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Measuring the quantity of harmful volatile organic compounds inhaled through masks

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ABSTRACT

An increase in the concentration of environmental particulate matter and the spread of the COVID-19 virus have dramatically increased our time spent wearing masks. If harmful chemicals are released from these masks, there may be harmful effects on human health. In this study, the concentration of volatile organic compounds (VOCs) emitted from some commonly used masks was assessed qualitatively and quantitatively under diverse conditions (including different mask material types, time between opening the product and wearing, and mask temperature). In KF94 masks, 1-methoxy-2-propanol ($221 \pm 356 \mu\text{g m}^{-3}$), *N,N*-dimethylacetamide ($601 \pm 450 \mu\text{g m}^{-3}$), *n*-hexane ($268 \pm 349 \mu\text{g m}^{-3}$), and 2-butanone ($160 \pm 244 \mu\text{g m}^{-3}$) were detected at concentrations 22.9–147 times higher than those found in masks made from other materials, such as cotton and other functional fabrics. In addition, in KF94 masks, the total VOC (TVOC) released amounted to $3730 \pm 1331 \mu\text{g m}^{-3}$, about 14 times more than that released by the cotton masks ($267.5 \pm 51.6 \mu\text{g m}^{-3}$). In some KF94 masks, TVOC concentration reached over $4000 \mu\text{g m}^{-3}$, posing a risk to human health (based on indoor air quality guidelines established by the German Environment Agency). Notably, 30 min after KF94 masks were removed from their packaging, TVOC concentrations decreased by about 80% from their initial levels to $724 \pm 5.86 \mu\text{g m}^{-3}$; furthermore, 6 h after removal, TVOC concentrations were found to be less than $200 \mu\text{g m}^{-3}$. When the temperature of the KF94 masks was raised to 40°C , TVOC concentrations increased by 119–299%. Since the types and concentrations of VOCs that will be inhaled by mask wearers vary depending on the mask use conditions, it is necessary to comply with safe mask wearing conditions.

1. Introduction

Masks are classified as health, surgical, droplet-blocking, dust-proofing, and cold-proofing depending on their purpose (Karuppasamy and Obuchowski, 2021; Palmieri et al., 2021; Rengasamy et al., 2017). Most masks are used to prevent humans from inhaling air pollutants, though some special purpose masks such as warm masks exist for other reasons (McDonald et al., 2020; Pacitto et al., 2019; Zorko et al., 2020). Masks for blocking pollutants can be further classified into disposable and multi-use (Karuppasamy and Obuchowski, 2021; O'Kelly et al., 2021; Rengasamy et al., 2009). Disposable masks are primarily composed of polypropylene, polyethylene, and melt-blown filters, and differ based on blocking efficiency and targeted particle size (i.e., KF94,

KF80, and KFAD) (Jung et al., 2014; Ryu et al., 2022). The formation of the charge that affects the blocking of particles and viruses varies depending on the mask material (Ghatak et al., 2021; Zhang et al., 2022). Multi-use masks are made of diverse materials (i.e., synthetic resin, polyurethane foam, etc.) depending on their purpose, and recently the use of multi-functional face masks with additional functions such as UV protection is increasing (Blevens et al., 2021; Hu et al., 2021; Pollard et al., 2021).

As the quality of life improves, the demand for masks has increased to protect humans from air pollutants such as fine dust (Lee et al., 2020; Zhang and Mu, 2018). Researchers have reported that the inhalation of fine dust causes various harms including respiratory diseases. As a response to ultrafine dust that can cause cerebrovascular diseases

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through the microvascular system, wearing a mask has been emphasized (Ritz et al., 2019; Wilker et al., 2015). In addition, the COVID-19 pandemic that began at the end of 2019 established a global norm of mandatory mask wearing (Betsch et al., 2020; Fischer et al., 2021; Lyu and Wehby, 2020). KF94, KF80, and KFAD masks, which have been verified for droplet blocking, are recommended (Esmeria et al., 2021; Kang et al., 2020; Noh et al., 2020; Safarpour et al., 2022).

As mask wearing has become mandatory to prevent the spread of COVID-19, the time spent wearing masks has significantly increased. Since masks are worn close to the face (mouth and nose), mask materials are directly or indirectly exposed to the human body through inhalation, the mouth, and skin (Bhatia et al., 2020; Jin et al., 2021; Raval and Sangani, 2021). If hazardous compounds are released from these masks, the human body is at risk (Aerts et al., 2020; Fernández-Arribas et al., 2021; Xie et al., 2022). For example, dimethylformamide (DMF) and dimethylacetamide (DMAC), which are organic solvents used in the production of masks and have been detected in KF masks in South Korea (Liu et al., 2022; Mariello et al., 2021), cause reproductive toxicity, liver toxicity, and cancer in the human body (Lamkarkach et al., 2022; Maxfield et al., 1975; Wang and Chen, 2020). Accordingly, South Korea has drafted a law to regulate the amount of DMF and DMAC allowed to be released from KF masks, setting the limit below 5 mg/kg. Of course, various hazardous chemicals other than DMF and DMAC can be emitted from masks, and there is no legislation for their regulation. Safe mask use is necessary to monitor and evaluate harmful chemicals emitted from the masks and to conduct research to confirm their harmful levels.

In this study, we assessed the types and concentrations of volatile hazardous chemicals (volatile organic compounds, VOCs) and how they are released depending on mask use conditions. Ultimately, we suggest some guidelines for safe mask use based on the experimental evidence

developed herein.

2. Materials and methods

2.1. Selection of target mask samples

Various masks were selected as target samples ($n = 14$). Target masks were selected on the basis of possible reuse (disposable and multi-use), material, and droplet blocking efficiency. Among disposable masks, three different brands of droplet blocking masks (KFAD: sample codes A1, A2, and A3) and three different brands of surgical masks (KF94: sample codes B1, B2, and B3) were prepared. Samples A and B, which were disposable masks, were made of polypropylene and polyurethane nylon. The multi-use masks were prepared in four different types of cotton masks (main materials (sample codes): 100% cotton (C1 and C2), cotton + ramie (D1), and cotton + polyurethane (D2)) and in four types of multi-functional masks (sample codes E1, E2, E3, and E4) made of materials with UV blocking function. The E samples did not provide information on their main materials. All mask samples were purchased from an online market. Detailed information of the target masks is presented in Table 1.

2.2. Experimental schemes (Exps 1, 2, and 3)

VOCs were generated from the target mask samples under various conditions, and analyzed. The experiments were classified according to the VOC generation conditions from the masks (Exps 1, 2, and 3) (Table 2). The VOCs were collected and analyzed by (1) a sorbent tube/thermal desorption-gas chromatography-mass spectrometry (ST/TD-GC-MS) system and (2) 2,4-dinitrophenylhydrazine cartridge-high

Table 1
Basic information associated with the tested masks.

Order	Sample code	Mask type	Main material	Photos
1	A1	Droplet blocking mask (KFAD)	Polypropylene, Polyurethane nylon	A1
2	A2			A2
3	A3			A3
4	B1	Surgical mask (KF94)	Polypropylene, Polyurethane nylon	B1
5	B2			B2
6	B3			B3
7	C1	Cotton mask (100% cotton)	Cotton	C1
8	C2			C2
9	D1	Cotton mask (Cotton + others)	Cotton and Ramie	D1
10	D2		95% cotton, 5% polyurethane	D2
11	E1	Functional mask (Functional fabric + UV protection)	Polyester, Graphene, and Somatid	E1
12	E2		Aerosilver fabric	E2
13	E3		Cooling fabric	E3
14	E4		Copper cotton fabric	E4

Table 2
Experimental schemes for mask emission VOC assessment.

Order	Variables	Experimental codes		
		Exp 1	Exp 2	Exp 3
1	Key variable	Mask type	Pre-purge time	Emission temperature
2	Target sample ^a	All masks	KF94 masks (sample code: B)	KF94 masks (sample code: B)
3	Pre-purge flow rate (L min ⁻¹)	-	0.2	-
4	Pre-purge time (min)	-	30, 60, 120, and 360	-
5	Temperature (°C)	25	25	40
6	Analytical method ^b	ST/TD-GC-MS system and DNPH cartridge-HPLC-UV system		

^a Refer to Table 1.

^b ST/TD-GC-MS system: sorbent tube/thermal desorption-gas chromatography-mass spectrometry system and DNPH cartridge-HPLC-UV system: 2,4-dinitrophenylhydrazine cartridge-high performance liquid chromatography-UV vis.

performance liquid chromatography-UV vis (DNPH cartridge-HPLC-UV) system.

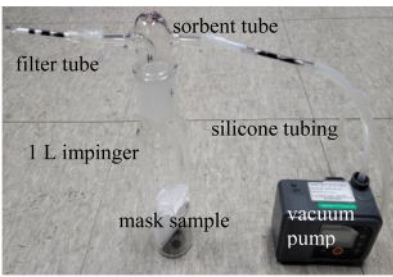

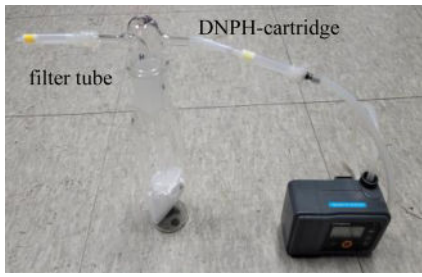

In short, VOCs emitted from each mask were subjected to qualitative and quantitative analysis through the ST/TD-GC-MS system. VOCs were adsorbed and collected by the ST, and after thermal desorption, they were induced by the TD system, then separated and analyzed by the GC-MS (Kim and Lee, 2022). The aldehydes (formaldehyde (FA), acetaldehyde (AA), and propionaldehyde (PA)), which were difficult to quantify

with the ST/TD-GC-MS system, were quantitatively analyzed using the DNPH cartridge-HPLC-UV system (Dutta et al., 2018; Kim and Kim, 2016). Elution of the three aldehydes from the DNPH cartridge was induced by injecting 5 mL of acetonitrile into the DNPH cartridge where aldehyde was collected, and the eluted aldehydes were loaded into the HPLC-UV system, followed by separation and quantitative analysis (Kim et al., 2020). Detailed information concerning our instrumental system is also provided in Table 3.

2.2.1. Assessment of VOCs emitted from masks depending on mask type (Exp 1)

In Exp 1, the types and concentrations of VOCs generated from the mask samples were compared (each mask having a different sample code: n = 14). The mask samples were taken out of the product packaging and injected into a 1 L capacity impinger. The inlet of the impinger was connected to a filter tube packed with Carbpac X (100 mg, Supelco, USA). The outlet of the impinger was connected to the inlet of the ST filled with Carbpac C, B, and X (each 50 mg, Supelco, USA). The outlet of the ST was connected to a vacuum pump interfaced with a mass flow controller (Sibata ΣMP-30, Japan) using silicone tubing. The VOCs generated from the mask samples in the impinger were swept into the ST by a 0.2 L min⁻¹ flow of gas over 5 min. The VOCs were finally collected while passing through the ST. However, three aldehydes (FA, AA, and PA) generated from the mask samples were collected using a DNPH cartridge instead of the sorbent tubes used for VOC collection. At this time, the sampling flow rate of the aldehydes was 2 L min⁻¹ for 5 min.

Table 3
System used to generate and collect VOCs from mask samples.

Order	Variables	Analytical methods	
		ST/TD-GC-MS	DNPH cartridge-HPLC-UV
1	Sampling approach	 	 
2	Target VOCs	VOCs detected by the GC-MS ^a (n = 72)	Formaldehyde, acetaldehyde, and propionaldehyde
3	Sampler	Three multi-bed adsorbents (Carbpac C, B, and X; each 50 mg) packed in quartz tube	2,4-dinitrophenylhydrazine cartridge
4	Sampling flow rate (L min ⁻¹)	0.2	2
5	Sampling time (min)	5	5
6	Pretreatment	Thermal desorption	Solvent extraction (Acetonitrile)
7	Instrument	GC-MS	HPLC-UV
8	Quantitative method	External calibration method using standard solutions and effective carbon number (ECN) method using statistics ^b	External calibration method using standard solutions

^a VOCs with the concentration below 0.1 µg m⁻³ or a library similarity of below 80% by mass spectrometry.

^b Statistical estimation approach for quantitative concentrations of VOCs based on linear correlations between directly measured detector responses and carbon number of different functional groups (Kim et al., 2014; Szulejko et al., 2013).

2.2.2. Mass flow rate of mask-emitted VOCs depending on time worn (Exp 2)

In Exp 2, KF94 masks (sample B) were employed to evaluate whether the concentration of VOCs emitted from the masks changes depending on the time elapsed after opening the packaging. To accomplish this, the mask was removed from its packaging, placed in a 1 L capacity impinger, and air was flowed through the filter tube at 0.2 L min^{-1} (pre-purge). VOCs emitted from the mask were collected and analyzed in the same manner as in Exp 1. The pre-purge times were set at 30, 60, 120, and 360 min.

2.2.3. Concentrations of mask-emitted VOCs depending on mask temperature (Exp 3)

Exp 3 assessed whether VOC concentrations increased as mask temperature increased. After putting the impinger with the masks in a 20 L water bath container filled with water, temperature was adjusted to 40°C by heating the water with an immersion electric heater (DAIHAN Scientific, Republic of Korea). VOCs were generated and collected in the same manner as in Exp 1.

2.3. Preparation and analysis of working standards for acquiring calibration curves

In this study, working standards including a total of 27 VOCs were prepared to evaluate the concentrations of VOCs generated from masks ((1) two alkanes: pentane (P) and hexane (H), (2) two aldehydes: butyraldehyde (BA) and valeraldehyde (VA), (3) three ketones: methyl ethyl ketone (2-butanone, MEK), methyl isobutyl ketone (MIBK), and acetone (AT), (4) three acetates: methyl acetate (MeAc), butyl acetate (BuAc), and ethyl hexanoate (EtHe), (5) two alcohols: isobutyl alcohol (i-BuAl) and 1-hexanol (HeAl), (6) four aromatics: benzene (B), toluene (T), p-xylene (p-X), and o-xylene (o-X), (7) two phenols: o-cresol (o-C) and m-cresol (m-C), (8) one amine: nicotine (Nic), (9) seven acids: acetic acid (ACA), propionic acid (PPA), butyric acid (BTA), isovaleric acid (IVA), valeric acid (VLA), hexanoic acid (HXA), and heptanoic acid (HPA), and (10) one sulfide: dimethyl disulfide (DMDS)).

The reagent grade chemicals (RGCs) of the 27 VOCs were purchased at a purity ranging from 96.5% (VA) to 99.9% (EtHe) (Sigma-Aldrich, USA). The working standards were prepared by gravimetric dilution of the RGCs with methanol: (1) 8.79 ± 1.09 , (2) 17.6 ± 2.17 , (3) 35.2 ± 4.35 , (4) 87.9 ± 10.9 , and (5) $176 \pm 21.7 \text{ ng } \mu\text{L}^{-1}$. The working standard was directly injected onto the ST via a temporary injection port made from a Teflon tube that connected the inlet of the ST and the outlet of the filter tube, while the back-up air flowed from the filter tube to the ST (0.2 L min^{-1} for 5 min) (Kim and Kim, 2016). The VOCs loaded on the ST was then thermally desorbed using the TD system to derive calibration curves prior to separation by the GC and the final detection by the MS (Kim and Kim, 2016).

For quantitative analysis of FA, AA, and PA, the primary standard including the three aldehydes was purchased at a concentration of $15 \text{ ng } \mu\text{L}^{-1}$ (TO11A, Supelco, USA). The primary standard was diluted using acetonitrile to create the working standards for the calibration curves: (1) 0.06, (2) 0.12, (3) 0.30, (4) 1.50, and (5) $3.00 \text{ ng } \mu\text{L}^{-1}$. The working standards were analyzed by the HPLC-UV system to obtain calibration curve data. Table S1 shows detailed procedures for making the working standards.

2.4. Instrumental system

2.4.1. ST/TD-GC-MS system

The analysis of the VOCs emitted from our mask samples was carried out using a GC (GC-2010, Shimadzu, Japan) equipped with MS (GCMS-QP2010, Shimadzu, Japan) and a TD (TD20, Shimadzu, Japan). The VOCs loaded on the ST were thermally desorbed at 280°C (5 min) at a reverse flow of 100 mL min^{-1} with helium ($> 99.9999\%$) carrier gas. The desorbed analytes were swept into the cold trap (held at 5°C) in the

stream of the carrier gas. The cold trap packed with quartz wool (10 mg) and Tenax TA (50 mg) in a Silcosteel holder (Shimadzu, Japan) was then rapidly desorbed (280°C) in a reverse flow of carrier gas in order to transfer (inject) the VOCs into the column (DB wax - length: 60 m, diameter: 0.25 mm, and thickness: $0.25 \mu\text{m}$, Agilent, USA). The transfer/injection of analytes from the cold trap into the GC column was carried out by splitting the flow between the column (2 mL min^{-1}) and the split vent (20 mL min^{-1}). Oven temperature was initially set at 40°C (for 5 min), ramped at $10^\circ\text{C min}^{-1}$ until reaching 250°C , and held at this temperature for 4 min (a total run time of 30 min). To detect VOCs, interface and ion source temperatures were set relatively high (at 230°C) in order to prevent contamination in the MS system. VOCs were examined in total ion chromatographic (TIC) mode over a mass range of 35–500 m/z . Detailed information on the instrumental system is included in Table S2.

2.4.2. HPLC-UV system

All liquid samples (DNPH cartridge solvent extraction samples and working standards) containing three aldehydes were analyzed with an HPLC-UV system (LC-2010, Shimadzu, Japan) equipped with an auto sampler (SIL-20A), pump (LC-20AD), oven (CTO-20A), and UV detector (SPD-20A). A fixed sample volume of $20 \mu\text{L}$ was injected into the HPLC system through the auto sampler. The analytes were separated on a Shim-Pack GIS-ODS column (length: 25 mm, diameter: 4.6 mm, particle size: $5 \mu\text{L}$) using a mobile phase of acetonitrile–distilled water (6:4 (v/v)) at a flow rate of 1.5 mL min^{-1} at 30°C (maintained by the oven). The total run time was 11 min. The separated aldehydes were detected by the UV detector at a wavelength of 360 nm (Table S2).

2.5. Quantitative method for the calculation of concentrations of the VOCs emitted from masks

In this research, a total of 27 VOCs that were prepared for working standards were selected for external calibration (Table S1). The calibration results obtained using the working standards were used to derive predictive equations based on the effective carbon number (ECN) method (Faiola et al., 2012; Kállai et al., 2003; Kim et al., 2014). The ECN method was then used to calculate the concentration of each VOC due to the absence of standard material (i.e., authentic compounds) or the complexity involved in standard preparation. Among the VOCs detected from the mask emission samples, VOCs that could not be quantified by external calibration were quantified through ECN.

The concentrations of the VOCs were derived from predictive equations based on a linear regression equation between response factor (RF) values of target standard compounds (Table S1) and their ECNs. Each ECN was determined by counting the number of the atoms (C, H, O, N, and S) and moieties in functional groups (e.g., aldehyde, ester, ketone, carboxyl, alcohol, cyclic, and acyclic groups) in terms of carbon number equivalent (CNE), accounting for the approximate relative contribution of each to the sensitivity (RF) in the MS system. This detailed calculation process is presented in Table S3.

3. Results and discussion

3.1. VOCs emitted from different mask samples (Exp 1)

In this study, VOCs emitted from masks were collected and analyzed from different mask samples. VOC concentrations were calculated as the TVOC and the sum of the concentrations of each functional group (i.e., alcohol, aldehyde, amide, aromatic, etc.) to facilitate a comparative analysis (Fig. 1, Table 4, and Fig. S2).

The highest concentration of TVOCs was recorded in sample B (KF94), a disposable mask ($3730 \pm 1331 \mu\text{g m}^{-3}$). Sample A (KFAD), another disposable mask, was associated with the next highest TVOC concentration ($1174 \pm 1271 \mu\text{g m}^{-3}$). Disposable mask samples A and B showed different TVOC concentrations of more than twice for each

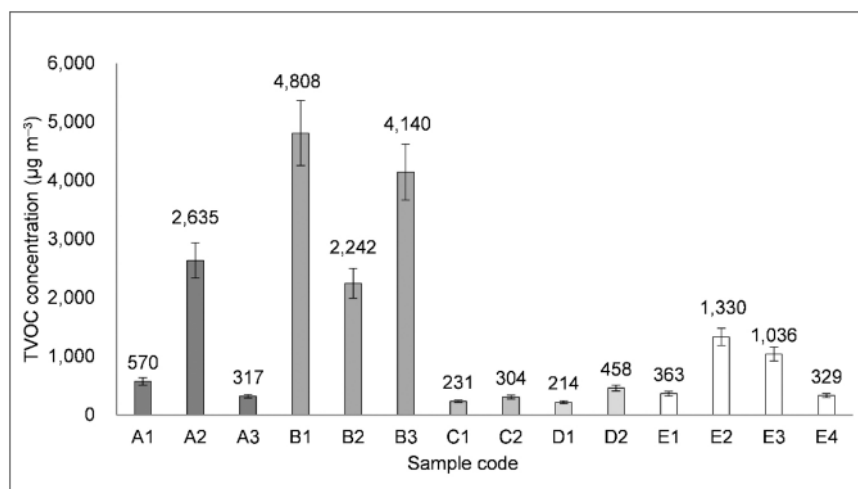


Fig. 1. TVOC concentrations ($\mu\text{g m}^{-3}$) emitted from each mask sample.

Table 4

Concentrations of VOCs emitted from mask samples (with VOCs sorted by functional group).

Order	Functional group	Concentration ($\mu\text{g m}^{-3}$)														Sum
		A1	A2	A3	B1	B2	B3	C1	C2	D1	D2	E1	E2	E3	E4	
1	Alcohol	109	231	59.8	203	140	731	76.8	53.4	23.1	46.9	41.7	56.7	37.3	54.6	1,864
2	Aldehyde	31.7	38.6	43.3	22.8	39.6	28.0	26.4	25.7	22.7	15.3	0.67	36.3	19.4	17.7	368
3	Amide	24.4	116	8.08	1,114	624	273	8.44	NA ^b	NA	40.7	NA	139	NA	NA	2,348
4	Aromatic	12.2	295	8.78	158	121	143	8.04	9.45	7.59	15.7	23.2	33.9	28.7	26.0	891
5	Carboxyl	80.9	NA	NA	NA	NA	NA	46.6	NA	97.6	199	77.8	153	626	65.6	1,346
6	Cyanide	16.8	45.3	81.0	45.1	17.2	87.3	20.5	27.1	22.5	88.3	68.1	20.4	52.3	10.5	602
7	Dioxane	2.99	15.9	NA	12.5	9.18	9.54	NA	NA	NA	NA	NA	9.44	2.45	13.0	75.1
8	Ester	172	855	4.92	1,073	445	1,076	7.62	13.8	13.9	3.46	15.2	384	197	11.3	4,272
9	Ether	249	144	19.2	82.3	194	980	68.7	37.5	27.7	38.4	27.1	47.4	36.4	25.2	1,977
10	Hydrocarbon ^a	108	908	96.1	1,968	687	1,204	23.3	168	18.1	31.4	120	462	61.5	116	5,973
11	Ketone	10.0	100	6.43	181	148	578	6.73	6.51	5.14	6.53	12.6	28.8	8.38	9.19	1,108
12	Oxane	1.29	64.5	NA	93.3	32.5	28.3	1.11	NA	NA	NA	NA	NA	NA	NA	221
13	Oxirane	1.53	23.6	1.08	23.0	7.60	7.54	3.62	NA	2.95	7.23	2.16	4.75	3.76	2.76	91.6
14	Siloxane	NA	1.88	7.89	2.20	1.15	0.83	2.69	1.50	0.77	3.10	1.31	0.78	NA	2.45	26.5

^aExcept for aromatics

^bNA: not available, The compounds with the concentration of below $0.1 \mu\text{g m}^{-3}$ or the library similarity of below 80% by mass spectrometry (MS).

> $100 \mu\text{g m}^{-3}$

> $1,000 \mu\text{g m}^{-3}$

manufacturer. That is, although the masks were made of the same materials, the concentrations of VOCs generated from the masks varied depending on the manufacturing processes. TVOC concentrations generated from samples B1 ($4808 \pm 957 \mu\text{g m}^{-3}$) and B3 ($4140 \pm 823 \mu\text{g m}^{-3}$), which are the most commonly used KF94 masks for COVID-19 protection, correspond to a high-risk level (health concerns, $\text{TVOC} = 3000$ to $10,000 \mu\text{g m}^{-3}$) as established by the TVOC guidelines set by the German Federal Environment Agency concerning Indoor Guide Values (AIR) (der Ad-hoc-Arbeitsgruppe, 2007; Heinzow and Sagunski, 2009; Salthammer, 2011). The multi-use masks showed relatively lower TVOC concentrations ($267 \pm 51.4 \mu\text{g m}^{-3}$ (sample C), $336 \pm 172 \mu\text{g m}^{-3}$ (sample D), and $764 \pm 498 \mu\text{g m}^{-3}$ (sample E)) compared to the disposable masks (samples A and B). Both samples C and D, which were made of cotton as the main material, had TVOC concentrations below $460 \mu\text{g m}^{-3}$. These TVOC concentration levels corresponded to a level that is harmless to the human body (no relevant

health-related concerns, $\text{TVOC} < 1000 \mu\text{g m}^{-3}$) (der Ad-hoc-Arbeitsgruppe, 2007; Fromme et al., 2019; Salthammer, 2022). In the case of sample E, the TVOC concentrations of E2 and E3 were relatively high at $1330 \pm 259 \mu\text{g m}^{-3}$ and $1036 \pm 204 \mu\text{g m}^{-3}$, respectively. It was difficult to assess the TVOC concentration patterns for the sample E with the mask materials because they could not be specifically identified about their main materials.

The concentrations of VOCs emitted from each mask sample are presented in Table 4, subdivided into 14 major functional groups (alcohol, aldehyde, amide, aromatic, carboxyl, cyanide, dioxane, ester, ether, hydrocarbon, ketone, oxane, oxirane, and siloxane). Individual VOCs detected at relatively high concentrations ($> 100 \mu\text{g m}^{-3}$) are presented in Table S4. In sample B, alcohol, amide, aromatics, ester, hydrocarbon, and ketone have relatively high concentrations above $100 \mu\text{g m}^{-3}$, regardless of manufacturer. In particular, in sample B1, amide, ester, and hydrocarbon compounds were detected at high

concentrations of above $1000 \mu\text{g m}^{-3}$ ($1114 \mu\text{g m}^{-3}$ (amide), $1073 \mu\text{g m}^{-3}$ (ester), and $1968 \mu\text{g m}^{-3}$ (hydrocarbon)). Here, the amide compounds were 100% DMAc and the ester compounds were 99.25% of ethyl acetate, accounting for most quantitatively. The hydrocarbons detected from sample B1 were mostly alkanes with 6–12 carbon atoms. Concentrations of ester and hydrocarbon compounds for sample B3 were also relatively high at $1076 \mu\text{g m}^{-3}$ and $1204 \mu\text{g m}^{-3}$, respectively, and most of the ester compounds were ethyl acetate (70.1%). The concentrations of the VOCs emitted from sample A were generally lower than those of sample B; however, the concentration patterns of VOCs for each functional group were similar between samples A and B. In sample A, there were instances in which concentrations of alcohol, amide aromatic, ester, hydrocarbon, and ketone compounds were detected reached $100 \mu\text{g m}^{-3}$ or greater. In other words, VOCs having relatively various functional groups were released at relatively high concentrations from each of the disposable masks, such as samples A and B. In samples C and D, which used cotton as their primary material, the VOC concentrations by functional groups were mostly low, below $100 \mu\text{g m}^{-3}$ (except for hydrocarbon in sample C2 ($168 \mu\text{g m}^{-3}$) and carboxyl in sample D2 ($199 \mu\text{g m}^{-3}$)). In sample E, a multi-functional mask, carboxyl, ester and hydrocarbon compounds were detected at relatively high concentrations ($231 \pm 266 \mu\text{g m}^{-3}$ (carboxyl), $152 \pm 178 \mu\text{g m}^{-3}$ (ester), and $190 \pm 183 \mu\text{g m}^{-3}$ (hydrocarbon)). The carboxyl compounds were detected at their highest concentrations (on average) in the sample E. The carboxyl compounds detected in the sample E were all acetic acids.

The number of VOCs detected above $100 \mu\text{g m}^{-3}$ concentration was clearly distinguished between the disposable masks (samples A and B) and multi-use masks (samples C, D, and E) (Table S4). DMAc was detected at relative high concentrations with $480 \pm 440 \mu\text{g m}^{-3}$ in samples A2, B1, B2, and B3. In sample B2, DMF, which has an amide group like DMAc, a high concentration was also detected ($208 \mu\text{g m}^{-3}$). We confirmed that amide compounds were emitted from most disposable mask samples. Among the multi-use masks, DMF was detected at a high concentration of $139 \mu\text{g m}^{-3}$ only in sample E2. In the case of toluene, relatively high concentrations of $155 \mu\text{g m}^{-3}$ (A2), $123 \mu\text{g m}^{-3}$ (B1), and $104 \mu\text{g m}^{-3}$ (B2) were recorded only in the disposable mask samples. In contrast, toluene was not detected (or below $100 \mu\text{g m}^{-3}$) in the multi-use masks. High concentrations of carboxyl compounds (above $100 \mu\text{g m}^{-3}$) were detected only in the multi-use mask samples, and all were acetic acid. 2-nonaone with a ketone group was detected at a high concentration of $142 \pm 16.0 \mu\text{g m}^{-3}$ only in sample B. In short, concentrations of individual VOCs generated from each mask differed based on mask type. We confirmed that VOCs with various functional groups were generated in relatively high concentrations in sample B, a KF94 mask.

Fifteen species of the VOCs detected from mask samples were consistent with the hazardous chemicals commonly found in work environments, as identified by the United States' National Institute for Occupational Safety & Health (NIOSH) (Barsan, 2007) (Table 5). Among these 15 hazardous chemicals, DMAc and DMF are known to potentially cause liver and reproductive toxicity, and aromatic compounds such as toluene and xylene are toxic to the nervous system (Gong et al., 2016; Niaz et al., 2015; Saito et al., 2011; Wegner et al., 2021). Acetonitrile is also a harmful substance that can cause inflammation to the skin and eyes, and can cause neurological disorders (Ahmed et al., 1992; Hashimoto, 1991; Joshi and Adhikari, 2019). n-Hexane is a skin irritant that can cause headaches and pulmonary edema when inhaled. Simultaneous exposure to n-hexane and 2-butanone can cause severe neurotoxicity (Todd and Melia, 2019). However, the concentration levels of the hazardous chemicals (VOCs) detected were very low, nearly 100–1000 times less than the recommended exposure limit set by NIOSH. Nevertheless, the guidelines related to safe mask wearing are required as these 15 VOCs are harmful substances.

Table 5
Concentrations of hazardous VOCs emitted from mask samples.

Order	Functional group	Compound name	CAS number	Formula	Molecular weight (g mol ⁻¹)	NIOSH REL ^a (mg m ⁻³)	Concentration (µg m ⁻³)													
							A1	A2	A3	B1	B2	B3	C1	C2	D1	D2	E1	E2	E3	E4
1	Alcohol, Ether	1-Methoxy-2-propanol	107-98-2	C ₄ H ₁₀ O ₂	90	360	NA ^b	32.0	NA	2.43	28.7	632	NA	4.26	NA	2.52	2.14	7.82	2.40	NA
2	Amide	Dimethylformamide (DMF)	68-12-2	C ₃ H ₇ NO	73	30	NA	NA	NA	NA	208	NA	NA	NA	NA	33.7	NA	139	NA	NA
3	Amide	N,N-Dimethylacetamide (DMAc)	127-19-5	C ₄ H ₉ NO	87	35	24.4	116	8.08	1114	417	273	8.44	NA	NA	6.99	NA	NA	NA	NA
4	Aromatic	Toluene	108-88-3	C ₇ H ₈	92	375	7.45	155	6.42	123	104	75.2	4.87	4.21	5.59	8.32	13.1	22.5	17.5	17.3
5	Aromatic	Ethylbenzene	100-41-4	C ₈ H ₁₀	106	435	1.61	27.0	1.19	8.33	4.57	5.09	1.08	1.51	0.96	2.66	3.78	3.77	3.83	2.74
6	Aromatic	p-Xylene	106-42-3	C ₈ H ₁₀	106	435	1.26	16.1	NA	5.36	3.56	25.5	NA	0.98	NA	0.85	1.48	2.50	1.22	1.57
7	Aromatic	m-Xylene	108-38-3	C ₈ H ₁₀	106	435	1.38	41.6	1.18	8.28	4.44	5.78	1.15	1.16	1.04	1.93	2.19	3.15	3.81	3.28
8	Aromatic	o-Xylene	95-47-6	C ₈ H ₁₀	106	435	0.47	50.1	NA	9.85	2.76	13.8	NA	1.61	NA	0.67	1.35	2.01	2.27	NA
9	Aromatic	1,3,5-Trimethylbenzene	108-67-8	C ₉ H ₁₂	120	125	NA	2.52	NA	3.29	1.87	16.5	0.93	NA	NA	1.24	1.36	NA	NA	1.07
10	Carboxyl	Acetic acid	64-19-7	C ₂ H ₄ O ₂	60	25	80.9	NA	NA	NA	NA	NA	46.6	NA	97.6	199	77.8	153	626	65.6
11	Cyanide	Acetonitrile	75-05-8	C ₂ H ₃ N	41	34	16.8	43.9	81.0	44.2	17.2	87.3	19.4	25.9	22.5	88.3	68.1	20.4	52.3	10.5
12	Ester	Ethyl acetate	141-78-6	C ₄ H ₈ O ₂	88	1400	1.37	831	4.92	1065	337	754	5.22	13.8	1.46	2.86	11.6	383	194	6.14
13	HC	n-Hexane	110-54-3	C ₆ H ₁₄	86	180	NA	3.43	NA	668	109	26.0	NA	NA	NA	NA	NA	0.80	1.29	1.79
14	HC	Cyclohexane	110-82-7	C ₆ H ₁₂	84	1050	NA	6.49	NA	7.10	23.9	NA	NA	0.85	NA	NA	NA	NA	NA	NA
15	Ketone	2-Butanone	78-93-3	C ₄ H ₈ O	72	590	6.72	14.8	2.54	20.6	17.7	443	3.29	2.53	2.05	3.88	4.36	26.0	5.34	5.42

^a The guidelines of recommended exposure limit (REL) for up to 8 hr workday were established by the agency of United States' National Institute for Occupational Safety & Health (NIOSH).

^b NA: not available. The compounds with the concentration below $0.1 \mu\text{g m}^{-3}$ or the library similarity below 80% by mass spectrometry (MS).

3.2. Exp 2: TVOC mass flow rates depending on mask wearing time

The VOCs adsorbed on the surface of the mask are easily volatilized into the air by breathing or wind. Accordingly, the amount of VOCs emitted from masks can vary depending on the elapsed time after the

mask is opened. In Exp 2, the mass flow rate and concentrations of the VOCs generated from the sample B masks were assessed at different times. The mass flow rate and concentrations of each VOC were calculated as TVOC and are presented in Fig. 2. Sample B, a KF94 mask, was selected as the target mask for evaluation in Exp 2 because it generated

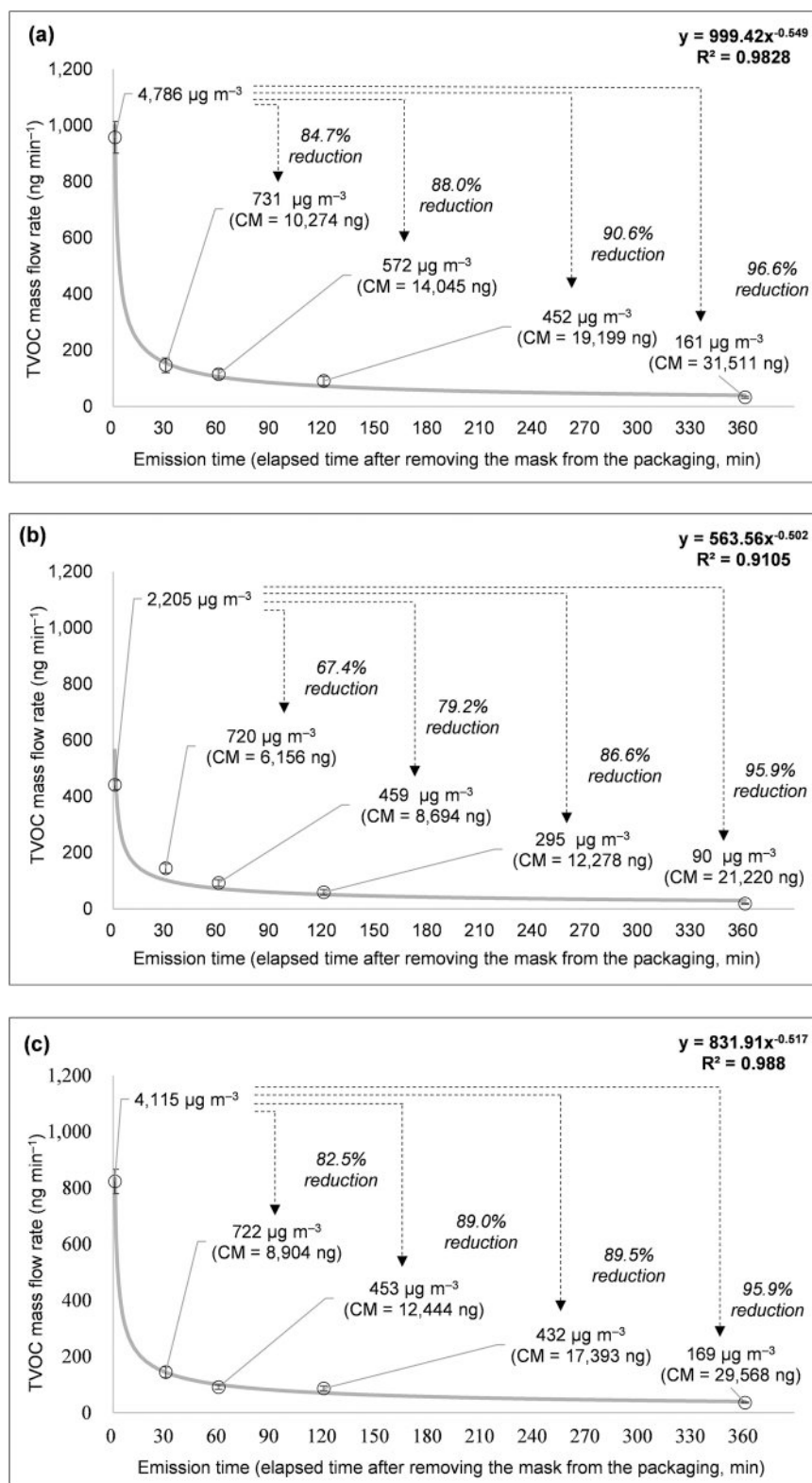


Fig. 2. Mass flow rates (ng m^{-3}) of VOCs emitted from KF94 mask samples at various times after each mask was removed from its packaging: (a) B1, (b) B2, and (c) B3.

the highest concentration of VOCs among all masks evaluated in Exp 1, and is a globally recommended mask for the prevention of COVID-19.

The TVOC mass flow rate of mask sample B ($n = 3 \times 3$) was a mean $740 \pm 268 \text{ ng min}^{-1}$ immediately upon package opening. However, 30 min after opening, the TVOC mass flow rate of the sample B had decreased by $78.2 \pm 9.44\%$ to $145 \pm 1.22 \text{ ng min}^{-1}$. After 6 h, the mass flow rate of the TVOC was $28.7 \pm 9.35 \text{ ng min}^{-1}$, and most of the VOCs had been volatilized from the masks. The mass flow rate of the TVOC generated from the mask decreased exponentially as the elapsed time increased and the correlation was high enough to show a mean R^2 value of 0.9604 ± 0.0433 . As we observed, as soon as the mask packaging was opened, the mass flow rate of the VOCs generated from the mask rapidly

declined. All experiments in Exp 2 were repeated three times to assess reproducibility in terms of RSD (%). Exp 2 showed good reproducibility with RSD below 20% (mean $19.1 \pm 8.15\%$).

Wearing a mask immediately upon opening the packaging could result in exposure to a TVOC concentration of $3702 \pm 1339 \mu\text{g m}^{-3}$. However, exposure can be significantly reduced if a mask is opened and left to sit for at least 30 min. With mask sample B1, for example, if worn for 6 h (immediately after opening the product), the accumulated TVOC mass that can be inhaled is $31.5 \mu\text{g}$. If the mask sample is left for 1 h after opening, the cumulative mass of inhalable TVOC is significantly reduced to $19.7 \mu\text{g}$ when worn for 6 h. When a new mask product every hour over a 6 h period, the total exposed TVOC mass is quite high at $84.3 \mu\text{g}$.

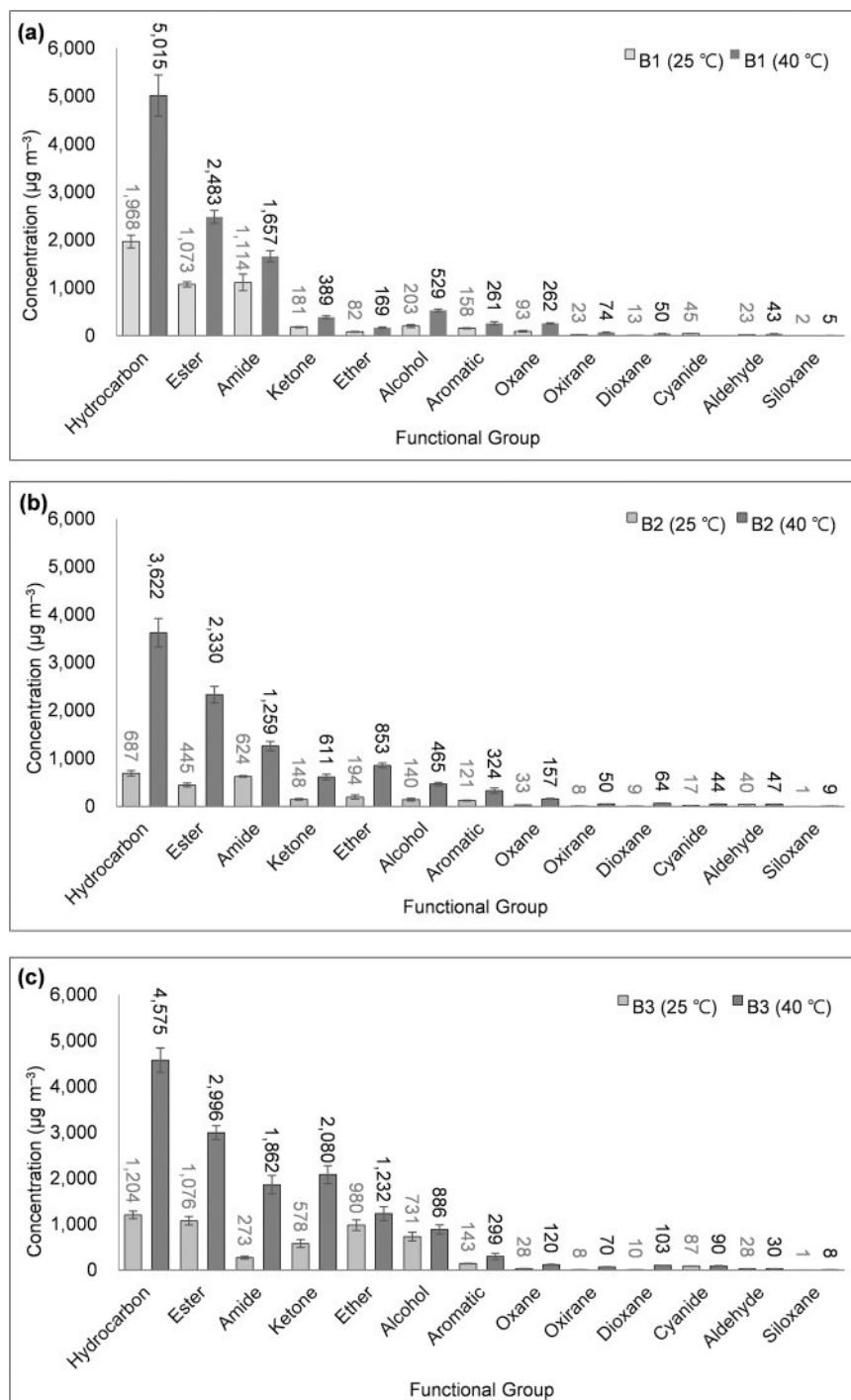


Fig. 3. VOC concentrations ($\mu\text{g m}^{-3}$) at different mask temperatures: (a) B1, (b) B2, and (c) B3.

3.3. Exp 3: differences in VOCs concentration of mask based on changes to temperature

As masks are worn close to the face, temperature may increase beyond the ambient temperature due to body heat. Sunlight and ambient temperature also act as a factor in increasing the temperature of the mask. When the temperature of the mask rises, the types and concentrations of the VOCs emitted from the mask can rise with it (Gravina et al., 2021; Kerkeling et al., 2021). In Exp 3, the changes in the concentration of VOCs emitted from each mask were assessed under different temperature conditions (room temperature: 25 °C and high temperature: 40 °C) using sample B. Due to the influence of weather conditions (i.e., temperature, sunlight intensity, humidity, etc.) and mask characteristics (i.e., color), the temperature of the mask may increase to the level of body temperature or beyond (Pal et al., 2021; Zhong et al., 2020). Therefore, we conducted the VOC emission experiment at a temperature of 40 °C, which is slightly higher than the body temperature, to account for these factors.

TVOC emission concentrations from sample B were $4808 \pm 489 \mu\text{g m}^{-3}$ (B1), $2242 \pm 144 \mu\text{g m}^{-3}$ (B2), and $4140 \pm 376 \mu\text{g m}^{-3}$ (B3) at 25 °C. When the temperature reached 40 °C, TVOC concentrations in mask sample B were recorded to be $10,521 \pm 1134 \mu\text{g m}^{-3}$ (B1), $8833 \pm 955 \mu\text{g m}^{-3}$ (B2), and $13,029 \pm 42.7 \mu\text{g m}^{-3}$ (B3), representing an increase of 119–299% over the concentrations recorded at 25 °C. The difference in TVOC concentrations among mask manufacturers (B1, B2, and B3) decreased as the temperature rose to 40 °C (RSD = 36.2% (25 °C) and 19.7% (40 °C)). We hypothesize that this is the result of active volatilization of the VOCs lightly adsorbed on the masks as mask temperature increased (Chang et al., 2022; Li et al., 2021).

Fig. 3 showed the emission concentrations of VOCs from the mask B samples under different mask temperature conditions by summing them by functional groups. As the mask temperature increased, VOC concentrations across all functional groups rose. Hydrocarbons, of which the highest concentrations were recorded at 25 °C, showed the highest concentration among all functional groups even at 40 °C ($1286 \pm 644 \mu\text{g m}^{-3}$ (25 °C) and $4404 \pm 712 \mu\text{g m}^{-3}$ (40 °C)). The rise in the concentration of hydrocarbons as mask temperature increased was also the largest at $287 \pm 136\%$. An increase in concentrations of ester, amide, and ketone was also observed ($244 \pm 157\%$ (ester), $244 \pm 294\%$ (amide), and $229 \pm 102\%$ (ketone)). The mean concentrations of the six functional groups (oxane, oxirane, dioxane, cyanide, aldehyde, and siloxane), which were recorded at relatively low concentrations at 25 °C (below $100 \mu\text{g m}^{-3}$), increased more than two-fold once mask temperature reached 40 °C ($23.7 \pm 18.6 \mu\text{g m}^{-3}$ (25 °C) and $68.4 \pm 59.0 \mu\text{g m}^{-3}$ (40 °C)). Concentrations of oxidants such as oxane, oxirane, and dioxane increased significantly ($25.0 \pm 22.8 \mu\text{g m}^{-3}$ (25 °C) and $106 \pm 64.3 \mu\text{g m}^{-3}$ (40 °C)). The reproducibility of these concentration assessments was fairly good with RSD values below 20% ($15.8 \pm 9.56\%$ (25 °C) and $12.3 \pm 8.14\%$ (40 °C)).

Exp 3 experimentally showed that as the temperature of the mask product grows, the concentrations of VOCs that mask wearers are exposed to increases. The exact exposure concentration varies depending on VOC types. Accordingly, masks should be used after accounting for factors, like weather conditions, that affect mask temperature.

3.4. Mask usage recommendations and study limitations

Since 2020, countries have issued recommendations for preventing the spread of COVID-19 through wearing masks (Dzisi and Dei, 2020; Rab et al., 2020). When social distancing is difficult, wearing a mask is recommended or mandatory, and it should cover both the nose and mouth tightly. Using masks designed to filter out at least 95% of particles, including viruses and bacteria (i.e., KF94, N95, FFP2), is highly recommended (Han et al., 2021; Knobloch et al., 2023; Ohara et al., 2022). In the United States, the Centers for Disease Control and Prevention (CDC) recommends using two or more layers of cotton masks or

N95 masks. Germany recommends using FFP2 or N95 masks, while Korea recommends using KF94 masks. Guidelines for handling harmful VOCs from masks are lacking. According to this study, it is recommended to open a mask made of a material such as KF94 for at least 30 min before wearing it and leave it at room temperature to remove harmful VOCs.

In this study, we evaluated VOC generation concentration based on mask type, wearing time, and mask temperature. Although various masks were evaluated, only the KF94 mask was focused on for evaluating VOC generation based on wearing time and temperature. Future studies should evaluate VOC generation on masks other than KF94 due to the rapidly increasing number of mask types (De Sio et al., 2020; Dharmaraj et al., 2021; Gereffi, 2020), and a sufficient number of mask samples should be evaluated to ensure statistically significant results. Additionally, since humidity can affect the concentration of water-soluble VOCs, the effect of humidity needs to be investigated (Markowicz and Larsson, 2015; Wolkoff, 1998).

4. Conclusions

As the number of problems that require mask wearing (including air pollution and COVID-19) grows, masks are increasingly important. Now that masks are all but required, the harmful chemicals that can be released from them must be evaluated. In this study, VOCs generated from various types of masks, including commonly used KF94 disposable masks, were assessed. The types and concentrations of VOCs that humans are likely to be exposed to from these masks under various conditions (i.e., emission time, temperature, and mask types) were calculated and compared. This study demonstrated that disposable masks (KF94) released higher concentrations of TVOCs in comparison to cotton masks, with values of $3730 \pm 1331 \mu\text{g m}^{-3}$ for KF94 and $268 \pm 51.6 \mu\text{g m}^{-3}$ for cotton masks. The concentrations of TVOCs in KF94 masks are high enough to pose a concern based on indoor air quality guidelines established by the German Federal Environment Agency. However, when KF94 masks were opened and left undisturbed for 30 min at room temperature, TVOC concentrations significantly decreased to $724 \pm 5.86 \mu\text{g m}^{-3}$ (a $78.2 \pm 9.45\%$ reduction from levels measured immediately upon opening). It is clear that particular attention must be paid to the VOCs associated with the use of KF94 masks their effects on human health. Based on our findings, we suggest that prior to wearing a KF94 mask, each product should be opened and not worn for at least 30 min, thereby reducing TVOC concentrations to levels that will not impair human health.

CRediT authorship contribution statement

Hajoo Ryu: Formal analysis, Investigation, Data curation, Writing – original draft. **Yong-Hyun Kim:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision.

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

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2023.114915.

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