Evaluation of hydrogen peroxide and ozone residue levels on N95 masks following chemical decontamination

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S U M M A R Y

Background: Hydrogen peroxide and ozone have been used as chemical decontamination agents for N95 masks during supply shortages. If left behind on the masks, the residues of both chemicals represent a potential health hazard by skin contact and respiratory exposure.
Aim: Characterization of hydrogen peroxide and ozone residues on mask surfaces after chemical decontamination.
Methods: Various N95 masks were decontaminated using two commercial systems employing either aerosol spray or vaporization of hydrogen peroxide in the presence of ozone. Following the decontamination, the masks were aired out to eliminate moisture and potential chemical residues. The residual hydrogen peroxide and ozone were monitored in the gas phase above the mask surface, and hydrogen peroxide residue directly on mask surfaces using a colorimetric assay.
Findings: After decontamination, hydrogen peroxide and ozone were detectable in the gas phase in the vicinity of masks even after 5 h of aeration. Hydrogen peroxide was also detected on all studied masks, and levels up to 56 mg per mask were observed after 0.5 h of aeration. All residues gradually decreased with aeration, likely due to decomposition and vaporization.
Conclusion: Hydrogen peroxide and ozone were present on N95 masks after decontamination. With appropriate aeration, the gaseous residue levels in the vicinity of the masks decreased to permissible levels as defined by the US Occupational Safety and Health Administration. Reliable assays to monitor these residues are necessary to ensure the safety of the mask users.

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Introduction

The coronavirus pandemic has amplified the demand for medical personal protective equipment (PPE), particularly N95 facepiece respirators (hereafter called N95 masks). This has resulted in a surge of interest in the reprocessing of these

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respirators. N95 masks are made using melt-blown or electro-spun polypropylene or by combining these materials, giving specific properties such as filtration mechanism, fibre diameter, surface area, and breathability. N95 masks are designed for single use [1]. However, if N95 masks are decontaminated for reuse, it should be ensured that reprocessing achieves: (i) maximum microbial reduction; (ii) retention of respirator filtration efficiency and fit; and (iii) no harmful chemical residues.

Ethylene oxide and hydrogen peroxide (H_2O_2) are used for sanitization of medical devices and N95 masks. Also ozone (O_3), ethanol, isopropanol, chlorine dioxides and quaternary ammonium compounds have been investigated for N95 mask decontamination with varying degrees of success [2−5].

Dilute hydrogen peroxide is used as an antiseptic and bleaching solution in cosmetic and household product formulations. Higher concentrations are used for the sterilization of medical devices. Hydrogen peroxide is delivered in the form of gas, plasma, aerosol, or liquid. Gaseous and plasma-generated hydrogen peroxide is widely applied for medical device decontamination and is preferable to liquid dispersion, due to reduced moisture load and consequently shorter turn-around times [6].

Ozone is produced from air or pure oxygen and generated on site by the ozone generator, by UV light, or corona discharge. Ozone is utilized in indoor air treatment. The use of ozone for disinfection of N95 masks has been investigated and found superior due to its high penetration efficiency and no hazardous residue [7,8].

The residues of hydrogen peroxide and ozone on N95 masks following chemical decontamination can potentially pose an inhalation and/or dermal exposure risk. As N95 masks are single use, no regulated limits for residual hydrogen peroxide and ozone on masks have been established. Additionally, there are no standardized, widely accepted methodologies for the determination of these chemicals. There is very limited information available on residues and potential exposure associated with mask-wearing and masks after decontamination [2]. Most of the studies on reusability have focused only on physical effects of the decontaminated process (filtration efficiency and efficacy) and largely ignoring the potential chemical hazards [3,9−11].

Therefore, the current study aimed to examine the residue levels on a variety of masks in a number of conditions. An 8 h total weight average (TWA) permissible exposure limit of the US Occupational Safety and Health Administration (OSHA) of ozone and hydrogen peroxide was selected as a benchmark for the gas released from masks in this study to evaluate adverse health effects to the users [12]. There are no permissible limits for hydrogen peroxide on N95 masks; consequently, the residue concentrations were benchmarked against untreated N95 masks and against the hydrogen peroxide levels used in cosmetics and household applications.

Methods

N95 mask samples

Six types of N95 mask were selected for this study (mask A is a surgical mask; the others are particulate and airborne protection masks) and are listed in Table I. Layers of the mask

Table I
N95 masks used in this study

Label	Brand model	NIOSH TC approval number	Shape	Manufacturer	Mask detail
A	3M 1860	TC 84A-0006	Cupped type	3M Company, USA	Total weight of 10.7−12.4 g, soft texture, four layers (green colour at the outer layer and white in all other layers), with an aluminium nose clip outside and grey sponge nose foam inside the mask, and fitting with white elastic bands attached by metal staples (21% weight)
B	3M 8210	TC 84A-0007	Cupped type	3M Company, USA	Total weight of 9.0−9.5 g, soft texture, three layers (white colour), with a white plastic nose clip outside and grey sponge nose foam inside the mask, and fitting with yellow elastic bands (16% weight)
C	3M 9205	TC 84A-8590	Folded type	3M Company, USA	Total weight of 8.4−8.7 g, soft thin texture, four layers (white colour), with a plastic nose clip and grey sponge nose foam inside the mask, and fitting with blue elastic bands attached by metal staples (9% weight)
D	FT-N040	TC 84A-7861	Folded type	Suzhou Fangtial Industries Co. Ltd, China	Total weight of 7.2−8.6 g, soft thin texture, four layers (white colour), with a white plastic nose clip and fitting with white elastic bands (18% weight)
E	FT-N058	TC 84A-7863	Cupped type	Suzhou Fangtial Industries Co. Ltd, China	Total weight of 10.4−11.6 g, hard texture, four layers (white colour), with grey sponge nose foam inside the mask, and fitting with white elastic bands (15% weight)
F	Gerson 2130	TC 84A-4123	Cupped type	Louis M. Gerson Co., Inc., USA	Total weight of 9.9−10.5 g, hard texture, four layers (white colour), with grey sponge nose foam inside the mask, and fitting with yellow elastic bands (18% weight)

were separated for hydrogen peroxide distribution analysis and are shown in Supplementary Figure S1.

Decontamination process

The masks were decontaminated according to the condition prescribed by the equipment manufacturers. Two decontamination processes were compared as follows:

Process I. Aerosol spray system delivered three ingredients; a maximum of six masks were arranged by facing up on a tray and placed on a flat-top belt conveyor driven by a motor. The tray carrying six masks was driven to a closed chamber. The masks were exposed to UV-C, ozone (minimum 2 mg/L), and 3% hydrogen peroxide aerosol (generated from a spray nozzle) at a flow rate of 40 mL/min for 30—40 s at room temperature. Before exiting the chamber, an excess amount of ozone was removed via an activated carbon filter.

Process II. Dual chemical decontamination system; masks were loaded in a chamber following a pre-condition at a vacuum pressure of 1 torr for 10 min. A 50% hydrogen peroxide solution was injected into the chamber as a vapour form and continuously injected (40 mg/pulse/s) until a pressure of 19 torr (the difference between the actual chamber pressure of 20 torr and the initial vacuum of 1 torr) was reached. Later an excess amount of hydrogen peroxide was removed by adding ozone (2 mg/L) and left for 5 min (min) dwell time. The process was repeated for another cycle before evacuation and ventilation in a total of 90 min [13].

After decontamination, the masks were aerated at room temperature before the residue analysis. The time profiles of the residue concentrations were monitored in this study to determine optimal aeration time.

Measurement of gaseous hydrogen peroxide and ozone

Hydrogen peroxide gas was measured using a handheld detector X-am 5100 from Dräger (Lübeck, Germany). The detection range of the instrument was 0.1—20 parts per million (ppm) by volume with a precision of 14%. A hydrogen peroxide detector was calibrated by the manufacturer and calibrated in-house using 10 ppm sulfur dioxide gas.

Ozone was detected using Aeroqual Series 500 ozone detector from Aeroqual (Ackland, New Zealand). The instrument detection range was from 0.001 to 0.50 ppm with a precision of 8%. The detector was calibrated by the manufacturer. Gas-phase measurements were carried out by placing one mask in an 11 L closed chamber (Figure 1), equilibrated for 3 min; headspace concentrations were then read and reported as ppm. Before placing a new mask, the plastic chamber was flushed with nitrogen gas to remove all gas residues and reduce carryovers.

Measurement of hydrogen peroxide on N95 mask surfaces

Three masks were selected after decontamination and individually weighed. From each mask, a 2 cm $\times$ 2 cm piece was cut and weighed (Supplementary Figure S2). Stamped areas or areas marked with ink were avoided. The hydrogen peroxide was extracted from the samples with 10 mL of deionized water in a 50 mL polypropylene vial and hand-shaken (end over end) for 2 min (120—150 times) or using an end-over-end mechanical shaker (at speed 30 rpm for 5 min) at room temperature. Five millilitres of the extracted solution was reacted with 0.4 mL of
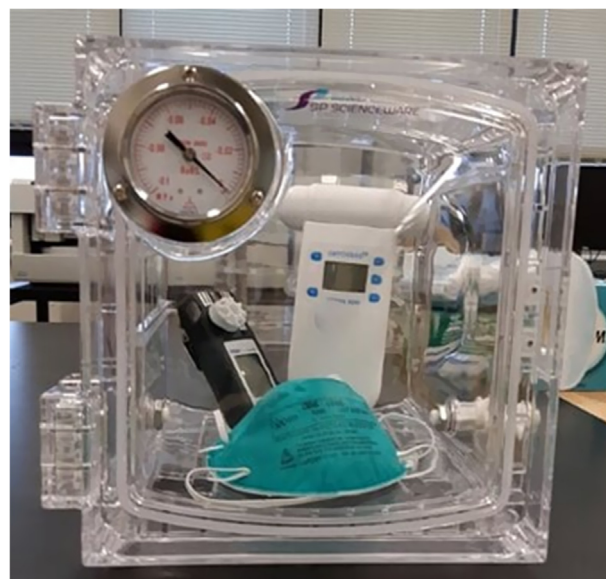

Figure 1. Measurement of hydrogen peroxide and ozone gas released from mask in a closed chamber using handheld detectors.

7.5% wt titanium oxysulphate in 2 mL of 25% wt sulfuric acid. All chemicals used are detailed in the Supplementary Appendix. The absorbance at a wavelength of 409 nm was chosen for quantification using a UV-visible spectrometer (Varian Easy 5000; Agilent, Santa Clara, CA, USA) [14]. The concentration of hydrogen peroxide (mmol/L) on the N95 masks from the extraction was obtained via a calibration graph of hydrogen peroxide standard solutions and reported as mg/mask (the calculation is explained in Supplementary Appendix: Data processing). Method validation was performed and reported in the Supplementary Appendix.

Results

Gas-phase detection of ozone from N95 masks

In the gas phase, in the vicinity of all mask types from all treatment approaches, ozone was detected as in Figure 2 (raw data are in Supplementary Tables S2 and S3). The levels ranged from 0.041 to 0.146 ppm after 3 h aeration and were well above background levels. Although similar residual ozone levels were observed in all masks by both decontamination processes, the aeration time profiles differed significantly (Figure 2). Masks treated with process II apparently required longer aeration times to observe measurable decrease. Masks treated with process I behaved as expected, and residual ozone levels fell with time.

Gas-phase detection of hydrogen peroxide from N95 masks

Hydrogen peroxide was detected in the gas phase in the vicinity of all masks with maximum concentrations of 2.4 ppm for process I and 14.5 ppm for process II after 0.5 h aeration (Figure 3; raw data are in Supplementary Tables S2 and S3). Higher levels of hydrogen peroxide were detected for N95 masks treated with decontamination process II compared to
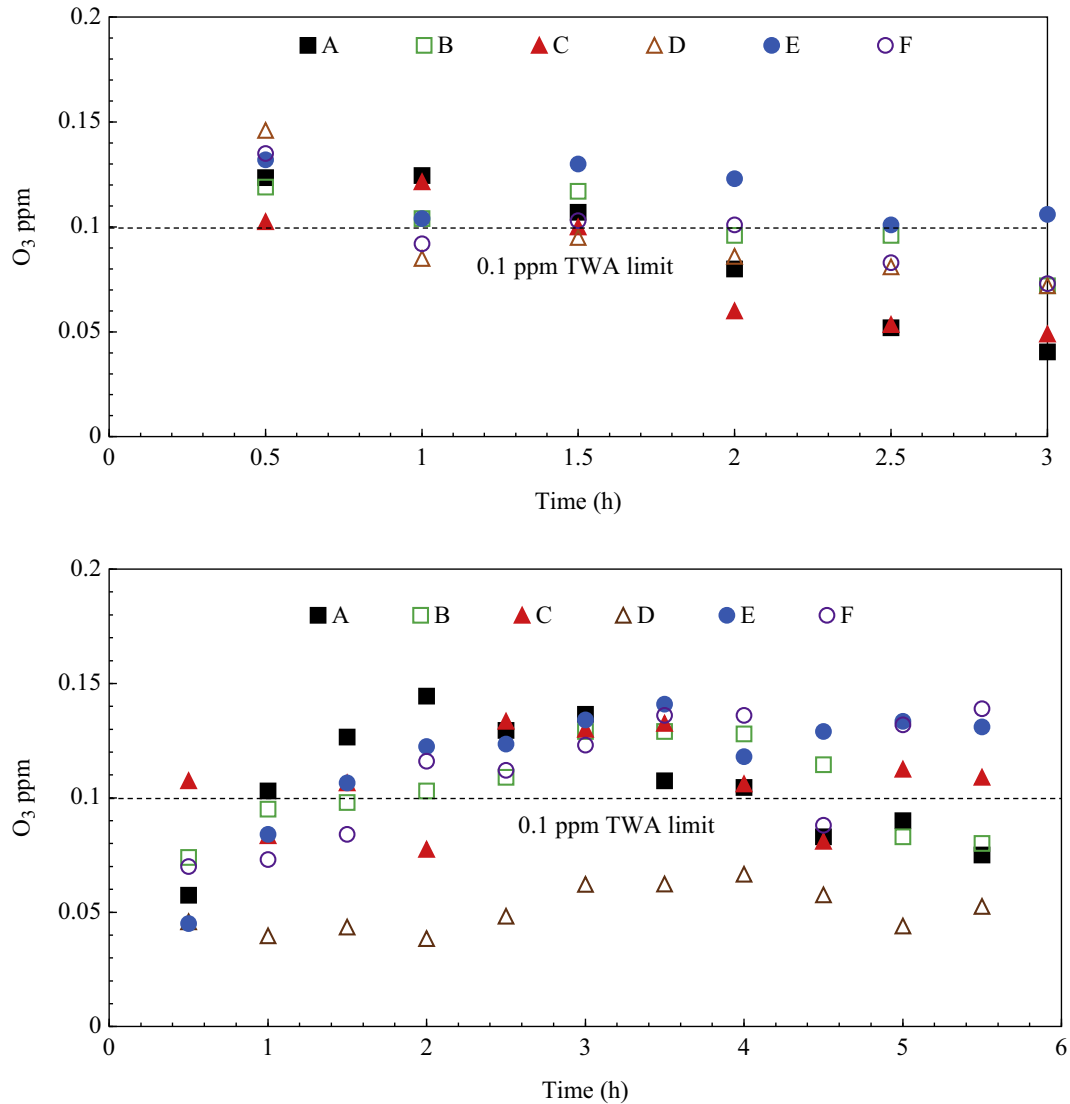
Figure 2. Ozone (ppm) released in a closed chamber from N95 masks (A to F) treated with process I (upper graph) and process II (lower graph), after aeration (h). TWA, total weight average.

process I. As expected, the concentration of hydrogen peroxide rapidly decreased with aeration time. After a 2 h aeration, the concentration was less than a permissible limit of 1 ppm TWA in all masks treated by process I. However, the concentration of hydrogen peroxide released from process II depended on the type of mask, and it could take 2–5 to be reduced to below the TWA limit.

Hydrogen peroxide extracted from N95 masks

The amount of residual hydrogen peroxide on the mask depends on the mask type and decontamination process (raw data in Supplementary Tables S4 and S5). The concentration of hydrogen peroxide (Figure 4) ranged from 1.01 to 4.84 mg/mask for process I and from 7.12 to 55.9 mg/mask for process II after 0.5 h aeration. Interestingly, only <0.2 mg was detected on mask C from both processes, and therefore mask C was not presented in Figure 4. A high amount of hydrogen peroxide was

observed in masks E and F, particularly from process II. The differences are likely due to the materials used for the mask construction and not to the shape of the masks (cupped vs folded type).

Distribution of hydrogen peroxide among the mask layers

N95 mask consists of multiple-layer filtering materials. After decontamination following 0.5 h aeration, layers of the masks were separated (Supplementary Figure S1) and analysed for hydrogen peroxide. It was found that a large proportion of hydrogen peroxide (33–50% from decontamination process I and 39–97% from process II) was apparently on a hard material of the inner layer of masks A and B and a middle layer (L2) of masks D, E, and F (Figure 5). Mask C was not presented because the amount of hydrogen peroxide was very low. Interestingly mask B has accumulated either on the inner or at the outer
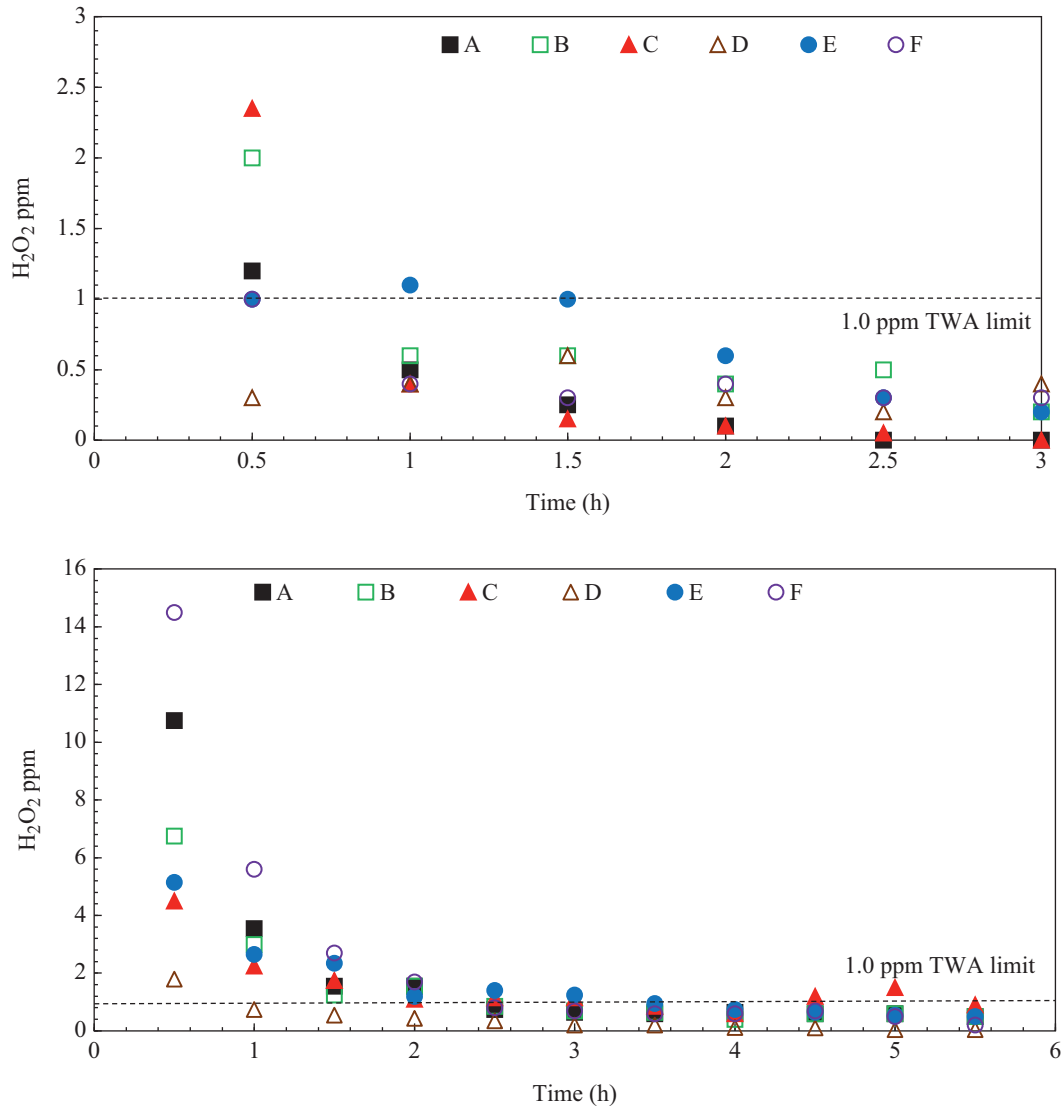
Figure 3. Hydrogen peroxide (ppm) released in a closed chamber from N95 masks (A to F) treated by process I and process II after aeration (h). TWA, total weight average.

layer depending on the decontamination process. The differences in the distribution among these layers likely explains the differences observed in aeration time profiles.

Discussion

It was observed that all masks after decontamination were visually dry. However, our study showed that residual hydrogen peroxide and ozone were detectable in the gas phase in the masks' vicinity.

Surprisingly, the elimination of residual ozone from both decontamination processes takes much longer compared to the hydrogen peroxide (Figures 2 and 3), which is counterintuitive considering a higher vapour pressure of ozone.

After the masks had been aerated for longer times, both residues in the 11 L chamber decreased to safe levels, compliant with TWA limits of 1.0 ppm for hydrogen peroxide and 0.1 ppm for ozone. It is not claimed that the 11 L exposure chamber study design provides data that are directly applicable to gas-exposure risk assessments, as the chamber volume is a small

fraction of that of inhaled air by a mask user during typical daily use. Nevertheless, it provides useful information on the residue elimination trends during mask processing.

Not surprisingly, hydrogen peroxide was detected after decontamination (Figure 4), particularly from process II on the mask materials. An exponential decrease of hydrogen peroxide concentration was observed during aeration at room temperature. The scatter plot of residual hydrogen peroxide vs aeration time with the correlation function is shown in Supplementary Figures S3 and S4. Using the exponential function, an 'aeration half-time' could be calculated for any residue levels. In our study, it takes 3 h by process I and 9 h by process II to reduce residual hydrogen peroxide to <0.5 mg/mask (Supplementary Tables S6 and S7).

Aeration of masks after decontamination was performed to reduce the hydrogen peroxide and ozone residue levels. The two decontamination processes showed similar ozone levels ranging from 0.04 ppm to 0.15 ppm. However, the results in this study were conducted in a confined space of 11 L. In real use, the mask is usually worn in an open area with ventilation that
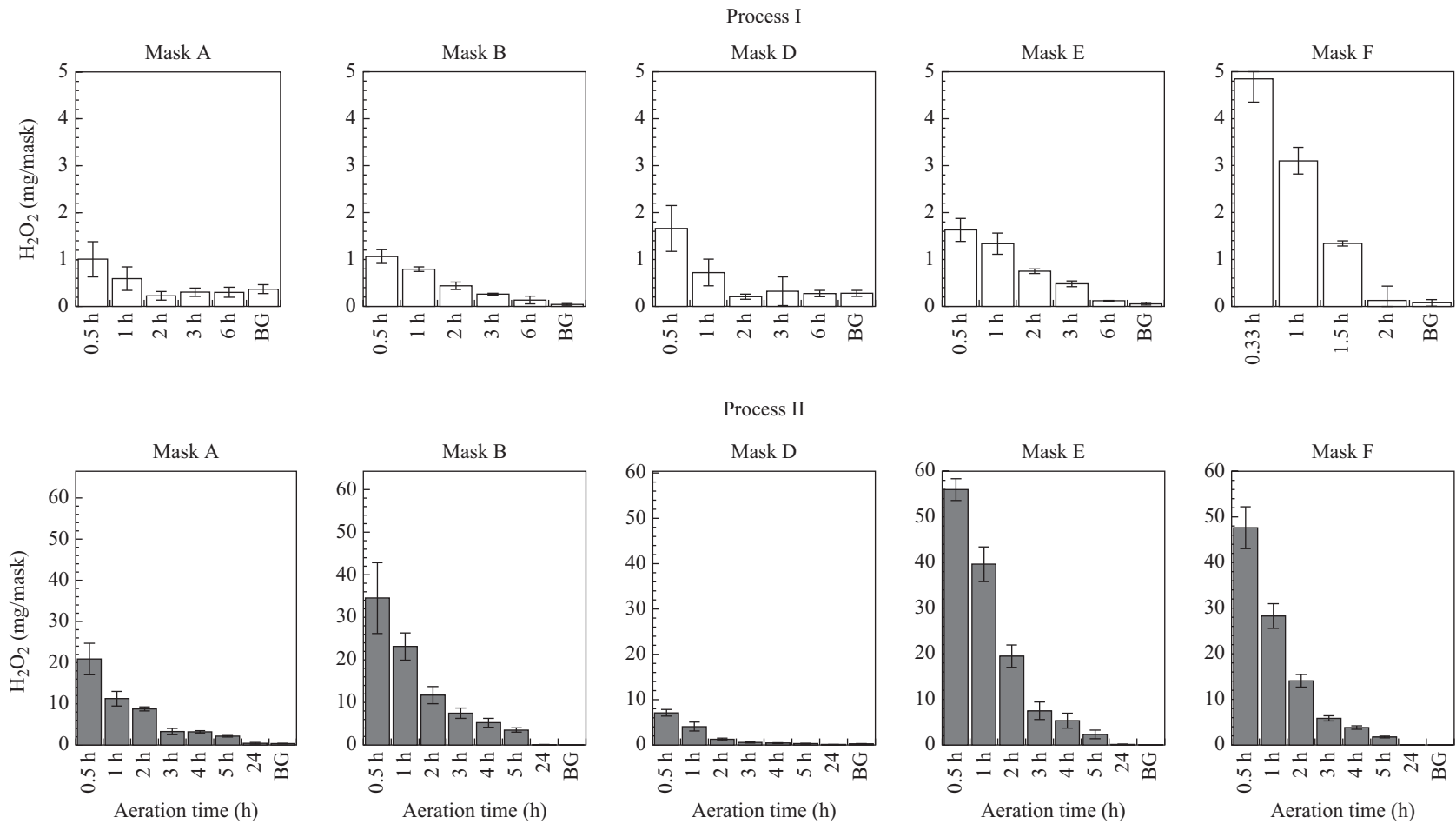
Figure 4. Residual hydrogen peroxide concentration and associated standard deviation (mg/mask) after aeration of N95 masks (A, B, D, E, and F) from decontamination process I and process II compared to untreated masks (BG).
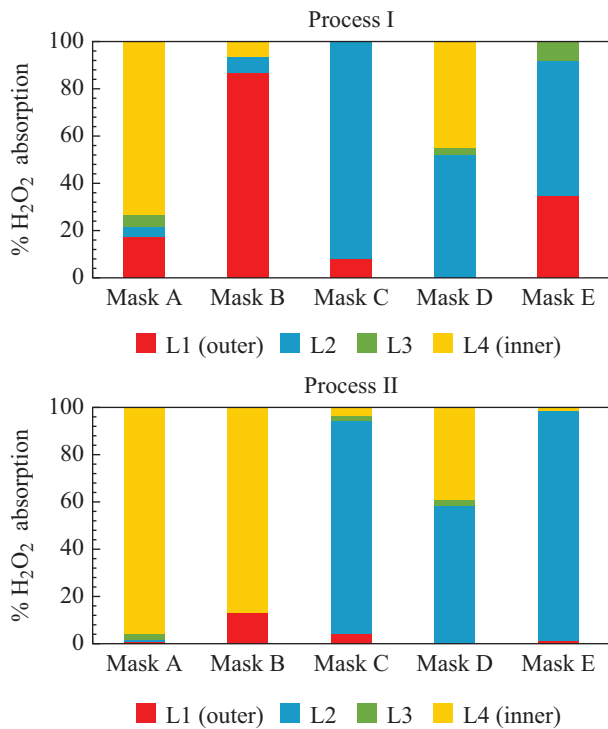
Figure 5. Residual hydrogen peroxide absorbed on individual layers of N95 masks from decontamination process I (upper row) and process II (lower row).

assists in dispersing hydrogen peroxide and ozone. Overall, ozone used in such concentrations is unlikely to pose a significant exposure risk to the masks' users after an appropriate aeration protocol is observed.

Higher amounts of hydrogen peroxide were detected in the gas phase and on the surface of N95 masks, so respiratory and skin contact risks should be considered. From the gas-phase experiments, it is evident that the hydrogen peroxide concentration in the 11 L confined space after 3 h of aeration falls below the TWA level of 1.0 ppm. However, at the same 3 h aeration, the amount of hydrogen peroxide residue on the mask surface was relatively high, particularly for the decontamination process II.

The results from this study demonstrated that hydrogen peroxide deposited on the mask was eliminated rapidly during aeration. Overall dermal exposure from properly aerated masks to hydrogen peroxide is likely minimal, especially at the 0.5 mg/mask levels targeted in this study, compared to other household hydrogen peroxide applications, which range from 720 mg per application for hair bleaching to 15 mg in mouth wash (see Supplementary Table S8) [15].

From this study, we conclude that: (i) monitoring of residues resulting from the decontamination process is important to ensure user safety; (ii) both ozone and hydrogen peroxide present as residues after decontamination; (iii) ozone and hydrogen peroxide levels in the gas phase above the mask are measurable but could be eliminated with proper post-decontamination aeration; (iv) hydrogen peroxide on the mask surfaces represent potential skin contact concern, but it could be eliminated with increasing aeration time. Higher air exchange rate, potential light exposure, and temperature increase might be ways of reducing the residual disinfectant levels in masks.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhin.2021.02.018.

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