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Article

Emissions of Volatile Organic Compounds from Human Occupants in a Student Office: Dependence on Ozone Concentration

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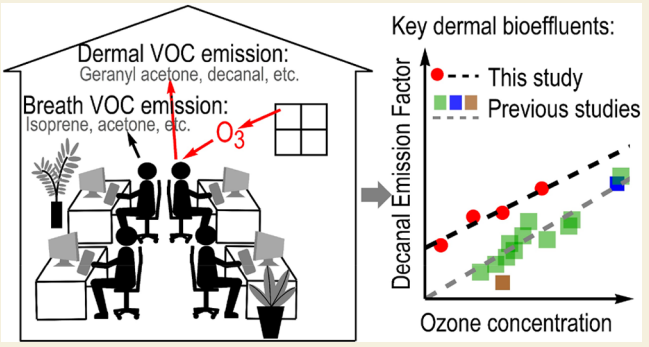
ABSTRACT: Human occupants themselves constitute an important source of volatile organic compounds (VOCs) in indoor environments through breath and dermal emissions. In order to quantify VOC emissions from occupants under real-world settings, previous indoor observational studies often determined emission factors (i.e., average emission rates per person). However, the values obtained across these studies exhibited large variability, and the causes of this variability still need to be understood. Herein we report 10-day real-time VOC measurements in a university student office, using a proton transfer reaction-quadrupole interface-time-of-flight mass spectrometer. A method was developed to identify VOCs of primary human origin and to quantify the corresponding emission factors, accounting for the dynamically changing occupancy level and ventilation rate in the assessed office. We found that the emission factors of many dermally emitted VOCs strongly increased as the ozone concentration increased from <3 to 10−15 ppb. These VOCs include geranyl acetone, 6-methyl-5-hepten-2-one (6-MHO), and C_{10}-C_{12} saturated aldehydes, which align with characteristic first-generation ozonolysis products of skin oil. The strongest increase occurred for 6-MHO, from 113 to 337 μg/h/p. In comparison, acetone and isoprene, which are primarily emitted from human breath, varied little with the ozone level. In light of this finding, we conducted an integrated analysis of emission factors reported in the literature for two frequently reported species, namely, 6-MHO and decanal. Ozone concentration alone can explain 94−97% of the variation in their emission factors across previous studies, and the best-estimated ozone dependence obtained using the literature data is consistent with those obtained in the current study. These results suggest that the ozone concentration is a key factor regulating emission factors of many dermally emitted VOCs in real indoor environments, which has to be considered when reporting or using the emission factors.



KEYWORDS: *ozonolysis, indoor, bioeffluents, air quality, exposure*

INTRODUCTION

Human occupants continuously emit volatile organic compounds (VOCs) into the indoor air from exhaled breath and skin. Such emission has been considered the primary contributor to unpleasant odor and poor perceived air quality in densely occupied indoor environments,[1] and has driven the development of indoor ventilation standards on a per-person basis.[2] The variety of VOCs emitted from the human body is extensive.[3] Commonly observed species include isoprene and acetone, primarily originating from exhaled breath,[4] as well as 6-methyl-5-hepten-2-one (6-MHO), 4-oxopentanal (4-OPA), geranyl acetone, and straight-chain aldehydes, predominantly released from the skin.[5] Some of the emitted VOCs are odorous (e.g., decanal),[6] some are irritating (e.g., 4-OPA),[7] some can further react with ozone in the indoor air to produce OH radicals (e.g., 6-MHO and geranyl acetone)[8] and to form secondary organic aerosol (e.g., geranyl acetone),[9] and many contribute to OH reactivity of the indoor air.[10,11] It is thus necessary to quantify VOC emissions from the human body at the species level.

An increasing number of indoor observational studies have investigated VOC emissions from the human body in real-world indoor environments. These observations were mainly conducted in densely occupied public spaces, such as commercial airplane cabins,[12−16] football stadiums,[17] classrooms,[18−20] movie theaters,[21] art museums,[22] gyms,[23] and office buildings.[24] A few other studies also observed human

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emissions in indoor spaces with lower occupancy, such as normally occupied residences[25] and test houses.[26] Results of these studies have confirmed that VOC emissions from the human body are substantial or even the dominant VOC source in indoor environments. Many studies further employed mass balance techniques to estimate speciated emission factors (i.e., average emission rates per person) based on measured VOC concentrations.[5,18−24,26] This simple metric serves to quantify VOC emissions from the human body and holds implications for their application in indoor air quality models.[18−20,24] There are, however, substantial variabilities in the values of the emission factors obtained across the existing observational studies. For example, the reported emission factor of 6-MHO ranged from 3 μg/h/p[21] to over 800 μg/h/p,[17] and that of decanal ranged from not detected[20] to over 300 μg/h/p,[17] both showing a difference of 2 orders of magnitude. These discrepancies hinder the direct application of these emission factors in indoor air quality models.

Various factors might contribute to the observed discrepancies. Measurement uncertainties might play a role, since concentrations of many VOCs were semiquantified in these studies (i.e., without calibration using authentic standards).[5,18−24,26] Additionally, some previous studies suggested potential impacts of variations among human occupants, stemming from factors such as age,[21] physical activity level,[23] clothing,[3,11] and inherent individual differences.[27] Furthermore, some environmental factors, such as temperature,[3,11] relative humidity,[3,11] and ozone concentration,[3,28,29] might also be important. Among the myriad of factors, the indoor ozone concentration is of particular importance. Many dermally emitted VOCs can originate from the reactions of ozone with reactive constituents in skin lipids, in addition to the metabolic processes within the human body. For example, ozonolysis of squalene forms acetone, 6-MHO, and geranyl acetone as the major first-generation volatile products, and 4-OPA as a key second-generation product.[30] Ozonolysis of unsaturated fatty acids and triacyl glycerols produces a range of straight-chain aldehydes. Controlled chamber experiments using human subjects have demonstrated that the emission factors of many VOCs, such as 6-MHO, 4-OPA, and decanal, are higher at high ozone levels compared with those at low ozone levels.[3,13,29] For example, Wang et al. reported a 6-MHO emission factor of 19 μg/h/p at near-zero ozone (<1 ppb) and of 430 μg/h/p at ∼36 ppb ozone;[3] our recent study further showed that the emission factors of most skin oil oxidation products linearly depended on ozone concentration.[29] Nevertheless, few studies have quantitatively examined the ozone dependence in real-world settings so far.

Herein we report VOC measurements in a normally occupied student office with a dynamically changing occupancy level and ventilation rate. A method was developed based on the obtained data feature to identify VOCs mainly emitted from human occupants and to quantify their emission factors. Taking advantage of the large natural variability of indoor ozone concentration during the observation period, we assessed how the indoor ozone concentration regulated the VOC emission factors from the human body. Based on the findings, we further integrated the existing literature data to explore the extent to which ozone dependence can explain the variability in emission factors reported in previous studies.

MATERIALS AND METHODS

Overview of the Observational Study

Continuous observation was conducted in an office building at Peking University, Beijing, China for one and a half weeks in April, 2019. Five sampling locations were chosen, including two faculty offices, one student office, the corridor, and the outdoor. Current analysis focuses on the data collected from the student office because it was densely occupied and hence the VOC emissions from occupants were stronger. To illustrate this point, Figure S1 shows the time series of a known human bioeffluent measured at all five locations during the whole observation period.

The volume of the student office is ∼70 m^3. It is simply furnished with PVC flooring and a foam ceiling. There are 10 workstations, a small fabric sofa, a compact refrigerator, a potted plant, and several cardboard boxes in the office. Eight young adults, all in their 20s, worked in the office, and up to six were present in the office simultaneously during the observation period. To monitor VOCs in real-world settings, no deliberate cleaning of surfaces took place before or during the observation and no interventions were made to control the daily activities of the occupants. The office has no mechanical ventilation system. Natural ventilation can occur through the door to the corridor and a window to the outdoors. Sensor measurements indicate that the door was sometimes open during occupancy, for 1−8 h per day, and generally closed during vacancy at night (Figure S2). The window was open for the majority of the time, with only a few exceptions (Figure S2). The air conditioner was not operated.

Concentrations of trace gases, including VOCs, CO_2, and O_3, were monitored. CO_2 concentrations were measured with a 5 min time resolution using portable sensors (AZ Instrument, China; Model 7798) deployed at individual sites. Specification of the sensor is provided in the SI. Concentrations of VOCs and O_3 were measured using a proton-transfer-reaction quadruple-interface time-of-flight mass spectrometer (PTR-Qi-ToF; IONICON Analytic GmbH, Austria) and an ozone monitor (Thermo Scientific; Model 49i), respectively, by switching between sampling locations. The two instruments were situated in a faculty office, and separate sampling lines (1/4" OD PFA tubing) were installed to actively draw air from the other locations at an approximate flow rate of 2 L/min. During most of the observation period, air was subsampled from each of the five sampling locations for 6 min sequentially using a multiple-way solenoid valve (inner surface with PTFE), and the measurement cycle was repeated every 30 min. To enhance the temporal resolution of VOC data in the student office, measurements were alternated between the student office (50 min) and the outdoor (10 min) for a two-day period during the latter observation phase. Data of the initial 2 min following each switch were excluded in the analysis, to mitigate measurement errors resulting from the alternation between sampling points.

Additional supplementary data were collected to aid in the interpretation of the observational results. An inert tracer, deuterated butane ($C_4H_5D_3$), was constantly released in the student office and measured using PTR-Qi-ToF. This tracer was employed to monitor ventilation rates, using a method described in a previous study.[31] Wireless sensors (Aqara; Model MCCGQ11LM) were installed to monitor the open/closed state of the doors and windows. Temperature and humidity were measured using the same portable sensors for CO_2 measurements. Additionally, occupants were required to maintain a daily record documenting their presence and activities in the office.

VOC Measurements and Calibration

The PTR-Qi-ToF employed for online VOC measurements in this study comprises an ion source, drift tube, ion interface, and mass analyzer.[32] Hydronium ions (H_3O^+), produced by the ion source, ionize VOCs with proton affinity higher than that of H_2O in the drift tube, which was operated at an E/N ratio of 120 Td in this study. The ionization is generally soft, often producing protonated ions ($VOCH^+$),[33] but fragmentation occurs in some cases. The quadruple

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interference ensures high ion transmission efficiency from the drift tube to a time-of-flight mass analyzer, which detects the product ions based on their exact masses. In this study, the PTR-Qi-ToF had a mass resolution of ~5000 m/Δm and a sensitivity >1000 cps/ppb for benzene (m/z 79). The mass spectrometry data of PTR-Qi-ToF were acquired with a 10-s time resolution and analyzed using the *Tofware* software (version 2.5.11., Tofwerk). A customized ion list was used to fit the spectral data, and the ion signals were outputted in counts per second (cps).

In total, 402 VOC signals were extracted from 745 ions detected on the mass spectra by applying the following signal processing procedure. Background ions predominantly arising from the instrument and from tubing were first filtered based on zero air measurements. The list of ions was further reduced by consolidating isotopic ions and major fragment ions (identified with the assistance of experience and correlation) and removing interference ions, tracer ions, and inorganic ions. An abundance threshold was then applied to refine the selection. Chemical formulas of ions can provide insights into the identity of VOCs to some extent. Educated compound assignments are reported together with the corresponding ion formulas whenever possible.

Calibrations were conducted before and after the observation using a standard gas mixture (including methanol, acetonitrile, acetaldehyde, acetone, methyl ethyl ketone, benzene, toluene, styrene, m-xylene, chlorobenzene, 1,3,5-trimethylbenzene, and 1,3-dichlorobenzene), to monitor response drift of the PTR-Qi-ToF and to construct a transmission curve (i.e., dependence of transmission efficiency on exact ion masses). For VOCs that were not directly calibrated, the sensitivity factors were estimated using the transmission efficiency at the mass-to-charge ratio of the VOC signals and an assumed rate constant of 2.5×10^9 cm^3/s for the reaction of the parent VOCs with H_3O^+ and $H_5O_2^+$. The uncertainty for this method is estimated to be ~50%.[24,34]

This study entails a focused analysis of isoprene (C_5H_8) and 6-MHO ($C_8H_{14}O$) and a nontargeted analysis covering all identified VOC signals. The concentrations of isoprene and 6-MHO were estimated from signal of $C_5H_9^+$ ion and summed signals of $C_8H_{15}O^+$ and $C_8H_{13}^+$ ions, respectively, consistent with previous observational studies.[18−20,23,24] A recent study suggests that fragmentation of certain aldehydes, such as nonanal, can contribute to the $C_5H_9^+$ signal.[35] In this study fragmentation is anticipated to be less pronounced due to lower E/N ratio employed (120 Td as compared to 137 Td). Direct application of the fragmentation ratio in the previous study to our data might result in an overcorrection of the $C_5H_9^+$ signal. Therefore, we choose not to consider this potential contribution in our analysis.

Source Strength Analysis

The indoor emission rates of VOCs and CO_2 in the office were quantified from their concentrations by mass balance. It was assumed that the air in the office was well-mixed. Furthermore, the effect of the air change occurring with the corridor was considered equivalent to that happening with the outdoor environment. Justification of this assumption is provided in detail in the SI. Based on the mass balance and the above assumptions, the change in the concentration of a gaseous compound in the office air, resulting from transport, emission, and gas-phase chemistry, can be described by the following equation

$$\frac{dc_{in}}{dt} = (c_{out} - c_{in}) \times ACR + \frac{E}{V} + P \quad (1)$$

where c_{in} and c_{out} are the concentrations of the compound in the office and outdoor air, respectively (ppb or ppm); ACR is the air change rate of the office (h^{-1}); V is the volume of the office (m^3); E is the total emission rate of the compound into the office air (ppb m^3 h^{-1} or ppm m^3 h^{-1}); and P is the net chemical production of the compound in the gas phase (ppb h^{-1} or ppm h^{-1}).

The average emission rate of a compound into the office air for a time interval of Δt can be obtained by integrating eq 1

$$\overline{E} = V \times \left[\frac{\Delta c_{in}}{\Delta t} + (\overline{c_{in}} - \overline{c_{out}}) \times ACR - P\right] \quad (2)$$

where Δc_{in} is the change in c_{in} for a time interval of Δt, and $\overline{c_{in}}$ and $\overline{c_{out}}$ are average indoor and outdoor concentrations for a time interval of Δt, respectively.

To use eq 2, we took Δt as 2 h. *ACR* was calculated from concentrations of the inert tracer with a 2-h time resolution.[31] For alternating sampling from five locations, we calculated average concentrations after each switch for VOCs and ozone, providing one data point for each location in each half hour. $\overline{c_{in}}$, $\overline{c_{out}}$, $\frac{\Delta c_{in}}{\Delta t}$, and P of VOCs over each 2 h period were then estimated (four data points in each 2 h period).

Gas-phase chemistry term P in eq 2 is accounted for calculating emission rates of geranyl acetone, 6-MHO, 4-OPA, and acetone by considering ozone reactions with two major ozone-reactive volatile products of squalene, 6-MHO and geranyl acetone. Even for these two reactions, some parameters have not been measured directly. In this study we followed the approach used in our recent chamber study for parametrization[29] and represented the reactions as follows

$$\text{6-MHO} + O_3 \xrightarrow{k_{6-MHO}} 0.3\ \text{acetone} + 0.8\ \text{4-OPA} \quad (R1)$$

$$\text{GA} + O_3 \xrightarrow{k_{GA}} 0.15\ \text{6-MHO} + 0.4\ \text{4-OPA} + 0.15\ \text{acetone} + 0.4\ \text{4-MON} \quad (R2)$$

where $k_{6\text{-MHO}}$ and k_{GA} are the ozone reaction rate coefficient with 6-MHO and geranyl acetone, respectively. They were assigned values of 0.035 and 0.070 ppb^{-1} h^{-1}. Other gas-phase reactions (e.g., reactions with OH and NO_3) were assumed negligible. A preliminary analysis suggests that OH chemistry has only a minor influence on the results (cf., SI).

The time-resolved indoor emission rate obtained using eq 2 encompasses the emissions from human occupants, building and furnishing materials, and other indoor items. For CO_2, emissions from sources other than human occupants can be considered negligible. For VOCs, the source proportion can differ by compounds. Herein we took advantage of differing temporal patterns of major VOC sources to conduct source apportionment. VOC emissions from occupants vary with occupancy level. In contrast, background VOC emissions in the office is expected to stay relatively constant over the 1.5-week observation period. This expectation is based on the fact that the office had been in use for about 3 years, and long-term VOC emissions from building and furnishing materials tend to change slowly over time.[36] Based on this difference, we utilized the correlation between indoor emission rates of VOCs and those of CO_2 to identify VOCs strongly affected by emissions from human occupants. The slope of the linear fit of the two can be used to estimate the VOC emission factor from the human body, while the intercept corresponds to the background room emission, as detailed in the SI.

RESULTS AND DISCUSSION

Analysis on Featured Compounds Emitted from the Human Body

Figure 1 illustrates the time series of indoor concentrations of three commonly known bioeffluents, CO_2, isoprene, and 6-MHO, on 2 days (6:00−6:00 the next day) characterized by low and high ozone concentrations, respectively. The three compounds correspond to an exhaled inorganic species, an exhaled VOC, and an dermally emitted VOC, respectively. Key factors that might influence indoor concentrations of these compounds are also shown in Figure 1, including door status, occupancy level, ozone concentration, and concentration of the steadily released tracer (indicating ventilation rate). On both days, the concentrations of CO_2, 6-MHO, and isoprene started

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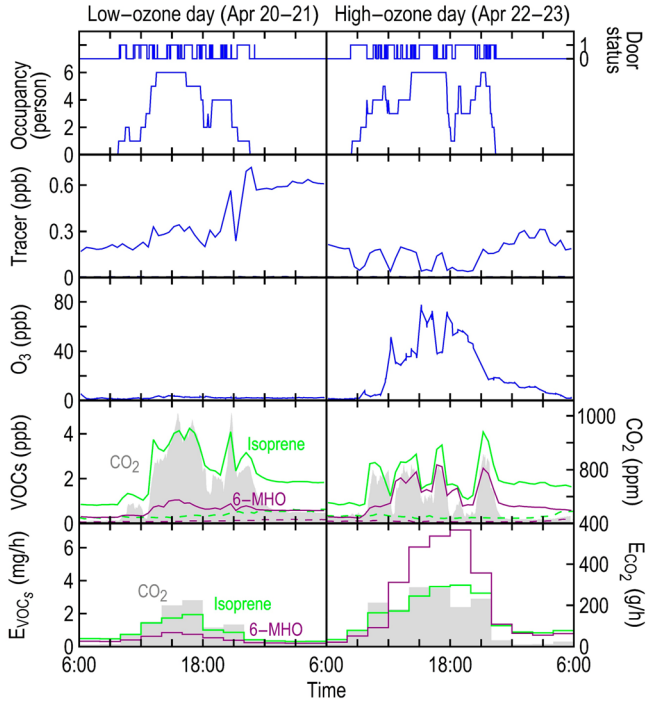

Figure 1. Time series of observed variables on 2 days. From top to bottom: present occupancy level, tracer gas concentration, ozone concentration, concentrations of three bioeffluents including CO_2, isoprene, and 6-MHO, and their emission rates. The panels on the left and right present measurements on a low-ozone day (Apr. 20, 2019) and a high-ozone day (Apr. 22, 2019), respectively. Data of isoprene and 6-MHO are denoted by the green and purple lines (left axis), respectively, and data of CO_2 by the gray shades (right axis). The solid and dashed lines represent VOC concentrations measured indoors and outdoors, respectively. The top panel also shows the door state, with 0 indicating closed and 1 indicating open.

to increase in the morning after the students arrived. During working hours (8:00−22:00), their concentrations exhibited rapid rise and fall closely following the tracer concentration, suggesting a strong influence of ventilation rates on the indoor concentrations of these gaseous compounds. As the students left the office one after another during 21:00−22:30, the concentrations of the three compounds gradually dropped, despite that the tracer concentration remained high. These results suggest that occupants were the major source of the three compounds, on the one hand. On the other hand, they also reveal that a direct correlation between the indoor concentrations of the three compounds and the occupancy level does not exist. The lack of correlation is due to that the concentrations were also substantially influenced by the ventilation rates, which exhibited large temporal variations during occupancy in this naturally ventilated office. This is a distinct feature compared with previous observational studies conducted in mechanically ventilated indoor spaces, which were characterized by constant ventilation rates.[18,20−22]

In order to further explore the relationship between indoor emissions of the three compounds and occupancy level without the interference of varying ventilation rates, their indoor emission rates were calculated with a 2h time resolution using eq 2. The bottom panels in Figure 1 show the time series of emission rates (another version of Figure 1 showing error bars for emission rates is presented in Figure S3). The emission rates of all three compounds followed a diel pattern that corresponded to the occupancy level on both days. Specifically, the emission rates peaked in the late afternoon, coincident with the period when more students were in the office. However, temporal variation of the emission rates of the three compounds also exhibited some glaring differences. On the afternoon with a high ozone level, characterized by an average ozone concentration of 48 ppb (12:00−18:00), the average emission rate of 6-MHO was five times higher than that observed in the afternoon when a low ozone level was present, with an average concentration of 3 ppb. In contrast, the emission rates of CO_2 and isoprene only increased by 40% and 70%, respectively, from the low-ozone afternoon to the high-ozone afternoon. The self-reported occupancy level in the office was also similar on both afternoons, with an average of 5.0 and 5.1 students present, respectively. The substantially higher 6-MHO emission rate observed on the high-ozone day is thus more likely related to a higher ozone concentration (48 ppb compared to 3 ppb), rather than differences in the number or status of the occupants. Another notable difference arises in the night-time emission rates of these compounds. Once all students left the office at around 22:00 on both days, indoor CO_2 emission rate exhibited a rapid decline, reaching near zero. In contrast, the indoor emission rates of isoprene and 6-MHO stabilized at levels ranging from 1/6 to 1/3 of the values observed in the afternoon, persisting overnight until 6 a.m. on the following day. One plausible explanation for this observation is that VOCs emitted from human occupants during daytime were partly absorbed by indoor surfaces and slowly released into the indoor air at night. It is also possible that there were VOC sources other than human occupants, such as ozone reactions with off-body skin lipids to produce 6-MHO.[24,25] Overall, Figure 1 suggests that the occupancy level was a key factor determining the indoor emission rates of all three compounds, but the net indoor emissions of isoprene and 6-MHO were also affected by other factors. In particular, indoor ozone concentration might regulate the 6-MHO emissions.

In light of the snapshot observations shown in Figure 1, we further explored the dependence of indoor emission rates of isoprene and 6-MHO on the occupancy level and ozone concentration using all available data. Figure 2 (left panels) plots indoor emission rates of isoprene and 6-MHO against indoor CO_2 emission rates, respectively, and the data points are with a 2 h time resolution and colored by ozone concentrations. Herein we use the indoor CO_2 emission rate to indicate the occupancy level instead of relying on the presence records maintained by the occupants because the quality of the records degraded over time at least for some occupants. During the whole observation period, indoor CO_2 emission rates varied from near zero to ∼300 g/h (over 97% of the data were in the range of 0−250 g/h), corresponding to the presence of 0−6 occupants based on manual records (cf. SI). Ozone concentrations varied from near zero to ∼55 ppb, with over 80% of the data below 20 ppb. The indoor emission rates of isoprene correlated well with those of CO_2 (R^2 = 0.76), and there was no clear influence of ozone concentration on the isoprene emission rate. In comparison, the correlation between the emission rates of 6-MHO and those of CO_2 was less tight (R^2 = 0.56). At similar CO_2 emission rates (occupancy levels), the 6-MHO emission rates at higher ozone levels were overall greater than those at lower ozone levels. As an additional note, we also colored the data points in the 6-MHO plot using

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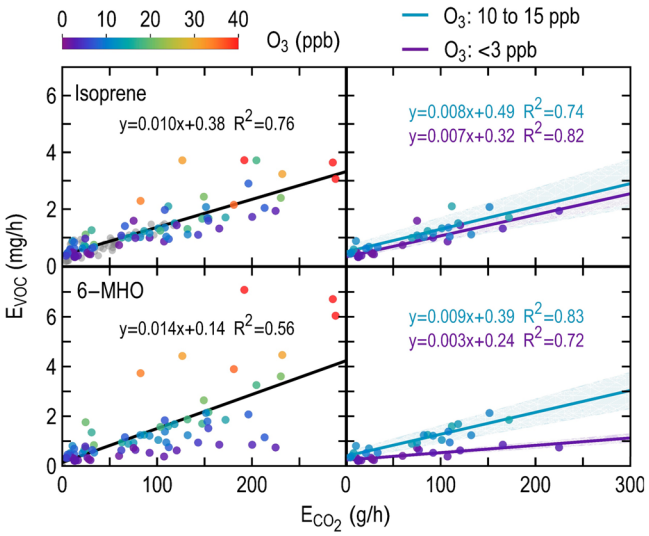

Figure 2. Dependence of indoor emission rates of isoprene (top) and 6-MHO (bottom) on indoor emission rates of CO_2. Emission rates were determined with a 2-h time resolution. The left panels show all data during the entire observation period and the right panels show subsets of data at two ozone levels, 10−15 and <3 ppb, respectively. Data points are colored by ozone concentrations. In the case that ozone concentration data are unavailable (due to a malfunction of the ozone monitor in the later part of the campaign), data points are shown in gray. The black lines represent the best linear fits to all data, and the blue and purple lines represent the best linear fits to data with ozone concentrations of 10−15 and <3 ppb, respectively.

temperature and relative humidity (Figures S4 and S5) and found indiscernible effects of these two factors.

To better quantify the influence of ozone, we compared two subsets of data with contrasting ozone concentrations, in the range of 10−15 and below 3 ppb, respectively, as shown in Figure 2 (right panels). They were selected for analysis because the observed variations in the CO_2 emission rates in both subsets were wide enough, allowing for quantifying the respective dependence of VOC emission rates on the CO_2 emission rates. As shown in Figure 2, the emission rates of both isoprene and 6-MHO exhibited a strong correlation with the CO_2 emission rates at both ozone levels (R^2 = 0.72−0.83).

The fitted slopes in the right panels in Figure 2 represent milligrams of 6-MHO or isoprene emitted per gram of CO_2 emitted in the office. Given that CO_2 was predominately emitted from the human occupants, we can estimate the emission factors of 6-MHO and isoprene by multiplying the best-fit slopes with the CO_2 emission factor. Herein the CO_2 emission factor is estimated to be 38 g/h/p based on the linear fit of indoor CO_2 emission rate and manual records of occupancy level (cf. Figure S6), and the value is consistent with previous estimates in office environments.[37] The isoprene emission factors obtained at ozone concentrations of below 3 ppb and in the range of 10−15 ppb were comparable (284 ± 35 versus 307 ± 43 μg/h/p). Conversely, the emission factor of 6-MHO increased from 113 ± 18 μg/h/p at ozone concentrations of below 3 ppb to 337 ± 36 μg/h/p at ozone concentrations of 10−15 ppb. The substantial increase quantitatively confirms a strong influence of ozone concentration on the 6-MHO emission rate from the human body.

Nontarget Analysis on VOC Emissions from the Human Body

Based on measurement data features of 6-MHO and isoprene presented in the last section, we further conduct a nontarget

Table 1. Best-Estimated Emission Factors (EF; Mean ± Standard Deviation) at High (10−15 ppb) and Low (<3 ppb) Ozone Levels for the Top 20 VOCs[a]

			high O_3 (10−15 ppb)		low O_3 (<3 ppb)		
VOC signal[b]	empirical compound	main source[c]	R^2	EF (μg/h/p)	R^2	EF (μg/h/p)	EF_{highO_3}/EF_{lowO_3}
$C_{13}H_{23}O^+$	geranyl acetone	skin (S)	0.86	159 ± 15	0.88	75.3 ± 7.3	2.11
$C_8H_{15}O^+$	6-MHO	skin (S)	0.83	337 ± 36	0.72	113 ± 18	2.98
$C_{13}H_{21}O^+$	damascone, ionone	fragrance	0.77	10.5 ± 1.4	0.74	8.1 ± 1.2	1.30
$C_3H_7O^+$	acetone	exhalation	0.76	1420 ± 190	0.67	1160 ± 210	1.22
$C_5H_9^+$	isoprene	exhalation	0.74	307 ± 43	0.82	284 ± 35	1.08
$C_{10}H_{21}O^+$	decanal	skin (F)	0.70	245 ± 38	0.57	151 ± 34	1.62
$C_{14}H_{29}O^+$	C14 saturated carbonyl		0.69	12.7 ± 2.0	0.45	8.6 ± 2.5	1.48
$C_{11}H_{23}O^+$	undecanal	skin (F)	0.68	41.0 ± 6.6	0.49	27.1 ± 7.1	1.51
$C_6H_{11}^+$			0.67	221 ± 3	0.67	185 ± 34	1.19
$C_7H_{13}^+$			0.65	77 ± 13	0.56	52 ± 12	1.47
$C_9H_{19}^+$			0.63	10.9 ± 2.0	0.41	6.5 ± 2.0	1.68
$C_{14}H_{29}^+$			0.62	3.1 ± 0.6	0.21	1.9 ± 1.0	1.57
$C_{14}H_{25}^+$			0.61	5.2 ± 1.0	0.50	4.3 ± 1.1	1.23
$C_{10}H_{11}^+$			0.61	3.3 ± 0.6	0.68	3.2 ± 0.6	1.03
$C_{12}H_{25}O^+$	dodecanal	skin (F)	0.61	25.5 ± 4.9	0.51	19.0 ± 4.8	1.34
$C_{12}H_{25}^+$			0.59	8.0 ± 1.6	0.48	6.5 ± 1.8	1.23
$C_9H_{17}O^+$	nonenal	skin (F)	0.58	36.9 ± 7.4	0.36	20.3 ± 6.9	1.82
$C_9H_{19}O^+$	nonanal	skin (F)	0.58	137 ± 27	0.50	92 ± 24	1.50
$C_7H_{15}^+$			0.58	6.7 ± 1.4	0.39	5.0 ± 1.6	1.34
$C_{16}H_{27}O^+$	Iso E Super	fragrance	0.56	35.0 ± 7.4	0.77	21.1 ± 3.0	1.65

[a]These VOCs were selected based on the strong correlation between their emission rates and CO_2 emission rates (indicated by R^2) at 10−15 ppb ozone. [b]The main fragmentation ions are also considered in the calculation. [c]Skin (S) represents ozonolysis of squalene in skin oil, and skin (F) represents ozonolysis of unsaturated fatty acids in skin oil.

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analysis to identify other VOCs of primary human origin and explore the ozone dependence of their emission factors. In reference to Figure 2, the correlation coefficient (R^2) between the indoor emission rates of individual VOC signals and those of CO_2 is used as a metric to identify potential human-emitted VOCs. When fitting all data points, the resulting R^2 value exceeds 0.5 for 83 out of 402 VOC signals detected by PTR-Qi-ToF, indicating that a large portion of VOC signals observed in this densely occupied office were likely emitted from the human occupants. Given the possible influence of ozone concentration, our following analysis focuses on the top 20 VOC signals that exhibit the highest R^2 values using a subset of data with ozone concentration in the range of 10−15 ppb. The emission factors of these VOCs obtained at ozone concentrations of 10−15 and <3 ppb are listed in Table 1 for comparison.

The VOC signals identified using the above criteria cover many featured VOCs emitted from the human body, including key metabolites in human breath: acetone ($C_3H_7O^+$) and isoprene ($C_5H_9^+$); first-generation products from ozonolysis of squalene: geranyl acetone ($C_{13}H_{23}O^+$) and 6-MHO ($C_8H_{15}O^+$); and products from ozonolysis of unsaturated fatty acids: nonenal ($C_9H_{17}O^+$), nonanal ($C_9H_{19}O^+$), decanal ($C_{10}H_{21}O^+$), undecanal ($C_{11}H_{23}O^+$), and dodecanal ($C_{12}H_{25}O^+$).[5,38,39] It is worth noting that 4-OPA, a commonly observed second-generation ozonolysis product of squalene, is not among the top 20. For the product ion of 4-OPA ($C_5H_9O_2^+$), the R^2 value is 0.23 at 10−15 ppb ozone, lower than those of the top 20 (0.56−0.86). One potential explanation is that some other compounds also contributed to the signal of the $C_5H_9O_2^+$ ion.

The other 11 VOC signals in Table 1 cannot be attributed to known human bioeffluents. For $C_{13}H_{21}O^+$ and $C_{16}H_{27}O^+$, detailed time series data suggest that their emissions were associated with the presence of one specific occupant (Figure S7). Their chemical formulas are consistent with some common fragrant chemicals, specifically $C_{13}H_{21}O^+$ to damascone or ionone ($C_{13}H_{20}O$; a series of isomers known as rose ketones) and $C_{16}H_{27}O^+$ to tetramethyl acetyloctahydronaphthalenes ($C_{16}H_{26}O$; a synthetic woody odorant). These compounds are commonly used as natural flavors or synthetic additives in perfumes and cosmetics.[40−44] These two VOC signals likely originated from the residual perfume of certain personal care products used by the occupant, who was often present in the office during periods of higher overall occupancy. In terms of $C_{14}H_{29}O^+$, the chemical formula is consistent with C_{14} saturated carbonyl ($C_{14}H_{28}O$) and the signal cannot be attributed to the presence of any specific occupant (result not shown). Although ozonolysis of fatty acids is known to produce a series of saturated aldehydes, C_{14} aldehyde has not been reported to the best of our knowledge, so the source of $C_{14}H_{29}O^+$ herein is uncertain. For all the other VOC signals, the chemical formulas are in the form of $C_xH_y^+$ ($y \leq 2x + 1$). Their signals can be contributed by both alkenes with the chemical formula of C_xH_{y-1} and some larger compounds through fragmentation. Given the ambiguity of the parent compounds and associated sources of these VOC signals, the following discussion focuses on those attributable to specific human bioeffluents.

Among all the identified human bioeffluents in Table 1, acetone has the highest emission factor of over 1000 μg/h/p, consistent with the results in previous studies.[17,18,20−23] Isoprene, 6-MHO, decanal, nonanal, and geranyl acetone had emission factors of 100−400 μg/h/p at 10−15 ppb ozone, while the corresponding emission factors of other bioeffluents are in the range of <50 μg/h/p.

For VOCs known to be produced from ozone chemistry with skin oil, the emission factors at 10−15 ppb ozone were consistently higher than those at <3 ppb. The ratios ranged from 1.34 for dodecanal to 2.98 for 6-MHO. In contrast, for VOCs known to be mainly emitted from exhaled breath, the emission factors at the two ozone levels were closer, with a ratio of 1.08 for isoprene and 1.22 for acetone. The slightly higher acetone emission factor at the higher ozone level might be attributed to the dual sources of acetone. Specifically, acetone can be produced by ozonolysis reactions of squalene in skin oil in addition to being emitted through exhaled breath.[4,5] These results provide further evidence that in real indoor environments, ozone concentration affects the emission factor of VOCs which can be produced from the ozone reaction with skin oil.

The ratios of VOC emission factors at high and low ozone levels in Table 1, which indicate the magnitude of the ozone influence, are all lower than the ratio of the ozone concentration itself. The mean ozone concentrations at the high and low ozone levels were 12 and 2.3 ppb, respectively, differing by 5 times. In contrast, the corresponding ratios of VOC emission factors at the two ozone levels were at a maximum of 2.98 (for 6-MHO). One plausible explanation is that there might also be baseline emissions of these VOCs from the human body, in addition to secondary emissions driven by ozone reactions. The baseline emissions have been reported in chamber experiments conducted under ozone-free conditions.[3,45] Along this line of thinking, the variations in the magnitude of ozone influence across VOC species (indicated by the ratios in Table 1) could potentially be linked to the relative contribution of the baseline emission. Specifically, relatively lower baseline emission of 6-MHO renders its overall emission factor more susceptible to changes in ozone concentration, as compared with other species such as nonanal and decanal. This hypothesis is corroborated by findings from prior controlled experiments, which observed a greater rise in the emission factor of 6-MHO from low to high ozone conditions compared with those of nonanal and decanal.[3,46]

Dependence of VOC Emission Factors on Ozone Concentration: Comparing Current and Previous Studies

To better quantify the ozone dependence of the emission factors for dermal oxidation products and the associated baseline emission, we further divided the observational data into 4 subsets based on ozone concentration: below 3 ppb, 5−10 ppb, 10−15 ppb, and 15−22 ppb. This division ensures that each subset contains at least 13 data points and covers a wide range of occupancy level. This approach allows for determining the VOC emission factors from the human body with reasonable accuracy for each subset of data. Figure 3 plots the obtained emission factors against corresponding ozone concentrations for the two most commonly reported oxidation products from skin oil, 6-MHO and decanal. The estimated emission factors for the two compounds strongly correlated with the ozone concentration (R^2 = 0.95−0.96). The slope and intercept of the best linear fit can be interpreted as the ozone dependence of the VOC emission factor and the baseline emission factor in the absence of ozone, respectively. The best-fit slope for 6-MHO (18.6 μg/h/p/ppb ozone) is higher than that for decanal (9.0 μg/h/p/ppb ozone), while the intercept-

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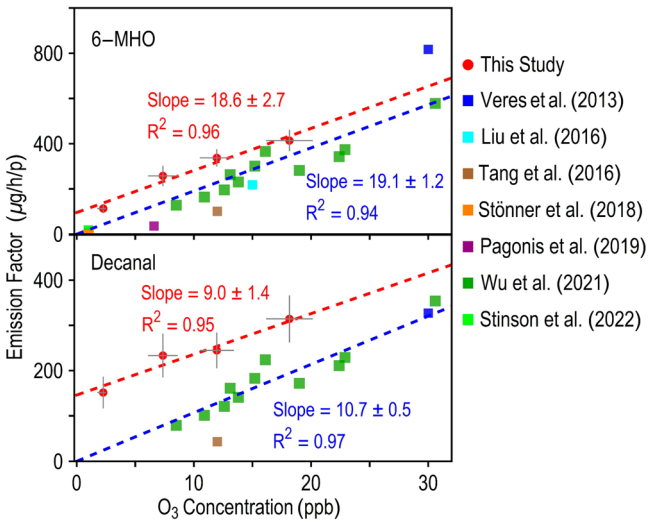

Figure 3. Dependence of 6-MHO and decanal emission factors on ozone concentrations. The red points represent measurements in this study, with gray error bars indicating the standard deviations. The squares represent literature data, colored by the data source. The ozone concentration associated with each reported emission factor corresponds to the mean value during the observation period. In the case that the mean value is unavailable, the mean of the upper and lower limits of the reported ozone range is used instead. The red and blue lines represent the best linear fits to the data obtained in this study and reported in previous studies, respectively.

to-slope ratio for decanal is higher than that for 6-MHO, indicating a higher fraction of baseline emission in overall emission factor for decanal.

In addition to the results from the current study, Figure 3 also plots the VOC emission factors reported in previous observational studies versus the corresponding ozone concentrations, as illustrated in solid squares. Among these studies, Wu et al. reported the ozone concentrations and VOC emission factors on a daily basis in an office building,[24] while each of the other studies only provided a single emission factor using all the data throughout the whole observation period.[17−22] As shown in Figure 3, the emission factors of 6-MHO and decanal reported by Wu et al.[24] also exhibit linear dependence on ozone concentration. The data points obtained from other previous studies were largely consistent with the results reported by Wu et al.[17−22,24] A linear fit using all data points from the previous studies can explain 94% and 97% of variations in the emission factors of 6-MHO and decanal, respectively. The suggestion is that the large variations in emission factors of dermal ozonolysis products reported in these previous studies were largely driven by variations in the indoor ozone concentration despite differences in occupants, measurement techniques, and environmental conditions across these studies.

There is good agreement on ozone dependence of the emission factors estimated using data from both the current and previous studies, indicated by the slopes of two linear fits in Figure 3. The agreement stands within 2.7% for 6-MHO and within 19% for decanal. Yields for 6-MHO and decanal from ozone reaction with the human body can be further derived from the ozone dependence, with the assumption of an average body surface area of 1.7 m^2 for the occupants, and utilizing an ozone deposition velocity on human body surfaces of 17 m/h.[29] The resulting yields for 6-MHO are 12% and 13%, using data from current and previous studies, respectively. The corresponding yields for decanal are 4.8% and 5.7%. These yields are comparable to those obtained in our recent chamber study involving three male human subjects (9.4% for 6-MHO and 2.7% for decanal).[29]

Another noticeable feature in Figure 3 is that the baseline emission, indicated by the intercept of the linear fits, is larger in this study than in previous studies, particularly for decanal. The baseline emissions can come from emissions of endogenous metabolites from the human body,[47] decompositions of stable secondary ozonides on human body surfaces,[48] and slow release of these VOCs from clothing and skin surfaces after production. The strengths of baseline emissions and the factors influencing them are still to be understood. Even in chamber experiments where the human subjects were controlled for bathing and clothing, divergent findings have been reported regarding baseline emissions for ozonolysis products. Some studies reported low baseline emissions,[3,13,45,49−51] while some others suggested substantially higher levels.[46] In real-world scenarios, the soiling conditions of skin and clothing can differ by occupants,[11] adding extra variability to the apparent baseline emissions. In general, the Chinese students in the current study tended to take showers at night due to the limited water supply duration in dormitories and typically changed their clothes every 2−3 days. In comparison, the previous studies were conducted in the United States and Europe, where people often take showers in the morning and change their clothes more frequently.[52−54] This difference might have contributed to a higher baseline emission in this study for decanal, which is stickier to human body surfaces than 6-MHO, among other factors such as the ethnicities of occupants.

In summary, herein, we report observations in a normally occupied student office and reveal that the emission factors of many VOCs from the human body are ozone-dependent. Furthermore, we find that a linear fit with ozone can explain over 90% of variations in the emission factors reported across previous studies for some featured ozonolysis products of skin oil. These results suggest caution in using VOC emission factors obtained from a single study to model human emissions without considering the ozone concentration in a specific indoor environment. The consistency between the ozone dependence calculated from this data set and previous results further supports the potential use of this dependency to estimate human body VOC emisisons in complex real-world scenarios with varying ozone concentrations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenvironau.3c00043.

Instrument specifications; comparison of VOC concentrations among different locations; justification for simplified treatment of air change in the student office; estimation of emission factors of CO_2 and VOCs from human occupants; influence of temperature and RH on indoor emissions of 6-MHO; impact of gas-phase chemistry treatment on emission factors; and supplementary figures (PDF)

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Notes

The authors declare no competing financial interest.

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