



Supplement of

Identifying and correcting interferences to PTR-ToF-MS measurements of isoprene and other urban volatile organic compounds

Matthew M. Coggon et al.

Correspondence to: Matthew M. Coggon (matthew.m.coggon@noaa.gov)

The copyright of individual parts of the supplement might differ from the article licence.

Additional Instrumentation

NOAA GC-MS

The NOAA GC-MS provided speciated VOC measurements during SUNVEx, RECAP-CA, and FIREX-AQ. During RECAP-CA, the NOAA GC-MS was deployed to the ground site to sample ambient air on a 20 minute duty cycle. The GC-MS collects two separate 240 mL samples and analyzes each on two channels. Channel 1 consists of a CO₂ trap (Ascarite II, Thomas Scientific), a water trap operated at -55°C, and a sample trap operated at -165°C. The series of traps are linked to an Al₂O₃-KCl porous layer open tubular column (Restek RT-Alumina bonded porous polymer/KCl; 30-m length × 0.25-mm I.D., and 4-µm film thickness) designed to separate light hydrocarbons. Channel 2 consists of the water and sample traps, but is coupled to a DB-624 column identical to the column used in the GC-PTR-ToF-MS. This column separates hydrocarbons up to C₁₂, as well as select oxygen-, halogen-, and nitrogen-containing VOCs. The effluent of each column is analyzed using a quadrupole mass spectrometer (Agilent 5975C) operated in selected ion monitoring/scan mode. The GC-MS was calibrated using a gravimetrically-prepared gas mixture containing 50 VOC components. Mixing ratios reported here have uncertainties < 10% (Lerner et al., 2017)

VOCs analyzed by NOAA GC-MS in Las Vegas and during FIREX-AQ were first sampled using a whole air sampling canister system (iWAS, Lerner et al., 2017). The iWAS system consists of a stainless steel compressor and 24 2.7 L electropolished stainless steel canisters. During SUNVEx, canisters were filled every 2 hours during stationary ground-based sampling, while targeted samples were taken during mobile drives. During FIREX-AQ, targeted samples were filled on demand up to a total number of 72 per flight. The canisters were shipped to either Boulder, CO, or Pasadena, CA, and analyzed by GC-MS within four days of collection to minimize sampling artifacts.

UCI WAS

The University of California, Irvine Whole Air Sampler (UCI WAS) was deployed on the DC-8 during FIREX-AQ to sample VOCs and halocarbons. The UCI WAS operated similarly to the NOAA canister system, where samples were collected into electropolished stainless steel canisters, then analyzed offline within seven days using a series of laboratory GC systems. The operation of the airborne WAS and laboratory GCs is fully described elsewhere (Colman et al., 2001; Simpson et al., 2020; Simpson et al., 2010). All samples were analyzed on a multi-column GC system coupled to flame ionization, electron capture, and mass selective detectors. The whole system is calibrated using a suite of VOC standards and mixing ratio uncertainties for the species reported here are ~5% (Simpson et al., 2020).

TOGA-TOF

The NCAR Total Organic Gas Analyzer with a TOFWERK electron ionization high-resolution time-of-flight mass spectrometer (TOGA-TOF) was deployed on the DC-8 during FIREX-AQ to provide

in situ GC measurements of a large suite of VOCs including hydrocarbons, oxygenated VOCs (OVOCs), and halogen-, nitrogen- and sulfur-containing VOCs. A full description of the TOGA system is provided by Apel et al. (2015). Briefly, during FIREX-AQ the TOGA-TOF continuously sampled 13-mL aliquots of ambient air for approximately 35 seconds every 105 seconds, concentrating the VOCs in two cryogenic preconcentration steps prior to injection onto a Restek MTX-624 column (I.D. = 0.18 μm , length = 8 m). Helium gas carried the samples through the column, which was heated from 25–120°C at a rate of 100°C min^{-1} , and the effluent was analyzed by the electron ionization time-of-flight mass spectrometer. The TOF-MS was operated at 70 eV and nominal mass resolution 3000 $\Delta m m^{-1}$. The system was calibrated several times per flight and in the laboratory before and after the campaign using a series of multicomponent VOC standards (Apel-Riemer Environmental Inc., Miami, FL, USA). Mixing ratio uncertainties for species reported here are estimated to be 9% (Apel et al., 2015).

Aerodyne GC-MS

The ARI GC-MS system consists of three main components: (1) a thermal desorption preconcentrator (TDPC) (Aerodyne Research, Inc.) for sample collection, (2) a GC (Aerodyne Research, Inc.) for sample separation, and (3) an electron ionization time-of-flight mass spectrometer (EI-ToF-MS) (TOFWERK AG, model EI-HTOF) for sample detection (Gilman et al., 2013; Obersteiner et al., 2016; Claflin et al., 2021). For the MOOSE campaign, the TOF-MS was operated at 70 eV and nominal mass resolution 3000 $\Delta m m^{-1}$. The GC is a 2-channel system, where both separation channels use identical preconcentration steps. The TDPC employed for this campaign relied upon two-stage adsorbent trapping for preconcentration of analytes. The sample is initially collected onto multibed (Tenax TA/Graphitized Carbon/Carboxen 1000), preconditioned glass sorbent tubes that are optimized for $\text{C}_{2/3}$ – C_{30} species. The first stage of trapping allows sampling rates up to 100 sccm, followed by forward-flushing with UHP nitrogen to remove water. For the higher volatility channel (Channel 1), additional H_2O was removed from the ambient sample stream via passing through a cooled PFA tube (1/8-inch O.D., 1/16-inch I.D., 3.375-inch length, 15°C) prior to trapping of VOCs to avoid water condensed in the sample tube. After the initial collection and water purge, the sample was then transferred to the focusing stage, which is a multibed (Tenax, Carbopack X, Carboxen 1003) glass cold trap. After preconcentration, the samples are transferred to different separation columns (Restek Rt-Q-Bond and Rxi-624) for Channels 1 and 2, respectively. Channel 1 is optimized for separation of C_3 – C_4 alkanes, C_1 – C_2 halocarbons and C_1 – C_3 oxygenates; Channel 2 is optimized for C_5 – C_{12} alkanes, C_6 – C_{10} aromatics, C_3 – C_6 oxygenates.

The GC inlet consisted of approximately 8 m of 0.25-inch O.D., 0.15625-inch I.D. PFA tubing connected to a sample pump, with an inlet flow of approximately 1 slpm. The GC pulled a sub-flow from the main GC inlet via 1-m length, 0.125-inch O.D., 0.0625-inch I.D. PFA tubing. The sample flow was 80 sccm to each GC channel for 10 minutes during each 30-minute analytical cycle. Before preconcentration, the ambient sample is passed through a bed of pre-cleaned sodium sulfite (nominal 1 g) to scrub ozone and thereby reduce sampling artifacts [Helmig, 1997].

Calibration was performed by multicomponent VOC calibrant gas (Apel-Riemer Environmental Inc., Miami, FL, USA) diluted in UHP N₂ at sufficient total flow to overflow the GC sub-inlet. Instrument calibrations were performed in-field each night throughout the campaign via automated valve switching. Note that this calibration mixture was the same as described in Section 2.2.3 and mixing ratio uncertainties are estimated to be < 10% (Lerner et al., 2017).

Supplemental Figures

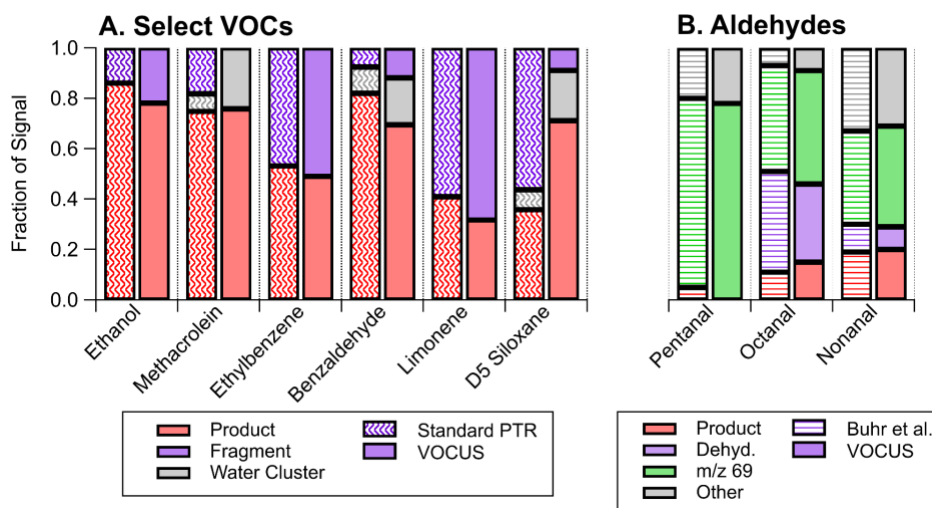


Figure S1. Comparison of ion product distributions for (a) select VOCs measured using a traditional drift tube described by Yuan et al. (2016) vs. the Vocus used in this work and (b) aldehydes reported by Buhr et al. (2002) and compiled in Pagonis et al. (2019) vs. the Vocus used in this work. Note that “product” refers to the proton-transfer product, “Dehyd.” refers to the product generated by the loss of neutral water, “fragment” refers to species-specific fragmentation processes, and “other” refers to the sum of multiple fragments. We exclude fragments below m/z 33 for these intercomparisons due to the BSQ mass discrimination employed in the Vocus (Krechmer et al., 2018).

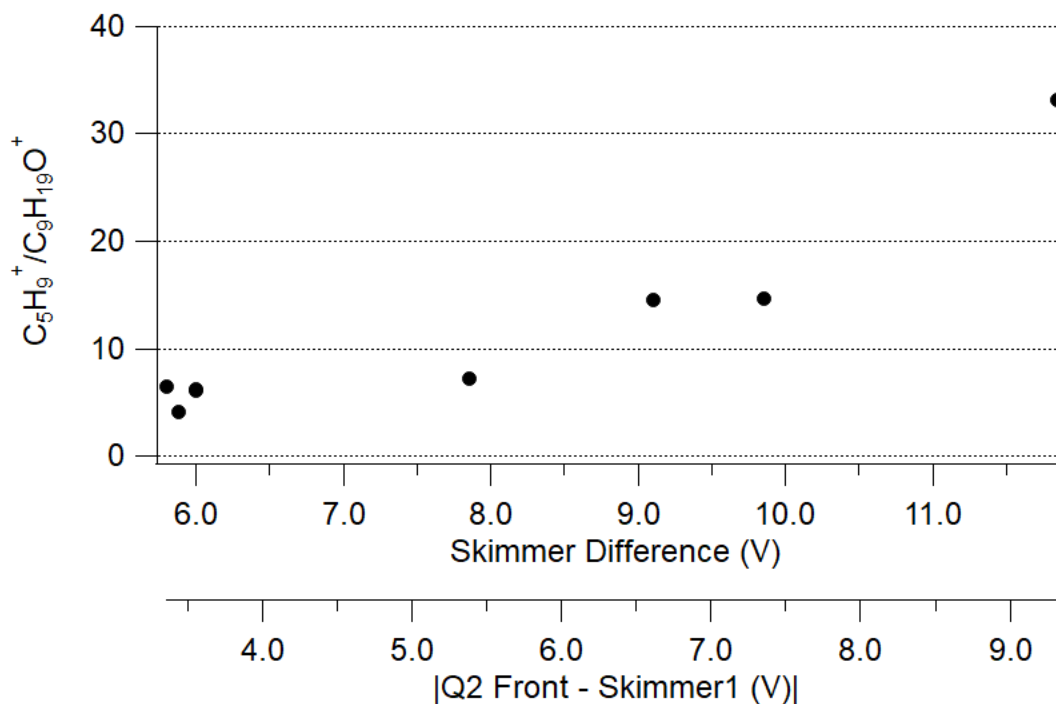


Figure S2. Nonanal fragmentation ratio of m/z 69 ($C_5H_9^+$) to m/z 143 ($C_9H_{19}O^+$) for a range of voltage gradients between the first skimmer (Skimmer 1), front voltage of the big segmented quadrupole (Q2 Front), and second skimmer (Skimmer 2) in the Berkeley Vocus PTR-ToF-MS. The “Skimmer Difference” is the difference between Skimmer 2 and Skimmer 1.

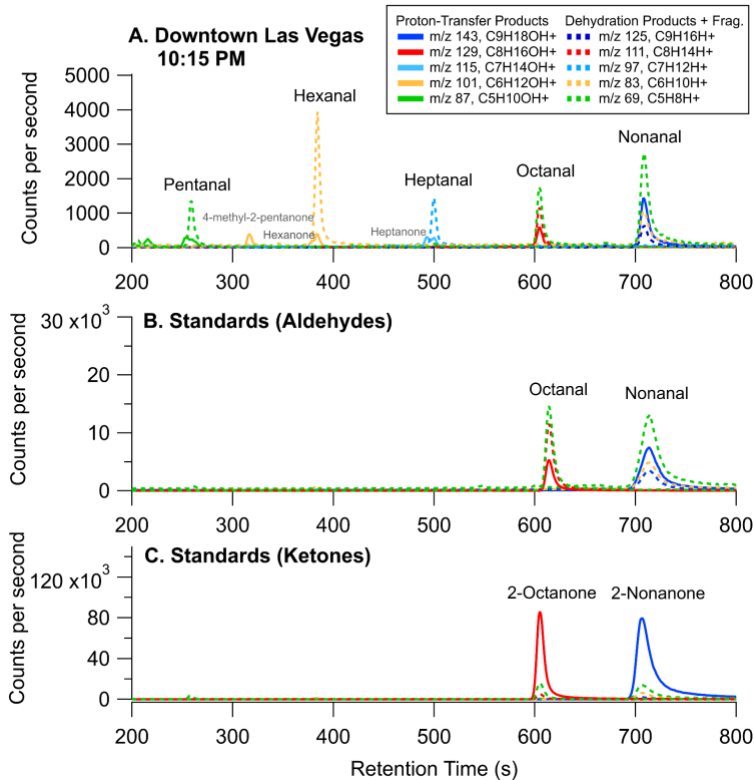


Figure S3. (a) Chromatographic distribution of C₅ - C₉ aldehydes measured in downtown Las Vegas (A). Standard additions of C₈-C₉ aldehydes (b) and ketones (c) are shown to demonstrate that fragmentation patterns for observed peaks match those of octanal and nonanal.

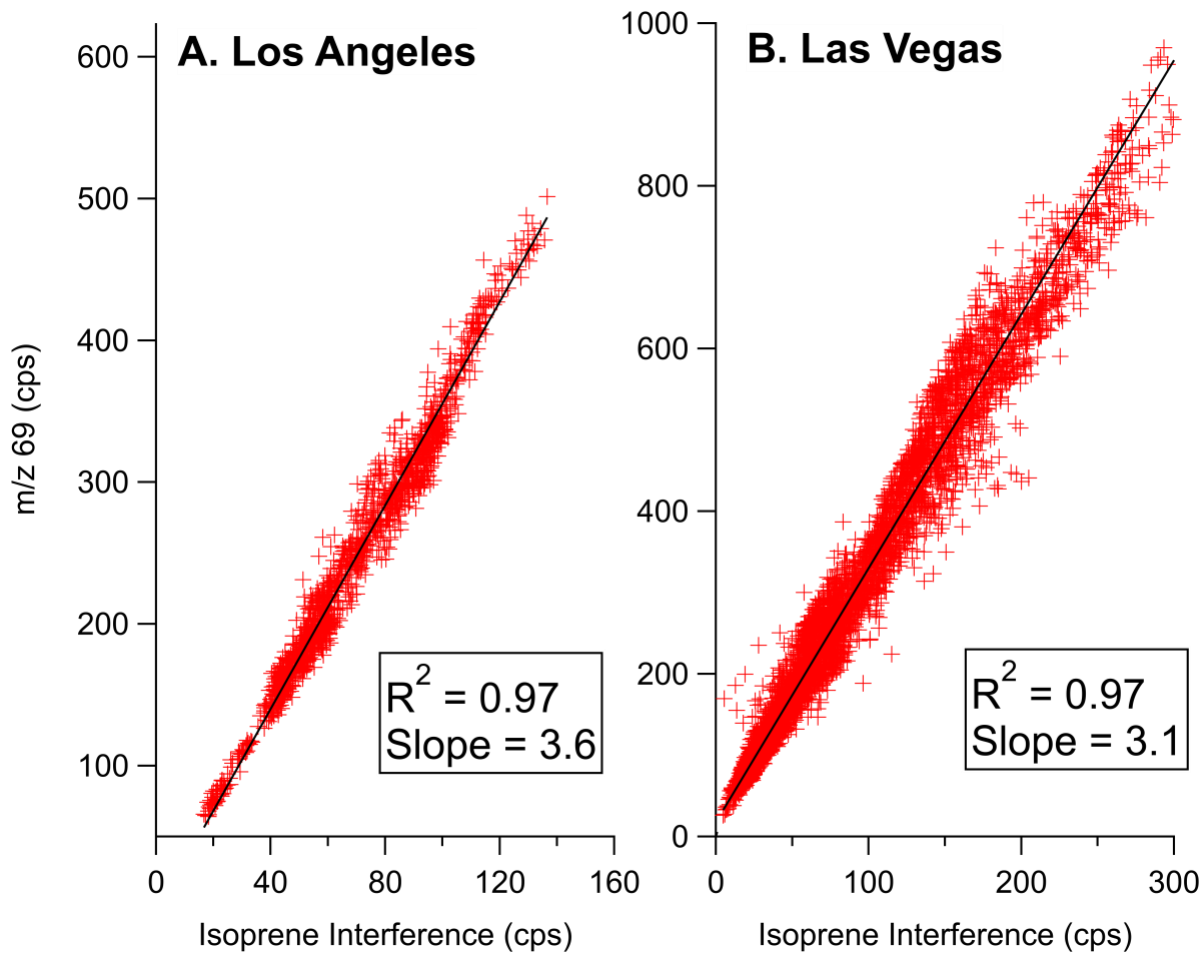


Figure S4. Slope of m/z 69 vs the sum of aldehydes (m/z 111 + m/z 125) from nighttime data (00:00-4:00 Local Time) in (a) Los Angeles and (b) Las Vegas during SUNVEx. The interference ratio is determined using an ODR linear regression.

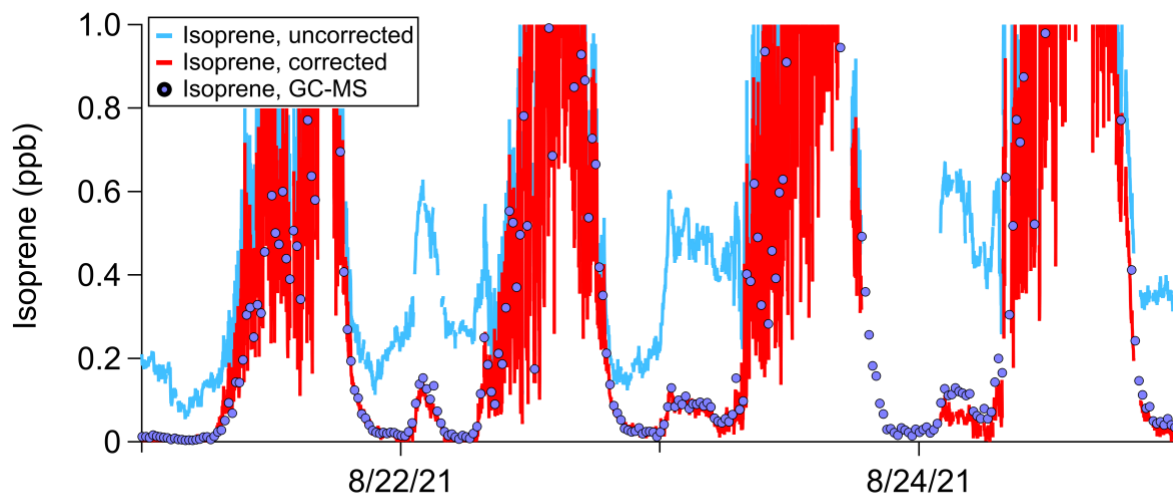


Figure S5. Time series of corrected and uncorrected isoprene signals on Los Angeles data with GC-MS isoprene data for comparison. The y-axis isoprene mixing ratio scale is enlarged to highlight nighttime data.

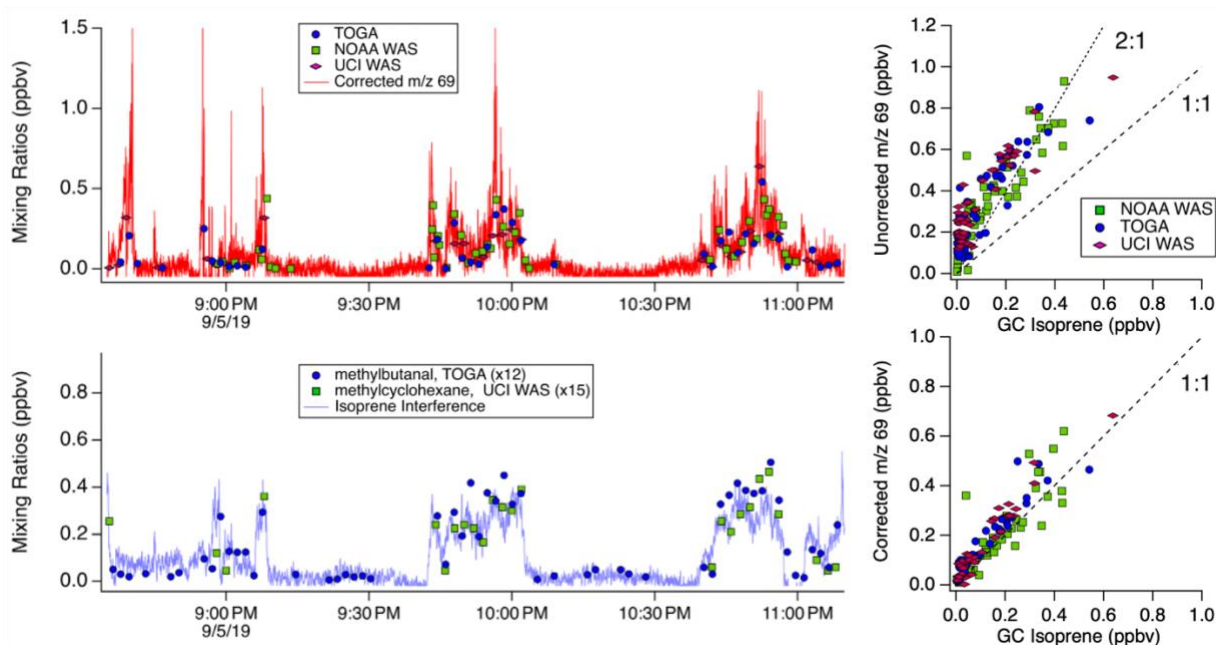


Figure S6. Impact of isoprene interference correction on m/z 69 measurements from the Oslo PTR-ToF-MS during FIREX-AQ. The time series at the top shows the corrected signal at m/z 69 and comparison to GC-MS measurements of isoprene. The bottom time series shows the estimated contribution of the isoprene interference to m/z 69 and a comparison to the GC-MS measurements of methylpropanal and methylcyclohexane, which are proxies for the key interfering species. The scatter plots show the comparison of the uncorrected (top) and corrected (bottom) signal at m/z 69 to GC-MS measurements of isoprene.

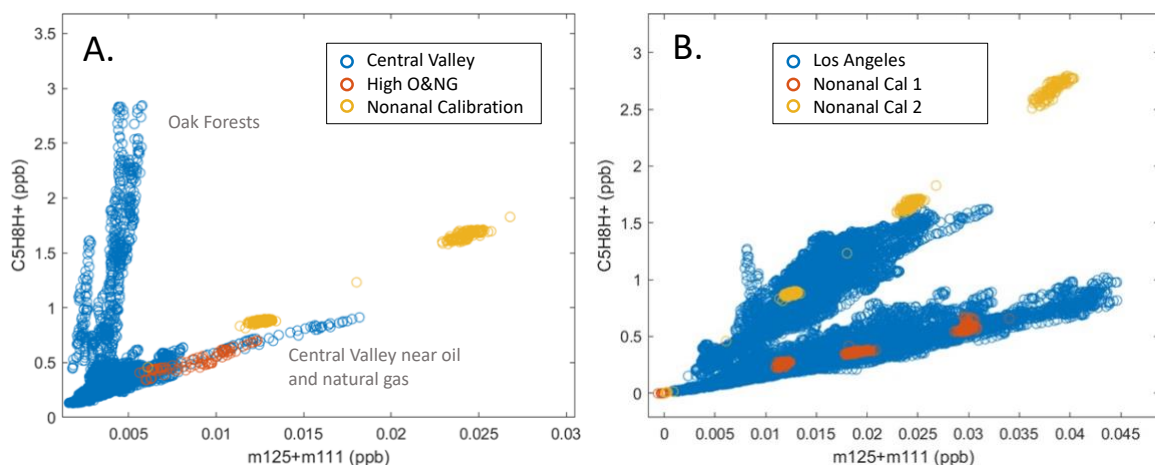


Figure S7. Observations of m/z 69 ($C_5H_8H^+$) and the sum of m/z 125 + m/z 111 in (a) the Central Valley and (b) Los Angeles Basin during RECAP-CA flights. Samples collected over dense oil fields in the Central Valley are highlighted in panel (a). For each dataset, the ratio of m/z 69 to m/z 125 + m/z 111 for nonanal are shown. Nonanal was calibrated regularly during the campaign, and changes to the slope in panel (b) result from different instrument operating conditions.

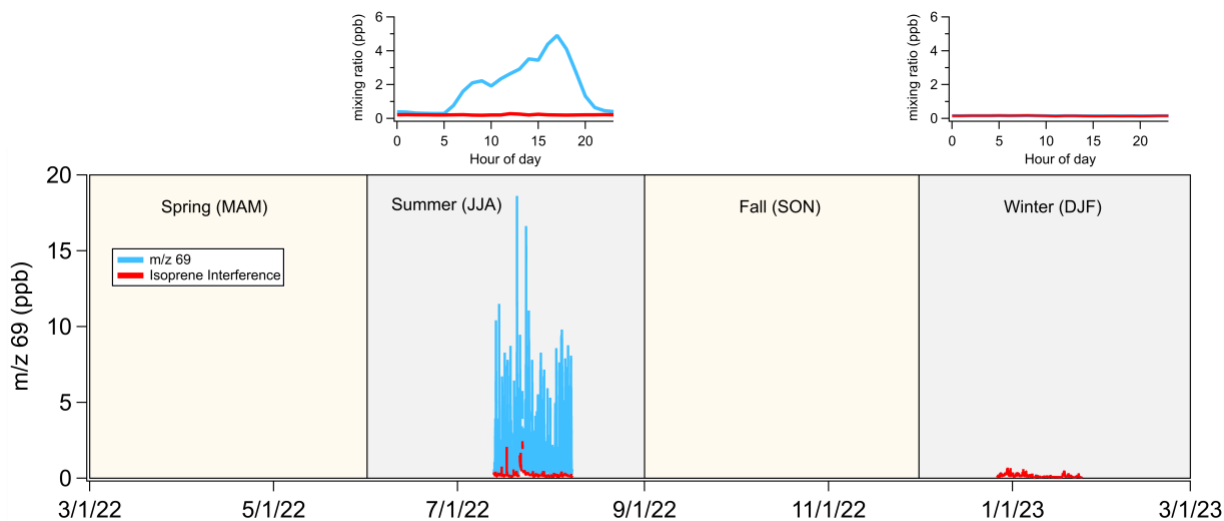


Figure S8. (bottom) Time series of m/z 69 and isoprene interference measured by the Stony Brook PTR-ToF-MS at the forested suburban Flax Pond ground site in Long Island. (top) Diel patterns of m/z 69 and isoprene interference mixing ratios for each season.

References

Apel, E. C., Hornbrook, R. S., Hills, A. J., Blake, N. J., Barth, M. C., Weinheimer, A., Cantrell, C., Rutledge, S. A., Basarab, B., Crawford, J., Diskin, G., Homeyer, C. R., Campos, T., Flocke, F., Fried, A., Blake, D. R., Brune, W., Pollack, I., Peischl, J., Ryerson, T., Wennberg, P. O., Crouse, J. D., Wisthaler, A., Mikoviny, T., Huey, G., Heikes, B., O'Sullivan, D., and Riemer, D.

D.: Upper tropospheric ozone production from lightning NO_x-impacted convection: Smoke ingestion case study from the DC3 campaign, *Journal of Geophysical Research: Atmospheres*, 120, 2505-2523, 10.1002/2014JD022121, 2015.

Buhr, K., van Ruth, S., and Delahunty, C.: Analysis of volatile flavour compounds by Proton Transfer Reaction-Mass Spectrometry: fragmentation patterns and discrimination between isobaric and isomeric compounds, *International Journal of Mass Spectrometry*, 221, 1-7, 10.1016/S1387-3806(02)00896-5, 2002.

Colman, J. J., Swanson, A. L., Meinardi, S., Sive, B. C., Blake, D. R., and Rowland, F. S.: Description of the Analysis of a Wide Range of Volatile Organic Compounds in Whole Air Samples Collected during PEM-Tropics A and B, *Analytical Chemistry*, 73, 3723-3731, 10.1021/ac010027g, 2001.

Krechmer, J., Lopez-Hilfiker, F., Koss, A., Hutterli, M., Stoermer, C., Deming, B., Kimmel, J., Warneke, C., Holzinger, R., Jayne, J., Worsnop, D., Fuhrer, K., Gonin, M., and de Gouw, J.: Evaluation of a New Reagent-Ion Source and Focusing Ion-Molecule Reactor for Use in Proton-Transfer-Reaction Mass Spectrometry, *Analytical Chemistry*, 90, 12011-12018, 10.1021/acs.analchem.8b02641, 2018.

Lerner, B. M., Gilman, J. B., Aikin, K. C., Atlas, E. L., Goldan, P. D., Graus, M., Hendershot, R., Isaacman-VanWertz, G. A., Koss, A., Kuster, W. C., Lueb, R. A., McLaughlin, R. J., Peischl, J., Sueper, D., Ryerson, T. B., Tokarek, T. W., Warneke, C., Yuan, B., and de Gouw, J. A.: An improved, automated whole air sampler and gas chromatography mass spectrometry analysis system for volatile organic compounds in the atmosphere, *Atmos. Meas. Tech.*, 10, 291-313, 10.5194/amt-10-291-2017, 2017.

Pagonis, D., Sekimoto, K., and de Gouw, J.: A Library of Proton-Transfer Reactions of H₃O⁺ Ions Used for Trace Gas Detection, *Journal of The American Society for Mass Spectrometry*, 30, 1330-1335, 10.1007/s13361-019-02209-3, 2019.

Simpson, I. J., Blake, N. J., Barletta, B., Diskin, G. S., Fuelberg, H. E., Gorham, K., Huey, L. G., Meinardi, S., Rowland, F. S., Vay, S. A., Weinheimer, A. J., Yang, M., and Blake, D. R.: Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C₂-C₁₀ volatile organic compounds (VOCs), CO₂, CH₄, CO, NO, NO₂, NO_y, O₃ and SO₂, *Atmos. Chem. Phys.*, 10, 11931-11954, 10.5194/acp-10-11931-2010, 2010.

Simpson, I. J., Blake, D. R., Blake, N. J., Meinardi, S., Barletta, B., Hughes, S. C., Fleming, L. T., Crawford, J. H., Diskin, G. S., Emmons, L. K., Fried, A., Guo, H., Peterson, D. A., Wisthaler, A., Woo, J.-H., Barré, J., Gaubert, B., Kim, J., Kim, M. J., Kim, Y., Knote, C., Mikoviny, T., Pusede, S. E., Schroeder, J. R., Wang, Y., Wennberg, P. O., and Zeng, L.: Characterization, sources and reactivity of volatile organic compounds (VOCs) in Seoul and surrounding regions during KORUS-AQ, *Elementa: Science of the Anthropocene*, 8, 10.1525/elementa.434, 2020.

Yuan, B., Koss, A., Warneke, C., Gilman, J. B., Lerner, B. M., Stark, H., and de Gouw, J. A.: A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions (H₃O⁺ ToF-CIMS) for measurements of volatile organic compounds in the atmosphere, *Atmos. Meas. Tech.*, 9, 2735-2752, 10.5194/amt-9-2735-2016, 2016.