Supplementary Information for

A New Approach to Characterizing the Partitioning of Volatile Organic Compounds to Cotton Fabric

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Supplementary Text and Figures

S1. Vocus PTR-TOFMS Operation

The VOCs desorbed from cloth samples upon heating in the stainless-steel cell were measured with a Vocus PTR-TOFM (Aerodyne Research Inc.). With a focusing ion-molecule reactor (FIMR), the detection efficiency of ions is improved as compared to conventional PTR instruments.[1] A 1.2 m long flight tube in the time-of-flight (TOF) analyzer enhances the mass resolving power up to 12,000.[1]

From the stainless-steel cell, sample air was drawn into the Vocus inlet through a 50 cm long PFA Teflon tubing (ID 3.97 mm, OD 6.35 mm, wrapped with heating tape maintained at 55 °C) at a flow rate of 600 cm^3/minute. 100 cm^3/minute of this flow was sampled into the Vocus, while the remainder passed to a KNF diaphragm pump (model UN911 KVP) to enhance the total flow. The Vocus operating conditions were as follows:

(i) reagent ions (H_3O^+) produced in the discharge ion source originated from HPLC-grade milli-Q water at 105 Pa and 273.15 K, at a flow rate of 20 cm^3/minute;

(ii) the focusing ion−molecule reactor (FIRM) was operated at a pressure of 220 Pascal;

(iii) discharge voltage: 425 V; discharge voltage current: 2 mA; E/N = 79 Td.

For measurements of thermal desorption and ambient air during exposure period, raw data were recorded with a time resolution of 10 seconds and 10 minutes, respectively. Tofware software (version 3.2.2) was used for analysis.

S2. VOC Calibration and PTR-TOFMS sensitivity

A "syringe pump" approach described in Liu and Abbatt (2021) was used to calibrate selected VOCs from the 3 homologous series.[2] The calibration was performed under dry conditions (0% RH), as the experimental RH condition was low and literature has demonstrated little RH impact on VOC sensitivities within the RH range of 0–60%.[1,2] C9 carbonyl-Nonanal, C4 carboxylic acid-butanoic acid, C4 carboxylic acid-hexanoic acid, C7 aromatic-toluene (all from Sigma-Aldrich) and C2 carboxylic acid-acetic acid (Fisher Scientific) were calibrated. The fractions of parent ion to fragment ion(s) fragmentation were calculated for predicting the sensitivity calibration factors (CFs) of the remainder VOCs of the same chemical class category. Table S3 (A) summarizes the sensitivities of calibrated VOCs.

The sensitivity calibration factors (CFs; unit of counts per second per parts per billion, or cps/ppb) of the remaining VOCs were predicted based on the proton-transfer reaction rate coefficients ($k_{proton\text{-}transfer}$; cm^3/ (molecule · s)). The $k_{proton\text{-}transfer}$ values for all VOCs can be

predicted from the approach proposed by Sekimoto et al., which is based on the polarizability (α; cm^3) and dipole moment (μ; D) of the targeted chemicals.[3] Similar to previous literature findings, the sensitivities of calibrated VOCs (corrected for fragmentation) correlates linearly with $k_{proton\text{-}transfer}$:[1,2]

$$\text{Sensitivity Calibration Factor (cps/ppb)} = 6.0 \times 10^{11} \cdot k_{proton\text{-}transfer} \qquad (1)$$

The set of sensitivity data used is a combination of VOCs calibrated in this study and in Liu and Abbatt (2021), as both calibrations were operated with the same instrument and parameters. [2] The $k_{proton\text{-}transfer}$ values for calibrated VOCs are obtained from an online publicly available library of proton-transfer reactions with H_3O^+ ions by Pagonis et al. (2019) and are listed in Table S3 (A).[4] The coefficient 6.0×10^{11} in equation (1) is obtained from the fitted linear equation of this set of sensitivity and $k_{proton\text{-}transfer}$ data. As a result, by combining the estimated $k_{proton\text{-}transfer}$ and the sensitivity–$k_{proton\text{-}transfer}$ correlation shown in equation (1), the sensitivity of the remainder VOCs can be predicted. The parent ion sensitivity can be obtained assuming the parent ion fraction is the same as the calibrated VOC from that homologous series (carbonyl, carboxylic or aromatics). Table S3 (B) lists the predicted sensitivities for all VOCs and the relevant parameters.

Due to the BSQ (big segmented quadrupole) bandpass properties in the Vocus, a VOC with molecular weight below 58 has an ion transmission efficiency < 100%.[1] For VOCs in this study, C1 carboxylic acid (ie. formic acid) is the only one with molecular weight below 58, Krechmer et al. obtained a transmission efficiency of 50%. This low transmission efficiency was taken into account in the sensitivity prediction.[1]

S3. Sample Calculations

S3.1. Partition ratio

Example for C3 Carbonyl

Known: Sensitivity calibration factor (CF) = 234 cps/ppb; Area under desorption time series (A) = 1.1 × 10^7 cps × s; 1 ppb = 2.46 × 10^{10} molecules/cm^3 at 298 K and 1 atm; flow rate = 600 cm^3/min; Mass of cloth piece = 0.2 g; Molecular weight = 58.08 g/mol; Density of cotton cloth = 1.5 g/cm^3; Average PTR-MS signal during air sampling (S_{avg}) = 2411 cps; Average gas-phase concentration ($C_{mr,air}$) = S_{avg} / CF = 2411 cps / (234 cps/ppb) = 10.4 ppb, i.e. $C_{conc,air}$ = 24.5 ug/m^3. [Note that this calculation assumes that the ambient from the heated cotton has returned close to room temperature (assumed to be 298 K) by the time it is sampled by the PTR-MS. While the flow might be somewhat hotter than true room temperature, there errors associated with this assumption are minor, well less than 10%.]

Method:

$$\text{Log } K_{CA\_V} = \log \frac{\frac{m_{desorbed}}{V_{cloth}}}{C_{conc,air}} = \log \frac{\frac{\frac{A \times F}{CF}}{V_{cloth}}}{\frac{S_{avg}}{CF}} = \log \frac{\frac{A \times F}{V_{cloth}}}{S_{avg}} = \log \frac{\frac{(1.1 \times 10^7 \text{ cps} \times \text{s}) \times (\frac{600 \text{ cm}^3}{min} \times \frac{1\, min}{60\, s})}{1.33 \times 10^{-7} \text{ m}^3}}{2411\, cps} = 5.53$$

(μg/m^3 of cloth) / (μg/m^3 of air)

where F = flow of air over the cotton. Since $K_{CA\_V} = K_{CA\_S} \times (SA_{cloth}/V_{cloth})$, and SA_{cloth}/V_{cloth} = 4.8 × 10^5 m^{-1} for this cloth sample specifically, log K_{CA_S} = - 0.161 (μg/m^2 of cloth) / (μg/m^3 of air).

S3.2. Surface coverage

Example for C3 Carbonyl

Known: Specific Surface area = 0.32 m^2/g; Mass of cloth piece = 0.2 g; Molecular weight = 58.08 g/mol; Mass of compound per cotton piece = 1.1 ug

Total surface area = 0.2 g × 0.32 m^2/g = 0.064 m^2

$$\text{Total number of molecules} = \frac{1.1\text{ug}}{\frac{10^6\text{ug}}{\text{g}} \times 58.08\text{g/mol}} \times \frac{6.02 \times 10^{23}\text{molecules}}{\text{mol}} = 1.25 \times 10^{16} \text{ molecules}$$

$$\text{Surface coverage} = \frac{1.25 \times 10^{16}\text{molecules}}{0.064 \text{ m}^2} \times \frac{1\text{m}^2}{10000 \text{ cm}^2} = 1.95 \times 10^{13} \text{ molecules/cm}^2$$

S4. Long-term exposure in a Toronto apartment

The desorption time series in Figure S3(A) were obtained from cloth samples deployed in the living room of a Toronto apartment from May 25 – July 27 2020, with exposure time of 2-10 weeks. The deployment procedure matched that described in the main text but no concurrent gas-phase measurements were made at this location, precluding calculation of partition ratios. The cloth samples were transported to the laboratory for analysis in clean, sealed vessels that led to no artifacts, as demonstrated using field blanks. Assuming that the gas-phase concentrations were stable in the apartment during this period, the mass desorbed data in Figure S4 indicate that equilibrated amounts are largely stable from 2 to 10 weeks exposure.

From an operational perspective, we note that the time at maximum temperature during thermal desorption was only 30 minutes for these analyses, as opposed to two hours for the data presented in the main paper. Comparing the shape of desorption time series for this shorter heating time with the corresponding long-time heating desorption time series (Figure S3(B), 1-5 day February 2021 laboratory samples used in main text, 2-hour heating at maximum temperature), the short-time heating desorption time series have captured the major part of the "complete" desorption time series. To evaluate the validity of the 30 minute data, in Figure S5 we compare results from an additional set of partitioning coefficient measurements conducted with exposures from 1 to 7 days in the laboratory setting in December 2020 (open data points, 30 minutes at maximum temperature) overlaid on top of the data presented in the main paper (closed data points, 2 hours at maximum temperature). Compared to the 2-hour heating desorption time series, the K_{CA} values are systematically lower when only 30 minutes time is used. Nevertheless, the relative positions of the log K_{CA} values from one species to another are steady.

S5. Justification on the variability of physicochemical properties of isomers

In PTR-MS detection, isomers are not differentiable and so confident identification of the identity of chemicals can be limited. However, the interpretation of the results may not be determined by accurate chemical identities, as the variabilities of physicochemical properties of isomers within homologous series is generally small. To illustrate, a collection of vapor pressure (VP) for selected carbonyls (aldehydes and ketones) and aromatic hydrocarbon isomers is presented in Table 1 below, sourced from the Stephenson and Malanowski (1987).[5] Log K_{OA} values are obtained from the ppLFER prediction in UFZ-LSER database.[6] Details of the sources can be found in Table S3.

Table S1. Saturated vapor pressure (VP) of liquid and log K_{OA} for selected isomers at 298 K.

Formula	Identity	CAS Registry Number	Vapor Pressure at 298 K [log (VP/Pascal)]	log K_{OA}
C3H6O	Propanal	123-38-6	4.626	2.22
	2-Propanone (Acetone)	67-64-1	4.486	2.31
C8H16O	Octanal	124-13-0	2.503	4.62
	2,5-dimethyl-3-hexanone	1888-57-9	2.856	NA
	2,2,4-trimethyl-3-pentanone	5857-36-3	2.469	NA
	2-octanone	111-13-7	2.165	4.61
	3-octanone	106-68-3	2.453	4.60
C8H10	Ethylbenzene	100-41-4	3.098	3.67
	o-xylene	95-47-6	2.943	3.86
	m-xylene	108-38-3	3.041	3.75
	p-xylene	106-42-3	3.069	3.75

As seen from Table S1, the physical chemical properties of isomers do not vary greatly.

Figure S1. Desorption time series collected by Vocus PTR-MS to derive partition ratios (K_{CA}) for C3-9 carbonyls **(A)**, C1,2,4-8 carboxylic acids **(B)**, and C6-11 aromatics **(C)**.

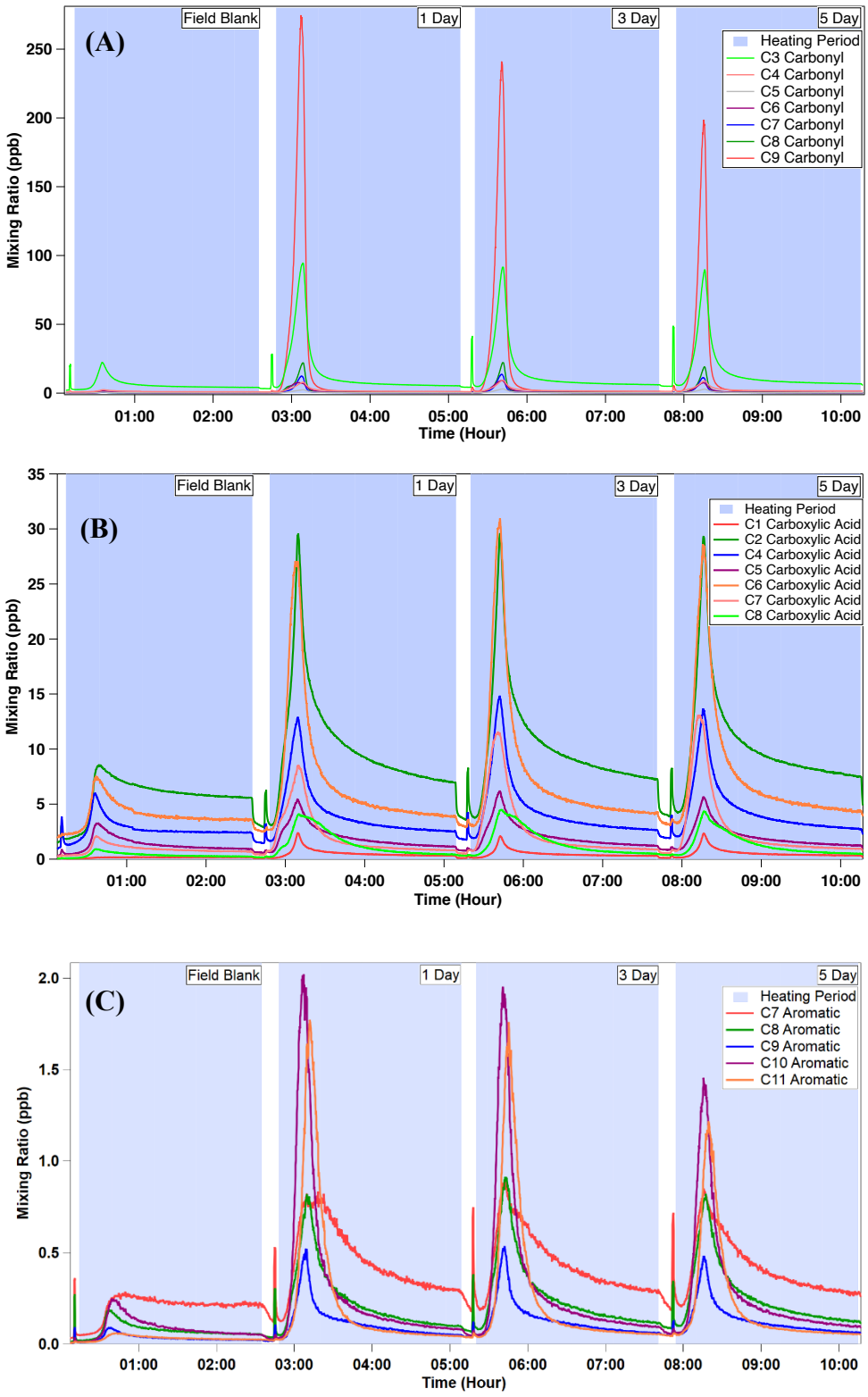


Figure S2. Real-time (5-day) ambient air signals during sample exposure period in February 2021 for corresponding species shown in Figure 1. With no use of chemicals near the instrument inlet during data collection, the spikes in signal are possibly due to human presence and circulation of room air.

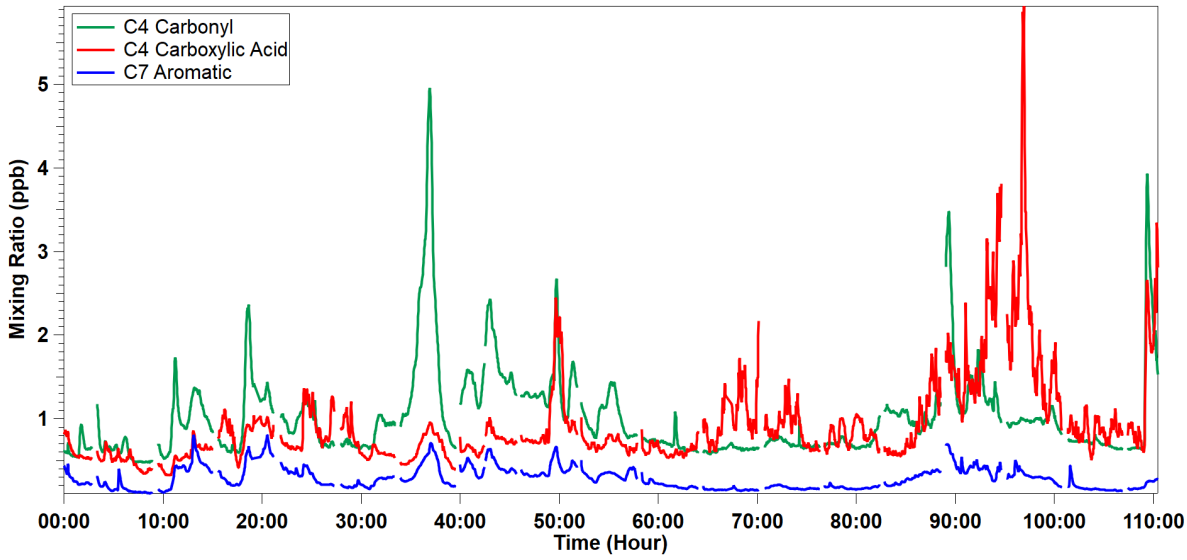
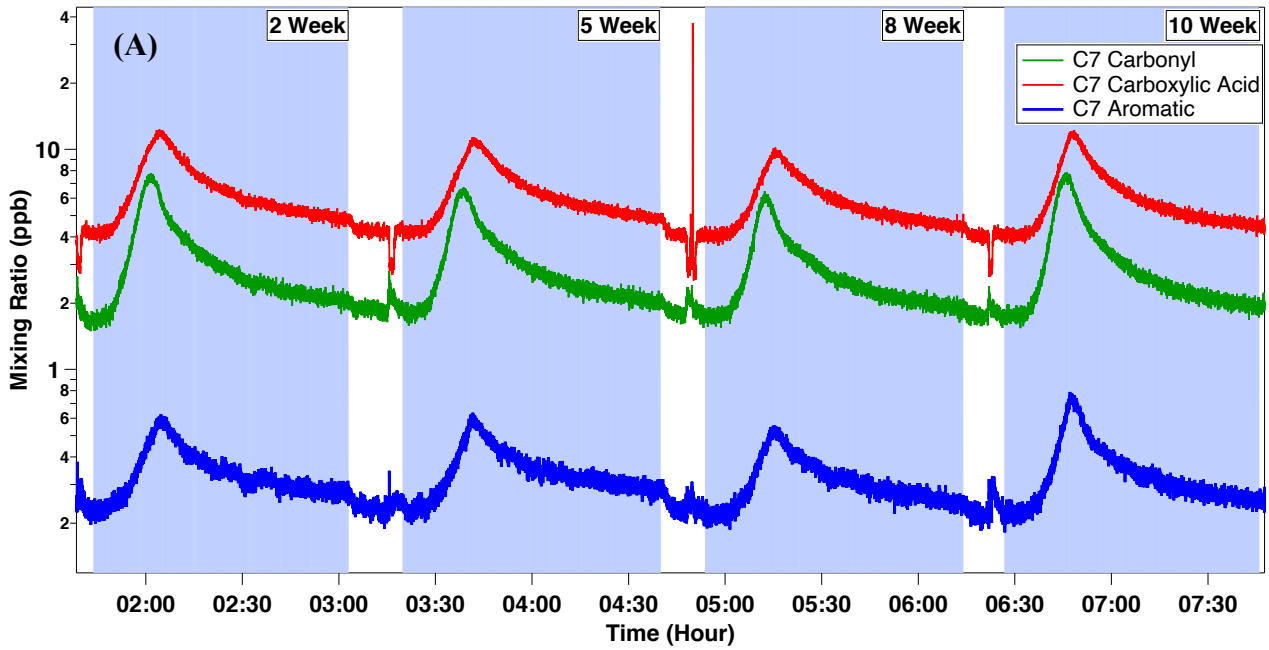


Figure S3. (A) Sample desorption time series of 30 minute short-time heating for cloth samples exposed in a Toronto apartment for a maximum of 10 weeks, in May to July 2020. Comparing with the corresponding desorption time series for 2-hour heating February 2021 **(B)**, this short-time heating has captured the major part of the corresponding desorption time series.



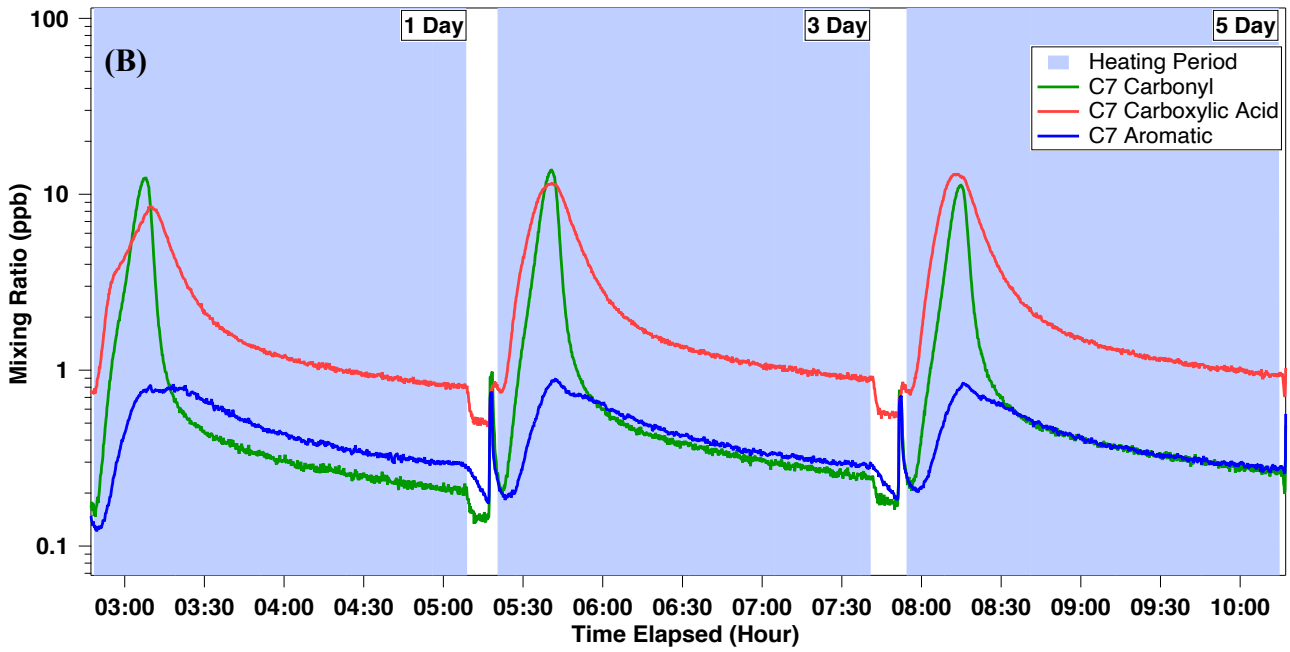


Figure S4. The mass desorbed (µg) from samples that are exposed to apartment air as a function of exposure time, calculated from the desorption time series in **Fig. S3 (A)**. Assuming the gas-phase concentrations were stable during the deployment period, the equilibrated amounts are largely stable from 2-10 weeks exposure, i.e. cloth-air equilibrium had been reached in less than 2 weeks of exposure.

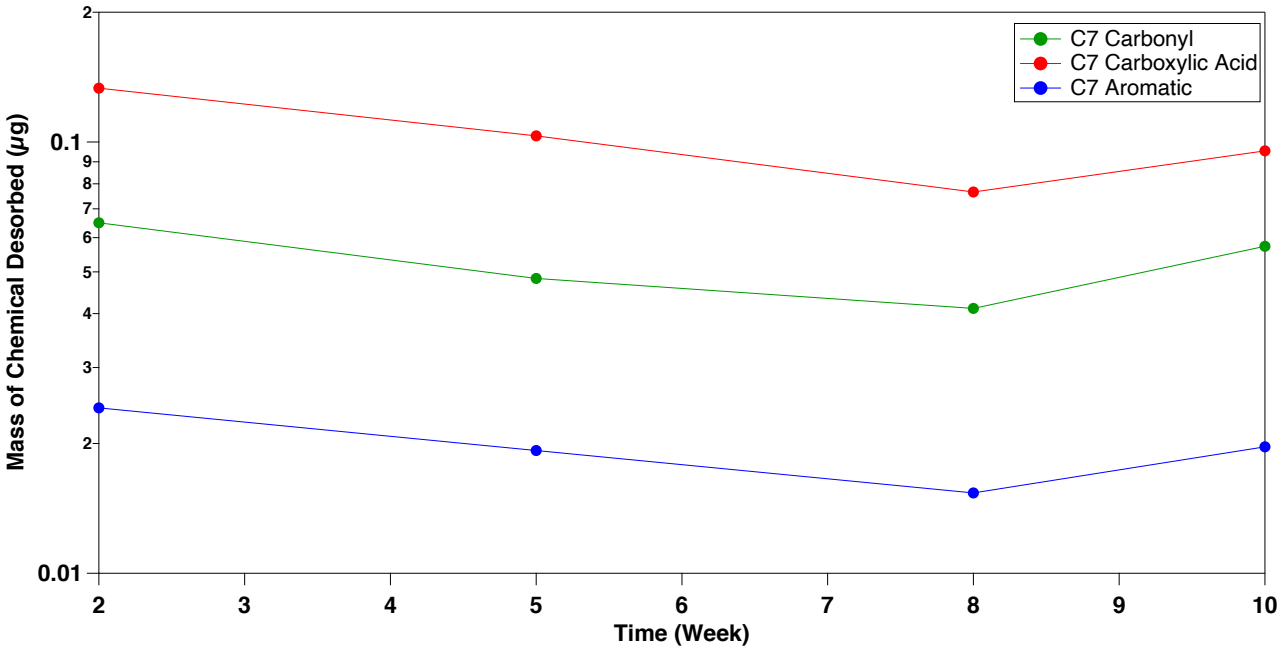


Figure S5. The validity of the 30-min short-time heating measurements is made via comparison of the K_{CA_V} values for long-time (2-hour heating; from data presented in the main paper in December 2020 and February 2021) vs short-time (30-minute heating; from an additional set of 1-7 day data in December 2020) thermal desorption. The K_{CA_V} values derived from short-time heating (open data points) are systematically lower but close to values from long-time heating (closed data points). However, the relative positions of the log K_{CA_V} values from one species to another are steady.

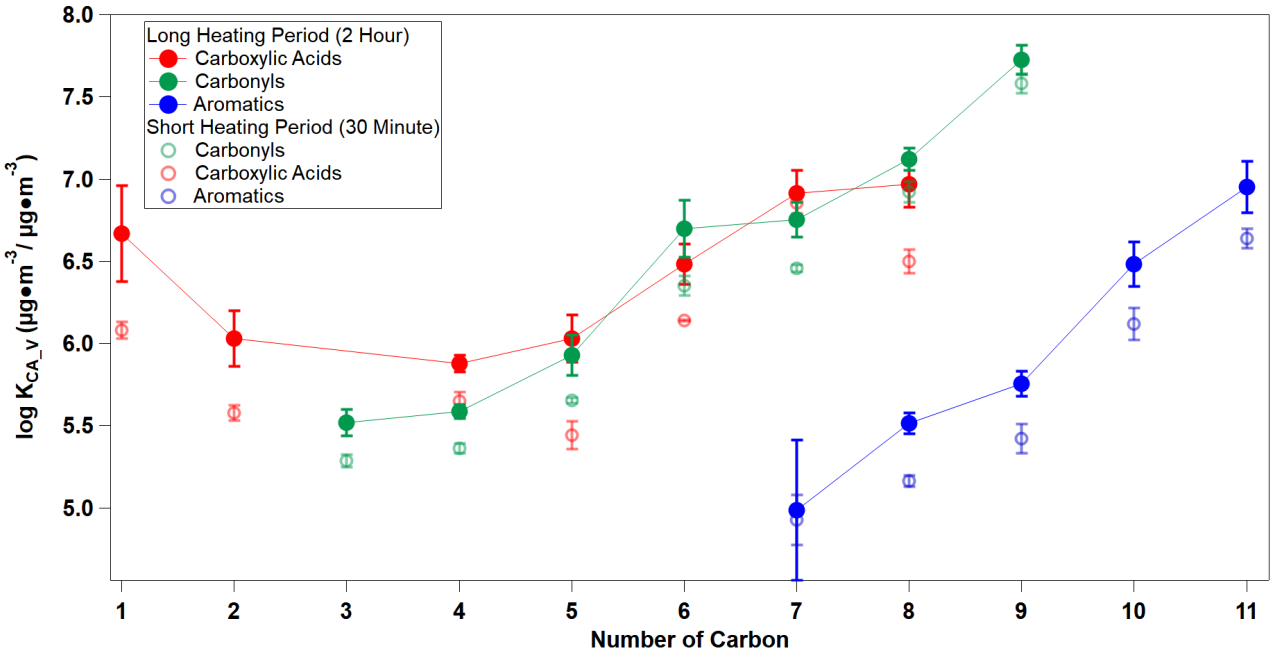


Figure S6. Time series of ambient temperature and relative humidity during exposure period in February 2021. The average temperature and relative humidity remained stable at 22.6 ± 0.3 ºC and 22.2 ± 2.1%, respectively.

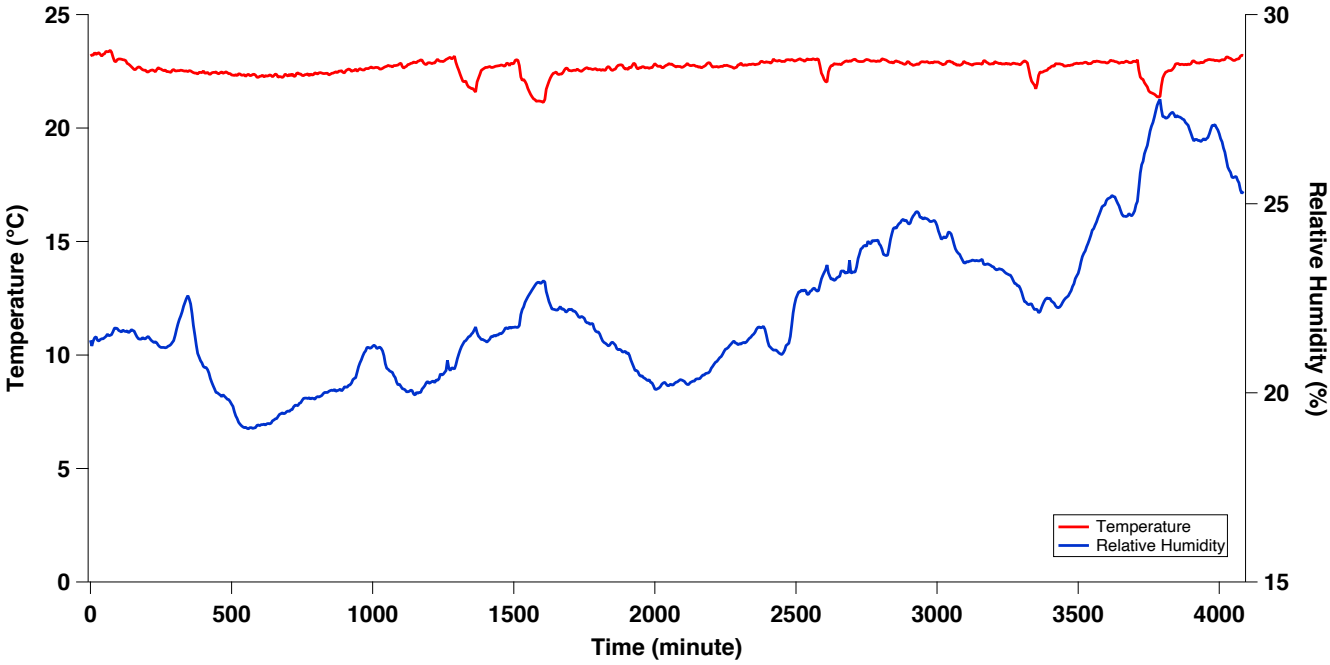


Figure S7. Surface adsorption partition ratio comparison for ethylbenzene: correlation of measured log K_{CA_S} values with ppLFER-predicted log K_S for Quartz-air system at 45% RH and NIST 2975 diesel soot – air system. The red square indicates the comparison of ethylbenzene with Aubin and Abbatt (2016): they obtained a log K_S of -1.522 m, the corresponding log K_{CA_S} is - 0.166 m in this study.

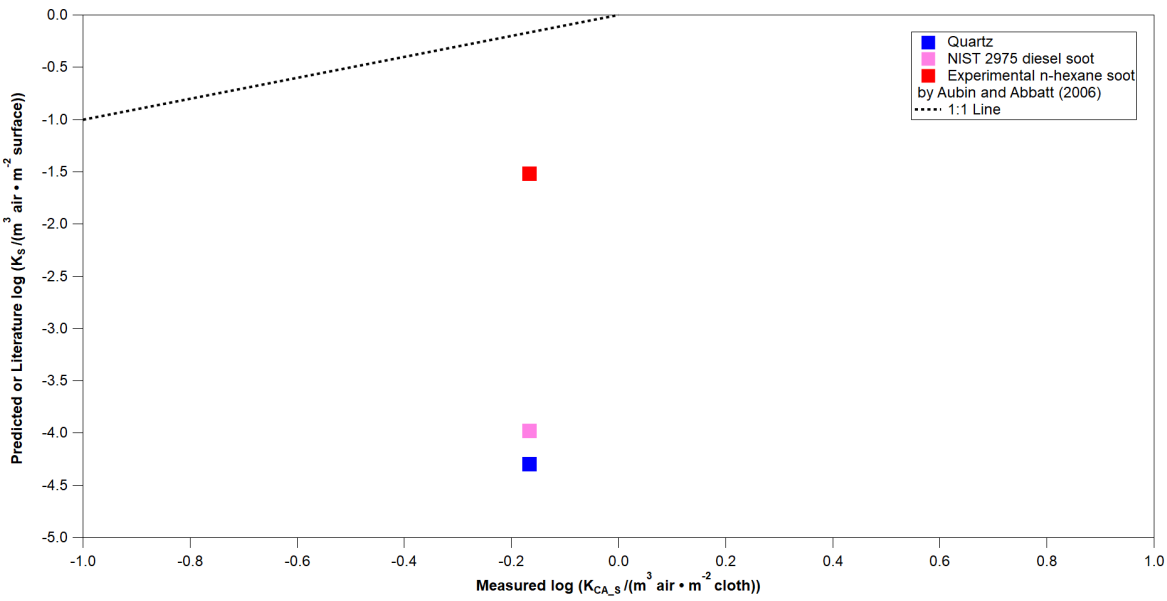
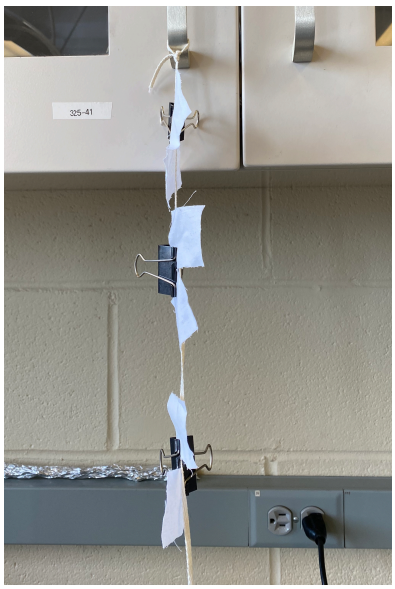


Figure S8. Illustrations for (A) Exposure set up; (B) Flow cell system.

(A) Cloth samples were hung vertically in the laboratory for various timed exposure periods.



(B) The stainless-steel flow cell system was situated in an old GC oven, cloth samples were placed inside the cell, one at a time for thermal desorption experiment at 135 °C. A nitrogen flow was sent through the system, and a heated Teflon sample line were used to transport desorbed signal to PTR-MS.

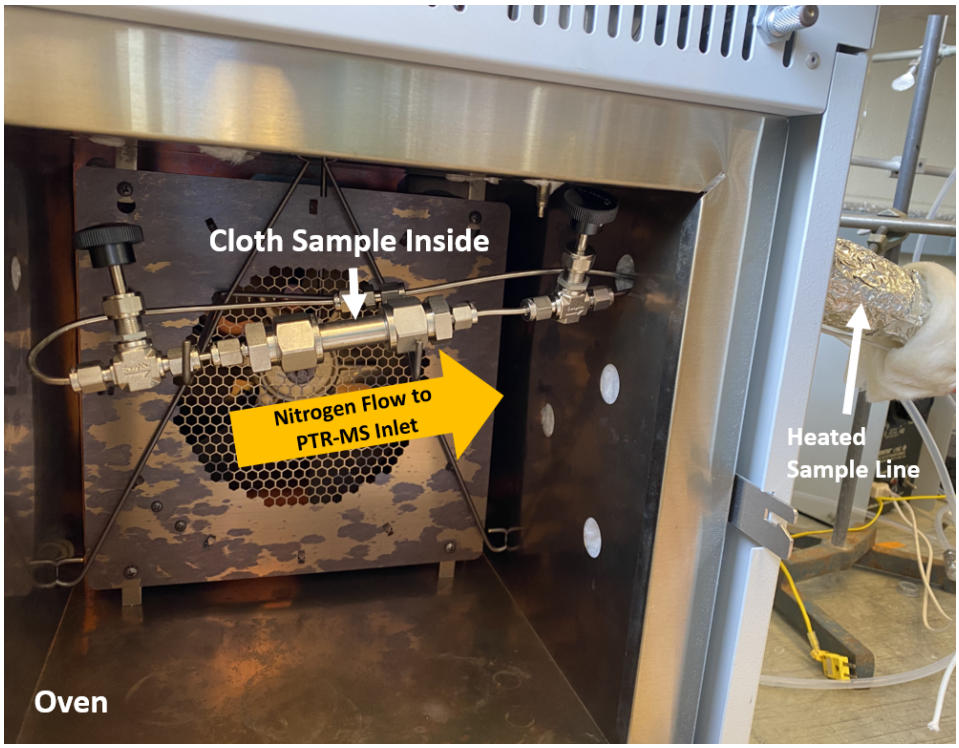


Table S2. (A) Measured sensitivity calibration factor (CF) of calibrated VOCs and predicted $k_{proton\text{-}transfer}$ values; (B) Predicted calibration factor for all VOCs and the relevant parameters.

(A)

Calibrated Chemical	Parent ion fraction	Measured parent ion CF (cps/ppb)	$k_{proton\text{-}transfer}$ (cm^3/ molecule • s)*[4]
Nonanal (C9 carbonyl)	0.13	188	3.13×10^{-9}
Acetic acid (C2 carboxylic acid)	0.53	577	2.2×10^{-9}
Butanoic acid (C4 carboxylic acid)	0.22	139	2.23×10^{-9}
Hexanoic acid (C6 carboxylic acid)	0.12	53	/
Toluene (C7 aromatic)	1	1286	2.06×10^{-9}

* $k_{proton\text{-}transfer}$ obtained from the online PTR library as described by Pagonis et al. (2019).[4]

(B)

Chemical	Assumed parent ion fraction	$k_{proton\text{-}transfer}$ (cm^3/ molecule • s)	Predicted parent ion CF (cps/ppb)
Carbonyls			
Propanal (C3)	0.13	3.13×10^{-9}	234
Butanal (C4)	0.13	3.17×10^{-9}	237
Pentanal (C5)	0.13	3.02×10^{-9}	226
Hexanal (C6)	0.13	3.05×10^{-9}	228
Heptanal (C7)	0.13	3.06×10^{-9}	229
Octanal (C8)	0.13	3.09×10^{-9}	231
Carboxylic Acids			
Formic acid (C1)	0.12	1.92×10^{-9}	260 (*assume 50% transmission efficiency)
Pentanoic acid(C5)	0.12	2.34×10^{-9}	157
Heptanoic acid(C7)	0.12	2.45×10^{-9}	165
Octanoic acid(C8)	0.12	2.56×10^{-9}	172
Aromatics Hydrocarbons			
Ethylbenzene (C8)	1	2.22×10^{-9}	1289
Propylbenzene (C9)	1	2.37×10^{-9}	1376
Butylbenzene (C10)	1	2.49×10^{-9}	1444
Pentamethylbenzene (C11)	1	2.60×10^{-9}	1509

Table S3. Summary of the numerical values of K_{CA}, error bar log K_{OA} values that are presented in Figure 3 - 5.

Proposed identity	Log K_{CA_V}	log K_{CA_V} Error bar	log K_{CA_S}	log K_{CA_S} Error bar	log K_{OA}*	Vapor Pressure [log (VP/Pascal)]**
Carbonyls						
Propanal	5.52	0.08	- 0.16	0.08	2.22	4.63
Butanal	5.58	0.04	- 0.097	0.04	2.65	4.17
Pentanal	5.93	0.12	0.25	0.12	3.20	3.33
Hexanal	6.70	0.17	1.02	0.17	3.68	3.08***
Heptanal	6.75	0.11	1.07	0.11	4.16	2.23
Octanal	7.12	0.07	1.44	0.07	4.62	2.50
Nonanal	7.72	0.09	2.04	0.09	5.08	1.92
Carboxylic Acids						
Formic acid	6.67	0.29	0.99	0.29	4.57	3.75
Acetic acid	6.03	0.17	0.35	0.17	4.28	3.32
Butanoic acid	5.88	0.05	0.20	0.05	5.26	2.13
Pentanoic acid	6.03	0.15	0.35	0.15	5.76	1.22
Hexanoic acid	6.48	0.12	0.80	0.12	6.28	0.75
Heptanoic acid	6.92	0.14	1.23	0.14	6.62	0.27
Octanoic acid	6.97	0.14	1.29	0.14	7.10	0.56
Aromatics Hydrocarbons						
Toluene	4.99	0.43	-0.70	0.43	3.25	3.58
Ethylbenzene	5.52	0.06	-0.17	0.06	3.68	3.10
n-Propylbenzene	5.76	0.08	0.075	0.08	4.09	2.65
n-Butylbenzene	6.48	0.14	0.80	0.14	4.57	2.13
Pentamethylbenzene	6.95	0.16	1.27	0.16	5.64	0.97

*PP-LFER fitting coefficients from Abraham et al.[7] The PP-LFER equation is log K_{OA} = 0.94L + 0.56S + 3.51A + 0.75B – 0.21E – 0.15 at 25 °C where the L, S, A, B and E are defined in Abraham et al.[7]

** The saturated vapor pressure values of the liquid are calculated for 298 K from the Antoine equation $\log_{10} P = A - \frac{B}{C+T}$, where the Antoine constants A, B, C are obtained from Stephenson and Malanowski (1987).[5]

*** Antoine constants unavailable, thus the vapor pressure value at 297K is referenced from Verevkin et al. (2003).[8]

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