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The impact of clothing on ozone and squalene ozonolysis products in indoor environments

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Multiphase reactions of ozone with human skin oils impact indoor air quality by depleting ozone and forming semi-volatile organic compounds, which can be respiratory and skin irritants. Here we demonstrate the impact of clothing on indoor air composition and human exposure by integrating indoor chemistry modeling over a wide range of different spatial and temporal scales. Constrained by molecular dynamics simulations that provide key kinetic parameters, the kinetic model reproduces experimental measurements and predicts that squalene could persist in clothing for several hours to over a day depending on ozone concentrations. Soiled clothing protects skin from ozone exposure even with high concentrations, but can enhance concentrations of oxidation products to a ppb level depending on air exchange rates. Computational fluid dynamics simulations reveal that primary products have ~1.6–2.0 times higher concentrations in the breathing zone than in bulk room air, while secondary products are distributed more uniformly throughout a room.

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Human occupants can affect the composition of indoor air in a variety of ways. It is well known that activities such as cooking, smoking, and cleaning can degrade indoor air quality. Less well recognized is the role of the occupants themselves. High concentrations of volatile organic compounds have been measured in human breath, which can lead to an increase in the concentrations of these species indoors^{1–3}. Primary emissions of volatiles from skin have also been measured⁴. Chemical reactions involving the human body can also alter the concentrations of indoor pollutants^{5–7}. Human skin oils contain unsaturated species including squalene, fatty acids and wax esters that react with O₃⁸. Experimental measurements have demonstrated that the reaction of ozone with human skin can lead to a decrease in ozone concentrations and to an increase in the concentrations of volatile and semi-volatile products, including mono-carbonyls and di-carbonyls, both in the gas phase and in skin oils^{9–13}. Carbonyls are likely to be respiratory and skin irritants and it is therefore important to be able to predict their concentrations under different indoor conditions^{14–17}.

The main source of O₃ indoors is from outdoor-to-indoor transport. Concentrations of O₃ indoors are usually 20–80% of the outdoor concentration depending on the rate of outdoor-to-indoor transport and the removal by indoor surfaces and other chemicals in indoor air¹⁸. Typical O₃ concentrations in buildings can vary significantly, from less than 5 ppb to over 50 ppb¹⁹. Concentrations of O₃ in aircraft cabins can be very high, with measurements ranging from ~30 ppb to several hundred ppb depending on altitude, latitude, time of year and the use of catalytic converters to remove ozone^{19,20}. Therefore, the rate of formation of carbonyls indoors due to reactions of O₃ with skin oils can vary considerably for different indoor environments.

Clothes, which often contain skin oil, have been shown to remove significant amounts of O₃ indoors and are important for the uptake of semi-volatile organic compounds (SVOCs), which can be accumulated on and released from clothes^{21–26}. Measurements have shown that a single soiled t-shirt can account for 70% of the total O₃ removed by a person²⁷. Other studies have also measured a decrease in O₃ concentrations and the evolution of significant concentrations of squalene ozonolysis products in the gas-phase from clothing worn by people for several hours^{20,28–30}. In addition, recent experimental studies have shown that the extent of dermal uptake will be influenced significantly by clothing^{31–37} and dermal uptake of species such as polycyclic aromatic hydrocarbons and phthalates is similar or larger than inhalation intake^{38,39}. Clean clothing can reduce the concentration of species being absorbed into the skin by acting as a protective barrier, whereas clothing which has had time to absorb these compounds from the gas phase before being worn may act as a source of the compound, leading to an increase of dermal uptake compared to bare skin^{32,33,36}. Modeling studies indicated that several factors, such as the clothing thickness, the gap between the clothing and the skin, and the time since laundering, would be important for the dermal uptake of SVOCs^{35,37}.

Therefore, it is important to quantify the impact of clothing on ozone–human interactions and indoor air quality. Recently, we developed the kinetic multilayer model of surface and bulk chemistry of the skin, which includes mass transport through the skin and chemical reactions of skin lipids and ozone in the skin and secondary chemistry in the gas phase⁴⁰. In this study we have further developed this model to include clothing (KM-SUB-Skin-Clothing), as shown in Fig. 1, by treating the following additional processes: gas-phase diffusion, partitioning between a gas-phase and condensed phase in the clothing, transfer of skin oil between the upper skin and clothing as well as chemical reactions in the clothing. Twelve ozonolysis reactions of squalene and resulting fourteen ozonolysis products are included. Reactions with other

reactive species present in skin and clothing are considered and air-exchange is also treated in the model. The surface mass accommodation of ozone to the skin oil, the diffusion coefficient of O₃ in skin oil, the gas-skin oil partition coefficient of ozone, and the ozone desorption lifetime are constrained by molecular dynamics (MD) simulations. Using the kinetic model and computational fluid dynamic simulations, we assess the impact of clothing on indoor concentrations and human exposure of ozone and carbonyl compounds.

Results

Derivation of parameters from molecular dynamics simulations. MD simulations of two systems containing a single ozone molecule and liquid squalene as a proxy for skin oil⁸ were carried out to calculate several thermodynamic and kinetic parameters for input into the KM-SUB-Skin-Clothing model. The details of the MD simulation setup and the methodology used to calculate the thermodynamic and kinetic parameters are provided in the Supplementary Methods. Representative data from the MD simulations are reported in Fig. 2. The ozone mean-squared displacement in bulk squalene is plotted in Fig. 2a along with a linear fit from which the bulk diffusion coefficient was calculated to be $3.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ using the Einstein relation (Eqn. E28). Figure 2b reports the free energy profile for ozone entering a slab of liquid squalene from the gas phase. The vertical dashed line indicates the depth, z_{cut} , at which ozone was considered to be absorbed in 250 trajectories of ozone impinging on the surface of liquid squalene. The Henry's law constant for ozone in squalene was derived to be $3.3 \times 10^{-3} \text{ mol cm}^{-3} \text{ atm}^{-1}$ using the free energy of solvation ΔG_s . Figure 2c depicts examples of the four classes of outcomes in the ozone impingement trajectories, the numbers of which were used to calculate the surface mass accommodation coefficient α to be 0.60. The histogram of desorption lifetimes calculated from trajectories in which the ozone molecule desorbed is plotted in the inset of Fig. 2c; the mean desorption lifetime is 147 ps.

Modeling the reactions of O₃ with clothing. Figure 3 shows measurements of O₃ and the formation of three major squalene ozonolysis products (4-OPA, 6-MHO, and acetone) when soiled cotton samples or t-shirts were exposed to O₃ in a simulated aircraft cabin under different conditions. It consists of three data sets, which have been published in the literature. In the experiments in Fig. 3a by Wisthaler et al.²⁰, 17-soiled T-shirts were exposed to ozone in a 28.5 m³ chamber and with an air exchange rate of 3 h^{−1}. When the t-shirts were present in the chamber the concentration of ozone decreased, compared to the empty room, while the concentration of three measured squalene ozonolysis products increased significantly. In Fig. 3b, Coleman et al.²⁸ quantified the ozone deposition velocity and concentration of ozone as well as emission rates of acetone and 6-MHO upon ozone exposure of a pre-worn 250 cm² soiled cotton sample in a 10.5 L chamber with an air exchange rate of 23 h^{−1}. In Fig. 3c, Rai et al.²⁹ measured concentrations of ozone, acetone and 4-OPA upon ozone exposure of a pre-worn 0.9 m² cotton t-shirt in a 5.1 m³ chamber with two different exchange rates of 0.5 and 2.7 h^{−1} (see further details of each experiments in the Supplementary Methods).

The kinetic modeling results are shown by the shaded areas in Fig. 3, reproducing experiments well. Ozone deposition rates and concentrations upon exposure of ozone to unsoiled cotton, as quantified by Coleman et al.²⁸ (Supplementary Fig. 1), as well as ozone and SVOC concentrations upon exposure of people to O₃, as measured by Wisthaler et al.⁹, were also reproduced well by the model. The model parameters are listed in Supplementary

Fig. 1 Schematic of the KM-SUB-Skin-Clothing model for interactions of O₃ with skin and clothing. Kinetic parameters determined from molecular dynamics (MD) simulations were used in the kinetic model and outputs from the kinetic model were inputted into the computational fluid dynamics (CFD) model to obtain the spatial distribution of species. O₃ can react with skin lipids such as squalene forming volatile and semi-volatile organic products including 4-OPA and 6-MHO. O₃ and products can diffuse through clothing, which consists of fibers and air, and also partition to oil in the clothing. They can also diffuse across the air gap separating the clothing from the skin, while skin oils can be transferred between the skin and clothing by contact transfer. They can also diffuse through the skin reaching the bloodstream. In the right panel the red arrows represent chemical reactions, while the green and blue arrows represent mass transport. [O₃], [Sq], and [P] are O₃, squalene and product concentrations, respectively. The subscripts g, bl, cl1, clm, gap, gs, oil1, oiln, sc1, sco, ve1, and vep represent the gas phase, boundary layer, first layer of the clothing, last layer of the clothing, the gap between the clothing and the skin, the near surface gas phase, the first layer of the skin oil, the last layer of the skin oil, the first layer of the stratum corneum, the last layer of the stratum corneum, the first layer of the viable epidermis and the last layer of the viable epidermis, respectively

Tables 1 and 2, which are similar among the different data sets, especially when considering the natural variability between people, clothing and laundering products^{34,39,41–43}. The model reproduced the temporal evolution of ozone and steady-state concentrations of squalene ozonolysis products very well. The decrease in O₃ deposition rates over time in Fig. 3b can be attributed to the consumption of the reactive species in the clothing over the timescale of the experiments. Dependence of ozonolysis products on ozone and air exchange rate (Fig. 3c) was captured well by the model such that product concentrations were higher at higher ozone and lower indoor-to-outdoor transport. Given that the model reproduces such a large variety of data sets with vastly different conditions, the model parameters are constrained to a reasonable range of values.

Impact of clothing on ozone and carbonyls. The model is applied to estimate the lifetime of squalene in clothing and product concentrations under different indoor conditions. Figure 4a shows the chemical half-life of squalene in clothing as a function of gas-phase O₃ concentration. The range of values of the squalene chemical half-life reflects the range of critical parameters

including the boundary layer length, the level of soiling, skin oil volume, and the concentration of reactive laundering species in the clothing (see Supplementary Fig. 2). The half-life varies from about one hour at high O₃ concentrations to several weeks under low O₃ conditions. This suggests that squalene may persist in soiled clothing over a relatively long period of time in typical indoor environments, which could occur if the clothing is left in a laundry pile. Under low O₃ conditions the depletion of squalene in soiled clothing would be relatively slow over a time-scale of days and low concentrations of carbonyl products would be formed continuously (Supplementary Fig. 3). Note that other oxidation processes such as OH and NO₃ uptake and potentially autooxidation may also degrade squalene but are likely to have smaller effects in comparison to ozonolysis^{44–46}. Under high O₃ conditions squalene in clothing would be reacted away relatively quickly, resulting in the rapid formation of squalene ozonolysis products. Thus, soiled clothing could become a major source of squalene ozonolysis products for a short period of time, until the squalene in the clothing was fully depleted.

Figure 4b shows the effect of air-exchange rate on the O₃ and carbonyl concentrations in a room. As the air exchange rate

Fig. 2 Molecular dynamics simulations for derivation of kinetic parameters. **a** Mean-squared displacement of the ozone center-of-mass in bulk squalene (red curve) and fit to eqn. E28 from 1.25 ns to 2 ns (black dashed line); the ozone diffusion constant is derived from the slope of the fitted line. **b** Fitted free energy profile for ozone entering the squalene slab. The free energy of solvation of ozone in squalene, ΔG_s , is indicated. The black dashed line denotes the location, z_{cut} , where the free energy profile becomes flat and, hence, denotes bulk solvation. **c** Example of each class of trajectory of ozone encounters with the squalene slab used in the calculation of the surface mass accommodation coefficient α and desorption lifetimes, τ_d . The black dashed line denotes the location, z_{cut} . Inset: histogram of desorption lifetimes of ozone adsorbed on the surface squalene. Details are described in the Supplementary Methods

Fig. 3 Effect of ozone exposure to soiled clothing. Experimental measurements and modeled O_3 and squalene ozonolysis products upon ozone exposure to soiled cotton samples or t-shirts. Experimental measurements are represented by the data points and dashed lines and are from **a** Wisthaler et al.²⁰, **b** Coleman et al.²⁸, and **c** Rai et al.²⁹. A 20% error for all measurements was assumed. Model results are shown by the shaded areas, which are due to the range of parameters in Supplementary Table 2

Fig. 4 The half-life of squalene in clothing and indoor air composition. **a** The estimated chemical half-life of squalene in soiled clothing as a function of O_3 concentration and without any replenishment of squalene. **b** O_3 , monocarbonyl, and dicarbonyl concentrations as a function of air exchange rate after two 0.9 m^2 soiled t-shirts are exposed to O_3 in a 30 m^3 room. In the absence of t-shirts the O_3 concentration in the room would be 5 ppb

decreases, the O_3 concentration decreases due to a decrease in ozone supply from outdoors, while gas-phase carbonyl concentrations increase as indoor-to-outdoor transport decreases allowing more time for these products to accumulate indoors. Note that at higher air exchange rates the boundary layer adjacent to the clothing is expected to be thinner⁴⁷, which would lead to higher O_3 flux and an increase in carbonyl generation rates. (Supplementary Fig. 4a). These sensitivity studies demonstrate the crucial importance of ventilation on indoor air quality. The level of soiling and reactive laundering species would also affect carbonyl concentrations: higher soiling would lead to increase of skin lipid-specific carbonyl concentrations, while a higher loading of reactive laundering species would decrease carbonyl concentrations by depleting O_3 (Supplementary Fig. 4b, c). Note that some types of laundering species such as natural soaps consisting of highly unsaturated fatty acids have the potential to produce other carbonyl species, which may remain in clothing or partition to the gas phase depending on their volatility.

In addition to soiled clothing affecting indoor air quality, total human exposure to ozone can be impacted strongly by wearing clothing and by the fraction of the body covered by clothing. It should be noted that a previous calculation estimated that less than 2% of ozone removal by a human body was due to inhalation, demonstrating the importance of dermal uptake and the importance of understanding how clothing can reduce exposure of skin to ozone⁹. Figure 5 shows contour plots of O_3 concentrations in clothing as a function of depth into the clothing for different levels of clothing reactivity and gas-phase O_3 concentrations of 5 and 50 ppb. For soiled clothing, O_3 concentrations penetrating through the clothing decreased substantially to <0.1 ppb (Fig. 5a, b and Supplementary Fig. 5). In the case where clothing is initially clean and contains no laundering species and is therefore unreactive, ozone may penetrate through clothing and skin would be exposed to significant amount of ozone especially at 50 ppb O_3 (Fig. 5d). The extent of O_3 penetration is expected to decrease gradually upon contact transfer of skin oils to clothing and strong concentration gradients of squalene within clothing is expected (Supplementary Fig. 6). These results indicate that clothing acts as a protective barrier leading to skin being exposed to much lower O_3 concentrations in typical indoor environments, while a significant fraction of ozone may still penetrate clothing to reach skin during the first few minutes of exposure if clothing is clean under high ozone concentrations, for example in an aircraft cabin without an ozone denuder. Overall wearing freshly laundered clean clothing would decrease carbonyl and dicarbonyl concentrations in the gas phase significantly, while ozone concentrations

would increase by ~ 1 ppb (Supplementary Fig. 7). This reinforces the importance of regularly laundering clothing and not re-wearing soiled clothing in order to reduce human exposure to squalene ozonolysis products. It is also important to understand the trade-off between a decrease in carbonyl concentrations and a slight increase in ozone concentrations in terms of overall health effects, which needs further investigation.

Implications for indoor air quality and human exposure. To provide further insights into implications of ozone–human interactions on indoor air quality, we simulate spatial distribution of ozone and squalene ozonolysis products in a room. We applied our model simulations to a benchmark experiment by Wisthaler and Weschler⁹, which measured concentrations of O_3 and squalene ozonolysis product when two fully-clothed people entered a 28.5 m^3 room with 33 ppb O_3 . As shown in Fig. 6a, the O_3 concentration decreased during the experiment to ~ 16 ppb, while concentrations of 6-MHO and 4-OPA increased to ~ 2 ppb, and these measured concentrations in a room were reproduced well by the KM-SUB-Skin-Clothing model as shown by the solid lines. Based on this simulation, O_3 uptake coefficients and product yields were calculated by KM-SUB-Skin-Clothing under soiled clothing condition, and the results were implemented to a computational fluid dynamic (CFD) model to investigate the extent of concentration gradients around an occupant that may develop within a room for different species (Fig. 6a).

Figure 6b–d present CFD simulation results that describe spatial distributions of ozone (Fig. 6b) and primary (6-MHO, Fig. 6c) and secondary (4-OPA, Fig. 6d) ozonolysis products. Figure 6b shows that ozone is depleted in the human surface boundary layer because of ozone reaction with the human surface. Ozone is moved upward by the occupant thermal plume that is created due to the temperature gradient between the human surface and the room air. The thermal plume draws air up and across the reactive human surface, thereby resulting in lower ozone concentrations in the breathing zone than in the bulk room air (Fig. 6b). Due to the reaction of ozone with soiled clothing, primary reaction products (6-MHO) are highly concentrated near the human surfaces (Fig. 6c). As a result, the 6-MHO concentration in the breathing zone is up to two times higher than the ambient bulk air. The primary reaction products are transported by the thermal plume and react further with ozone in the ambient room air, leading to the formation of secondary reaction products such as dicarbonyls (4-OPA, 1,4 butanediol). Figure 6d shows that the secondary products (4-OPA) are mainly formed in the ambient air and are relatively well distributed in the

Fig. 5 O_3 concentration profiles within clothing. Clothing was exposed to gas-phase O_3 concentrations of **a, c** 5 and **b, d** 50 ppb. The distance of 0 cm refers to clothing closest to the skin while the distance of 0.1 cm refers to clothing adjacent to the room air. Panels **a, b** are for soiled clothing with laundering species, while **c, d** are for clean clothing without laundering species. For both cases squalene replenishment due to contact transfer is included

Fig. 6 Spatial distribution of ozone and squalene ozonolysis products in a room. **a** Average concentrations of O_3 and four squalene ozonolysis products with an initial O_3 concentration of 33 ppb. The markers represent measurements from Wisthaler and Weschler⁹, while the solid lines are modeled with KM-SUB-Skin-Clothing. Spatial distributions of **b** ozone, **c** 6-MHO (primary product), and **d** 4-OPA (secondary product) as simulated by computational fluid dynamics

room compared to the primary products with a concentration range of 2.2–2.8 ppb.

Overall, our model is quantitatively consistent with measurements showing that clothing can impact indoor air quality and human exposure to O_3 and carbonyls, which can be respiratory and skin irritants. Squalene may persist in clothing for several days in the low-ozone environment typical of U.S. residences and clothing can release substantial amounts of carbonyls once O_3 levels become elevated. Note that other fabrics, such as bedding, also have the potential to contain high concentrations of squalene and could also become a major source of carbonyls indoors under elevated O_3 conditions, especially if it is not laundered regularly and skin oils accumulate within it. Using KM-SUB-Skin-Clothing it has been demonstrated that human exposure to O_3 would be substantially lower with pre-worn clothing especially at high O_3 concentrations such as in an aircraft cabin, but exposure to carbonyls would be lower with laundered clean clothing.

There are several ways in which indoor air quality and human exposure to squalene ozonolysis products can be improved. Regularly laundering clothing, bedding and any other fabrics that come into contact with people would substantially reduce the concentrations of squalene ozonolysis products that would be emitted upon reactions with O_3 . In addition, pre-worn soiled clothing awaiting laundering could be stored in a room that is not regularly used by people in order to reduce their exposure. It would be important to ensure that the reactions of O_3 with laundering products do not result in harmful or irritating products. Finally, good ventilation would reduce carbonyls in indoor air as well as human exposure to these species by increasing their transport from indoors to outdoors. It is also interesting to note that there are some concerns about ozone-skin chemistry generating squalene hydroperoxides, which are associated with acne⁴⁸. Wearing clothing would protect from the direct formation of these species at the skin. These products could also potentially form at greater concentrations in soiled clothing than laundered clothing, where they could be transported back to the skin.

It has been demonstrated experimentally that squalene ozonolysis products including 4-OPA, acetone, geranyl acetone, and 1,4-butanediol can be irritants^{15,49,50} and a link has been found between low molecular weight carbonyls and an occupational asthma hazard¹⁷. It is still unclear what the overall risk of exposure to carbonyl species at parts-per-billion levels would be, although it has been speculated that long term chronic exposure or the effect of being exposed to the summation of the mono-carbonyls and di-carbonyls could adversely impact health¹⁴. As clothing reduces ozone concentrations and increases carbonyl concentrations, it is important to understand at what level the trade-off between exposure to ozone and exposure to carbonyls becomes important and this question still needs to be investigated. Until this is understood, the best way to reduce risk indoors would be to reduce ozone penetrating indoors, for example, by using activated carbon filtration⁵¹. Reducing O_3 concentrations indoors would also reduce the concentrations of squalene ozonolysis products in indoor air as well as human exposure to these products.

Methods

Kinetic model. The kinetic multilayer model of surface and bulk chemistry of the skin and clothing (KM-SUB-Skin-Clothing) is developed by extending the KM-SUB-Skin model⁴⁰ by including a clothing layer and a boundary layer. The model includes diffusion of O_3 and carbonyls to and from the surface of the clothing, through the clothing, in the gap between the clothing and the skin and in the different layers of the skin; the skin oil, stratum corneum, and viable epidermis. Gas-phase diffusion in the clothing was effectively slowed down by rapid partitioning to oils or other substances covering the fibers in the clothing and partitioning into the skin was also included. Mass transport of species through clothing and skin is consistent with the model of Morrison et al. using partial differential

equations³⁵ (Supplementary Figs. 8, 9). Contact transfer of species between the upper skin oil layer and the clothing was treated in the model (Supplementary Fig. 10) as well as reactions in the gas phase, clothing and skin. The required kinetic parameters are listed in Supplementary Tables 1 and 2 and were kept consistent with literature values whenever possible. Uncertain parameters which were varied to fit experimental data included the volume of skin oil and other substances present in soiled clothing, the concentration of squalene, other reactive skin oil species and laundering species in this volume, the rate coefficients of laundering species with O_3 , the thickness of the boundary layer, and the rate of contact transfer. Molecular dynamics simulations were conducted to estimate the surface accommodation coefficient, Henry's law constant, desorption lifetime, and the bulk diffusion coefficient of ozone in skin oil (Supplementary Fig. 11; Supplementary Table 3). Further details regarding the values used for different parameters are given in the SI. CFD simulations were performed to evaluate the spatial distribution of O_3 and specific squalene ozonolysis products around humans in a room by using ozone uptake coefficients and product yields as determined by KM-SUB-Skin-Clothing (Supplementary Figs. 12, 13, 14; Supplementary Tables 4, 5, 6). More details are described in the Supplementary Methods.

Data availability

The codes used to generate the data in the current study are available from the corresponding author on reasonable request.

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Author contributions

P.L., G.M., and M.S. designed and performed kinetic modeling and wrote portions of the manuscript. K.P., M.D., and D.T. designed and performed MD simulations and wrote portions of the manuscript. Y.W. and D.R. designed and performed CFD modeling and wrote portions of the manuscript. P.L. and M.S. led manuscript writing with inputs from all coauthors.

Additional information

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