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Article

Bleach Emissions Interact Substantially with Surgical and KN95 Mask Surfaces

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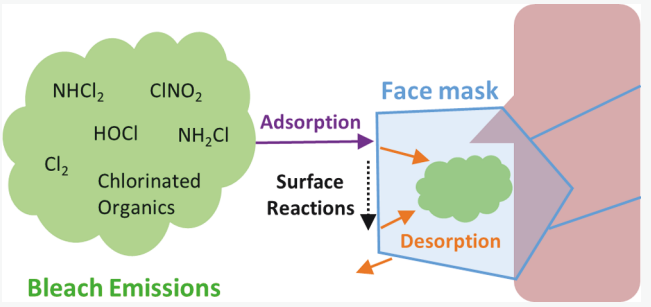
ABSTRACT: Mask wearing and bleach disinfectants became commonplace during the COVID-19 pandemic. Bleach generates toxic species including hypochlorous acid (HOCl), chlorine (Cl_2), and chloramines. Their reaction with organic species can generate additional toxic compounds. To understand interactions between masks and bleach disinfection, bleach was injected into a ventilated chamber containing a manikin with a breathing system and wearing a surgical or KN95 mask. Concentrations inside the chamber and behind the mask were measured by a chemical ionization mass spectrometer (CIMS) and a Vocus proton transfer reaction mass spectrometer (Vocus PTRMS). HOCl, Cl_2, and chloramines were observed during disinfection and concentrations inside the chamber are 2−20 times greater than those behind the mask, driven by losses to the mask surface. After bleach injection, many species decay more slowly behind the mask by a factor of 0.5−0.7 as they desorb or form on the mask. Mass transfer modeling confirms the transition of the mask from a sink during disinfection to a source persisting >4 h after disinfection. Humidifying the mask increases reactive formation of chloramines, likely related to uptake of ammonia and HOCl. These experiments indicate that masks are a source of chemical exposure after cleaning events occur.



KEYWORDS: *bleach, disinfection byproducts, indoor air, masks, mass spectrometry*

INTRODUCTION

The 2020 SARS-CoV-2 pandemic increased disinfectant usage to curb viral transmission.[1,2] Bleach (sodium hypochlorite solution) is a recommended disinfectant for SARS-CoV-2[3,4] and is utilized in public spaces, homes, offices, industrial plants, and medical facilities.[5−8] In the process of spraying surfaces or fogging air with bleach, sanitation workers are exposed to high concentrations of chlorine gas (Cl_2), hypochlorous acid (HOCl), trihalomethanes, and chloramines.[9−11] These species are detrimental to human health, and respiratory tract symptoms have been observed in cleaning workers, lifeguards, and household users after bleach cleaning.[12−14] Bleach emissions undergo further reactions in the gas phase, in aqueous films, and on human skin to form oxygenated and chlorinated organics that may cause further irritation and can be carcinogenic.[15−18]

Masks were also widely adopted to reduce virus spread, with the first recommendation by the Center for Disease Control and Prevention for masks outside of hospital environments in April 2020[19] and a stronger stance for universal masking in July 2020.[20,21] The prevalence of masks resulted in masked workers using bleach in healthcare, industrial, hospitality, and home settings. Previous indoor air studies have demonstrated the importance of surfaces in providing an adsorptive sink and reactive environment for bleach emissions,[22−24] and masks add an additional surface between the user and the environment. Bleach emissions including HOCl and chloramines show substantial uptake to surfaces and organic films and undergo further reaction to form additional Cl_2, nitryl chloride ($ClNO_2$), chloramines, or oxidized organics.[9,10] Scheme 1 summarizes the general reactive pathways that commonly occur in aqueous bleach surface films. Many relevant pathways including formation of Cl_2 are pH-dependent, while chloramine and nitryl chloride formation are dependent on ammonia uptake and nitrite salts, respectively.

The confluence of bleach disinfection and mask usage raises questions about best practices for workers during and after disinfection to reduce exposure to primary and secondary emissions from bleach disinfection and associated health impacts. To assess how masks affect the behavior of bleach disinfection emissions, bleach was injected into a ventilated

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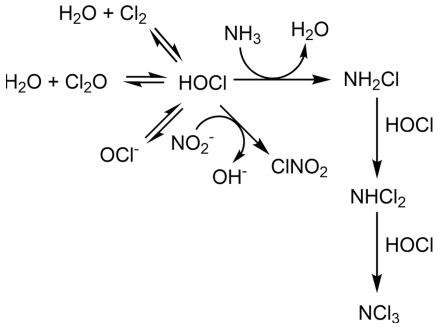
Scheme 1. Mechanism of Aqueous-Phase Bleach Chemistry Involving Chlorine Species



stainless steel chamber containing a thermal manikin inhaling through (1) surgical and (2) KN95 masks. The behavior of gas-phase species including Cl_2, HOCl, $ClNO_2$, chloramines, and oxidized organic compounds is explored across the mask surface and basic recommendations on mask usage during bleach disinfection are made.

MATERIALS AND METHODS

Chamber Measurements. Experiments were conducted in a 67 m^3 stainless steel chamber at the University of Texas at Austin JJ Pickle Research Center. The chamber contained two gypsum wall boards, six classroom tables, a bleach injection system, a plastic chair, a thermal manikin, and sampling lines. Prior to this study, bleach disinfection measurements with additional building materials including ceiling tiles and carpet were conducted. Variation in HOCl concentration among experimental replicates was higher than that observed from the addition of building materials, so a simple indoor environment (without carpet or ceiling tiles) was chosen for this mask impact study.

The chamber was ventilated with filtered laboratory air without recirculation at an air exchange rate (AER) of 1.9−2.4 h^{-1} typical of classroom ventilation rates.[25] While higher AER rates were recommended during the pandemic to reduce viral exposures, these recommendations often could not be implemented, and poor maintenance of HVAC retrofits regularly failed to deliver sufficient ventilation.[26] Thus, the AER used in this work is realistic for classrooms during the pandemic. AER was measured by injected CO_2 decay using a LI-7000 H_2O/CO_2 gas analyzer (LI-COR). The average chamber temperature and relative humidity (± 1 standard deviation) were 22.7 ± 1.7 °C and 41.3 ± 14.4%.

A thermal manikin was placed in the chamber in a sitting position and fitted with a fresh surgical (BYD Electronics) or KN95 (Kingfa) mask for each experiment. These mask types were used because they are two of the most commonly used types of masks. Differences in these masks including material, thickness, number of layers, and particle removal effectiveness are broad. However, we observed minimal differences in the behavior of disinfection emissions and byproducts across mask surfaces. The manikin simulated breathing by inhaling twelve 0.5 L breaths per minute. The manikin and chamber used here have been described in detail in other studies,[27,28] although we note that the manikin was not heated in this work. The manikin did not exhale during sampling to avoid dilution during measurements. However, realistic mask surfaces are not dry, and uptake of water vapor from human breath has been observed on masks, increasing the relative humidity in the air behind the mask.[29] Given the propensity of bleach emissions to partition to aqueous films, humidified mask experiments were conducted by simulating human exhalation from the manikin. Prior to bleach injection in humidified mask experiments, the manikin exhaled humid air (>95% RH) at 37 °C into the mask with 12 intermittent 0.5 L breaths per minute. The humidified mask contained ∼1 g additional water compared to a dry mask. Exhalation ended before bleach injection began in humidified mask experiments. Real human exhalation contains a wide range of additional components, including carbon dioxide, ammonia, and VOCs that may alter the mask surface pH and reactivity. While outside the scope of this study, additional work utilizing human breath analogues would be valuable.

The bleach solution was generated by diluting 500 mL of liquid consumer bleach with tap water to 0.1% NaOCl typical for household usage. The solution was injected into the chamber with an ultrasonic adiabatic humidifier fogger (Holmes) on the "High" or "Low" setting for ∼4 h. This injection method was used to inject bleach at a constant rate (0.25 and 0.15 L h^{-1} for the "High" and "Low" settings, respectively) and achieve stable concentrations in the chamber after 2−3 h. This injection method was chosen to facilitate assessment of transport across the mask surface in this study and avoid complexity from rapidly changing emissions in disinfectant mopping experiments. Stable HOCl and Cl_2 concentrations achieved by this injection method were similar to peak concentrations observed from bleach mopping and spraying as discussed later. HOCl and Cl_2 concentrations varied by up to 50% between replicate experiments, likely driven by differences in surface uptake characteristics and use of a commercial fogging device rather than a scientifically calibrated injection system. Mask behavior and trends discussed later in this manuscript are consistent, independent of experimental variability in disinfectant injection and concentrations.

Sampling inlets to instruments were placed throughout the chamber including a position 20 cm in front of the manikin and 80 cm from the ground (referred to as the "inside chamber" position) and a position within the manikin's mouth (referred to as the "behind mask" position). The Teflon sampling line in the "behind mask" position originated just behind the mask to minimize the interaction with manikin surfaces inside the mouth cavity. Room intake air and outlet air were also sampled. Sampling positions were switched every 5 min; thus each of the 4−6 positions was sampled every 20−30 min (for a 5 min period). Comparison between "inside chamber" and "behind mask" positions provides insight into transport across the mask surface.

Gas-phase concentrations were measured with an iodide mode chemical ionization mass spectrometer (I-CIMS) and a Vocus 2R proton transfer reaction mass spectrometer (Vocus PTRMS). These two instruments detect a wide range of organic and inorganic gas-phase species and have been described previously in the literature.[30,31] In this study, I^- CIMS was calibrated for chlorine by standard Cl_2 injection (100.3 ppm Cl_2 in N_2, Airgas) to a 10 m^3 Teflon chamber and multipoint calibration was performed at 10, 20, 30, and 40 ppb Cl_2. Nitryl chloride was calibrated by standard injection after being formed by passing Cl_2 in nitrogen over an aqueous slurry of sodium nitrite as previously discussed in the literature.[32] HOCl was calibrated by passing air bubbled through a sodium hypochlorite solution (0.1% NaOCl, Sigma-Aldrich) over an

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acidified slurry of sodium chloride in hydrochloric acid to convert HOCl to Cl_2 as previously described.[10,33,34] Measured CIMS sensitivities for Cl_2, $ClNO_2$, and HOCl were 909, 61, and 11 cps ppb^{-1}, respectively. All other CIMS signals are normalized to the I^- reagent ion signal at a constant 10^5 ions per second, meaning signal time series were divided by the measured I^- time series and multiplied by 10^5. High-resolution peak fitting of the mass spectra was conducted in the Tofware data analysis package. The Vocus PTRMS was calibrated daily using a standard gas mixture and species not within the gas mixture were calibrated according to their proton transfer reaction rate.[35] Peak fitting for Vocus data was conducted using the automated PTRwid package.[36] Additional peak assignment, particularly for chlorinated species, was conducted afterward based on best available fit to exact mass to charge ratios and confirmed in Tofware. A list of experiments analyzed and available data are shown in Table 1.

Table 1. List of Experiments and Data Availability

#	mask	humidified mask?	injection setting	AER (h^{-1})	instrumentation
1	surgical	no	high	2.3	CIMS
2	surgical	no	low	1.9	CIMS, Vocus
3	surgical	yes	high	2.4	CIMS, Vocus
4	KN95	no	high	2.3	Vocus
5	KN95	yes	high	2.3	Vocus
6	KN95	yes	high	2.3	Vocus

Mass Transport Modeling and Net Source−Sink Estimation. For some species, the mask appeared to operate as a sink, while for others it was a source. To assess the mask as a source or sink, a simple mass transfer model was developed (Figure 1). In this model, the chamber and mask were treated

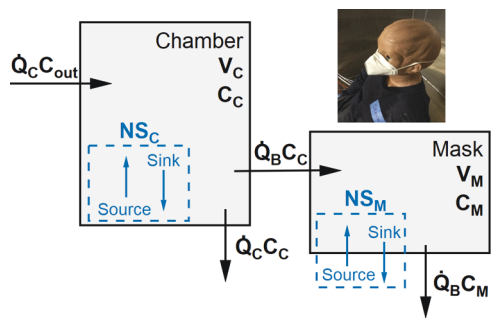

Figure 1. Diagram of mass transfer model. Q_C is the flow rate through the chamber. Q_B is the breathing rate of the manikin. C_C and C_M refer to chamber and mask concentrations, while NS_C and NS_M refer to the net source and sink present in the chamber and mask. V_C is known and V_M is estimated. Manikin wearing KN95 mask is shown in the upper right.

as two separate, internally mixed volumes (V_C and V_M) and the only transport between the volumes was across the mask barrier by the manikin's inhalation at a rate of 6 L min^{-1} ($\dot{Q}_B$). Ventilation through the chamber was represented ($\dot{Q}_C$) and concentrations outside the chamber (C_{out}), inside the chamber (C_C), and inside the mask volume (C_M) were accounted for. Any variation not associated with ventilation through the chamber or mask was ascribed to an additional net source or sink term in the chamber (NS_C) and in the mask (NS_M). These net source/sink terms are positive for a source and negative for a sink. The model mass balance in the chamber and mask volumes are shown in eqs 1 and 2.

$$V_C \frac{dC_C}{dt} = NS_C + \dot{Q}_C C_{out} - \dot{Q}_C C_C - \dot{Q}_B C_C \quad (1)$$

$$V_M \frac{dC_M}{dt} = NS_M + \dot{Q}_B C_C - \dot{Q}_B C_M \quad (2)$$

Equations were rearranged and evaluated numerically based on the measured C_C concentrations to calculate NS_C. With measured C_C and C_M concentrations, estimates for the net mask source or sink (NS_M) were calculated. The final equations used are shown in eqs 3 and 4. C_{out} was assumed to be zero for all pollutants in this analysis. The mask volume represents the mask "box" where emissions across the mask are diluted. A mask volume of 6 L is assumed based on typical healthy adult total lung volume.[37] While other choices of mask volume were appropriate or possible, changes in the mask volume impacted magnitudes of the calculated source or sink variables, not the qualitative time-varying behavior.

$$NS_C = V_C \frac{\Delta C_C}{\Delta t} - \dot{Q}_C C_{out} + \dot{Q}_C C_C + \dot{Q}_B C_C \quad (3)$$

$$NS_M = V_M \frac{\Delta C_M}{\Delta t} + \dot{Q}_B C_M - \dot{Q}_B C_C \quad (4)$$

RESULTS AND DISCUSSION

Bleach Emissions Include Toxic and Reactive Species. A wide variety of emissions were observed from bleach, including hypochlorous acid (HOCl), molecular chlorine (Cl_2), and nitryl chloride ($ClNO_2$) (Figure 2A). Stable concentrations were achieved after about 2 h of injection. Peak HOCl concentrations inside the chamber reached 800 ppb, while Cl_2 (80 ppb) and $ClNO_2$ (70 ppb) were much lower, consistent with previous bleach-cleaning observations.[9,10,38] Emission of trichloramine or nitrogen trichloride (NCl_3) were also observed by CIMS measurements, while monochloramine (NH_2Cl) and dichloramine ($NHCl_2$) emissions were measured by Vocus. Peak monochloramine and dichloramine concentrations ranged from 1 to 2 ppb, similar to previous bleach-cleaning observations and peak monochloramine concentrations near a recreational facility.[10,39] Chloroform ($CHCl_3$) was observed by the Vocus, with concentrations from 0.5 to 0.9 ppb during injection similar to bleach mopping observations in Mattila et al.[11] Many of these species, including Cl_2, NCl_3, and chloroform, have induced acute and potentially chronic respiratory symptoms, while mono- and dichloramines form carcinogenic byproducts in water disinfection.[13,18,40]

The Vocus PTRMS captured the complexity of bleach emissions (Figure 3). Due to hundreds of species measured and identified, and the lack of structural information from the Vocus, we have grouped the identified species by chemical families including organics containing oxygen, chlorine, and nitrogen ($C_XH_YO_ZN_{1-2}Cl_{1-2}$) and organics containing chlorine and nitrogen but no oxygen ($C_XH_YN_{1-2}Cl_{1-2}$). These groups of species were observed in all experiments and may be related to HOCl and chloramine reactions with amines, aldehydes, and ketones. HOCl chlorinates amines in solution and at the air−water interface.[41,42] Chloramines can initiate addition to aldehydic C=O double bonds as in cyanogen-forming reactions with formaldehyde.[43] The two most abundant species containing chlorine and nitrogen were C_2H_4ONCl

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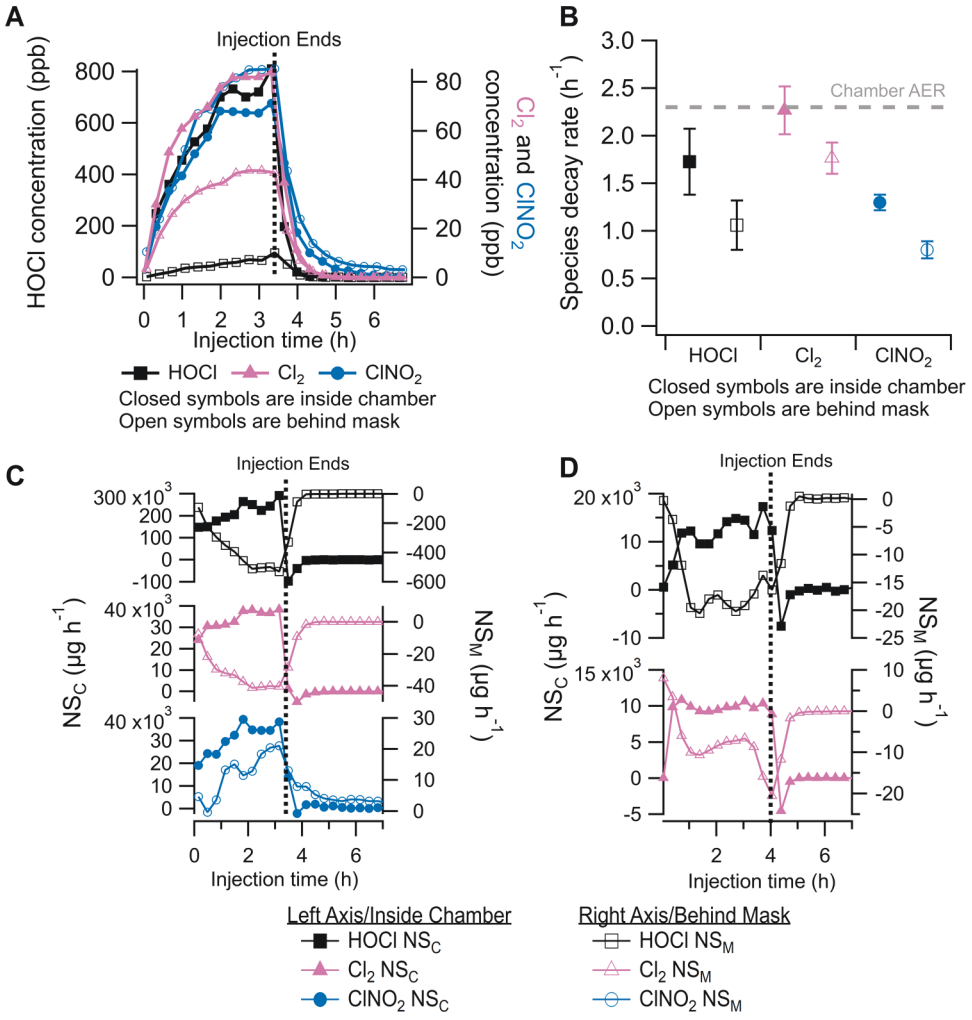

Figure 2. (A) Concentrations, (B) decay rates, and (C) mass transfer modeling of net sources and sinks for selected inorganic chlorinated species emitted from bleach inside the chamber and behind the mask during experiment 1. (B) Decay rate error bars indicate ±1 standard deviation in the linear least-squares regression fit. (C, D) NS_C refers to the source/sink inside the chamber and is represented by closed symbols read on the left axis. NS_M refers to the source/sink behind the mask and is represented by open symbols read on the right axis. (D) Mass transfer modeling for HOCl and Cl_2 for experiment 3 using a humidified surgical mask.

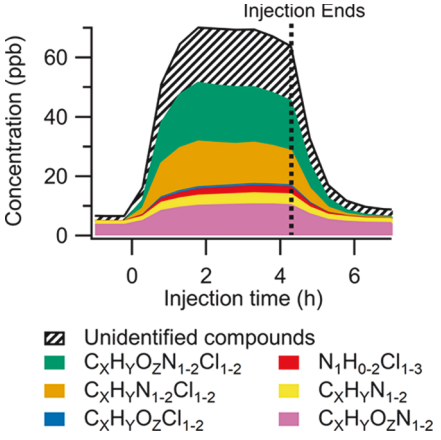

Figure 3. Stacked Vocus PTRMS time series of inside chamber concentrations during experiment 4.

and $C_2H_5ONCl_2$, which may correspond to chlorinated amines and imines. C_2H_4ONCl is consistent with an *N*-chloraldimine observed from dichlor disinfection of an athletic facility and formed from reaction of HOCl and free amines.[44] Non-halogenated nitrogen-containing organic emissions from bleach ($C_XH_YO_ZN_{1-2}$) also appear to be dominated by amines, amides, and other nonnitrate functionalities. Nitrates make up a small fraction of observed $C_XH_YO_ZN_{1-2}$ and are identified by an oxygen-to-nitrogen ratio of 3−1 or greater. Non-nitrates include toxic isocyanate species (C_2H_3NO and C_3H_5NO) that have been previously observed.[11]

The set of reactive organics in this study was substantially different from realistic conditions. Sources of organic species in this study may include hydrocarbons and oxygenated species off-gassed from building materials and the polymer "skin" of the manikin, along with modest human emissions from experiment preparation. Humans continuously emit organics from their breath and skin including acetone, squalene, oleic acid, and other species that are likely to react with hypochlorous acid and chloramines.[45] Ozone reactions with skin oil have been observed broadly,[46−49] while work on bleach-skin oil reactions is more limited[17] and deserves further research. In addition, water treatment studies have shown rapid reaction of bleach with organics in the aqueous phase to form a variety of volatile disinfection byproducts that may have substantial health impacts,[18,50] relevant to indoor environ-

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ments of greater humidity or reactions in mucous membranes. Taken together, we anticipate that under realistic conditions, there would be a greater variety and higher concentration of reactive species and products compared to this study. Simulation of these realistic conditions would further capture impacts of bleach exposure and reaction on human health.

Mask Surface Interactions Elevate Concentrations behind the Mask after Disinfection. HOCl, Cl_2, and $ClNO_2$ concentrations inside the chamber and behind the mask are shown in Figure 2A. For HOCl and Cl_2, concentrations behind the mask were lower than those inside the chamber. This indicates a sink for HOCl and Cl_2 across the mask that may be related to uptake to the mask surface, reaction with species on the mask surface, or some combination. HOCl surface uptake has been previously observed in bleach-cleaning studies.[10] Higher-volatility Cl_2 may be more prone to reactive losses than adsorption to surfaces, with enhanced losses across the mask that are not observed in the chamber. $ClNO_2$ concentrations behind the mask were higher than inside the chamber. This indicates a source for $ClNO_2$ across the mask surface. The primary pathway of $ClNO_2$ production in ambient air is nocturnal reaction of particulate chloride with dinitrogen pentoxide (N_2O_5).[51] The primary formation pathway during indoor bleach cleaning is thought to be an aqueous reaction of HOCl with nitrite.[10,52,53] While the mechanism of $ClNO_2$ formation on the mask is unclear, it is plausible that HOCl and NO_2 are both taken up by the mask and form $ClNO_2$. While these measurements cannot confirm the presence of NO_2 or nitrous acid (HONO), one or both are commonly present in environmental chambers and indoor environments.[54,55]

Bleach injection resulted in elevated concentrations of many compounds after disinfection ended. Inside the chamber, HOCl and $ClNO_2$ both decayed more slowly than the chamber air exchange rate, indicative of a source in the chamber, perhaps surface-adsorbed droplets or gases that later desorb (Figure 2B). The decay rate was calculated using an exponential decay function from a typical chamber mass balance. Cl_2 did not have a clear source in the chamber and decayed at the air exchange rate, consistent with its high volatility. In studies which apply bleach using mops, decay of HOCl was more rapid than AER, which was attributed to uptake and reaction on indoor surfaces.[9,10] The misting method in this study formed a less aqueous film for production and loss of gas-phase species than mopping with bleach solution. In addition, mopping procedures required human occupancy during disinfection, which contributed additional reactive sinks for HOCl and other species. When a chlorinated disinfectant (sodium dichloro-s-triazinetrione or dichlor) was aerosolized in another study,[56] HOCl decay was more rapid than AER (ascribed to reaction with surfaces and organics), although other chlorinated species decayed more slowly than AER, indicative of production sources after disinfection.

Decay inside the mask was slower than in the room for HOCl, Cl_2, and $ClNO_2$, evidence of an additional source from the mask surface that elevated concentrations behind the mask. HOCl and $ClNO_2$ likely adsorb to the mask surface during disinfection and then desorb and elevate concentrations behind the mask. Cl_2 is a higher-volatility species and is unlikely to adsorb to mask fibers. Instead, Cl_2 is likely formed following HOCl uptake to the mask surface and subsequent disassociation and reaction with available acids.[9]

To better quantify the source strength inside the chamber and mask, we calculated the net source and sink for the chamber (NS_C) and the mask (NS_M) using our mass balance model. For positive values of NS_C and NS_M, a net source is present for the compound of interest inside the chamber and mask. For negative values, a net sink is present. Figure 2C shows the evolution of source and sink strengths during and following disinfection for Experiment 1. Outside the mask, the injection served as a stable source ($NS_C > 0$) for all three species until the end of injection. HOCl and Cl_2 show a net sink across the mask surface ($NS_M < 0$) that increased alongside their concentration growth, indicative of a concentration dependence of this mask sink. $ClNO_2$ shows a net source behind the mask ($NS_M > 0$) during injection, consistent with reactive formation of $ClNO_2$ on the mask surface from nitrite and HOCl reaction.

Following disinfection, NS_M had a small positive value for all species and the mask served as a source of additional exposure, consistent with previous observations of adsorption and subsequent desorption of many indoor gas-phase contaminants to indoor surfaces.[10,23] For HOCl and Cl_2, the resulting net mask source was 2−3 orders of magnitude smaller than the mask sink during disinfection. Processes which remove HOCl from the mask include disassociation reactions, reactions with available organics, and reactions with nitrites to form $ClNO_2$, which drive this low source strength. However, chamber and mask sources persisted for more than 4 h after injection ended, lengthening the period of exposure to toxic species.

In experiment 4, monochloramine and dichloramine source/sink behavior is similar to that of HOCl and Cl_2 (Figure 4A). These inorganic chloramines form from aqueous ammonia and HOCl chemistry.[57] The monochloramine chamber source term was stable throughout injection, while the dichloramine chamber source term (NS_C) rose throughout injection. Slower reactive formation of dichloramine than monochloramine may drive this difference. Inside the mask, we find the magnitude of the monochloramine mask sink (NS_M) falls during the injection period, perhaps driven by saturation of adsorption sites or consumption of adsorbed species on the mask. The behavior of chloramines may not be representative of realistic conditions, given ammonia in human breath that could drive formation of additional chloramines. Chloroform shows similar concentration inside the chamber and behind the mask during disinfection and decay, indicating that no strong source or sink exists across the mask surface.

A variety of organics were emitted during bleach injection. Vocus measurements of organics from experiments 4 and 6 are grouped by elemental composition and averaged for 2 h periods during and after disinfection. Averages were taken from 2 to 4 h after disinfection began and 2−4 h after disinfection ended. In Figure 5, these grouped averages inside the chamber and behind the mask are background-subtracted to remove VOC contributions from chamber or mask sources. For all species categories shown, during the disinfection period, concentrations in the chamber were higher than those behind the mask because of sinks across the mask surface. However, following the end of disinfection, concentrations behind the mask were elevated above those inside the chamber and show the mask was a source for a wide range of species. Within each species category, individual species followed the group trend though the strength of source/sink behavior varied. As previously discussed, formation of chlorine- and nitrogen-containing organics was observed in the chamber. Concen-

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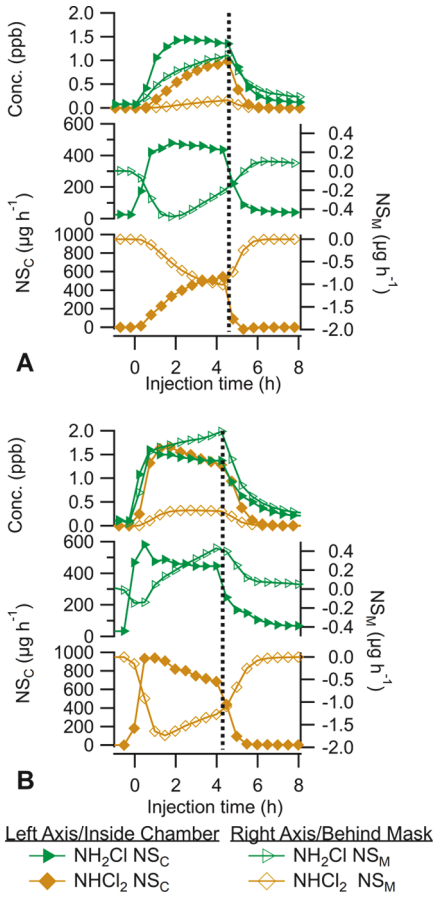

Figure 4. Concentrations and source/sink profiles for mono- and dichloramines from (A) Experiment 4-Dry KN95 and (B) Experiment 6-Humidified KN95. Vertical dashed line indicates end of bleach injection. NS_C refers to the inside chamber source/sink and is represented in closed symbols read on the left axis. NS_M refers to the behind mask source/sink and is represented in open symbols read on the right axis.

trations of chlorine- and nitrogen-containing organics were elevated behind the mask following disinfection, indicating desorption from the mask or reactive formation on the mask surface. Elevated concentrations indicate availability of reactive sites in the mask surface, which would be supplied with human breath and skin organics under realistic conditions. The presence of additional organics on the mask or in the room would substantially alter the products observed, as discussed previously. The presence of ammonia and carbon dioxide in human breath would alter mask surface pH and reactive uptake, while volatile organic compounds including skin oils may react with disinfectant emissions, altering their concentrations in the breathing zone and forming a different set of reaction products.

While sinks and sources across the mask were lower-magnitude on a mass basis than those observed in the chamber, emissions confined to the breathing zone of the mask user may result in more substantial exposure impacts. The behaviors of the mask as a sink during disinfection and a source as disinfectant concentrations in the room fall are consistent across all experiments for a wide range of compounds. Masks may reduce exposures to HOCl, Cl_2, chloramines, and other species during disinfection but increase exposure afterward. However, while these mask surfaces may appear protective during disinfection, they are not designed for this use and cannot be recommended as personal protective equipment for bleach emissions. In addition, increased exposure to $ClNO_2$ behind the mask is evident. Although the toxicological impacts of nitryl chloride are unclear, other species may show similar behavior, and the general behavior of the mask as a prolonged source of exposure is of concern.

Mask Humidification Impacts Species Uptake and Emission. HOCl and Cl_2 net source and sink behavior are compared for dry (Experiment 1, Figure 2C) and humidified (Experiment 3, Figure 2D) mask conditions. A reduced chamber source and mask sink is observed for both species under humidified mask conditions during disinfection. However, HOCl and Cl_2 concentrations were lower inside the chamber during the humidified experiment, which was attributed to system variability including chamber history and disinfectant product age. Therefore, the impacts of humidity on the interactions between masks and HOCl and Cl_2 were unclear. Qualitative source/sink analysis suggests little impact of humidity. This is surprising given the observed uptake of both species to the mask and the solubility of HOCl. HOCl uptake and subsequent reaction on wetted surfaces require further study.

For NH_2Cl and $NHCl_2$, behavior and concentrations were compared side by side from the dry KN95 experiment 4 (Figure 4A) and the humidified KN95 experiment 6 (Figure 4B). Similar monochloramine concentration and source behavior in the chamber were observed under dry and humidified mask conditions as expected, but behind the mask, the behavior changed substantially. Under humid conditions, higher monochloramine concentrations were observed behind the mask than inside the chamber. This corresponded with a weaker mask sink during injection under humid conditions. The presence of water may have increased NH_2Cl production through increased uptake of ammonia. However, at the end of injection, the mask was a source of similar magnitude under dry and humidified conditions. The mask visibly dried during the experiment, which likely drove this similarity.

Under humidified conditions, dichloramine chamber concentrations were slightly higher and peaked earlier as opposed to the gradual increase observed under dry conditions, which may be related to factors including recent chamber history, shifts in relative humidity, age of bleach solution, and other variables. A stronger mask sink for dichloramine was observed during injection under humidified conditions, perhaps related to uptake and reaction in the aqueous film. The multistep reaction required to generate dichloramine may limit the formation of dichloramine on mask surfaces. After injection, dichloramine concentrations and net source/sink behind the mask were similar for dry and humidified conditions, again related to mask drying.

For the broader range of organics, concentrations in the humid experiment were reduced for most species groups (Figure 5), although the relative ratio across the mask surface was similar. Under both dry and humid conditions, emission of chlorine- and nitrogen-containing organic species was observed behind the mask after disinfection ends. Variations in organic emissions and formation here cannot be conclusively related to mask humidification as the available organics in the chamber may have varied due to repeated cleaning events. Again, during real building disinfection events, inorganic and organic emissions from human breath and skin will impact the mask

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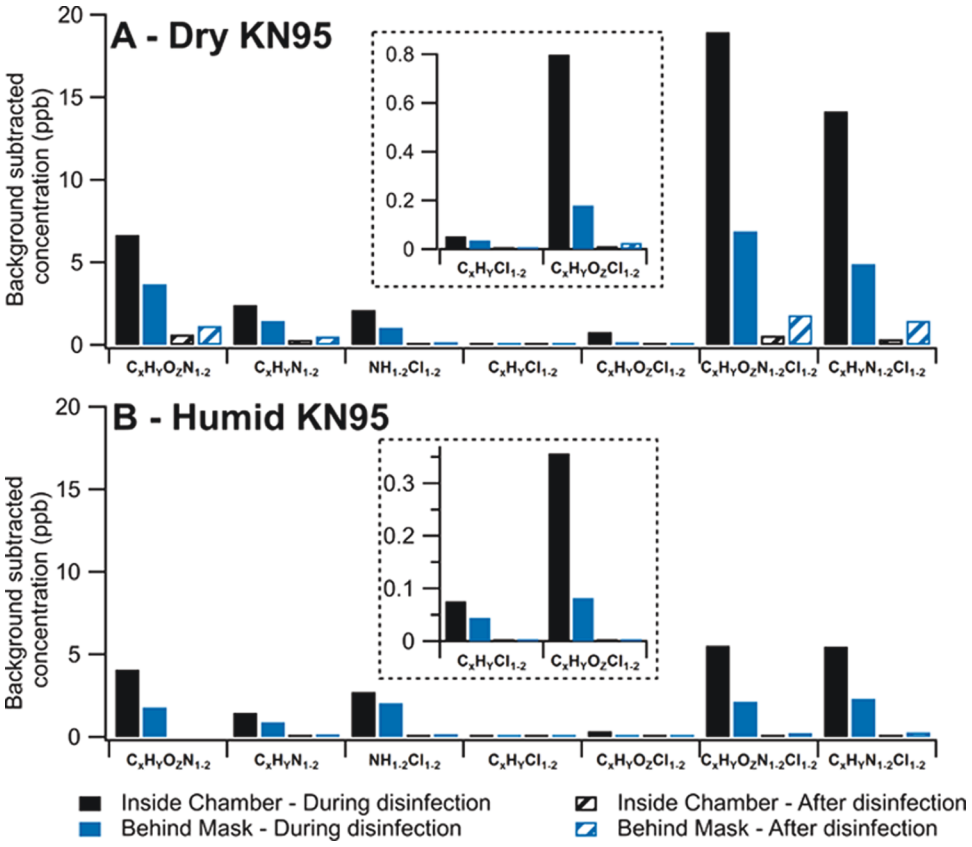

Figure 5. Background-subtracted mean concentrations of elementally grouped species identified in Vocus for (A) Experiment 4 and (B) Experiment 6. $C_XH_YCl_{1-2}$ and $C_XH_YO_ZCl_{1-2}$ species are presented in the inset. Averages are taken from 2 to 4 h after the beginning of injection and 2−4 h after the end of injection. Each category varies in the number of species identified and included in sum. From left to right on the main axis, the categories contain 40, 7, 3, 2, 5, 10, and 8 species, respectively.

environment by altering the surface pH and reactivity and result in a different set of reaction products.

Health and Environmental Implications. Elevated concentrations of bleach disinfectant emissions including HOCl, Cl_2, $ClNO_2$, chloroform, chloramines, and oxidized organics (including chlorine- and nitrogen-containing species) were observed during injection, consistent with the existing literature.[9,10,16] These species have substantial health impacts. HOCl concentrations in the 100s of ppb are observed and have been previously associated with chlorohydrin formation upon reaction with squalene present in human skin oil.[17] These reactions may drive skin and respiratory tract irritation from bleach. While Cl_2 inhalation is associated with acute respiratory damage in high parts per million concentrations, the World Health Organization recommends ambient Cl_2 below 34 ppb to reduce chronic exposure impacts.[58,59] Chloroform derived from drinking water disinfection can be taken up through inhalation and has been shown to increase the rates of bladder cancers.[40,60,61] Exposure to nitrogen trichloride has been associated with respiratory distress,[13] while monochloramine and dichloramine have been previously shown to react with a wide range of organic molecules to form toxic species.[18,43] Broadly, these emissions are toxic upon inhalation and react to form other toxic species, driving respiratory irritation and increased cancer risk. While concentrations present during bleach disinfection are unlikely to cause acute injury, exposure over a long time period could present a health concern.

Beyond exposure impacts, indoor bleach usage introduces a substantial source of chlorine radical precursors to the indoor and outdoor environment. While not explored in detail here, indoor illumination can photolyze HOCl, $ClNO_2$, and Cl_2 to form chlorine radicals and drive further oxidation of skin oils and volatile organic compounds.[62] In addition, increases in ventilation utilized to reduce virus exposures may drive HOCl, Cl_2, and $ClNO_2$ outdoors where they may be photolyzed and generate chlorine radicals that drive formation of secondary organic aerosol and ozone.[63,64]

Here, we find that surgical and KN95 masks consistently act to prolong the exposure time for a wide range of species. During disinfection, masks reduce exposures to many species as they sorb and react on mask surfaces. However, after disinfection ends, the concentrations in the room rapidly fall, while concentrations inside the mask remain somewhat elevated. These mask-adsorbed species continue to react and desorb, prolonging exposure to harmful species in the gas phase. Under realistic conditions with human subjects, mask wearing will likely result in additional formation of potentially toxic halogenated species due to the presence of human skin oils and other organics on mask surfaces.[17] The presence of inorganic and organic species from human breath and skin, as well as other indoor emissions, will substantially alter the reaction products observed here, though general behaviors are likely to be similar. The masks discussed here are not designed for filtration of disinfectant emissions and their protective utility is unclear, particularly for longer-term cleaning events under realistic conditions. However, if masks are worn during cleaning events to reduce exposure to airborne disease, they should be removed (and replaced if needed) following cleaning

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or when moving to another space. This is likely relevant for chemical handling and exposure in industrial and research settings as well. Further examination of interactions with human emissions with realistic proxies will improve estimations of disinfection byproduct lifetimes on mask surfaces. In addition, development, recommendation, and deployment of additional personal protective equipment to reduce worker exposures to disinfectants and disinfection byproducts is necessary.

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Notes

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