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EXPOSURE ROUTES AND RISK ASSESSMENT OF PHTHALATES FOR UNIVERSITY STUDENTS IN CHINA

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Introduction

Phthalates are widely used chemicals in household products, which severely affect human health. Increased exposure to phthalates in humans was associated with reproductive system variations. In China, there are approximately 15 million undergraduate students and 1.8 million graduate students. They have to live in the dorms for four or more years. The specific indoor environment of university dorms may result to varying exposures to phthalates, and lead to significant risks on students' health status. And the effects may last for years, which may affect the health of their next generation.

The objectives of this study were a) to analyze the concentrations and profiles of 6 phthalates (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), and di-(2-ethylhexyl) phthalate (DEHP)) in personal care products (PCPs); b) to study the daily intakes (DIs) of phthalates for university students via inhalation, oral ingestion, and dermal absorption, combined with phthalates in dorm dust from our previous study and phthalates in dorm air and foodstuffs in China from other studies[1-3]; and c) to study the carcinogenic risk assessment of DEHP for university students using Monte Carlo simulation.

Materials and methods

Sample collection. A total of 65 PCP samples were collected from university students (24 from male students and 41 from female students) in Harbin, China, in March and April, 2014. The PCP samples included face cleanser (11), toner (8), lotion (10), shampoo (10), body wash (8), hand lotion (4), body lotion (6), and makeup (8).

Sample preparation. PCP samples (0.10-0.20 g) were spiked with 100 ng of surrogate standards (deuterated DMP, DEP, DiBP, DBP, BBP, and DEHP) in 10 mL glass tubes, 2 mL of Milli-Q water was added. Samples were shaken for 30 min with 4 mL of methyl tert-butyl ester, and centrifugation at 4000 rpm for 10 min. The extraction was repeated for three times, and the combined upper layer solvent was concentrated to nearly dry, and reconstituted with1 mL of hexane for instrumental analysis.

Instrumental analysis. The total target phthalates were analyzed with Agilent 6890 gas chromatography/5975B mass spectrometry in electron capture negative ionization mode equipped with a DB-5 column (60 m×0.25 mm×0.25 μm), using following temperature program: 80 ^{o}C for 1 min, 25 ^{o}C /min to 230 ^{o}C, and held for 3 min, 20 ^{o}C /min to 270 ^{o}C, and held for 2 min, 15 ^{o}C /min to 300 ^{o}C, and held for 3 min. The temperatures were 150 ^{o}C, 230 ^{o}C, and 250 ^{o}C for the quadrupole, ion source, and interface, respectively.

QA/QC. For each batch of 10 samples, a method blank and a spiked blank were processed. The average recoveries of target compounds in spiked samples ranged from 97% to 126%. The recoveries of surrogate standards in method blanks, spiked blanks, and real samples were 91-113%, 104-115%, and 112-125%, respectively. All concentrations of phthalates in PCP samples were corrected with blank values and recoveries.

Results and discussion

Phthalates in PCPs. The detection rate of 6 phthalates in PCPs was 3.1-60%. The median concentration of the total phthalates in PCPs was 0.696 μg/g (not detected (nd)-189 μg/g). DEP was found to be the most abundant phthalate in PCPs (median: 0.042 μg/g). Among 8 types of PCPs, the highest median concentration of phthalates was found in body lotions (**Fig. 1**). The median concentrations of phthalates in PCPs from female students were approximately 3 times higher than those from male students, with the values of 0.943 μg/g and 0.320 μg/g, respectively.

Daily intakes of phthalates via different routes. Human exposure to phthalates occurs via inhalation, oral ingestion, and dermal absorption. The DIs of phthalates from PCPs for male and female students were estimated according to the equations in the previous studies[4]. Combined with phthalate concentrations in university dorm dust from our previous study[1], and dorm air and foodstuffs in China[2, 3], the DIs of phthalates from these media were estimated using the equations reported by previous studies[3, 5]. Due to lacking of DiBP level in dorm air, this compound was not included in this section. The median DIs of phthalates for university students via three exposure routes were summarized in **Table 1**.

Female students' exposure to phthalates was much severer than male students. Among three routes, oral ingestion contributed most for students' exposure. The DIs of phthalates for male and female students via oral ingestion were comparable, but the DI of phthalates for male students via inhalation or dermal absorption was approximately 2 times lower than those for female students. Among 5 phthalates, DEHP contributed most for students' exposure, followed by DBP and BBP. Oral ingestion was found to be the most abundant source of exposure to DEHP, whereas dermal absorption was the dominant source of exposure to DMP and DEP. And both oral ingestion and dermal absorption were the important source of exposure to DBP and BBP.

The DI values of phthalates via three routes in this study were much lower than those for Chinese young adults in a previous study (based on urinary concentrations of phthalate metabolites)[6]. Compared to some recommended intake doses, such as the tolerable daily intake (TDI), the reference dose (RfD) and reference dose for anti-androgenicity (RfD AA), the median DIs of phthalates for male and female students were all within the acceptable levels.

Carcinogenic risk assessment of DEHP. In this study, carcinogenic risk (CR) of DEHP for male and female students via oral ingestion (dust and foodstuffs) was estimated. The threshold of CR value is 1×10^{-5} that indicates potential adverse effects. In order to demonstrate the overall trend, the predicted probability density functions were applied using Monte Carlo simulation (**Fig. 2**). The predicted CR values for male and female students were comparable, and the maximum values severely exceeded the threshold level. It indicated that students are in the risk of exposure to DEHP.

In summary, the median concentration of 6 phthalates in PCPs was 0.696 μg/g, and DEP was the most abundant phthalate in PCPs. Female students' exposure to phthalates via inhalation, oral ingestion, and dermal absorption was much severer than male students. DEHP contributed most for students' exposure. Oral ingestion was found to be the most abundant source of exposure to DEHP, whereas dermal absorption was the dominant source of exposure to DMP and DEP. And both oral ingestion and dermal absorption were the important source of exposure to DBP and BBP. DEHP could pose risk to student health according to carcinogenic risk assessment.

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Table1. The median daily intakes of phthalates for university students via three exposure routes[1-3] (ng/kg·day)

Routes	Media	Student Groups	DMP	DEP	DBP	BBP	DEHP	Total
Inhalation	Air	Male	85.2	85.3	116	87.3	169	543
		Female	224	185	180	159	260	1010
Oral ingestion	Foodstuffs	Male	85.4	30.5	544	461	1240	2360
		Female	90.9	31.5	565	491	1290	2470
	Dust	Male	0.14	0.14	9.83	0.071	52.6	67.5
		Female	0.21	0.24	13.5	0.046	76.9	88.1
Dermal absorption	Air	Male	161	161	308	232	544	1410
		Female	469	388	532	471	931	2790
	Dust	Male	0.0094	0.0095	0.65	0.0047	3.15	4.15
		Female	0.012	0.014	0.79	0.0027	4.06	4.85
	PCPs	Male	nd	0.0013	nd	nd	nd	0.0053
		Female	nd	0.0096	nd	nd	nd	0.12
Total	-	Male	332	277	978	780	2010	4380
		Female	784	605	1290	1120	2560	6360

nd: not detected.

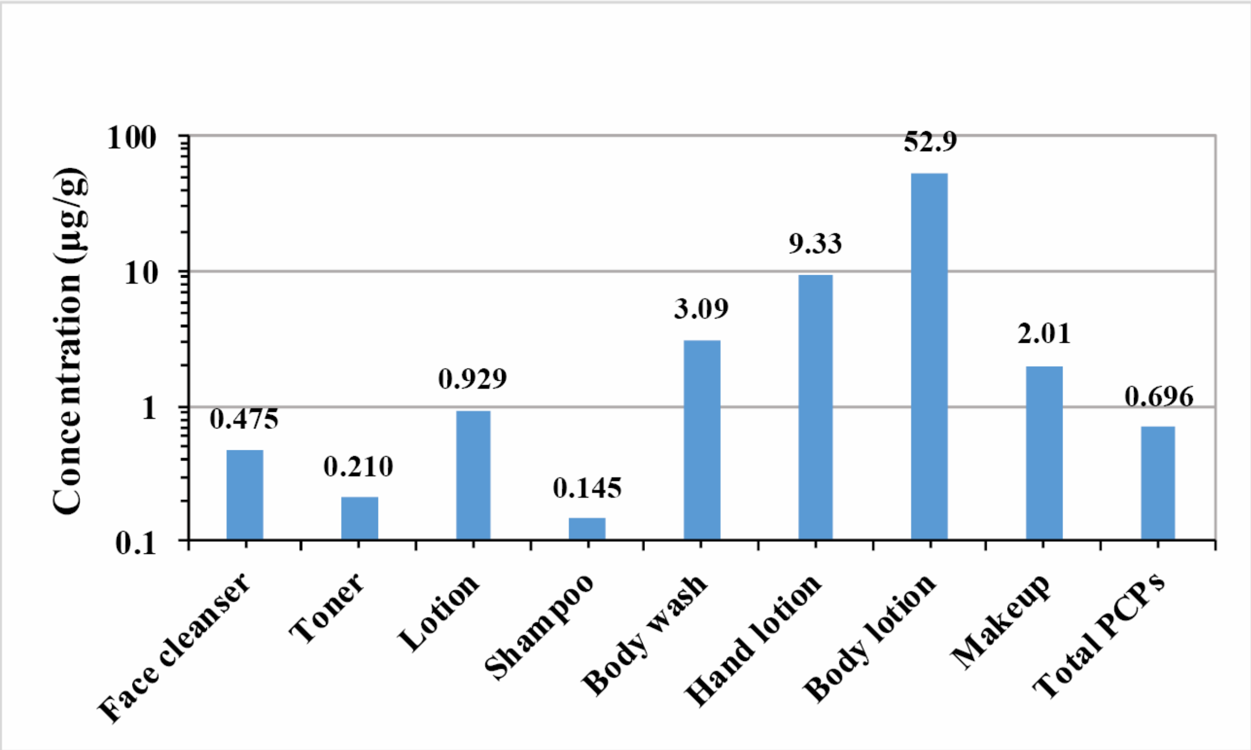

Fig. 1. The median concentrations of phthalates in PCPs (µg/g)

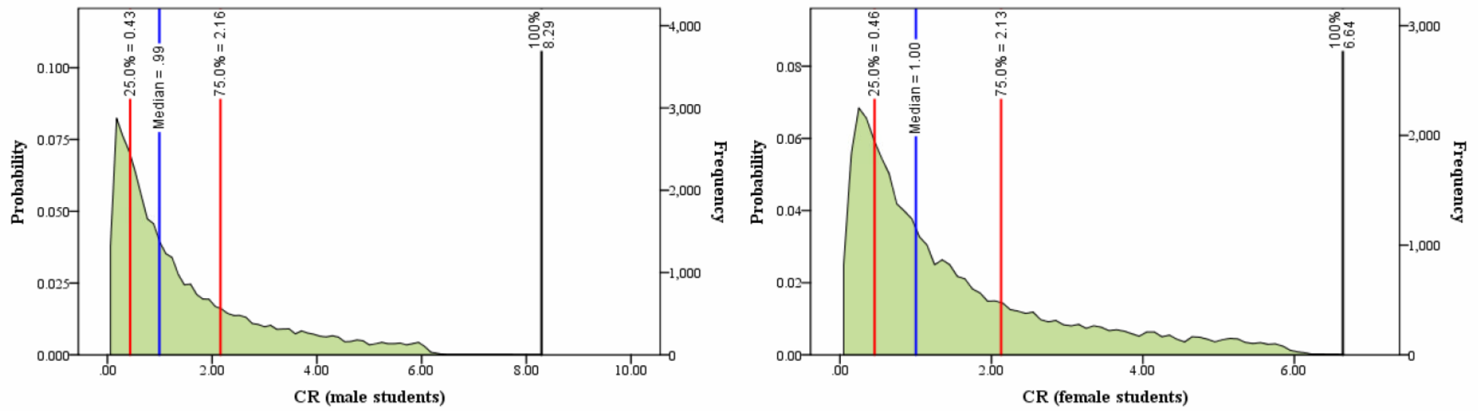

Fig. 2. Predicted probability density functions of carcinogenic risk of DEHP. ($\times10^{-5}$)