

Supplementary Materials for

Surface reservoirs dominate dynamic gas-surface partitioning of many indoor air constituents

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Supplementary Materials and Methods

Text S1. Surface nitrite analysis during HOMEChem.

Surface wipe samples from the glass sheets deployed in the kitchen were acquired and analyzed daily for nitrite during the HOMEChem campaign in June 2018. The procedure follows the method described previously (17). In brief, surface samples were collected by wiping the glass with nylon membrane filters (47 mm; Whatman 7404-004) and kept in the dark before analysis. The filters were subsequently (on the same day) extracted in deionized water (18.2 M Ω) and analyzed for nitrite concentration using the Griess assay (Invitrogen/Molecular Probes G-7921) with a UV-vis spectrophotometer (Ocean Optics, USB2000+UV-VIS-ES) with a waveguide capillary cell (World Precision Instruments, LWCC-3050). Measurement was at $\lambda = 548$ nm. A calibration curve was derived from measurement of absorbance for NaNO₂ solutions using the Griess assay following the same procedure. An average surface concentration on the order of 10¹² molecules cm⁻² during HOMEChem campaign was detected. This result should be considered a lower limit, considering collection efficiency less than unity and possible loss of nitrite during analysis. This surface concentration is in agreement with measurement for different surfaces in a Toronto residence (17).

Text S2. Detrending data and response time calculation.

1. A new data series (the green trace in Fig. S2) was created for each species, which includes only data for the 30 mins before the start of each enhanced ventilation experiment (data for the other time periods were masked).
2. A linear fit was derived from the new data of the two adjacent 30-min periods before and after an enhanced ventilation experiment assuming a linearly increasing trend. For example, the fit for experiment 6 is shown in the red box in Fig. S2. This procedure is similarly done for 5 enhanced ventilation experiments (EV2-EV6) when the air conditioning was off, i.e. when temperature was increasing in the house.
3. The equation of the linear fit (signal as a function of elapsed time, $fit [t] = At + B$) was then applied to derive the detrended data set for each enhanced-ventilation period, i.e. the dark blue trace in Fig. S2.

For each detrended time period, the original data (*original data [t]*) was detrended by dividing the fitted data (*fit [t]* from the linear fit) to derive a detrended data (*detrended data [t]*):

$$detrended\ data [t] = original\ data [t] / fit [t] * original\ data [0]$$

Where *detrended data [t]*, *original data [t]* and *fit [t]* are the detrended data, the original data and the linear fit at time t (elapsed time since the beginning of the enhanced ventilation period),

respectively. The term *original data [0]* is the original data at time zero of the enhanced ventilation period.

4. The response time constant was calculated by fitting the detrended signal to a first-order exponential curve after each enhanced ventilation period (the lighter blue curve in Fig. S2), using the built-in curve fitting function (exp_XOffset) in Igor Pro (Version 7.08; Wavemetrics, Inc.) with the following equation

$$y = y_0 + A \exp\left(\frac{x - x_0}{\tau}\right)$$

Where y_0 , A and x_0 are fitting parameters, and τ is the calculated response time constant.

Text S3. Phase distribution calculation.

Consider the indoor abundance of a species in three compartments: air, sorbed in a weakly-polar organic reservoir, and partitioned into a polar reservoir. The equilibrium abundance in these three states can be expressed in relation to two thermodynamic constants and three volumes. Specifically, the fraction of a chemical in indoor air, weakly-polar organic and polar reservoirs (F_{gas} , F_{org} , and F_{p}) at equilibrium can be calculated from the following equations

$$F_{\text{gas}} = 1/(1 + K_{\text{Oa}} V_{\text{org}}/V_{\text{gas}} + K_{\text{wa}} V_{\text{p}}/V_{\text{gas}}) \quad \text{Eq. (S1)}$$

$$F_{\text{p}} = 1/(1 + 1/(K_{\text{wa}} V_{\text{p}}/V_{\text{gas}}) + K_{\text{Oa}}/K_{\text{wa}} V_{\text{org}}/V_{\text{p}}) \quad \text{Eq. (S2)}$$

$$F_{\text{org}} = 1/(1 + 1/(K_{\text{Oa}} V_{\text{org}}/V_{\text{gas}}) + K_{\text{wa}}/K_{\text{Oa}} V_{\text{p}}/V_{\text{org}}) \quad \text{Eq. (S3)}$$

where V_{gas} , V_{p} and V_{org} (in unit of m^3) are, respectively, the volumes of indoor air (i.e. house volume), surface polar (represented by water) and weakly-polar organic (represented by octanol) reservoirs. The thermodynamic parameters, K_{wa} (in units of m^3 air per m^3 water) and K_{Oa} (in units of m^3 air per m^3 octanol), are water-air and octanol-air partitioning coefficients, respectively. These parameters determine the apportionment of the chemical among the three phases.

If the weakly-polar organic and polar reservoirs are uniformly spread on indoor surfaces as surface films, the volume ratios between different phases can be related to the surface weakly-polar organic and polar (e.g. water) film thickness (X_{org} and X_{p} , in unit of m) and surface area to volume ratio (S/V , in unit of m^{-1}). Note that in indoor environments $V_{\text{gas}} \gg V_{\text{p}}$ and $V_{\text{gas}} \gg V_{\text{org}}$. Consequently, to a good approximation, $V_{\text{gas}} = V$ (volume of the house)

$$V_{\text{org}}/V_{\text{gas}} = X_{\text{org}} S/V \quad \text{Eq. (S4)}$$

$$V_p/V_{\text{gas}} = X_p S/V \quad \text{Eq. (S5)}$$

$$V_{\text{org}}/V_p = X_{\text{org}}/X_p \quad \text{Eq. (S6)}$$

Text S4. CIMS calibration and data analysis.

C1-C5 monocarboxylic acids were calibrated with their corresponding *n*-acid standards. It is possible that some of the intensity in these signals is attributable to branched acids, in addition to the straight chain acids for which the calibration was conducted. The calibration was carried out weekly during the campaign using permeation tubes (VICI, Dynacal) with known emission rates at controlled temperatures (40 °C) in dry zero air. Calibration for HONO was conducted before and after the campaign using a custom-built HONO source following the method described previously (17). In brief, a known flow of gas-phase HONO was collected by bubbling into deionized water (18.2 MΩ), which was subsequently analyzed for aqueous phase nitrite with UV-vis spectrometry following the Griess assay (17, 52). A HONO calibration was also conducted daily on-site during the field campaign by collecting gas-phase HONO from a known flow of indoor air bubbled through deionized water (18.2 MΩ) and analyzed similarly with the Griess assay. The overall sensitivity of the instrument was obtained by averaging the sensitivity from the on-site calibration, and the pre- and post-campaign calibrations. HNCO calibrations were obtained after the campaign using a custom-built HNCO source described elsewhere (34). The influence of humidity on the mass spectral sensitivities of HONO, HNCO and formic acid was confirmed to be minor (48). Overall, we estimate that the systematic uncertainties in the reported mixing ratios are ± 20% for HONO and HNCO, and ± 10% for the other species.

Tofware (Version 3.0.3, Aerodyne Research, Inc.) based on Igor Pro (Version 7.08; Wavemetrics, Inc.) was used to analyze CIMS data, especially peak fitting. The 1 Hz signals acquired during the experiments were time-averaged to 10 s resolution for further analysis. Ion signals were first normalized to the reagent ion signal ($\text{CH}_3\text{C}(\text{O})\text{O}^-$, *m/z* 59.01). Mixing ratios were calculated by applying a calibration factor to the normalized data. For uncalibrated molecules, the normalized signals were used for further analysis. Data collected within 30 s of a valve-switching event were disregarded to avoid interference of potential line effects.

Text S5. PTR-TOF-MS calibration and data analysis.

The PTR-TOF-MS collected mass spectra at 1 Hz, which were processed with the PTRwid package (53) and averaged to 1 min. Data from the first 4 minutes after valve switching were excluded. Isoprene, D5 siloxane, and ethanol were directly calibrated every 48 hours. Phenol, furfural, and monoterpene mixing ratios were derived using a default proton reaction rate constant of $2.5 \times 10^9 \text{ cm}^3 \text{ s}^{-1}$ for the reaction of

the VOC species with H_3O^+ . The default proton reaction rate method has an uncertainty of $\pm 50\%$ while direct calibration has an uncertainty of $\pm 10\%$ (54). Sesquiterpene signals were not calibrated.

Supplementary Figures

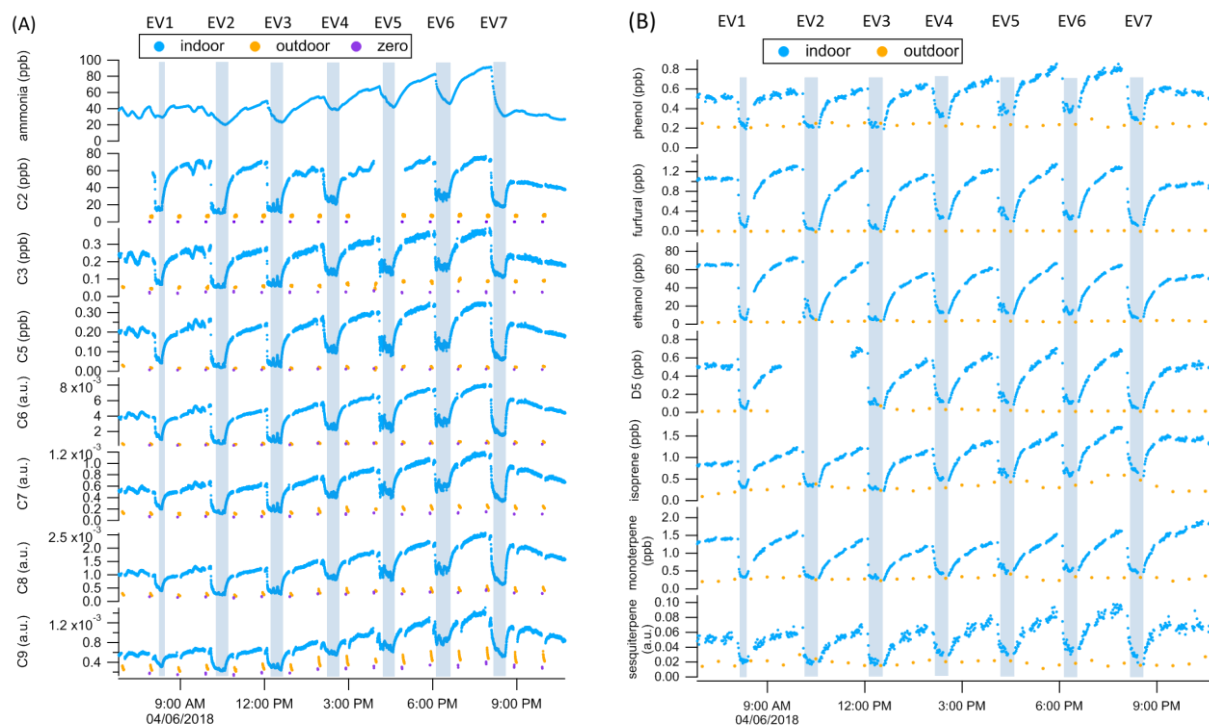


Fig. S1. Time-series of different species during EV experiments. (A) ammonia and C2 - C9 monocarboxylic acids and (B) other VOCs. The C2 and C3 - C9 acids were measured with iodide and acetate CIMS, respectively. Note that the mass spectrometry indicates only the molecular weight of the carboxylic acids and signals of C2 - C5 monocarboxylic acids were calibrated with *n*-acids. It is possible that some of the intensity in these signals is attributable to branched acids, in addition to the straight chain acids for which the calibration was conducted. C6 - C9 monocarboxylic acid and sesquiterpene signals were not calibrated and are shown in arbitrary unit (a.u.). Ammonia mixing ratios were measured with cavity ring-down spectroscopy (Picarro G2103 Analyzer) and are published in (49). The shaded areas (blue) show when doors and windows were open to increase the ventilate rate of the test house. Data for D5 siloxane during the EV1 and EV2 were excluded due to interferences.

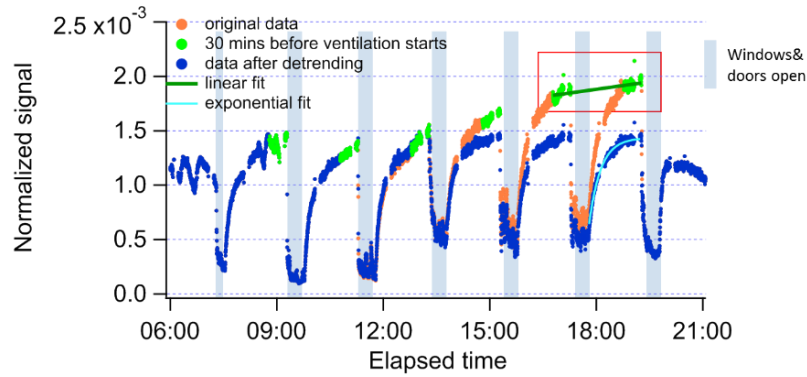


Fig. S2. Detrending data during the EV experiments. Butyric acid signal is shown as an example.

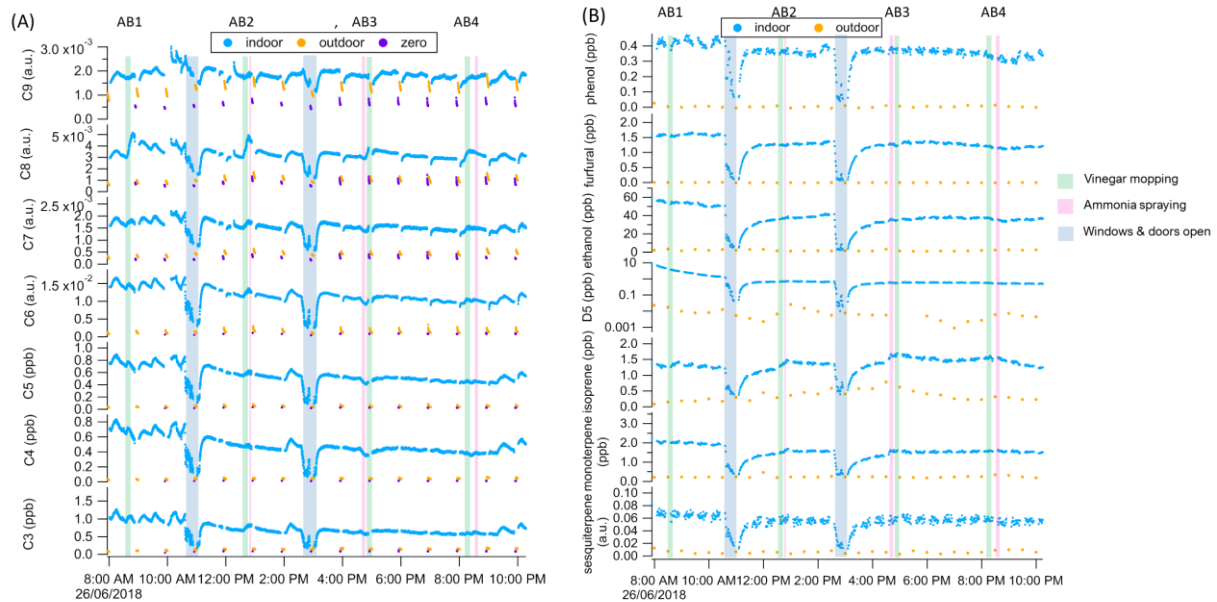


Fig. S3. Indoor air signals during vinegar and ammonia cleaning. (A) C3 - C9 monocarboxylic acids signals and (B) VOCs (acid base experiments, AB1-AB4). Mixing ratios (ppb) of C3 - C5 acids were calibrated with propionic, butyric and pentatonic acid, respectively. The C6 - C9 acid and sesquiterpene measurements were not calibrated and are shown with arbitrary units (a.u.). The shaded areas show when doors and windows were open to ventilate the house (blue), mopping the floor with vinegar solution (green) and spraying ammonia on indoor surfaces (pink). Signals for outdoor air and zero air are the orange and purple circles. The air conditioning system was off during the two ventilation periods.

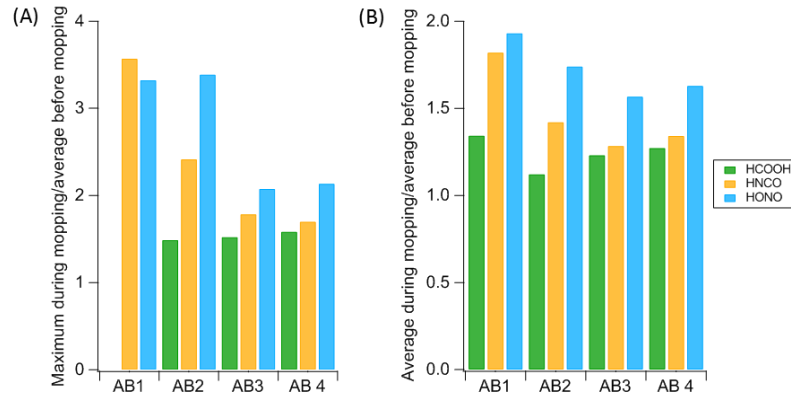


Fig. S4. Comparison of mixing ratios before and during vinegar cleaning. (A) Ratio of the maximum mixing ratio during mopping to the average mixing ratio for the 15 min before mopping. (B) Average mixing ratio during (10 min) and after (50 min) mopping to the average mixing ratio before mopping (15 min). AB1 - AB4 represents the four acid-base experiments. Maximum HCOOH mixing ratio was not quantifiable during AB1. The estimated mass of acetic acid and ammonia used during each experiment is reported in Table S3.

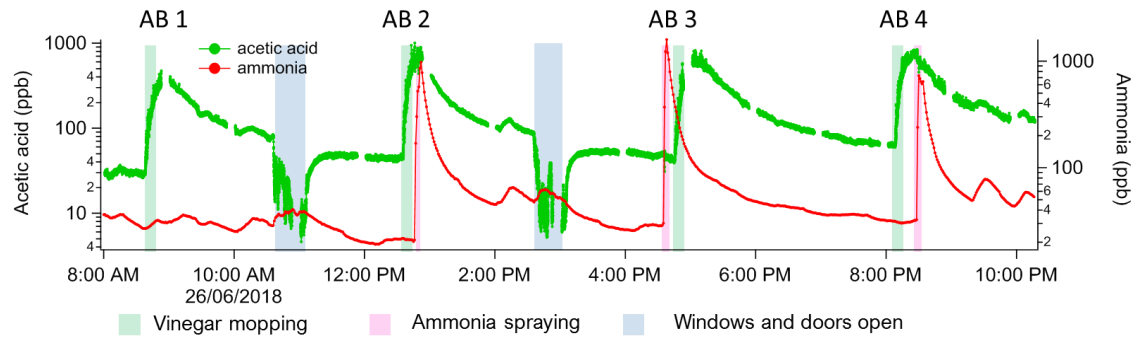


Fig. S5. Indoor acetic acid and ammonia mixing ratio during vinegar and ammonia cleaning. The shaded areas show when doors and windows were open to rapidly ventilate the house (blue), mopping the floor with vinegar solution (green) and spraying ammonia on indoor surfaces (pink).

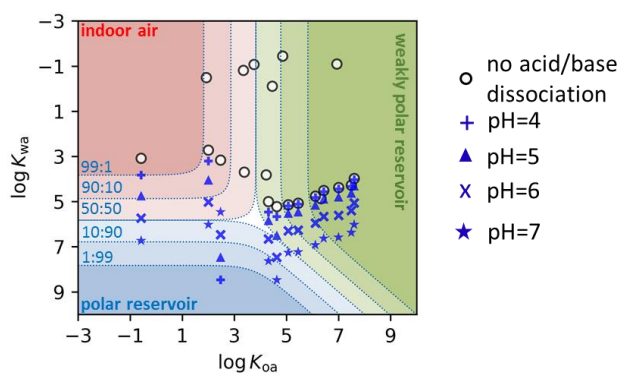


Fig. S6. Partitioning space plot for an indoor environment. A surface area/volume ratio of 3 m^{-1} , 500 nm thick surface polar reservoir, and 50 μm thick weakly-polar organic reservoir are assumed. Names of the individual species are labeled in Fig. 4 (A). The dashed lines in the space indicate boundaries for different fractions of compounds in each phase and the blue text shows the fraction in gas vs. polar phase for the dashed line below the blue label. The different symbols indicate the pH of the polar phase, as indicated in the legend.

Supplementary Tables

Table S1. Physical and chemical properties of different compounds at 25°C: acid dissociation constant (pK_a), vapor pressure (Pa), octanol-air partitioning coefficient ($\log K_{oa}$, with K_{oa} in units of m^3 air per m^3 octanol), water-air partitioning coefficient (i.e. Henry's law constant, $\log K_{wa}$, with K_{wa} in units of m^3 air per m^3 water).

Species	pK_a	vapor pressure (Pa)	$\log K_{oa}^a$	$\log K_{wa}$
Nitrous acid	3.35	-	-0.58	3.08
Isocyanic acid	3.70	1.33×10^5	2.00	2.72
Formic acid	3.75	5.68×10^3	4.63	5.22
Acetic acid	4.76	2.29×10^3	4.31	5.00
Propionic acid	4.88	471	5.07	5.14
Butyric acid	4.82	220	5.45	5.07
Pentanoic acid	4.84	26.1	6.11	4.76
Hexanoic acid	4.88	5.80	6.43	4.51
Heptanoic acid	4.80	15.6	7.00	4.38
Octanoic acid	4.90	6.51	7.49	4.27
Nonanoic acid	4.95	2.85	7.60	3.97
Furfural	-	295	4.22	3.81
D5 siloxane	-	26.7	6.93	-1.10
Phenol	-	46.7	6.33	4.87
Ethanol	-	7.91×10^3	3.38	3.69
Isoprene	-	7.33×10^4	1.92	-0.50
Sesquiterpene ^b	-	4.16	4.85	-1.45
Limonene	-	192	4.45	-0.12
α -Pinene	-	633	3.75	-1.08
β -Pinene	-	391	3.34	-0.82
Ammonia	9.3 ^c	-	2.47	3.16

EPI-Suite (EPA) experimental values (vapor pressure, K_{oa} and K_{wa}) are used for chemicals with experimental values. For compounds with no available experimental values, EPI-suite estimates are used. Physical and chemical properties are also taken from the NIST Chemistry WebBook and reference (19, 55).

^a K_{oa} values for nitrous acid and ammonia have larger uncertainties because values for these species lie outside of the estimation domain of EPI-Suite for inorganic compounds.

^b Caryophyllene was used as a representative sesquiterpene species.

^c pK_a for NH_4^+

Table S2. Time-averaged steady-state mixing ratios (parts per billion) for indoor air during enhanced-ventilation (EV) period, the following closed-house (CH) period and time-averaged mixing ratio in outdoor air following each EV period.

Experiment	C1	C2	C3	C4	C5	HNCO	HONO	D5 siloxane	ethanol	furfural	isoprene	mono- terpene	phenol	sesqui- terpene ^f	AER ^g (h ⁻¹)	WS ^h (m/s)	
EV1 ^a	indoor EV ^b	6.49	15	0.08	0.05	0.06	0.04	1.04	0.07	7.51	0.14	0.34	0.36	0.24	0.02		
	indoor CH ^c	21.1	66	0.26	0.23	0.23	0.1	3.84	0.49	67.9	1.23	1.07	1.42	0.55	0.06	0.47	5.0
	outdoor ^d	1.66	6.33	0.05	0.02	0.02	0.03	0.55	0.02	2.75	n.d. ^e	0.22	0.27	0.22	0.02		
EV2	indoor EV	3.51	11.7	0.06	0.02	0.03	0.04	0.66	-	15.6	0.06	0.37	0.35	0.23	0.02		
	indoor CH	22.9	63.7	0.25	0.21	0.21	0.09	3.69	0.66	55.2	1.04	1.08	1.14	0.55	0.06	0.42	4.3
	outdoor	1.92	6.84	0.05	0.02	0.02	0.04	0.54	-	3.62	nd.	0.39	0.31	0.25	0.03		
EV3	indoor EV	6.2	16	0.08	0.04	0.04	0.04	0.83	0.11	5.71	0.08	0.28	0.32	0.23	0.02		
	indoor CH	27	58.2	0.26	0.23	0.23	0.1	3.7	0.48	48.6	1.00	1.04	1.02	0.59	0.06	0.62	1.6
	outdoor	2.48	7.01	0.06	0.02	0.02	0.04	0.53	0.05	3.64	n.d.	0.25	0.26	0.25	0.02		
EV4	indoor EV	15.8	25.8	0.14	0.10	0.11	0.06	1.6	0.17	17.0	0.36	0.57	0.50	0.36	0.03		
	indoor CH	32.7	60	0.30	0.27	0.28	0.1	4.11	0.56	54.7	1.11	1.26	1.14	0.65	0.07	0.47	1.0
	outdoor	3.16	6.83	0.07	0.02	0.02	0.04	0.53	0.04	3.38	n.d.	0.31	0.33	0.24	0.02		
EV5	indoor EV	17.5	-	0.16	0.12	0.13	0.07	1.66	0.16	16.9	0.36	0.65	0.58	0.39	0.04		
	indoor CH	35.5	67.8	0.34	0.31	0.32	0.11	4.27	0.58	56.7	1.15	1.40	1.28	0.75	0.08	0.47	0.9
	outdoor	3.95	7.43	0.07	0.02	0.02	0.05	0.62	0.02	3.26	n.d.	0.44	0.38	0.22	0.02		
EV6	indoor EV	19.4	31	0.18	0.12	0.14	0.07	1.71	0.13	14.3	0.31	0.65	0.56	0.40	0.04		
	indoor CH	38.3	70.9	0.35	0.32	0.33	0.11	4.32	0.59	57.1	1.15	1.54	1.40	0.77	0.09	0.55	0.1
	outdoor	4.34	7.46	0.09	0.03	0.02	0.05	0.6	0.01	2.61	n.d.	0.36	0.30	0.26	0.02		
EV7	indoor EV	11.4	20.4	0.13	0.07	0.08	0.06	1.14	0.07	8.96	0.18	0.75	0.52	0.32	0.03		
	indoor CH	20.4	44.8	0.22	0.20	0.22	0.09	2.73	0.49	67.9	1.23	1.07	1.42	0.55	0.06		0.6
	outdoor	3.58	7.09	0.09	0.03	0.02	0.05	0.66	0.01	3.54	n.d.	0.47	0.32	0.23	0.02		

^a EV1-EV7 represents enhanced-ventilation experiments 1 to 7.

^b Indoor EV: average indoor mixing ratio when doors and windows were open (15 min for the first and 30 min for the following EV periods).

^c Indoor CH: average steady state indoor mixing ratio (the 1-hour average prior to an EV experiment)

^d Outdoor: average outdoor mixing ratio prior and following an EV experiment

^e not detected

^f in arbitrary unit

^g Air exchange rate (AER) during house closed (indoor CH) period after each enhanced-ventilation experiment

^h Average wind speed (WS) during EV period, measured approximately 100 m from the house.

Table S3. Vinegar and ammonia cleaning experiment details

Experiment time	activities	air conditioning	product used (g) ^a	
AB1	8:38-8:48 AM	mopping with vinegar solution	on	1.3-1.9
	10:35-11:05 AM	windows and doors open	off	
AB2	12:35-12:45 PM	mopping with vinegar solution	on	1.4-2.1
	12:46-12:51 PM	cleaning surfaces with ammonia cleaner	on	1.5-4.5
	2:35-15:05 PM	windows and doors open	off	
AB3	4:35-4:40 PM	cleaning surfaces with ammonia cleaner	on	1.5-4.4
	4:45-4:55 PM	mopping with vinegar solution	on	1.7-2.5
AB4	8:08-8:18 PM	mopping with vinegar solution	on	1.9-2.9
	8:28-8:33 PM	cleaning surfaces with ammonia cleaner	on	0.7-2.2

^aThe estimated mass of pure acetic acid or ammonia used during cleaning events.

Table S4. EV experiment details

experiment	time	windows and doors	air conditioning operation	outdoor air supply fan ^a	window light ^b	external mixing fan ^c
EV1	8:05-8:20 AM	open	off	on	on	off
	8:20-10:05 AM	closed	on	off	on	off
EV2	10:05-10:35 PM	open	off	on	on	off
	10:35-12:05 PM	closed	off	off	on	off
EV3	12:05-12:35 PM	open	off	on	on	off
	12:35-2:05 PM	closed	off	on	on	off
EV4	2:05-2:35 PM	open	off	on	on	off
	2:35-4:05 PM	closed	off	on	on	off
EV5	4:05-4:35 PM	open	off	on	on	on at 4:20 PM
	4:35-6:05 PM	closed	off	on	off	off
EV6	6:05-6:35 PM	open	off	on	on	on
	6:35-8:05 PM	closed	off	on	off	off
EV7	8:05-8:35 PM	open	off	on	on	on
	8:35 PM and after	closed	on	on	off	off

^aThe outdoor air supply fan was set to provide outdoor air at an air-exchange rate of 0.5 h⁻¹ when it is turned on. When the fan was off, infiltration controlled the rate of air exchange.

^bAll windows were blocked with blinds or aluminum foils (off) or unblocked (on).

^cTwo external box fans in the house were turned on to facilitate indoor air mixing. The built-in indoor mixing fan of the HVAC system was continuously on, providing air mixing throughout the house.