

**Title:** ReadMe for CAVE 2019 NO<sub>x</sub>/PAN data

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**1.0. Data Set Description**

Final data for the NO<sub>x</sub> and PAN measurements collected in Carlsbad Caverns National Park. Data status is final data. NO<sub>x</sub> data are collected every minute. PAN and PPN data are measured at 10-minute frequency. All data are reported as mixing ratios in units of parts per billion by volume (ppbv). Measured species include: NO, NO<sub>2</sub>, NO<sub>x</sub>, NO<sub>y</sub>, PAN, and PPN. Instruments for NO<sub>x</sub> and PAN measurements were collocated at the “Biology” Building (32.18° N, 104.44° W) located within Carlsbad Caverns National Park. The field study took place from July 25, 2019 to September 5, 2019.

The instrument inlets were positioned 1-2 m above the roofline of the building (roughly 6-7 m above ground level). All measurements used in this analysis are averaged to 1 hour, although instrument data collection rates varied from 1 minute to 1 hour.

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.

**2.0. Instrument Descriptions**

**NO<sub>x</sub> Instrument:** NO, NO<sub>2</sub>, and NO<sub>y</sub> were measured using a single-channel commercial NO analyzer (Eco Physics, model CLD 780 TR) employing NO-O<sub>3</sub> chemiluminescence detection and outfitted with two custom-built inlets. One inlet is an LED-based converter employing 395 nm LEDs for UV photolysis of NO<sub>2</sub> to NO [Pollack *et al.*, 2010]. The other is a molybdenum converter heated to 320°C used to reduce NO<sub>y</sub> species to NO for detection by the NO analyzer. The converters are housed in a light-tight, insulated and weather-proof enclosure positioned roughly 1 m above the roofline of the building. A common inlet tip protruding from the enclosure allows calibration gases to be injected into the sample tubing as close to the inlet tip as possible. The NO analyzer is located inside the building and connected to the inlet/converter enclosure via sample tubing housed inside an opaque, insulated, and weather-proof conduit. A pair of 3-way solenoid valves positioned inside the inlet enclosure directs sample flow through the molybdenum converter for 20 s and the LED converter for 40 s on rotation. When the air sample is being directed through the LED converter, the LEDs are turned off for 20 s to measure NO only and illuminated for 20 s to measure NO plus the fraction of NO<sub>2</sub> converted by 395 nm

photolysis. The rotation allows for 20 s of sampling (5 s of flush time followed by 15 s of averaging) through each inlet channel at a rate of  $1 \text{ min}^{-1}$ .

**PAN Instrument:** PAN and PPN were measured every 10 minutes using a custom-built gas chromatography instrument employing a commercial electron capture detector (Shimadzu, model Mini-2) that was thermally stabilized at  $40^{\circ}\text{C}$ . The detection technique is similar to that described in Flocke et al. (2005) and the instrument configuration is similar to that described in Zaragoza et al. (2017). The instrument was configured to only separate and quantify PAN and PPN. The output voltage from the electrometer was converted to a digital signal by custom Labview software (Original Code Consulting, MICAS-X). The sampling inlet was located at a total height of 5 m above the ground and 2 m above the roof of the historical building where the instruments were housed. Ambient air was sampled through a pumped bypass inlet constructed of  $\frac{3}{8}$ " o.d. x  $\frac{1}{4}$ " i.d. x 7.6 m long Teflon tubing and a diaphragm pump (GAST). A  $1 \mu\text{m}$  Teflon filter was positioned at the tip of the pumped bypass inlet. Flow through the pumped bypass inlet line was approximately 9 SLPM corresponding to a residence time of 1.2 s. Under the afternoon conditions typical of Carlsbad Caverns in summer, the lifetime of PAN is  $\sim 2$  hours, thus we do not expect significant decomposition in the inlet. The GC instrument sub-samples from the pumped bypass inlet at a slower flow rate of 200 mL/min through 1 m of  $\frac{1}{4}$ " o.d. and 1 m of  $\frac{1}{8}$ " o.d. Teflon tubing.

A 1.5 mL sample was injected every 5 minutes onto a pre-column using a 10-port Valco sampling valve. The sample loop was made from  $\frac{1}{8}$ " polyetheretherketone (PEEK) tubing and the connecting tubing material from the sampling valve to the column was also PEEK. Ultrahigh purity (UHP) helium (He) was used as a carrier gas, and UHP nitrogen ( $\text{N}_2$ ) was used as a make-up gas. The carrier and make-up gases were both further purified with a Valco Helium Purifier (HP2) and a Supelpure-O (22449) trap, respectively. The carrier gas flow was  $\sim 25 \text{ mL/min}$ , and the make-up gas flow was  $\sim 6 \text{ mL/min}$ . Similar to Flocke et al. (2005), we humidified the carrier gas by flowing it through a cartridge filled with copper(II) sulfate pentahydrate, temperature controlled to  $35^{\circ}\text{C}$ . We used a 15 m column (Restek Rtx-200, 1 mm film thickness, 0.53 mm ID) capillary column for separation. The 6-port valve, the columns, the connecting tubing, and needle valves were situated in an insulated box controlled to  $22^{\circ}\text{C}$  using a bi-directional temperature controller (TE Technology TC 36-25 RS232) and a thermoelectric device (TE Technology AC-073). This combination of temperature, flow rates and valve switch time yielded a PAN retention time of approximately 2 minutes. The instrument box is temperature stabilized to  $20^{\circ}\text{C}$ . At this temperature, PAN has a lifetime against thermal dissociation of  $\sim 85$  minutes, which yields a potential thermal loss of  $<5\%$  from thermal dissociation within the instrument; however, our calibration procedure also corrects for this.

### 3.0. Data Collection and Processing

$\text{NO}$  and  $\text{NO}_y$  are measured directly;  $\text{NO}_2$  is determined by subtracting each 15-s average data point from the interpolated average of two surrounding 15-s  $\text{NO}$  data points and then applying a measured  $\text{NO}_2$  to  $\text{NO}$  conversion efficiency determined during calibration. All three inlet channels are calibrated by standard addition of a known mixing ratio of  $\text{NO}$  to a flow of synthetic ultrapure "zero" air (UZA). The calibration standard is a National Institute of Standards and Technology (NIST) traceable 1 ppmv  $\text{NO}$  in  $\text{N}_2$  mixture (Praxair, California) diluted in the sample stream to match the maximum range of expected  $\text{NO}$  emission mixing ratios. The

converters are additionally calibrated using a known mixing ratio of NO<sub>2</sub> generated by gas-phase titration of the NO standard with O<sub>3</sub> produced by irradiation of UZA at 185 nm. The O<sub>3</sub> mixing ratio and reaction time is set to provide 85% titration of the NO standard to NO<sub>2</sub>. Given the plug flow residence time in the LED converter, the NO<sub>2</sub> conversion fraction during the measurement period was 0.75. The molybdenum converter is further challenged daily by standard addition of a known mixing ratio of HNO<sub>3</sub> generated from a temperature-regulated permeation device. The HNO<sub>3</sub> permeation device is validated before and after the field intensive using the NOAA UV optical absorption system (Neuman et al., 2003). The sensitivity of the analyzer to NO, the unreacted NO in the NO<sub>2</sub> calibration mixture, and the NO<sub>2</sub> conversion efficiency of each converter are determined from the calibrations and taken into account in the final data reduction. A correction for the sensitivity of the NO-O<sub>3</sub> chemiluminescence technique to water vapor is also applied to the final reported data according to the procedure outlined in Ridley et al., 1992. Water vapor measurements were collected at 1 minute using a Picarro model G2508 analyzer and directly applied to the NO<sub>xy</sub> dataset. The estimated uncertainty for the NO, NO<sub>2</sub>, and NO<sub>y</sub> measurements are ±5%, ±10%, and ±15%, respectively. The precision of the analyzer is 13 pptv and the limit of detection is 50 pptv at 1 Hz (or 10 pptv in 15 s).

A multi-point calibration curve was collected before and after the field campaign and once during the middle of the campaign. Automated calibrations were also performed once every 4 hours for a duration of 30 minutes throughout the campaign to a known quantity of PAN generated using the NCAR calibrator [Flocke et al., 2005]. Briefly, PAN calibration gas is generated using an acetone photolysis cell with accurately measured flows of acetone in UHP zero air (20 ppbv acetone) and 1.02 ppm NO in nitrogen (Praxair Cylinder Number: DT0030814). We used a zero air generator (Teledyne 701H) to dilute the output of the calibrator output. The calibrator efficiency was assumed to be 95% for the conversion of NO to PAN following Flocke et al. [2005]. The uncertainty of the calibrator was checked prior to the campaign and determined to be 10%. On the basis of chromatograms collected during the most pristine periods, we estimate an on-site detection limit of 25 pptv.

#### **Additional Data Averaging:**

1-hour averaged data for NO<sub>xy</sub> and PANs are reported here for easy use with respect to other variables collected at Carlsbad Caverns Nation Park during the 2019 Study. Hourly averages are generated by taking the average of the datapoints within the time window of each hour (e.g., average of all datapoints between 01:00 and 01:59). A 1-hour average value for PANs is generated when there are 3 or more values within the specified time window. A 1-hour average value for NO<sub>xy</sub> species is generated if there are 4 or more values in the specified time window.

#### **4.0. Data Format**

Data can be found in the excel file named CAVE2019\_NO<sub>xy</sub>PAN\_R1\_final\_data.xlsx. The file contains 4 sheets of data, including (a) 1-hour average values of all measured species, (b) 10-minute averaged NO<sub>xy</sub> data, (c) 10-minute collected PAN and PPN data, and (d) 1-minute NO<sub>xy</sub> data unflagged for missing values. Each sheet is also available as a .csv file to ensure long-term usability. Each sheet contains the start time, end time, and mixing ratios in units of ppbv for each species. The start and end times are provided in Mountain Daylight Time.

#### Associated Data Flags:

Dataset	Flag Value	Reason
NO <sub>xy</sub>	-999	Instrument performing an externally applied zero or span calibration
NO <sub>xy</sub>	-888	Instrument performing an internal routine calibration
NO <sub>xy</sub>	-777	Removal of spurious data points
PAN	-999	Missing data due to times when the instrument was performing calibrations
PAN	-888	Below detection limit
PAN	-777	Less than 3 data points available for 1-hour average; check individual 10-minute data flags

#### 5.0. Data Remarks

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#### 6.0 Description of Variables

Variable Name	Units	Description	Time Resolution
Start_time_MDT	MM/DD/YYYY HH:MM	mountain time zone date time (24-hour)	
End_time_MDT	MM/DD/YYYY HH:MM	mountain time zone date time (24-hour)	
NO_1hr_avg	ppbv	1-hour average mixing ratios of NOxy species	1-hour
NO2_1hr_avg			
NOx_1hr_avg		1-hour average mixing ratios of PAN and PPN	
NOy_1hr_avg			
PAN_ppb_1hr_avg			
PPN_ppb_1hr_avg			
NO_10min_avg	ppbv	10-minute average mixing ratios of NOxy species	10-minute
NO2_10min_avg			
NOx_10min_avg			
NOy_10min_avg			
Injection_Time	MM/DD/YYYY HH:MM:SS	mountain time zone date time (24-hour) of sample injection to the GC	
PAN (ppbv)	ppbv	Mixing ratio of PAN and PPN	10-minute
PPN (ppbv)			
Start_time_1min	MM/DD/YYYY HH:MM	mountain time zone date time (24-hour)	

End_time_1min	MM/DD/YYYY HH:MM	mountain time zone date time (24-hour)	
NO2_ppbv_1min	ppbv	1-minute mixing ratios of NOxy species	1-minute
NO_ppbv_1min			
NOy_ppbv_1min			
NOx_ppbv_1min			

## 7.0. References

- Flocke, F.M., Weinheimer, A.J., Swanson, A.L. et al. On the Measurement of PANs by Gas Chromatography and Electron Capture Detection. *J Atmos Chem* **52**, 19–43 (2005). <https://doi.org/10.1007/s10874-005-6772-0>
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