

Supplementary Information for:

## **Evaluating a commercially available in-duct bipolar ionization device for pollutant removal and potential byproduct formation**

Yicheng Zeng<sup>1</sup>, Prashik Manwatkar<sup>1</sup>, Aurélie Laguerre<sup>2</sup>, Marina Beke<sup>1</sup>, Insung Kang<sup>1</sup>, Akram Ali<sup>1</sup>, Delphine Farmer<sup>3</sup>, Elliott Gall<sup>2</sup>, Mohammad Heidarinejad<sup>1</sup>, and Brent Stephens<sup>1\*</sup>

<sup>1</sup> Department of Civil, Architectural, and Environmental Engineering, Illinois Institute of Technology, Chicago, IL USA

<sup>2</sup> Department of Mechanical and Materials Engineering, Portland State University, Portland, OR USA

<sup>3</sup> Department of Chemistry, Colorado State University, Fort Collins, CO USA

\*Corresponding Author:

Brent Stephens, PhD

Professor and Department Chair

Department of Civil, Architectural, and Environmental Engineering

Illinois Institute of Technology

Alumni Hall Room 228E

3201 S Dearborn Street

Chicago, IL 60616 USA

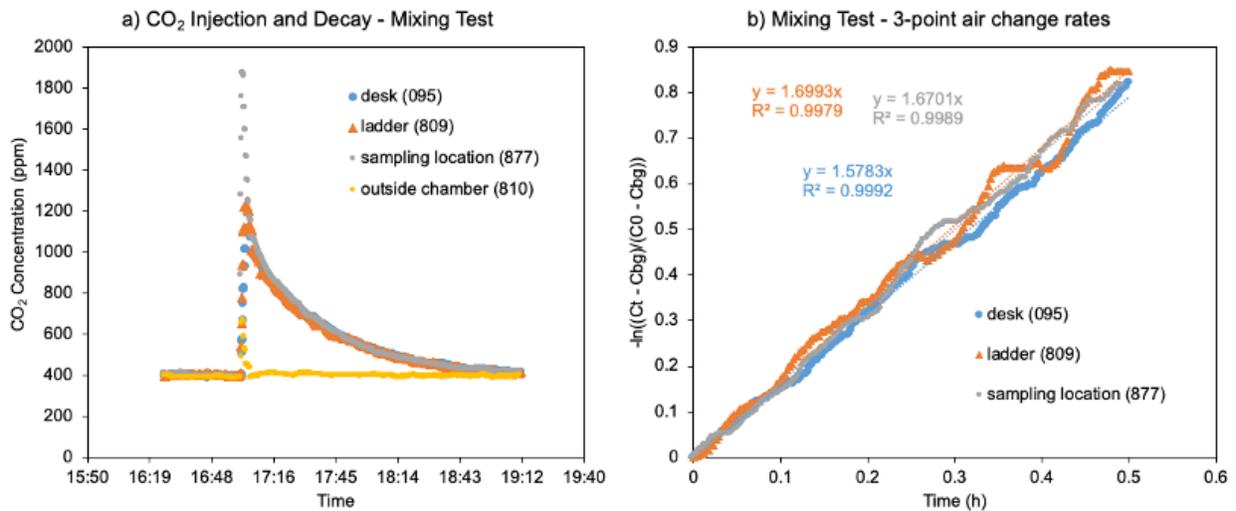
SI Contents Include:

- Additional methods and results
- Figures S1-S4
- Appendix 1-4
- Additional References

### **Chamber Mixing Investigation**

A CO<sub>2</sub> injection and decay test was conducted to investigate mixing conditions in the test chamber with the air handling unit (AHU) operating. Four Extech SD800 CO<sub>2</sub> monitors, which were calibrated against each other using short-term co-location measurements, were placed in three different locations within the chamber (middle of the room on a desk, at the sampling location, and elevated in a corner on a ladder) and one location outside the chamber (near the AHU). CO<sub>2</sub> was briefly injected into the AHU from outside the chamber and each CO<sub>2</sub> monitor logged data at 5-second intervals. Figure S1a shows time-series CO<sub>2</sub> concentrations measured in the three monitoring locations before, during, and after CO<sub>2</sub> injection. The time-series data

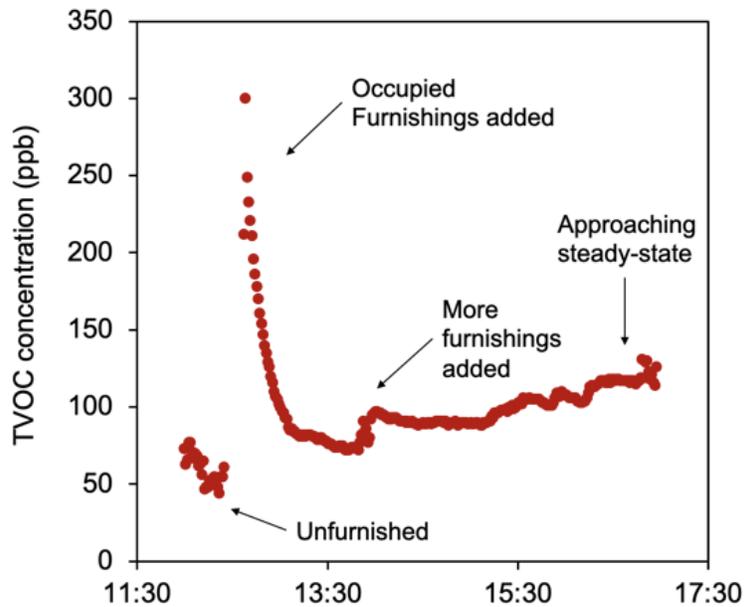
show good agreement between CO<sub>2</sub> measurements at each location, especially after the first ~15 minutes of CO<sub>2</sub> injection after allowing for mixing of the point source CO<sub>2</sub> entry. The mean CO<sub>2</sub> concentration measured during the subsequent decay period was 717 ppm in the central (desk) location, 707 ppm at the elevated (ladder) location, and 729 ppm at the primary instrument sampling location (i.e., a maximum relative difference in mean concentrations of ~3%). Figure S1b shows estimates of air change rates made at each of the three sampling locations inside the chamber using data from the CO<sub>2</sub> decay period. Air change rate estimates ranged from 1.57 per hour in the central (desk) location, 1.69 per hour at the elevated (ladder) location, and 1.67 per hour at the primary instrument sampling location (i.e., a maximum relative difference in of ~7%). Both measures of mixing confirm the chamber was operated at reasonably well-mixed conditions for the purposes of the tests conducted herein (i.e., <10% differences among chamber sampling locations for both of these metrics).



**Figure S1.** Chamber mixing tests: a) time-series CO<sub>2</sub> concentrations measured in three inside-chamber locations and outside the chamber before, during, after CO<sub>2</sub> injection and b) estimated air change rates in the three monitoring locations inside the chamber. The three-digit numbers next to each monitoring location corresponds to a portion of the serial number for each instrument.

## Steady-State Conditions: TVOCs

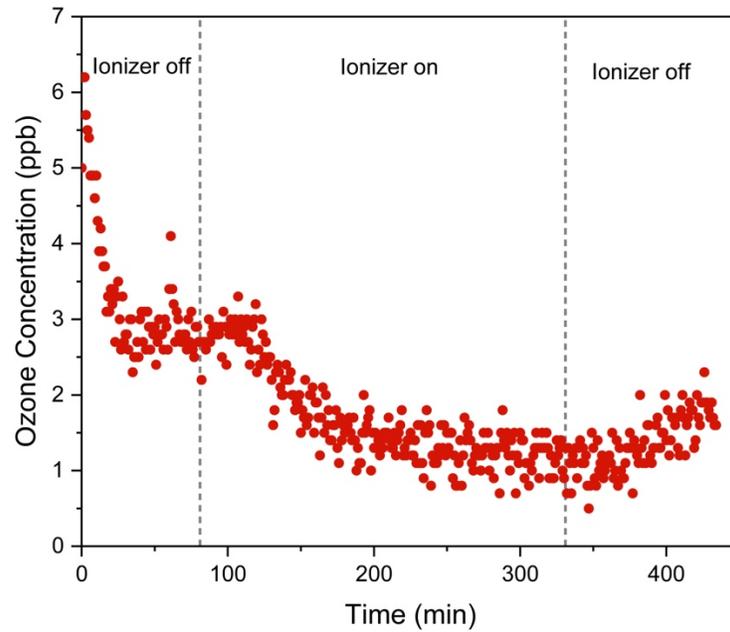
Figure S2 shows time varying TVOC concentrations (as isobutylene equivalents) measured in the chamber as furniture and materials were brought in to create an indoor VOC mixture prior to testing.



**Figure S2.** TVOC concentrations (as isobutylene equivalents) measured on October 9, 2020 as the chamber went from completely unfurnished to furnished and eventually approaching steady-state

### Time-series O<sub>3</sub> Concentrations

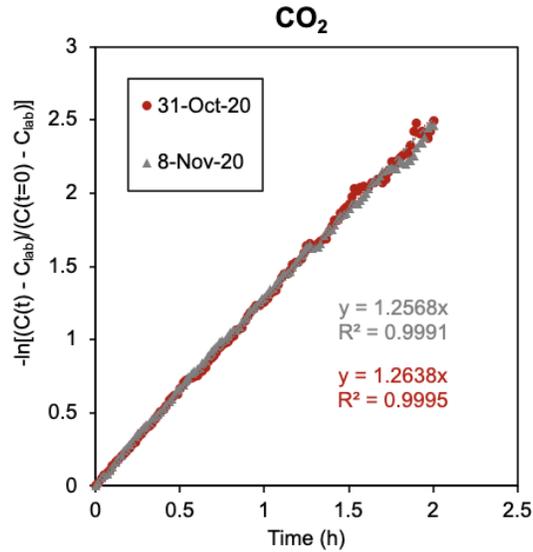
Figure S3 shows time-series O<sub>3</sub> concentrations measured in the chamber during normal operating conditions.



**Figure S3.** Time-resolved O<sub>3</sub> concentration in the chamber on one of the normal condition test days (October 24, 2020).

### Air Change Rate Estimates during Particle Injection and Decay

Figure S4 shows results from air change rate measurements using CO<sub>2</sub> injection and decay made during the particle injection and decay experiments conducted on October 31, 2020 (with the ionizer on) and November 8, 2020 (with the ionizer off).



**Figure S4.** Air change rate estimates using CO<sub>2</sub> tracer injection and decay after particle injection and decay experiments were conducted on October 31, 2020 (ionizer test day) and November 8, 2020 (background, i.e., no ionizer, test day).

**Appendix 1: List of TO-15 VOC analytes and reported concentrations from chamber tests**

Test Method	Analyte	Units	Ionizer On		Ionizer Off	
			Inside	Outside	Inside	Outside
TO-15	1,1,1-Trichloroethane	mg/m <sup>3</sup>	< 0.0033	< 0.0033	< 0.0033	< 0.0033
TO-15	1,1,2-Trichloroethane	mg/m <sup>3</sup>	< 0.0033	< 0.0033	< 0.0033	< 0.0033
TO-15	1,1-Dichloroethane	mg/m <sup>3</sup>	< 0.0024	< 0.0024	< 0.0024	< 0.0024
TO-15	1,1-Dichloroethene	mg/m <sup>3</sup>	< 0.0024	< 0.0024	< 0.0024	< 0.0024
TO-15	1,2,4-Trichlorobenzene	mg/m <sup>3</sup>	< 0.0046	< 0.0046	< 0.0045	< 0.0045
TO-15	1,2-Dibromoethane	mg/m <sup>3</sup>	< 0.0046	< 0.0046	< 0.0045	< 0.0045
TO-15	1,2-Dichlorobenzene	mg/m <sup>3</sup>	< 0.0036	< 0.0037	< 0.0036	< 0.0036
TO-15	1,2-Dichloroethane	mg/m <sup>3</sup>	0.0041	< 0.0024	< 0.0024	< 0.0024
TO-15	1,2-Dichloropropane	mg/m <sup>3</sup>	< 0.0027	< 0.0027	< 0.0027	< 0.0027
TO-15	1,4-Dichlorobenzene	mg/m <sup>3</sup>	< 0.0036	< 0.0037	< 0.0036	< 0.0036
TO-15	1,4-Dioxane	mg/m <sup>3</sup>	< 0.0055	< 0.0055	< 0.0054	< 0.0055
TO-15	2-Butanone	mg/m <sup>3</sup>	< 0.0046	< 0.0046	< 0.0045	< 0.0045
TO-15	Acetone	mg/m <sup>3</sup>	0.023	0.036	0.041	0.037
TO-15	Benzene	mg/m <sup>3</sup>	< 0.0018	< 0.0018	< 0.0018	< 0.0018
TO-15	Bromodichloromethane	mg/m <sup>3</sup>	< 0.0039	< 0.0040	< 0.0039	< 0.0039
TO-15	Bromoform	mg/m <sup>3</sup>	< 0.016	< 0.016	< 0.016	< 0.016
TO-15	Bromomethane	mg/m <sup>3</sup>	< 0.0058	< 0.0058	< 0.0057	< 0.0058
TO-15	Carbon disulfide	mg/m <sup>3</sup>	< 0.0019	< 0.0019	< 0.0019	< 0.0019
TO-15	Carbon tetrachloride	mg/m <sup>3</sup>	< 0.0039	< 0.0040	< 0.0039	< 0.0039
TO-15	Chlorobenzene	mg/m <sup>3</sup>	< 0.0027	< 0.0027	< 0.0027	< 0.0027
TO-15	Chloroform	mg/m <sup>3</sup>	< 0.0030	< 0.0030	< 0.0030	< 0.0030
TO-15	cis-1,2-Dichloroethene	mg/m <sup>3</sup>	< 0.0024	< 0.0024	< 0.0024	< 0.0024
TO-15	cis-1,3-Dichloropropene	mg/m <sup>3</sup>	< 0.0027	< 0.0027	< 0.0027	< 0.0027
TO-15	Dibromochloromethane	mg/m <sup>3</sup>	< 0.0052	< 0.0052	< 0.0051	< 0.0052
TO-15	Dichlorodifluoromethane	mg/m <sup>3</sup>	0.0036	< 0.0030	< 0.0030	< 0.0030
TO-15	Ethylbenzene	mg/m <sup>3</sup>	0.0075	< 0.0027	< 0.0027	< 0.0027
TO-15	m,p-Xylene	mg/m <sup>3</sup>	0.024	< 0.0052	< 0.0051	< 0.0052
TO-15	Methyl tert-butyl ether	mg/m <sup>3</sup>	< 0.0021	< 0.0021	< 0.0021	< 0.0021
TO-15	Methylene chloride	mg/m <sup>3</sup>	< 0.021	< 0.021	< 0.021	< 0.021
TO-15	Naphthalene	mg/m <sup>3</sup>	< 0.0030	< 0.0030	< 0.0030	< 0.0030
TO-15	o-Xylene	mg/m <sup>3</sup>	< 0.0027	< 0.0027	< 0.0027	< 0.0027
TO-15	Styrene	mg/m <sup>3</sup>	< 0.0027	< 0.0027	< 0.0027	< 0.0027
TO-15	Tetrachloroethene	mg/m <sup>3</sup>	< 0.0042	< 0.0043	< 0.0042	< 0.0042
TO-15	Toluene	mg/m <sup>3</sup>	0.0026	0.0045	0.0034	0.0051
TO-15	trans-1,2-Dichloroethene	mg/m <sup>3</sup>	< 0.0024	< 0.0024	< 0.0024	< 0.0024
TO-15	trans-1,3-Dichloropropene	mg/m <sup>3</sup>	< 0.0027	< 0.0027	< 0.0027	< 0.0027
TO-15	Trichloroethene	mg/m <sup>3</sup>	< 0.0033	< 0.0033	< 0.0033	< 0.0033
TO-15	Trichlorofluoromethane	mg/m <sup>3</sup>	< 0.0033	< 0.0033	< 0.0033	< 0.0033
TO-15	Vinyl acetate	mg/m <sup>3</sup>	< 0.021	< 0.021	< 0.021	< 0.021
TO-15	Vinyl chloride	mg/m <sup>3</sup>	< 0.0015	< 0.0015	< 0.0015	< 0.0015
TO-15	Xylenes, Total	mg/m <sup>3</sup>	0.025	< 0.0079	< 0.0079	< 0.0079

**Appendix 2: List of TO-11A analytes and reported concentrations from chamber tests**

Test Method	Analyte	Units	Ionizer On		Ionizer Off	
			Inside	Outside	Inside	Outside
TO-11A	2,5-Dimethylbenzaldehyde	µg/m <sup>3</sup>	< RL <sup>1</sup>	< RL	< RL	< RL
TO-11A	Acetaldehyde	µg/m <sup>3</sup>	5.9	5.4	5.7	4.6
TO-11A	Acetone	µg/m <sup>3</sup>	29.6	23.0	26.0	19.4
TO-11A	Acrolein	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	Benzaldehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	Butyraldehyde	µg/m <sup>3</sup>	2.1	2.0	2.2	1.6
TO-11A	Crotonaldehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	Formaldehyde	µg/m <sup>3</sup>	11.4	5.9	10.6	5.3
TO-11A	Hexaldehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	Isovaleraldehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	m,p-Tolualdehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	o-Tolualdehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	Propionaldehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL
TO-11A	Valeraldehyde	µg/m <sup>3</sup>	< RL	< RL	< RL	< RL

<sup>1</sup> RL = Reporting limit

### Appendix 3: Sampling and analysis protocol TD-GC/MS used at the field site

**Sorbent tubes.** VOCs were collected by glass sorbent tubes (Perkin Elmer) packed with 180 mg of Carbotrap B followed by 70 mg of Carboxen 1000 (Pankow et al, 1998) using a portable sampling pump (Universal PCXR8, SKC Inc., USA) to draw in the air. The sorbent tubes were conditioned prior to the sampling at 320°C for an hour using pre-cleaned N<sub>2</sub> gas at 100 mL/min. Each sorbent tube was then sealed with stainless steel Swagelok end caps that had been baked for 90 min at 100°C. The endcaps were fitted with PTFE ferrules. The sealed tubes were then stored in two clean Ziploc bags at -18°C in a freezer and kept cold during transportation using a cooler containing reusable ice packs. The sampling and the analysis of the sorbent tubes occurred within a few days after conditioning.

**VOC sampling.** The sampling was performed at a flow rate around 50 mL/min for 60 minutes with a total sample volume of 3 L for samples upstream and downstream of the ionization unit. The outdoor and indoor air samplings were performed at a flow rate around 50 mL/min for 30 minutes with a total sample volume of 1.5 L. The flow rate was measured for each sample using a primary standard air flow calibrator (Gilian, Gilibrator 2). After sampling, the sorbent tubes were capped and stored in two clean Ziploc bags and kept cold during transportation using a cooler containing reusable ice packs. Back to the laboratory, they were stored in the freezer at -18°C until analysis.

**Calibration standards loading.** A six-point calibration curve was achieved using a TO-15 gas mixture containing a representative mix of VOCs (65 components) at 1 ppmv in N<sub>2</sub> from Linde (Alpha, NJ, USA) certified to ± 5% accuracy. This mixture allows for the identification and quantification of compounds. Six calibration sorbent tubes were spiked with 0.16 – 6.2 mL of the gas mixture using a 50 mL/min flow of pre-cleaned N<sub>2</sub> gas for 10 min. The spiked volume was withdrawn using a gastight syringe at atmospheric pressure and then injected into the sidearm of a Swagelok tee. The tee was connected to the N<sub>2</sub> flow on one side and to the inlet end of the sorbent tube on the other side (Pankow et al, 1998). The mass of compounds loaded into the standard sorbent tubes ranged from 0.3 to 71.7 ng (depending on the compounds). Standard sorbent tubes were analyzed following the same analysis method as for the samples, described below. Four internal standards were injected at a constant concentration in each sorbent tubes (including standards, samples and blanks): fluorobenzene, toluene-D8, bromofluorobenzene and 1,2-dichlorobenzene-D4. An internal standard normalized response ratio (e.g., compound area/internal standard area using the closest internal standard in terms of retention time) was then calculated and plotted against the theoretical mass loaded into the sorbent tube. The response of the analytical system was linear through the origin over this range.

**Breakthrough test.** Volume breakthrough tests have been performed at a mass spectrometry facility at Portland State University in the past, and showed that sample volume should not exceed 5 L using these sorbent tubes.

**Sorbent tubes analysis.** A total of 22 sorbent tubes including blanks were then analyzed using an Absorption/Thermal Desorption (ATD) instrument (TurboMatrix 650, PerkinElmer) connected

to a gas chromatograph (model 7890 A, Agilent Technologies) with a DB-VRX column (60 m length × 0.25 mm i.d. × 1.4 μm film thickness, Agilent J&W) coupled to a mass selective detector (model 5975 C, Agilent Technologies). The ATD instrument desorbed each sorbent tube at 300 °C during 10 min, and samples were then concentrated into a cold trap at -30 °C after which they were injected in a split/splitless injector kept at 180 °C. The injector was in split mode with a split flow of 2.76 mL.min<sup>-1</sup>. Helium was used as the carrier gas at a constant flow of 0.92 mL.min<sup>-1</sup>. The oven temperature started at 45 °C for 10 min, was then raised at 12 °C.min<sup>-1</sup> up to 190 °C and kept isothermal for 2 min, then raised again at 6 °C.min<sup>-1</sup> up to 240 °C and kept isothermal for 1 min and finally decreased at 10 °C.min<sup>-1</sup> to 210 °C. The MS conditions were: transfer line at 230 °C, ion source at 250 °C and EI voltage at 70 eV. Data were recorded in full scan mode (*m/z* range: 34-400 amu). Peaks integration was performed using Agilent ChemStation software. Compounds were identified on the basis of their mass spectra and the injection of standards when available. The mass spectra were compared with those from two databases: NIST Mass Spectral Database (2008) (NIST08) and W8N08 library (John Wiley & Sons, Inc., USA). Peak integration was based on extracted ion chromatograms (quantifier ions). Moreover, four internal standards were injected in each sample in order to i) use the internal standard normalized response factor to calculate the concentration of target compounds, ii) check the method (desorption and analysis) efficiency, evaluate the instrument and method performance, iii) get a relative concentration for the compounds for which we do not have standards. 98 compounds were extracted from the mass spectra for identified peaks with a signal/noise ratio of > 3 standard deviations. 40 compounds were above the quantification threshold (signal/noise ratio of > 10 standard deviations and within the external calibration range).

### **Quantification**

Compounds included in the TO-15 mixture: Compounds mass on each sorbent tube was calculated by imputing the compound internal standard normalized area into the linear fit line equation from the corresponding calibration curve. Concentrations were then calculated by dividing mass by sampling volume for each sorbent tube.

Compounds not included in the TO-15 mixture: Semi-quantification was estimated using the response factor determined for the nearest compounds in the TO-15 mixture in terms of retention time. The response factor (RF) is calculated using the following equation:

$$RF = ((A_X) \times (C_{ISTD})) / ((A_{ISTD}) \times (C_X))$$

Where  $A_X$  is the area of the nearest compound,  $C_X$  the concentration of the nearest compound,  $A_{ISTD}$  is the area of the internal standard,  $C_{ISTD}$  is the concentration of the internal standard. The response factor is calculated for each level of the calibration and an averaged response factor is then calculated ( $RF_{AVE}$ ). The following equation is then used to calculate the concentration of the target compound:

$$C_X = [((A_X) \times (C_{ISTD})) / ((A_{ISTD}) \times (RF_{AVE}))] / \text{sample volume}$$

**QA/QC.** A field blank was prepared and consisted in handling the sorbent tube the same way we do with the sample: take the sorbent tube from the Ziploc bag from the cooler bag, remove the end cap, plug the sorbent tube onto the pump, tight the fittings, prepare the pump, unplug the sorbent tube from the pump, cap the tube and place it in a new Ziploc bag into the cooler. A

transportation blank was analyzed consisting in a sorbent tube never uncapped until analysis and that was transported in the same way as other sorbent tubes. A storage blank was also analyzed consisting in a sorbent tube placed into the freezer after conditioning and analyzed at the same time as the other sorbent tubes. The transportation and storage blanks showed no contamination compared to freshly conditioned sorbent tubes.

## References

Pankow et al, 1998: Pankow, J. F.; Luo, W.; Isabelle, L. M.; Bender, D. A.; Baker, R. J. Determination of a Wide Range of Volatile Organic Compounds in Ambient Air Using Multisorbent Adsorption/Thermal Desorption and Gas Chromatography/Mass Spectrometry. *Anal. Chem.* 1998, 70 (24), 5213–5221.  
<https://doi.org/10.1021/ac980481t>.

**Appendix 4: Summary of compounds identified and quantified in the field site sampling  
(occupied office environment) by TD-GC-MS ( $\mu\text{g}/\text{m}^3$ )**

Compounds	Calibration <sup>1</sup>	Upstream	Downstream	Outdoor	Office
Dichlorodifluoromethane	internal	2.12	1.52	4.69	4.23
Ethanol*	internal	44.96	104.97	3.06	372.95
Trichlorofluoromethane	internal	0.56	0.32	1.83	5.52
Isopropanol*	internal	7.32	22.89	5.37	53.99
Acetone*	internal	11.31	30.35	18.37	103.75
Vinyl acetate	internal	0.00	0.00	1.07	1.39
Methyl ethyl ketone	internal	0.65	0.66	0.19	1.00
Ethyl Acetate	internal	2.02	2.18	0.35	3.02
Tetrahydrofuran	internal	0.16	0.19	0.00	0.00
Heptane	internal	0.17	0.55	0.00	0.87
Methyl methacrylate	internal	0.09	0.45	0.28	0.54
Toluene	internal	1.12	1.28	0.86	1.33
m-,p-Xylene	internal	0.75	0.65	0.35	0.98
<b>Aldehydes</b>					
Acetaldehyde	semi-quant	1.03	0.99	0.00	4.27
n-Hexanal	semi-quant	0.77	0.27	0.00	0.49
Furfural	semi-quant	3.29	2.19	0.17	1.37
Benzaldehyde	semi-quant	0.61	0.59	0.18	1.65
Nonanal	semi-quant	1.88	1.24	0.84	1.55
Decanal	semi-quant	1.57	0.97	0.54	1.53
<b>Total aldehydes</b>		<b>9.15</b>	<b>6.25</b>	<b>1.73</b>	<b>10.86</b>
<b>Acids</b>					
Formic acid	semi-quant	0.00	1.18	0.00	0.00
Acetic acid	semi-quant	1.39	0.54	2.72	10.61
2-Methylpropanoic acid	semi-quant	0.14	0.23	0.00	0.00
Butanoic acid	semi-quant	2.06	1.11	0.00	0.48
Hexanoic acid	semi-quant	0.37	0.27	0.00	0.05
<b>Total acids</b>		<b>3.96</b>	<b>3.33</b>	<b>2.72</b>	<b>11.14</b>
<b>Other alcohols</b>					
1-Propanol	semi-quant	0.07	0.20	0.00	0.25
2-Methyl-3-buten-2-ol	semi-quant	0.73	0.97	0.31	0.87
1-Butanol	semi-quant	5.07	4.65	0.00	6.68
1-Methoxy-2-propanol	semi-quant	0.00	2.17	0.00	0.00
1-Pentanol	semi-quant	0.06	0.12	0.00	0.00
Phenol	semi-quant	1.03	0.97	0.46	0.70
2-Ethylhexanol	semi-quant	2.21	1.11	0.22	2.44
<b>Total other alcohols</b>		<b>9.18</b>	<b>10.19</b>	<b>0.98</b>	<b>10.94</b>
<b>Other compounds</b>					
Decamethylcyclopentasiloxane	semi-quant	31.45	13.97	0.84	51.95
Butyrolactone	semi-quant	0.00	0.40	0.00	0.00
Acetophenone	semi-quant	0.94	0.47	0.19	0.36
$\alpha$ -Pinene	semi-quant	0.63	0.34	0.08	0.37
Limonene	semi-quant	4.26	1.80	0.25	1.24
2-Methylhexane	semi-quant	0.38	0.41	0.00	0.53
Methylcyclohexane	semi-quant	0.36	0.44	0.00	0.66
1-Methoxy-2-propyl acetate	semi-quant	0.00	0.33	0.00	0.00
2-Methylbutane	semi-quant	1.90	1.50	3.94	4.08
<b>Total other</b>		<b>39.92</b>	<b>19.67</b>	<b>5.29</b>	<b>59.19</b>

<sup>1</sup>Internal = quantified using standard calibration (TO-15 mixture); Semi-quant = quantified using response factor calculated using internal standard and nearest compounds in the TO-15 standard