantly greater than the related wipe for keyboards without polymer covers. Masses of DEHP, DnBP, DnOP on wipes of polymer covers were 2.1~21.0, 2.5~107 and 6.6~16.9 times greater than that on wipes of keyboards without polymer covers. Masses of DEHP, DnBP and DnOP on wipes of keyboards without polymer covers were correlated with concentrations of PAEs in office dust. This result is consistent with results reported previously which indicated the strong association between the mass on hands and the masses on indoor surfaces [17]. These results indicated that using keyboard with polymer covers can result in greater exposure of office workers to PAEs. Nowadays, polymer covers for keyboards or screen protectors are wildly used for computers, tablets and smartphones, which are touched frequently. Polymer covers are commonly made of polyvinylchloride (PVC) from which PAEs can be easily emitted. In the present study, for the very first time, a significant correlation between masses of PAEs on wipes of keyboard polymer covers and hands of users was observed.

Table S1. Properties and limits of quantification (LOQ) for phalate esters (PAEs).

Chemicals	Abbreviation	CAS no.	Purity (%)	LOQ dust (ng/g)	LOQ wipe (ng)	Log-K_{oa}	Log-K_{ow}
Dimethyl phthalate	DMP	131-11-3	99.5	10	1.5	6.69	1.6
Diethyl phthalate	DEP	84-66-2	99.5	10	0.6	7.02	2.42
Dibutyl phthalate	DnBP	84-74-2	99.0	23	3	8.63	4.5
Benzyl butyl phthalate	BBP	85-68-7	99.5	10	1.5	9.02	4.73
Di-2-ethylhexyl phthalate	DEHP	117-81-7	99.0	30	6	12.56	7.6
Di-*n*-octyl phthalate	DnOP	117-84-0	99.5	20	5	12.08	8.1

Table S2. Method recoveries and matrix spike recoveries for phthalate esters (PAEs).

Chemicals	Procedural recovery (n=3)				Matrix spike recovery (n=3)							
	Dust		Wipe		Dust		Hand wipe		Mobile phone wipe		keyboard wipe	
	Recovery (%)	RSD[1] (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
DBP	97	4.2	99	5.7	105	6.2	103	12.2	93	6.1	98	9.2
DIBP	89	6.7	97	5.3	99	5.5	101	14.3	99	11.1	105	6.7
BBP	89	3.2	96	8.8	100	9.2	107	7.9	99	10.1	113	3.5
DEP	84	1.3	90	4.3	98	7.6	90	3.1	98	14.7	93	2.0
DEHP	94	2.0	86	5.3	101	11.5	108	8.5	98	12.1	110	6.0
DnOP	89	3.7	93	6.0	99	10.8	101	8.1	94	4.2	108	10.1

1 RSD=Relative Standard Deviation

Table S3. Relevant physical-chemical properties of phthalate esters (PAEs).

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Chemicals	Molecular mass g/mol	$Log(K_{lw})$	k_{p_w} cm/h	k_{p_l} µm/h
BBP	312	3.6	0.019	0.048
DnBP	278	3.4	0.023	0.092
DEP	222	1.9	0.0027	0.340
DEHP	391	5.5	0.10	0.003

Table S4. Phthalate esters (PAEs) on wipes of hands, keyboard, mobile phones and in office dust (n = 55).

Sample type	Phthalate esters	Percent detection (%)	Mean	GM	Range	50th percentile	75th percentile	95th percentile
Wipes of hands (μg)	DMP	47	0.157	0.007	nd-5.23	nd	0.04	0.272
	DEP	52	0.837	0.01	nd-14.4	0.004	0.017	7.28
	DnBP	100	16.0	9.23	0.3-55.66	12.5	20.5	41.9
	BBP	96	2.34	0.599	nd- 31.2	1.01	2.09	7.95
	DEHP	100	381	37.5	0.07-4298	21.6	141	1981
	DnOP	96	2.52	0.423	nd-21.1	0.758	2.43	10.4
Office dust (μg/g)	DMP	65	0.20	0.024	nd-1.52	0.016	0.242	0.952
	DEP	89	1.54	0.157	nd-15.5	0.271	2.00	7.18
	DnBP	96	238	32.5	nd-6828	47.5	146	592
	BBP	100	9.31	2.27	0.03-173	3.76	7.70	33.0
	DEHP	100	566	148	0.51-5698	174	573	2336
	DnOP	100	60.6	4.57	0.02-2335	4.46	22.8	84.3
Wipes of keyboard (μg)	DMP	71	0.71	0.033	nd-7.64	0.045	0.752	3.19
	DEP	75	1.98	0.041	nd-22.0	0.063	1.67	7.07
	DnBP	100	41.9	20.7	1.93-174	22.5	58.2	145
	BBP	87	1.92	0.249	nd-22.8	0.431	1.80	6.77
	DEHP	100	415	83.6	0.27-2658	64.8	450	1894
	DnOP	99	5.22	0.977	nd-83.7	1.27	3.38	16.1
Wipes of mobile phones (μg)	DMP	69	0.630	0.009	nd-23.1	0.006	0.096	1.54
	DEP	64	1.98	0.008	nd-45.7	0.006	0.04	8.55
	DnBP	100	42.5	4.42	0.02-1296	6.12	13.8	86.8
	BBP	75	1.06	0.033	nd-37.1	0.048	0.290	1.75
	DEHP	98	116	10.2	nd-1356	8.17	49.2	467
	DnOP	96	1.54	0.169	nd-22.6	0.169	0.667	8.71

GM: geometric mean; nd: not detected

Table S5. Mean concentrations (μg/m^2) of phthalate esters (PAEs) in wipes of hands measured in this study as well as those reported in the literature.

Area	n	DnBP	BBP	DEHP	References
Korean children at play ground	5	140	20	10700	34
Korean children at play room	6	710	<LOD	1250	34
Korean children at day care center	4	3900	<LOD	3340	34
Korean children at kindergarten	5	810	20	7540	34
Beijing, China	20	989 [a]	<LOD	11825 [a]	35
Nanjing, China	18	584 [b]	108	13406	this study
Nantong, China	19	334 [b]	35	9113	this study
Zhenjiang, China	18	303 [b]	40	7421	this study

[a] Adjusted from reference [35] by assuming the mean value of PAEs on hands were the sum of mean PAEs on left back-of-hand, right back-of-hand, left palm and right palm.

[b] Normalized by masses on wipes of hands and surface area of the hand by use of equations 1 and 2 in SI.

Table S6. Predictors of masses of phthalate esters (PAEs) in wipes of hands collected in offices.

Predictor		Wipes of keyboard	Hand washing times		Use of keyboard polymer covers	
			<4 times	>4 times	No	Yes
ΣPhthalate esters	n	55	39	16	15	24
	GM (μg)	144	127	13.5	25.2	348
	r	0.59	0.74	0.53	0.65	0.88
	p	<0.001	<0.001	0.72	<0.001	<0.001
DEHP	n	55	39	16	15	24
	GM (μg)	83.6	83.8	5.3	14.4	252
	r	0.47	0.72	0.59	0.57	0.87
	p	<0.001	<0.001	0.128	<0.001	<0.001
DNBP	n	55	39	16	15	24
	GM (μg)	20.7	12.4	4.50	5.05	21.8
	r	0.58	0.41	0.59	0.38	0.66
	p	0.01	<0.001	<0.001	<0.001	<0.001

GM: geometric mean

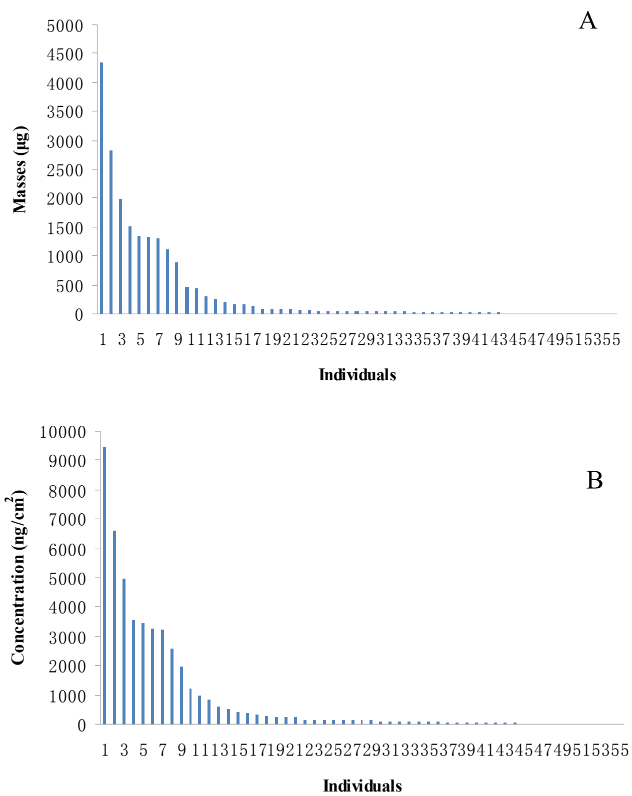

Figure S1. Distribution of Σphthalate esters: (A) concentrations normalized to surface area; (B) measured on wipes of hands.

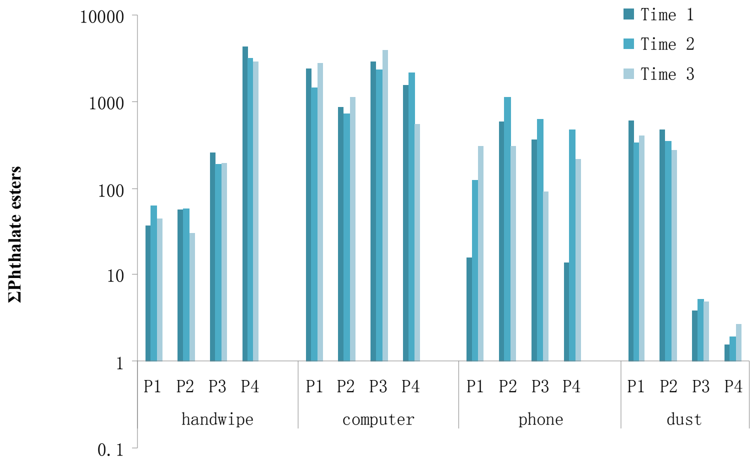

Figure S2. Masses or concentrations of phthalate esters (PAEs) in wipes of hands (μg), computers (μg), mobile phones (μg) and office dust (μg/g, dm) from four individuals (P1, P2, P3 and P4) for three times (Time 1, Time 2 and Time 3).

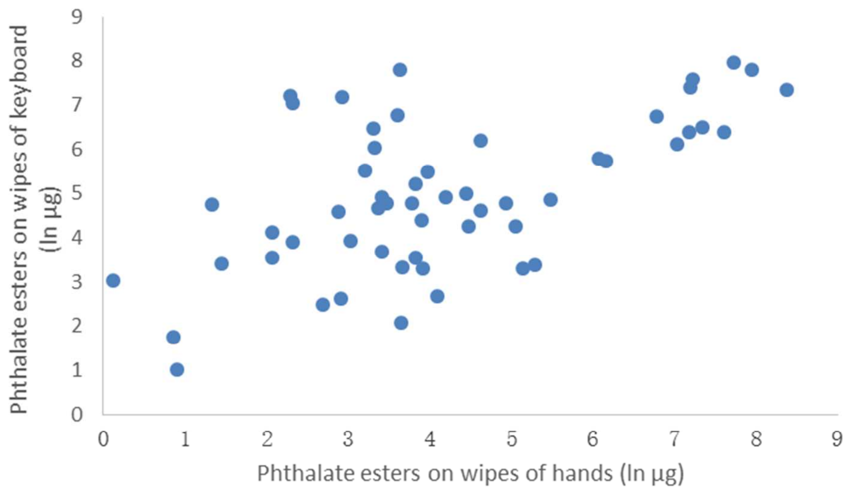

Figure S3. Correlations between masses of Σphthalate esters (PAEs) in wipes of computer keyboards versus those of hands (n = 55, data were natural log transformed).

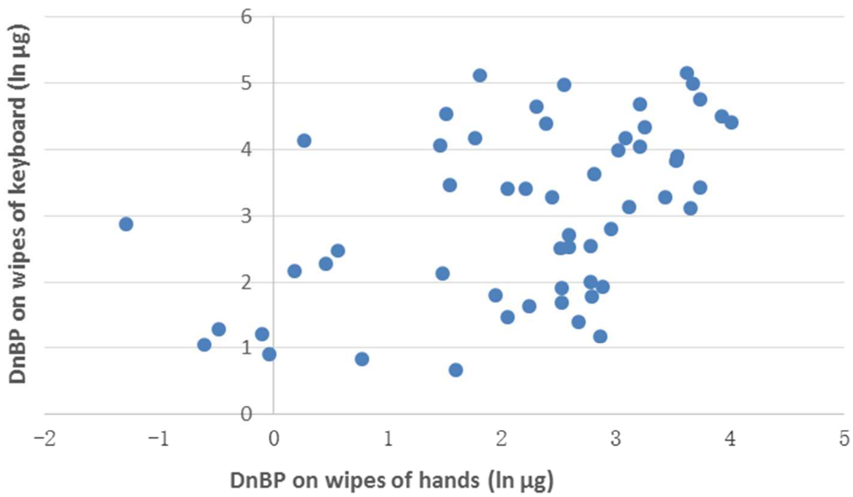

Figure S4. Correlation between masses of dibutyl phthalate (DnBP) on wipes of computer keyboard versus masses on wipes of hands (n = 55, data were natural log transformed).

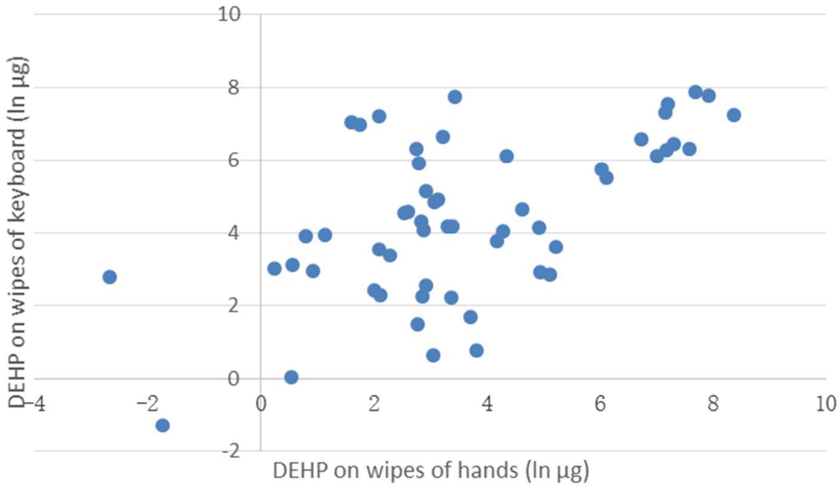

Figure S5. Correlation between masses of di-2-ethylhexyl phthalate (DEHP) on wipes of computer keyboard versus masses on wipes of hands (n = 55, data were natural log transformed).

AUTHOR INFORMATION

Corresponding Author:

* E-mail: zhangxw@nju.edu.cn (Xiaowei Zhang) and yuhx@nju.edu.cn (Hongxia Yu). Telephone: 86 25 89680623. Fax: 86 25 89680623.

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