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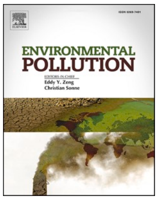

Organophosphate ester exposure in nail salons: Health implications for workers☆

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ABSTRACT

Organophosphates esters (OPEs) have become a preferred alternative in nail polish as plasticizers due to health concerns over previously used additives like dibutyl phthalate. However, the true extent of nail technicians' exposure to OPEs is largely unknown. This study shows that nail salon workers are significant exposed to OPEs, with varied concentrations found in air, dust, masks, and urine. The total concentrations of 11 OPEs in ultrasonic personal air samplers (UPAS) ranged from 251 to 1007 ng/m^3, and in air conditioner filter dust from 371 to 14473 ng/g. Triphenyl phosphate (TPHP) was the most abundant compound found in the nail polishes used in these salons. On average, the concentrations of TPHP and diphenyl phosphate (DPHP) in workers' urine after work were 5.2 and 1.8 times higher than those before work, respectively. Two nail salons that had the highest nail polish usage also had very high concentrations of TPHP in surgical masks, dust, and UPAS. TPHP concentrations in workers' urine after work were 19 and 13 times those before work, respectively, in these two salons. Human internal exposure assessment showed that the average exposure dose of TPHP after work was 1.8 times higher than that before work. On average, use of masks reduced OPEs in urine by 77%. In conclusion, frequent mask replacement is highly recommended, especially in long working circumstances. Without regular replacement, masks may accumulate OPEs from the air, potentially becoming another source of human exposure to OPEs. Therefore, more attention should be paid to the occupational exposure of nail salon workers to OPEs, particularly considering that most practitioners in this industry are young women of reproductive age.

1. Introduction

Organophosphates esters (OPEs) are widely used as additives in nail polish because of their low acute toxicity and low cost. OPEs can make nail polish chip-resistant and pliable, quick to dry and brightly colored (Young et al., 2018). The most common semi volatile organic compound added to nail polish in the past was dibutyl phthalate, which has been associated with birth defects and detrimental effects on development and the reproductive system. By 2006, companies in the United States initiated voluntary labeling of nail polishes as "3-Free", signifying the absence of dibutyl phthalate, toluene, and formaldehyde. Triphenyl phosphate (TPHP) has emerged as a prominent substitute for dibutyl phthalate, being extensively incorporated into nail polish formulations. As of 2015, nearly half of all nail polishes listed TPHP on their ingredient lists, with concentrations reaching as high as 16.8 mg/g (equivalent to 1.68% by mass) in nail polish (Mendelsohn et al., 2016). Notably, recent studies have revealed TPHP as an endocrine disruptor (Liu et al., 2021), capable of influencing thyroid hormone levels and even reducing semen quality (Welch et al., 2021). In addition to TPHP, other OPEs are also present in small amounts in nail polish. For example, in our previous study, we found that tris(2-ethylhexy) phosphate (TEHP) and tris [(2R)-1-chloro-2-propyl] phosphate (TCIPP) exceeded 10 μg/g in some

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nail polishes (Jia et al., 2024).

Nail salons are one of the fastest-growing industries in China. In 2021, the nail art market size was 25.4 billion USD. It is expected that the market size will reach 36.4 billion USD in 2027. Currently, there are 640,000 nail-related companies in China, employing more than 2.6 million nail salon workers. A total of 115,000 were registered in the first half of 2022, reflecting a 109.1% increase compared with the previous year. Most of the manicurists are young women who may experience pregnancy and breastfeeding in the coming years. This chronic exposure to nail products subjects them to higher concentrations of OPEs than the general public (Nguyen et al., 2022).

OPEs can affect the function of the endocrine system and lead to various health problems, such as reproductive toxicity, female malignancies, and developmental disorders (Tao et al., 2019). Disturbances in the balance of the endocrine system in women can have serious health implications, for example, inappropriate responses to estrogen have been shown to underlie the pathology of most breast and uterine cancers (Luo et al., 2021). Since 2012, tris(2-chloroethy) phosphate (TCEP) has been banned from use in children's foam products. Additionally, TCEP and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) have been listed as carcinogens under California Proposition 65 (Nguyen et al., 2022).

Both manicurists and consumers are exposed to OPEs from nail polish, which are predominantly women that thus may have increased health risks. Currently, studies on occupational exposure of nail workers are very limited. Craig et al. analyzed phthalates and a few OPEs in the urine of nail salon workers in the United States and found that the level of some phthalates in the urine after work was more than three times higher than before work (Craig et al., 2019). Through the analysis of air and wristbands worn by Canadian nail salon workers, Nguyen et al. found that the TPHP content in the wristbands of nail salon workers was significantly higher than that of e-waste workers (Nguyen et al., 2022).

However, there are many sources of OPEs in nail salons and the factors influencing occupational exposure of nail salon workers to OPEs are complex. At present, there is a lack of comprehensive research that tracks OPEs from their sources in the indoor environment to their presence within workers' bodies. This study aimed to comprehensively investigate the exposure of nail salon workers to OPEs, using ultrasonic personal air samplers (UPAS) for air sampling and collecting air conditioner (AC) filter dust, workers' masks, and urine samples. The study aimed to assess and compare the influencing factors related to the occupational exposure of nail salon workers. Furthermore, a multiple linear regression model was developed to predict occupational exposure, and measures were proposed to reduce occupational exposure. This study could be a great help for the nail salon industry to reduce occupational exposure hazards and protect workers' health.

2. Materials and methods

2.1. Study design

We conducted field and online surveys of nail salons in China. Based on the popularity of commonly used nail polish brands and nail salons, we selected 10 nail salons located on the nail beauty street in Beijing (Beijing, China). The analysis of the nail polishes employed in these 10 salons, as well as the simulated emission experiments, can be found in our previous research (Jia et al., 2024). These nail salons primarily offer manicure services, including both fingernails and toenails, with some also providing additional services like eyelash extensions and eyebrow trimming. All participating salon workers ($n = 10$) provided their consent for the study. Between January and April 2022, one worker was selected from each salon to wear a UPAS (Access Sensor Technologies, Fort Collins, CO) during the average 10-h workday. The UPAS is an active air sampler that utilizes an ultrasonic piezoelectric pump to drive airflow efficiently and with low noise. Designed to be quiet and lightweight, the UPAS can be worn directly in the worker's breathing zone. Its portability, light weight, and ability to operate continuously for extended periods make it suitable for personal exposure assessment in occupational environments (Volckens et al., 2017). This approach yielded a collection volume of 0.6 m^3 per worker on the sampled day. Additionally, dust samples were collected from the AC filter of the nail salon on the same day as the UPAS sample collection. Masks worn by the participants during their shifts and urine samples before and after work were also collected. To ensure consistency, participants refrained from using nail polish for 72 h before sampling. Information such as sex, age, work hours, and daily client count was obtained from all participants (Tables S3 and S4).

2.2. Sample collection and analysis

Eleven OPEs were analyzed in UPAS samples ($n = 10$) and AC filter dust ($n = 10$) using gas chromatography with tandem mass spectrometry (GC-MS/MS). The extraction of 200 mg AC filter dust and UPAS samples involved ultrasonication and purification using ENVI™-Florisil cartridges. To more comprehensively assess workers' exposure, we added the measurement of di-OPEs in addition to OPEs when analyzing masks worn during work ($n = 10$) and urine samples ($n = 20$) collected before and after work, using liquid chromatography with tandem mass spectrometry (LC-MS/MS). The selection of di-OPEs was based on a comprehensive consideration of their metabolism, usage, and relevant literature (Hou et al., 2021; Wang et al., 2021; Hou et al., 2022) (Table S2). The sampling was approved by the Ethical Commission of the Research Center for Eco-Environmental Science, Chinese Academy of Sciences. The extraction method for dust, mask, and UPAS samples was adapted from a previous study (Jia et al., 2023). Briefly, a mixture of n-hexane and dichloromethane (1:1, v/v) in a volume of 15 mL was used for ultrasonic extraction, and the supernatants were combined after three rounds of extraction. Extraction and purification of OPEs from urine were performed using an ENVI-18 column, while for di-OPEs, extraction and purification were conducted using a Bond-Elut C18 column (Hou et al., 2020). Further details regarding sampling, analysis, and materials can be found in the Supporting Information. The target compounds consisted of eleven OPEs and seven di-OPEs. The chemical names, abbreviations, molecular formulae, and properties of these target compounds are listed in Tables S1 and S2.

2.3. Instrumental analysis

The OPEs in the UPAS samples and AC filter dust were determined using a gas chromatograph triple quadrupole mass spectrometer (7890/7010, Agilent). The oven temperature was initially set at 80 °C for 5 min, followed by an increase to 190 °C at 5 °C/min, then increased to 220 °C at 15 °C/min, and finally increased to 305 °C at 10 °C/min. The temperature was then held at 305 °C for 2 min. OPEs and di-OPEs in urine and mask samples were determined using high-performance liquid chromatography with triple quadrupole mass spectrometry (LCMS-8050, Shimadzu Scientific Instruments, Columbia, MD). The target compounds were separated using a Shimadzu Shim-pack GIST C18 column. Additional information regarding the instrument analysis can be found in the Supporting Information.

2.4. Quality assurance and quality control

All glassware was baked at 350 °C for 4 h before use and then washed once with each of methanol, acetone, and dichloromethane to minimize potential interference. Three unexposed masks were randomly selected and analyzed before sampling, with OPEs concentrations ranging from ND to 1.39 ng/g and di-OPEs concentrations ranging from ND to 0.52 ng/g. The recoveries of OPEs internal standards in UPAS, AC filter dust, mask, and urine samples were 66%–124%, 67%–112%, 62%–111%, and 55%–102%, respectively. The recoveries of di-OPEs internal standards in mask and urine samples were 77%–115% and 83%–102%, respectively. Further details are provided in the Supplementary Information.

2.5. Mask protection efficiency

Masks can serve as crucial protective measures to effectively reduce the inhalation of OPEs by workers. The following equation was used to estimate the protection efficiency of masks for nail salon workers:

$$\text{Protection efficiency} = \text{Mask} \times G_{\text{mask}} / \text{UPAS} \times V \times H \tag{1}$$

Here, G_{mask} represents the weight of the mask worn by the worker during work (g); Mask is the total concentration of OPEs in the mask (ng/g); V represents the amount of air inhaled by the worker during work (0.48 m^3/h) (Hagman et al., 2016), and H is the worker's working time (h); UPAS indicates the total concentration of OPEs in the UPAS (ng/m^3).

2.6. Human internal exposure assessment

The exposure doses (D_p) of parent OPEs were calculated from the urine concentration of OPE metabolites using the following equation:

$$D_p = (C_{\text{urine}} \times UV_{\text{excr}} / F_{\text{ue}}) / (MW_p / MW_m) \tag{2}$$

where UV_{excr} is the daily volume of urine excreted by adults (20 mL/kg bw/day); C_{urine} is the concentration of the OPE metabolite in urine (ng/mL); MW_p and MW_m are the molecular weights of the parent OPEs and corresponding metabolites, respectively; and F_{ue} is the excreted molar fraction. The values of F_{ue} were obtained from a previous study (Wang et al., 2019). The F_{ue} for diethyl phosphate (DEP), dibutyl phosphate (DnBP), bis(butoxyethyl) phosphate (BBOEP), and BEHP were all 0.18, and that for DPHP was 0.63.

3. Results and discussion

Women aged 20–30 years are the main consumers of nail art in China, and the nail salon workers are also mostly young women (18–35 years old). The participants in this study ranged in age from 19 to 28 years, with a median age of 22 years (Table S3). The median number of hours they worked in nail salons per week was 65 h (50–67 h). All workers used personal protective equipment, including surgical masks, nitrile/latex gloves, and work aprons when working. Among all the services offered by a salon, manicures are the most common. The median number of services performed on the day of sampling was seven manicures, one pedicure, and two other services (Table S4).

3.1. OPEs in the nail salon environment

The presence of OPEs in UPAS and AC filter dust samples was investigated to characterize the external exposure of workers to OPEs. Compared with stationary samplers, UPAS provide more accurate assessments of the inhalation exposure of workers (Fuchao Xu et al., 2016). The total concentrations of 11 OPEs ($\sum_{11}$ OPEs) in the UPAS ranged from 251 to 1007 ng/m^3 (with an average of 524 ng/m^3 and a median of 485 ng/m^3). TEHP and TCEP were detected in 8 of the 10 salons, while tri-n-butyl phosphate (TBP) was detected in 9 of 10 salons. All other OPEs were detected in every UPAS from the nail salons. The highest median concentrations of TCIPP (148 ng/m^3), TPHP (57.2 ng/m^3) and triethyl phosphate (TEP, 57.0 ng/m^3) found in the UPAS accounted for 41%, 14%, and 12% of $\sum_{11}$OPEs, respectively (Fig. 1).

The total concentration of $\sum_{11}$ OPEs in AC filter dust ranged from 371 to 14473 ng/g, with an average of 4315 ng/g and a median of 3485 ng/g (Table S5). The 11 OPEs were detected in all AC filter dust samples. Similar to the distribution pattern observed in the UPAS, TCIPP (311 ng/g) was the most abundant OPE in AC filter dust, accounting for 15% of the total $\sum_{11}$ OPEs. This result is similar to our previous study on OPEs in nail polish and their emission rates (Fig. S3) (Jia et al., 2024). TPHP has the highest concentration in nail polish, accounting for 87% of the total concentration, followed by TCIPP, which accounts for 10% of the total concentration. Additionally, TCIPP also has a relatively high proportion (16%) in the emission rate from nail polish. Our previous research on OPEs in six typical indoor environments also found that chlorinated OPEs, including TCIPP, dominate in the air and dust, as they are mainly used in indoor decorations and building materials (Jia et al., 2023). For instance, a study found that spray foam insulation is a major source of TCIPP contamination in indoor environments (Truong et al., 2017). Therefore, the cumulative emissions from nail polish and indoor decorations may explain the high concentration of TCIPP in nail salons.

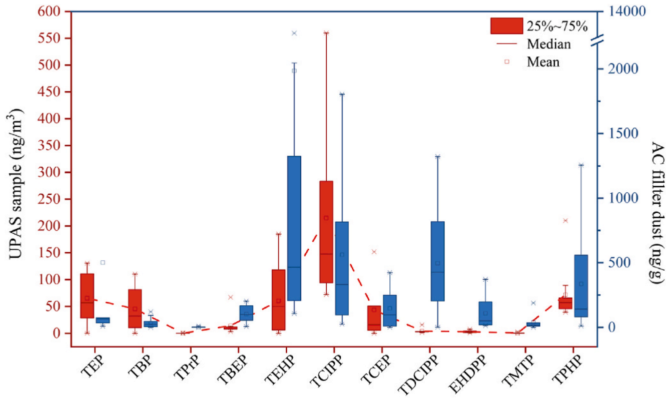

Fig. 1. Concentrations of OPEs in the UPAS (in red) and AC filter dust (in blue) samples. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The concentration of TPHP in the UPAS in this study (median: 57.2 ng/m^3) was higher than that in the air of Canadian nail salons (Nguyen et al., 2022) and American nail salons (Estill et al., 2020). It was also found to be higher than the concentration in Chinese bedroom and office air (Tang et al., 2020), but lower than those recorded in chemical manufacturing plants and electronic scrap plants (Estill et al., 2020) (Table S7). The concentrations in the AC filter dust in our study were comparable to those found in AC filter dust in Chinese bedrooms (Tang et al., 2020) (Table S8).

3.2. OPEs and di-OPEs in mask and urine

The concentrations of OPEs in masks worn during work can directly reflect the exposure of nail shop workers to OPEs. The total concentration range for OPEs in masks worn by workers during work was 1393–2483 ng/g, and the total concentration range for di-OPEs was 85.2–300 ng/g. OPEs were detected in all mask samples except TBEP, while di-OPEs were detected in 60%–100% of the mask samples. Among the measured OPEs, the highest concentrations were found for TCIPP (average: 992 ng/g), TPHP (488 ng/g), and TDCIPP (241 ng/g). DPHP and BEHP were the main di-OPEs, accounting for 50% and 34% of the

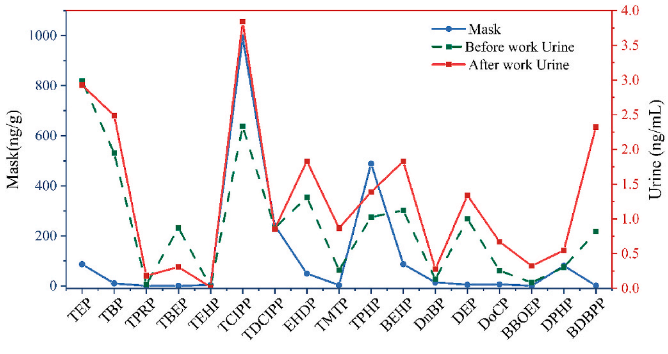

Fig. 2. The average concentrations of OPEs and di-OPEs in mask and urine samples.

total concentration, respectively (Fig. 2). The concentrations of TPHP, TCIPP, and TDCIPP in masks showed a significantly positive correlation with each other (Fig. S1, $p < 0.01$), suggesting a potential common source for TPHP, TCIPP, and TDCIPP. However, there was no correlation between BEHP and DPHP.

Masks can serve as a crucial protective measure to effectively reduce the inhalation of OPEs by workers. The protective efficacy of the masks was assessed by calculating the ratio of OPEs content in the mask to UPAS. The average protective efficiency of masks against OPEs for nail salon workers was 77% ± 24%. This finding underscores the masks' effective capability to intercept OPEs and offer protection to the staff. However, it is important to note that in the case of two nail salons with prolonged working hours ($H = 13$h), the masks became enriched with high levels of OPEs, which could potentially be released and inhaled by the workers. Therefore, in extended work scenarios, we strongly recommend frequent replacement of masks. Neglecting to do so might lead to the masks becoming a source of OPEs to the workers, thereby contributing to additional human exposure to these compounds.

OPEs and di-OPEs were detected in urine samples collected before and after work (Table S6). The concentrations of OPEs in urine ranged from 1.12 to 18.62 ng/mL, while the concentrations of di-OPEs ranged between 2.49 and 10.8 ng/mL. TPHP, tri-*m*-tolyl phosphate (TMTP), di-*o*-tolyl-phosphate (DoCP), and BEHP were present in all urine samples, and DPHP was detected in 95% of the samples. The average detection rate of di-OPEs (94%) was higher than that of OPEs (89%). Among the OPEs in urine, TEP had the highest concentration (3.28 ng/mL), and its metabolite DEP was also found in high concentrations (0.84 ng/mL). In contrast, the concentration of TEHP in urine was low (median: 0.02 ng/mL), while its metabolite BEHP was abundant (mean: 1.20 ng/mL). TCIPP was the most abundant monomer in AC filter dust, masks, and UPAS, and it was also present in very high concentrations in urine (median: 2.26 ng/mL). The second-highest average concentration among di-OPEs is BDBPP (1.01 ng/mL). Some studies have indicated that halogenated OPEs and di-OPEs have the highest concentrations in abiotic matrices (Greaves et al., 2016) (see Fig. 2).

The time of day for sample collection can also affect biomonitoring results. Morning (before work) urine samples usually provide the most accurate reflection of long-term exposures, whereas afternoon urine samples reflect human exposures in occupational settings (Wang et al., 2021). The concentration ranges of $\sum$OPEs and $\sum$di-OPEs in workers' urine before work were 1.54–18.6 ng/mL and 2.49–5.80 ng/mL, respectively. The corresponding concentrations after work were 4.48–19.9 ng/mL and 3.31–10.80 ng/mL. Notably, our findings suggest that nail salon workers might face significant occupational exposure to TPHP and DPHP. The TPHP concentration in urine before work showed a significant correlation with the DPHP concentration after work (Fig. S2, $p < 0.01$). A recent study found that TPHP is metabolized into DPHP after entering the human body, with a half-life of 9.58 days (Wang et al., 2020). The correlation between TPHP and DPHP is likely due to continuous and cumulative exposure to TPHP in the nail salon environment. This persistent exposure results in relatively high and stable concentrations of TPHP, subsequently leading to its consistent metabolization into DPHP. Urine concentrations of TPHP and DPHP after work were on average 5.2 and 1.8 times those before work (Fig. 3). In two nail salons, urine TPHP concentrations after work were 19 and 13 times greater than those before work. Interestingly, these two salons also had the highest TPHP concentrations in masks and UPAS among the nail salons, implying that the elevated TPHP levels in urine might indeed stem from occupational exposure.

3.3. Correlations between OPEs, di-OPEs, and the characteristics of nail salon workers

To further investigate if nail salon workers experienced substantial occupational exposure, Spearman correlation and cluster analysis were performed between total concentrations of OPEs and di-OPEs, concentrations of TPHP and DPHP, and characteristics of the nail salon workers. On average, 0.6 g of UV nail polish is used for a single manicure, while 0.55 g is used for a single pedicure. For this study, we calculated nail polish usage by workers by summing the number of manicures and pedicures performed in a day.

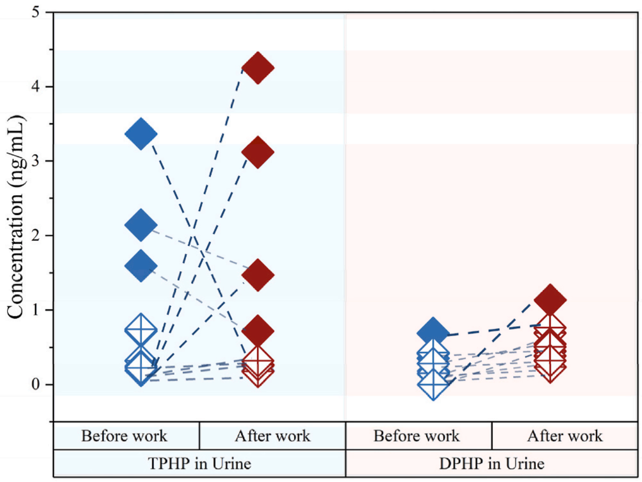

Fig. 3. Concentrations of TPHP and DPHP in urine samples collected before and after work.

The results of multilevel clustering indicated that work hours and nail polish usage affected both the TPHP concentration in the nail salon environment and the TPHP concentrations in the workers' urine samples (Fig. 4). It was further found that TPHP levels in urine samples after work were significantly associated with several factors, including nail polish usage, DPHP level in masks, TPHP level in UPAS, daily working hours, and DPHP level in urine after work. The two nail salons with the highest nail polish usage had higher concentrations of TPHP and DPHP in UPAS, AC filter dust and masks. Additionally, a significant association was observed between daily working hours and OPE concentrations in UPAS. Nail polish usage, along with TPHP levels in urine before and after work, showed a significant association as well. These findings suggest the potential for long-term exposure issues among workers in nail salons.

3.4. Human internal exposure assessment

D_p was calculated based on the urine concentration of OPE metabolites, providing a comprehensive perspective on internal dosing that

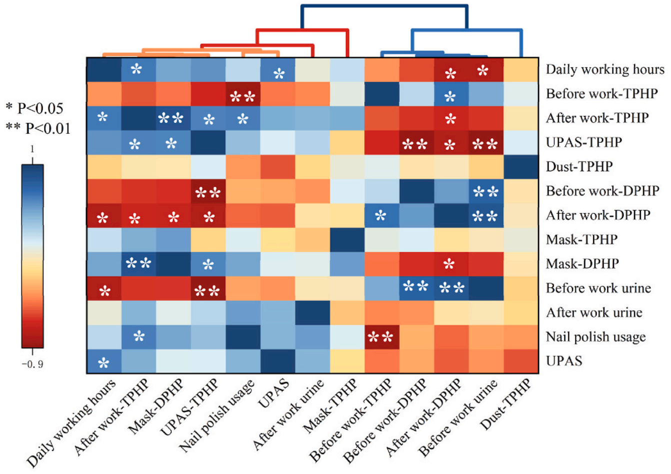

Fig. 4. Correlation and cluster analysis between nail polish usage, work hours, and the concentrations of OPEs and di-OPEs.

encompasses all routes of occupational exposure in nail salons. However, data regarding the bioavailability and toxicokinetic of OPEs are still very limited (Wang et al., 2019). Therefore, the daily intake calculated here is only an approximation (Wang et al., 2021). The average D_p of ΣOPEs before and after work were 343 and 560 ng/kg bw/day, respectively (Fig. 5). This was an increase of 1.63 times after work compared with before work. Similarly, the average D_p for TPHP before and after work were 12.7 and 22.8 ng/kg bw/day, respectively, which was an increase of 1.8 times. The median D_p of ΣOPEs calculated in this study before and after work were 5.0 and 8.6 times the OPEs exposure doses of the general population in the United States (65.3 ng/kg bw/day) (Wang et al., 2019), and 1.9 and 3.3 times higher than the OPEs exposure doses in Guangzhou, China (172 ng/kg bw/day) (Chen et al., 2018).

We also calculated the health risks faced by nail salon workers exposed to OPEs using the formulas provided in Section 1.7 of the Supporting Information. A carcinogenic risk (CR) value lower than 10^{-6} is considered to be indicative of a negligible increase in cancer risk. A CR value between 10^{-6} and 10^{-4} suggests a potential cancer risk, while a CR value greater than 10^{-4} indicates a high potential cancer risk. A hazard index (HI) value exceeding 1 suggests the presence of a possible adverse health risk (Chen et al., 2019). Toddlers were included in the health risk assessment because many of the women working in nail salons are also mothers, and their children often spend extended periods in the salons. Furthermore, customers frequently bring their children with them when getting their nails done. To provide a more comprehensive assessment of exposure risks, toddler CR and HI values were therefore included in the analysis. The HI values for OPEs ranged from 0.07 to 0.44 for toddlers and from 0.18 to 1.04 for adults. The CR values for OPEs ranged from 10^{-6} to 10^{-5} for toddlers and from 10^{-5} to 10^{-4} for adults (Fig. S4). The results indicate that only one nail salon had both CR and HI values for adults exceeding the corresponding theoretical risk thresholds, suggesting potential health risks. This salon also had relatively higher concentrations of OPEs in masks, dust, and UPAS, as previously mentioned. Therefore, more attention should be paid to the occupational exposure to OPEs among nail salon workers, especially considering that most workers in this industry are young women of childbearing age.

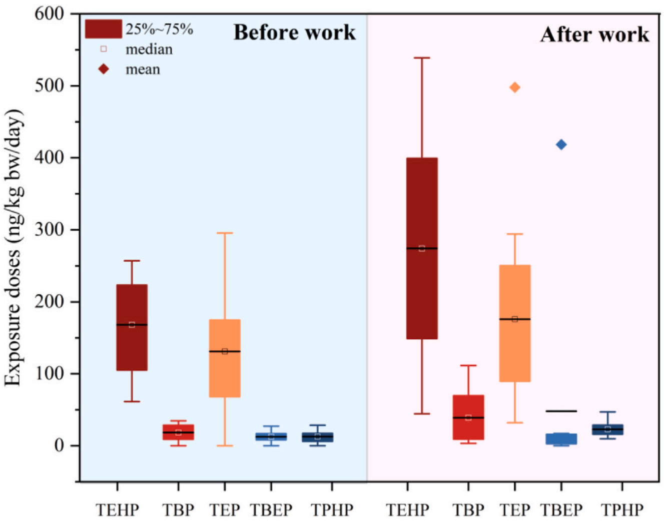

Fig. 5. Exposure doses to OPEs before and after work.

4. Conclusions

Relatively little is known about the true extent of exposure of nail technicians to OPEs and this study represents the first comprehensive investigation of Chinese nail salon workers. The study's findings demonstrate that nail salon workers are indeed exposed to significant levels of OPEs. Considering the protective effect of masks, which can reduce workers' exposure to OPEs by up to 77%, it is important to note that this estimate assumes proper usage. We highly recommend that workers consider frequent mask changes and proper usage during their work shift, and ensure proper indoor ventilation. The findings of the human internal exposure assessment suggest that working in a nail salon substantially increases the risk of OPEs exposure, potentially endangering the health of workers, especially considering that the majority of practitioners in this industry are young women of reproductive age. However, regulations regarding exposure to OPEs are still at a preliminary stage and have only been implemented for children and only in some countries (e.g., BEHP). Unfortunately, these protections have not yet been extended to nail salon workers, and we call for more attention to occupational exposure to OPEs among these workers.

CRediT authorship contribution statement

Tianqi Jia: Writing – original draft. **Arturo A. Keller:** Writing – review & editing. **Lirong Gao:** Writing – review & editing. **Wenbin Liu:** Writing – review & editing. **Sasha Liu:** Formal analysis. **Xiaotian Xu:** Data curation. **Fei Yin:** Data curation. **Yunchen He:** Investigation. **Tianao Mao:** Methodology. **Jinglin Deng:** Methodology. **Javid Hussain:** Software. **Chunci Chen:** Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.125013.

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