



Spatiotemporal variations in ozone and carbon dioxide concentrations in an HVAC system of a LEED-certified office building

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ABSTRACT

Indoor air quality (IAQ) is crucial for the health, well-being, and productivity of office occupants. IAQ is strongly influenced by occupancy and the operational mode of the heating, ventilation, and air conditioning (HVAC) system. This study investigates the spatiotemporal variations in ozone (O₃) and carbon dioxide (CO₂) concentrations throughout the HVAC system of a LEED-certified office building. A four-month field measurement campaign was conducted at the Ray W. Herrick Laboratories, employing an automated multi-point sampling system to monitor O₃ and CO₂ at eight locations throughout the HVAC system. The objectives of this study are to characterize the spatiotemporal distribution of these gases under different ventilation modes and occupancy levels, and to identify O₃ loss mechanisms in the office and its HVAC system. Spatiotemporal variations in O₃ and CO₂ concentrations were observed throughout the HVAC system. Results indicate that outdoor air exchange rates (AERs) significantly impact indoor O₃ levels, with higher AERs resulting in increased indoor O₃ but reduced CO₂ concentrations. Measurements reveal that HVAC filters and ducts contribute to O₃ loss, with up to 18% O₃ removal observed in the longest HVAC duct segment. Additionally, occupancy influences O₃ deposition onto human skin and clothing surfaces. This research underscores the limitations of ventilation standards that focus only on CO₂, highlighting the need for ventilation strategies that consider the effects of occupancy and outdoor AERs on different gases. By integrating multi-point gas sampling into building automation systems, more effective control strategies can be developed to enhance IAQ and occupant health while reducing energy consumption.

1. Introduction

Indoor air quality (IAQ) in office buildings can impact the health, well-being, and productivity of the occupants [1–3]. Operation of building heating, ventilation, and air conditioning (HVAC) systems and occupant activities are two important factors that may affect the dynamics and chemistry of indoor air pollutants, including airborne particles, volatile organic compounds (VOCs), nitrogen oxides (NO_x: NO and NO₂), ozone (O₃), and carbon dioxide (CO₂). Among these indoor air pollutants, O₃ and CO₂ are two important trace gases that are strongly connected to IAQ. In most buildings, especially in office buildings without combustion sources, the exhaled breath of occupants is the major source of CO₂ [4,5]. O₃ is an important driver of indoor oxidative reactive chemistry. O₃ can react with VOCs such as monoterpenes emitted by human activities, including cleaning and disinfecting surfaces, and initiate the formation of secondary organic aerosol (SOA) [6–11]. In addition, O₃ can react with compounds on indoor surfaces

including building surfaces and human body surfaces. O₃ reacts with unsaturated compounds in human skin oil, including squalene, glycerides, fatty acids, and cholesterol, leading to the formation of volatile skin oil ozonolysis products and SOA [12–16]. O₃-skin oil reactions are considered one of the major O₃ sinks in occupied indoor environments [12]. Both O₃ itself and its secondary reaction products can have adverse effects on human health. Human exposure to O₃ has been associated with respiratory and cardiovascular morbidity and mortality [17–21]. 4-oxopentanal (4-OPA), a reaction product of O₃ and skin oil, can cause irritation of the respiratory system and skin [22–25].

LEED-certified office buildings often implement sophisticated HVAC systems with building automation systems to control parameters related to the indoor thermal environment and IAQ, while minimizing energy consumption. Mixing ratios of indoor CO₂ are strongly associated with the design and operation of mechanical ventilation systems [26–29]. Outdoor and exhaust volumetric airflow rates determine the air exchange rate (AER) of the building, which directly impacts CO₂ loss and

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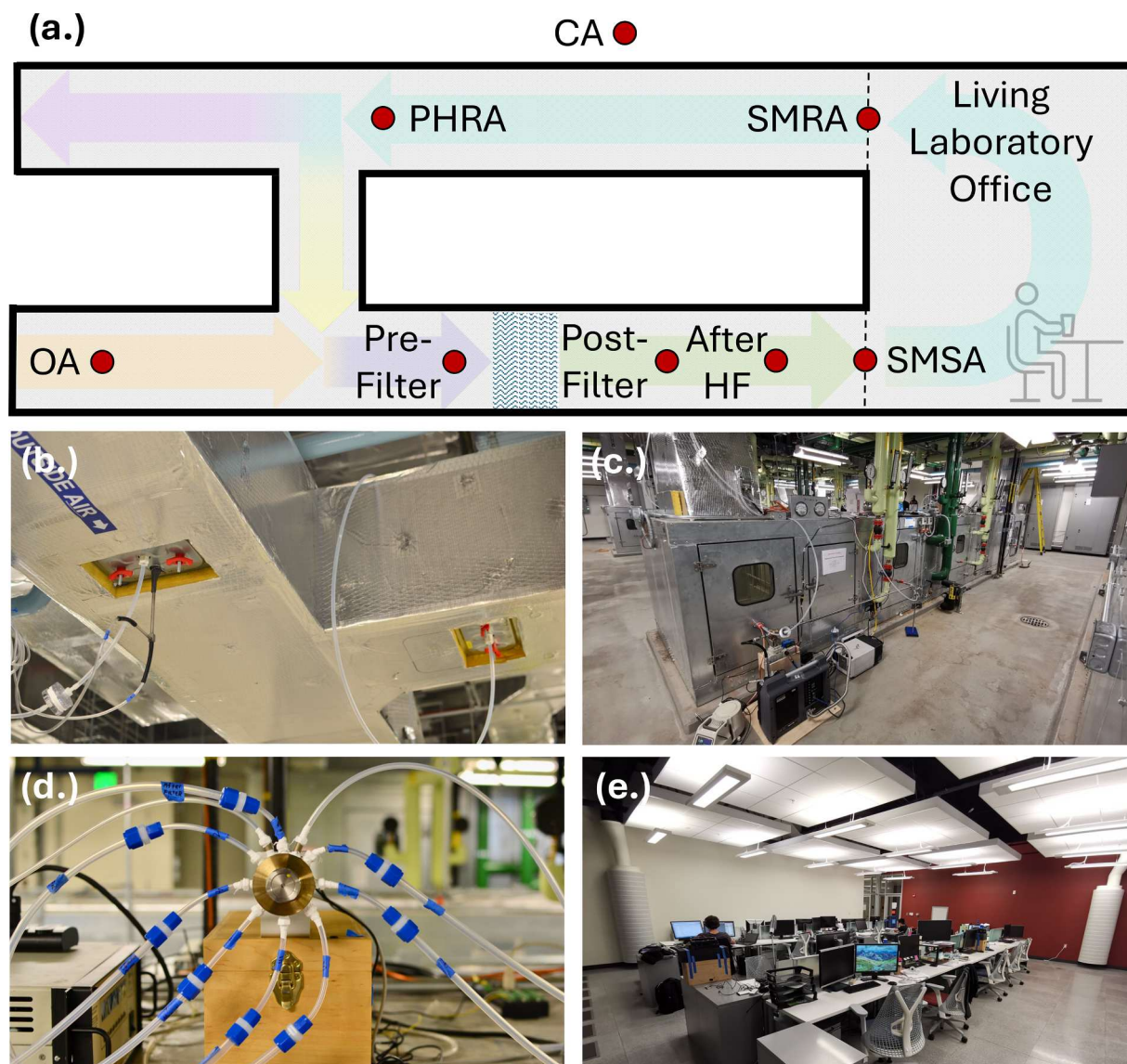


Fig. 1. (a.) Schematic of the experimental setup for multi-point sampling of O₃ and CO₂ mixing ratios throughout the HVAC system of the living laboratory office. The eight sampling locations are noted in the schematic and include: the outdoor air intake (OA), upstream of the HVAC filter bank (Pre-Filter), downstream of the HVAC filter bank (Post-Filter), after the steam humidifier (After HF), supply air duct located in the small mechanical room (SMMSA), return air duct located in the small mechanical room (SMRA), return air duct located in the penthouse (PHRA), and the common area (CA) adjacent to the office; (b.) photo of the OA and PHRA sampling locations in the penthouse; (c.) photo of the Pre-Filter and Post-Filter sampling locations from the HVAC system; (d.) photo of the programmable multi-flow path selector connected to the O₃ and CO₂ gas analyzers; and (e.) photo of the living laboratory office.

CO₂ mixing ratios in buildings. CO₂ mixing ratios are commonly monitored in building automation systems as an indicator of ventilation conditions, occupancy levels, or other indoor air pollutants [30–32]. ANSI/ASHRAE Standard 62.1–2022 has been established to regulate the minimum outdoor volumetric airflow rate in buildings based on the number of people present or the area of the office space [33]. However, most standards primarily focus on CO₂ levels and do not adequately address the complexities of IAQ, such as the presence and dynamics of other critical air pollutants like O₃. This limitation can lead to ventilation strategies that fail to comprehensively protect occupant health and well-being.

A building's mechanical ventilation system may impact indoor O₃ mixing ratios and dynamics differently than that for CO₂, which is an inert gas. Ventilation systems are the major pathway for outdoor O₃ to enter indoor environments [34–36], which could further impact indoor oxidative reactive chemistry and the formation of secondary gas- and particle-phase products. In addition, the surfaces of HVAC ducts and the

components of HVAC systems, including the HVAC filter bank and heating and cooling coils, could be a sink for outdoor O₃ as it is transported through the HVAC ducts before being supplied to the office [37–39]. However, current common HVAC system control strategies for IAQ are predominantly based on CO₂ sensing or modeling [40–43]. Furthermore, very few systems monitor trace gas concentrations at multiple locations within the HVAC system, failing to account for the impact of HVAC ducts and the operational conditions of HVAC components on IAQ in their control logic. Simultaneous real-time monitoring of the mixing ratios of these trace gases throughout building HVAC systems is critical to improve our understanding on indoor air pollutant dynamics and chemistry, providing data and information to determine appropriate ventilation strategies that improve IAQ.

However, to the authors' knowledge, there have been no prior long-term, multi-location measurements of O₃ and CO₂ throughout a commercial HVAC system under different ventilation and occupancy conditions. This study proposes and presents a novel automated multi-

location sampling system that has a wide range of applications, especially for ventilation control and improving IAQ. Specifically, this study investigates how the HVAC system operational mode and occupancy impact the spatiotemporal distribution of O₃ and CO₂ mixing ratios, as well as O₃ dynamics, in a ventilation system of a LEED-certified office building. A four-month field measurement campaign was conducted from February to June 2019 in one of the four occupied open-plan living laboratory offices at the Purdue University Ray W. Herrick Laboratories, which was awarded a LEED Gold Certificate. An automated multi-point sampling system was designed and built to monitor O₃ and CO₂ mixing ratios throughout the HVAC system in real-time. The objectives of this study are: (1.) to characterize the spatiotemporal distribution of O₃ and CO₂ mixing ratios at eight different sampling locations throughout the ventilation system of the office building under different HVAC system operational modes, including outdoor AERs and pressurization conditions, and different occupancy levels; (2.) to understand how the indoor/outdoor (I/O) ratio of O₃ and CO₂ mixing ratios are related to the operational mode of the mechanical ventilation system and human occupancy levels; and (3.) to understand loss mechanisms for O₃ in the office and throughout its HVAC system.

2. Materials and methods

2.1. Site description: Herrick living laboratory open-plan offices at Purdue University

The study site, one of the four Herrick living laboratory offices, is part of a LEED-certified building at Purdue University in West Lafayette, IN, U.S. (40°25'19.4"N 86°55'11.6"W). The living laboratories are four reconfigurable, side-by-side large open-plan office spaces, with a maximum occupancy of 20 and interior volume of 333 m³. Each office includes its own HVAC system, which is equipped with a MERV-8 pre-filter and a MERV-14 final-filter (Fig. 1). A building automation system (Niagara/AX, Tridium Inc., Richmond, VA, U.S.), along with hundreds of sensors, is applied to achieve real-time monitoring and precise control of the HVAC system. These sensors monitor air temperatures, relative humidities, volumetric airflow rates, damper positions, and fan speeds at different locations throughout the HVAC system; this provides a detailed airflow profile for the entire system. Damper positions and fan speeds were changed throughout the campaign to adjust the supply, return, and outdoor volumetric airflow rates.

2.2. Experimental setup and air quality instrumentation

2.2.1. Automated multi-point sampling system for the monitoring of O₃ and CO₂ mixing ratios

An automated multi-point sampling system was built with a programmable multi-flow path selector (EUTA-2VLSC8MWE2, Valco Instruments Co. Inc., Houston, TX, U.S.) to sample O₃ and CO₂, as well as NO_x and VOCs, at eight locations throughout the HVAC system (Fig. 1). The sampling locations included: the outdoor air intake (OA), upstream of the HVAC filter bank (Pre-Filter), downstream of the HVAC filter bank (Post-Filter), after the steam humidifier (After HF), supply air duct located in the small mechanical room (SMSA), return air duct located in the penthouse (PHRA), and the common area (CA) adjacent to the living laboratory office (Fig. 1). Perfluoroalkoxy (PFA) tubing (3/8" (9.5 mm) OD) was used for the sampling lines to connect each sampling location to the multi-flow path selector. The selected flow path outlet was connected to trace gas analyzers. The unselected streams were purged by a rough pump to prevent accumulation of stagnant air in the lines. This was done to eliminate a time delay in sampling. The total flow rate of the selected stream was maintained at 11.25 L min⁻¹ with a vacuum pump drawing the sample air at 9 L min⁻¹. This ensured that the residence time of the sample air was no more than 8 s. A polytetrafluoroethylene (PTFE) membrane filter was installed at the inlet of each sampling line to

Table 1

Multi-point sampling sequences implemented during the field measurement campaign.

| Sequence | Multi-Point Sampling Sequence |
|------------------|--|
| Spatial | 4 min outdoor air (OA) + 4 min Pre-Filter + 4 min Post-Filter + 4 min after humidifier (After HF) + 4 min supply air (SMSA) + 4 min return air (SMRA) + 3 min return air (PHRA) + 3 min common area (CA) |
| Temporal | 5 min outdoor air (OA) + 5 min supply air (SMSA) + 20 min return air (SMRA) |
| Pre-/Post-Filter | 4 min Pre-Filter + 4 min Post-Filter |

remove particles and was replaced daily to ensure its efficacy.

2.2.2. Instrumentation for the real-time monitoring of O₃ and CO₂ mixing ratios and office occupancy

An O₃ gas analyzer (Model M400E, Teledyne Technologies Inc., Thousand Oaks, CA, U.S.) and a CO₂ gas analyzer (LI-830, LI-COR Biosciences, Lincoln, NE, U.S.) were connected to the selected flow path outlet of the multi-flow path selector to alternatively monitor O₃ and CO₂ mixing ratios at the eight locations in real-time (1 Hz). The CO₂ analyzer was operated at a flow rate of 0.75 L min⁻¹. The O₃ gas analyzer monitored O₃ mixing ratios with a precision of 1 ppb using a photometric analyzer based on ultraviolet absorption of O₃ at 254 nm, with a sample flow rate at 0.8 L min⁻¹. Nitrogen oxides (NO and NO₂) were measured by a chemiluminescence NO-NO₂-NO_x analyzer (Model 42C, Thermo Electron Corp., Waltham, MA, U.S.) with a sample flow rate at 0.6 L min⁻¹. VOCs with a proton affinity greater than water were monitored by a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS, PTR-TOF 4000, Ionicon Analytik Ges.m.b.H., Innsbruck, Austria) using H₃O⁺ as the reagent ion. The inlet flow rate was maintained at 0.1 L min⁻¹. Details of the PTR-TOF-MS measurements can be found in Wu et al. (2021 and 2024) [44,45]. The O₃, CO₂, and NO-NO₂-NO_x analyzers were calibrated before the measurement campaign. The PTR-TOF-MS was calibrated daily following protocols described in previous studies [6,45–49]. Human occupancy in the living laboratory was tracked via chair-embedded thermocouples during the measurement campaign as described in Wagner et al. (2021) [50].

2.2.3. Multi-point sampling system sequences

During the measurement campaign, three different sequences for the multi-point sampling system were implemented. (1.) Sequence 1: a 30 min spatial sequence. The spatial sequence was designed to monitor spatial variations in O₃ and CO₂ mixing ratios across the eight locations of the HVAC system, which can inform how different HVAC components impact O₃ chemistry. During the spatial sequence, the valve system switched to OA, Pre-Filter, Post-Filter, After HF, SMSA, and SMRA for 4 min each, then PHRA and CA for 3 min each. (2.) Sequence 2: a 30 min temporal sequence, which specifically focused on O₃ and CO₂ dynamics in the office. This enabled for a more detailed investigation into the impact of occupants and ventilation conditions on indoor O₃ and CO₂ mixing ratios. During the temporal sequence, SMRA was sampled for 20 min, and then SMSA and OA were sampled for 5 min each. (3.) Sequence 3: an 8 min pre-/post-filter sequence. To investigate the role of the HVAC filter bank on O₃ dynamics, a pre-/post-filter sequence was designed to sample only the pre-filter and post-filter locations with 4 min of sampling at Pre-Filter and 4 min of sampling at Post-Filter. Details of each valve sequence are provided in Table 1. The O₃ and CO₂ mixing ratios for each location presented in the results are the mean values during the 30-min sample sequence for sequences 1 and 2. The first minute and last minute of data at each sampling location was disregarded to avoid the impact of the valve switching. For the pre-/post-filter sequence, data when the valve was sampling from another location was interpolated to better compare the difference in O₃ mixing ratios upstream and downstream of the HVAC filter bank.

Table 2

Ventilation modes and their corresponding outdoor AERs and office pressurization conditions.

| Ventilation Mode | Outdoor AER | Office Pressurization |
|------------------|---------------------|-----------------------|
| 1 | Low | No |
| 2 | Medium | No |
| 3 | High | No |
| 4 | Low | Yes |
| 5 | Medium | Yes |
| 6 | High | Yes |
| 7 | Natural Ventilation | - |

2.2.4. HVAC system operational modes during the measurement campaign

To investigate how the operation of the HVAC system impacts indoor O₃ and CO₂ dynamics, the supply, return, and outdoor volumetric airflow rates were adjusted to achieve different outdoor AERs and room pressurization conditions under different ventilation modes. The ratio of the recirculation airflow rate to the total supply airflow rate was adjusted from 0 to 1 to achieve different AERs. Throughout the campaign, based on the AERs and pressurization conditions, the ventilation modes can be categorized as follows: (1.) Mode 1: low AER (≤ 2.7 h⁻¹), no pressurization; (2.) Mode 2: medium AER (2.7 h⁻¹ < AER ≤ 5.4 h⁻¹), no pressurization; (3.) Mode 3: high AER (> 5.4 h⁻¹), no pressurization; (4.) Mode 4: low AER, pressurization; (5.) Mode 5: medium AER, pressurization; (6.) Mode 6: high AER, pressurization; and (7.) Mode 7: natural ventilation with unfiltered outdoor air via a south-facing, full-size double-skin glass façade. Table 2 summarizes the ventilation modes implemented during the campaign. The corresponding dates for each ventilation mode are summarized in a calendar in Fig. 2.

2.3. Material balance model to characterize O₃ loss terms in the office

To quantify the dynamics of O₃ in the living laboratory office, a simplified material balance model was developed to estimate the overall loss rate for O₃ under different ventilation and occupancy conditions:

$$\frac{dC_i(t)}{dt} = p\lambda_{in}(t)C_o(t) + \frac{C_o(t)Q_o(t)}{V} - L(t)C_i(t) \tag{1}$$

where C_i(t) is the indoor O₃ mixing ratio (ppb) sampled at SMRA; p is the penetration factor for O₃ (-); λ_{in}(t) is the infiltration rate (h⁻¹); C_o(t) is the outdoor O₃ mixing ratio (ppb) sampled at OA; Q_o(t) is the outdoor air volumetric airflow rate (m³ h⁻¹); V is the volume of the living laboratory office (m³); and L(t) is the overall O₃ loss rate (h⁻¹). The office was treated as a completely mixed flow reactor (CMFR). There were no obvious indoor O₃ sources in the office, such as photocopiers or air purifiers, thus, an indoor emission term for O₃ is not included in the material balance model.

The time-dependent overall loss rate L(t) for O₃ can be estimated by rearranging Eq. (1) as follows:

$$L(t) = -\frac{C_i(t+dt) - C_i(t)}{dt} - p\lambda_{in}(t)C_o(t) - \frac{C_o(t)Q_o(t)}{V} \tag{2}$$

For a 30 min spatial sequence or a 30 min temporal sequence, the time interval was defined as: dt = 30 min. The mean SMRA and OA O₃ mixing ratios during the 30 min period were taken as the values for C_i(t) and C_o(t), respectively. Similarly, the mean value of the outdoor air volumetric airflow rate during the 30 min period was taken as the value for Q_o(t).

The overall loss rate for O₃ includes indoor O₃ removal by exfiltration, deposition to building surfaces and human body surfaces, building ventilation (outdoor air exchange), and gas-phase reactions with indoor NO_x and selected VOCs, as shown in Eq. (3):

$$L(t) = \lambda_{ex}(t) + \frac{v_{d,bldg}S_{bldg}}{V} + \frac{v_{d,occ}(t)S_{occ}(t)}{V} + \frac{Q_o(t)}{V} + L_{reaction}(t) \tag{3}$$

where λ_{ex}(t) is the exfiltration rate (h⁻¹); v_{d,bldg} is the O₃ deposition velocity to interior building material surfaces in the office (m h⁻¹); S_{bldg} is the surface area of interior building material surfaces in the office, assumed to be constant over time (m²); v_{d,occ}(t) is the O₃ deposition velocity to office occupant surfaces (m h⁻¹); S_{occ}(t) is the surface area of

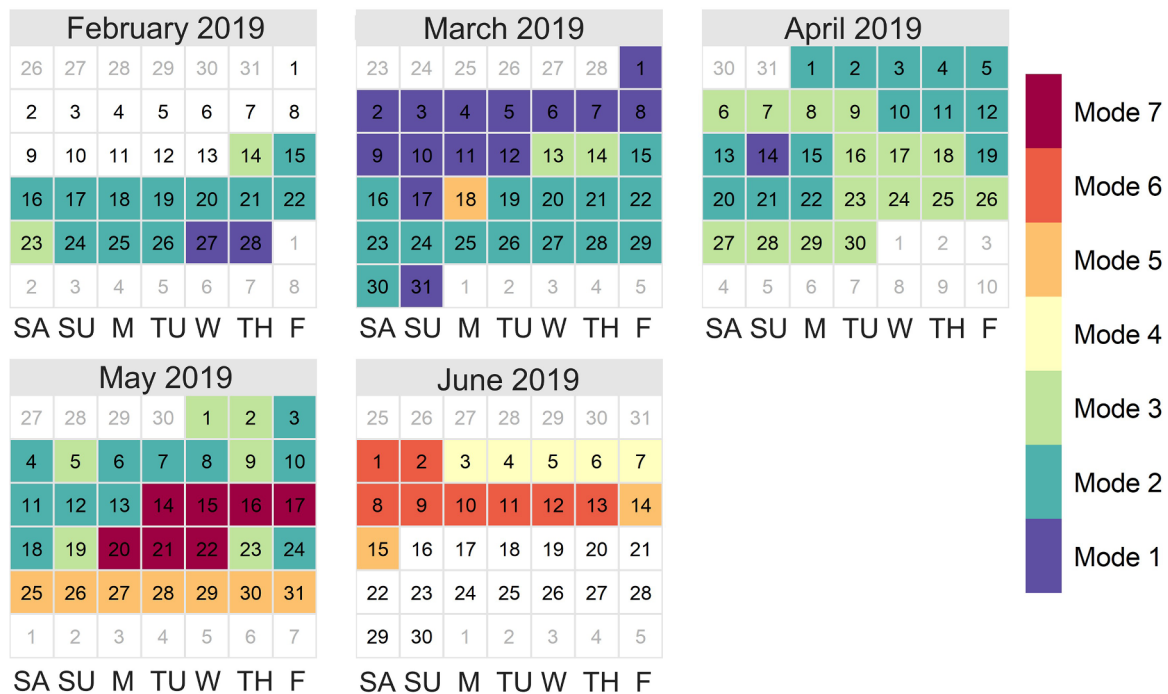


Fig. 2. Ventilation modes implemented throughout the four-month measurement campaign, including: (1.) Mode 1: low AER (≤ 2.7 h⁻¹), no pressurization; (2.) Mode 2: medium AER (2.7 h⁻¹ < AER ≤ 5.4 h⁻¹), no pressurization; (3.) Mode 3: high AER (> 5.4 h⁻¹), no pressurization; (4.) Mode 4: low AER, pressurization; (5.) Mode 5: medium AER, pressurization; (6.) Mode 6: high AER, pressurization; and (7.) Mode 7: natural ventilation with unfiltered outdoor air.

Table 3
Reaction rate constants of O₃ reactions with various gas-phase compounds.

| Chemical Formula | Compound Name | Reaction Rate Constant (cm ³ molecule ⁻¹ s ⁻¹) | Indoor Concentration Range (ppb) |
|---------------------------------|-------------------|--|----------------------------------|
| C ₄ H ₈ | 1-Butene | 1.00E-17 [52] | 0 – 10 |
| C ₅ H ₈ | Isoprene | 1.28E-17 [52] | 0 – 2 |
| C ₁₀ H ₁₆ | Limonene | 2.08E-16 [51] | 0 – 10 |
| NO | Nitrogen monoxide | 1.40E-12 [53] | 0 – 1 |
| NO ₂ | Nitrogen dioxide | 3.50E-17 [53] | 0 – 2.5 |

the office occupants, which varies with the occupancy in the office (m²); and $L_{reaction}(t)$ is the loss rate due to O₃ reactions with indoor NO_x and selected VOCs, including butene (C₄H₈), isoprene (C₅H₈), and monoterpenes (C₁₀H₁₆) (h⁻¹). $L_{reaction}(t)$ can be expressed as:

$$L_{reaction}(t) = \sum_i k_i [M_i(t)] \quad (4)$$

where $[M_i(t)]$ is the concentration of compound M_i (molecule cm⁻³) and k_i is the reaction rate constant of the reaction between O₃ and compound M_i (cm³ molecule⁻¹ s⁻¹). Limonene and isoprene, two VOCs associated with human-related emissions, and NO_x, with outdoor air as the major source, were considered for O₃ reactions. 1-Butene, with relatively high concentrations observed during the campaign and a relatively high

reaction rate with O₃, was considered as well. Their corresponding reaction rate constants and range of concentrations are summarized in Table 3. The reaction rate constants were obtained from the National Institute of Standards and Technology (NIST) Chemical Kinetics Database [51–54]. An average deposition velocity to interior building material surfaces in the office of $v_{d,bldg} = 1.62 \text{ m h}^{-1}$ was applied throughout the loss rate calculation. With all other parameters known, the O₃ deposition velocity to human body surfaces, $v_{d,occ}(t)$, can be back calculated with the assumption that the surface area of each occupant is approximately 1.7 m² [55].

The loss mechanisms of indoor O₃ listed above contribute to the difference between indoor and outdoor O₃ mixing ratios, which can be described by the “O₃ loss” ($C_{loss}(t)$). O₃ loss is a metric to evaluate the adverse health effects from human exposure to oxidation products from O₃ reactions and separate them from exposures to indoor O₃ itself [56]. The O₃ loss can be expressed as:

$$C_{loss}(t) = C_o(t) - C_i(t) \quad (5)$$

3. Results and discussion

3.1. Spatiotemporal variations in O₃ and CO₂ mixing ratios throughout the HVAC system

The diurnal trends of O₃ and CO₂ mixing ratios at the seven sampling locations (CA not shown) throughout the HVAC system under the three

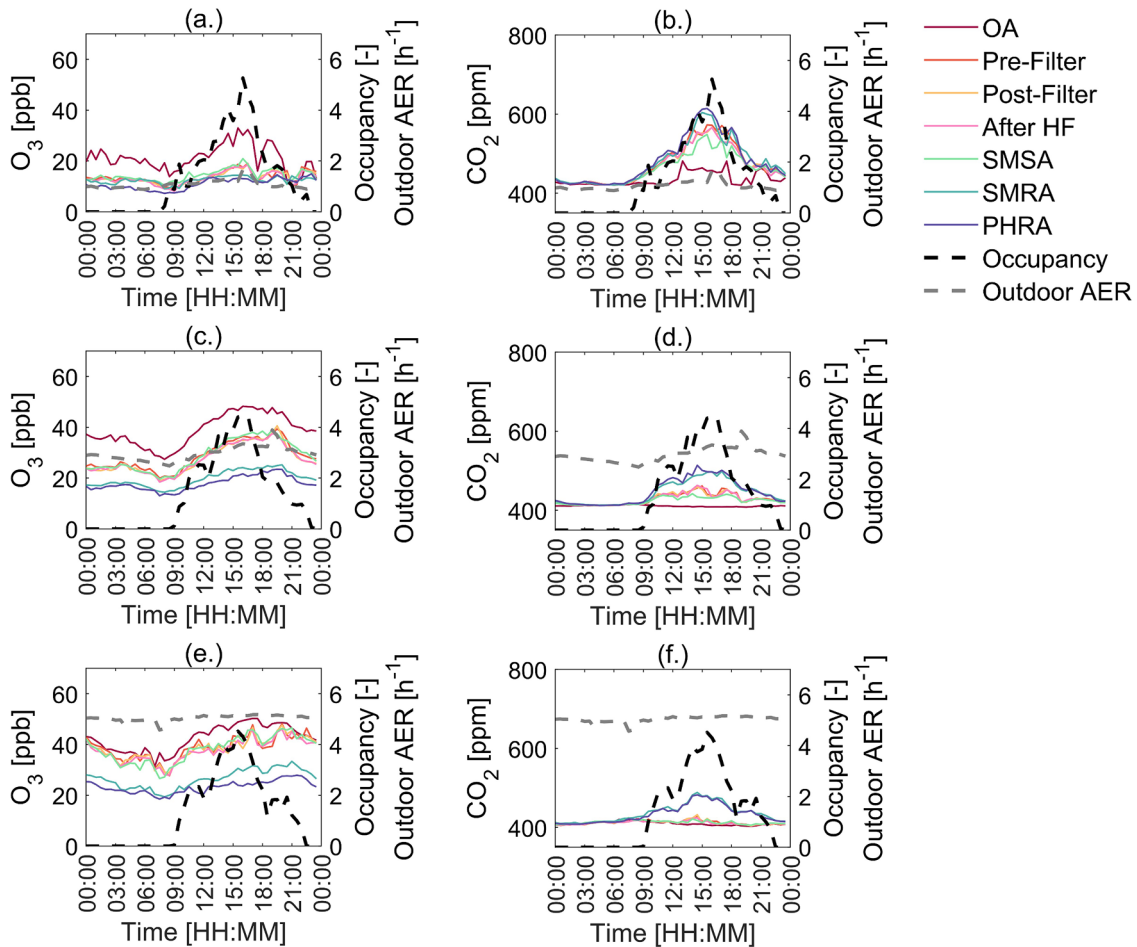


Fig. 3. Diurnal trends of (a.) O₃ and (b.) CO₂ mixing ratios under ventilation mode 1: low AER, no pressurization; (c.) O₃ and (d.) CO₂ mixing ratios under ventilation mode 2: medium AER, no pressurization; (e.) O₃ and (f.) CO₂ mixing ratios under ventilation mode 3: high AER, no pressurization. Occupancy (black dashed line) and outdoor AER (gray dashed line) are plotted on the right axis. The O₃ and CO₂ mixing ratios, outdoor AER, and occupancy are the median values of all days under the same ventilation mode category.

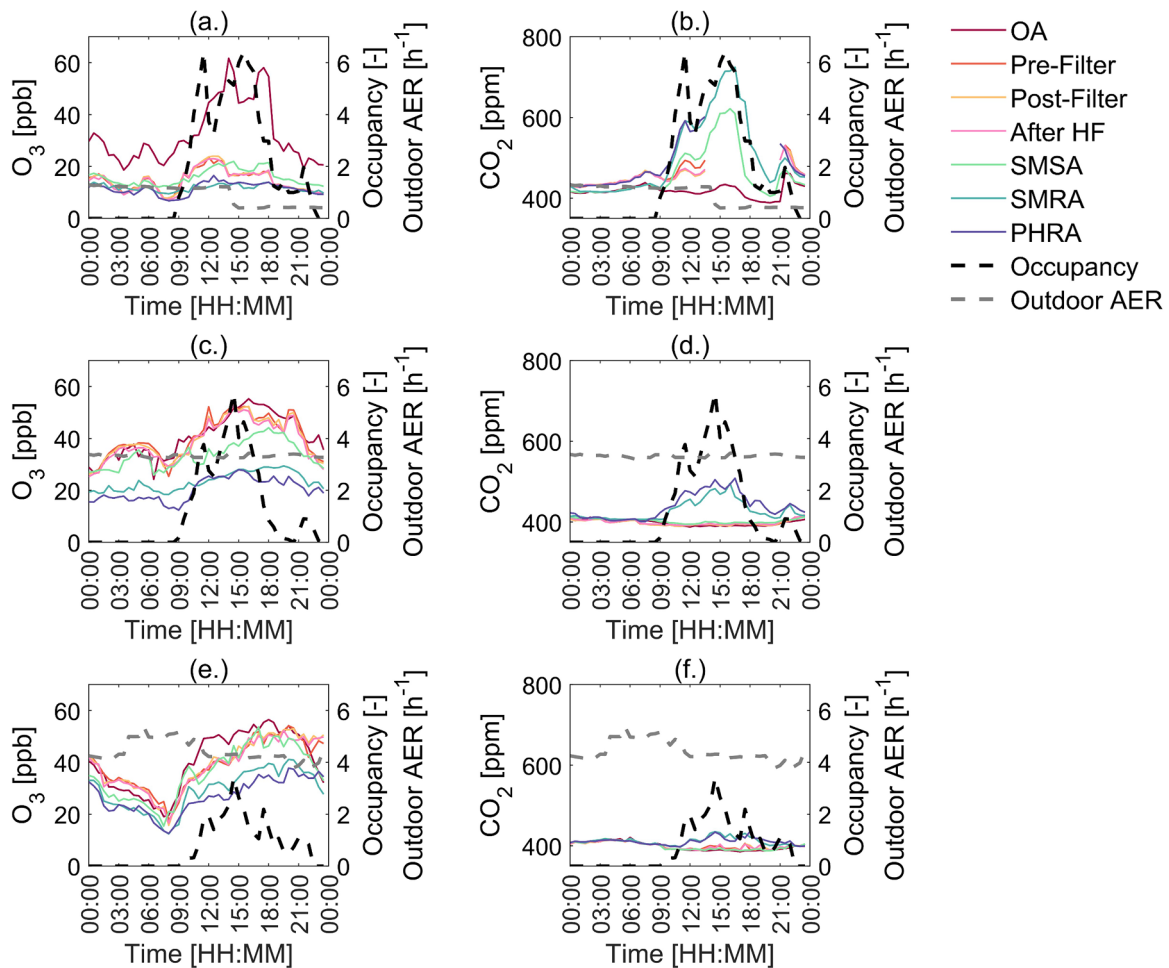


Fig. 4. Diurnal trends of (a.) O₃ and (b.) CO₂ mixing ratios under ventilation mode 4: low AER, pressurization; (c.) O₃ and (d.) CO₂ mixing ratios under ventilation mode 5: medium AER, pressurization; (e.) O₃ and (f.) CO₂ mixing ratios under ventilation mode 6: high AER, pressurization. Occupancy (black dashed line) and outdoor AER (gray dashed line) are plotted on the right axis. The O₃ and CO₂ mixing ratios, outdoor AER, and occupancy are the median values of all days under the same ventilation mode category.

non-pressurized ventilation operational modes 1 to 3 are presented in Fig. 3. O₃ mixing ratios at OA started increasing gradually at around 08:00 in the morning and peaked in the afternoon at around 17:00, which is consistent with previous observations of diurnal trends in outdoor O₃ mixing ratios [57–59]. Under ventilation modes 1 to 3 with low, medium, and high outdoor AERs, the SMRA O₃ mixing ratios peaked at 14, 25, and 33 ppb, respectively. As outdoor O₃ introduced via mechanical ventilation is the major source of indoor O₃ for this office, the outdoor AER has a strong impact on indoor O₃ mixing ratios. The SMRA CO₂ mixing ratio peaked at 15:00 to 16:00 in the afternoon, following the trend of the human occupancy level in the office. For example, as shown in Fig. 3(b), the occupancy level started increasing from 07:00 and reached its peak of 5.3 at around 16:00, while the indoor CO₂ mixing ratio started increasing from about 420 ppm at 07:00 and peaked at about 600 ppm at 15:30. As expected, human exhaled breath is the major source of CO₂ in this office environment. However, monitoring indoor CO₂ remains critical in environments where other CO₂ sources exist, such as in indoor swimming pool facilities (e.g. CO₂ addition for maintaining water pH balance) and cooking with combustion sources (e.g. gas stoves).

The automated multi-point sampling system enables further examination of the spatial distribution of O₃ and CO₂ mixing ratios throughout the HVAC system. The O₃ mixing ratios along the supply air duct (sampled at Pre-Filter, Post-Filter, After HF, and SMSA) were relatively consistent, whereas the difference between SMSA and SMRA is markedly

greater. This indicates that the contribution of the HVAC filter bank and supply air duct surfaces to the loss of O₃ is less than that for the office space itself (see discussion in Section 3.3). The spatial distribution of O₃ and CO₂ at OA, RA (SMRA and PHRA), and SMSA are strongly connected with the HVAC system operational mode. Comparing indoor O₃ and CO₂ mixing ratios under the three ventilation modes, mode 3 with the highest outdoor AER resulted in the highest SMRA O₃ mixing ratio and the lowest SMRA CO₂ mixing ratio. At low outdoor AERs (Fig. 3(a.) and 3(b.)), indoor O₃ and CO₂ mixing ratios peaked at approximately 14 ppb and 610 ppm, respectively. When outdoor AERs were raised to medium (Fig. 3(c.) and 3(d.)) and high levels (Fig. 3(e.) and 3(f.)), the peak indoor O₃ mixing ratios increased to about 25 and 34 ppb, while the peak indoor CO₂ mixing ratios dropped to around 510 and 490 ppm, respectively.

Similarly, under the three pressurized ventilation operational modes 4 to 6, spatiotemporal trends were observed across the seven sampling locations (CA not shown) throughout the HVAC system (Fig. 4). The SMRA O₃ mixing ratios peaked at 16, 29, and 41 ppb under ventilation modes 4 to 6 with low, medium, and high outdoor AERs, respectively. The indoor O₃ mixing ratios under the pressurized ventilation modes were generally higher than those under the non-pressurized ventilation modes mainly due to the bias of the sampling periods – the pressurized ventilation modes were implemented in May and June 2019, during which the outdoor O₃ mixing ratios were also higher. With lower outdoor O₃ mixing ratios, the modeled indoor O₃ ratios under the

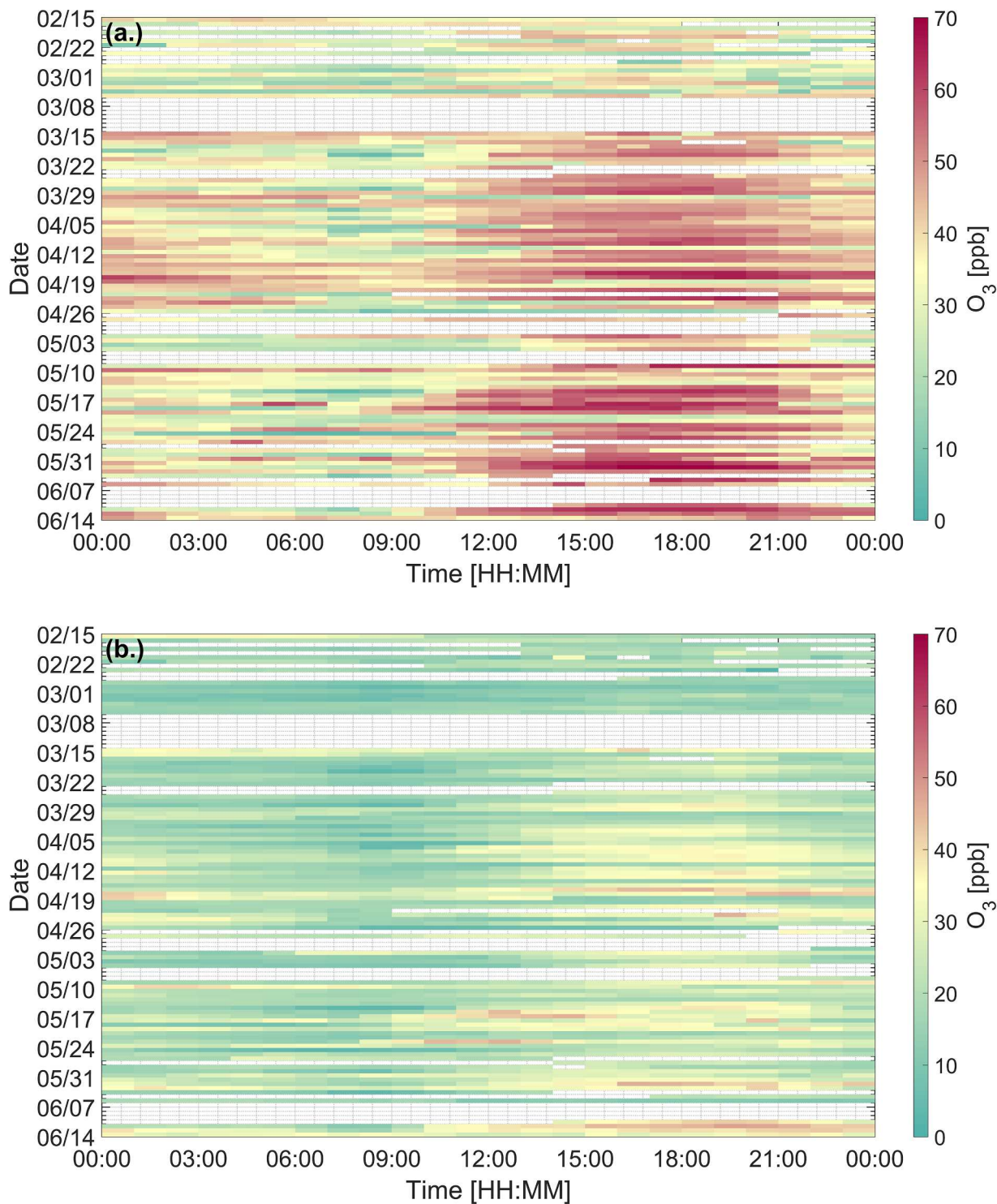


Fig. 5. Seasonal variation of (a.) outdoor O₃ mixing ratios and (b.) indoor O₃ mixing ratios. The blank areas indicate when measurement data was not available.

pressurized ventilation modes dropped as compared to their original levels (Fig. S1). Comparing mode 1 and mode 4 – low outdoor AER without and with pressurization – the outdoor O₃ mixing ratios under mode 4 were about 1.5 to 2 times higher than the outdoor O₃ mixing ratios under mode 1, while the indoor O₃ mixing ratios under the two modes were around the same levels. This indicates that pressurizing the room can effectively prevent outdoor air pollutants from infiltrating into indoor environments.

Fig. 5 shows the diurnal and seasonal variations of indoor and outdoor O₃ mixing ratios during the measurement campaign. The ranges for

diurnal outdoor O₃ mixing ratios increased from 10 to 30 ppb in February/March to 20 to 60 ppb in June with the increase in the duration of daylight. The trend observed in this study agrees with the seasonal O₃ variations observed in the Midwest region of the U.S. [57]. The median indoor O₃ mixing ratios during the campaign varied from 15 to 25 ppb throughout the day, while the median outdoor O₃ mixing ratios varied from 15 to 60 ppb (Fig. 6). This suggests that the building operation strategy for maintaining acceptable IAQ cannot be simply based on CO₂ mixing ratios. For instance, when the occupancy level is high, the typical control strategy is to increase the outdoor AER.

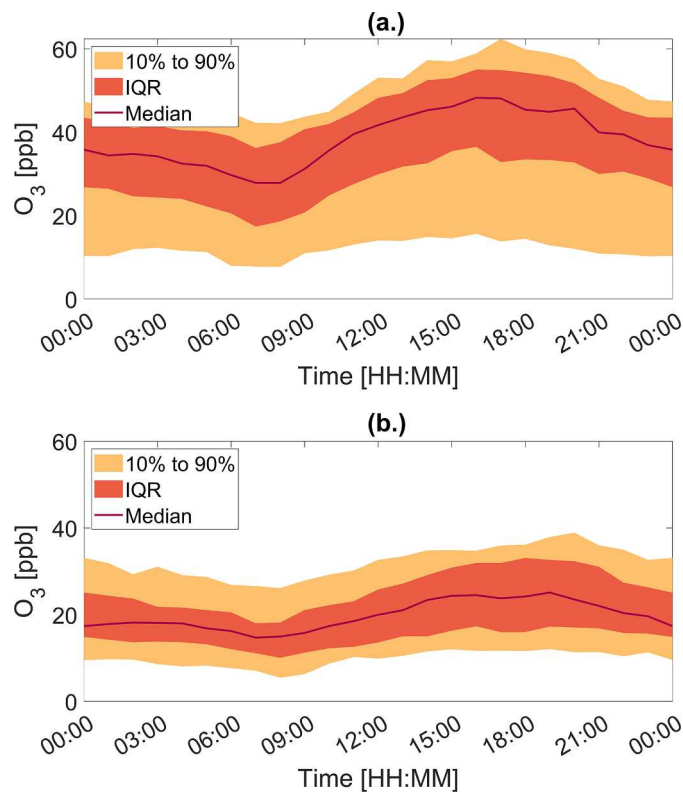


Fig. 6. Median, interquartile range, and 10th- to 90th-percentile of (a.) outdoor O_3 mixing ratios and (b.) indoor O_3 mixing ratios.

However, introducing more outdoor air to dilute indoor-generated CO_2 in the summer can lead to significant increases in indoor O_3 mixing ratios due to the high outdoor O_3 mixing ratios. With high occupancy levels and elevated O_3 mixing ratios, it is more likely that O_3 reactions with human skin lipids and body surfaces would form more secondary products that may potentially lead to adverse health effects. Thus, it is critical to consider the combined effects of different trace gases on IAQ when controlling a building ventilation system.

3.2. O_3 and CO_2 I/O ratios under different outdoor AERs and human occupancy levels

Spatiotemporal sampling of O_3 and CO_2 under different HVAC system operational modes revealed relationships between human occupancy, outdoors AERs, and O_3 and CO_2 mixing ratios. Given that outdoor O_3 is the major source of indoor O_3 in the office environment, the dependence of indoor O_3 mixing ratios on the outdoor AER and occupancy could be biased by the outdoor O_3 concentration. The indoor/outdoor (I/O) ratio normalizes indoor mixing ratios by outdoor mixing ratios, providing a more unbiased term to examine the contribution of indoor- and outdoor-associated sources of trace gases. Fig. 7 groups the I/O ratios of O_3 and CO_2 mixing ratios by outdoor AERs and office occupancy levels. The occupancy levels were categorized as: (1.) low occupancy where occupancy < 4; (2.) medium occupancy where $4 \leq$ occupancy < 8; and (3.) high occupancy where occupancy \geq 8.

Generally, the I/O ratio of O_3 increases with an increase in the outdoor AER (Fig. 7(a.)). Median O_3 I/O ratios ranged from 0.35 to 0.43, 0.45 to 0.55, and 0.60 to 0.65 at low, medium, and high AERs, respectively. O_3 I/O ratios observed in this study are consistent with the I/O ratio reported for an office in the U.S. with similar AERs [60], but higher than those reported in offices in Europe and Asia where AERs were not specified [61,62]. The dependency of the O_3 I/O ratio on occupancy levels varies with outdoor AERs. The median O_3 I/O ratio decreased by 11 to 22% from low/medium occupancy to high occupancy levels at low

outdoor AERs, and by 4 to 22% at medium outdoor AERs. Interestingly, at high outdoor AERs, the median O_3 I/O ratios were around the same level as at low and medium occupancy, and only elevated by 8% from low/medium to high occupancy levels. At lower AERs, air exchange due to ventilation contributed less to the loss mechanisms of indoor O_3 , while O_3 deposition to human body surfaces contributed more to the loss of indoor O_3 . Thus, with higher occupancy, lower I/O ratios can be observed, as the increase of O_3 deposition leads to lower indoor O_3 mixing ratios. In contrast, at higher AERs, outdoor air ventilation via the HVAC system became the major sink for indoor O_3 and deposition to occupant surfaces contributed less to indoor O_3 loss, so the O_3 I/O ratio can be less dependent on occupancy levels at higher AERs. An ANOVA analysis (Table 4) also verified the dependence of the O_3 I/O ratio on occupancy and AER ($p < 0.001$).

Fig. 7(b.) presents the “ O_3 loss” at different AERs and occupancy levels. The median value of the O_3 loss at different outdoor AERs and occupancy levels varies from 14.7 to 26.5 ppb, similar to the O_3 loss ranges modeled by Weschler and Nazaroff (15.5 to 27.8 ppb) for different indoor environments with AERs from 0.25 to 6 h^{-1} and occupancy levels from 2 to 35 occupants [56]. At low and medium AERs, the O_3 loss increased with the increase in occupancy levels due to deposition onto human body surfaces. This indicates more secondary products can be formed indoors with higher occupancy, which may lead to adverse health effects. The O_3 loss decreased when the outdoor AER increased, as higher AER leads to elevated indoor O_3 mixing ratios. This suggests that HVAC system control and building ventilation strategies need to be adjusted accordingly based on the outdoor AER and occupancy levels.

Fig. 7(c.) illustrates the dependency of the CO_2 I/O ratio on the AER and occupancy levels. Occupants are the major source of indoor CO_2 and the median CO_2 I/O ratios increased with the increase of occupancy levels, increasing from 1.01 to 1.03 (low occupancy) to 1.22 to 1.45 (high occupancy) at various AERs. However, the increase in the outdoor AER did not always lower the CO_2 I/O ratio. At low and medium occupancy (less than 8 occupants), the median CO_2 I/O ratios were similar across low, medium, and high AERs. The consistency in CO_2 I/O ratios across different AERs indicates that with lower occupancy, a low AER would be sufficient to control the indoor CO_2 mixing ratio at low levels, with an I/O ratio very close to 1. At high occupancy levels (> 8 occupants), the CO_2 I/O ratio dropped by 5% and 15% when the AER increased from low to medium and high levels, respectively. Increasing outdoor AERs can effectively dilute indoor-generated CO_2 at higher occupancy levels. Fig. 7 demonstrates that the outdoor AERs and occupancy levels may have different effects on O_3 and CO_2 I/O ratios. Building ventilation strategies may need to be implemented with careful and comprehensive consideration of their impact on different indoor air pollutants. Recent studies have evaluated the performance of low-cost metal oxide and electrochemical sensors for trace gases, including O_3 , CO, and NO_x [63–65]. With proper calibration, these low-cost sensors showed good correlation with reference analytical instruments. A multi-point trace gas sampling system such as that presented in this study, or implemented through the use of low-cost sensor arrays, has the potential to be integrated into building automation systems to aid the ventilation control of buildings and improve IAQ.

3.3. O_3 loss in the office and its HVAC system

Fig. 8 illustrates diurnal trends of overall and itemized O_3 loss rates during representative days for three different ventilation operational modes – 1, 2, and 3. The loss rate due to O_3 deposition to human body surfaces generally follows the trend of indoor occupancy levels, indicating that the occupancy level is strongly connected to indoor O_3 loss mechanisms and indoor O_3 mixing ratios. For the ventilation mode 1 with the lowest AER, the overall O_3 loss rate ranges from 5.3 to 9.2 h^{-1} throughout the day. This variation is mainly due to the variation in O_3 deposition to human body surfaces, which ranges from 0 to 2.3 h^{-1} with occupancy ranging from 0 to 9.5. O_3 loss due to ventilation and

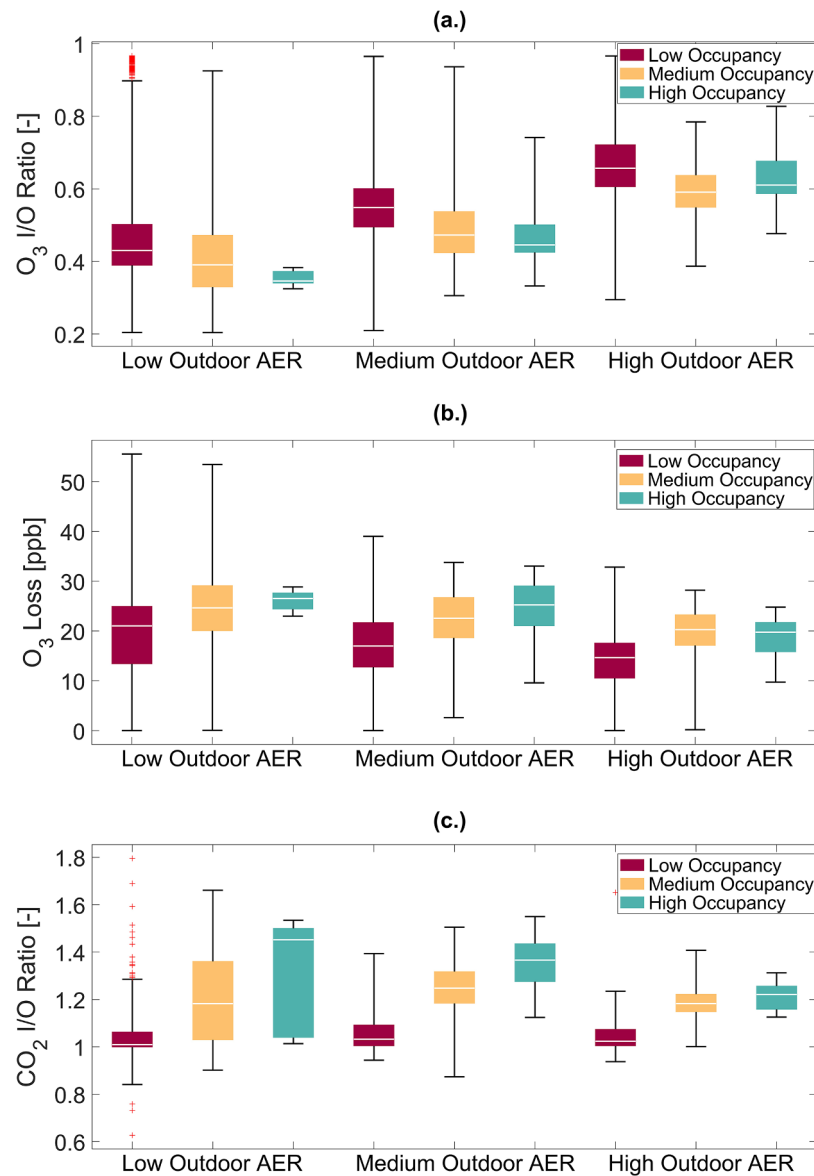


Fig. 7. (a.) I/O ratios of O₃ mixing ratios, (b.) O₃ loss, and (c.) I/O ratios of CO₂ mixing ratios for different outdoor AERs and office occupancy levels during the field measurement campaign.

Table 4
ANOVA test for the dependence of the O₃ I/O ratio on AER and occupancy.

| | Sum of Squares | DF | Sum of Squares | F | p-Value |
|-----------|----------------|------|----------------|--------|-----------|
| AER | 19.007 | 3 | 6.3357 | 394.82 | 1.46E-226 |
| Occupancy | 2.5740 | 2 | 1.2870 | 80.203 | 6.33E-35 |
| Error | 69.114 | 4307 | 0.016047 | | |
| Total | 90.296 | 4312 | | | |

exfiltration dominated the overall O₃ loss rate under all three ventilation modes for our study site, an office environment without indoor combustion sources (e.g. gas stoves). Outdoor air ventilation and exfiltration, deposition to building material surfaces, and deposition to human body surfaces account for 37 to 64%, 36 to 37%, and 0 to 26% of the overall O₃ loss rate, respectively. The contribution of gas-phase reactions to the overall O₃ loss rate was negligible. It should be noted that in other indoor environments, especially those with combustion sources and the use of personal care products, O₃ reactions with NO_x and VOCs could be important sinks. The overall O₃ loss rates were the highest,

approaching a peak of around 14 h⁻¹, under ventilation mode 3 with the highest outdoor AER. Outdoor air ventilation contributed 44 to 51% to the overall O₃ loss rate under mode 2 and 56 to 69% to the overall O₃ loss rate under mode 3. For O₃ deposition to human body surfaces, the loss rate peaked at 3.0 h⁻¹ and 2.6 h⁻¹ when the office occupancy level peaked at 8.7 and 5.5 under ventilation modes 2 and 3, respectively. Average O₃ deposition velocities to human body surfaces during the three days selected from ventilation modes 1 to 3 were estimated to be 48, 68, and 93 m h⁻¹, which results in O₃ loss rates of 0.25, 0.35, and 0.47 h⁻¹ person⁻¹, respectively. The deposition velocities to human body surfaces observed in this study were 2 to 10 times higher than the values reported in previous studies [12,16,66–68]. O₃ loss rates reported in these studies vary from 0.02 h⁻¹ person⁻¹ to 1.5 h⁻¹ person⁻¹, with room volumes ranging from 22.5 to 670 m³. O₃ loss rates observed in our study were 1.5 to 4.7 times higher than the O₃ loss rates for a simulated office with a similar room volume [69]. Such inconsistencies might be explained by differences in the application of personal care products to the skin and hair [70] or the clothing the occupants were wearing [13, 71], especially for mode 3 which occurred in late April. The deposition velocities can be enhanced due to O₃ reactions with hair (large surface

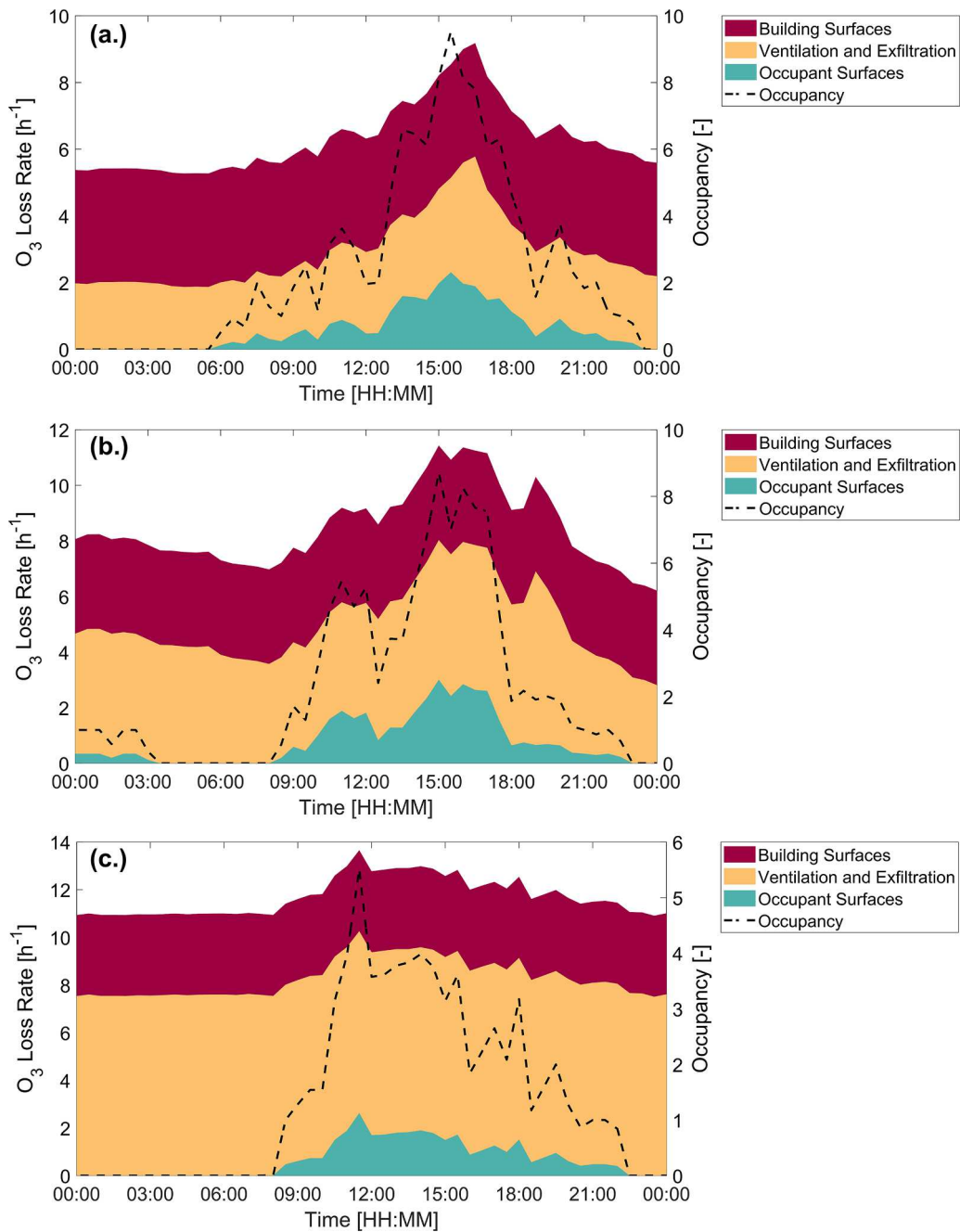


Fig. 8. Diurnal trends of the overall and itemized O₃ loss rates (left axis) and occupancy (right axis) during representative days for three different ventilation modes: (a.) ventilation mode 1, (b.) ventilation mode 2, and (c.) ventilation mode 3.

area), soiled clothing (multiple layers may be worn), and soiled backpacks. Thus, the assumed occupant surface area might be underestimated. Time delays in indoor and outdoor O₃ sampling and the time-averaged loss rate calculation may also lead to uncertainties in the estimation of the deposition velocities.

Considering the large surface area of the HVAC system and its components, the HVAC system can be another important sink of outdoor O₃ being supplied to indoor environments. The multi-point sampling system allows for the investigation of how each HVAC component can impact O₃ dynamics. Fig. 9(a.) presents the diurnal trend of O₃ loss across the HVAC filter bank during the pre/post-filter sequence. Pre-Filter O₃ mixing ratios were consistently higher than the Post-Filter mixing ratios, indicating O₃ deposition to the filter media. Up to 8 ppb of O₃ could deposit to the HVAC filter bank when passing through,

resulting in 0 to 10% of O₃ loss across the filter. O₃ removal by other HVAC system components is presented in Fig. 9(b.). O₃ mixing ratios dropped by a median of 3.9, 1.2, 0.5, and 6.0% when travelling from Pre-Filter to SMSA, Post-Filter to SMSA, After HF to SMSA, and SMRA to PHRA, respectively. The difference between O₃ removal percentages from Pre-Filter and Post-Filter to SMSA verifies the contribution of the HVAC filter bank to O₃ deposition. For the other parts of the HVAC system, the HVAC duct itself could be major contributor of O₃ loss. The HVAC duct between SMRA and PHRA was the longest among the four segments, with only one return fan installed along the duct. Both sampling locations were located along the return air duct, however, up to 18% of O₃ loss was observed. With the two sampling locations at two different mechanical rooms that are > 10 m apart, the large surface area of the long HVAC duct contributes to the high O₃ loss from SMRA to

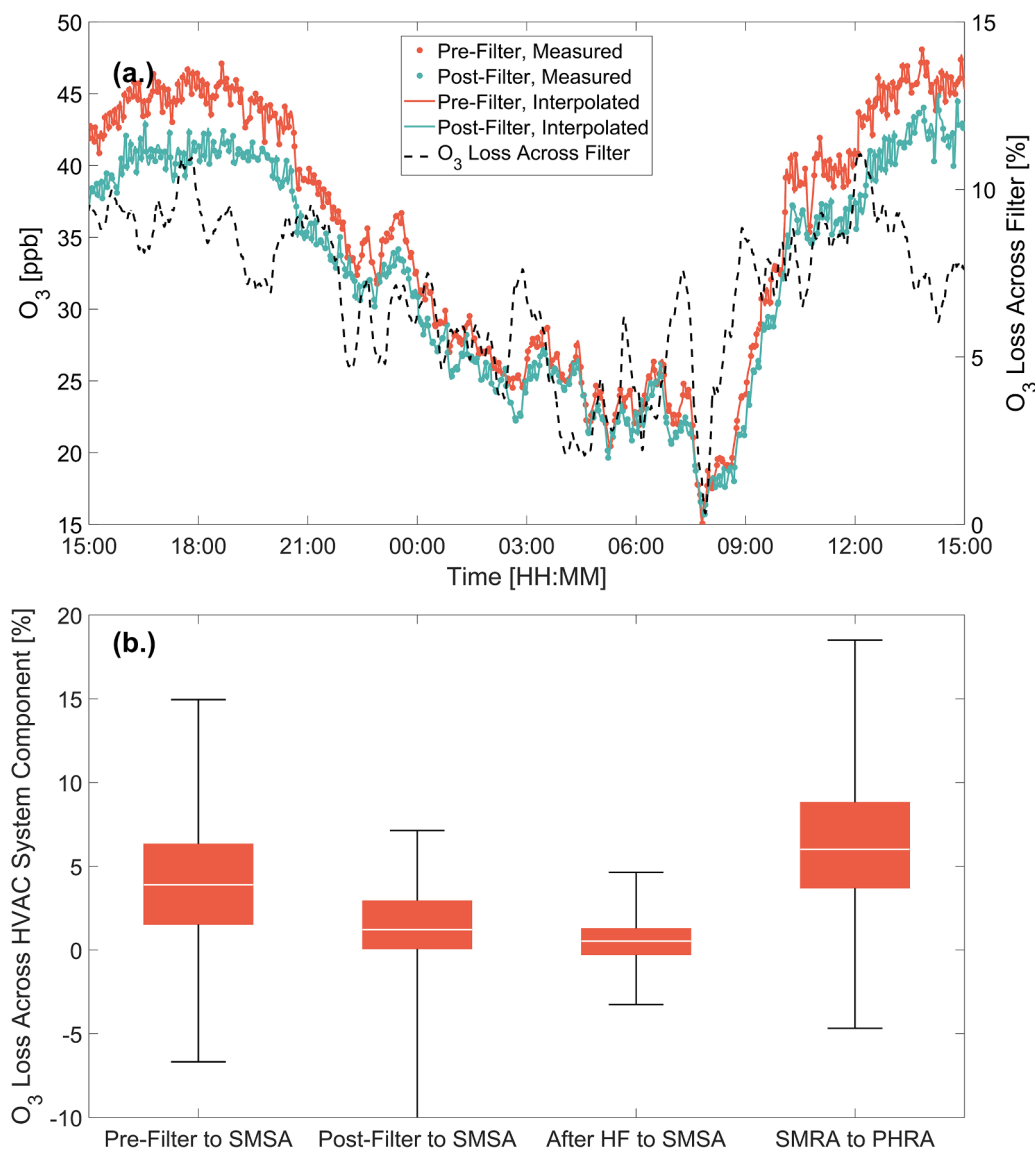


Fig. 9. (a.) Diurnal trend of the O₃ loss across the HVAC filter bank during the pre-/post-filter sampling sequence and (b.) O₃ loss across different HVAC system components during the field measurement campaign.

PHRA.

It is important to note that the findings presented here may be specific to the office environment studied. In office settings, as demonstrated in this study, occupants are major contributors to O₃ loss, with large-scale and complex HVAC systems also playing an important role in the removal of O₃. In contrast, in residential environments with lower occupancy and simpler HVAC systems, the contribution of occupants and HVAC systems to O₃ loss may be less significant. However, other indoor activities – such as cooking with gas stoves, which emit NO_x, or the use of personal care products that release VOCs – can lead to O₃ reactions with these compounds and the production of secondary pollutants. These processes may become the dominant mechanisms for O₃ loss in such environments. This highlights the need for multi-point sampling of trace gases across diverse indoor environments and their associated HVAC systems to fully understand the fate and dynamics of indoor air pollutants.

4. Conclusions and future directions

This study introduced a novel automated multi-point sampling system for the real-time monitoring of spatiotemporal trends of trace gases

in the HVAC system of a LEED-certified office building. A four-month field measurement campaign at the Purdue University Ray W. Herrick Laboratories provided valuable insights into the dynamics of O₃ and CO₂ within the HVAC system under varying ventilation modes and occupancy levels. Through O₃ and CO₂ measurements with the multi-point sampling system at eight different locations throughout the HVAC system in a LEED-certified office building, spatiotemporal variations in O₃ and CO₂ mixing ratios were observed. The results revealed significant diurnal and seasonal variations in both indoor and outdoor O₃ mixing ratios, emphasizing the influence of outdoor air on IAQ. Higher outdoor AERs were associated with increased indoor O₃ levels but reduced CO₂ concentrations, demonstrating the complex interplay between ventilation rates and indoor air pollutant levels. Spatial variations of O₃ and CO₂ mixing ratios were observed as well, especially across supply air, return air, and outdoor air sampling locations. Minor variations were also observed among different locations along the supply duct (Pre-Filter, Post-Filter, After-HF, and SMSA) and return duct (SMRA and PHRA), indicating that the HVAC filter bank and duct surfaces can contribute to O₃ loss.

I/O ratios of O₃ and CO₂ ranged from 0.35 to 0.65 and 1.01 to 1.45, respectively, at different outdoor AERs and occupancy levels.

Ventilation and occupancy impact the I/O ratio of O₃ and CO₂ differently, which needs to be carefully accounted for when implementing building ventilation strategies to improve IAQ. Overall O₃ loss rates and the contribution of each loss mechanism were estimated, including building ventilation and exfiltration (outdoor air exchange), gas-phase O₃ reactions with NO_x and selected VOCs, and O₃ deposition to building material surfaces and human body surfaces. Ventilation and exfiltration contributed most to the overall O₃ loss rate, and the contribution of deposition on human body surfaces cannot be neglected when the occupancy level is high. Human occupancy significantly influenced O₃ deposition onto skin and clothing, further complicating the dynamics of IAQ. This study also highlighted the role of HVAC components, such as filters and ducts, in contributing to O₃ loss, with up to 18% O₃ removal observed in the longest HVAC duct segment.

Current ventilation standards, which primarily consider CO₂ mixing ratios in the design of the ventilation rate, may not adequately address the complexities of indoor air composition and the interactions between various pollutants. This study emphasizes the need for a more comprehensive IAQ sensing system and ventilation control strategies that consider multiple trace gases to effectively optimize IAQ. The automated multi-point sampling system presented in this study has the potential to be implemented in building automation systems to aid in the control of building ventilation. This system can be connected not only to CO₂ and O₃ analyzers as demonstrated in this study, but also to advanced analytical instruments, including online mass spectrometers such as PTR-TOF-MS, which can characterize a wide range of VOCs. While installing individual instruments at each sampling location would be impractical due to their size, cost, and calibration needs, a multi-point sampling system with an automatic multi-port valve offers a practical solution for precise spatiotemporal trace gas monitoring. By integrating this system into building automation systems, real-time data of multiple trace gases (e.g. CO₂, O₃, NO_x, VOCs) can be utilized to develop dynamic ventilation strategies that respond to varying indoor and outdoor conditions. For example, by measuring trace gases at the supply, return, and outdoor air ducts, building automation systems can better understand the sources, transport, and fate of these air pollutants.

Real-time monitoring of the spatial distribution of trace gases at these locations can be further inputted into indoor chemistry models to predict the concentration of these pollutants and their possible secondary reaction products in order to find optimal settings for the HVAC system. This dynamic approach helps maintain a healthy indoor environment while minimizing energy consumption by avoiding unnecessary ventilation during periods of high outdoor air pollution. In addition, by arranging the sampling locations upstream and downstream of in-duct air filtration and purification devices (such as HVAC filter banks, UV disinfection units, or bi-polar ionization devices), the system can evaluate the in-situ performance of these technologies, ensuring that these devices are functioning properly and informing when maintenance is needed. We believe that the innovative integration of automated multi-point sampling, analytical instrumentation, and building automation systems opens up new possibilities for real-time air quality monitoring and predicting and enabling more accurate and efficient HVAC system operation and maintenance across diverse indoor environments. Such systems have the potential to help reduce building maintenance and operational costs while improving the health and productivity of office workers. Future research should focus on exploring their integration with other smart building technologies, optimizing the control of HVAC systems, analyzing their cost benefits, and evaluating their long-term benefits in diverse building types and climates.

CRediT authorship contribution statement

Jinglin Jiang: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Junkai Huang:** Visualization, Methodology, Formal

analysis. **Nusrat Jung:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Brandon E. Boor:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.buildenv.2025.112651](https://doi.org/10.1016/j.buildenv.2025.112651).

Data availability

Data will be made available on request.

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