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Modelling the time-dependent concentrations of primary and secondary reaction products of ozone with squalene in a university classroom

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Abstract

Volatile organic chemicals are produced from reactions of ozone with squalene in human skin oil. Both primary and secondary reaction products, i.e., 6-methyl-5-hepten-2-one (6-MHO) and 4-oxopentanal (4-OPA), have been reported in indoor occupied spaces. However, the abundance of these products indoors is a function of many variables including the amount of ozone and occupants present as well as indoor removal processes. In this study, we develop a time-dependent kinetic model describing the behavior of ozone/squalene reaction products indoors, including the reaction process and physical adsorption process of products on indoor surfaces. The key parameters in the model were obtained by fitting time-resolved concentrations of 6-MHO, 4-OPA, and ozone in a university classroom on one day with multiple class sessions. The model predictions were subsequently tested against observations from four additional measurement days in the same classroom. Model predictions and experimental data agreed well (R^2=0.87-0.92) for all test days including ~7 class sessions covering a range of occupants (10-70) and ozone concentrations (0.09-32 ppb), demonstrating the effectiveness of the model. Accounting for surface uptake of 6-MHO and 4-OPA significantly improved model predictions (R^2=0.52-0.76 without surface uptake), reflecting the importance of including surface interactions to quantitatively represent product behavior in indoor environments.

Introduction

Ozone is typically the dominant oxidant in indoor air for chemicals containing unsaturated carbon bonds, and thereby plays an important role in indoor air chemistry.[1] Indoor ozone generally originates from ventilation with outdoor air, and in some environments could have additional sources such as ozonolysis air purifiers, photocopiers or printers.[2-4] Early studies on indoor ozone were mainly confined to interactions with cleaning products and building materials, [5-10] while just a few studies referred to the direct interaction of ozone with humans. Later research discovered that in highly occupied indoor spaces the main loss process for ozone is typically reaction with the unsaturated carbon-carbon double bonds in human skin oil. For example, human occupants were shown to be the most important sinks for ozone in a simulated aircraft cabin environment, accounting for ~60% of ozone removal.[11] Ozone has also been shown to react with human skin oil remaining on hair and worn clothing.[12-14]

Human skin oil is composed of fatty acids, glycerides, wax esters and squalene. Squalene, a triterpenoid hydrocarbon containing six unsaturated carbon-carbon double bonds, is the most abundant ozone-reactive constituent in skin oil, and is ubiquitous in occupied indoor environments.[15] Squalene ozonolysis products include acetone, 6-methyl-5-hepten-2-one (6-MHO), geranyl acetone (Ga), 4,9,13,17-tetramethyl-octadeca-4,8,12,16-tetraeneal (TOT), 4,8,13,17,21-tetramethyl-octadeca-4,8,12,16,20-pentaene-al (TOP), and 5,9,13-trimethyl-tetradeca-4,8,12-triene-al (TTT). Primary products with remaining unsaturated carbon-carbon double bonds can react with ozone again generating secondary products,[16] such as 4-oxopentanal (4-OPA), which is

recognized as an asthma trigger and sensitizer, and has been shown to induce irritation and allergic response.[17-20] The ozonolysis of fatty acids also leads to formation of various aldehydes (i.e., decanal, nonanal, hexanal, octanal, undecanal), and the yields of the last three products are generally lower.[21] The reaction of ozone with human skin oil has also been shown to result in the indoor formation of secondary organic aerosols.[14,22,23]

The heterogeneous reaction rate constants of ozone with pure squalene films under different conditions have been reported from laboratory studies.[21,24-26] Wells et al.[24] applied a pseudo first-order model to analyze the kinetics of ozone/squalene reaction by coupling a second-order reaction with surface ozone. The first-order rate constant was reported to be 1.58×10^{-3} s^{-1} with 50 ppb ozone. The kinetics were further examined by Petrick and Dubowski,[21] and the first-order rate constant was obtained as 1.22×10^{-5} s^{-1} with 50 ppb ozone, much lower than that found by Wells et al. Fu et al.[25] analyzed the reaction probability of squalene upon exposure to ozone, and acquired first-order rate constants of $(2.5 \pm 0.3) \times 10^{-4}$ s^{-1} and $(6.3 \pm 0.6) \times 10^{-3}$ s^{-1} for C=C band and C=O band with 250 ppb ozone. Zhou et al.[26] investigated squalene film changes when exposing to ozone and the reactive uptake coefficients were determined to be $(1.3 \pm 0.1) \times 10^{-3}$ s^{-1} and $(6.0 \pm 0.4) \times 10^{-4}$ s^{-1} for ozone mix ratio of 50 ppb and 25 ppb. These studies represent a range of second-order rate constants of $(0.02\text{-}3.15) \times 10^{-5}$ s^{-1} ppb^{-1} for primary products of ozone/squalene reactions. A few studies also investigated the rate constants for secondary products.[27,28] The large discrepancy in the rate constants of ozone with pure squalene film in laboratory among different studies implies the reaction

dynamics are not fully understood. Wisthaler and Weschler[29] observed that the predicted secondary product (4-OPA) concentration based on rate constants determined from lab tests was much lower than the measured data in a simulated office. Tang et al.[30] reported observations of these products and their dynamic behavior in a classroom regularly occupied by students over a period of several weeks, providing the dataset used here for further study of the processes determining their abundance in indoor air.

A few model investigations have been reported simulating the dynamic interactions of airborne chemicals with human skin. These models are generally limited to physical transport processes,[31,32] while one model is specifically simulating chemical reactions of ozone with squalene. Lakey et al.[16] extended a kinetic multilayer model used for predicting the oxidation of oleic acid particles to skin oil, and developed a kinetic multilayer model of surface and bulk chemistry of the skin (KM-SUB-Skin) to simulate the emission of squalene ozonolysis products from people exposed to ozone. They applied this model to simulate ozone, 6-MHO, and 4-OPA for comparison with three sets of data collected in simulated office and small enclosure. The model includes tens of parameters that must be determined, thus presenting a barrier to its wide use in engineering applications. In addition, the model ignores adsorption and desorption processes of products onto indoor surfaces, which should cause prediction discrepancies in real indoor environments since surface interactions are important for these types of chemicals and must influence the indoor composition as well as chemical dynamics.[33]

The objectives of the present study are to: (1) develop a novel kinetic model that

predicts the products of chemical reactions between ozone and squalene including their interaction with indoor surfaces; (2) analyze data from a previously reported measurement campaign in a university classroom[30] to validate the model and examine the behavior of reaction products in this typical indoor setting with varying occupant density and ozone concentrations.

Methods

Heterogeneous oxidation of squalene by ozone produces aldehydes, ketones and some bicarbonyl compounds.[21] Two of the most abundant primary and secondary products are 6-MHO and 4-OPA,[29] which can irritate the digestive tract, respiratory tract, skin and eyes (6-MHO), and induce allergic response (4-OPA),[17-20,34] and these are selected as typical main products for our modeling analysis. Formation of 6-MHO occurs as a product of the primary reaction between ozone and squalene, while formation of 4-OPA is a product of the secondary reactions of ozone with 6-MHO, as well as ozone with geranyl acetone.[21,29] The detailed chemical reactions are given by equations (S1)-(S3) in Section S1 of the Supporting Information (SI). The time-dependent ozone concentration in indoor air (classroom for the present study) can be characterized by the following equation:

$$V\frac{dC_{O3}(t)}{dt} = Q[C_{in,O3}(t) - C_{O3}(t)] - v_{d,h}A_hC_{O3}(t) - v_{d,r}A_rC_{O3}(t) \quad (1)$$

where C_{O3} is the ozone concentration in the classroom air, ppb; $C_{in,O3}$ is the ozone concentration introduced into the classroom in the supply air, ppb; V is the volume of the classroom, m^3; A_h and A_r are the surface areas of the human bodies and room

surfaces, respectively, m^2; Q is the ventilation rate, $m^3\ s^{-1}$; $v_{d,h}$ and $v_{d,r}$ are the deposition velocities of ozone at the human skin surfaces and indoor surfaces, respectively, $m\ s^{-1}$.

Prior modeling studies generally focused on ozone/squalene reactions with constant inlet ozone concentrations,[21,24-29] while the present study examines the reactions with naturally varying ozone concentrations in the ventilation supply air which comes from outdoors. The formation rate of 6-MHO and 4-OPA are described in SI Section S2. In real indoor environments, the chemicals (e.g., 6-MHO, 4-OPA) will adsorb/desorb onto the wall surfaces. This surface partitioning for squalene oxidation products was not considered in previous indoor modelling.[16,35] Previous studies generally focused on chamber experiments or indoor spaces with high air change rates such as an aircraft cabin at 25-30 h^{-1},[16,36] and assumed wall effects were negligible. Our model explicitly account for wall effects to determine their significance for indoor environments such as the classroom we are studying which has an air change rate of 5 h^{-1}.[37] For surface partitioning, we assume that a convective boundary layer exists along the wall surface, and the wall uptake/release rate can be represented as:

$$E(t) = h_{m,s}(C_a - C_s) = K_s \frac{dC_s}{dt} \quad (2)$$

where C_s is the surface concentration of chemicals, ppb; K_s is the surface/air partition coefficient, m (for 6-MHO and 4-OPA, the partition coefficients are expressed as K_{6M} and K_{4O}, respectively); $h_{m,s}$ is the convective mass transfer coefficient across the wall surface, $m\ s^{-1}$.

The mass balance equation for 6-MHO and 4-OPA can then be represented as:

$$V\frac{dC_{6M}(t)}{dt} = A_h \cdot k_{6M} \cdot C_{O3} + Q \cdot [C_{in,6M}(t) - C_{6M}(t)] - V \cdot k_{4O} \cdot C_{O3} \cdot C_{6M}(t) + V \cdot k_{Ga} \cdot C_{O3} \cdot C_{Ga}(t) - A_r \cdot E_{6M}(t) \quad (3)$$

$$V\frac{dC_{4O}(t)}{dt} = V \cdot k_{4O} \cdot C_{O3} \cdot C_{6M}(t) + V \cdot k_{Ga} \cdot C_{O3} \cdot C_{Ga}(t) + Q \cdot [C_{in,4O}(t) - C_{4O}(t)] - A_r \cdot E_{4O}(t) \quad (4)$$

where C_{6M} is the concentration of 6-MHO in the classroom air, ppb; C_{4O} is the concentration of 4-OPA in the classroom air, ppb; C_{Ga} is the concentration of geranyl acetone in the classroom air, ppb; $C_{in,6M}$ is the 6-MHO concentration in the supply air, ppb; $C_{in,4O}$ is the 4-OPA concentration in the supply air, ppb; k_{6M} is the pseudo-first-order rate constant of 6-MHO, m s^{-1}; k_{4O} is the second-order rate constant of 4-OPA, s^{-1} ppb^{-1}; k_{Ga} is the second-order rate constant of geranyl acetone, s^{-1} ppb^{-1}.

The concentrations of ozone, 6-MHO and 4-OPA in indoor environments can be characterized by equations (1), (3) and (4). Eight key parameters should be pre-determined to calculate three pollutant concentrations (C_{O3}, C_{4O}, C_{6M}), i.e., $v_{d,h}$, $v_{d,r}$, k_{6M}, k_{4O}, k_{Ga}, K_{6M}, K_{4O}, C_{Ga}. Previous study assumes that 6-MHO and geranyl acetone have equal production rates from the reactions of ozone with squalene, and the second-order rate constant of geranyl acetone (k_{Ga}) is half of that for 6-MHO.[16] In order to determine the remaining key parameters, experiments must be performed to measure the time-resolved concentrations of ozone, 6-MHO and 4-OPA in the indoor environment, including the amount coming in through ventilation. Then the remaining parameters can be extracted by fitting the kinetic model with experimental data through nonlinear curve regression. In the present study, to ensure the accuracy of the obtained parameters, data collected on one test day were generally used to determine the key parameters in

the kinetic model, and data from other four test days were then used to assess model performance by comparison with observations.

Experimental section

Measurements were carried out over a period of five days (Nov 4, Nov 5, Nov 6, Nov 12, Nov 13, 2014) in a typically occupied classroom located at the University of California, Berkeley. The experimental setup, and results of concentrations and fluxes from outdoor, indoor, and occupant sources have been previously reported,[30,38] thus only a brief description is provided here. The volume of the classroom was 670 m^3, and ambient ozone was introduced from outdoors directly through the single-pass ventilation system (the outdoor ozone concentration changed over time). The number of occupants (students) in the classroom was recorded manually, and fluctuated from 10-70 during different class sessions, as seen in SI Table S1. The ratio of male to female was 66%:34% during the test, and the use of personal care products and its influence on indoor air composition was analyzed in a prior study.[32] Measurements were also made during unoccupied conditions when classes were not in session. During the experiments (field campaign), a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) (IONICON Analytik GmbH) was used to measure the concentrations of 6-MHO and 4-OPA as well as other volatile organic compounds in the classroom and supply air (switching at 5-minute intervals), daily from 8:10 am to 20:45 pm. This instrument uses H_3O^+ as the primary reagent, and can scan the mass spectrum for mass-to-charge ratio (*m/z*) of 30-500. PTR-TOF-MS enables fast response

time measurements (full mass spectrum in seconds or minutes), has high sensitivity (tens of parts per trillion or ppt in a second), and high mass resolution.[30,39] After 18:00 pm, the classroom was always empty but the ventilation remained on for several more hours. The time-dependent ozone concentrations in the classroom and supply air were continuously monitored with an ozone analyzer (Thermo Scientific 49i) through the same sampling lines.

The walls and ceiling in the classroom were covered with latex paint, and the floor was made of hard tile and cleaned periodically outside of normal class times. The total surface areas of walls, floor, and ceiling in the classroom was estimated to be 534 m^2 based on the physical dimensions (length, width, height). The surface area of tables and chairs exposed to ambient air in the classroom was estimated to be 65 m^2 in total. The mechanical single-pass ventilation system provides an air change rate (N) of 5 ± 0.5 h^{-1},[37] using outdoor air for the supply so ozone concentration of air entering the classroom varies with outdoor air concentrations. The surface area of each human body is assumed to be 1.7 m^2.[40] The convective mass transfer coefficient along the wall surface is about 0.002 m s^{-1}, calculated by empirical correlations, consistent with the commonly reported range (0.0007-0.004 m s^{-1}).[41-43] The parameters used for modeling are summarized in SI Table S2.

Results and discussion

Observations and relationships among occupant number, ozone level and oxidation products

208 The measured data of five test days in the classroom covers a series of squalene
209 oxidation products concentrations and some important influencing factors (ozone,
210 occupancy, 6-MHO, and 4-OPA), thus it makes sense to probe their relationships from
211 this dataset. We averaged the measured data for each classroom session and took the
212 processed data for analysis. The processed ozone concentration covers a wide range (0-
213 23 ppb). For the convenience of visualization, the ozone concentration is divided into
214 three intervals (0-1 ppb, 1-10 ppb and 10-23 ppb for each interval). After data transform,
215 we bin all the data according to the ranges of ozone concentration, and then plot bins
216 (6-MHO vs occupancy, 4-OPA vs product of 6-MHO and ozone bins) into Figure 1. In
217 the figure, ozone concentrations are marked by different colors (red, blue and green).
218 To more clearly show the relevance of 4-OPA with 6-MHO and ozone, further data
219 transform is performed for Figure 1(b). We divide 6-MHO concentrations into three
220 intervals (0-0.2 ppb, 0.2-0.4 ppb and 0.4-0.7 ppb for each interval) and mark them in
221 the manner of the circle size (circle size from small to large indicates concentration
222 from low to high). With above processing, we can more clearly examine the impact of
223 occupants and ozone levels on the squalene oxidation products.
224 As is shown in Figure 1(a), two clusters are differentiated by the number of
225 occupants and ranges of ozone concentration to determine if certain behaviors exist. In
226 the left cluster, the number of occupants is small (10-30 persons) and the average 6-
227 MHO concentration is low (0.07-0.30 ppb); while in the right cluster, the number of
228 occupants is large (50-70), with high average 6-MHO concentration (0.24-0.64 ppb). It
229 is clear that occupants do influence the abundance of 6-MHO, with an increasing

tendency. The observed behavior is consistent with our fundamental understanding, i.e., low 6-MHO at low ozone and occupancy levels, high 6-MHO at high ozone and occupancy levels. Figure 1(b) indicates that the concentration of 4-OPA is approximately in a linear relationship with the product of concentrations of 6-MHO and ozone. When the concentrations of ozone and 6-MHO are low (smallest red circle), 4-OPA concentration is at a low level. When the concentrations of ozone and 6-MHO are high (largest blue and green circles), 4-OPA concentration is accordingly at a high level. It should be pointed out that, 4-OPA will continue to produce even if without occupants because the reactions between ozone with 6-MHO and geranyl acetone in gas phase are still in process.

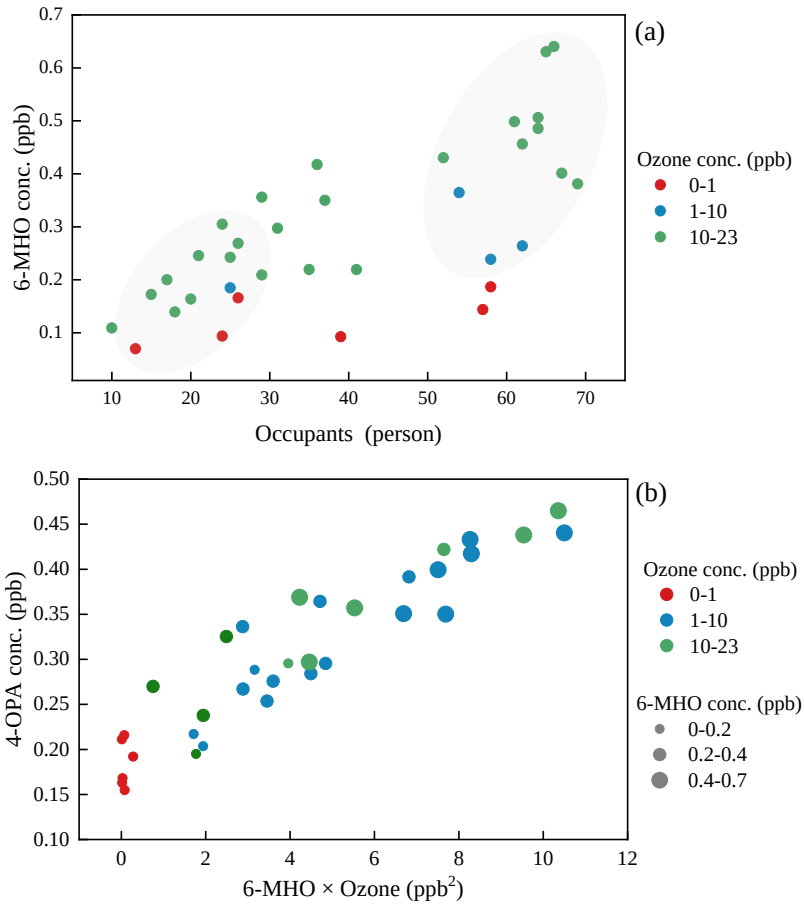


Figure 1. Scatter plots of (a) 6-MHO versus number of occupants and (b) 4-OPA versus

the product of 6-MHO and ozone, for average data from each class session of five test days (Ozone concentration bins are marked by different colors; 6-MHO concentrations are marked in the manner of circle size).

Determining ozone deposition velocity to room surfaces

The measured classroom/supply ozone data during the unoccupied period from 18:10 pm to 20:45 pm on Nov 6, 2014 is used in equation (1) to determine the ozone deposition velocity to room surfaces ($v_{d,r}$). To simplify the calculation, we assume all the indoor surfaces have the same deposition velocity and the objective function is then a 2-norm solution of the difference between the predicted value and measured value. The optimal parameter value is obtained by minimizing the objective function. During the global optimization process, a pattern search algorithm is applied. The determined ozone deposition velocity to room surfaces is 0.03 cm s^{-1}, in agreement with typical values published for common indoor materials (0.02-0.058 cm s^{-1}, listed in SI Table S3). Model predictions of ozone concentration in the classroom are compared with measured data in some other days as shown in SI Figure S1. The good agreement suggests the reliability of the determined deposition velocity.

Determining ozone deposition to human surfaces

The measured ozone data with occupants in the classroom on the same day (Nov 6) is then used for determining ozone deposition velocity to human surfaces ($v_{d,h}$). Classroom occupancy varied from 15 to 58 during this period, and human surface area

was scaled accordingly in a time-dependent manner. While ozone removal to human surfaces is fairly sensitive to the near surface air movement,[13] and ozone deposition velocity can vary between different individuals, the range of occupancy in the classroom during this day provides a good opportunity to determine an average value relevant to highly occupied spaces. The fitted value as well as model prediction for classroom ozone are listed in Table 1 and Figure 2(a). The 9-h average deposition velocity for ozone removal by occupants for the classroom of 0.25 cm s^{-1} is in the range of literature values (0.20 to 0.62 cm s^{-1}, SI Table S3). It is clear that ozone deposition velocity to human skin surfaces is nearly one order of magnitude larger than that to indoor surface, thus when human surface area approaches one tenth of the room surface area, these removal processes become approximately equivalent.

It is also instructive to compare the relative contribution of ozone deposition to occupant and room surfaces with removal to human breathing and gas-phase reaction. The rate constants of typical indoor VOCs (excluding squalene ozonolysis products) reacting with ozone are in the range of 10^{-13}-10^{-7} s^{-1} ppb^{-1}, which is much lower than that of ozone/squalene reaction probability (see the "Introduction" section).[44] It should be noted that the chemical loss of ozone due to gas-phase reaction could potentially be competitive in transient cases of high levels (10-100 ppb) of typical indoor VOCs (e.g., monoterpenes that react with ozone) during fresh emission episodes. Nevertheless, the influence from monoterpene chemistry did not seem apparent in the classroom based on the low level of monoterpene oxidation products (<5 ppb) which makes sense given the high air change rates (5 h^{-1}). Undoubtedly, peeling citrus fruit, and using detergents,

287 can release a series of monoterpenes, and the concentration of some common
288 monoterpenes (such as limonene, terpene alcohol, α-pinene) can be high in some places.
289 For the present study, the 8-h average concentration of these reactive species was less
290 than 2 ppb in the classroom for Nov 13.[38] Morawska et al.[45] also measured the limonene
291 concentration in a classroom located in Brisbane and found that the 24-h average
292 mixing ratio of limonene was less than 2 ppb. Based on these data, we simplify the
293 model and ignore the gas-phase chemistry of ozone with monoterpenes for the cases
294 studied. The caveat should be kept in mind that the developed model is more applicable
295 for low-monoterpene circumstances.

296 For the convenience of calculation, the determined deposition velocities are
297 converted into ozone removal rates, and the number of occupants in the classroom is
298 set as 57 persons. The estimated first-order removal rates for occupant surfaces and
299 room surfaces are 1.3 h^{-1} and 0.97 h^{-1}, respectively. Ozone can be also removed by
300 respiration. By assuming the breathing rate of a sedentary adult is 0.52 $m^3 h^{-1}$,[11,46] and
301 that breathed ozone is completely removed in the body before the breath is exhaled, the
302 ozone removal by occupants breathing in the classroom is estimated to be 0.043 h^{-1}. SI
303 Figure S2 presents the relative contribution of various sinks to ozone removal in the
304 classroom. Among these sinks, occupants account for the largest relative contribution,
305 almost 60%. This ratio is similar to values reported in the literature (58% in a simulated
306 aircraft cabin).[11] Although the deposition velocity of ozone removal to indoor surfaces
307 is only one-tenth of that to human surfaces, considering that the total surfaces of the
308 classroom are about 600 m^2, the relative contributions of both are comparable in this

classroom when occupant number reaches 40 persons. Because breathing accounts for only 2% of the total removal, and gas-phase ozone removal is negligible according to the above analysis, it is reasonable to model without considering these two ozone removal effects.

Determination of key parameters in the kinetic model for 6-MHO and 4-OPA

A similar method is used to determine the remaining key parameters by fitting model (equations (3) and (4)) with the occupied experimental data on Nov 6. The determined key parameters as well as model predictions are summarized in Table 1 and Figure 2(b), (c). The pseudo first-order rate constant of ozone with squalene in the classroom is determined to be 2.5×10^{-4} m s^{-1}, which is calculated by assuming that the squalene concentration adjacent to human skin surfaces is constant. This assumption is reasonable since squalene is naturally occurring and continuously produced by the human body. The first-order rate constant can be converted into the second-order rate constant. The surface coverage of squalene in the skin calculated ranges from 1.2×10^{13} molecules cm^{-2} to 1.2×10^{14} molecules cm^{-2}.[24] Thus, by dividing the average surface coverage (6×10^{13} molecules cm^{-2}), the second-order rate constant is determined to be 3.09×10^{-5} s^{-1} ppb^{-1}, which is within the range of prior studies (see the "Introduction" section). Actually, the formation rate of 6-MHO will vary for different parts of the body. Experiments performed on different parts of the human body indicated that the 6-MHO mixing ratio adjacent to the human forehead was nearly 1.4-fold larger than that next to the cheek and forearm.[29] The reason is that more skin oil exists on the forehead

surface compared with other parts of human body. Generally, the pseudo first-order rate constant of ozone with squalene can vary over the skin surface, depending on the reaction probability of the occupant surface, as shown by computational fluid dynamics (CFD) simulations.[47]

The reaction rate constant of ozone with 6-MHO is measured to be 3.8×10^{-5} s^{-1} ppb^{-1} (1.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1} after unit conversion), which is higher than experiments conducted by Grosjean et al. and Leonardo et al. ($3.94 \pm 0.4 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} and 5.9×10^{-16} cm^3 $molecule^{-1}$ s^{-1}, respectively).[27,28] The above two cases are all conducted without human presence. Wisthaler and Weschler[29] used the gas-phase reaction rate constant (4.03×10^{-16} cm^3 $molecule^{-1}$ s^{-1}) to estimate the 4-OPA concentration in an office occupied by occupants, and found that the calculated concentration was much lower than the measured data (<5%), meaning the rate constant should be higher when occupant is involved. Therefore, the difference of the reaction rate constant in different studies can be ascribed to the effect of occupants to a large extent. That is to say, part of the product (i.e., 4-OPA) measured in the gas phase in the classroom may originate from surface reaction, causing 4-OPA concentrations in the classroom greater than that originating only from gas-phase reactions between ozone with 6-MHO and geranyl acetone. In summary, 6-MHO is derived from surface reaction adjacent to the surface of human skin, while 4-OPA can come from both surface and gas-phase reactions. Further study is needed to determine surface reaction rate constant in different parts of the human skin surface.

353 **Table 1.** Determined key parameters for ozone/squalene reactions

Parameters	Value
$v_{d,h}$	0.25 (cm s^{-1})
$v_{d,r}$	0.03 (cm s^{-1})
k_{4O}	3.8×10^{-5} (s^{-1} ppb^{-1})
k_{6M}	2.5×10^{-4} (m s^{-1})
K_s (6-MHO)	0.5 (m)
K_s (4-OPA)	0.9 (m)

354

355 Figure 2(a) shows that the outdoor ozone concentration was routinely higher than
356 indoors, and the average ozone indoor-to-outdoor (I/O) concentration ratio was 0.7,
357 which is within the expected range of 0.05 to 0.85 summarized in literature for different
358 air change rates (0.05 for buildings tightly sealed and 0.85 for buildings with very high
359 air change rates).[44] The temporal trend of indoor ozone concentration is similar to that
360 of outdoors, reflecting that the air introduced into the classroom has variable amounts
361 of ozone and classroom air volume is exchanged on a timescale of 12 min. Figure 2(b)
362 and (c) show the fitted results for 6-MHO and 4-OPA. We can see that the
363 concentrations of 6-MHO and 4-OPA outdoors are negligible in comparison to the
364 classroom, and the trends of these two products are distinct from that of outdoors,
365 reflecting the dominance of their sources due to ozone reactions with human skin oil.

366

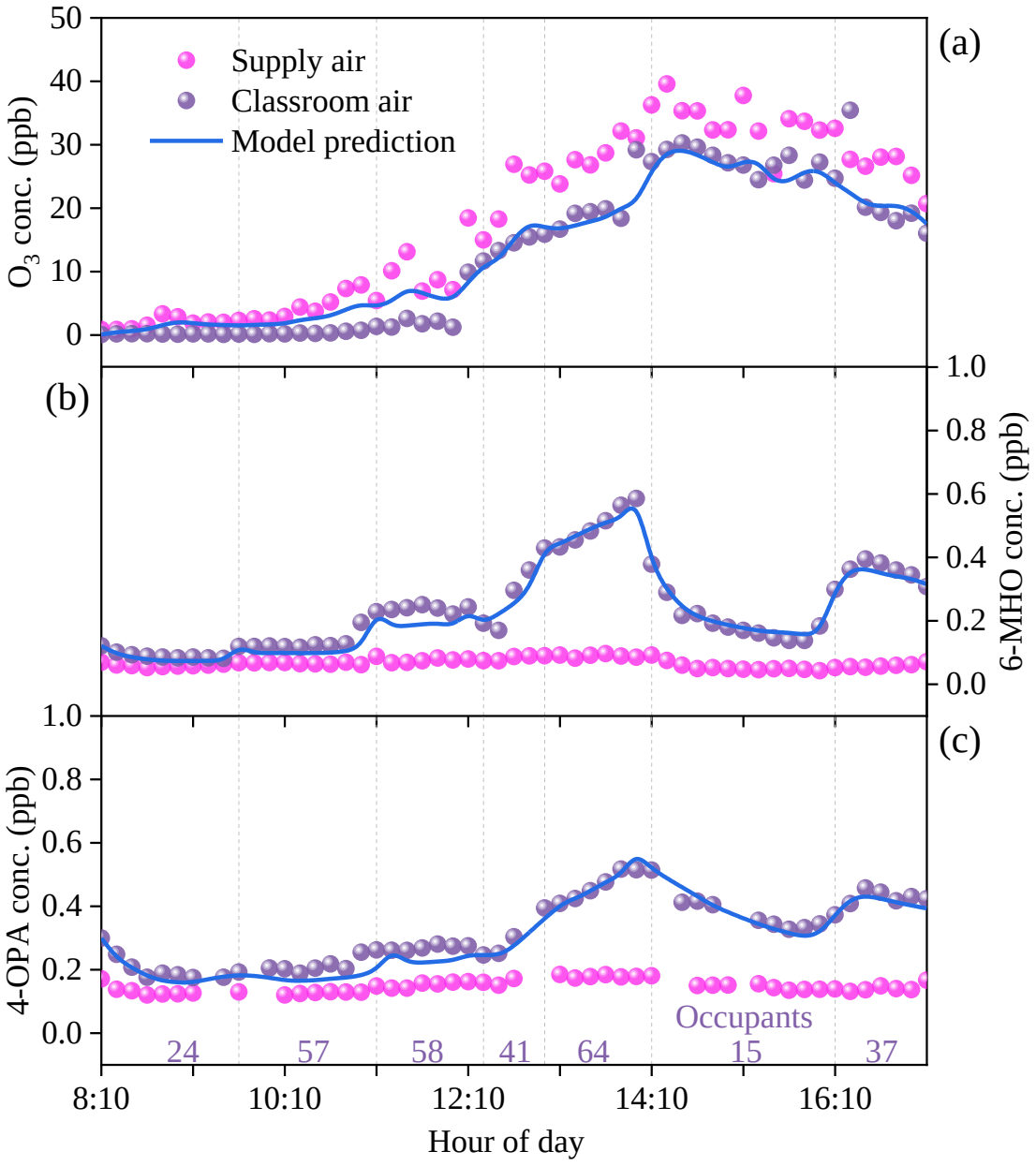


Figure 2. Fitting results of modeled (a) ozone, (b) 6-MHO, and (c) 4-OPA compared with experimental observations from Nov 6, 2014, which were used to parameterize the model.

Impact of surface partitioning

Prior kinetic models focused on the reaction details of ozone with squalene, while the surface partitioning (adsorption/desorption) of products on the wall was not

considered. This effect should be included in typical indoor environments since the surfaces of real buildings certainly will adsorb/desorb VOCs,[48] which will affect their indoor concentrations. Figure 3 as well as Table 1 suggest that partitioning to surfaces is significant both for 6-MHO and 4-OPA, because the model prediction departs from the measured data when surface partitioning is excluded (K_s=0 m). The surface partition coefficients for 6-MHO and 4-OPA are determined from the model fitting procedure to be 0.5 m and 0.9 m, respectively. Predicted results without surface partitioning are lower than the measured data in the morning because 4-OPA is adsorbed by wall surface during the previous day and continues to desorb from surfaces in the morning when production rates are low (low ozone). Later in the day around 14:00 pm when more students are in the classroom and ozone is high, there is uptake by the classroom surfaces, but during the subsequent class session when student occupancy drops to 15, the 4-OPA begins coming off the walls enhancing the concentration in the classroom. As far as we know, this is the first report that uses time-resolved measurements to demonstrate and model the partition effects of 6-MHO and 4-OPA onto wall surface in a real indoor environment.

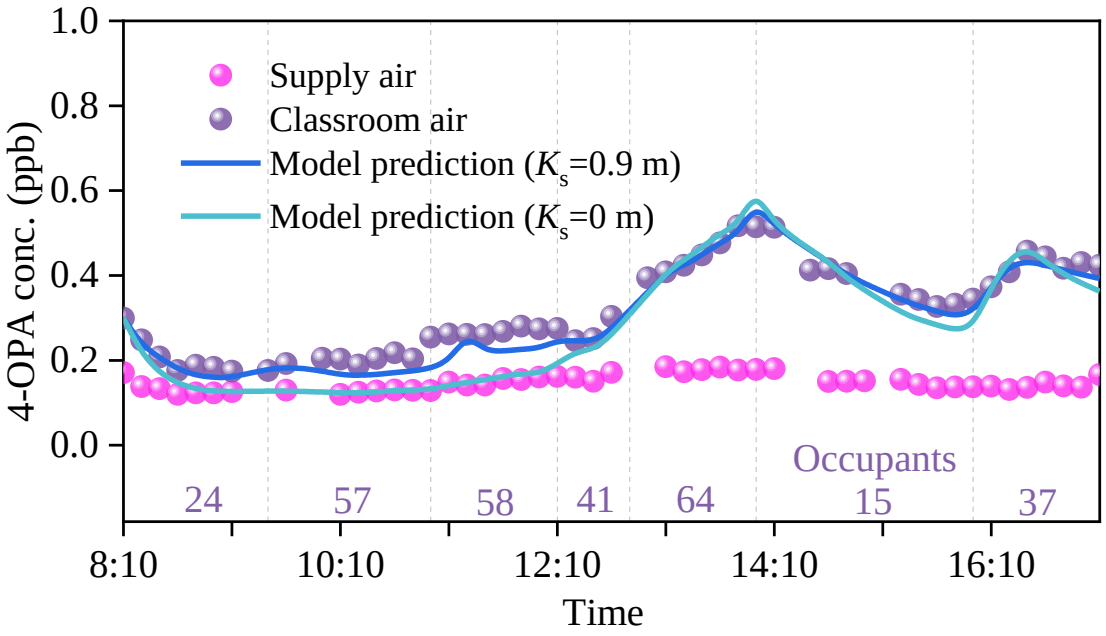


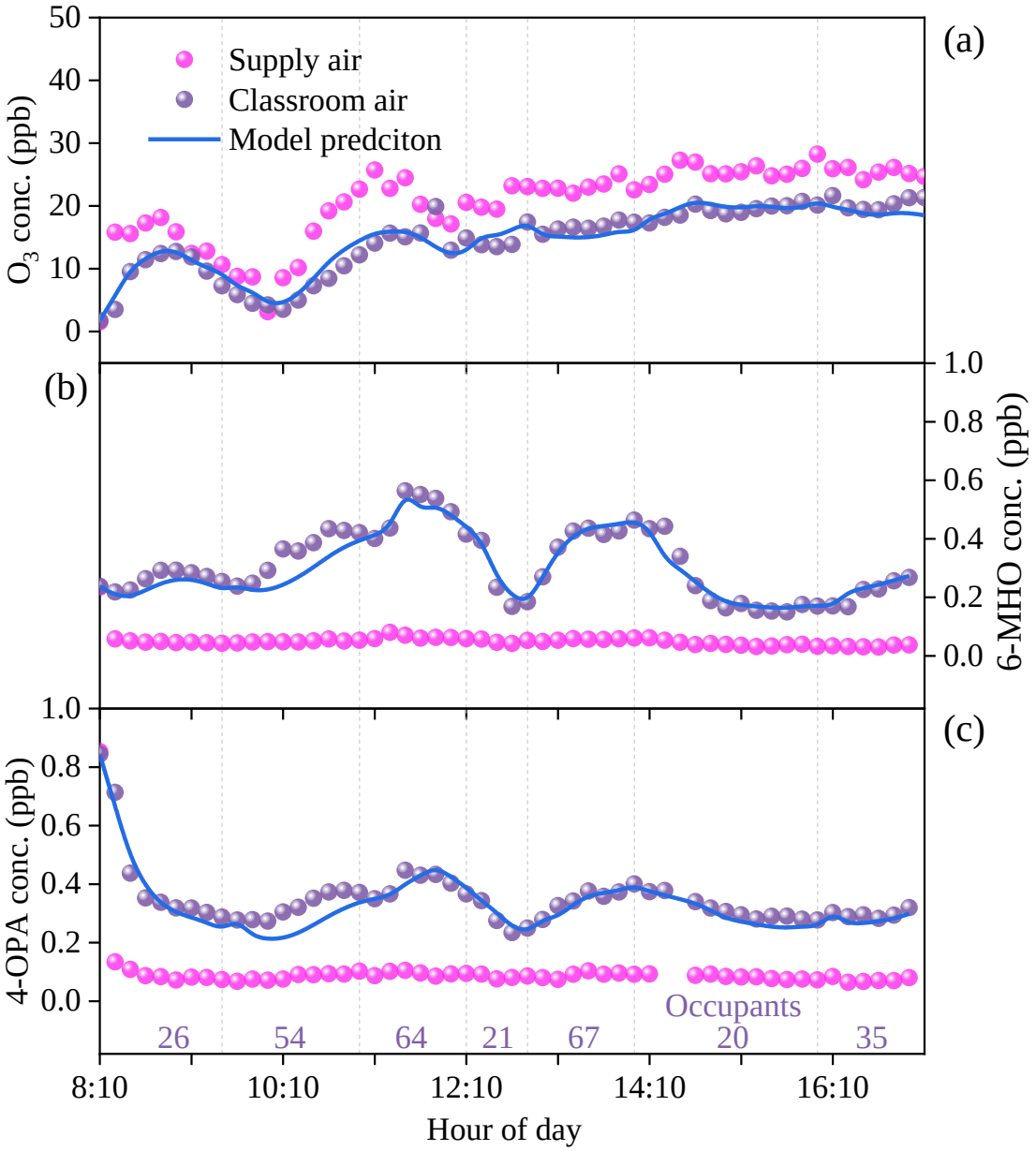
Figure 3. Impact of surface partitioning on the modeled concentration of 4-OPA.

Model validation

In order to verify the efficacy of the kinetic model using the key parameters determined from data on Nov 6, 2014 (listed in Table 1), it is applied to predict the concentrations of ozone, 6-MHO and 4-OPA in four additional days of classroom observations (Nov 4, Nov 5, Nov 12, Nov 13). Measured and modeled results for Nov 13 are presented in Figure 4 (comparisons for the other three test days are presented in SI Figures S3-S5). The number of occupants during this comparison day varied from 20 to 67, and the class sessions were similar to Nov 6 (SI Table S1). The peak concentration of 6-MHO and 4-OPA reached 0.56 ppb and 0.45 ppb, respectively, at ~11 am. Then concentrations rapidly decreased when occupancy was reduced to 21, consistent with the data measured in the previous week during similar occupancy variations. The agreement between model predictions (parameters extracted from Nov

6) and observed data for the concentrations of three compounds on Nov 13 demonstrates the effectiveness of the model with the fitted key parameters to simulate the time-resolved changes in concentrations observed in the classroom. For a more complete and quantitative comparison, Figure 5 provides scatter plots of all the model predictions versus observations for ozone, 6-MHO and 4-OPA for the five test days at the 3-min time resolution of the measured values. Correlations are strong with the square of the correlation coefficient (R^2) in the range of 0.87-0.92, showing that the model can explain approximately 90% of observed variability in the classroom with excellent quantitative agreement (slopes show 1:1 lines). Besides, the analysis of model prediction without surface interactions demonstrate that the R^2 of 6-MHO and 4-OPA are reduced to 0.76 and 0.52, respectively. Thus, surface uptake can significantly influence the accuracy of the model predictions.

The above analysis focuses on modelling ozone/squalene dynamics in a classroom. To check the feasibility of extending the developed model to other indoor settings, we compare the model predictions with published data from experiments in a simulated occupied office conducted by Wisthaler and Weschler[29]. For the modelling, the reaction rate constants of 6-MHO and 4-OPA are taken from the values obtained in this study from classroom tests. Detailed information is included in SI Section S3 and Figure S6. The good agreement between model prediction and experimental data in Figure S6 (R^2=0.92-0.94) demonstrates that the model can be applicable for predicting the ozone/squalene dynamics in other indoor settings.



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429 **Figure 4.** Comparison of model predictions with classroom observations for (a) ozone,

430 (b) 6-MHO, and (c) 4-OPA on Nov 13, 2014.

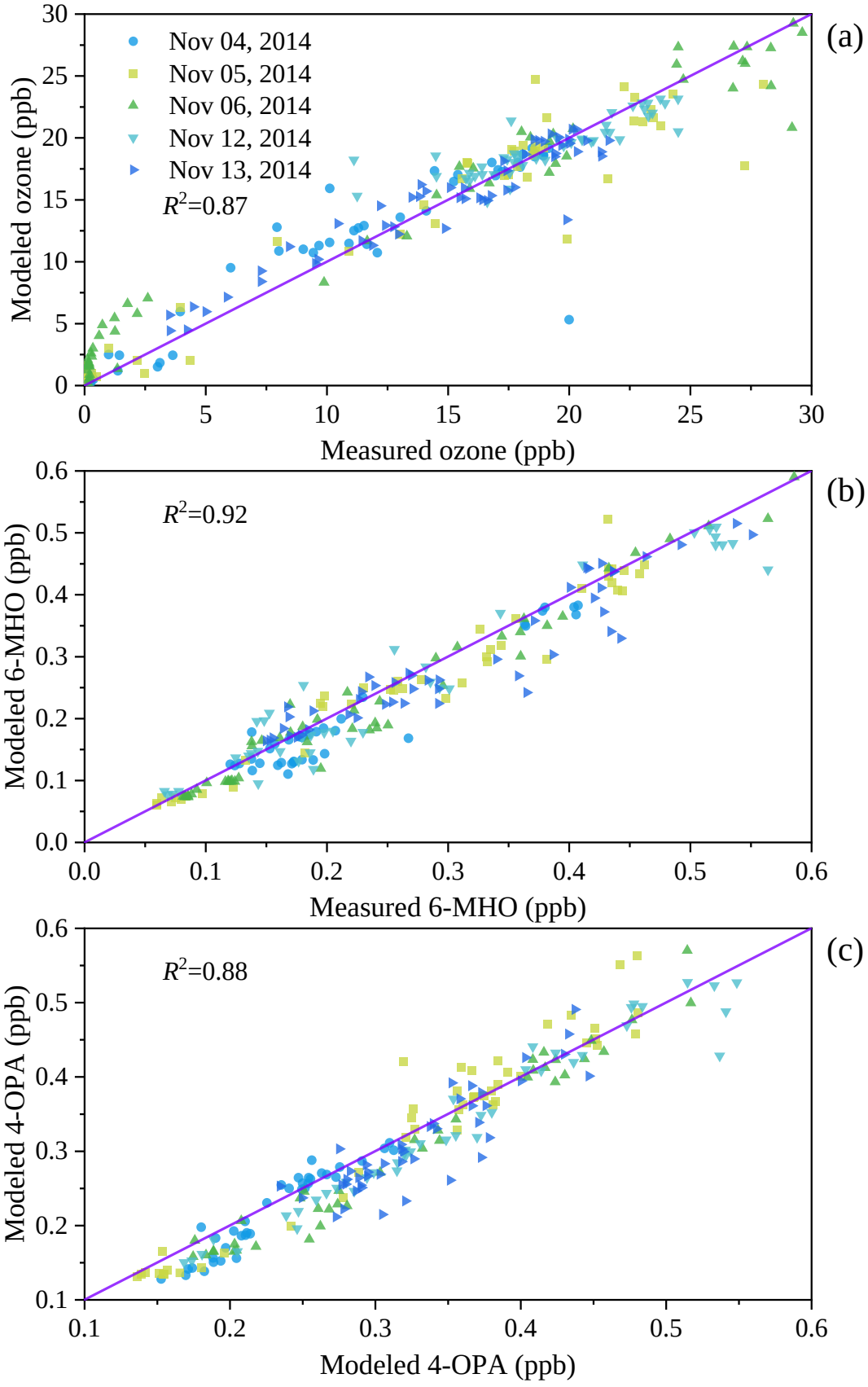

Figure 5. Correlation modeled results with measurements for (a) ozone, (b) 6-MHO, and (c) 4-OPA.

Limitations

Although some real indoor environments (e.g., classroom, office) are investigated in the presence of humans, there are limitations remaining in this study. For the present study, we assume the squalene ozonolysis process occurs from the outer surface of human skin, to simplify the interaction between ozone and occupants. In real reaction processes, part of the human skin is bared to the ambient air, which can directly react with ozone; part of the human skin is covered by clothing, the ozone may firstly penetrate the clothing layer (barrier layer), then react with skin oil. So, the interaction between human skin and ozone in real scenarios is very complicated, which deserves further study to explore the relevance of squalene ozonolysis production and the kind of clothing as well as skin coverage rate. In addition, the surface partition coefficients should be different for different indoor material surfaces. In this study, to make the model simple and practical, we assume all the surfaces have the same partition coefficients, which is certainly not true for real scenarios. Detailed description for different surface types is still needed to give a more accurate prediction with the model.

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Supporting Information

Additional details on chemical reaction of ozone with squalene (Section S1), formation rate of 6-MHO and 4-OPA (Section S2), application of model for other indoor settings (Section S3); comparison of model prediction with observations for unoccupied period (Figures S1), relative contribution of ozone removed by the various sinks (Figure S2), comparison of model predictions with observations for Nov 4, Nov 5, and Nov 13 (Figure S3-S5), comparison of model prediction with measurements in literature in a simulated office (Figure S6); occupants in the classroom during different class sessions (Tables S1), parameters for modelling ozone/squalene reactions (Table S2), ozone deposition velocity in different studies (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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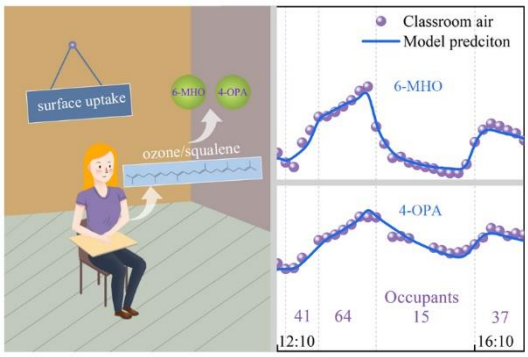

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