

# Supplemental Information

## **Bridging temporal resolution and molecular specificity with a compact GC-PTR for the measurement of volatile organic compounds**

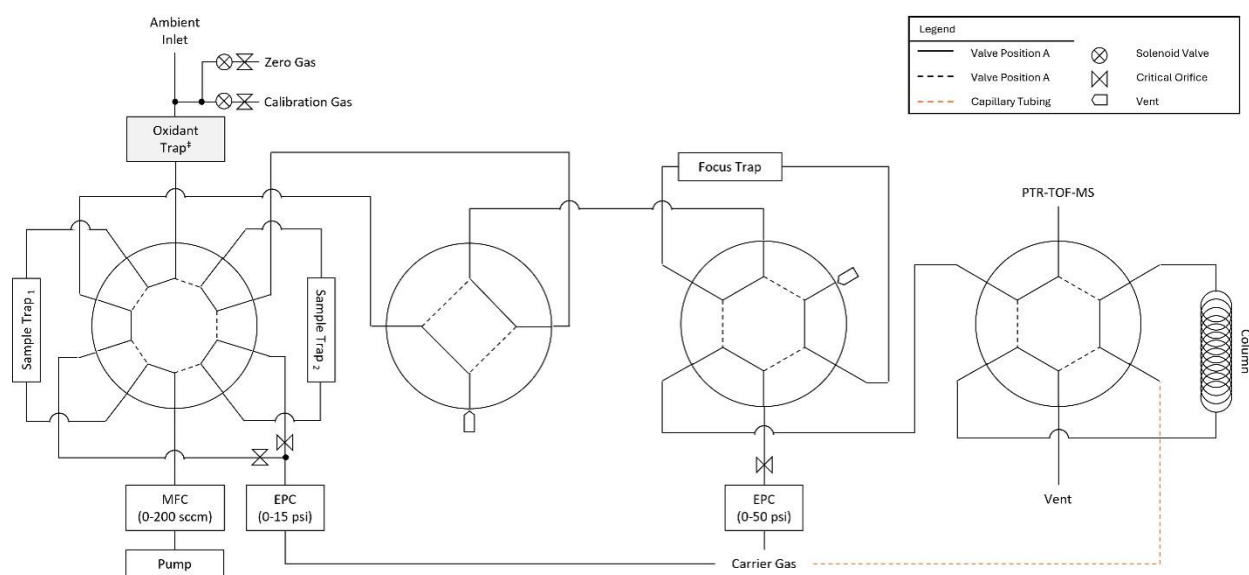
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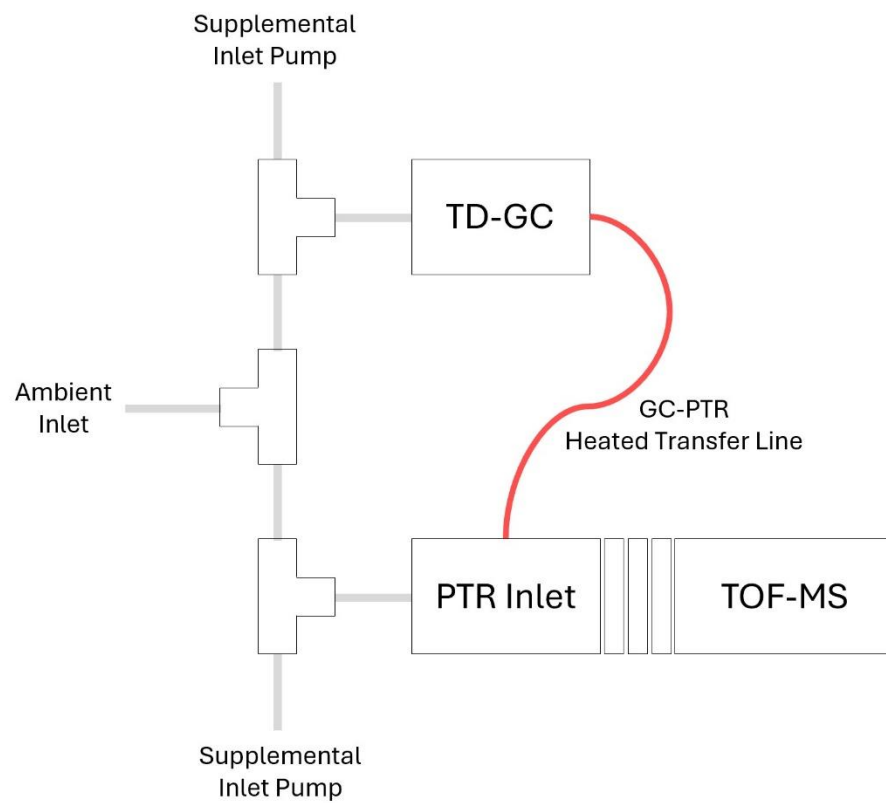
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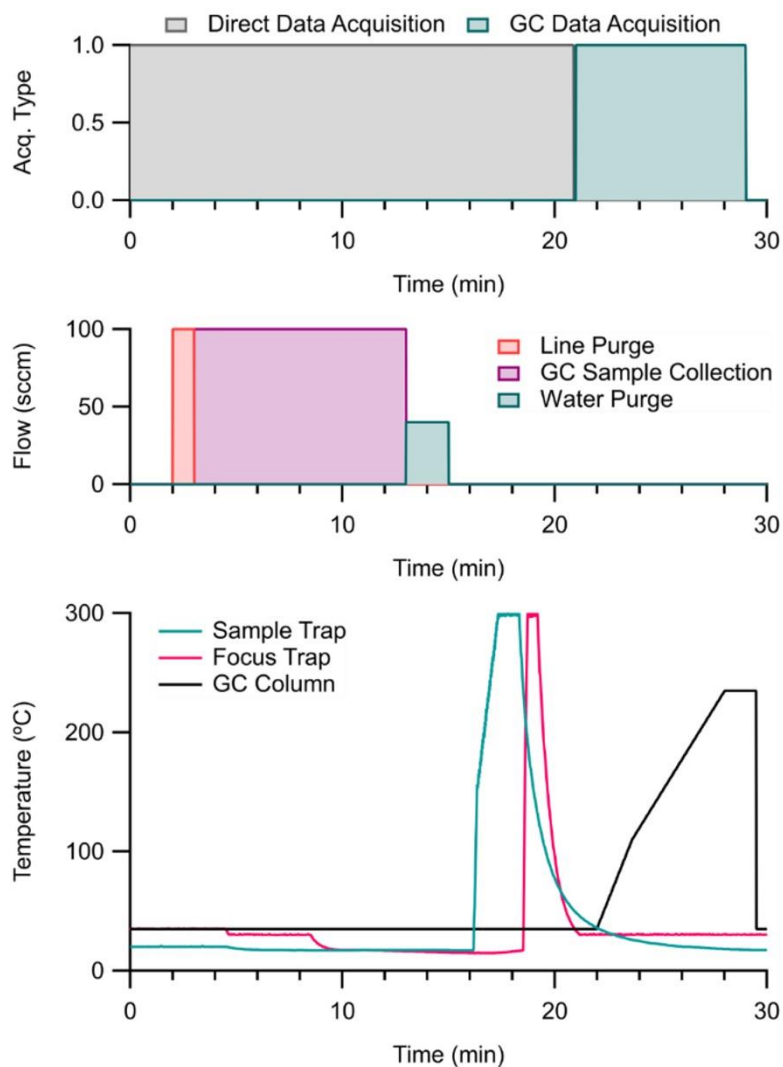
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**Figure S1.** TD-GC flow path schematics of single channel systems.



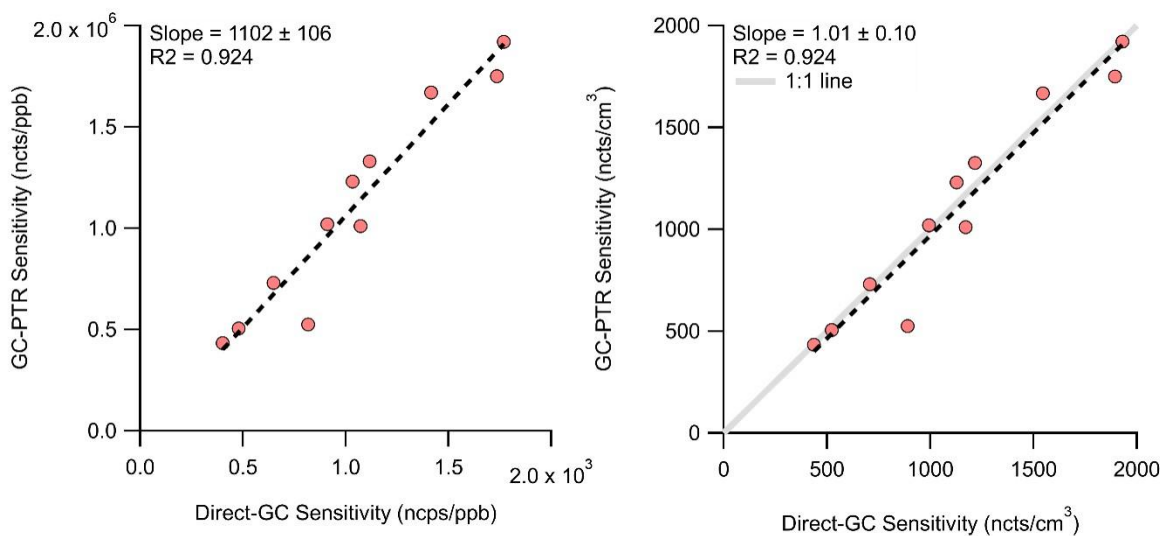
**Figure S2.** Schematic of ambient inlet configuration for TD-GC coupled with PTR-TOF-MS.



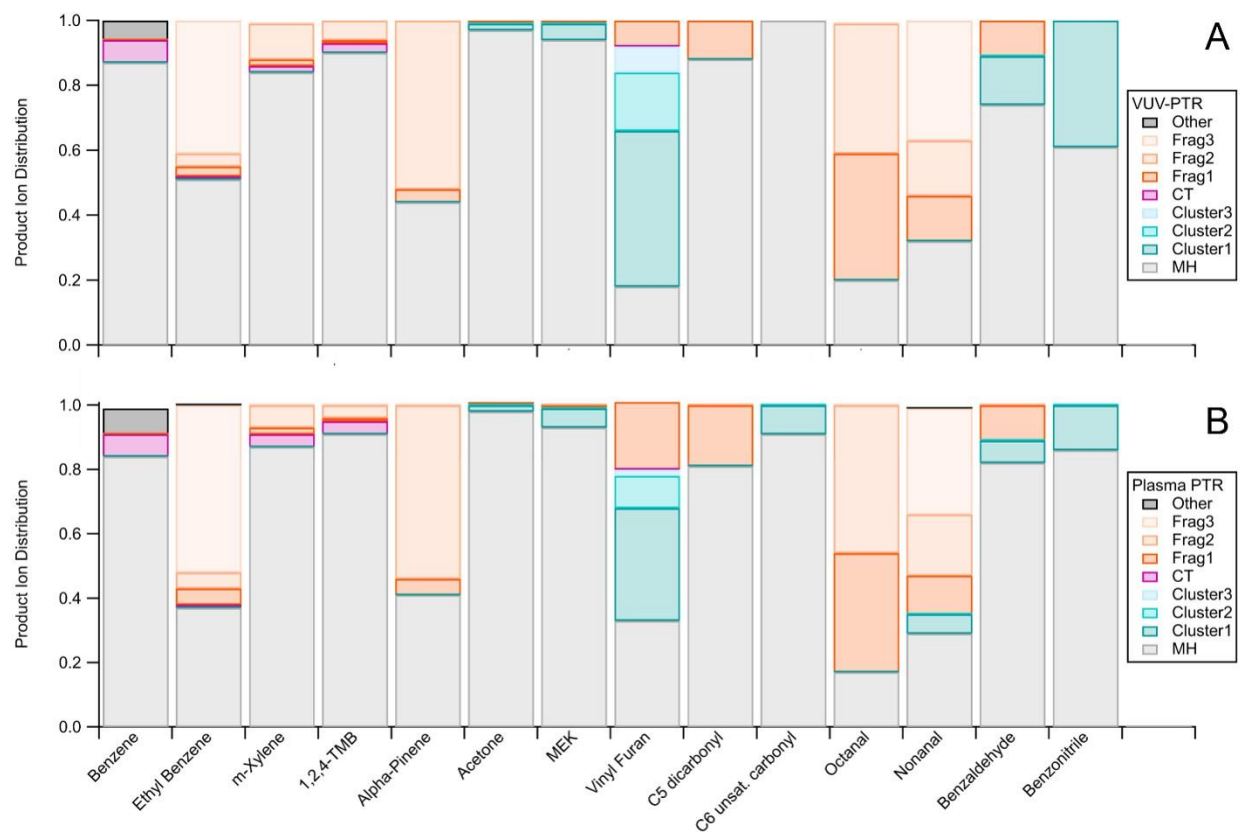
**Figure S3.** Sampling methodology for a single channel TD-GC coupled with PTR-TOF-MS. The cycle overview is split into three axes for ease of visualization. Methodology shown is an example, all timings, flow rates, heat rates, etc. can be modified depending on use case.



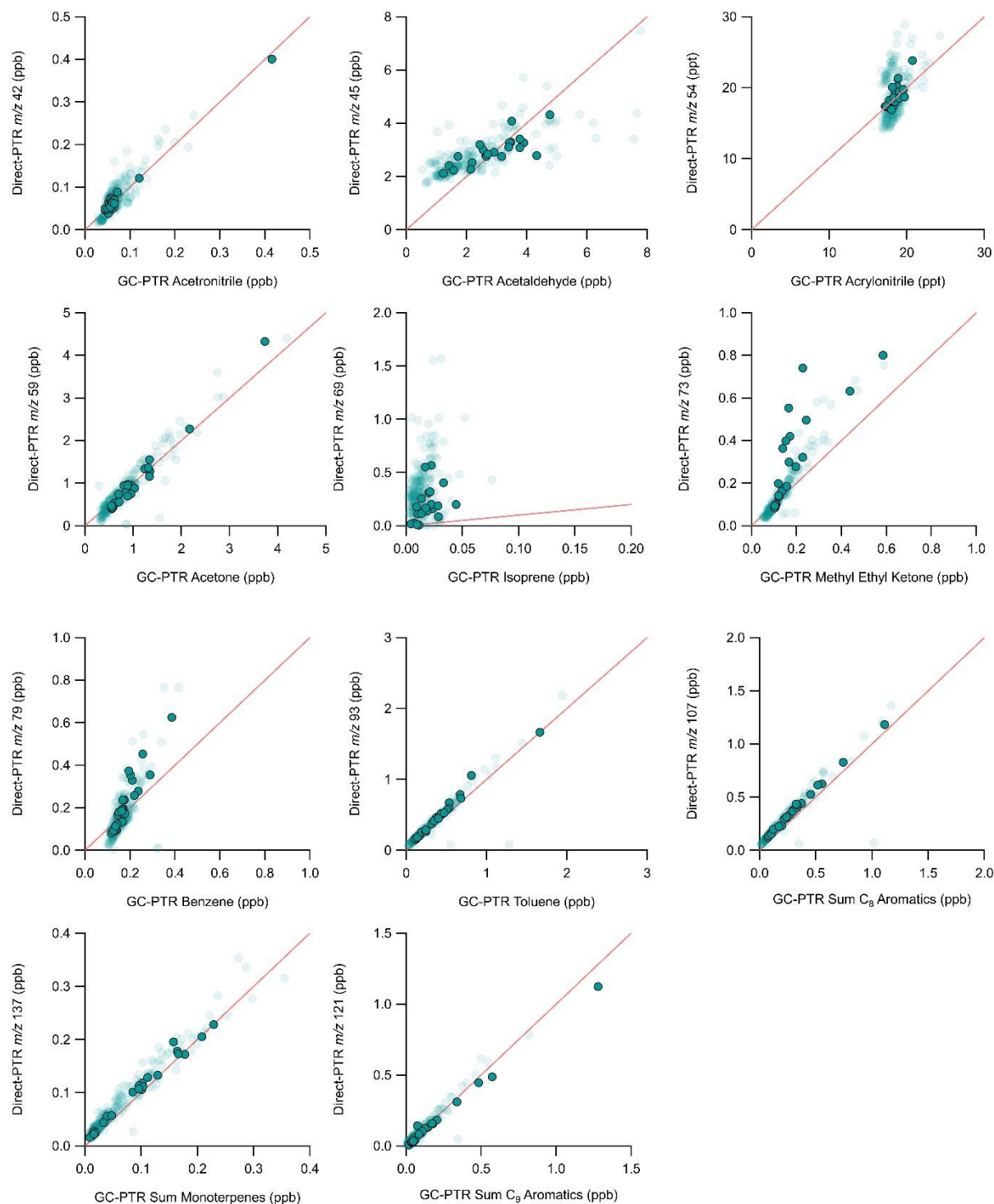
**Figure S4.** Wind rose diagram for Thun, Switzerland from February 27 to March 28, 2025 (left). The plot shows the distribution of wind speed and direction, where the length of each spoke represents the frequency of time (in percent) the wind blew from that direction. Colors represent different wind speed intervals (m/s). Continental (middle) and local (right) maps, indicating the location of Thun, Switzerland where the ambient measurements occurred.



**Figure S5.** Left: correlation between the measured sensitivities for the 11 calibrant species by GC-PTR (normalized counts / parts per billion; ncts/ppb) and direct-PTR (normalized counts per second / parts per billion; ncps/ppb). Right: correlation between the measured sensitivities for the 11 calibrant species with differences in sampling time and flow rate accounted for both the GC-PTR and direct-PTR, resulting in both axes being reported in normalized counts per volume of air sampled (ncts/cm<sup>3</sup>).



**Figure S6.** Product ion distributions (PIDs) for a variety of VOCs resolved in ambient air detected by the GC-PTR equipped with **(a)** a VUV-PTR ion source and **(b)** a plasma PTR ion source.



**Figure S7.** Correlations for the 11-calibrant species, or sum of associated isomers, detected in ambient air between GC-PTR and direct-PTR. Datapoints shown in dark blue with black outlines represent the subset of data shown in Figure 4. Points in light blue represent data measured across the entire 30-day measurement period. The 1:1 line is shown in red for reference.

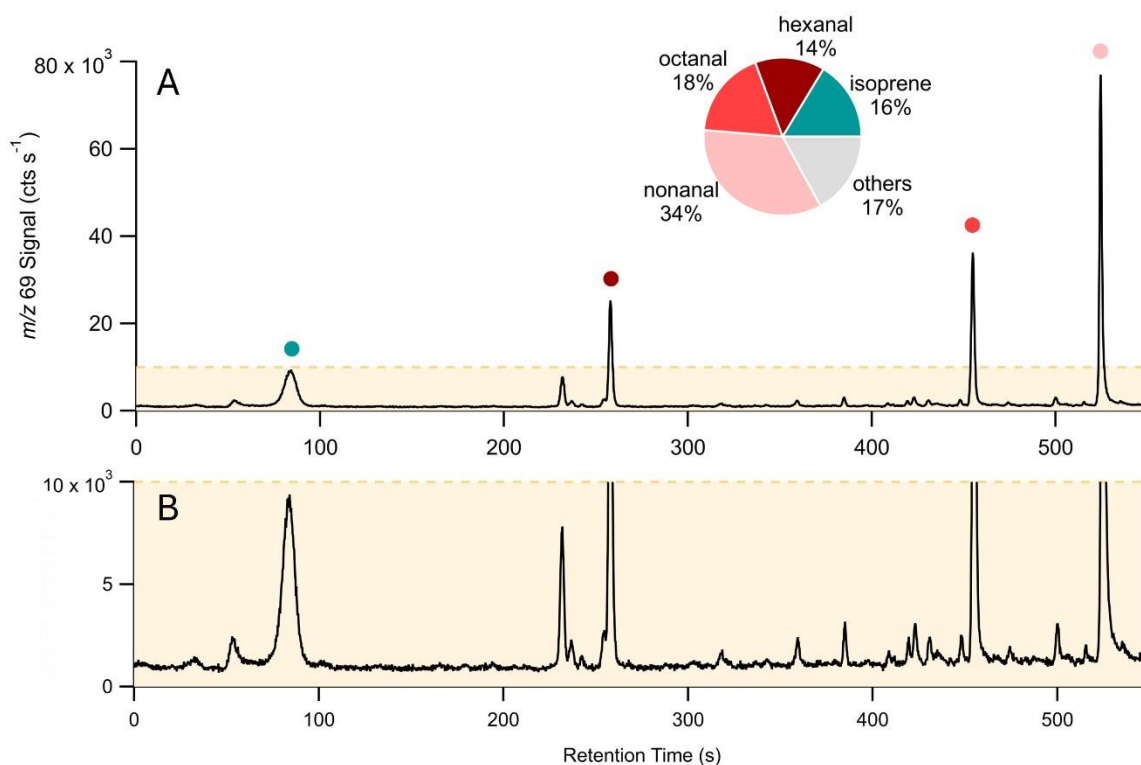
**Table S1.** Correlation statistics for the detection of calibrant species, or their associated sum of isomers, in ambient air between the GC-PTR and direct-PTR modes for the subset of data shown in Figure 4.

| Compound(s) Resolved by GC    | Quantitation Ion [ $\text{MH}^+$ ] | Slope <sup>a,b</sup> | Intercept <sup>a,b</sup> | $\text{R}^2$ <sup>a,c</sup> |
|-------------------------------|------------------------------------|----------------------|--------------------------|-----------------------------|
| acetonitrile                  | 42                                 | $0.97 \pm 0.06$      | $0.002 \pm 0.006$        | 0.984                       |
| acetaldehyde                  | 45                                 | $0.49 \pm 0.08$      | $1.532 \pm 0.240$        | 0.605                       |
| acrylonitrile                 | 54                                 | $1.49 \pm 0.27$      | $-0.001 \pm 0.001$       | 0.645                       |
| acetone                       | 59                                 | $1.22 \pm 0.08$      | $-0.252 \pm 0.096$       | 0.982                       |
| isoprene                      | 69                                 | $43.02 \pm 50.70$    | $-0.608 \pm 0.971$       | 0.149                       |
| methyl ethyl ketone           | 73                                 | $7.26 \pm 6.37$      | $-0.996 \pm 1.340$       | 0.188                       |
| benzene                       | 79                                 | $2.02 \pm 0.32$      | $-0.197 \pm 0.082$       | 0.856                       |
| toluene                       | 93                                 | $1.03 \pm 0.07$      | $0.054 \pm 0.036$        | 0.980                       |
| sum of $\text{C}_8$ aromatics | 107                                | $1.03 \pm 0.03$      | $0.058 \pm 0.012$        | 0.996                       |
| sum of $\text{C}_9$ aromatics | 121                                | $0.88 \pm 0.03$      | $0.004 \pm 0.010$        | 0.994                       |
| sum of monoterpenes           | 137                                | $0.99 \pm 0.06$      | $0.011 \pm 0.007$        | 0.982                       |

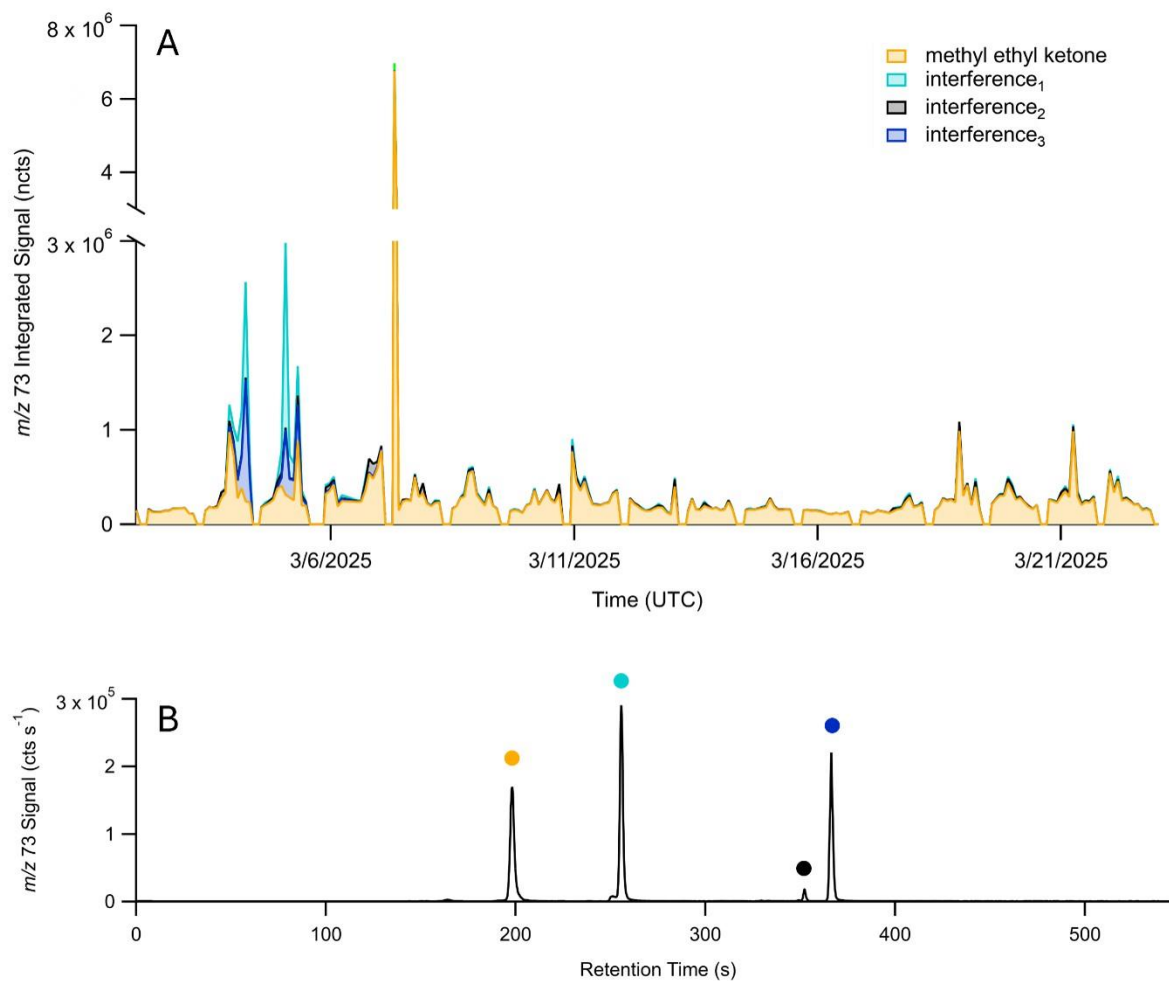
<sup>a</sup> Slope, intercept, and  $\text{R}^2$  values are for the correlation between GC-PTR and direct-PTR ambient detection from March 3 at 12:00 UTC – March 5 at 12:00 UTC.

<sup>b</sup> Slope and intercept values were calculated using orthogonal distance regression.

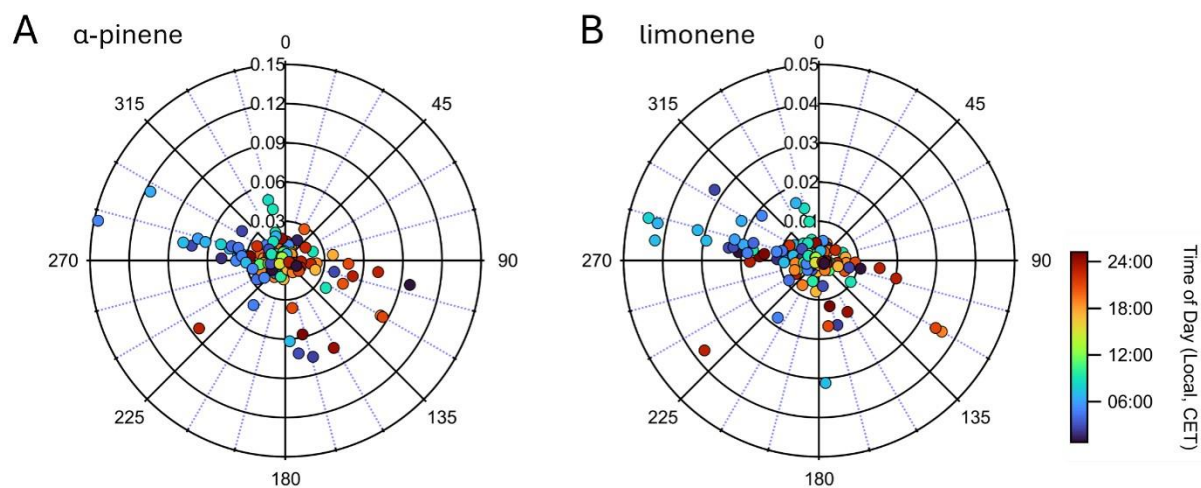
<sup>c</sup>  $\text{R}^2$  values were calculated using standard linear regression.



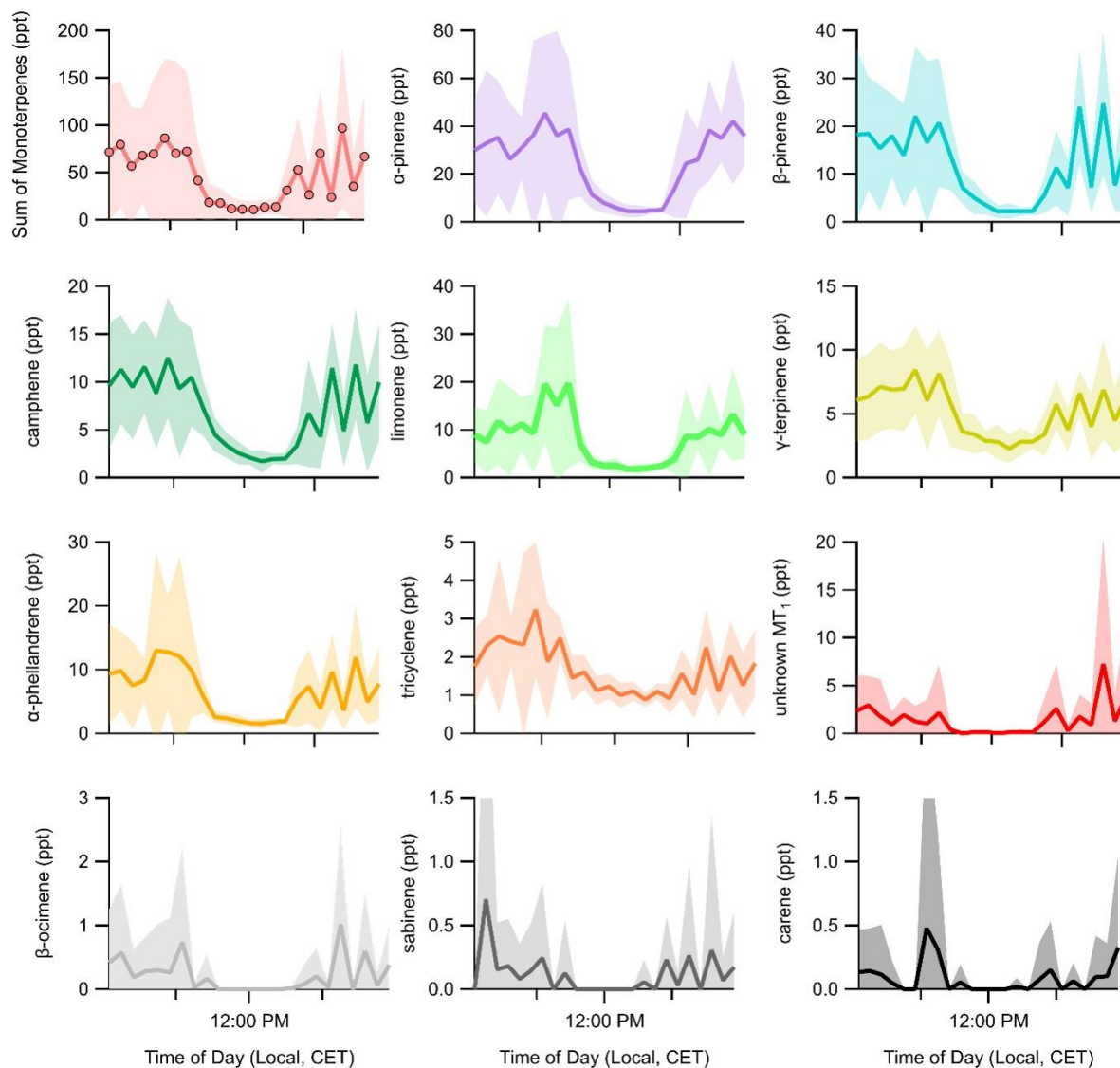
**Figure S8. (a)** Exemplary ambient chromatogram showing resolved species that result in detected signal at  $m/z$  69 by the PTR. Isoprene elutes early (blue dot), while contributions to  $m/z$  69 from long chain aldehydes ( $C_7 - C_9$ ) are separated by the GC column and elute later. Their percent contributions to the total  $m/z$  69 signal in this ambient sample are shown in the pie chart. Area highlighted in yellow is shown again in **(b)** with zoomed in y-axis to show details in the number of species giving response at  $m/z$  69 in this sample.



**Figure S9. (a)** Ambient timeseries of species resolved by the GC-PTR giving response at  $m/z$  73, including methyl ethyl ketone and three larger species that undergo fragmentation to form the  $m/z$  73 ion. **(b)** Exemplary ambient chromatogram of  $m/z$  73 ion, showing the resolution of methyl ethyl ketone (yellow dot) from the interfering species that elute later (light and dark blue, black).



**Figure S10.** Wind rose diagrams for (a)  $\alpha$ -pinene and (b) limonene during the 30-day ambient measurement period. The wind rose shows the distribution of isomer concentration with respect to wind direction, where the length of each spoke represents compound concentration in parts per billion (ppb). The data are colored by time of day (local time, CET).



**Figure S11.** Diurnal profiles for the 11 monoterpenes, and their sum, resolved by GC-PTR during the ambient measurement period.