Role of location, season, occupant activity, and chemistry in indoor ozone and nitrogen oxide mixing ratios†

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Understanding the oxidizing environment indoors is important for predicting indoor air quality and its impact on human health. We made continuous time-resolved measurements (30 s) of several oxidants and oxidant precursors (collectively referred to as oxidant*): ozone (O3), nitric oxide (NO), and NO2 – the sum of nitrogen dioxide (NO2) and nitrous acid (HONO). These species were measured in three indoor environments – an occupied residence, a chemistry laboratory, and an academic office – in Syracuse, New York, during two seasons in 2017 and 2018. Oxidant* levels differed greatly between the residence, the lab and the office. Indoor-to-outdoor ratios (I/O) of O3 were 0.03 and 0.67 in the residence and office; I/O NO (I/O NO2*) were 11.70 (1.26) in the residence and 0.13 (1.70) in the office. Little seasonal variability was observed in the lab and office, but O3 and NO2* levels in the residence were greater in spring than in winter, while NO levels were lower. Human activities such as cooking and opening patio doors resulted in large changes in oxidant* mixing ratios in the residence. In situ chamber experiments demonstrated that the increase in O3 and NO2* levels during door-open periods was due to a combination of physical mixing between indoor and outdoor air, gas-phase production of NO2 from O3–NO chemistry, and heterogeneous formation of HONO on indoor surfaces. Our results also highlight the importance of chemistry (with NO, alkenes, and surfaces) in O3 mixing ratios in the residence, especially during door-open periods.

1 Introduction

Ozone (O3) exposure is a major public health concern. Many studies have reported associations between outdoor O3 mixing ratios and morbidity and mortality. Since North Americans spend the majority (~85%) of their time indoors, most O3 exposure is expected to occur in indoor environments. Ozone can be generated indoors by appliances such as photocopiersons, printers, and air cleaning devices, but in most buildings the predominant source of indoor O3 is transport from outdoors through ventilation. Whether originating indoors or outdoors, O3 in indoor environments can undergo homogeneous and heterogeneous chemistry. Secondary organic aerosols and other potentially irritating species, such as aldehydes, ketones, acids, and epoxides can be generated and cause additional adverse health effects. Indoor exposure to O3 is accompanied by exposure to the products of O3-initiated indoor chemistry.

Ozone-initiated chemistry in indoor environments has received significant attention. As an oxidant, O3 reacts in ventilation systems and on interior materials, including carpets and indoor furnishing surfaces. It also initiates gas-phase reactions with common indoor volatile organic compounds (VOCs) and those from tobacco smoke, cleaning products, and air fresheners. Recently, the human envelope has received increasing attention as skin oils on human surfaces and soiled clothing are an important O3 sink. In addition to reducing the oxidizing environment indoors is important for predicting indoor air quality and its impact on human health. We made continuous time-resolved measurements (30 s) of several oxidants and oxidant precursors (collectively referred to as oxidant*): ozone (O3), nitric oxide (NO), and NO2 – the sum of nitrogen dioxide (NO2) and nitrous acid (HONO). These species were measured in three indoor environments – an occupied residence, a chemistry laboratory, and an academic office – in Syracuse, New York, during two seasons in 2017 and 2018. Oxidant* levels differed greatly between the residence, the lab and the office. Indoor-to-outdoor ratios (I/O) of O3 were 0.03 and 0.67 in the residence and office; I/O NO (I/O NO2*) were 11.70 (1.26) in the residence and 0.13 (1.70) in the office. Little seasonal variability was observed in the lab and office, but O3 and NO2* levels in the residence were greater in spring than in winter, while NO levels were lower. Human activities such as cooking and opening patio doors resulted in large changes in oxidant* mixing ratios in the residence. In situ chamber experiments demonstrated that the increase in O3 and NO2* levels during door-open periods was due to a combination of physical mixing between indoor and outdoor air, gas-phase production of NO2 from O3–NO chemistry, and heterogeneous formation of HONO on indoor surfaces. Our results also highlight the importance of chemistry (with NO, alkenes, and surfaces) in O3 mixing ratios in the residence, especially during door-open periods.
O<sub>3</sub> levels, O<sub>3</sub>-initiated reactions are a source of two other important indoor oxidants: hydroxyl and nitrate radicals. Ozone/alkene reactions are considered an important source of hydroxyl radicals (OH) indoors, while the reaction of O<sub>3</sub> with nitrogen dioxide (NO<sub>2</sub>) is the major source of nitrate radicals indoors. With these recent scientific efforts, our knowledge of O<sub>3</sub> reactivity indoors has expanded greatly. However, the listed studies have been conducted in either mechanically ventilated buildings, under laboratory settings, or in simulated office environments; all are non-residential environments.

A large number of studies focused on understanding O<sub>3</sub> levels in commercial buildings, museums, and classrooms have been undertaken in the past four decades. The air exchange rate (AER) has been shown to affect the indoor concentration of O<sub>3</sub>, with a higher AER yielding higher indoor to outdoor ratios (I/O), which often range from 0.3–0.8. Far fewer measurements of O<sub>3</sub> mixing ratios have been made in residences, where people spend most of their time. Mean O<sub>3</sub> mixing ratios in homes range from sub-ppbv levels to 60 ppbv and I/O span a large range between <0.1 and 0.7, depending on ventilation rates. Most measurements conducted in residences were made with passive O<sub>3</sub> samplers that were exposed to the indoor environment for extended periods of time (1 to 14 days). The few studies that report time-resolved O<sub>3</sub> in American homes were conducted prior to the implementation of the 8 hour O<sub>3</sub> National Ambient Air Quality Standard (NAAQS) in 1997. For measurements made in US homes subsequent to the NAAQS implementation, indoor O<sub>3</sub> levels were generally lower than 2 ppbv. However, model studies investigating O<sub>3</sub> chemistry and predicting OH and hydroperoxy (HO<sub>2</sub>) radicals in indoor environment use O<sub>3</sub> levels of up to 50 ppbv. Many laboratory experiments studying O<sub>3</sub>-initiated reactions in residential settings use O<sub>3</sub> levels ranging from 30 to 250 ppbv. There is a lack of real-time characterization of the mixing ratio of O<sub>3</sub> in residences and investigation of O<sub>3</sub>-initiated chemistry under realistic residential conditions.

To help fill this knowledge gap, we deployed the Mobile Indoor Laboratory for Oxidative Species (MILOS), a custom-built non-invasive mobile laboratory that provides time-resolved measurements of a suite of oxidants and oxidant precursors (collectively referred to as oxidant*), in three different indoor environments including an occupied residence. The mixing ratios, sources, and sinks of O<sub>3</sub>, nitric oxide (NO), NO<sub>2</sub>, and nitrous acid (HONO) were characterized in the residence and compared to those in a chemistry lab and an office. Secondary gas-phase and heterogeneous reactions involving these species were also investigated.

2 Methods

2.1 Experimental design

Continuous, time-resolved measurements were conducted in three indoor environments in Syracuse, New York, including an occupied single-family residence, a chemistry laboratory, and an academic office using MILOS. A detailed description of the instrumental setup, including limits of detection (LOD) for the various analyzers, can be found elsewhere. In brief, air was drawn through a perfluoroalkoxy (PFA) tubing inlet placed at head height followed by a 1 inch PFA tubing before entering a UV photometric analyser for O<sub>3</sub> measurements (Ecotech Serinus 10, UV photometric) and a chemiluminescence NO<sub>2</sub> analyzer (Ecotech Serinus 40) that nominally measures NO<sub>x</sub> (NO + NO<sub>2</sub>) and NO<sub>2</sub>. The NO<sub>2</sub> channel of this instrument responds quantitatively to HONO and nitric acid (HNO<sub>3</sub>) in addition to NO<sub>2</sub> and NO<sub>x</sub>, and has an unquantified response to alkyl nitrates. Interference from alkyl nitrates is assumed to be small based on the current knowledge about oxidation chemistry indoors, measured indoor HNO<sub>3</sub> levels have been reported to be very low relative to that of HONO. The nominal NO<sub>2</sub> (NO<sub>x</sub> = NO + HONO) was measured throughout the field study. Distinct separate measurements of NO<sub>2</sub> and HONO were made occasionally following the method described by Zhou et al. for CO<sub>2</sub>, relative humidity (RH), and temperature indoors were monitored with a TSI IAQ7545 air quality monitor. Data were acquired at 30 s intervals for all species except speciated HONO, for which data were acquired every 5 minutes.

Air sampling was carried out sequentially between three indoor environments. Each location was sampled in fall/winter and in spring, with the purpose of capturing seasonal differences. The fall/winter campaign lasted for more than 2 months from September 27 to December 9, 2017, and the spring campaign spanned 5 weeks from March 23 to May 2, 2018. Outdoor mixing ratios were measured intermittently by moving the inlet to an outdoor location. Average I/O was calculated for individual species.

2.2 Site description

The single-family residence is a 4-bedroom 1.5-storey house in an urban residential area. The main floor (where measurements were made) has an open floor plan with doors and windows on all four sides. Gas appliances include a stove (5 burners and an oven), water heater, fireplace, and furnace for space heating. The sampling inlet was placed in the kitchen (approximately the center of the main floor) or occasionally in the living room at head height (1.5 m above the floor). The chemistry lab (basement, no window) and office (2nd floor, 1 window) are in the same building in the Syracuse University campus, ~1.8 km away from the residence. All appliances in the university use electricity. The estimated air volume is 250, 90, and 24 m<sup>3</sup> in the residence, lab, and office, respectively. The residence utilized natural ventilation (sometimes opening patio doors) and a forced-air system (heating or air conditioning) during the sampling periods, whereas the lab and office used mechanical ventilation that exchanged room air with outdoor air. During the sampling period, the residence was occupied by two non-smoking adults, one child, and a dog. The lab was occupied by five to seven non-smoking adults and the office was occupied by one non-smoking adult. Occupants performed their usual daily activities throughout the field campaign. Activities such as cooking using the stove and opening doors and windows were logged by the occupants.
2.3 In-house environmental chamber

To investigate the indoor oxidizing environment under higher O₃ levels in the residence, O₃-perturbation experiments were conducted in the residence during both measurement campaigns. A 5 L Pyrex glass environmental chamber (60 cm in length x 10 cm in diameter) was placed in the shade and connected to the sampling line between the sampling inlet and MILOS. MILOS continuously sampled room air through the chamber. A known amount of O₃ was then injected into the environmental chamber, where it mixed with ambient indoor air. Air composition in the chamber was monitored for approximately one hour during O₃ injection, followed by a ~30 minute injection of zero air as a negative control. In all perturbation experiments, the chamber air flow was 1.3 L min⁻¹, yielding a residence time of 4.5 min.

2.4 Air exchange rate

The air exchange rate (AER) was estimated using a decay method of the indoor CO₂ concentration. Only periods with a dominant indoor source (e.g., cooking in the residence, occupants or dry ice in the lab and office) which led to CO₂ concentrations significantly higher than the background values, followed by a non-source period, were considered for these calculations. Assuming constant removal rates and background mixing ratios of CO₂ during the decay period and an even distribution of the indoor CO₂ concentration the AER can be calculated.

\[ C_t = e^{-kt} C_o + C_b \]

where \( C_t \) is the indoor mixing ratio after time \( t \), \( C_o \) is the initial (peak) mixing ratio, and \( C_b \) is the background mixing ratio of CO₂ during the decay event. The AER was determined using an exponential regression of the observed mixing ratio versus time for each decay period.

3 Results and discussion

3.1 Oxidant levels in the three indoor environments

The statistics of the air exchange rate and oxidant* levels in the residence, chemistry lab, and office over the entire sampling period are shown in Fig. 1. The residence had a distinctly different oxidizing environment than the academic building. The average (±SD) AER in the residence was 0.69 (±0.30) h⁻¹, substantially lower than that in the lab (3.80 (±0.45) h⁻¹) and the office (5.02 (±0.24) h⁻¹). This is consistent with the reported low AER for US residences and the higher recommended AER for commercial buildings (4–15 h⁻¹). Indoor O₃ levels followed the same trends as the AER. The lowest average O₃ was observed in the residence, 0.62 (±1.77) ppbv, which is on average 30 times lower than outdoor O₃ levels measured over the same time period (20.5 (±9.6) ppbv), yielding an average I/O₃ of 0.03. Mean O₃ levels measured in US homes prior to the implementation of the 8 hour O₃ National Ambient Air Quality Standards in 1997 were 13–60 ppbv. Studies subsequent to the implementation, on the other hand, reported substantially lower O₃ levels that ranged from 0.027 to 1.9 ppbv, similar to our observations. In these studies, I/O₃ generally spanned from 0.1 to 0.3, but increased substantially to 0.6–0.7 when windows were open. O₃ levels in the lab and office were comparable (average of 21.5 (±8.7) vs. 22.5 (±6.8) ppbv; Fig. 1); mean values were approximately 30 times higher than those in the residence. Outdoor measurements were made during the office sampling campaign in spring, but not during office sampling in fall/winter, or during either of the laboratory sampling periods. The average I/O₃ in the office was 0.67 based on the spring data, well within the range of I/O in buildings with negligible indoor O₃ sources (<0.1–0.8).

Lower O₃ levels and I/O₃ in the residence than in the academic building may be due to the low AER. Without significant indoor sources, O₃ indoors is transported from outside through air change. The literature has shown that homes and offices tend to have comparable O₃ loss rates to indoor surfaces, ranging from 2.5 to 5.4 h⁻¹. Surface loss rates in this and other US residences are generally much larger than the AER, whereas surface loss rates in the academic building is comparable to the AER. As a result, O₃ levels and I/O₃, in the residence are lower. This is consistent with reported observations that an increased outdoor ventilation rate increases indoor O₃ concentrations and I/O₃, as less O₃ will be lost (e.g., between walls) as it makes its way into the indoor space.

NO showed an opposing trend compared to O₃. Its mixing ratios were substantially higher in the residence (16.8 (±31.0) ppbv) than in the lab (1.0 (±3.7) ppbv) and the office (0.5 (±1.5) ppbv). The average I/NO, in the residence was 11.7 over the entire campaign and 0.13 in the office based on the spring data. The higher NO levels in the residence likely resulted from the combined effect of direct indoor sources and lower loss to O₃. Cooking was an important source of NO in the residence, with peak NO levels of ~350 ppbv. The low AER and lower O₃ levels in the house resulted in high NO mixing ratios after cooking which were sustained for hours, as discussed in detail by Zhou et al. Low NO mixing ratios in the lab and office were likely explained...
by a lack of indoor sources and by titration by O₃, NO₂* followed a similar trend as O₃, with lower mixing ratios in the residence (8.4 (±6.8) ppbv) followed by the lab (9.1 (±5.3) ppbv) and the office (11.3 (±5.5) ppbv), although the differences between the residential and non-residential locations were much less pronounced than for O₃ or NO. The average I/O₂NO₂ was 1.26 for the residence (all data) and 1.70 for the office (spring data only). Outdoor-to-indoor transport has been shown to be important for NO₂*. It could be a major source of NO₂* in the office and lab as a result of a high AER in the academic building. Secondary production from reactions between NO and O₃ may also be important. The residence had negligible influence from outdoor NO₂ emissions due to a low AER; cooking was often the dominant source of NO₂*, and – as discussed in Sections 3.3 and 3.4 – the reaction between NO and O₃ was also an important NO₂* source under some conditions.

3.2 Influence of season and occupant activity on oxidant levels in the residence

Background periods without human perturbations in the residence (i.e., patio doors closed and no cooking events) were selected for seasonal comparisons of indoor oxidant* levels. The AER in the residence in spring was ~15% higher than that in fall/winter (0.74 (±0.24) vs. 0.65 (±0.36) h⁻¹; Fig. 2), consistent with previous studies that have demonstrated a higher AER in spring and summer compared to winter. Daytime (8 am to 4 pm) outdoor O₃ mixing ratios were also higher in spring than in fall/winter, by an average of 10.3 ppbv. Although indoor background O₃ mixing ratios were low and noisy in both seasons, only 10% of fall/winter background O₃ data was above the limit of detection (LOD: 0.6 ppbv), while 36% of the spring data was above the LOD. Since there was a negligible indoor source of O₃ in the residence, the higher indoor O₃ levels in spring were likely a result of the higher AER and outdoor O₃ during warmer months. This subsequently affected background NO and NO₂* levels. As seen in Fig. 2, the background NO in spring was 1.7 ppbv lower than that in fall/winter, while the oxidation products (NO₂ and HONO, reported as NO₂*) were ~2 ppbv higher in spring. This is consistent with O₃ reacting with NO indoors to form NO₂ – and subsequently HONO – in spring. Some small seasonal differences in the AER and oxidant* levels during background periods (closed window and no cooking) were observed in the lab and office (Fig. S1 in the ESI†), but no firm conclusions could be drawn.

Human activities greatly influenced oxidant* mixing ratios in the residence. As seen in Fig. 3a, the average mixing ratios of O₃, NO, and NO₂* under background conditions during the residual sampling periods averaged 0.47, 3.96, and 5.29 ppbv, respectively. While cooking did not affect O₃ levels, it led to substantially higher levels of nitrogen oxides. Peak NO and NO₂* mixing ratios during cooking events (N = 98) were on average about 30 and 6 times greater, respectively, than the background levels (Fig. 3a). A detailed discussion of the influence of cooking from the fall data in this residence has been previously reported.

During the fall/winter 2017 campaign, the patio doors were sometimes opened (1–3 hours; N = 14) for increased ventilation. Although the AER was not measured during these door-open events, the AER was likely much larger during these periods than when doors were closed. Opening windows has been shown to increase the AER by up to 3 h⁻¹. The increase of the AER is associated with several factors including the width of the opening and the elevation of windows/doors, number of windows/doors opened, indoor-outdoor temperature

**Fig. 2** Average AER, ambient outdoor O₃ levels, and mixing ratios of O₂ and nitrogen oxides in the residence under background conditions in two seasons. Data below the detection limit were included to calculate averages. Text above the bars indicates the percentage of data above the detection limit.

**Fig. 3** Statistics of oxidant* observed (a) in the residence during background, cooking peak (5 min), and patio door open periods; (b) outside the residence (outdoor), indoors during undisturbed background conditions over a period of 1–2 hours prior to opening patio doors (pre-door open), and indoors with open patio doors (door open). The box and whisker plots show the median (line), mean (marker), upper and lower quartiles (box), and the 10th and 90th percentiles (whiskers).
difference, and wind speed and direction. During the door-open events, large (4.8 m²) patio doors were fully opened; differences between indoor and outdoor temperature ranged from ~3 °C to 18.2 °C and outdoor wind speed reached 11.8 m s⁻¹ (based on meteorology data at Syracuse Hancock International Airport, 7.3 km north of the residence). Given this combination of factors, it is possible that the AERs during the door-open periods in our campaign exceeded those reported in other studies, which had smaller area of openings and smaller indoor–outdoor temperature differences. As shown in Fig. 3b, outdoor O₃ mixing ratios averaged 13.1 (±7.9) ppbv. Indoor O₃ levels under background conditions measured prior to opening the patio doors were substantially lower with an average of 0.53 (±0.60) ppbv, consistent with the typical background O₃ levels in this residence. When the patio doors were open, indoor O₃ mixing ratios increased substantially from the background sub-ppbv level to an average of 8.1 (±6.5) ppbv, approximately 62% of the level outdoors. This is due to a combination of increased ventilation rates and decreased filtration by the building envelope with open doors.

While the majority of O₃ loss during transport from outdoors can be attributed to reaction with building materials and surface deposition, gas phase chemistry may have also contributed. The average mixing ratios of outdoor NO and NO₂* were 1.5 (±3.7) and 5.0 (±3.4) ppbv, respectively, and those for the pre-door-open periods were 5.4 (±3.1) and 6.0 (±1.4) ppbv, respectively. If only physical mixing occurred during the door-open periods, NO and NO₂* levels would lie between the background and outdoor values, because the house volume would contain a mixture of the original indoor air and infiltrated outdoor air. However, NO decreased to an average of 0.67 (±1.7) ppbv during the door-open periods, which was even lower than outdoor ambient values. This indicates an extra loss mechanism in addition to dilution. On the other hand, NO₂* increased by ~1.7 ppbv during the door-open periods, resulting in levels higher than those outdoors. This is suggestive of secondary production. These observations together suggest that O₃ introduced indoors via door opening reacted with NO indoors to yield secondary oxidation products (specifically NO₂). Although windows in this residence were often closed in winter, they can be open for more than half the time in warmer months. This highlights the importance of considering door/window open conditions in investigations of indoor chemistry.

### 3.3 Ozone–NO₂ chemistry implied from temporal trends

Temporal trends of oxidant* in the residence and the lab on a typical day during the sampling periods are shown in Fig. 4. Distinct features of the indoor oxidant* can be seen. In the residence, O₃ was stable and often below the LOD, whereas NO and NO₂* had stable background levels of approximately 5 and 8 ppbv, respectively (Fig. 3a and 4a). Sharp increases of NO and NO₂* (up to 230 and 50 ppbv) were observed during meal times due to cooking, as reported previously. In the lab, O₃ levels were generally between 10 and 30 ppbv. Mixing ratios of NO in the lab were very low and remained below the LOD except during periods consistent with morning rush-hour traffic or night-time traffic possibly associated with evening events at the university, during which high NO₂* levels were also observed (Fig. 4b). Similar temporal profiles were observed in the office and the lab; both showed clear diurnal patterns with an O₃ trough and NO and NO₂* peaks during morning rush-hour (Fig. S2†). The fact that O₃ and NO were inversely related in these indoor environments suggests that one species was generally titrated by the other. In addition, O₃ showed a clear anti-correlation with NO₂* in the lab and office (Fig. 4b and S2†), which further suggests the importance of chemical reactions between O₃ and NO₂.

When doors were closed, NO and NO₂* mixing ratios displayed a smooth exponential decay after cooking (Fig. 4a), with mean decay rate constants of 0.92 (±0.37) and 1.5 (±0.54) h⁻¹, respectively. These levels remained elevated above background mixing ratios often for more than four hours. Opening the patio doors changed the profiles dramatically. For example, after cooking lunch on October 7, 2017, NO and NO₂* levels in the residence rose rapidly and then decayed to ~70 and 11 ppbv, respectively (Fig. 5). Indoor O₃ remained low (~0.6 ppbv) throughout this time period. When the patio doors were opened O₃ levels rose rapidly to 20–30 ppbv and NO quickly dropped below the LOD. The behavior of O₃ and NO could be explained by physical mixing of outdoor and indoor air masses. However, NO₂* showed a rapid initial increase to 20 ppbv when the doors opened.
were opened and then remained elevated higher than the mixing ratios observed prior to opening doors until the doors were closed. This suggests chemical production of NO₂* in the residence when doors were open, consistent with previous discussions (Section 3.2). We note that NO₃ photolysis has been suggested to be a source of O₃ indoors. Given the NO₂ mixing ratios measured in this campaign, as well as photon fluxes measured previously, we predict that NO₂ photolysis could increase O₃ levels by up to 3× in sunlit regions in this residence. Low O₃ levels, small illuminated volumes, and rapid mixing of air inside the house prevented us from testing this hypothesis.

3.4 Chamber experiments (O₃-perturbation experiments)

To validate the hypothesis that NO reacts with O₃ and generates NO₂* under door-open conditions in the residence, O₃-perturbation experiments were performed in the residence. One was performed under background conditions and six were performed after cooking. In these experiments approximately 35 ppbv of O₃ was added into the environmental chamber (after accounting for dilution) while MILOS continuously pulled room air through it. Fig. 6 shows an example of a typical experiment performed after cooking. Prior to perturbation the combustion products NO, NO₂, and HONO decayed exponentially with rate constants of 0.7, 1.1, and 1.0 h⁻¹, respectively. With an addition of 35 ppbv of O₃, a sharp drop in NO occurred concomitantly with an increase of NO₂ and HONO. This provides direct evidence that O₃ reacts with NO and forms NO₂* in indoor air. A negative control replacing O₃ with zero air (ZA) following O₃ perturbation resulted in the same dilution factor yet removed the oxidant from the chemical reactions. This resulted in a slight increase in NO (~8 ppbv), while both NO₂ and HONO (as well as NO₂*) dropped rapidly. This behaviour was reproducible, as shown in Fig. S3–S5 in the ESI.† This supports the hypothesis that O₃–NO chemistry occurs in the indoor atmospheric environment.

Similar changes of oxidant* levels were observed in the other five experiments performed after cooking (Fig. S3–S5†). In the post-cooking experiments, the O₃ mixing ratio decreased by an average of 29.1 (±4.7) ppbv (after accounting for dilution). After accounting for dilution in the chamber, NO mixing ratios decreased by 21.1 (±4.1) ppbv following O₃ injection. Concurrent increases in NO₂* mixing ratios (17.4 (±4.2) ppbv) were observed. For individual experiments, the observed increase in NO₂* was 64–108% of the observed NO loss (average 84 (±18)%), suggesting that the majority of NO loss was due to reaction with O₃. Speciated NO₂ and HONO were detected during these experiments. Ratios of NO₂ to HONO were variable, with NO₂ contributing 22–66% to the total increase in NO₂* (with an average of 42%). Thin films of water have been observed to form on indoor surfaces at a relative humidity (RH) as low as 20%. Heterogeneous “wet” chemistry of NO₂ on indoor surfaces (RH > 20%) has been shown to generate HONO. Comparing elevated surface area to volume (S/V) ratios in indoor environments to those outdoors, heterogeneous reactions of NO₂ have been projected to be important indoors. The NO₂-to-HONO conversion is greatly enhanced in the presence of light (λ < 400 nm). However, as the chamber was in the dark (i.e., shade), heterogeneous photochemistry likely did not contribute to HONO formation in these experiments. Since the RH during the perturbation experiments was between 30% and 40%, our results are consistent with gas-phase NO₂ (formed from reactions between O₃ and NO) reacting on “wet” glass surfaces to form HONO, as would happen on indoor surfaces with the intrusion of O₃-containing outdoor air.

We performed control experiments (N = 3) injecting O₃ in ZA only (no room air) into the environmental chamber to investigate the contribution of uptake to glass on O₃ mixing ratios in the chamber. In these experiments, the O₃ mixing ratio immediately dropped by 5–17 ppbv in the chamber and recovered exponentially with an average rate constant of 5.5 (±0.35) h⁻¹. Over the course of the experiments, which ranged from 41 to 60 minutes, an average of 3.8 (±1.2) ppbv O₃ was consumed. No clear trends in ozone uptake were observed with successive experiments. The shape of the recovery curve is consistent with the reactive uptake of O₃ onto the glass chamber surface. Clean glass has very low O₃ uptake rates. However, thin organic films have been observed to form on impervious indoor glass surfaces. Since the chamber was exposed to room air during the entire field campaign, and it was preconditioned (room air pulled...
through the chamber before instrumentation) prior to most perturbation experiments, we expect the surface composition of the chamber walls to reflect that of indoor surfaces in the residence. Reactive uptake of O₃ by adsorbed surface materials could be responsible for the observed O₃ depletion. This will be relevant to many indoor locations due to high S/V ratios.

Reaction with NO and uptake to the chamber surface accounted for, on average, 86.0 (± 8.9)% of the observed ozone loss. The remaining O₃ sink (~4.2 ppbv) is likely unsaturated hydrocarbons in the residential air. These were scrubbed in the ZA but would be components in the sampled residential air. They can be emitted from building materials, carpets, paints, and indoor plants, and tend to be present at higher levels in residences than outdoors. ⁷⁻¹⁷ Using speciated alkene mixing ratios from Weschler and Shields⁷ and associated reaction rate constants, we calculated a loss of approximately 1.3 ppbv O₃ due to reaction with alkenes in the environmental chamber. This is smaller than the average unattributed O₃ loss of 4.2 ppbv, but it does, when combined with NO and surface uptake, account for between 93 and 100% of the observed O₃ loss in four of the six post-cooking experiments; an additional 7–9 ppbv O₃ remains unattributed in the other two experiments. Given the variability of indoor alkene mixing ratios, the three processes considered (reaction with NO, uptake to surfaces, and reaction with alkenes) appear to account for the majority of O₃ loss in the environmental chamber and in the residence.

While only one perturbation experiment was performed under background conditions (Fig. S6†), it is worth discussing briefly. Initial NO levels were much lower prior to O₃ injection compared to those in the post-cooking experiments (~4.3 vs. 77.3 ppbv). Accordingly, the decrease in the O₃ mixing ratio was smaller in this experiment (13.8 ppbv vs. ~29 ppbv in the post-cooking experiments). After accounting for dilution, NO increased by 3.3 ppbv and NO₂* increased by 1.7 ppbv following injection of O₃. Approximately 6.7 ppbv of consumed O₃ remains unattributed after accounting for uptake to the chamber walls. This is within the range determined for the post-cooking experiments (1.3–8.6 ppbv) and is likely due to reaction with alkenes. Fig. 7 shows relative strengths of the O₃ sinks considered (NO, alkene, and surface uptake) under post-cooking and background conditions. It is clear that different O₃ loss processes dominate under different conditions. While NO dominates O₃ loss after cooking (73%), alkene reactions are the most important single sink under background conditions (accounting for 48% of O₃ loss). Uptake to the chamber surface accounted for less than 14% of O₃ loss in the post-cooking experiments but was as large a sink as NO under background conditions (27%). While conditions in the environmental chamber (especially the surface composition and S/V ratio) do not fully reflect those in most residences, the conclusion that human activities such as cooking and opening doors will affect oxidant* mixing ratios and fates is likely generalizable to many indoor environments.

4 Conclusions and implications

We made continuous time-resolved measurements of O₃ and nitrogen oxides in three indoor environments (home, laboratory, and office) in Syracuse, New York, in two seasons. Oxidant* mixing ratios were very different in different indoor environments. Ozone, which is typically considered a major (or the only) indoor oxidant, was present at very low levels (~1 ppbv) in the residence, whereas NO and NO₂* levels were higher compared to those in the laboratory and office environments with higher AERs. As NO concentrations have been reported to be quite high in North American residences (mean values ranging from 30 to 77 ppbv [ref. 28 and references therein]), O₂ will likely often be fully titrated by NO. This suggests that the observation of low O₃ levels in such residences may be generalizable. This will have implications for the fate of other species indoors. For example, alkene oxidation will be slow, and OH steady state mixing ratios – in the absence of other OH sources – will be lower than those often predicted based on higher (~20 ppbv) indoor O₃ mixing ratios.

Our work highlights the effects of perturbations caused by human activity on the relative levels of oxidants* in the residence compared to those in the office and laboratory environments. Cooking increased NO and NO₂*, while opening patio doors for natural ventilation increased O₃ and reduced NO. In situ chamber experiments further confirmed that chemistry was responsible for the observed NO₂* increase during natural ventilation periods – specifically the formation of NO₂ from reactions of O₃ with NO in the gas phase and the heterogeneous production of HONO on indoor surfaces. These results suggest that when predicting chemistry in indoor environments, the type of building (residence vs. commercial) and perturbations (e.g., cooking and opening windows/doors) need to be taken into account.

Conflicts of interest

There are no conflicts to declare.

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