

**Title:** ReadMe for CAVE 2019 VOC data

**Data Authors:**

Barkley C. Sive

Chemist, Air Resource Division, US National Park Service

[barkley\\_sive@nps.gov](mailto:barkley_sive@nps.gov)

Yong Zhou

Research Scientist II, Colorado State University, Department of Atmospheric Science

[Yong.Zhou@colostate.edu](mailto:Yong.Zhou@colostate.edu)

Da Pan

Research Scientist I, Colorado State University, Department of Atmospheric Science

[da.pan@colostate.edu](mailto:da.pan@colostate.edu)

Andrey Marsavin

Graduate Research Assistant, Colorado State University, Department of Atmospheric Science

[marsavin@rams.colostate.edu](mailto:marsavin@rams.colostate.edu)

Jeffrey L. Collett, Jr.

Project PI

Professor, Colorado State University, Department of Atmospheric Science

[jeffrey.collett@colostate.edu](mailto:jeffrey.collett@colostate.edu)

## **1.0 Data Set Description**

Final data for volatile organic compound (VOC) measurements collected in Carlsbad Caverns National Park. Measured species include C1-C10 nonmethane hydrocarbons, C1-C2 halocarbons, C<sub>1</sub>-C<sub>5</sub> alkyl nitrates, select oxygenated VOCs (OVOCs), isoprene, dimethyl sulfide, and acetonitrile. Measurements were made at the Biology Office and Building 58 (32.18° N, 104.44° W) located within Carlsbad Caverns National Park. The field study took place from Jul. 25-Sept. 5, 2019.

## **2.0 Instrument Descriptions**

An automated five-channel online gas chromatographic (GC) system was used for in situ VOC measurements. The GC system used five different separation columns and five detectors (three flame ionization detectors (FID), one electron capture detector (ECD), and one mass spectrometry (MS)) to measure 56 individual VOCs including C2-C10 nonmethane hydrocarbons (NMHCs), C1-C2 halocarbons, and C1-C5 alkyl nitrates with hourly time resolution (Russo et al., 2010a; Sive et al., 2005; Zhou et al., 2008; Zhou et al., 2005). The version of the GC system deployed for this project used a cryogen-free concentration system for

the online preconcentration of ambient samples that was similar to Sive et al. (2005) but was equipped with a different cryogen-free cooler (Q-Drive, Model 2S102K).

A quadrupole proton transfer reaction mass spectrometer (PTR-MS; PTR-MS HS, Ionicon Analytik, Innsbruck, Austria) was used to measure acetonitrile, isoprene, dimethyl sulfide, and select oxygenated VOCs (OVOCs).

### **3.0 Data Collection and Processing**

For the GC system, ambient air was collected on 1 mm silica beads at -160°C for 5 min at a flow rate of 200 mL/min for a total sample volume of 1 L. Water was removed prior to sample trapping with a higher-temperature cold trap. The GC columns used for this deployment included the following: (1) a CP-Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub> PLOT column (50 m × 0.53 mm I.D. 10 µm film thickness; Varian, Inc.) connected to an FID for the C<sub>2</sub>-C<sub>6</sub> hydrocarbons, (2) a VF-1 ms column (60 m × 0.32 mm I.D. 1 µm film thickness, Agilent Technologies) connected to an FID for the C<sub>7</sub>+ hydrocarbons and aromatics, (3) a CP-PoraBond-Q column (25 m × 0.25 mm I.D. 3 µm film thickness, Varian, Inc.) coupled to an XTI-5 (30 m × 0.25 mm I.D. 0.25 µm film thickness, Restek) connected to an FID for the OVOCs, (4) an OV-1701 column (60 m × 0.25 mm I.D. 1 µm film thickness, Varian, Inc.) connected to an ECD for C<sub>1</sub>-C<sub>5</sub> alkyl nitrates and C<sub>1</sub>-C<sub>2</sub> halocarbons, and (5) an OV-624 column (60 m × 0.25 mm I.D. 1.4 µm film thickness, Ohio Valley Specialty) connected to a Shimadzu QP-5050A MS for duplicate measurements of hydrocarbons, aromatics, and halocarbons.

Additional analyses were carried out in order to verify and validate the mixing ratios of the whole air working standards. The working standards were analyzed on the Colorado State University canister analytical system against one of the high-pressure pontoons (HPPA, D. Blake, UCI) and one of the low-pressure pontoons (Pont S) routinely in order to ensure the standard integrity and accuracy of the mixing ratios (Russo et al., 2010b; Sive et al., 2005; Swarthout et al., 2013; Swarthout et al., 2015; Zhou et al., 2005). The post campaign analyses included cross-referencing to two additional standards. An additional high-pressure pontoon (HPPB, D. Blake, UCI) was analyzed against the same group of standards in order to confirm consistent and comparable mixing ratios for the target gases, including the alkyl nitrates. Dilutions of a certified 1 ppmv Airgas Specialty Gases NMHC multicomponent high-pressure synthetic standard were analyzed against the group of standards to further verify the calibration standards. Multipoint calibrations using primary standards evaluated the detector response and linearity over the observed mixing ratio ranges for all classes of compounds.

The measurement precisions of all species measured by the on-line GC system were determined from replicate analysis of the whole air standard prior to deployment. Method Detection Limits (MDLs) were calculated as the mixing ratio required to generate a peak with a signal-to-noise

ratio of 3 from replicate whole air standard analyses, where noise is defined as the standard deviation of the chromatogram baseline adjacent to the peak.

The PTR-MS was installed in a climate-controlled shelter and sampled outside air continuously. The sample inlet was ~10 m above the ground; a diaphragm pump drew air at ~ 9.5 mL/min through a PFA Teflon tube with a sample sub-stream of ~ 2 mL/min. The instrument drift tube pressure and temperature were 2.2 mbar and 45 °C, respectively; a potential of 570 V was applied over the 9.3 cm of the drift tube resulting in an E/N of 122 Td (Townsend). Ultrapure water was used to produce the H<sub>3</sub>O<sup>+</sup> reagent ion source, and its flow rate was 6 ml/min with a discharge current of 4 mA. We applied the specific rate constant for the species of interest according to the reaction rate between individual neutral compounds with H<sub>3</sub>O<sup>+</sup> ions to derive raw readings (Taipale et al., 2008). Raw observations were then multiplied by transmission rates derived from calibrations for all species reported here. Calibrations for the system were done before and after the campaign using two different calibration standards containing synthetic blends of selected VOCs in nitrogen at ppbv levels. The calibration standards were then diluted with zero air (from zero air generator) to the ambient levels. The accuracy for the calibration standards were < ±5 % for all species, and the measurement precision of the PTR-MS was 10% for individual compounds.

For calculated MDLs of all measured species, refer to Table S1 in Pan et al. (2023).

#### 4.0 Data Format

GC and PTR-MS data can be found in the Excel files named CAVE2019\_VOCs\_GC.xlsx and CAVE2019\_VOCs\_PTRMS.xlsx, respectively. All data are provided in local time (Mountain Daylight Time). Data units are indicated as either ppbv or pptv. -8888 indicates data below the detection limit and -9999 indicates missing data.

#### 5.0 Data Remarks

Those interested in using these data are encouraged to contact the authors listed above for more information. In case of planned publication, we request that data users contact Jeff Collett (collett@colostate.edu) to discuss appropriate recognition of those that collected the data and the agencies that sponsored data collection

#### 6.0 Description of Variables

For the file: CAVE2019\_VOCs\_GC.xlsx:

| Variable Name       | Units        | Description                  | Time Resolution |
|---------------------|--------------|------------------------------|-----------------|
| Start_Date_and_Time | M/DD/YY H:MM | Mountain Daylight Time (MDT) |                 |

|  |              |                              |        |
|--|--------------|------------------------------|--------|
| Midtime  | M/DD/YY H:MM | Mountain Daylight Time (MDT) |        |
| Stop Date and Time                                   | M/DD/YY H:MM | Mountain Daylight Time (MDT) |        |
| Ethane....12-diethylbenzene                          | ppbv         | Species concentration        | Hourly |
| CH <sub>2</sub> Cl <sub>2</sub> ...CHBr <sub>3</sub> | pptv         | Species concentration        | Hourly |

For the file: CAVE2019\_VOCs\_PTRMS.xlsx:

| Variable Name     | Units              | Description                  | Time Resolution |
|-------------------|--------------------|------------------------------|-----------------|
| Date Time (local) | M/DD/YYYY<br>HH:MM | Mountain Daylight Time (MDT) |                 |
| MeOH...Toluene    | ppbv               | Species concentration        | 4 minutes       |

## 7.0 References

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