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Face mask—A potential source of phthalate exposure for human

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ABSTRACT

Face masks are necessary for fighting against the coronavirus disease 2019 around the world. As the face mask is usually made from polymers and phthalates are widely-used additives into the polymers, the face mask could be a potential source of phthalate exposure to humans. However, limited knowledge is available on the occurrence and risks of the phthalates from the face mask. In this study, twelve phthalates were determined in 56 mask samples collected from different countries. The phthalates were detected in all the samples with total levels ranging from 115 ng/g to 37,700 ng/g. Estimated daily intakes (EDIs) of the phthalates from the masks ranged from 3.71 to 639 ng/kg-bw/day, and the EDIs of the phthalates from masks for toddlers were approximately 4–5 times higher than those for adults. Non-carcinogenic risks in relation to the phthalates in masks were found to be within safe levels, yet 89.3% of the mask samples exhibited potential carcinogenic effects to humans. The extent of the risks for wearing masks located at a moderate level comparing with other skin-contacted products. This study unveiled a potential source of phthalate exposure to human, and indicated necessity of managing types and levels of additives in the face masks.

1. Introduction

Since the outbreak of the coronavirus disease 2019 (COVID-19) which was claimed to be a pandemic by the World Health Organization (WHO), more than 114 million (by March 3, 2021) people have been infected by this virus (WHO Coronavirus Disease, 2021). The COVID-19 is highly contagious and it attacks not only lung but also heart, kidney, brain and many other organs (Lukiw et al., 2020; Vasquez-Bonilla et al., 2020). According to the WHO, the impact of the COVID-19 may last for decades. Fortunately, it has been convinced that protective face masks can be applied to prevent the spread of the coronavirus and the masks can reduce the spray of droplets when worn over the nose and mouth (Zhang et al., 2020; Cheng et al., 2020; Prather et al., 2020). Therefore wearing a mask has gradually become a habit of people.

Millions of masks can be consumed within 1 day protecting millions of people from infection (Li et al., 2020). However, the numerous masks have simultaneously brought some adverse effects on the environment and human health. For instance, the rising consumption and production of the face masks globally can increase the plastic waste and plastic particle pollution (Aragaw, 2020; Fadare and Okoffo, 2020; Patricio Silva et al., 2021). Furthermore, recent studies reported that long-term use of plastic mask could lead to various skin problems (Aerts et al., 2020; Bhatia et al., 2020; Xie et al., 2020). It was speculated that these skin problems were mainly caused by the chemicals released from the mask. The mask is usually made of polymers (mostly polypropylene) and the polymers can involve lots of additives (Jung et al., 2020; Camargo et al., 2020). Among the additives, phthalate is a group of high production volume (HPV) chemicals that needs to be concerned.

Phthalates are usually used as plasticizers to reduce shear in the polymer producing process and to improve flexibility and versatility of the polymers (Guo and Kannan, 2013; Rahman and Brazel, 2004; Vieira et al., 2011). Although the use of phthalates has been partly regulated in some countries, their annual usage amount is still up to several million tons (Net et al., 2015). The phthalates are usually applied as additives and they are not chemically bonded to the materials, therefore they can be easily released into the environment and enter human body, and further exert a series of adverse effects (Gong et al., 2016). For instance, the phthalate exposure was reported to affect fetal growth and had reproductive toxicity (Martino-Andrade and Chaboud, 2010; Yost et al., 2019; Kay et al., 2013). Butyl benzyl phthalate (BBP) and diisononyl phthalate (DINP) were proved to affect testosteron and semen parameters (Radke et al., 2018). Bis(2-ethylhexyl)phthalate (DEHP) was also found to be associated with penile birth defects and other effects related to androgen disruption (Bornehag et al., 2015).
Previous studies reported that the phthalates were widely deter-
mined in textiles and skin contacted products, including cotton clothing
(Li et al., 2019), sanitary napkin (Tang et al., 2019; Gao et al., 2019),
paper diaper and toys (Negev et al., 2018) et al. The phthalates from
these products can enter human body through dermal absorption, as
well as ingestion. It is reported that these phthalate exposures might lead
to contact allergy and even pose carcinogenic risks to humans (Li et al.,
2019; Rovira and Domingo, 2019). Compared with the mentioned tex-
tiles and skin contacted products, the face mask can directly contact
people’s nose and mouth, then the phthalates can be taken up through
dermal absorption, ingestion and inhalation. These joint exposure
pathways may increase the phthalates intakes comparing with other
products. However, there is no regulation or standard on the use of
phthalates in mask products around the world. The phthalate occurrence
and exposure from the mask and its potential risk to human health are
still knowledge gaps.

Under this circumstance, in the present study, 56 mask samples were
collected and 12 phthalates in the masks were analyzed. The phthalate
contents in the masks among different countries and different produc-
tion standards were investigated. In addition, the daily intakes of the
phthalates from the masks were estimated, and the phthalate exposures
for adults and toddlers were compared. Finally, the health risks of the
phthalate exposure were assessed, including carcinogenic risk and non-
carcinogenic risk. We hope the results can be employed to fill the
knowledge gap for the mask production standards as well as phthalate
management policies.

2. Materials and methods

2.1. Chemicals

Twelve phthalates were analyzed in this study, including dimethyl
phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP),
di-n-butyl phthalate (DBP), bis(2-methoxyethyl)phthalate (DMEP),
diamyl phthalate (DAP), dihexyl phthalate (DHP), dicyclohexyl
phthalate (DCHP), bis(2-Ethylhexyl)phthalate (DEHP), diphenyl
phthalate (DPhP), di-n-octyl phthalate (DNOP) and dinonyl phthalate
(DNP). Three deuterated compounds were used as surrogates, including
diisobutyl phthalate-d4 (DiBP-d4), dimethyl phthalate-d4 (DMP-d4) and
diethyl phthalate-d4 (DEP-d4). All of the targets and surrogates were
purchased from AccuStandard Inc. (New Haven, USA). Hexame-
thylbenzene was acted as an international standard and it was obtained
by J&K Scientific Ltd. (China).

2.2. Sample collection and preparation

Fifty-six brands of masks from different countries and regions were
collected through online or local shops in May of 2020, including 44
Chinese brands, 6 European brands, 3 American brands, 2 Japanese
brands and 1 South Korean brand. All of these masks were manufactured
locally and widely used in daily life. The 44 Chinese brands contained 28
masks for adults and 16 masks for toddlers, and the masks from other
countries were all for adults. The 28 Chinese adult mask brands con-
tained 11 KN95 masks and 17 disposable masks. Detailed information on
the masks is shown in Table S1 in supporting information.

In order to avoid potential contamination during storage, the mask
samples were prepared immediately after collection. Elastic band and
metal nose strip in the mask were removed, and then the net weight of
the masks was determined (listed in Table S1). The mask samples were
cut into small pieces through stainless steel scissors within 2 mm × 2
mm. Three masks from each brand were cut together and mixed as a
representative sample, and then placed in a pre-cleaned glass bottle. 0.5
g sample was accurately weighed, then 50 ng of each surrogate standard
was added. After equilibration for 4 h, the samples were extracted twice
with 10 mL of dichloromethane/ethyl acetate (1:1, V/V) for 30 min in an
ultrasonic bath. The eluent was separated with the sample through a
glass syringe. Then the combined eluent was blown down to approxi-
mately 0.5 mL with N2. Finally, 50 ng of internal standard was spiked.

2.3. Instrumental analysis

The phthalates were analyzed through an Agilent gas chromatog-
raphy mass spectrometry (GC-MS, 6890N-5975) in selected ion moni-
toring mode, operating with EI source. Separation was performed by a
HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm), and high pu-
rity helium was used as carrier gas at a flow rate of 1 mL/min. Tem-
peratures of GC injection port and transfer line were both kept at 290 °C.
The GC oven temperature was performed with a thermal gradient as
following: 60 °C for 1 min, 20 °C/min to 220 °C, held for 1 min, 5 °C
/min to 250 °C held for 1 min, 20 °C/min to 290 °C, held for 6 min, and
finally programmed to 300 °C at 10 °C/min, held for 6 min. Tempera-
tures for the ion source and quadrupole region were set at 230 °C and
150 °C, respectively. The retention time and precursor ion/product ions
of the 12 phthalates are provided in the Supporting Information and
Table S2.

2.4. Quality assurance and quality control

Only glass and stainless steel containers and tools were used during
the whole procedures. All the containers and tools were rinsed with
hexane and ethyl acetate prior to use. A procedural blank, as well as
a duplicated sample, was processed in every ten samples as a batch. The
relative standard deviations measured from duplicate samples were
proved to be within 20%. DEHP, DBP, DEP, DMP, and DiBP were
detected with low levels in the blank samples. The contamination of the
phthalates during the pretreatment procedures seems inevitable. Similar
results for the contamination were also found in lots of previous studies
on phthalate analysis (Guo and Kannan, 2013; Li et al., 2019; Gao
et al., 2019; Tang et al., 2020). The recoveries of the phthalates ranged
from 79.3% to 113.2%, indicating the matrix effect did not affect the
analyzing results based on the internal standard method. The surrogate
recoveries for DiBP-d4, DMP-d4 and DEP-d4 in all samples were 91.1 ±
10.9%, 87.2 ± 8.1% and 89.2 ± 8.8%, respectively. All phthalate con-
centrations in the samples were corrected with the blank and the sur-
rogate recoveries. Method detection limits (MDLs) of the 12 phthalates
fluctuated between 4.8 ng/g and 26.5 ng/g (listed in Table S2). Levels
below the MDLs were set as zero for statistical analysis.

2.5. Estimation of phthalate exposure

Estimated daily intakes (EDIs) for phthalates in the masks were
estimated with the following equations according to previous studies
(Tang et al., 2019):

$$EDI = \frac{C_l \times M \times N \times A}{BW}$$

where $C_l$ is the measured phthalate concentration in the mask (ng/g); $M$
is the weight (g) of the mask measured in this study (Table S1); $N$ is
the number of masks used per day, in this study the $N$ value was set as 1; $A$
is the absorption rate of phthalate in mask by human body. In previous
studies, the skin absorption rates of the phthalates were set as 5% for
cosmetics and personal care products, 5–10% for paper diapers and 15%
for sanitary napkins when estimating phthalates intake (Tang et al.,
2019). Here, for the masks, the phthalate exposure can take place in two
forms: through the direct contact with human skin, and through inha-
lation of the air gap between mask and skin surface. The respiration can
lead to increase of temperature and moisture content, this might further
increase the release rate of phthalates from mask as well as the intake
rate into human body. Therefore, the absorption rate was selected as a
higher value than the other products, i.e., 20%; BW represents body
weight, assumed as 60 kg for adult and 8 kg for toddler according to the

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European Union Risk Assessment Report. In this model, the product of C, M and A was regarded as the intake of the phthalates from one mask in one day. Usage duration of a single mask was considered as 3–4 h, which was similar to that of a single paper diaper or sanitary napkin. The usage period of the masks within one day was distinguished with the paper diaper or sanitary napkin by adjusting the N values.

2.6. Risk assessment

The non-carcinogenic risks to adults and toddlers associated with the phthalates in the masks were estimated using hazard quotient (HQ) and the cumulative non-carcinogenic risks were estimated by the hazard index (HI), which is a sum of the HQ of individual phthalate. The calculation of the cumulative risks was based on assumption that the phthalates had similar mode of toxic action (Martino-Andrade and Chahoud, 2010). The HQ can be calculated using Eq. (2) (Li et al., 2019):

\[ HQ = \frac{EDI}{RfD} \]  

(2)

where RfD is the reference dose of the individual phthalate. In this study, the RfD values were assumed to be equal to their corresponding oral RfD. The oral RfD values were obtained from the database of the United State Environmental Protection Agency (U.S. EPA) and listed in Table S3 in the supporting information. Carcinogenic risks (CRs) of the phthalates for adults and toddlers from the masks were conducted with the following equation:

\[ CR = EDI \times CFS \]  

(3)

where CFS is a slope factor of exposure to the individual phthalate. The CFS values of the phthalates were also assumed to be equal to their corresponding oral CFS (listed in Table S3).

2.7. Data analysis

SPSS version 21 was applied to analyze the data acquired (IBM SPSS, Armonk, NY, USA). The Kolmogorov-Smirnov test was employed to examine the normal distribution of the data. A nonparametric test was performed to compare various groups in the case that the data was not consistent with the assumption of normality. The Mann-Whitney test was applied for the comparison between two groups, while the Kruskal Wallis test was applied to compare multiple sets of measured data. This study set the statistical significance at less than 0.05.

3. Results and discussion

3.1. Phthalate concentrations

The phthalates contents in the 56 mask samples were listed in Table S4 and summarized in Table 1. Eleven phthalates were detected among the 12 targets. DEHP was detected in all samples, and DMP, DEP, DiBP, DBP, DPP, DPhP and DNP were detected with detection frequencies of > 50%, indicating that multiple phthalates were generally present in the face masks. DCHP was not found in any of the mask samples. The Kolmogorov-Smirnov test indicated that concentrations of most phthalates exhibited non-normal distribution (p < 0.05). The total concentrations of the phthalates ranged from 115 ng/g to 37,700 ng/g, with a median level of 1950 ng/g. DEHP, DBP and DiBP were found to be predominant phthalates with median levels of 590 ng/g, 322 ng/g and 321 ng/g. The maximum concentration was found for DEHP (36,700 ng/g), followed by DBP (4780 ng/g). The mask is mainly made of hot melt adhesive and non-woven fabric, and DEHP was reported to be a major plasticizer in these two materials (Wang et al., 2011; Lee et al., 2014). Thus the DEHP showed the highest detection level and detection frequency. Similar results were also found in other products, such as preschool children’s clothing (Tang et al., 2020) and feminine hygiene products (Gao et al., 2019).

Although the occurrence of the phthalates in masks was rarely reported in previous studies, some investigations on the phthalates in textiles and clothes can be used to compare with the results of this work. Previous studies reported that phthalates in crib mattress, nylon sheets and diaper-changing mats were above 0.1% by mass (Negev et al., 2018), which were much higher than those detected in the masks here. In addition, the concentrations of the phthalates in masks were 2–3 times lower than those in cotton clothing (Li et al., 2019), and 10–20 times lower than those in jeans (Gong et al., 2016). These can be mainly caused by adsorption of phthalates from surrounding air and environment during production and storage for the clothes (Li et al., 2019). While the environment for mask producing can be relatively clean and the masks were usually independently packaged, therefore the contamination of phthalates for the masks can be less.

3.2. Phthalate contamination profile

Masks from 5 countries and regions were analyzed to examine whether the phthalate content depend on the geographical origin. As the samples collected from South Korea and Japanese were too few, they were not considered in the statistical analysis. According to the statistical test results, the total concentrations of the 11 detected phthalates

Table 1

Detection frequencies (DF, %) and concentrations (ng/g) of phthalates in mask samples (n = 56).

| Compound | Mean | Median | IQRa | Range | DF |
|----------|------|--------|------|-------|----|
| DMP      | 22.8 | 12.0   | 37   | < MDL−126       | 76.8 |
| DEP      | 76.2 | 13.1   | 61.4 | < MDL−1780      | 53.6 |
| DiBP     | 321  | 43.4   | < MDL−1450     | 98.2 |
| DBP      | 523  | 246    | < MDL−4780     | 98.2 |
| DMEP     | 9.4  | < MDL  | 246  | < MDL−252       | 10.7 |
| DPP      | 47.4 | 36.8   | 50.3 | < MDL−149       | 80.4 |
| DHxP     | 131  | 41.6   | < MDL−1530     | 44.6 |
| DEHP     | 1590 | 590    | 789  | 37.4−36,700     | 100 |
| DiPhP    | 93.8 | 71.1   | 43.4 | < MDL−1960      | 50.0 |
| DNOP     | 47.4 | 36.8   | 50.3 | < MDL−149       | 80.4 |
| DNP      | 158  | 256    | < MDL−1500     | 57.1 |
| Total    | 3150 | 1950   | 2620 | 115−37,700      | 25.0 |

a IQR represents interquartile range.

b MDL represents method detection limit.
did not differ significantly among the masks from different countries ($p = 0.423$, Fig. 1). The median values of the total phthalate concentrations ranged from 1730 ng/g to 2890 ng/g among the countries. In addition, the individual phthalate between countries showed the same result ($p$ varied from 0.058 to 0.926) except for DEP and DPP (with $p$ values of 0.001 and 0.035, respectively). The median concentrations of the DEP and DPP were both highest in the USA samples, with the mean values of 108 ng/g and 86.0 ng/g, respectively. The total and individual concentrations of the masks from South Korea seemed lower than those from other countries, however, the sample number was limited and the representativeness should be further investigated. These results indicated that the phthalate contents in the masks from different countries were similar on the whole, which goes against previous studies on children’s clothing (Tang et al., 2020) and sanitary napkin samples (Tang et al., 2019). The phthalate concentrations differed significantly in clothing and sanitary napkin between countries due to various use of materials and individual phthalates by countries. For the mask, the raw material and producing process were generally similar in the world and therefore the phthalate content showed consistent results.

The phthalate contents were compared among the masks with different production standards and different applicable users. The detected levels of the masks were shown in Fig. 2. Significance test exhibited that there was no significant difference between phthalate levels in the masks for adults and toddlers ($p$ ranged from 0.157 to 0.825). Similar result was also observed between the KN95 and disposable masks for most phthalates ($p$ ranged from 0.059 to 0.926) except for DPP ($p = 0.001$) and DPhP ($p = 0.019$). The median levels for DPP and DPHP were 71.5 ng/g and 65.3 ng/g for the KN95 mask, while 23.5 ng/g and 115.2 ng/g for the disposable mask. No matter whether the mask was KN95 type or disposable type, for adults or toddlers, they were produced according to the production standards. While the essential difference among these standards was about filtration efficiency, appearance, respiratory resistance and leaking test, but not about materials or additives. In fact, most of the masks were made of hot melt adhesive and non-woven fabric, and therefore the masks had similar phthalate content.

In all the samples ($n = 56$), significant differences ($p < 0.05$) in concentrations between individual phthalates were observed. The composition profile of phthalates in the mask samples was shown in Fig. 3. Although the DEHP has been reported to be replaced gradually in the global market (ECHA, 2013), it still showed the highest percentage (39.3%) among the plasticizers in all mask samples. DBP has also been reported to be gradually replaced by DiBP, the result showed that their levels were both predominant (19.2% and 16.3%, respectively). Similar compositions for these three phthalates were also observed in infant cotton clothing and sanitary napkin samples (Li et al., 2019; Gao et al., 2019), indicating DEHP, DBP and DiBP are the most common phthalate plasticizers in the textiles and skin contacted products.

### 3.3. Estimation of phthalate exposure

The estimated daily intakes (EDIs) of phthalates from the 56 masks were calculated and the results were listed in Table S5. The total EDIs of the 11 detected phthalates ranged from 3.71 ng/kg-bw/day to 639 ng/kg-bw/day, with a median value of 33.9 ng/kg-bw/day. Among the detected phthalates, DEHP had the highest contribution for the phthalates exposure accounting for 39.1% (mean value), followed by DiBP and DBP with mean contributions of 16.2% and 19.2%, respectively. Similar results for these three predominant phthalates were also observed in phthalate exposure from sanitary napkins (Gao et al., 2019).

![Fig. 2. Concentrations (C) of phthalates in different masks.](image_url)
The weight and corresponding phthalate content of the adult masks were compared with those from other skin-contacted products. In addition, the median values of the phthalates in the masks ranged from 115 ng/g to 37,700 ng/g, with a median level of 1950 ng/g. Significance test showed that there was no significant difference for the phthalate concentrations in the masks from different countries. Based on the results of determination, the estimated daily intakes (EDIs) of phthalates from the masks were calculated with a median value of 33.9 ng/kg-bw/day. In addition, the EDIs of the phthalates from masks for toddlers were approximately 4–5 times higher than those for adults. In the risk assessment, the hazard index of phthalates from the masks located in acceptable levels.

3.4. Risk assessment

The risks of the phthalate exposure to adults and toddlers were estimated respectively and the results were shown in Table S7. The median hazard index (HI) of the phthalate exposure to adults and toddlers were 7.08 × 10⁻⁴ and 3.92 × 10⁻³, respectively, which were both much lower than the safe value. Even the maximum HI values for the adult mask and toddler masks were 3.17 × 10⁻² and 1.44 × 10⁻², respectively, indicating the 11 detected phthalates in the masks were within the acceptable levels in terms of non-carcinogenic risks. Similar results were also found for other skin contacted products, such as sanitary napkin, paper diaper and cotton clothing (Li et al., 2019; Gao et al., 2019; Ishii et al., 2015).

According to previous studies, the CR value of 1 × 10⁻⁶ was regarded as an acceptable limit. As can be seen from Table S7, the cumulative CR values of phthalate exposure to adults and toddlers were in the range of 5.30 × 10⁻⁷ - 1.45 × 10⁻⁵ and 6.29 × 10⁻⁸ - 4.26 × 10⁻⁵, respectively. It should be noted that the cumulative CR values for 50 mask samples (accounting for 89.3% of the mask samples) were higher than 1 × 10⁻⁶, indicating their potential adverse effects to human health. Thus, the potential carcinogenic effects of phthalates from the mask should not be ignored.

4. Conclusion

In this study, the occurrence, exposure and risks of phthalates from face mask were investigated. Twelve phthalates were determined in 56 mask samples from different countries. The total concentrations of the phthalates in the masks ranged from 115 ng/g to 37,700 ng/g, with a median level of 1950 ng/g. Significance test showed that there was no significant difference for the phthalate concentrations in the masks from different countries. Based on the results of determination, the estimated daily intakes (EDIs) of phthalates from the masks were calculated with a median value of 33.9 ng/kg-bw/day. In addition, the EDIs of the phthalates from masks for toddlers were approximately 4–5 times higher than those for adults. In the risk assessment, the hazard index of phthalate exposure from all masks located in acceptable levels.
However, 50 mask samples could exhibit carcinogenic risks to humans. The face mask has made a great contribution to the fighting against the epidemic and wearing masks will still last for a long time. This study convinced the face mask as a novel source of phthalate exposure. The results can be beneficial for awareness of management on additives in the face mask production.

CRediT authorship contribution statement

Huaijun Xie: Methodology, Investigation, Writing – original draft. Wenjing Han: Conceptualization, Supervision. Qing Xie: Data curation. Tong Xu: Writing – review & editing. Minghua Zhu: Writing – original draft. Jingwen Chen: Conceptualization, Project administration, Writing – review & editing.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126848.

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