

Supplemental Information (SI)

The Fate of Organic Peroxides Indoors: Quantifying Humidity-Dependent Uptake on Naturally Soiled Indoor Window Glass

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S1. Uptake Experiments on Clean and Soiled Glass

Table S1. Experiments, RH conditions, exposure times, sampling locations and number of measurements.

Compound (mixing ratio at reactor inlet)	Surface	RH (%)	Total exposure time (hr)	Sampling locations along reactor (cm)*	Number of measurements at each location (total number of measurements)
O ₃ (500 ppb)	Potassium Iodide	15	2	0-93 (12 steps)	3-4 (42-50)
(100 ppb)	Halocarbon wax	5	0.5	48, 63, 78, 93	4 (16)
(35 ppb)	Clean glass	2, 54, 94	0.5	48, 63, 78, 93	4 (16)
1,2-ISOPROOH (<1-300 ppb)	Halocarbon wax	5	6	0, 33, 63, 93	12 (48)
(<1-300 ppb)	Clean glass	5, 55, 80	6	0, 38, 53, 68	12-17 (48-68)
(<1-300 ppb)	Soiled glass (Houses A-C)	5, 55, 80	6-13.5	0, 33, 63, 93	12-17 (48-68)

*initial sampling positions for obtaining C_0 are denoted as x_0 after in the manuscript. The sampling locations for experiments on House A glass at mid RH were 0, 48, 63, and 93 cm. Other experiments on soiled glass used 0, 33, 63 and 93.

S2. Parallel Plate Flow Reactor Details

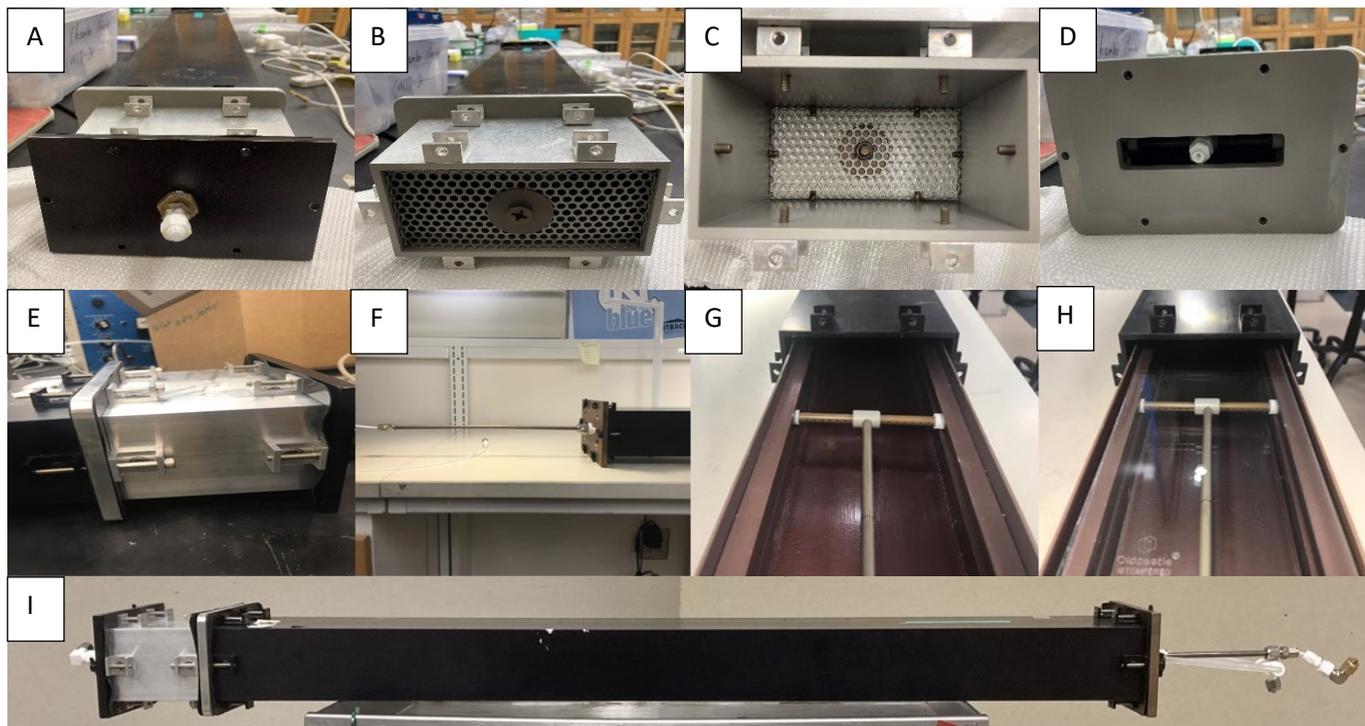


Figure S1. A) Fixed injection point at reactor entrance. B) Mixing chamber (front view; injection point cover plate removed to show mesh screen). C) Mixing chamber interior, which tapers from 15 cm x 8 cm to 10 cm x 2 cm over a distance of 8 cm (back view). D) Movable sampling inlet at position 0 cm at 20 cm² tapered exit of mixing chamber (inside view). E) Mixing chamber (side view). F) Movable sampling inlet at position 50 cm on exit side of reactor (outside view). G) Empty flow reactor interior and movable sampling inlet (inside view). H) Glass loaded flow reactor and movable sampling inlet (inside view). I) Flow reactor (outside view).

Table S2. Parallel plate flow reactor characteristics.

Interior flow chamber dimensions	1 m x 0.1 m x 0.02 m (LWH)
Sampling inlet	1 m long, 0.318 cm diameter (1/8 in) Teflon tubing
Reactor flow rate	2.5-4 L min ⁻¹
Sampling flow rate	600 cm ³ min ⁻¹ (organic gas sampling) 960 to 1000 cm ³ min ⁻¹ (O ₃ sampling)
Residence time	30-50 s
Reynolds Number	46-74
Boundary layer thickness	0.009 m

Reynolds numbers were calculated using the hydraulic diameter $D_h = 2WH^*(W+H)^{-1}$. The measured transport-limited velocity for ozone (v_{tO_3} : $0.161 \text{ cm sec}^{-1}$) and known diffusion coefficient for ozone ($D_{O_3} = 0.14 \text{ cm}^2 \text{ sec}^{-1}$)¹ were also used to estimate the boundary layer thickness (δ , cm) in the flow reactor as described by Hinds et al.²:

$$v_{tO_3} = \frac{D_{O_3}}{\delta} \quad (\text{S1})$$

S3. Ozone Experimental Details

For each O_3 experiment, the window glass loaded reactor was first conditioned at the experimental flow rate and RH for 90 minutes. O_3 (2.5 L min^{-1} ; mass flow controlled) generated from a U.V. photometric O_3 calibrator (Thermo Environmental Instruments; New Delhi, India) was then added to the flow. The movable sampling line pulled air from the flow reactor into the O_3 monitor at 0.980 L min^{-1} (**Figure S2**). Roughly 5-10 min of O_3 exposure was needed to achieve a stable starting O_3 concentration (20-35 ppb) in the glass-loaded flow chamber at x_0 before measurements began. O_3 was measured for 2 min each at x_0 , x_{15} , x_{30} and x_{45} cm and repeated for a total of 5 trials. The O_3 analyzer sampled every 10 s during 2-min sampling intervals and the average O_3 concentrations during the last 30 s after the system stabilized at each sampling location was used.

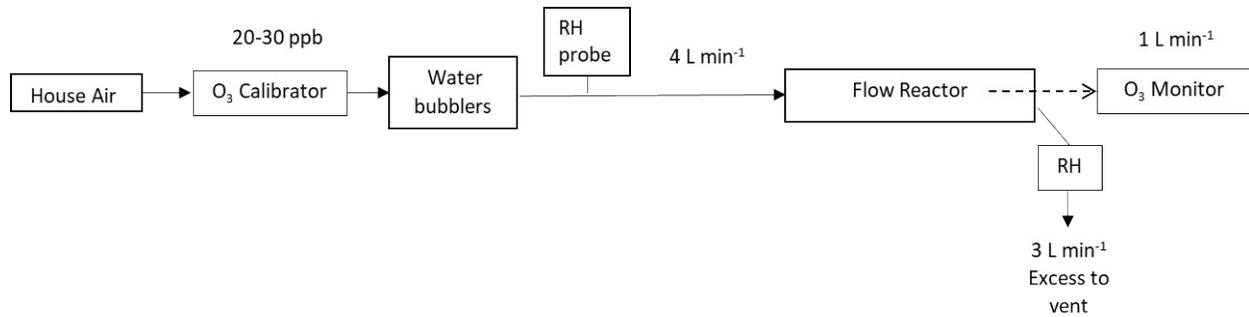


Figure S2. Simplified O_3 uptake set-up. The internal 0.980 L min^{-1} pump on the O_3 monitor was connected directly to the movable sampling line and excess flow at the dual exit ports was vented to the house exhaust system. O_3 was pushed through water bubblers for humid experiments until a stable O_3 concentration was achieved. The wet O_3 flow was then combined with another wet sheath flow and introduced into the reactor at appropriate RH.

S4. Preparation and Chemical Analysis of Surfaces

Clean glass

Several 0.635 cm (¼ in) thick 1 m by 10 cm custom tempered glass windows (Rice’s Glass Company) were obtained from a local glass shop. Window plates were wiped twice using Kimwipes wetted with hexane, followed by 2-propanol and then methanol. The window plates were then loaded into the flow reactor and dried under 20 L min⁻¹ house air for 30 min. Glass microscope slides were also wiped twice using Kimwipes wetted with hexane, 2-propanol, and methanol before being sonicated in water to remove Kimwipe fibers. Glass slides were stored in 2-propanol and allowed to air dry once deployed in homes.

Halocarbon wax coated glass

One gram of halocarbon wax (Halocarbon Products Corporation) was dissolved in 100 mL of acetone (10 g L⁻¹) and pipetted onto cleaned, dried glass plates and patted with a Teflon bag for even coverage. The acetone was allowed to evaporate for 2 h, leaving behind a film of wax.

Potassium iodide (KI) surface for “perfect sink” experiment

Gold’s Bond 0.95 cm (3/8 in) thick gypsum board was cut to size (1 m x 0.1 m) and painted with Gilden light base semi-gloss interior paint/primer, which was the most popular brand of paint sold at Walmart at the time. Paint was applied in 2 coats using a paint roller in opposite directions for each coat. A 4 h drying period was allowed after applying each coat. It takes approximately 2 weeks for paint to cure. To speed up the curing process painted drywall was cured in the reactor under high 20 L min⁻¹ clean dry air flow for 24 h. Steps were not taken to verify complete curing of the paint, but the number of air changes in the reactor over this time far exceeds the number of air changes in a typical house over the course of 2 weeks. After the expedited curing, 10 g of KI was dissolved in a 20 mL water: 10 mL methanol mixture (333 g L⁻¹) was pipetted along the surface of the painted drywall sheets, patted with a Teflon bag for even coverage, and allowed to dry for 4 h, leaving behind adsorbed/absorbed KI crystals for a highly reactive surface with O₃. The painted and KI-coated gypsum board was oriented in the reactor as the top plate parallel to a halocarbon wax-coated glass. This orientation allowed the distance between the parallel plates to be the same (2.62 cm) for the perfect sink experiments with gypsum and 1,2-ISPOOH experiments with glass, so as to maintain similar flow geometry. For the perfect sink experiment, **Equation 1** was modified to account for having only 1 reactive surface loaded in the reactor, yielding **Equation S2**:

$$v_t \approx v_d = \frac{Q * k_{wall}}{-1 * W} \quad (S2)$$

where “-1” represents ozone instantaneous removal to 1 plate as opposed to 2 parallel surfaces.

Study House Glass Substrate Deployment (authentically-soiled glass)

Table S3. Study house dates of glass plate deployment, average temperature, and average RH. The house temperature and RH were recorded once an hour daily using a HOBO data logger collocated with the deployed glass plates over an 8-month period. The soiling dates refer specifically to the deployment and removal dates of the glass window plates.

House	Dates of soiling	Location of glass plates	Average temperature (°C)	Average RH (%)
A ^{1,2}	11/1/2018-7/27/2020	Living room	24	59
B ³	10/18/2018-10/2/2020	Dining area	22	47
C ³	1/30/2019-1/22/2021	Kitchen	21	51

¹The walls in House A were mainly constructed of wood. Walls in the other houses were mainly painted gypsum drywall.

²Kitchen and living rooms were separate rooms.

³The kitchen and living room were an open concept layout.

For House A, the exposed faces of each pair of window plates were pressed together, and the pair was wrapped in aluminum foil and transported to the lab freezer for 1-2 weeks before experiments. For Houses B and C, the flow reactor was brought to the House and the window plates were loaded directly into the reactor and taken to lab for uptake experiments. The glass microscope slides were transported from the houses to the lab in glass amber bottles that had been deployed and the same initial date to equilibrate with House air (bottles were uncapped for exposure to room air). In some cases, glass slides were left in houses for up to 2 months after removing the glass window plates.

Total water-soluble organic carbon (WSOC) on soiled glass

To measure total WSOC, each (single) glass slide was extracted three times by submerging in 45 mL of deionized water in a pre-rinsed polypropylene tube, including soiled glass slides and clean unexposed glass slides (blanks). Extracts (and blanks) were analyzed for total WSOC via persulfate-ultraviolet oxidation with membrane conductometric detection using a Sievers Total Organic Carbon Analyzer. The analyzer has a linear range from 0.03 ppb to 50 ppm TOC at less than 1 % RSD precision and the greater of ± 2 % or ± 0.5 ppb accuracy. The TOC was calibrated using potassium hydrogen phthalate (KHP) standard solution. Extraction efficiency was 96%, calculated from 3 consecutive extracts from House A. Extracts were analyzed the same day or stored in refrigerator and analyzed within 2 days.

Ion chromatography (IC) on soiled glass

To measure ions, a set of 3 glass slides was extracted 2-3 times by submerging the slides in 60 mL of deionized water in a rinsed staining dish, then sonicated for 15 min. Extracts (and blanks) were analyzed for acetate, chloride, formate, nitrate, sulfate and oxalate anions using an ion chromatograph (Dionex ICS 3000, Thermo Fisher Scientific, Waltham, MA) with an IonPac AG11-HC guard column (2 x 50 mm) and AS11-HC anion-exchange column (2 x 250 mm) at a flow rate of 0.4 mL min⁻¹ as described previously³. Lab blanks were obtained by extracting cleaned glass slides in water following the same procedure applied to samples. Ions were quantified using an authentic standard mixture of the reported ions. After the second extraction, ion signals were not significantly different from the lab blanks, suggesting that extraction efficiencies were close to 100%. Extracts were analyzed the same day or stored in the refrigerator before analysis.

Atomic Force Microscopy (AFM) Fourier Transform Infrared (IR) Spectroscopy on soiled glass

AFM and AFM-IR were performed using the Bruker nanoIR3 AFM-IR system. The instrument combines the high spatial resolution of AFM with the chemical identification of IR spectroscopy, allowing the user to simultaneously take an AFM topographic image simultaneous with an absorption map at a specified IR wavenumber. Alternatively, an IR spectrum can be taken at a single spatial point by sweeping the IR laser over a range of 901-1897 cm⁻¹ wavenumbers. These scans were performed in Tapping Mode AFM-IR, using a stiff tip (PR-EX-TnIR-C-10 tip) to minimize tip-sample adhesion. AFM scans were taken with a 0.5 Hz scan rate, with (20 x 20) μm map dimensions. The scans had a resolution of 512 x 512 points, while the other scans were 256 x 256 points. The spectra have a resolution of 4 cm⁻¹ and are averaged over three measurements.

S5. 1,2-ISOPOOH Experimental Details

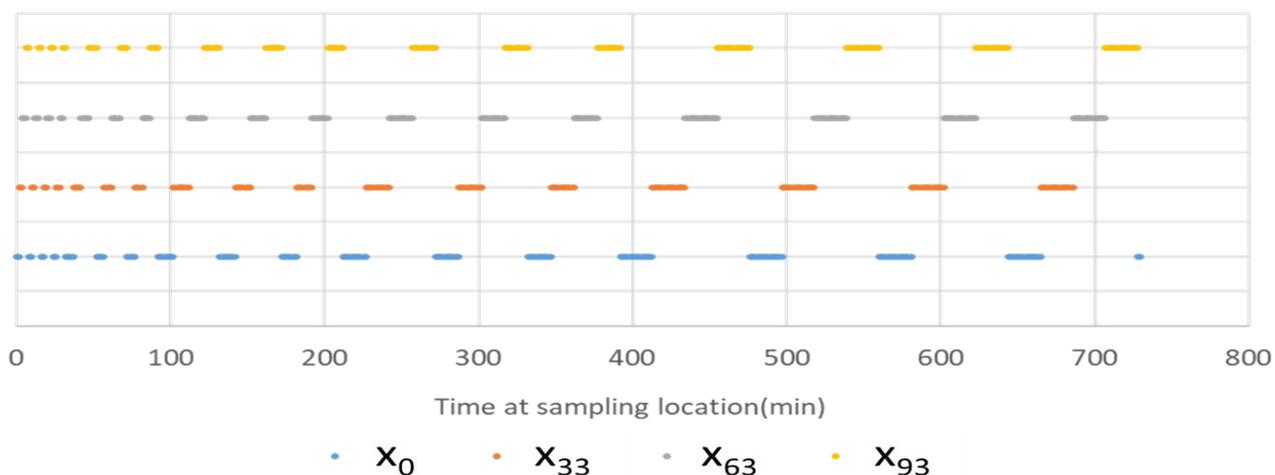


Figure S3. The movable sampling inlet movement pattern for 1,2-ISOPOOH experiments. The sampling position, x , of the movable inlet during each minute of the uptake experiment is shown. The movable inlet is moved from $x = 0$ cm (blue) to 33 (orange), 63 (grey), and 93 cm (yellow), then back to 0 cm to continue the pattern.

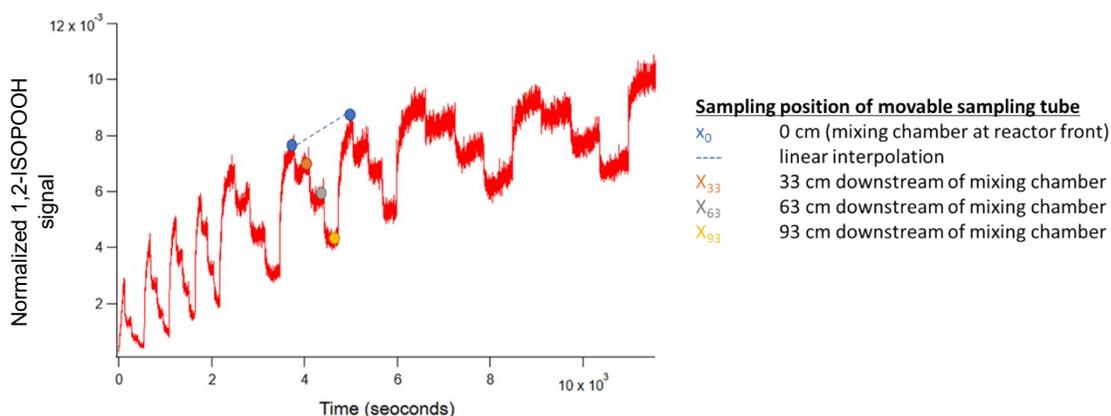


Figure S4. Example of raw data during a 1,2-ISOPPOOH uptake experiment on glass soiled in House B. Moving the movable sampling tube downstream consecutively to position x_i and resetting at position x_0 creates the repeating stepwise pattern. A linear interpolation between x_0 position allowed estimation of the C_0 at all time points in order to compare C_i to a C_0 at equivalent exposure time.

During the first 32 min of exposure, the sampling tube was moved every 2 min. For the next 3 h it was moved every 5 min, then 10 min for the next 2 h, 15 min for the next 3 h, and 21 min for the last 5.5 h for maximum exposure time of 13 h and 32 min. In this way, there were multiple measurements at each location including C_0 , over the course of each experiment. C_i was obtained by averaging the signal from the last 20-100 data points collected at each location after system stabilized. The concentration of 1,2-ISOPPOOH entering the reactor increased with time as 1,2-ISOPPOOH losses in the upstream mixing chamber decreased, making it important that we had measurements of C_0 throughout the experiment. Because all locations were not sampled at the same time (**Figure S3**), linear interpolation was used to compare C_i to C_0 at identical times (**Figure S4**). The formula $1-(C_i/C_0)$ provided the percent removal of 1,2-ISOPPOOH along the length of the reactor as a function of exposure time.

S6. O₃ Uptake

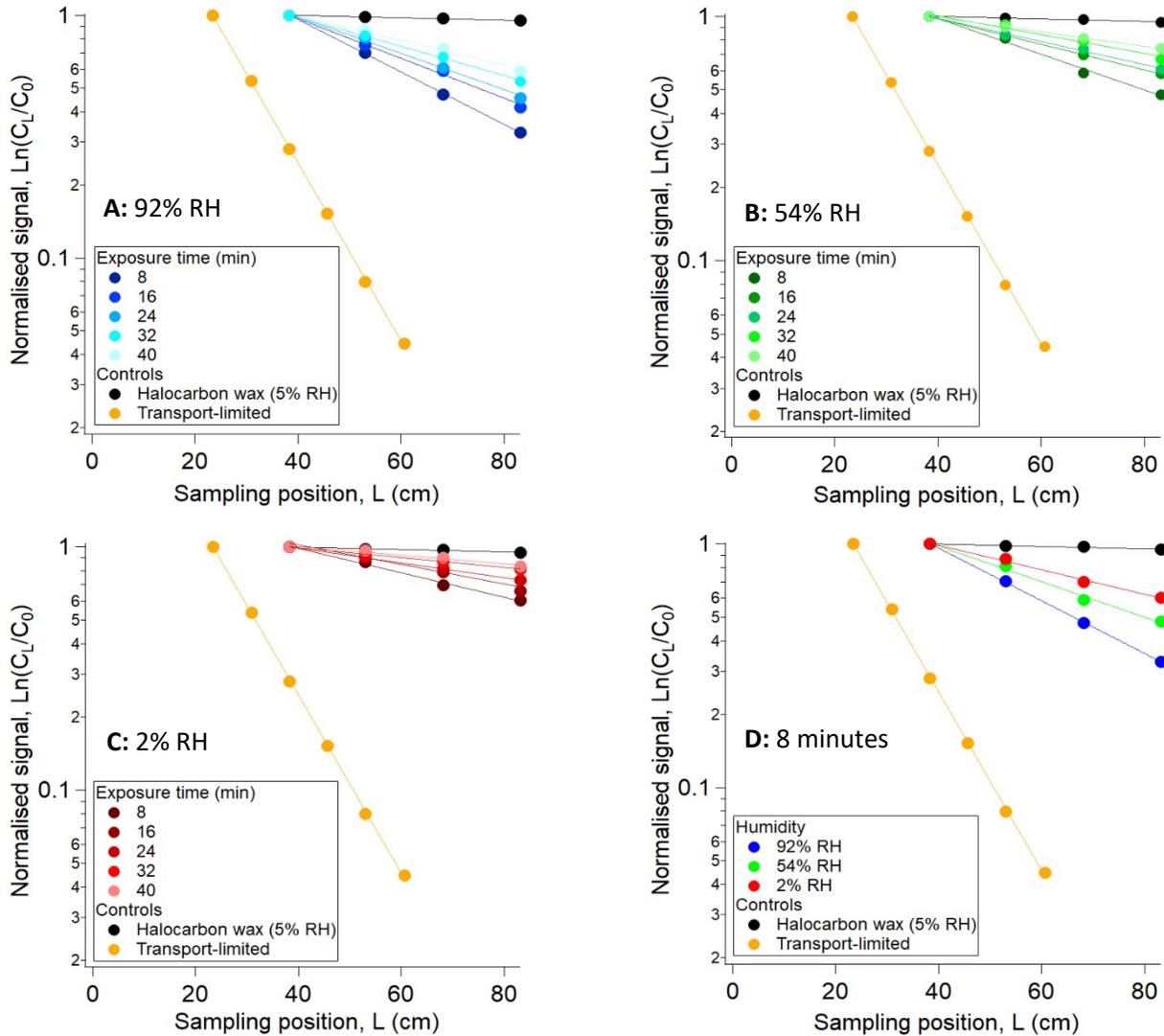


Figure S5. Normalized O₃ concentration at sampling location (denoted L above) ($\ln C_L/C_0$) vs sampling position for clean glass under dry, mid, and high RH conditions: (A) 92% RH (blue markers); (B) 54% RH (green markers); (C) 2% RH (red markers); and (D) RH comparison after initial 8 min of exposure. Initial uptake on halocarbon wax (black markers, 16 min of exposure) and on KI (gold markers, 12 min of exposure) are shown as minimum and uptake constraints, respectively. Exposure time is provided in the plot legends. Error bars represent the standard deviation in average C_0 , determined through propagation of error; error bars are too small to see beneath the markers on log scale.

Plotting the natural log of normalized signal vs sampling position yields a slope that equals K_{wall} . As expected, when ozone was injected between glass plates coated with halocarbon wax (16 min of exposure), uptake of ozone to the plates was not significant (black line; k_{wall} : -0.001 cm^{-1}). In contrast, KI is a perfect sink and O_3 uptake (12 min of exposure) was substantial (orange line; k_{wall} : -0.054 cm^{-1}). Uptake to clean glass fell between these maximum and minimum constraints. Initial K_{wall} coefficients after 8 min of total O_3 exposure were 0.027 cm^{-1} , 0.017 cm^{-1} , and 0.013 cm^{-1} for high, mid, and dry RH, respectively. The rate of O_3 uptake slowed as the glass was aged with O_3 .

S7. Transport-limited Deposition Velocity for 1,2-ISOPOOH (v_{ti})

$$v_{ti} = v_{t\text{O}_3} * \left(\frac{D_i}{D_{\text{O}_3}}\right)^{2/3} \quad (\text{S3})$$

The diffusivity of 1,2-ISOPOOH (D_i) was estimated using Graham's law [$D_i/D_{\text{O}_3} = (\text{MW}_{\text{O}_3}/\text{MW}_i)^{0.5}$]; MW refers to molecular weight for each species. The calculated D_i for 1,2-ISOPOOH was $0.09 \text{ cm}^2 \text{ s}^{-1}$. By this method, v_{ti} was estimated to be 0.74 times $v_{t\text{O}_3}$. From the measured $v_{t\text{O}_3}$ and estimated D_i ($0.09 \text{ cm}^2 \text{ s}^{-1}$), the transport limited deposition velocity for 1,2-ISOPOOH, v_{ti} , was calculated to be 0.119 cm s^{-1} (**Equation S3**). When v_t and v_d for a species in a flow system are known, γ can be calculated by **Equation S4**:

$$\gamma_i = \frac{4}{\langle v \rangle \left(\frac{1}{v_{d_i}} - \frac{1}{v_{t_i}} \right)} \quad (\text{S4})$$

S8. Characterization of Soiled Glass Substrates – Atomic Force Microscopy

The presence of deposited particles (~ 50 - 100 nm) and $\sim 50 \text{ nm}$ discontinuous organic thin films (**Figure S6A**) containing carbonyl functionalities (mostly distributed in particles) (**Figure S6B**) and spatial heterogeneity in vibrational response when scanning different locations on the same glass slides (**Figure S6C**) were verified in AFM-IR images on samples from Houses B and C. Organic films did not appear to be continuous (**Figure S6A**), and some deposited particles had different compositions than the surrounding thin films, as indicated by the spatially varied response to specific vibrational modes (**Figure S6B**). As expected for chemically complex films, IR scans demonstrated broad modes (**Figure S6C**). House C seemed to have stronger peaks in the carbonyl region ($\sim 1733 \text{ cm}^{-1}$) suggesting a higher quantity of C=O bonds than House A (**Figure S6C**). C=O functionalities on the glass from House C suggest more carbonyl accumulation in the deposited particles than in the thin films (**Figure S6B**). Significant spatial heterogeneity was observed on

length scales from hundreds of nanometers up to hundreds of microns. Most of the variations were in the 1200-1500 cm^{-1} range and in the range above 1700 cm^{-1} ; the 1400 cm^{-1} range is likely related to C-H and O-H modes in monocarboxylic acids. A strong, broad response was observed around 1600 cm^{-1} especially in House B (**Figure S6B**). This appeared to be more spatially homogeneous. The origin of this feature is not clear, but it could have contributions from C=C vibrational modes. House B glass was not imaged using AFM-IR due to limited availability of glass slides.

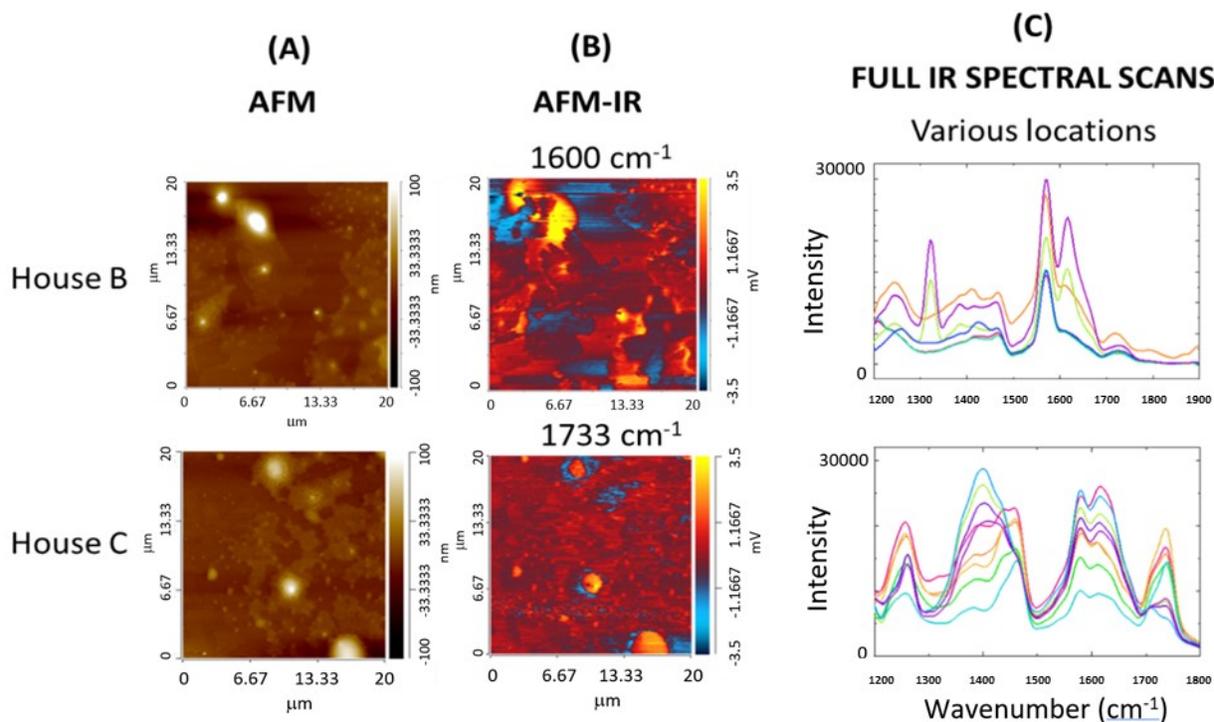


Figure S6. (A) AFM images of soiled glass slides from House B and C including 20 x 20 μm scanned AFM images; (B) AFM-IR scans at 1600 cm^{-1} (C=C likely contributes to this region, House B) and 1733 cm^{-1} (carbonyl region, House C); and (C) full IR scans on different locations on the same glass slide from House B and C.

S9. 1,2-ISOPHOH Uptake

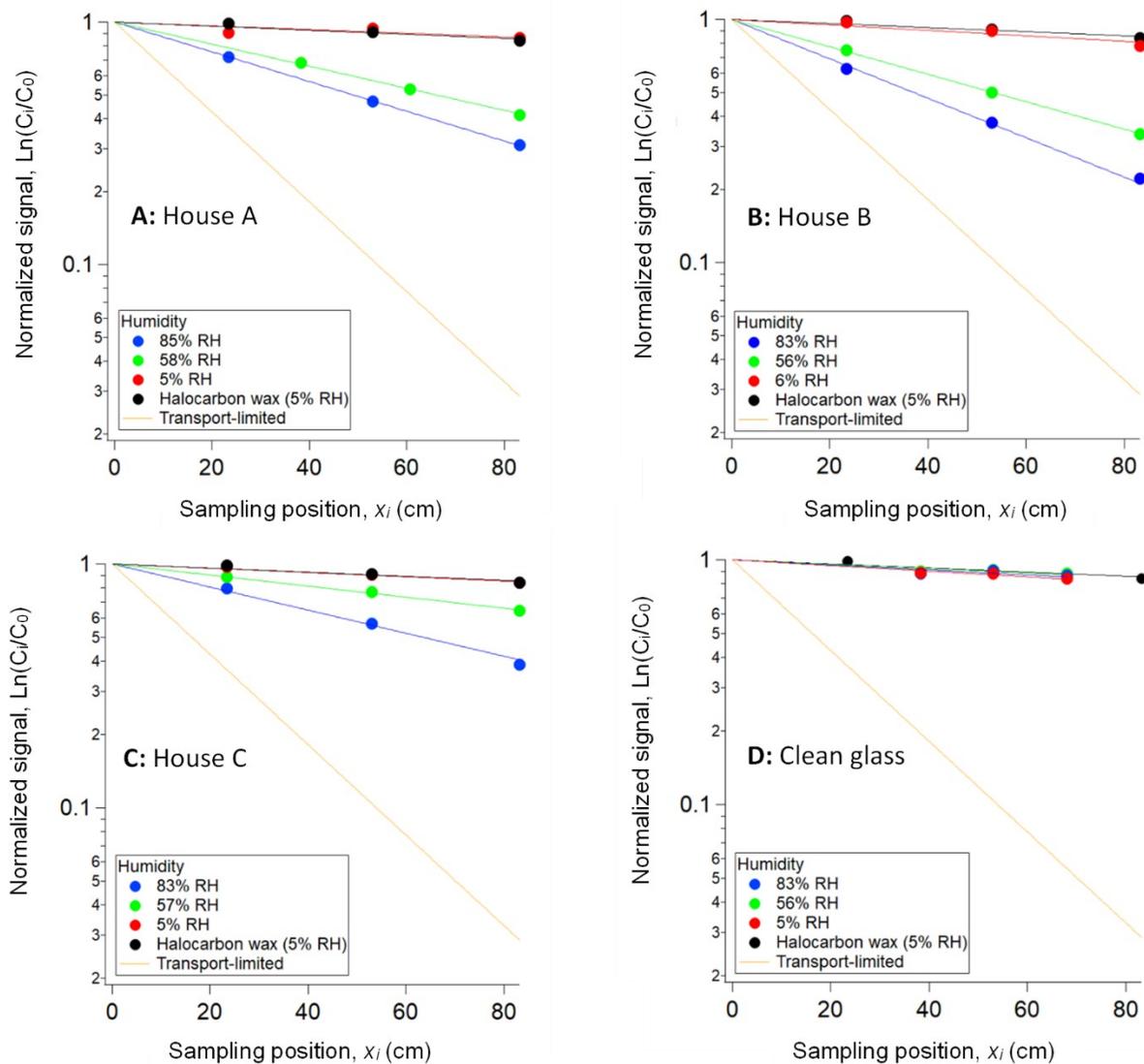


Figure S7. RH dependence of the normalized 1,2-ISOPHOH signal at location x_i ($\ln C_i/C_0$) vs sampling position for glass soiled in Houses A, B, C and clean glass. (A) House A glass. (B) House B glass. (C) House C glass. (D) Clean glass. Exposure time at x_{g3} for soiled glass and halocarbon wax coated glass was 16 min. Exposure time at x_{78} for clean glass was 16 min.

The minimum K_{wall} was measured directly on halocarbon wax-coated glass and the transport-limited K_{wall} (0.046 cm^{-1}) was inferred from the calculated v_t for 1,2-ISOPOOH. Initial K_{wall} coefficients ranged from $0.014\text{-}0.002 \text{ cm}^{-1}$, $0.018\text{-}0.002 \text{ cm}^{-1}$, $0.011\text{-}0.002 \text{ cm}^{-1}$, and $0.002\text{-}0.002 \text{ cm}^{-1}$ across the RH range for Houses A, B, C, and clean glass, respectively. Initial removal of 1,2-ISOPOOH to soiled glass was largest at high RH followed by mid RH and then dry RH conditions. RH effect was most significant for initial wall-losses to House B glass, where K_{wall} increased by 650% and 900% under mid and high RH, respectively. Similarly, a 550% and 700% increase in K_{wall} was observed for House A glass under the same RH conditions. The smallest RH effect for soiled glass was observed from House C, where mid RH and high RH conditions only increased K_{wall} by 250% and 550%, respectively. Initial uptake to clean glass was too small across the RH range to confidently discern any RH effect.

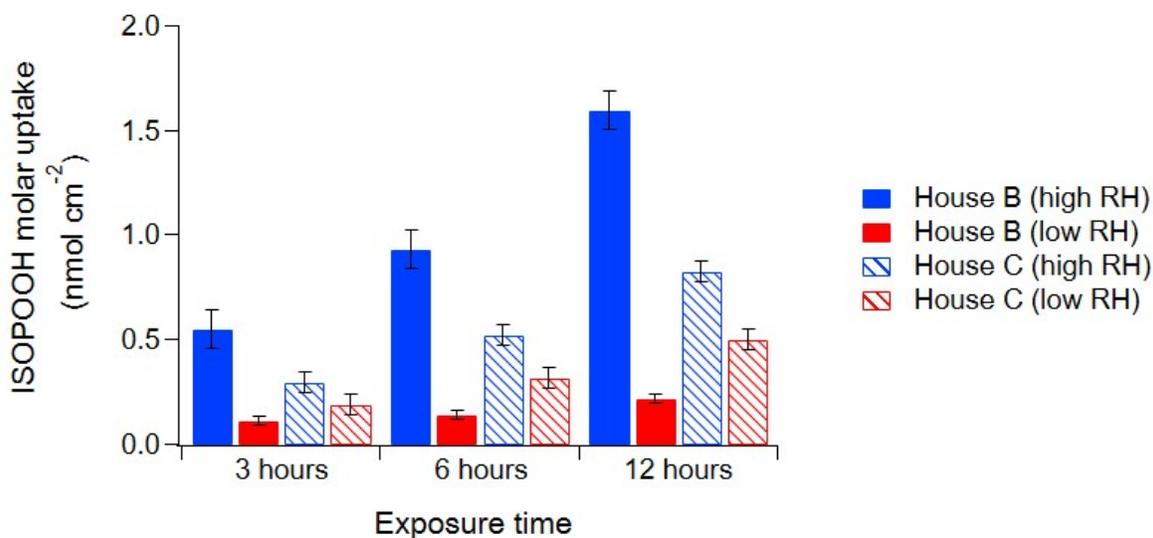


Figure S8. The total molar uptake of 1,2-ISOPOOH (nmol cm^{-2}) on clean glass and glass soiled in Houses B and C after 3, 6 and 12 h of exposure.

S10. Characteristic Time to Steady State (τ_{ss})

The mass of 1,2-ISOPOOH in the surface film at equilibrium with the inlet concentration C_0 divided by the mass rate (\dot{m}) at which 1,2-ISOPOOH is delivered to the flow reactor can be used to estimate a characteristic time to steady state (τ_{ss}). The τ_{ss} for 1,2-ISOPOOH partitioning with an octanol film, a surrogate for organic layers, on a flat surface can be estimated.

$$M_{film} = 2LWdC_0K_{oa} \quad (S5)$$

$$\dot{m} = C_0Q \quad (S6)$$

$$\tau = \frac{M_{film}}{\dot{m}} = 2LWd * \frac{K_{oa}}{Q} \quad (S7)$$

where L is the length of the glass plates, d is the thickness of organic film (~50 nm) assumed to completely cover the glass surface, K_{oa} is the octanol-air partitioning coefficient and octanol is used as surrogate organic film on a flat surface. The estimation is based primarily on partitioning theory and was expected to provide an order of magnitude value for τ_{ss} . The K_{oa} for 1,2-ISOPPOOH was estimated to be on the order of 10^6 - 10^7 based on the K_{oa} of similarly-sized WSOC. Using the dimensions of the glass plates and the estimated K_{oa} , the characteristic τ_{ss} was ~0.3-3 min for a pure octanol film. For a water film, the characteristic time is given by:

$$\tau = \frac{M_{film}}{\dot{m}} = 2LWd * \frac{K_H}{Q} \quad (S8)$$

Assuming the theoretical film was a 50 nm layer of pure water and using the K_H of 1,2-ISOPPOOH converted to dimensionless units ($K_H = 4.5 \times 10^6 \text{ mol m}^{-3} \text{ water/mol m}^{-3} \text{ air}$), the characteristic τ_{ss} was 1.5 min for a water film.

References

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