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Dynamic variation and inhalation exposure of organophosphates esters and phthalic acid esters in face masks

Can Wang a, Zi-Han Su a, Ming-Jing He a,b,*

a College of Resources and Environment, Southwest University, Chongqing, 400716, China
b Chongqing Key Laboratory of Agricultural Resources and Environment, Chongqing, 400716, China

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ABSTRACT

The coronavirus pandemic (COVID-19) has posed a huge global health threat since December 2019. Wearing face masks is known as an effective measure for controlling the wide spread of COVID-19 and its variants. But on the other hand, face masks could be a potential source of organophosphate esters (OPEs) and phthalic acid esters (PAEs) as they are extensively added in masks. However, knowledge associated with the occurrence as well as inhalation risks of OPEs and PAEs in masks is limited. In this study, OPEs and PAEs were determined in mask samples collected from the local market. OPEs and PAEs were detected in mask samples ranging from 36.7 to 855 ng/g, and from 251 to 3830 ng/g, respectively. Relatively lower OPEs and PAEs concentrations were observed in disposable mask for toddlers. Simulated inhalation experiment indicated that the mass loss of OPEs and PAEs was 136 and 3910 ng/mask in disposable masks, 71.9 and 763 ng/mask in disposable mask for toddlers, 924 and 1020 ng/mask in N95 mask after 12 h, respectively. Significantly negative correlations were exhibited between the decrement of OPEs in masks and the increment of OPEs in corresponding polyurethane foams (PUFs) during the course, elucidating OPEs released from masks could be well captured by PUFs. With regard to the variation over time, predominant OPE and PAE analogues showed semblable release and absorption tendency in mask and corresponding PUF. Inhalation exposure risk of OPEs and PAEs was estimated based on the increment of pollutants in PUF. The estimated daily intakes (EDIs), hazard index (HI) and carcinogenic risk (CR) were also calculated and they were within the threshold levels. This study provides the evidence of OPEs and PAEs releasing from the face masks during wearing and unveiled a potential source of OPEs and PAEs exposure to humans.

1. Introduction

At the end of 2019, the coronavirus pandemic (COVID-19) wreaked havoc around the world, posing a vital threat to human health. What’s worse, a growing number of confirmed cases as well as death cases has been reported globally (WHO, 2022). Due to the high infectivity of COVID-19, wearing a face mask in public places has been proven to be an efficient measure to control the wide spread of COVID-19 (Cheng et al., 2021; Leung et al., 2020; Santana et al., 2020). According to the World Health Organization (WHO, 2020), the demand of medical masks is estimated to be 89 million per month, while 129 billion face masks for the general public (Prata et al., 2020). As a result, it can be speculated that masks have become necessities in our daily life in the long term. Undoubtedly, adverse effects have been aware not only on the environment derived from large-scale consumption of masks, but also on human health owing to the frequent use of masks. For instance, numerous studies have indicated a variety of skin damage induced by long-term use of masks (Aerts et al., 2020; Bhatia et al., 2020; Lee and Goh, 2021; Xie et al., 2020).

Single-use medical masks are generally made of two layers of spun-bonded non-woven fabric with a melt-blown non-woven fabric in the middle, and the non-woven fabric is made from plastic polymers such as polypropylene, polyurethane, and polyacrylonitrile (Potluri and Needham, 2005). In most cases, a variety of chemical agents including plasticizers and flame retardants are added into polymers in order to enhance the performance of materials (Bodaghi, 2020; Zhu et al., 2020). Phthalic acid esters (PAEs) and organophosphate esters (OPEs) are high productive volume chemicals that are widely used as plasticizers and
flame retardants in polymer production (Darbre, 2015; Marklund et al., 2005). Because OPEs and PAEs are both physically bonded with host materials rather than chemically bonded, they can easily release into the environment during the production and usage of products (Navarro et al., 2010; van der Veen and de Boer, 2012). Inevitably, daily use of masks is bound to raise inhalation risks of OPEs and PAEs since the face masks can contact human skin and mouth directly (Fernandez-Arribas et al., 2021; Wang et al., 2022; Xie et al., 2022). Toxicological studies have confirmed the hazardous effect in regard to OPEs and PAEs so far. For example, tris(2-chloroisopropyl) phosphate (TCIPP) is considered to be potentially carcinogenic and tris-(2-chloroethyl) phosphate (TCEP) is toxic to aquatic organisms and carcinogenic for animals (Lehner et al., 2010; van der Veen and de Boer, 2012). Some PAE congeners such as butyl benzyl phthalate (BBP) and diisononyl phthalate (DINP) were reported to affect testosterone and semen parameters (Radke et al., 2010; van der Veen and de Boer, 2012). Relatively varying degrees of mass loss among PAE congeners (Wang et al., 2022). Small high PAE mass loss was detected through the off-gassing test, with levels among various types of face masks (Fernandez-Arribas et al., 2021). Some PAEs including triphenyl phosphate (TPhP), tricresyl phosphate (TCP) and 2-ethylhexyl diphenyl phosphate (EHDP) can result in androgen disorders (Bormelag et al., 2015).

The ubiquitousity of OPEs and PAEs in environment have been extensively reported across a diverse range of environmental media, which has been well documented in latest reviews (Wei et al., 2015; Zhang et al., 2022). The information referred to the face mask is rare mostly due to the fact that there is no relevant regulation or standard for OPEs and PAEs added in face masks. Till date, only several studies revealed the OPEs and PAEs occurrences in face masks, exhibiting heterogeneous levels among various types of face masks (Fernandez-Arribas et al., 2021; Wang et al., 2022; Xie et al., 2022). Apart from that, relatively high PAE mass loss was detected through the off-gassing test, with varying degrees of mass loss among PAE congeners (Wang et al., 2022).

Generally, a mask can be worn continuously for up to 10 to 12 h, so OPEs and PAEs in masks are likely to release at varying extents in different time frames, because both of these two compounds are characterized with a wide range of physicochemical properties. e.g., (log $K_{ow}$ ranging from 0.65 for trimethyl phosphate (TMP) to 9.49 for tris-(2-ethylhexyl) phosphate (TEHP); from 1.64 for dimethyl phthalate (DMP) to 7.73 for di (2-ethylhexyl) phthalate (DEHP)) (Net et al., 2015; Wei et al., 2015). But unfortunately, limited data is available for the dynamic variation of OPEs and PAEs in face masks during people wearing. Further, human exposure to OPEs and PAEs via use of face masks is ineluctable and health risk assessments have become particularly relevant and significant for the public, especially in vulnerable groups, but the related information is still knowledge gaps. To this end, three categories of face masks including disposable surgical, N95 and KN95 masks which are commonly consumed in China were collected. The aims of this study were (i) to analyze the concentrations and compositions of OPEs and PAEs in various types of face masks; (ii) to capture the dynamic variation of OPEs and PAEs in face masks via simulation experiment; (iii) to evaluate the health risks of human exposure to OPEs and PAEs via wearing masks. This study will help to fill the knowledge gap and recommend appropriate time for the public wearing face masks.

2. Materials and methods

2.1. Sample collection

From July to September 2021, we collected three categories of face masks including disposable surgical face masks (S1–S7), N95(N1) and KN95 (K1) that were commonly available in local grocery stores and pharmacies. Among the disposal surgical face masks, four of which were blue facing outside while the other three were black, green, and patterned facing outside, respectively. In terms of the N95 and KN95 masks, both of them were white facing outside, the difference is that the KN95 mask has the air valve while the N95 doesn’t. Detailed information about the face masks studied in this study was shown in Table S1. All the face masks were stored in aluminum foil bag which were pretreated with methanol and acetonitrile at room temperature prior to analysis.

2.2. Standards and reagents

Eleven OPE standards including alkyl-OPEs (trimethyl phosphate (TMP), triethyl phosphate (TEP), tripropyl phosphate (TPPr), tributyl phosphate (TBNP) and tris (2-butoxy ethyl) phosphate (TBEP)), CI-OPEs (tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP) and tris(1,3-dichloroisopropyl) phosphate (TDCCIPP)) and ary-OPEs (triphenyl phosphate (TPhP), tricresyl phosphate (TCP) and 2-ethylhexyl diphenyl phosphate (EHDP)) were purchased from Accustandard (USA). The internal standards for OPEs including TMP-d$_9$, TEP-d$_{16}$, TNP-d$_{27}$, TCEP-d$_{12}$, TCIPP-d$_{18}$, and TPhP-d$_{15}$ were purchased from Toronto Research Chemicals (Canada). Six individual PAE analogues including diethyl phthalate (DEP), dimethyl phthalate (DMP), butyl benzyl phthalate (BBP), dibutyl phthalate (DBP), diisobutyl phthalate (DiBP), and di-(2-ethylhexyl) phthalate (DEHP), were obtained from o2si smart solutions (USA). Internal standards for PAEs (DEP-d$_4$ and DnBP-d$_4$) were purchased from Dr. Ehrenstorfer GmbH (Germany). Acetone and n-hexane were HPLC-grade and obtained from J. T. Baker (USA). Methanol and acetonitrile applied in the instrumental analysis were obtained from Merck (Germany). The syringe filter with PTFE (Polytetrafluoroethylene) was provided by JinTeng (China).

2.3. Inhalation simulation via wearing face masks

To assess the scenario of human inhaling OPEs and PAEs via use of face masks, an experimental simulation was conducted using a modified SPE device (Fig. 1). Briefly, an SPE column (packed with florisoril) is added on the top of the device to filter out interfering substances from the air. The vacuum pump is operated to pump air with a constant flow rate of 20 L/min based on the rate of human inhalation in a steady state while people sitting (Kuga et al., 2022; Shang et al., 2015), and the air flowed through the face mask which was tied to the bracket of the device. The above process could simulate the air movement during use of face masks to some extent. To capture the potential OPEs and PAEs released from the face masks during the process, PU foam (PUF) disk which was pretreated with methanol and acetonitrile was employed and placed 3–4 cm below the face mask due to its satisfactory absorption performance for air pollutants (Rauert et al., 2018). For this simulation experiment, we analyzed S4, S7 and N1, which represented disposable surgical, N95 and KN95 face masks, respectively. Each mask was tested for 4/8/12 h (based on the average time people wearing face masks). Field blank sample was conducted with no mask tied on the bracket of the device. The experiment was repeated three times in fuming cupboard for each point of time. After the experiment, all the face masks and corresponding PUF samples were collected and stored in aluminum foil bag prior to analysis.

2.4. Sample preparation and OPE/PAE analysis

To avoid potential interference, the ear loops, metal nose strips, and valves in the mask were removed before mask analysis. Each face mask (including all layers of the face mask) was cut into small pieces within 3 mm $\times$ 3 mm using stainless steel scissors. Then, three face masks from same brand were pooled together as a representative sample. Approximately 1.0 g of mask samples were weighed and placed into a pre-cleaned polytetrafluoroethylene (PTFE) centrifuge tube. After adding 40 μL of 5 pg/μL internal standards (TMP-d$_9$, TEP-d$_{16}$, TNP-d$_{27}$, TCEP-d$_{12}$, TCIPP-d$_{18}$, TPhP-d$_{15}$, DEP- d$_4$, and DnBP-d$_4$), mask samples were extracted with a 15 mL mixture of acetonitrile/n-hexane (1:1, v/v) for 30 min in an ultrasonic bath for three times. All the extracts were combined, concentrated to nearly 2 mL using a rotary evaporator, and solvent-exchanged by adding 2 mL of acetonitrile for three times, and filtered with a glass syringe. Finally, the solvent was blown down to nearly 0.1 mL with N$_2$, and redissolved in 200 μL of methanol. PUF...
samples were cut into small pieces within 3 mm × 3 mm using stainless steel scissors, weighed and went through the same procedure as mask samples.

The analysis of OPEs and PAEs was determined by UPLC-Q-TOF (Waters, Xevo G2, USA) with positive electrospray (ESI) and sensitivity mode. Target compounds of OPEs and PAEs were separated using an ACQUITY BEH C18 column (100 mm × 2.1 mm i.d., 1.7 μm, Waters, USA). The mobile phase A was acetonitrile, and the mobile phase B consisted of Milli-Q water with 0.1% formic acid. The gradient program for separation was performed as follows: 0–1.0 min, 5% A; 1–4.0 min, 5% A-30%A; 4.0–6.0 min, 30%A-70%A; 6.0–10.0 min, 70%A-80%A; 10.0–13.0 min, 100%A; 13.0–15.0 min, 5% A. The flow rate was held at 0.4 mL/min, and the column temperature was controlled at 40 °C. The injection volume was 1 μL. Mass Spectrometry Elevated Energy (MSE) mode was used to quantify PAEs and OPEs, and the specific quantification ions were shown in Table S2.

2.5. QA/QC

The stainless-steel scissors and centrifuge tubes were rinsed with acetone and n-hexane prior to use. The glassware for analysis was solvent rinsed and baked at 450 °C before use to avoid potential contamination of OPEs and PAEs in the laboratory. Matrix spiking experiments were conducted by adding known amounts (100 ng) of target OPEs/PAEs and their internal standards (100 ng) into the solvent and mask samples to evaluate the matrix effects. The recoveries of each OPE and PAE analogue as well as the internal standards were presented in Table S2. Triplicated mask samples were analyzed, and the relative standard deviation (RSD) ranged from 13.59% to 22.40% for OPEs, while from 5.45% to 18.8% for PAEs.

TMP-d₉ and TEP-d₁₅ were used to quantify TMP and TEP, respectively, while TPrP, TNBP, and TBEp were quantified by TNBP-d₂₇. TCEP-d₁₂ was used as the internal standard of TCEP, whereas TCIPP-d₁₈ was used to calculate the concentrations of TCIPP and TDCIPP. TPhP, TCP, and EDHPP were quantified by TPhP-d₁₅. DnBP-d₄ was used to quantify DnBP, DiBP, DEHP, and BBP, while DMP and DEP were quantified by DEP-d₄. Procedure blanks were conducted with every batch of ten samples, and only a small amount of DnBP was detected in blanks which was subtracted from corresponding samples. The recoveries for TMP-d₉, TNBP-d₂₇, TPhP-d₁₅, TCEP-d₁₂, TEP-d₁₅, and TCIPP-d₁₈ in the blanks were 61.2 ± 2.6%, 96.2 ± 0.6%, 100.4 ± 1.5%, 86.3 ± 6.9%, 70.7 ± 2.6% and 82.7 ± 4.8%, respectively. And the recoveries for DnBP-d₄ and DEP-d₄ were 105.4 ± 6.0% and 102.4 ± 6.7%, respectively in the blanks. The limits of detection (LODs) were defined as a signal-to-noise ratio of 3: 1, while the limits of quantification (LOQs) were defined as a signal-to-noise ratio of 10: 1 in the samples. The LOQs of target OPEs and PAEs were listed in Table S2.

2.6. Statistical analysis

In this study, statistical analysis was performed using Origin 2018 for Windows. ANOVA (P < 0.05) was applied to determine the significant differences of OPEs and PAEs concentrations among different types of face masks. Pearson correlation analysis was used to establish the relationship between the decrement of OPE/PAE analogues in mask and the increment of OPE/PAE analogues in corresponding PUF samples. Raw data for instrumental analysis were processed using MassLynx TM.4.1 software. (Waters, USA).

2.7. Exposure risk

To obtain a complete picture of human exposure to OPEs and PAEs via wearing face masks, the estimated daily intakes (EDI) were calculated based on the increment of OPE or PAE analogues in PUF during the process and expressed in ng/kg body weight (bw)/day. The non-carcinogenic risks to adults, adolescents and toddlers were estimated using hazard index (HI). HI and carcinogenic risk (CR) were conducted with the following three equations:

\[
EDI_{\text{inhalation}} = \frac{C_{\text{inhalation}} - C_{\text{blank}}}{BW}
\]

(1)

\[
HI = \frac{EDI_{\text{inhalation}}}{RfD}
\]

(2)

\[
CR = EDI_{\text{inhalation}} \times SFO
\]

(3)

where \(C_{\text{inhalation}}\) (ng/d) was the amounts of OPEs or PAEs in PUF at different wearing time a day (4 h, 8 h, or 12 h), and \(C_{\text{blank}}\) (PFU) (ng/d) was the amounts of OPEs or PAEs in field blank at initial time. The average body weight (BW) values of adults, adolescents and toddlers were 58.55, 38.61 and 16.58, respectively (U.S. EPA, 2004; 2011). RfD (ng/kg/d) is the reference dose of individual OPEs and PAEs while SPO ((ng/kg/d)^-1) is the oral cancer slope factor. The RfD and SFO values were obtained from the database of the United State Environmental Protection Agency (U.S.EPA, 2019) which were listed in Table S3–S5.

3. Results and discussion

3.1. Characteristics of OPEs in different types of mask

The levels of OPEs in each mask were listed in Table 1. Targeted OPEs were detected in all face masks, indicating the extensive additions of OPEs in face masks. Except for TMP, TCEP, TCP, and EDHPP, the remaining OPE analogues were mostly detected with detection frequencies (DFs) higher than 66%. In terms of the disposable medical mask, the \(\sum_{\text{OPE}}\) concentrations varied across a wide range from 36.7 ng/g to 390 ng/g, with S5 showing the highest OPE level. Apparently, S5 had a black color on the surface, thus the extra addition of dyestuff in the
face mask may elevate the OPE levels in face masks (Cristale et al., 2021). As expected, the lowest OPE levels (36.7 ng/g) were found in S7 which was designed for the toddlers. This observation was in accord with the stringent regulation of chemicals added to children’s products (Zhu et al., 2020; Peng et al., 2020). OPE concentration was 855 ng/g and 117 ng/g in N1 and K1, respectively. According to ANOVA test, no significant differences can be found among the face masks, except that N1 was statistically higher than the other face masks ($p < 0.01$). In comparison with other studies, OPE levels in disposable medical masks in present study were in the same range with another study by Fernandez-Arribas et al. (from 38.4 to 717 ng/mask, mean: 118 ng/mask), but significantly lower when compared with KN95 masks (from 323 ng/mask to 20.4 μg/mask, mean: 11.6 μg/mask) (Fernandez-Arribas et al., 2021). Moreover, KN95 masks have been banned to sale in Europe from January 2021 due to the failure of requirement established by the European homologation (BOE, 2020). Under this circumstance, disposable medical masks may be more suitable for COVID-19 protection in comparison with KN95 masks. Due to the limited data on OPEs in face masks, some investigations of OPEs in textiles can be used to compare with the results of this work. Zhu et al. (2020) reported the concentrations of $\sum_{20}$OPEs in raw textiles collected from the United States ranging from 4.85 to $1.18 \times 10^6$ ng/g, which were tens and hundreds of times higher than those detected in face masks here. Further, Peng et al. (2020) reported nine OPE analogues in children’s play mats in China, with concentrations varying from 6.6 to 7400 ng/g, which were several times higher than those in face masks.

The percentage contribution of target OPEs in different face masks was presented in Fig. 2. In general, the profile of OPEs varied in each type of face mask, and for the same type of disposable medical mask (S1–S4). TCI(58.0%), TDCIPP (42.9%), and TPhP (61.6%) were the most abundant analogues in S1, S2 and S3, while S4 was dominated by

| Code  | TMP | TEP | TPrP | TNBP | TBEP | TCIP | TDCIPP | TPhP | TCP | EHDPP | $\sum$OPEs | $\sum$PAEs |
|-------|-----|-----|------|------|------|------|--------|------|-----|-------|----------|-----------|
| S1    | nd  | nd  | 1.43 | 4.68 | nd   | 71.5 | 39.1   | nd   | nd  | nd    | 123      | 120       |
| S2    | nd  | nd  | 1.63 | 3.08 | 2.25 | 31.2 | 105    | 102  | nd  | nd    | 245      | 41.8      |
| S3    | nd  | 1.53 | 1.43 | 4.73 | 2.20 | 17.3 | 18.8   | 73.8 | nd  | nd    | 120      | 48.7      |
| S4    | 0.48| 1.75 | nd   | 1.17 | 12.1 | nd   | 22.1   | nd   | nd  | nd    | 245      | 6.38      |
| S5    | nd  | nd  | nd   | 1.15 | 1.63 | 0.08 | 4.93   | 6.98 | nd  | nd    | 124      | 21.0      |
| S6    | nd  | nd  | nd   | nd   | nd   | 7.14 | 1.69   | 23.6 | nd  | nd    | 124      | 13.6      |
| S7    | 0.36| 0.53 | 1.04 | 3.39 | 0.13 | 8.43 | 6.71   | nd   | 7.33| 8.52  | 36.7     | 0.25      |
| N1    | nd  | 719 | 1.59 | 31.0 | 1.02 | 8.52 | 6.71   | nd   | 7.33| 8.52  | 855      | 0.47      |
| K1    | 1.10| nd  | 6.33 | 79.3 | nd   | 24.5 | 24.5   | 66.7 | nd  | nd    | 117      | 1.52      |

DF (%) 44.4 66.7 88.9 100 90.0 44.4 50.0 88.9 88.9 33.3 66.7 100 100 100 22.2 88.9

nd: below limit of detection.
TCP (36.8%), TBEF (17.8%) and TPhP (12.6%). As for the colored ones, TEP and TPhP accounted for more than 90% of total OPEs in S5, whereas TDCIPP was the dominating analogue in S6. For S7 which was designed for toddlers, TCP, TPhP, TCIPP and TCEP were evenly distributed. Disparate OPE compositions were observed in two kinds of N95 masks, where TEP was the major analogue in N1, responsible for 84.0%, while TDCIPP and TNBP were the dominating analogues in K1, with percentage contribution of 29.5% and 64.1%, respectively. Similar OPE compositions in face masks can be found in elsewhere with TEHP, TNBP and TEP dominating in surgical masks, while TEHP and TPhP dominating in N95 masks (Fernandez-Arribas et al., 2021). In general, TEP, TNBP, TPhP, TCP, TDCIPP and TEHP were most frequently detected OPE analogues in masks as the raw material as well as the manufacturing process for the mask were similar in the world. Similarly, TPhP and TCIPP were also the predominant compounds in flame retardant-treated textiles (Zhu et al., 2020).

### 3.2. Characteristics of PAEs in different types of mask

As shown in Table 1 and Fig. 2, the majority of PAEs were detected in mask samples except for DEHP, which was only observed in S1 and S4. DMP, DEP, and DnBP were all detected in masks, followed by DiBP and BBP with detection frequencies of 88.9%, suggesting that these PAE analogues were generally presented in face masks. The concentrations of \( \Sigma^{\text{PAEs}} \) ranged from 251 to 3830 ng/g in disposable medical masks, and the \( \Sigma^{\text{PAEs}} \) levels in N1 and K1 were 595 and 1530 ng/g, respectively. The result of this study was in the same range with another study by Wang et al. (2022) where PAEs in disposable medical masks ranged from 55 to 1700 ng/mask, and from 2300 to 5000 ng/mask in N95 masks. Xie et al. (2022) where PAEs in disposable medical masks ranged from 115 to 37,700 ng/mask. The result of this study was in the same range with another study by Wang et al. (2022) where PAEs in disposable medical masks ranged from 55 to 1700 ng/mask, and from 2300 to 5000 ng/mask in N95 masks. Xie et al. (2022) reported PAEs in face masks with range from 115 to 37,700 ng/mask. The result of this study was in the same range with another study by Wang et al. (2022) where PAEs in disposable medical masks ranged from 55 to 1700 ng/mask, and from 2300 to 5000 ng/mask in N95 masks. Xie et al. (2022) reported PAEs in face masks with range from 115 to 37,700 ng/mask.

Disparate OPE compositions were observed in two kinds of N95 masks, where TEP was the major analogue in N1, responsible for 84.0%, while TDCIPP and TNBP were the dominating analogues in K1, with percentage contribution of 29.5% and 64.1%, respectively. Similar OPE compositions in face masks can be found in elsewhere with TEHP, TNBP and TEP dominating in surgical masks, while TEHP and TPhP dominating in N95 masks (Fernandez-Arribas et al., 2021). In general, TEP, TNBP, TPhP, TCP, TDCIPP and TEHP were most frequently detected OPE analogues in masks as the raw material as well as the manufacturing process for the mask were similar in the world. Similarly, TPhP and TCIPP were also the predominant compounds in flame retardant-treated textiles (Zhu et al., 2020).

**Fig. 3.** Correlations between the decrement of OPEs/PAEs in face mask and the increment of OPEs/PAEs in corresponding PUF samples.
Table 2
Dynamic variation of predominant OPE and PAE analogues in mask and corresponding PUF samples.

| Contaminants (ng/mask) | Analogues | Mask Samples | 0 h | 4 h | 8 h | 12 h | PUF Samples | CK | 4 h | 8 h | 12 h |
|------------------------|-----------|--------------|-----|-----|-----|------|-------------|----|-----|-----|------|
| Disposable medical mask - S4 | OPEs | TCIPP | 32.7 | 25.1 | 15.4 | 6.32 | 14.0 | 15.8 | 87.8 | 96.7 |
|                         |        | TPhP | 34.9 | 42.5 | 45.3 | 39.1 | 1.17 | 1.94 | 1.12 | 2.41 |
|                         |        | TCP | 102 | 41.2 | 20.1 | 5.70 | 5.86 | 7.51 | 13.0 | 74.1 |
|                         |        | TBP | 49.2 | 22.2 | 28.5 | 31.9 | 0.35 | 0.20 | 0.62 | 0.36 |
|                         |        | ∑OPEs | 219 | 131 | 109 | 83.0 | 21.4 | 25.5 | 103 | 174 |
|                         | PAEs | DEHP | 4160 | 3480 | 743 | 259 | 65.4 | 98.7 | 195 | 327 |
|                         |        | ∑PAEs | 4160 | 3480 | 743 | 259 | 65.4 | 98.7 | 195 | 327 |
| Disposable medical mask for toddlers – S7 | OPEs | TCEP | 27.4 | 1.08 | 4.01 | 1.77 | 2.97 | 3.14 | 4.62 | 5.88 |
|                         |        | TCIPP | 21.8 | 7.27 | 4.98 | 6.12 | 1.40 | 5.43 | 12.7 | 18.5 |
|                         |        | TPhP | 23.8 | 14.7 | 5.19 | 4.63 | 1.17 | 0.67 | 1.07 | 1.22 |
|                         |        | TCP | 27.7 | 20.6 | 24.1 | 16.6 | 5.86 | 0.72 | 0.56 | 0.53 |
|                         |        | ∑OPEs | 101 | 43.7 | 38.3 | 29.1 | 11.4 | 9.96 | 19.0 | 26.1 |
|                         | PAEs | DMP | 371 | 550 | 373 | 239 | 7.29 | 14.4 | 15.9 | 25.4 |
|                         |        | DnBP | 1320 | 1050 | 846 | 686 | 28.1 | 46.9 | 56.3 | 49.9 |
|                         |        | ∑PAEs | 1690 | 1600 | 1220 | 924 | 35.4 | 61.3 | 72.2 | 75.3 |
| N95 mask - N1 | OPEs | TEP | 3160 | 3130 | 2670 | 2310 | 3.37 | 36.1 | 46.9 | 49.6 |
|                         |        | TPhP | 312 | 246 | 235 | 230 | 1.17 | 0.48 | 0.40 | 0.32 |
|                         |        | ∑OPEs | 3470 | 3380 | 2900 | 2540 | 4.54 | 36.6 | 47.3 | 49.9 |
|                         | PAEs | DMP | 360 | 482 | 434 | 103 | 7.29 | 8.68 | 9.05 | 9.21 |
|                         |        | DnBP | 792 | 625 | 648 | 461 | 28.1 | 27.6 | 33.1 | 33.5 |
|                         |        | BBP | 588 | 0.00 | 16.1 | 127 | 0.01 | 0.52 | 4.34 | 7.10 |
|                         |        | ∑PAEs | 1710 | 1110 | 1100 | 691 | 35.4 | 37.3 | 46.1 | 49.7 |

medical masks. But in most cases, people tend to wear masks for a short time, and the mass loss of OPEs after 4 h was 88.0 ng/mask in S4, 57.3 ng/mask in S7, and 90.0 ng/mask in N1. So, under this circumstance, S4 and N1 exhibited a higher risk of release than S7. For the corresponding PUF, the total mass increase of OPEs was 153 ng/mask in PUF for S4, and N1 exhibited a higher risk of release than S7. For the corresponding PUF, and both the mass loss and capture process were well performed using binomial fitting. Similar results were also observed in a study by Xu et al. (2020) where DnBP dramatically released from polyethylene terephthalate (PET) bottles into PET-bottled drinking water along with the storage time. It tends to be somewhat arduous to interpret in depth these disparate release and absorption behaviors among PAE analogues. Different physico-chemical properties (e.g., MW, Vapor pressure) of PAE analogues as well as the material of the mask may play a role in this observation, but it seemed that PAE analogues exhibited semblable release and absorption behavior in mask and corresponding PUF, respectively. In addition, temperature and humidity were constant during the experiment, which could be considered as influencing factors of pollutants emission from the mask, and further investigations should be conducted to reveal relevant issues.

3.4. Human exposure

Current studies associated with human exposure to OPEs and PAEs via inhalation during the use of masks were mostly assuming 100% of the off-gassed PAEs from the masks or 5–10% of OPE levels in masks were inhaled by the wearer (Fernandez-Arribas et al., 2021; Xie et al., 2022; Wang et al., 2022). Nevertheless, we view both methods as possibly leading to an over estimation of OPEs and PAEs inhaled. In this part, we used the increment of OPEs and PAEs in PUF of S4, S7, and N1 to calculate estimated daily intake (EDI)inhalation and the results were listed in Table S3–S5. The total EDIs of OPEs and PAEs ranged between 0.04 and 4.69 ng/kg bw/day and between 0.04 and 15.8 ng/kg bw/day, respectively, and EDIs via wearing S4 displayed the highest values both for OPEs and PAEs. In addition, the EDIs of OPEs and PAEs increased along with the wearing time, so the longer ones wear masks, the higher exposure to OPEs and PAEs ones may have. Notably, The EDIs of OPEs and PAEs for the toddlers were approximately 2–3 times higher than those for adolescents and adults, most likely due to the much lower body weight of toddlers.

Luckily, the EDIs of OPEs and PAEs for S7 (children’s mask) were

0–8 h, exhibiting an exponential decay function of time in S4. Likewise, DEHP in corresponding PUF also presented an exponential increase along with time. Interestingly, DMP and DnBP in S7 and N1 were both slightly descending, whereas it showed a smooth growth in corresponding PUF, and both the mass loss and capture process were well performed using binomial fitting. Similar results were also observed in a study by Xu et al. (2020) where DnBP dramatically released from polyethylene terephthalate (PET) bottles into PET-bottled drinking water along with the storage time. It tends to be somewhat arduous to interpret in depth these disparate release and absorption behaviors among PAE analogues. Different physico-chemical properties (e.g., MW, Vapor pressure) of PAE analogues as well as the material of the mask may play a role in this observation, but it seemed that PAE analogues exhibited semblable release and absorption behavior in mask and corresponding PUF, respectively. In addition, temperature and humidity were constant during the experiment, which could be considered as influencing factors of pollutants emission from the mask, and further investigations should be conducted to reveal relevant issues.

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Fig. 4. Dynamic variation of individual OPEs in mask and corresponding PUF samples over time.
Fig. 5. Dynamic variation of individual PAEs in mask and corresponding PUF samples over time.
20% of PAE content in mask (3.71 ng/kg bw/day) were one or two orders of magnitude lower compared to EDIs based on ranging between 1.2 and 2.1 ng/kg bw/day (Cao et al., 2019), and be negligible. Compared with other studies, the obtained EDIs inhalation values of only 1.21 and 2.41 ng/kg bw/day, respectively even after wearing 12 h. Reducing the wearing time could mitigate the release risks of OPEs and PAEs in comparison with real conditions. Lastly, it remains unknown how much OPEs and PAEs are potentially inhaled by people during wearing masks was estimated using calculated EDI, HI and CR, all of which were much lower than the threshold levels, indicating inhalation of OPEs and PAEs via using COVID-19 face mask may not be hazardous for people.

Author statement
Can-Wang sampled, conducted the experimental treatment and wrote the manuscript.Zihan-Su sampled and conducted the experimental treatment.Mingjing-He conceived the project, and revised the manuscript. All of the authors contributed to the final review of the submitted manuscript, and gave final approval for publication.

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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