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TRACER-VOC: Speciated Volatile Organic Compounds at the Tracking Aerosol Convection Interactions Experiment Field Campaign Report

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Acronyms and Abbreviations

ACSM	aerosol chemical speciation monitor
ANC	ancillary site
ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
CCN	cloud condensation nuclei
IOP	intensive operational period
iSOA	isoprene secondary organic aerosol
PMF	positive matrix factorization
PNNL	Pacific Northwest National Laboratory
SOA	secondary organic aerosol
SVOOA	semi-volatile oxidized organic aerosol
TBS	tethered balloon system
ToF-PTR-MS	time-of-flight proton transfer reaction-mass spectrometer
TRACER	Tracking Aerosol Convection Interactions Experiment
TRACER-CAT	TRACER-Carbonaceous Aerosol Thrust
TRACER-CCN	TRACER-Cloud Condensation Nuclei
TRACER-MAP	TRACER-Mapping Aerosol across Houston
TRACER-PFM	TRACER-Particle Flux Measurements
TRACER-UFI	TRACER-Ultrafine Aerosol Formation and Impacts
VOC	volatile organic compound

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1.0 Summary

Formation of secondary organic aerosol (SOA) is responsible for the growth of particles into cloud condensation nuclei (CCN)-relevant sizes (Ehn et al. 2014) and accounts for a substantial fraction of aerosol mass in the troposphere (Jimenez et al. 2009). Despite its wide abundance and importance, capturing SOA in regional and climate models is still challenging due to complex chemical transformations involved in production of SOA (Shrivastava et al. 2017). Oxidation products of biogenic hydrocarbons, such as isoprene, monoterpenes, and sesquiterpenes account for the largest fraction of SOA mass over the continents. As such, biogenic SOA is an important source of continental CCN, and has been recently shown to nucleate ice in the deposition mode (Wolf et al. 2020). To better account for the processes involved in SOA formation in global and regional climate models, we need better measurements of sources and transformations of volatile organic compounds (VOCs), the precursors to SOA formation in the atmosphere.

Understanding aerosol-deep convection interactions is an important science driver of the Tracking Aerosol Convection Interactions Experiment (TRACER), requiring a characterization of the critical controls on aerosol properties and processes, and how those properties and processes vary spatially and temporally in the Houston area (Jensen et al. 2022). In that environment, the atmospheric photo-oxidative chemistry that drives the evolution and transformation of aerosol properties and processes is strongly impacted by the emission of VOCs, which have both anthropogenic (e.g., industrial, urban, transportation, biomass burning) and biogenic (e.g., marine) sources in the region. Understanding (and disentangling) the complex role of VOCs in such a heterogenous region requires high-time-resolution, speciated VOC measurements that are spatially resolved. To meet these measurement requirements, the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's time-of-flight proton transfer reaction-mass spectrometer (ToF-PTR-MS) was deployed during the TRACER intensive operational period (IOP) from June to September, 2022 at the ancillary site (ANC), which was sited to provide a characterization of the rural atmospheric environment in contrast to the main site (Figure 1).

01 Oct. '21 – 30 Sep. '22
IOP June – Sep. 2022

1. AMF1 – La Porte
2. C-SAPR Site - Pearland
3. ARM Ancillary Site – Guy
4. UH Coastal Center (UAV, CUBIC)
5. Lemon Reservoir (UAV)
6a. Seawolf Park (TAMU)
6b. Hempstead (TAMU)
6c. Waller (TAMU)
6d. Hocksley (TAMU)
7. Moody Tower, UH
8. Aldine (CUBIC)
9. Jones Forest (MAP)
10. Battleground (MAP)

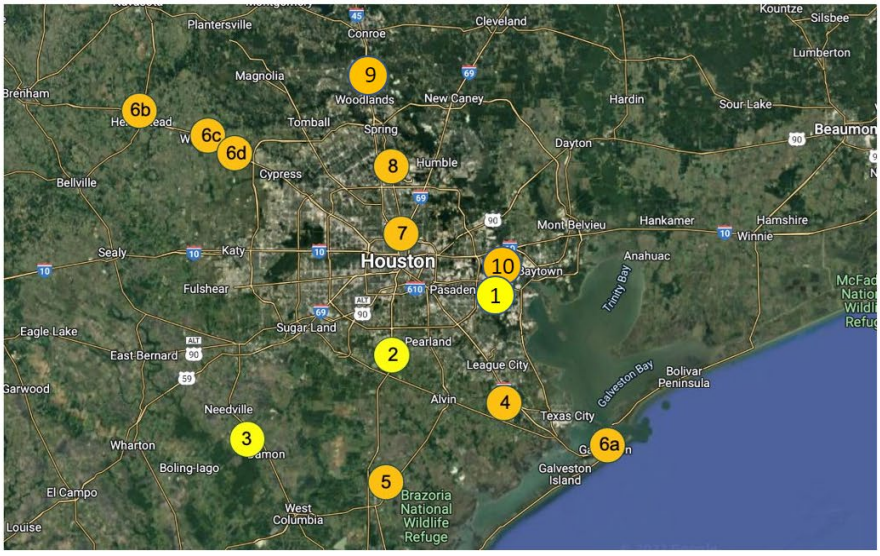

Figure 1. Locations of measurement sites during the TRACER campaign, for both ARM facilities and Atmospheric System Research (ASR)-funded projects.

Instrument Issues: Prior to the TRACER IOP, the PTR-MS was refurbished, outfitted with a calibration system, and deployed. However, during deployment preparation, it became clear that the instrument condition was worse than originally estimated. While the factory refurbishment with Ionicon (vendor) included an upgrade of the vacuum system and cleaning of vacuum components, both of which were damaged by years of atmospheric pressure exposure, it did not include repairs on the high-voltage power supply, which is produced by another manufacturer, ToFWerk. While such repairs would not normally be needed, it was found when the power supply was opened, following a sudden failure weeks ahead of the planned TRACER deployment, that the power supply was contaminated with metal shavings. ToFWerk (vendor) evaluated the power supply for damage and repaired the affected module, but a few weeks into the TRACER-VOC deployment, another high-voltage module in the affected power supply stopped working, likely either due to age or the metal contamination.

2.0 Results

Strong biogenic VOC emissions were detected at the ANC site. These emissions combined with urban pollution from Houston and marine sulfate emissions to produce biogenic SOA. Using positive matrix factorization (PMF) technique on the ANC site measurements of aerosol chemical composition obtained from the aerosol chemical speciation monitor (ACSM), general biogenic semi-volatile oxidized organic aerosol (SVOOA) and isoprene SOA (iSOA) were approximated, as shown in Figure 2.

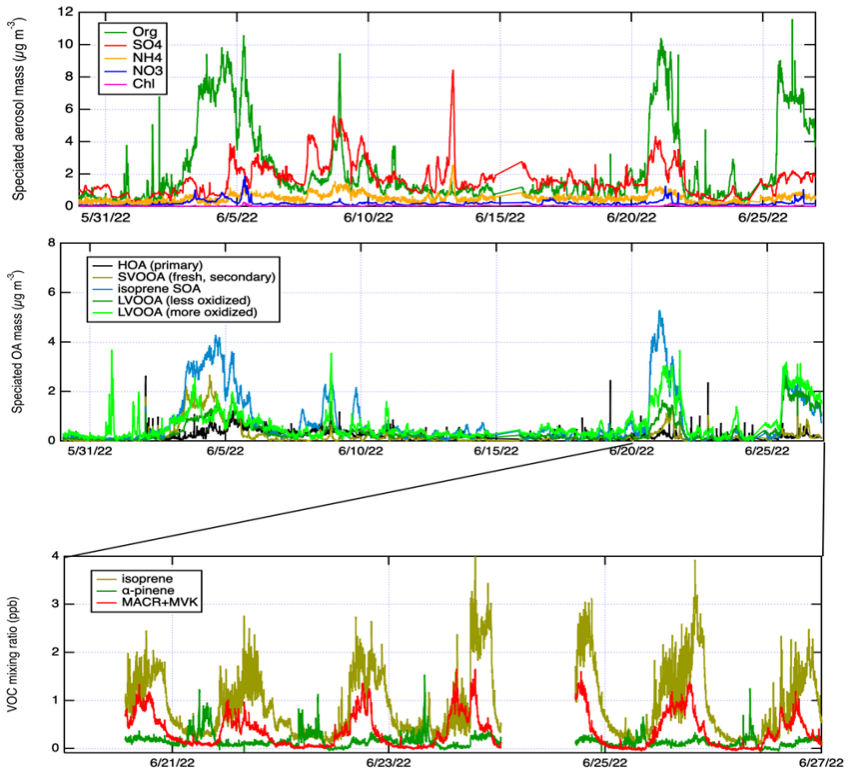

Figure 2. Overview of select aerosol measurements at the ANC site. Top panel: speciated aerosol mass. Middle panel: speciated organic aerosol mass derived from PMF analysis. Bottom panel: VOC concentrations.

Even though instrumental challenges discussed below made it impossible to operate for the duration of the four-month IOP, as originally planned, the PTR-MS collected a two-week time series of VOC concentrations, which greatly enhances the interpretation of the ACSM measurements, as shown in Figure 3.

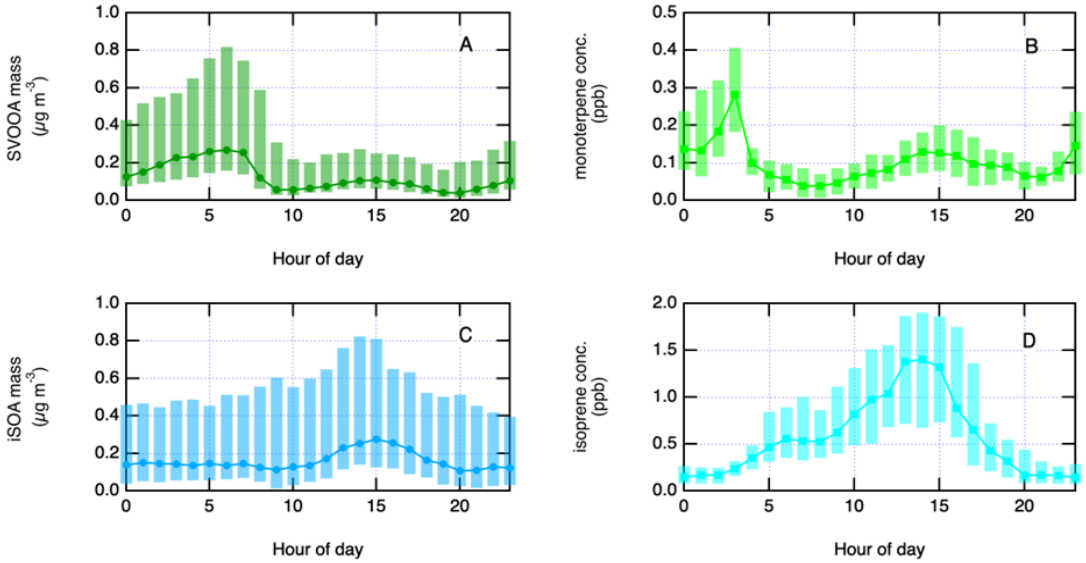

Figure 3. Diurnal cycles of (A) semi-volatile oxidized organic aerosol ACSM PMF factor (corresponding to biogenic SOA), (B) total monoterpene mixing ratio, (C) isoprene SOA ACSM PMF factor, and (D) isoprene mixing ratio. Total monoterpene and isoprene mixing ratios were measured by the PTR-MS. The figure suggests different chemical compositions of night-time (monoterpene) and day-time (isoprene) SOA.

Future research opportunities include coordination, collaboration, and comparison with other mobile VOC measurements during the IOP period (e.g., ARM tethered balloon system [TBS]-based, TRACER-MAP [Mapping Aerosol across Houston]) to provide more spatially-distributed characterization of VOCs within the TRACER domain. Furthermore, these VOC measurements will help to establish a baseline for the critical aerosol precursors that will support several additional TRACER-aerosol campaigns (e.g., TRACER-CAT [Carbonaceous Aerosol Thrust], TRACER-UFI [Ultrafine Aerosol Formation and Impacts], TRACER-MAP, TRACER-PFM [Particle Flux Measurements], and TRACER-CCN [Cloud Condensation Nuclei]).

3.0 Publications and References

3.1 Presentations

M Zawadowicz. 2023. “Long-term measurements of composition, optical properties and hygroscopicity of aerosol in Houston, TX.” Presented at the TRACER-Aerosol, Cloud, Precipitation, and Climate (ACPC) workshop.

3.2 References

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4.0 Lessons Learned

Due to the condition of the ARM TOF-PTR-MS, we believe is difficult to guarantee problem-free operation during future deployments. Note that we cannot buy a new power supply to avoid the issue of metal contamination because its manufacturer, ToFWerk, no longer works with Ionicon. Our only option is to work with the legacy system and exchange parts of it when they fail.

Following discussions with the scientific community and members of ARM infrastructure, we have therefor presented four options for future PTR-MS deployment to ARM.

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