Supplement of Simultaneous leaf-level measurement of trace gas emissions and photosynthesis with a portable photosynthesis system

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S1 Additional method details on TOF-CIMS

For CIMS experiments, sample air is pulled from either the SAM or REF subsampling ports through 0.25 m of PFA tubing (6.35 mm o.d.) into an ion-molecule reaction chamber, where analytes of interest react with I^- reagent ions. We generate I^- ions by flowing ultrahigh purity nitrogen over a methyl iodide (CH_3I) permeation tube and through a ^{210}P ionizer. We detect

10 analytes as $[I + analyte]^-$ adducts. TOF-CIMS mass resolution ($m/\Delta m$) = 4000 and mass accuracy of less than 15 ppm throughout experiments performed herein.

We calibrate our TOF-CIMS for formic acid (CH_2O_2) using a permeation tube standard (KIN-TEK Analytical, Inc.) housed in a homebuilt oven held at 50 °C. We flow UHP N_2 (Airgas) over the formic acid permeation tube to generate a steady

15 calibrant flow (Brophy and Farmer, 2015). The TOF-CIMS detection limit for formic acid was 12 parts-per-trillion by volume (ppt_v) over a 60 second average, with a sensitivity of 2630 ± 40 normalized counts second^{-1} ppt_v^{-1}.

S2 Additional method details on Thermal Desorption Gas Chromatography Mass Spectrometry

We calibrated the TD GC/MS for monoterpenes using a mixed calibration standard. The calibration standard is a mixture of methanol (gradient grade OmniSolv®, CAS:67-56-1) and the same concentration of α-pinene (99%, CAS:80-56-8), β-pinene

20 (99%, CAS:18172-67-3), α-terpinene (85%, CAS:99-86-5), p-cymene (99%, CAS:99-87-6), (R)-(+)-limonene (97%, CAS:5989-27-5), γ-terpinene (97%, CAS:99-85-4), and terpinolene (technical, ≥85% (GC), CAS:586-62-9). All chemicals were purchased from Sigma Aldrich, Co. We created calibration standards at concentrations of 0.5, 1, 5, 25, 50, and 100 ng μL^{-1}, and we used a 1 μL syringe (Hamilton Co.) to inject aliquots of calibration standard in volumes of 0.5, 1.0 or 2.0 μL onto the front end of the sorbent tube. We observed a linear range between 0.25 and 100 ng mass loadings. Table 2 shows

25 data from calibrations performed with mass loadings between 0.25 and 1 ng.

We collect gas phase samples using Tenax TA adsorbent material in inert-coated stainless steel tubes (Markes Intl., C1-CXXX-5003). We use a low-flow handheld sampling pump (ACTI-VOC, Markes Intl., C-LFP-01) at a constant flow rate of

0.20 L min^{-1} for 20 minutes, for a total sample volume of 4 L. Cartridges are sealed with brass storage caps and PTFE

30   ferrules and are stored in an airtight container and refrigerated prior to sample analysis on the TD-GC/MS, typically within 10 days. The autosampler (Ultra-xr, Markes Intl.) and the thermal desorption unit (Unity-xr, Markes Intl.) desorb gases from the cartridge. Cartridges are pre-purged with helium for 3 min. The cartridge tubes are then heated to 300 °C for 6 min while carrier gas (high purity helium) flows through the tubes at a rate of 0.100 L min^{-1}. Desorbed analytes are focused onto a cold trap (Air Toxics Analyzer, Markes Intl.) at 20 °C before the trap is heated to 300 °C at a rate of 40 °C min^{-1}. The cold trap is

35   maintained at 300°C for 7 min to allow the analytes to fully desorb.

Desorbed analytes are immediately sent through a gas chromatograph (TRACE 1310, Thermo Scientific with a ZB-5HT-MS column) mass spectrometer (TSQ 8000 Evo Triple Quadrupole GC-MS/MS, Thermo Scientific) with an electron impact source. A split ratio of 5.2:1 prevents overloading of the column during the desorption process. Helium carrier gas flows at

40   0.0012 L min^{-1}. The MS transfer line and the ion source temperatures are held at 300 °C. The GC oven temperature is maintained at 90 °C for 8 min and then raised to 280 °C (20 °C min^{-1}; hold at 280°C for 2.5 min). Full scan mass spectra covered *m/z* 35-300, while extracted ion chromatogram for monoterpenes were obtained using *m/z* 136, 135, 93, 91. BVOCs were identified using the NIST library and, when possible, retention time (RT) and mass spectra of available standards (Table 2). We also show the mass-based limit of detection (LOD) and emission rate LOD in Table 2. The emission rate LOD

45   is calculated using the mass-based LOD, a 20 minute sampling time, and 6×10^{-4} m^2 leaf area. For background-subtracted emission measurements, the emission rate LOD depends on the background concentration of the analyte and should be calculated separately. For calibration, liquid standards are injected onto sorbent tubes by syringe. Standards and calibration methodology are described in detail in S1.

50   GC/MS peaks are integrated using Chromeleon™ Chromatography Data System 7.1 (Thermo Fisher Scientific). Integrated peaks of non-calibrated compounds are identified only if integrated area exceeded 50,000 counts×min and if a NIST library match score exceeded 500.

S3 Background contamination minimization efforts
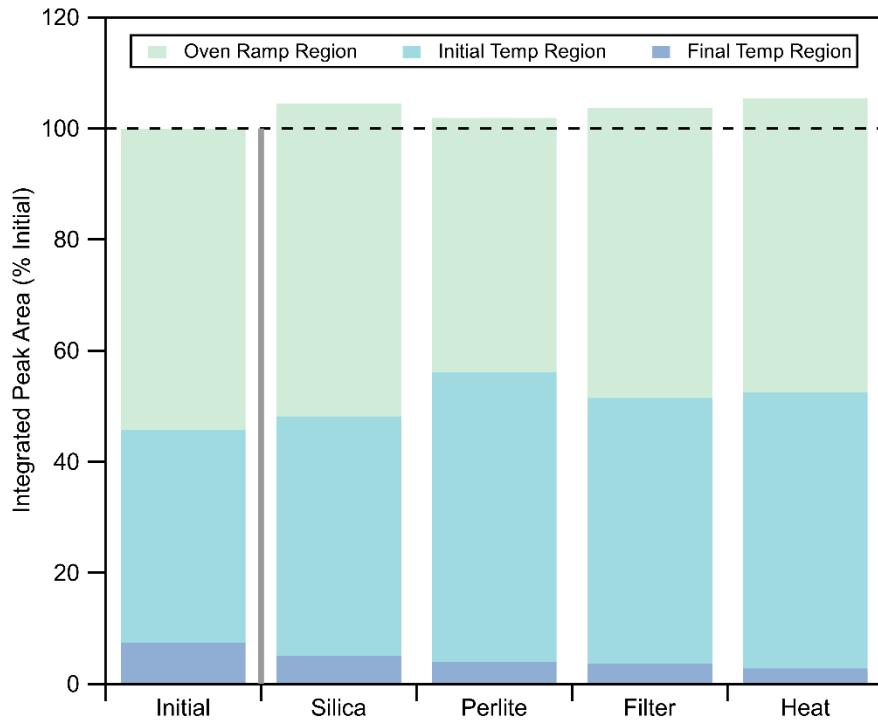
Figure S3. Stacked bar chart of LI-6800 system blanks, resulting from different system alterations. We show the change in total ion counts of the resulting chromatograms in terms of % initial integrated peak area. The results are split into three regions, based on the GC oven program. The oven remains at 90 °C for 8 minutes (Initial Temp Region), then ramps at 20 °C min^{-1} for 9.5 minutes (Oven Ramp Region), and remains at 280 °C for 2.5 minutes (Final Temp Region). The solid line denotes 100% of initial integrated peak area, and the dashed line delineates initial conditions from the affected conditions.

References

Brophy, P., and Farmer, D.: A switchable reagent ion high resolution time-of-flight chemical ionization mass spectrometer for real-time measurement of gas phase oxidized species: characterization from the 2013 southern oxidant and aerosol study, Atmos Meas Tech, 8, 2945-2959, 2015.