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How Do Breath and Skin Emissions Impact Indoor Air Chemistry?

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ABSTRACT

People are an important source of pollution indoors, through activities such as cleaning, and also from ‘natural’ emissions from breath and skin. This paper investigates natural emissions in high occupancy environments. Model simulations are performed for a school classroom during a typical summer in a polluted urban area. The results show that classroom occupants have a significant impact on indoor ozone, which increases from ~9 ppb to ~20 ppb when the pupils leave for lunch and decreases to ~14 ppb when they return. The concentrations of 4-OPA, formic acid and acetic acid formed as oxidation products following skin emissions attained maximum concentrations of 0.8, 0.5 and 0.1 ppb respectively when pupils were

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present, increasing from near-zero concentrations in their absence. For acetone, methanol and ethanol from breath emissions, maximum concentrations were ~22.3, 6.6 and 21.5 ppb respectively, compared to 7.4, 2.1 and 16.9 ppb in their absence. A rate of production analysis showed that occupancy reduced oxidant concentrations, whilst enhancing formation of nitrated organic compounds, owing to the chemistry that follows from increased aldehyde production. Occupancy also changes the peroxy radical composition, with those formed through isoprene oxidation becoming relatively more important, which also has consequences for subsequent oxidant concentrations.

KEYWORDS

Human emissions, indoor air chemistry, occupied indoor environments, detailed chemical model, indoor air quality

Practical Implications

This modelling study investigates the impact of occupancy in a school classroom and the subsequent consequences for indoor air chemistry. Occupants in buildings enhance the formation of indoor air pollutants following emissions from skin and breath. Further, the presence of occupants indoors decreases the level of oxidants, such as ozone, hydroxy radicals (OH), hydroperoxy radicals (HO₂) and peroxy radicals (RO₂), and can affect the formation of nitrated organic species, a potentially toxic class of compounds. The impact of emissions from humans could be potentially important in highly occupied spaces, such as classrooms, particularly as energy efficiency measures are making buildings more airtight. Ventilation is therefore key to mitigate such impacts and in order to maintain healthy buildings. However, in some locations it may also allow the ingress of harmful pollutants from outdoors. Clearly then, it is important to understand the impact of human occupancy

indoors and crucially, the impact ventilation can have on the concentrations of different indoor air pollutants before defining appropriate mitigation strategies.

1 INTRODUCTION

The impact of humans on indoor air quality is a growing area of research, both in terms of what might be thought of 'natural' emissions (from skin or breath) and also through occupant activities such as cooking and cleaning. Several studies^{1,2,3,4,5} have shown that the presence of humans in the indoor environment decreases ozone concentrations, while volatile organic compound (VOC) (e.g. mono- and dicarbonyls) concentrations increase⁶. Therefore, humans are recognized as a sink for ozone in the indoor environment, but also a source of secondary oxidation products⁷ and the chemistry of an empty room is likely to differ significantly from one which contains occupants. In particular, highly occupied spaces, such as classrooms, might be expected to show large differences in air quality when empty or occupied.

The chemicals that constitute human skin oils can be classified as wax esters, glycerols, fatty acids, squalene, esters and sterols and contain unsaturated carbon bonds (C=C) which readily react with ozone⁴. For instance squalene (a non-volatile triterpene) constitutes ~ 10% and the fatty acids approximately 25% of human skin lipids⁸. Following reactions of such species with ozone, a wide range of secondary products can be formed, including aldehydes, ketones, acids and secondary organic aerosols (SOA), some of which might be harmful to health^{2,4,5,9,10,11}.

The main products of the ozone-squalene reaction are 4-oxopentanal (4-OPA), 6-methyl-5-hepten-2-one (6-MHO), acetone and geranyl acetone¹². Additionally, following ozonolysis of unsaturated fatty acids, higher aldehydes can be formed, namely hexanal, heptanal, octanal, nonanal, decanal, dodecanal and undecanal⁴. Such compounds may be a concern particularly when the indoor ozone concentration is high. For instance, Wolkoff et

al.¹³ showed that 4-OPA and 6-MHO formed through the squalene-ozone reaction are potential sensory and pulmonary irritants and may cause airflow limitation. The rate of ozone deposition and subsequent secondary pollutant formation clearly depends on the level and duration of occupancy in the indoor environment, given reactive chemistry processes occur on human skin, hair or soiled clothes^{14,15,16}

Breath is also a significant source of pollutants emitted indoors, including alcohols, hydrocarbons, aldehydes and ketones¹⁴. Several studies^{17,18,19,20,21} have quantified the major VOCs emitted in the exhaled breath of healthy individuals and their concentrations are in the range of ppb to ppm. However, their concentrations in the indoor environment depend on the volume of the indoor space, the air exchange rate, the number of individuals indoors and also individual variations such as dietary habits²². For instance, a large number of VOCs are present in food and drinks, which may contribute to the VOCs detected in exhaled breath. Aldehydes can be used as flavoring agents and alcohols (i.e. ethanol) are typically found in coffee, tea, beverages and food (i.e. vegetables, fruits, cheese or meat)²³.

Children are at a higher risk of exposure to air pollutants compared to adults²⁴. As well as inhaling a higher volume of air relative to their body weight when compared to adults²⁵, their immune systems are still developing and less able to deal with potential irritants²⁶. For this reason, indoor air pollution in classrooms has become a significant concern²⁷.

A number of studies have investigated the relationship between the role of ventilation indoors and the resulting performance of school pupils^{28,29,30,31,32}. For instance, Bakó-Biró et al.³¹ reported that the performance of more than 200 pupils in different classrooms improved by 2-15% when ventilation rates increased. Lower ventilation rates allow pollutants emitted indoors to accumulate. However, whilst increasing ventilation rates lowers concentrations of pollutants emitted indoors, in some locations it may also allow the ingress of harmful

pollutants from outdoors, e.g. near a busy road. For instance, Mendell and Heath²⁷ reported indoor/outdoor concentration ratios of outdoor pollutants measured at schools as 0.3-0.8 for ozone and 0.6-0.9 for carbon monoxide. Clearly then, it is important to understand the impact of human occupancy indoors and crucially, the impact ventilation can have on the concentrations of different indoor air pollutants.

In the absence of comprehensive indoor air measurements, indoor air pollutant concentrations and chemical processes indoors can be simulated using models. The aim of this paper is to investigate the impact of high occupancy on indoor air chemistry, using a detailed chemical model for indoors. This work follows on from Kruza et al.³³ which used the same model to investigate the impact of emissions from materials on indoor air chemistry. The main findings were that ozone loss was dominated by deposition onto painted walls, a range of C₆-C₁₀ aldehydes were produced following the deposition process and emissions from these materials promoted the formation of organic nitrates indoors. This work now extends the work of Kruza et al.³³ by examining the chemistry that arises following skin and breath emissions in a classroom in Milan during typical outdoor conditions and for a range of air exchange rates.

2 METHODOLOGY

An Indoor Detailed Chemical Model (INDCM)^{33,34,35} has been developed to investigate human occupancy in the indoor environment. The INDCM uses a comprehensive chemical mechanism called the Master Chemical Mechanism, MCM v3.2³⁶, which considers the chemical degradation of 143 VOCs^{37,38,39}. The degradation of VOCs is initiated by reactions with OH, O₃, NO₃ and photolysis where relevant. Radicals are generated as intermediate products, such as oxy (RO) and peroxy (RO₂) radicals, excited and stabilized Criegee (R'R''COO) species, which can undergo a number of further reactions. A range of

products such as alcohols, carbonyls and nitrates are formed, until carbon dioxide and water are produced. The MCM also includes an inorganic scheme including reactions of ozone, nitrogen oxides (NO_x) and carbon monoxide³⁷. The INDCM includes approximately 20,000 gas-phase chemical and photolysis reactions, as well as a representation of indoor-outdoor exchange, VOC emissions, surface deposition and gas to particle partitioning for limonene³⁵.

The INDCM considers a single well-mixed environment and assumes that the concentration of each species is calculated according to equation 1³⁴:

$$\frac{dC_i}{dt} = -\nu_d \left(\frac{A}{V_i} \right) C_i + \lambda_r f C_o - \lambda_r C_i + \frac{E_i}{V_i} + \sum_{j=1}^n R_{ij} \quad (1)$$

where C_i (C_o) is the indoor (outdoor) concentration of species (molecule cm^{-3}), ν_d its deposition velocity (cm s^{-1}), A the surface area indoors (cm^2), V_i the volume of air in the indoor environment (cm^3), λ_r the air exchange rate between indoors and outdoors (s^{-1}), f the building filtration factor, E_i the indoor emission rate for species i ($\text{molecule cm}^{-3} \text{ s}^{-1}$) and R_{ij} the reaction rate between species i and j ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

Outdoor photolysis rates were calculated following the method described in detail by Carslaw³⁴. Basically, a 2-stream isotropic scattering model uses the longitude, latitude, time of year and day to calculate location and time specific clear-sky photolysis rates³⁷, which are attenuated to be representative for indoors. Values of 10% and 3% respectively for transmission of outdoor visible and UV light are assumed³⁴. The building filtration factor is assumed to be equal to 1⁴⁰.

For this study, the INDCM has been developed to consider ozone deposition onto skin, as well as the subsequent emissions of oxygenated products following skin surface interaction. The ozone loss rate to a skin surface is calculated according to equation 2:

$$F_{skin} = v_{dO_3} \frac{A_s}{V_i} \quad (2)$$

where, F_{skin} is the ozone deposition flux to the skin surface (s^{-1}), v_{dO_3} is the total ozone deposition velocity to the skin surface ($cm\ s^{-1}$), A_s is the skin surface area (cm^2) and V_i is the total volume of the indoor environment (cm^3).

The emission of the skin surface products was calculated using equation 3⁴¹:

$$E_{sec} = \frac{A_s Y C_{O_3} v_{dO_3}}{V_i} \quad (3)$$

where E_{sec} is the secondary product emission rate from the skin surface ($molecule\ cm^{-3}\ s^{-1}$), Y is the yield of the emitted pollutant and C_{O_3} is the ozone concentration at the skin surface ($molecule\ cm^{-3}$). Since degradation schemes for some of the species emitted from skin are not available in the MCM (e.g. geranyl acetone and 6-MHO), this study focuses on those species that are already present, namely acetone, nonanal, decanal, 4-OPA, formic and acetic acids. The inclusion of 6-MHO and geranyl acetone would involve significant new mechanism development. In the case of 6-MHO, we note that Wisthaler and Weschler⁴ concluded from their measurements in a simulated aircraft cabin that most 4-OPA was derived from surface reactions rather than the reaction of 6-MHO with ozone.

The skin surface was defined as 2 m² for an adult and 1 m² for a child⁸. Although some of the skin surface will be covered by clothing, we assume that the rate of ozone deposition and secondary product formation is not significantly different to bare skin^{5,6}. This assumption appears to be reasonable given the good agreements between our model predictions and the measurements of Wisthaler and Weschler⁴ presented in figure 1 in the

model validation section. A median value (calculated based on 12 measurements) of the ozone deposition velocity onto human bodies (0.285 cm s^{-1}) was derived from a literature review^{1,3,4}. Product yields of various species following ozone-skin interactions were measured by Weschler et al.² in an aircraft cabin and were incorporated in this study (table 1).

TABLE 1 Average yields (from 4 experiments) of oxidized products of chemistry following skin emissions following exposure to ozone with a stated uncertainty of 15-25%². Note that the yields of acetone, nonanal, formic and acetic acids have been halved (see text).

| Compounds | Skin emission product yield |
|-------------|-----------------------------|
| Acetone | 0.049 |
| Nonanal | 0.018 |
| Decanal | 0.026 |
| 4-OPA | 0.026 |
| Formic acid | 0.0085 |
| Acetic acid | 0.0065 |

The yields of decanal and 4-OPA reported by Weschler et al.² derive almost exclusively from ozone-skin oil chemistry, but those of acetone, nonanal, formic and acetic acids also reflect emissions from internal surfaces in the aircraft cabin: the yields of the latter four species were therefore halved to represent oxidized products of chemistry following skin emissions only based on the experimental conditions (Professor Charles J. Weschler, EOHSI, Rutgers University, NJ, USA; personal communication).

To calculate breath emissions, this study includes weighted averages from several studies of the major VOCs found in exhaled breath¹⁴. The measured values showed large variations, owing to differences between individual subjects, but also the sampling and measurement methods. For instance, there is a significant difference in the concentration range of VOCs in exhaled breath when the subjects of the study had different occupational

exposures or habits (i.e. smoking). The highest emissions from breath are for acetone, methanol, ethanol, isoprene and isopropanol and we focus on those here.

The review of Fenske and Paulson¹⁴ focused on breath emission concentrations from adults, but there is a substantial difference in metabolic processes between adults and children. Enderby et al.⁴² presented an analysis of VOCs detected in the exhaled breath of 200 children and a summary of the values used for adults and children are presented in table 2. Note that the concentration of isopropanol was not included in the study of Enderby et al.⁴² and was calculated based on correlation with other alcohol species identified in both adults and children.

TABLE 2 Weighted average concentrations of VOCs [ppb] in exhaled breath of adults and children (based on the measurements from 200 children). n.d. indicates no detectable concentration.

| Compound | Adults | | Children |
|-------------|--|------------------------|--|
| | Weighted average concentration (concentration range) (ppb) | Number of subjects (n) | Median concentration (concentration range) (ppb) |
| Acetone | 985 (1.2-1880) | 24 | 297 (89-2342) |
| Ethanol | 770 (13-1000) | 64 | 187 (13-580) |
| Methanol | 330 (1.3-2000) | 68 | 193 (31-685) |
| Isopropanol | 150 (50-260) | 94 | 41 (n.d.) |
| Isoprene | 210 (12-580) | 107 | 37 (n.d.-184) |

The number of breaths per unit time and the volume of each breath vary according to age^{43,44}. Recent research indicates that the tidal volume of a single exhaled breath of an adult is approximately 500 ml and that the adult respiratory rate is 20 breaths per minute⁴⁵. This equates to 167 ml s⁻¹ of expired air for adults. For a healthy 10 year old child, the respiratory

rate is typically 20 breaths per minute, with a tidal volume of approximately 10 ml kg⁻¹ of body weight⁴³. The average weight of a 10-year old child is 31.2 kg²⁴. Accordingly, the calculated expiration rate for a child is 104 ml s⁻¹.

The emission of VOCs from exhaled breath in the indoor environment is calculated according to equation 4:

$$E_{VOC} = \frac{V_t * C_t * n * N_A}{V_m * V_i * 10^{18}} \quad (4)$$

where E_{voc} is the relevant VOC emission rate from exhaled breath (molecule cm⁻³ s⁻¹), V_t is the breathing rate of an individual (ml s⁻¹), C_t is the weighted average concentration of a particular species in a single breath (ppb), n is number of people indoors, N_A is the Avogadro constant (6.02 x 10²³ molecule mol⁻¹), V_m is the molar gas volume (22.4 litres mol⁻¹ at room temperature and pressure), V_i is the room volume (m³) and 1x10¹⁸ provides the necessary unit conversion.

The impact of human emissions in a classroom was investigated, assuming thirty 10 year old pupils and one teacher. We adopted the measurements carried out in 51 French classrooms described by Canha et al.⁴⁶, whereby the median volume of the classroom was 171 m³. The school day was assumed to run from 09:00-15:00h with an hour lunch break at noon. Canha et al.⁴⁶ indicated that 73% (n= 37) of the studied classrooms had natural ventilation and 27% (n=14) had a mechanical ventilation system, so this study focuses on classrooms with natural ventilation. The mean measured values of the indoor temperature, indoor relative humidity (RH) and air exchange rate (AER) were ~23.3°C, 47% and 1.2±0.6 per hour respectively⁴⁶.

Emissions from skin for the classroom occupants were calculated according to equation 3. With 30 children and one adult, the total surface area of skin was 32 m², and the surface to volume ratio (A/V) of skin ~0.19 m⁻¹. The breath emission rates of 30 children and one adult were calculated according to equation 4 and are presented in table 3.

TABLE 3 Emission rates of VOCs [ppb s⁻¹] calculated for exhaled breath in the classroom.

| Compound | VOC emission rate of 30 children [ppb s⁻¹] | VOC emission rate of one adult [ppb s⁻¹] |
|-----------------|--|--|
| Acetone | 5.83 x 10 ⁻³ | 1.03 x 10 ⁻³ |
| Ethanol | 3.67 x 10 ⁻³ | 8.08 x 10 ⁻⁴ |
| Methanol | 3.79 x 10 ⁻³ | 3.46 x 10 ⁻⁴ |
| Isopropanol | 8.04 x 10 ⁻⁴ | 1.57 x 10 ⁻⁴ |
| Isoprene | 7.26 x 10 ⁻⁴ | 2.20 x 10 ⁻⁴ |

Along with emissions from skin and breath, those from other internal surfaces (linoleum, wood or painted wall) were included as described by Kruza et al.³³, using a similar process to that described above for skin emissions. The internal materials in the classroom considered as a source of ozone-derived surface emissions (and hence competing with skin surface for ozone removal) included: linoleum on the floor (58 m²); painted wall (~138 m²); wooden furniture such as the desks, chairs and the internal door (~25 m²)⁴⁶. The total surface area available for ozone-initiated chemistry in the classroom including 30 children, the teacher and internal materials amounts to 252.6 m², with a total surface to volume ratio of ~1.48 m⁻¹.

The outdoor NO_x and O₃ concentrations were based on those from an urban area (Milan) in the summer of 2009 as described by Terry et al.⁴⁷ and are shown in Supplementary Information (Figure S1). The outdoor VOC concentrations (listed in Table S1 in Supplementary Information) were available from the EU OFFICAIR project⁴⁸ or set to typical outdoor values in an urban area^{49,50}. Of relevance to this study, the mean outdoor

concentrations of acetone, methanol, isoprene, isopropanol and ethanol were set to be 7.95, 4.40, 1.90, 1.90 and 63.70 $\mu\text{g m}^{-3}$ respectively.

3 RESULTS AND DISCUSSION

3.1 Model validation

In order to test the model framework, we have used it to simulate the conditions described in Wisthaler and Weschler⁴ and Weschler⁷. A simulated aircraft cabin was reconfigured to represent an office with a carpeted floor. The walls and ceiling of the ‘office’ were panels from a used aircraft interior and were likely to be relatively inert when clean, but more reactive towards ozone over time as they became covered with skin flakes and oil. It is reasonable to assume that the ozone reactivity of the walls and ceiling was much less than that of the carpet and, to a first approximation, can be ignored (Professor Charles J. Weschler, EOHSI, Rutgers University, NJ, USA; personal communication). Therefore, the deposition velocity of ozone onto the aircraft walls was set to zero in the model and onto carpet at 0.15 cm s^{-1} ³³, but all other parameters are defined as described above.

Two occupants (without having showered or used personal care products) entered the office at around 10:00 h and then left at around 14:00 h. The concentrations of ozone and 4-OPA were measured over this time period. The 4-OPA concentration reached ~2 ppb whilst ozone decreased to 17 ppb⁷. The model predicts a 4-OPA concentration of ~2 ppb, with a final ozone concentration of 23 ppb (figure 1).

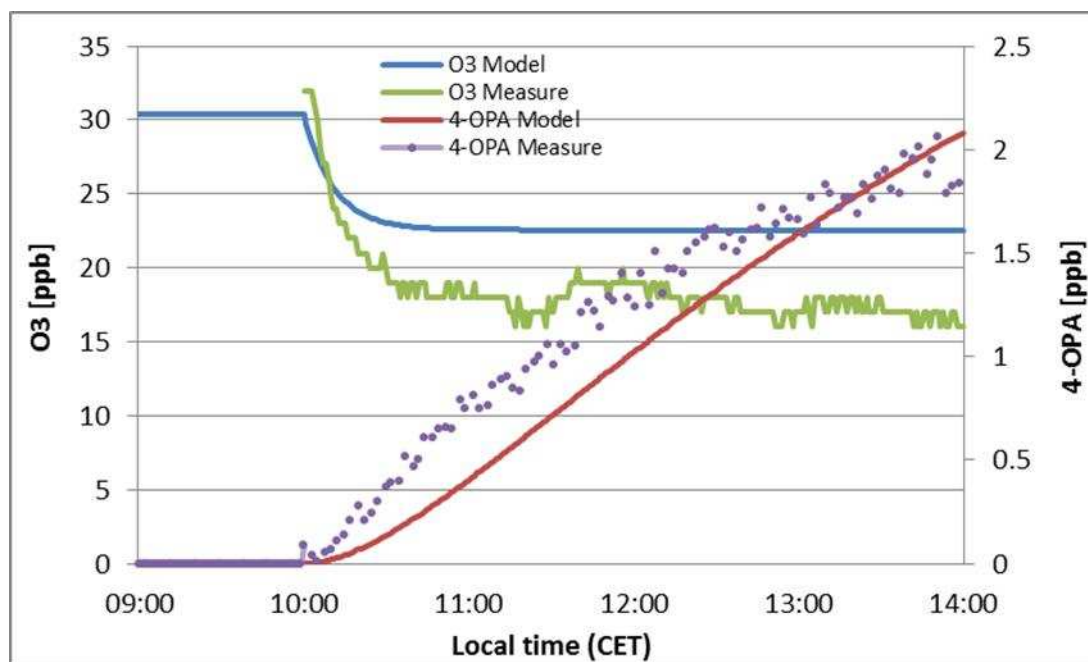


FIGURE 1 Comparison of the measured⁴ and modelled concentration profile of ozone and 4-OPA [ppb] in the simulated office.

The modelled 4-OPA concentration profile shows reasonable agreement with the measured values. There is less ozone removed than observed, but there is likely to be some additional deposition to the walls that we have not considered here that would improve the model-measured agreement. Further, there is no information available about indoor and outdoor NO_x and VOC concentrations during this experiment. Therefore, this degree of agreement seems reasonable and provides confidence that the model framework is suitable for further investigation of the impacts of occupancy on indoor air chemistry.

3.2 Model sensitivity analysis

Given the uncertainty in the input parameters, a series of sensitivity tests have been carried out to investigate the effect of changing key parameters on the predicted concentrations of the species following skin and breath emissions. Transmission of outdoor UV and visible light through the windows were varied between 0.15% and 25% for UV light and between 0.7% and 75% for visible light.³⁴ Ozone deposition velocities onto skin were varied to the 25

percentile (0.2 cm s^{-1}) or the 75 percentile (0.4 cm s^{-1}) values of the range reported in Kruza et al.³³ Given that there are fewer measurement values, outdoor concentrations of isoprene, skin emission product yields and breath emission concentrations were either decreased or increased by 50%. For the latter two parameters, the values of all species were increased or decreased by 50% together. The concentrations of the skin and breath emission products predicted by the model were then investigated for 9:00-15:00 h excluding an hour lunch break, relative to baseline conditions. The results from the sensitivity analysis are shown in table 4.

TABLE 4 Sensitivity test results: the % change in concentrations of products arising from skin and breath emissions, in an occupied classroom in Milan during typical summer conditions (air exchange rate = 1.2 h^{-1}) for 9:00-15:00 h (excluding an hour lunch break), relative to baseline conditions, as well as the estimated overall uncertainty for each species based on these tests.

| Scenario | Nonanal | Decanal | 4-OPA | Formic acid | Acetic acid | Acetone | Methanol | Ethanol | Isopropanol | Isoprene |
|--|---------|---------|-------|------------------|-------------|---------|----------|---------|-------------|----------|
| UV=0.15%, VIS=0.7% | -2.5 | -3.4 | -9.7 | -9.9 | -9.6 | -0.8 | 0.1 | 0.1 | 0.1 | 2.7 |
| UV=25%, VIS=75% | 13.5 | 18.4 | 53.7 | 57.0 | 55.1 | 4.4 | -0.1 | -0.3 | -0.5 | -13.5 |
| ν_d skin = 0.2 cm s^{-1} | -1.4 | -4.6 | -42.0 | -41.4 | -38.3 | -2.7 | -0.1 | -0.1 | -0.1 | -0.4 |
| ν_d skin = 0.4 cm s^{-1} | 2.5 | 7.0 | 59.0 | ⁵⁷ .8 | 53.7 | 3.9 | 0.1 | 0.1 | 0.1 | 0.5 |
| Outdoor isoprene*0.5 | -0.1 | -0.1 | -0.2 | -0.2 | -0.2 | -0.1 | -0.1 | -0.1 | -0.1 | -12.1 |
| Outdoor isoprene*1.5 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 0.1 | -0.1 | -0.1 | -0.1 | 12.1 |
| Skin emission product yield*0.5 | -2.9 | -6.3 | -43.7 | -43.3 | -40.6 | -2.9 | -0.1 | -0.1 | -0.1 | -0.1 |
| Skin emission product yield*1.5 | 2.3 | 5.0 | 34.5 | 33.9 | 31.9 | 2.3 | -0.1 | -0.1 | -0.1 | 0.1 |
| Breath emissions*0.5 | -0.1 | -0.2 | -0.4 | -0.5 | -0.4 | -38.3 | -38.1 | -12.7 | -37.7 | -38.0 |
| Breath emissions*1.5 | 0.1 | 0.2 | 0.5 | 0.6 | 0.4 | 38.4 | 38.1 | 12.7 | 37.7 | 38.1 |
| Estimated uncertainty | 27 | 37 | 107 | 116 | 110 | 77 | 76 | 25 | 75 | 76 |

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These sensitivity tests provide an estimate of the likely range of predicted model concentrations for the species of interest in this study. The largest source of uncertainties in the model output are driven by the uncertainty in the assumed deposition velocity onto skin, the yield of production following deposition onto skin and the indoor photolysis rates. The uncertainties for the breath emissions species are generally lower than those from skin emissions. Based on these results, we estimate conservatively that the model uncertainty is double that for the largest individual source of uncertainty for each species, ranging from 27-116% as shown in the last line of table 4.

3.3 Skin emissions

The indoor air quality for a naturally ventilated (AER 1.2 h⁻¹) classroom during school hours (09:00-15:00h) with a 1-hour lunch break (12:00-13:00h) was investigated, assuming that 30 children and one teacher were present in the classroom. The concentrations of ozone and ozone-derived oxygenated products following skin emissions for typical summer conditions are shown in figure 2.

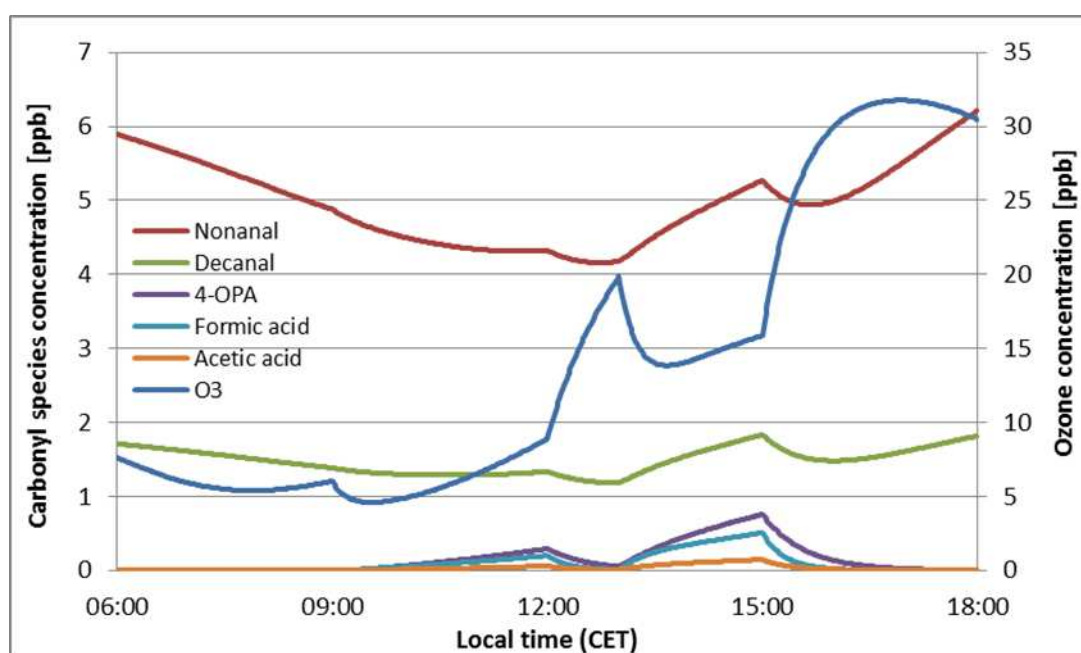


FIGURE 2 Diurnal profile of the concentrations of ozone and carbonyl species following skin emissions (and other internal surface emissions for nonanal and decanal) in the classroom during typical summer conditions (air exchange rate = 1.2 h^{-1}).

Oxidized products of chemistry following skin emissions increase when occupants are in the classroom (09:00-12:00h and 13:00-15:00h), although concentrations of carboxylic acids and 4-OPA are relatively low (up to ~ 0.8 ppb during typical summer conditions and up to ~ 1.3 ppb during the extreme summer conditions (not shown)). Nonanal and decanal concentrations are enhanced with occupants, though these species derive mainly ($\sim 90\%$) from material rather than human emissions in the classroom. Prior to the occupants arriving (after they leave) the concentration of these two species decreases (increases) because the OH concentration is increasing (decreasing).

Liu et al.⁵¹ reported measurements of carboxylic acids in a university classroom. The measured concentration of formic acid was in the range of 0.2-3.5 ppb, whereas the predicted range of concentration from the model was 0.2-0.5 ppb. Fischer et al.⁸ presented averaged measured 4-OPA concentrations of 0.5-0.7 ppb in an occupied school classroom (24 pupils), compared to the modelled range here of 0.2-0.7 ppb.

There is substantial variation in the ozone concentration in the classroom, which reflects the outdoor profile (figure S1). The average outdoor O_3 concentration during school hours was 43.4 ppb. Indoors, the concentration was 15.2 ppb on average for the periods without occupants and 9.6 ppb when they are present. There is a clear increase in O_3 concentration when the pupils are at lunch (from ~ 9 ppb to ~ 20 ppb in figure 2). When the occupants return to the classroom after the break, the ozone concentration decreases to ~ 14 ppb. When the school day finishes at 3 p.m. there is again an increase in the ozone concentration, as ozone rich air from outdoors replenishes the supply indoors (outdoor concentrations of ozone peak at 4 p.m.). Note that we repeated these simulations for more polluted conditions, based on outdoor concentrations measured during a heatwave in 2003

(outdoor ozone concentration profile shown in Figure S2 in Supplementary Information). The results showed similar % reductions and increases in ozone concentrations as pupils entered and left the classroom, despite the much higher ozone concentrations outdoors and indoors.

Fischer et al.⁸ measured ozone loss of $6.3 \times 10^{-4} \text{ s}^{-1}$ in an occupied (24 pupils and one teacher) classroom (volume = 182 m^3) in semi-rural area in Sweden, whereas in our study (volume = 171 m^3) it is $7.8 \times 10^{-4} \text{ s}^{-1}$. Each person in the classroom in the study of Fischer et al.⁸ removed ozone at a rate of $2.5 \times 10^{-5} \text{ s}^{-1}$ and in our study with a rate of $1.8 \times 10^{-5} \text{ s}^{-1}$. Therefore, our results seem to be in reasonable agreement with the Fischer et al.⁸ study.

3.4 Breath emissions

Figure 3 shows the diurnal profile of modelled VOCs due to breath emissions in the classroom for typical summer conditions with natural ventilation ($\text{AER} = 1.2 \text{ h}^{-1}$). Again, the concentrations increase when the occupants enter the classroom at 9:00 a.m., then decrease when children leave the classroom for an hour lunch break (12 p.m.).

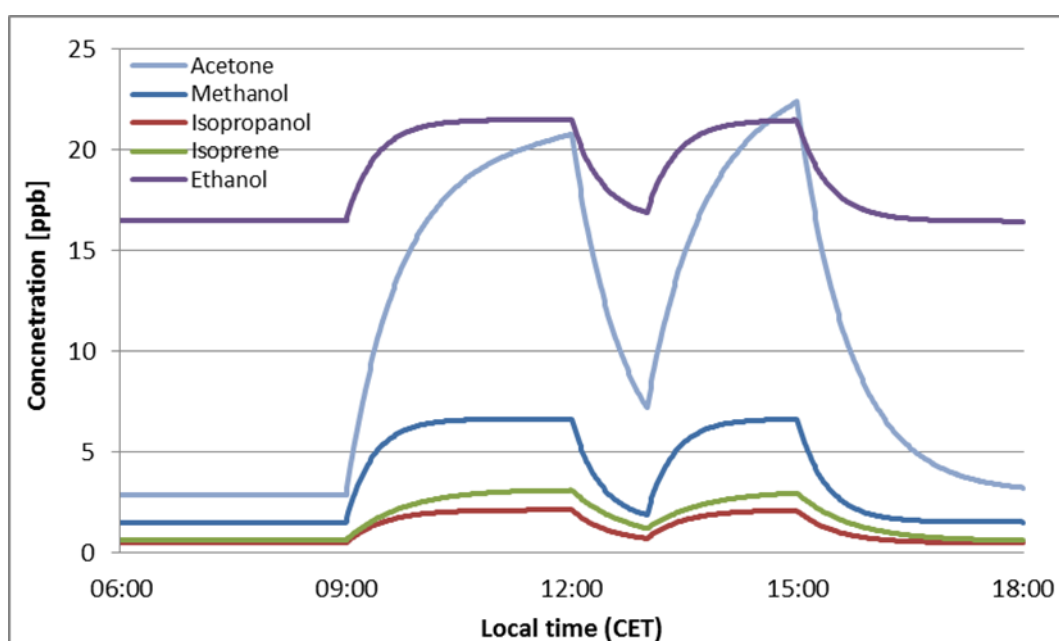


FIGURE 3 Diurnal profile of the modelled concentrations of VOCs from breath emissions [ppb] in the classroom during typical summer conditions and with natural ventilation (air exchange rate = 1.2 h⁻¹).

Acetone shows the most significant variation in concentration with occupancy, increasing from ~3 ppb before the children enter the classroom up to ~22 ppb at the end of the day. Note that the acetone concentration profile in figure 3 includes skin and breath emissions together but breath emissions contribute ~90% to the total. The concentrations of methanol and ethanol increase from ~2 to 7 ppb and from ~16 to 22 ppb respectively when pupils are present.

It is interesting to explore the effect of ventilation on emissions from skin and breath. For breath emissions, there is a negative relationship between the air exchange rate and resultant concentrations, as higher ventilation rates dilute breath emissions as shown for isoprene in figure 4. However, skin emissions products are ozone-derived species and higher ventilation rates lead to higher indoor ozone concentrations, as indoor ozone derives largely from outdoors in the absence of indoor sources such as photocopiers and laser printers⁵². Consequently, the concentrations of species derived from oxidized products of chemistry following skin emissions increase with ventilation, but only up to the point where production exceeds the loss to dilution at higher exchange rates. It can be seen from figure 4 that 4-OPA increases as AER increases from 0.2 to 1.2 h⁻¹, but then decreases thereafter.

So far we have focused on skin and breath emissions, rather than including additional emissions that may arise following the use of personal care products, such as fragrances and body sprays. Tang et al.⁵³ measured mixing ratios of selected VOCs in a university classroom and also the emission rates/person based on these concentrations. The measurements were conducted over a two-week period on five weekdays (during 08:00-20:45h) when at least 17 adult occupants were present in the classroom. The volume of the classroom was 670 m³ and air exchange rate with the use of mechanical ventilation was 5.0 ± 0.5 h⁻¹. The study

presented time-series measurements of VOCs, CO₂ and O₃, sampling the classroom and supply air six times per hour.

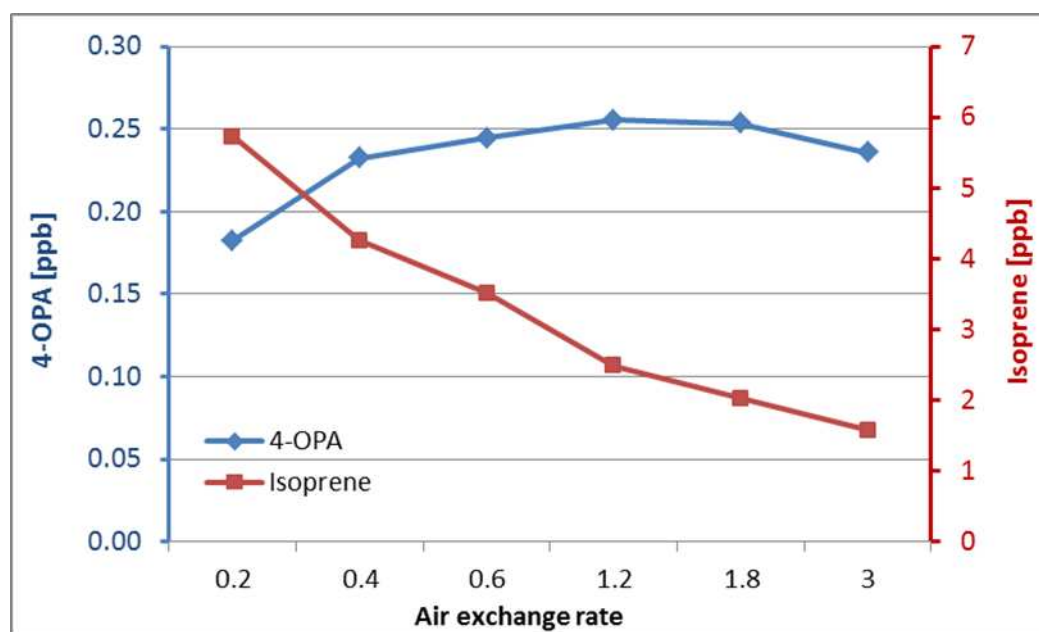


FIGURE 4 Modelled 4-OPA and isoprene concentrations following skin and breath emissions respectively [ppb] in the classroom during typical summer conditions for different air exchange rates.

The calculated VOC emission rates by Tang et al.⁵³ were ~50-100 times higher than those used to drive the model runs described here. In fact, there was a clear decline in emissions over the course of the day, as the personal care products worn by the students gradually degassed from their bodies⁵³. Given that the model described here accounted only for the ‘natural’ human emissions, it can be estimated that these emissions were only~ 5% of the total human emissions, presented by Tang et al.⁵³, which included personal care products.

To test the sensitivity of the model to higher emissions rates which also include the use of personal care products, we increased our calculated emission rates by 50% and 100% and then compared the results to those we presented earlier (table 5).

The increase in emission factors enhances the production of oxygenated products indoors, particularly for those species that are mainly derived from occupants (e.g. 4-OPA, formic and acetic acids, acetone, methanol, isopropanol and isoprene), whilst those that are dominated by internal material emissions (nonanal, decanal) or outdoor concentrations (ethanol) are less sensitive to changes. Clearly, the use of personal care products can have a large impact on the resulting concentrations in an indoor environment such as a classroom.

TABLE 5 Sensitivity test results: the % change in concentrations of the species following increases to baseline skin and breath emissions in the classroom in Milan for typical summer conditions (AER=1.2 h⁻¹) during school hours when the occupants were present.

| Scenario | Nonanal | Decanal | 4-OPA | Formic acid | Acetic acid | Acetone | Methanol | Ethanol | Isopropanol | Isoprene |
|------------------------|---------|---------|-------|-------------|-------------|---------|----------|---------|-------------|----------|
| Human emissions * 50% | 2.4 | 5.2 | 35.1 | 34.6 | 32.4 | 40.6 | 38.1 | 12.7 | 37.7 | 38.1 |
| Human emissions * 100% | 4.4 | 9.4 | 63.6 | 62.5 | 58.6 | 80.9 | 76.2 | 25.3 | 75.5 | 76.3 |

3.5 Impact of human occupancy on chemical processing in the classroom

Table 6 presents a detailed comparison of average oxidant concentrations for an occupied and an unoccupied classroom during the school day during typical and polluted summer conditions. Outdoor ozone concentration and hence indoor ozone concentrations were elevated during the latter episode, making such conditions ideal for the study of reactive chemistry indoors. The unoccupied classroom was a model simulation of the furnished classroom without the occupants. The concentrations of O₃, OH, HO₂ and RO₂ for the unoccupied classroom were higher compared to the occupied classroom. Weschler⁷ suggested that the presence of humans in a building would decrease the net level of oxidants, as ozone is deposited onto skin. However, these results also confirm that the OH, HO₂ and RO₂ radical concentrations decrease with occupancy, across a range of ventilation rates and outdoor

conditions. During typical summertime conditions and for an AER of 1.2 h^{-1} , the concentration of O_3 , OH, HO_2 , RO_2 decrease by ~40%, 16%, 32% and 44% respectively for the occupied versus unoccupied classroom.

TABLE 6 Average oxidant concentrations for occupied and unoccupied classroom (during typical and polluted summer conditions) and different air exchange rates (0.6 ; 1.2 ; 1.8 h^{-1}) for 9:00-15:00 h excluding the lunch break. Ozone concentrations are given in ppb, OH in units of $10^5 \text{ molecule cm}^{-3}$, both HO_2 and RO_2 in ppt.

| | | Typical summer conditions | | | Polluted summer conditions | | |
|---------------|--------------|---------------------------|------|------|----------------------------|------|------|
| | | AER (h^{-1}) | | | AER (h^{-1}) | | |
| | | 0.6 | 1.2 | 1.8 | 0.6 | 1.2 | 1.8 |
| O_3 | No occupants | 12.4 | 15.9 | 18.3 | 20.3 | 27.8 | 33.2 |
| | Occupants | 6.6 | 9.6 | 11.9 | 10.7 | 16.4 | 20.6 |
| OH | No occupants | 4.0 | 4.5 | 4.7 | 4.4 | 5.0 | 5.2 |
| | Occupants | 3.2 | 3.8 | 4.0 | 3.6 | 4.2 | 4.5 |
| HO_2 | No occupants | 5.4 | 3.4 | 2.8 | 7.3 | 5.1 | 4.3 |
| | Occupants | 3.6 | 2.3 | 1.9 | 5.1 | 3.6 | 3.1 |
| RO_2 | No occupants | 10.6 | 6.1 | 4.7 | 16.3 | 10.5 | 8.6 |
| | Occupants | 5.6 | 3.4 | 2.8 | 8.4 | 5.6 | 4.8 |

The higher the air exchange rate, the higher the indoor concentrations of O_3 , NO_2 and NO. The OH radical concentration increases along with the higher air exchange rate, as more OH can be formed through ozone oxidation of terpenes. However, the concentrations of HO_2 and RO_2 are suppressed by higher NO_x concentrations indoors as the AER increases. Therefore, the concentrations of HO_2 and RO_2 decrease, while those of ozone and OH radicals increase with AER.

Figure 5 presents the reaction rates for (i) the unoccupied classroom and for (ii) the occupied classroom (in units of 10^4 molecule cm^{-3} s^{-1}) for typical summer conditions and an AER of 1.2 h^{-1} . When the occupants are present, O_3 and hence OH concentrations are lower as discussed above. Thus the propagation reaction of OH with alkanes, alkenes, dicarbonyls and aldehydes become less important and the production rate of RO_2 radicals also decreases. However the reaction rate of OH with isoprene is enhanced given that there is a higher concentration of isoprene when the occupants are present in the classroom. When OH reacts with aldehydes, acyl peroxy radicals are formed, which then react with NO_2 to form PAN (peroxy acetyl nitrate)-type species. When isoprene reacts with OH on the other hand, alkyl peroxy radicals are formed which can then react with NO to form organic nitrates. Therefore, as more OH reacts with isoprene and less with aldehydes, the termination products of RO_2 shift more towards organic nitrates and away from PANs.

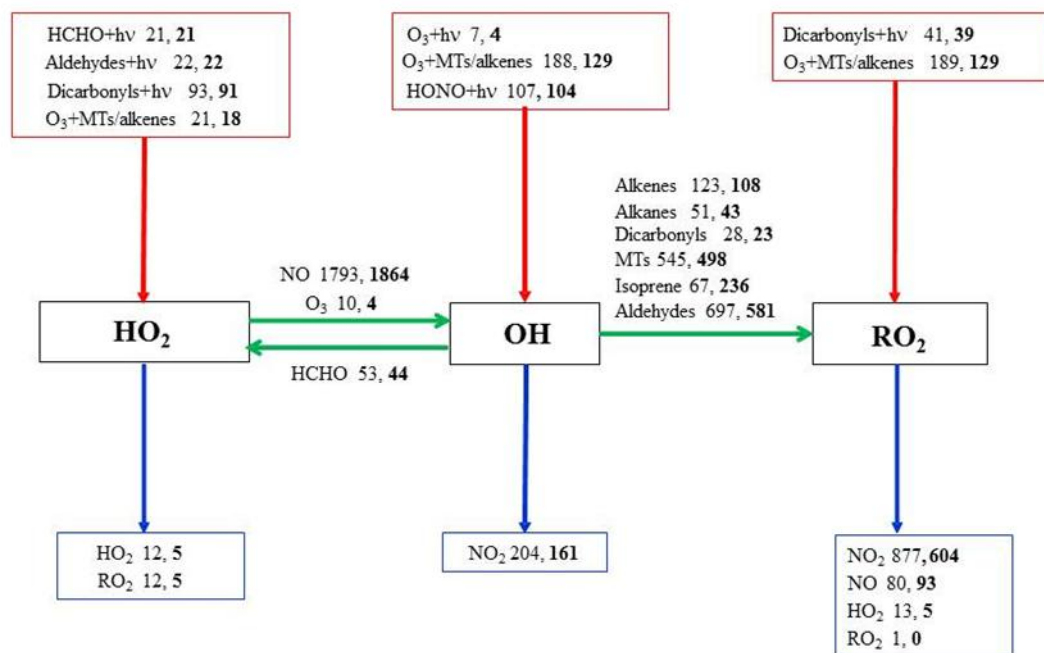


FIGURE 5 Simplified rate of production analysis for the major rates of reaction for the unoccupied classroom (figures in normal font) and the occupied classroom (figures in bold) in Milan during

typical summer conditions ($AER = 1.2 \text{ h}^{-1}$) in units of $10^4 \text{ molecule cm}^{-3} \text{ s}^{-1}$. MTs denotes monoterpenes. Red arrows denote radical initiation processes, blue arrows are termination processes with green arrows representing radical propagation.

We also compared RO_2 composition in the occupied and unoccupied classroom. The main difference between the two scenarios is that RO_2 produced from isoprene oxidation become more important (increased from ~ 2 to 9% of the total) when occupants were in the room and those produced from limonene oxidation become less important (decreased from ~ 42 to 34% of the total) as expected from the rate of production analysis in figure 5. Isoprene reacts more slowly than limonene with both OH and ozone. Therefore as isoprene becomes more important, fewer RO_2 radicals are formed (table 6) and the feedback to OH radicals via VOC oxidation by ozone also becomes less significant (figure 5). Clearly, occupancy affects both quantity and composition of radicals indoors.

Finally, we investigated the different loss processes for ozone in the occupied classroom (table 7). The results show that for the average AER of 1.2 h^{-1} , loss of ozone is dominated by reaction with NO (39%), deposition to the occupants ($\sim 29\%$) and the internal materials ($\sim 13\%$), and air exchange (18%) with minor contributions from reactions with limonene and NO_2 . However, at the lower AER of 0.6 h^{-1} , deposition became relatively more important with 37% to occupants, 17% to internal materials, $\sim 33\%$ through reaction with NO and $\sim 12\%$ through air exchange. Therefore, the removal of ozone by occupants is the most important removal process for ozone for this low air exchange rate under our study conditions.

TABLE 7 The rate of ozone loss [%] to different pathway processes for a range of air exchange rates (0.6; 1.2; 1.8 h⁻¹).

| | AER (h ⁻¹) | | |
|---------------------|------------------------|------|------|
| | 0.6 | 1.2 | 1.8 |
| NO | 32.5 | 39.0 | 39.7 |
| NO ₂ | 0.5 | 0.6 | 0.6 |
| Limonene | 1.6 | 0.8 | 0.5 |
| Material deposition | 16.6 | 12.9 | 11.1 |
| Human deposition | 37.3 | 28.9 | 25.0 |
| Exchange | 11.5 | 17.8 | 23.1 |

4 CONCLUSIONS

This study has examined the changes in indoor air chemistry when occupants are present in a classroom. The model results show that people can remove a significant quantity of indoor ozone, just by being present and particularly when the air exchange rate is low. Also, occupants in a building can deplete oxidants and affect the concentration and composition of radicals and nitrated organic material. The results also demonstrate the importance of ventilation rate: whilst higher ventilation rates can provide more ozone to indoor environments and aid surface production of secondary species such as on the skin surface, there is also more dilution of the products under these conditions and also of emissions from breath. Therefore, the point at which maximum impact from human emissions can be found on indoor concentrations will be a function of the number of occupants, the ventilation rate and the dimensions of the room and the other indoor surfaces.

Highly occupied indoor environments, such as classrooms, could experience relatively high concentrations of species derived from human emissions indoors. Such concentrations could be a concern for human health, though there is relatively little known about the toxicological effects of many of these pollutants at present. In addition, there is increasing evidence that there may be many more VOCs emitted from skin than those we consider here: future model simulations will need to consider more of this newly available information⁵⁴. Finally, occupants also add to the reactivity of surfaces via transferring skin oils to surfaces, and through cooking or cleaning activity⁷. Such processes may result in increased reactivity of indoor surfaces over time. In the future, models will benefit from more extensive field measurements of indoor air chemistry in occupied homes, as well as information on surface interactions for indoor pollutants other than ozone. More comprehensive information on emissions from breath would also be beneficial.

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