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Arctic Methane, Carbon Aerosols, and Tracers Study Field Campaign Report

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CLIMATE RESEARCH FACILITY

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Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
BC	black carbon
BRW	Barrow station (NOAA)
DOE	U.S. Department of Energy
LGR	Los Gatos Research
NOAA	National Oceanic and Atmospheric Administration
NSA	North Slope of Alaska
OCS	carbonyl sulfide
SNL	Sandia National Laboratory
SP2	single-particle soot photometer
UTC	Coordinated Universal Time

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1.0 Summary

The Arctic Methane, Carbon Aerosols, and Tracers Study was a measurement campaign at the National Oceanic and Atmospheric Administration (NOAA) Barrow Observatory and U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility North Slope of Alaska (NSA) sites in Barrow (formerly known as Utqiagvik) that involved the deployment of instruments to measure CH_4, black carbon (BC), and source tracers. The campaign ran from September 1, 2014 to September 1, 2016 and was extended until July 30, 2017. We deployed an in situ instrument to measure methane, the ratio of its isotopologues $^{13}CH_4/^{12}CH_4$, and ethane. We deployed a second instrument to measure carbon monoxide, carbonyl sulfide (COS), carbon dioxide, and water vapor. We also deployed an in situ instrument to measure BC, a single-particle soot photometer (SP2), at the nearby NOAA Barrow Observatory, co-located with the other NOAA aerosol instruments. Changes in emissions across different regions and seasons will be inferred using atmospheric transport and inverse modeling techniques.

During the first year of the campaign we prepared the shelter for the instruments, installed inlets, and deployed instruments. The trace-gas instruments were deployed in the guest-instrument shelter at the ARM-NSA site. The instruments are not weatherproof and must be operated indoors; therefore, they were connected to an outdoor inlet through tubing. The instruments and the inlet were located on the northeast end of the shelter. We employed passivated stainless steel tubing to make the inlet general purpose and suitable for sampling volatile organic compounds. Because blockage of the inlet due to frost was a significant concern, the tubing was insulated and was heated using self-regulating heat tape. During the first winter prior to deploying instruments, we ran the inlet, set up a weather station, and installed a networked computer to monitor the inlet and test the communications with the site. Initially, we intended to install two inlets, one for the trace gases and one for aerosols, and these were designed to extend approximately 12 feet above the roof of the shelter. Concerns that the inlet would block a Cimel sun photometer prompted us to keep the gas inlet at the level of the hand rail on the roof and move the aerosol measurements to the NOAA Barrow site. Both of the trace gas instruments are state of the art, semi-custom, and purchased specifically for this campaign. Delays in procuring and characterizing the instruments prevented us from deploying them before the second year of the campaign.

In September 2015, we installed the $CO/OCS/CO_2/H_2O$ instrument (LGR, Los Gatos Research, Inc.) and began sampling ambient air. In the initial phase of installation, the full calibration system was not deployed, but a partial calibration of the carbonyl sulfide (OCS) measurement was made using a permeation tube diluted with OCS-free ambient air scrubbed by a zero-air generator. Calibration using whole-air reference cylinders was started in December 2015 along with reference cylinders for CO and OCS calibration. We tested the stability and remote control of the instrument initially while the rest of the system was installed. In October 2015, we installed the instrument that measures $^{13}CH_4/^{12}CH_4/C_2H_6$ (Aerodyne Research, Inc.) along with its calibration system. Both the LGR and Aerodyne instruments employ mid-infrared tunable diode lasers to measure absorption spectra and report mixing ratios for their target species, and they require periodic introduction of calibration standards to achieve traceable results. The Aerodyne instrument was required to make measurements with exceptionally high precision in the ratio of $^{13}CH_4/^{12}CH_4$ ($\delta^{13}CH_4$) to be useful, and the associated calibration system was complex. A set of four small cylinders of air with elevated, isotopically characterized methane was used to calibrate the isotope ratio. These isotopic references were diluted using zero-air to ambient concentration during

calibration. An unfortunate property of the spectroscopy employed in the Aerodyne instrument is that the $\delta^{13}CH_4$ measurement is concentration-dependent. Therefore, an additional measurement of the concentration dependence of the isotopic ratio was performed with an additional concentrated reference cylinder. Zero-methane background measurements were also performed. The LGR and Aerodyne instruments shared the whole-air calibration cylinders, but they had independent valve systems to isolate them from one another. Both instruments started whole-air calibration in December 2015, but a valve in the Aerodyne system failed within a month after deployment, and this valve failure precluded calibration of the methane system until the end of January when a repair could be implemented. The LGR instrument and the Aerodyne instrument collected data until October 2016, before they were shipped back to Sandia National Laboratory (SNL).

Figure 1. Inlet on NSA shelter (left) and instruments (right) inside NSA shelter. The black insulated inlet extended from the northeast corner of the shelter roof at the level of the handrail. Within the shelter were the LGR $CO/OCS/CO_2/H_2O$ instrument (left side of photo) and the Aerodyne $^{13}CH_4/^{12}CH_4/C_2H_6$ instrument.

The SP2 was installed along with the other ARM/NOAA aerosol instruments in October 2015. The instrument performance degraded in the first two weeks after installation. The instrument was cleaned and recalibrated in December, and the instrument performance degraded again as before. In late January 2016, we serviced the instrument, added filtration, modified flows, and recalibrated, and, beginning early February 2016, the SP2 ran without need for another cleaning or maintenance for over six months. Once fully installed and running in Barrow, the SP2 required maintenance, cleaning, and calibration approximately every three months. The SP2 ran and collected data until July 2017 when it was removed and shipped back to SNL.

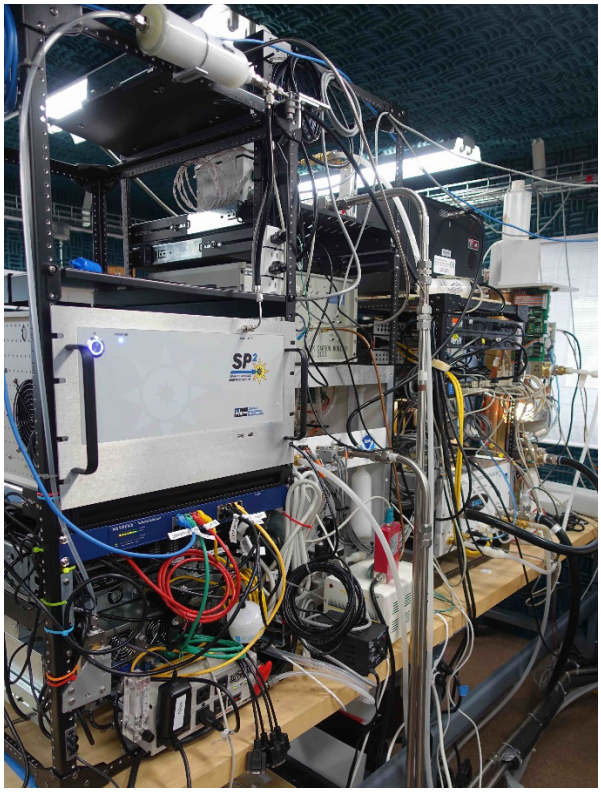

Figure 2. SP2 installed at the NOAA BRW Station. The SP2 was on the same inlet as the other instruments in the aerosol suite. The SP2 rack included a computer for external communication, a data storage unit, keyboard-video-mouse unit, and an uninterruptible power supply.

2.0 Results

The data collected represent the longest continuous measurements in the North Slope of Alaska of methane, methane isotopologues, ethane, carbonyl sulfide, and black carbon. Preliminary analysis of the data from the first half-year of data shows some interesting trends, and further analysis and data collection of a complete annual cycle is expected to be very interesting. Figure 3 shows seasonal variation of OCS and CO_2 and provides observational details about diel and synoptic-scale behavior of OCS in the boundary layer. Further analysis is required to more adequately interpret these patterns and to understand how the observations relate to carbon and OCS exchange between the atmosphere and the terrestrial biosphere.

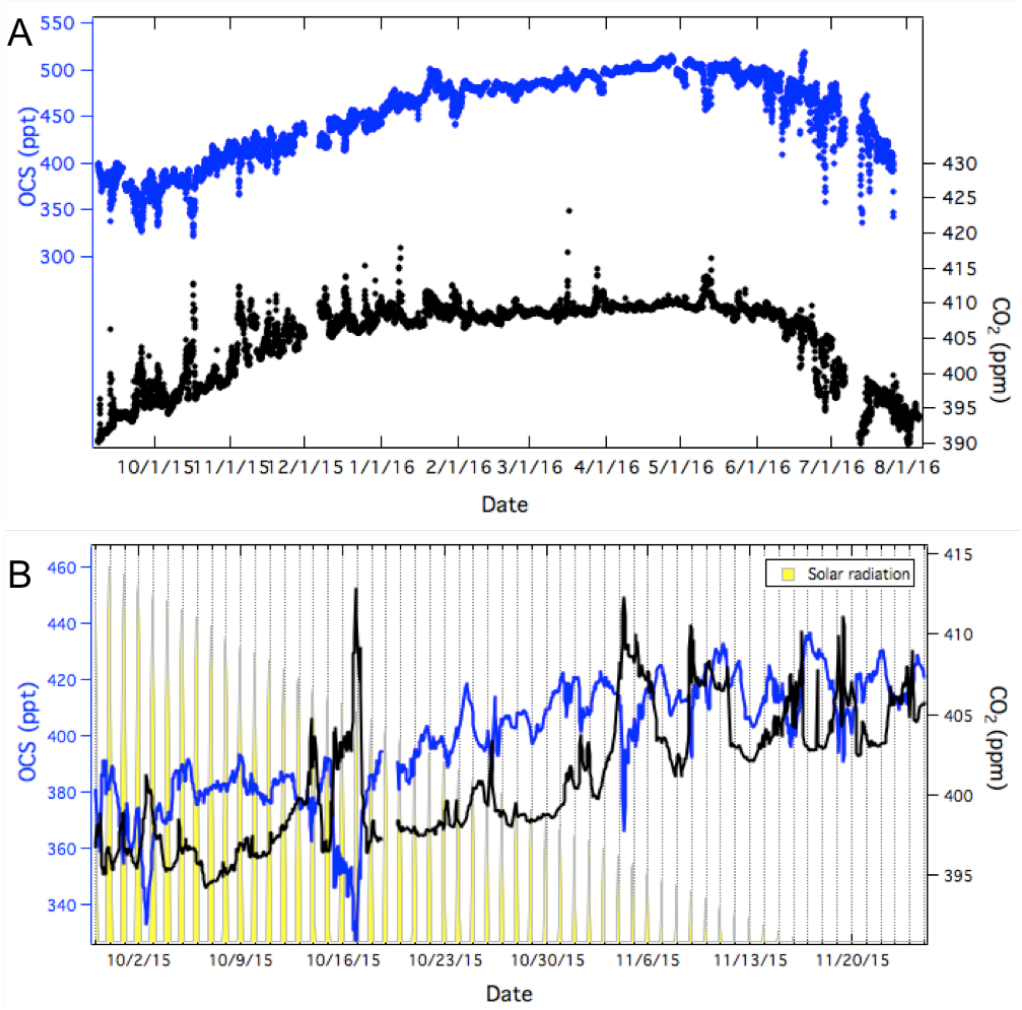

Figure 3. Time series of OCS (left, blue) and CO_2 (right, black) at NSA. The entire observation period is shown in (A), demonstrating seasonal variability, and a zoomed-in segment is shown in (B) to illustrate the anti-correlation of OCS and CO_2. Date ticks (in B) are located 00:00 UTC, with the theoretical clear-sky solar radiation shown to indicate periods of daylight.

Measurements of methane, methane isotopologues, and ethane give an indication of the source of methane in Barrow. Ethane has negligible natural sources and is a good tracer for thermogenic methane, particularly oil and gas sources. Our data demonstrate a strong correlation of methane and ethane during portions of the data set (Figure 4a), suggesting fossil methane contributions to the ambient mixing ratio during those times. The composition of the carbon-stable isotopes of methane, commonly depicted as a standardized shift ($\delta^{13}CH_4$) in the ratio of $^{13}CH_4/^{12}CH_4$, provides another indication of the methane source (Quay et al., 1999). Preliminary analysis of the early spring data using a Keeling plot (Figure 4b) shows a strong biogenic component with an intercept of -66 per mil, indicating a background wetlands contribution. This observation contrasts with published data from the Arctic Zeppelin Station in Norway for which springtime methane isotopologues suggest a background that is substantially less depleted in $^{13}CH_4$, indicating thermogenic sources (Fisher et al., 2011).

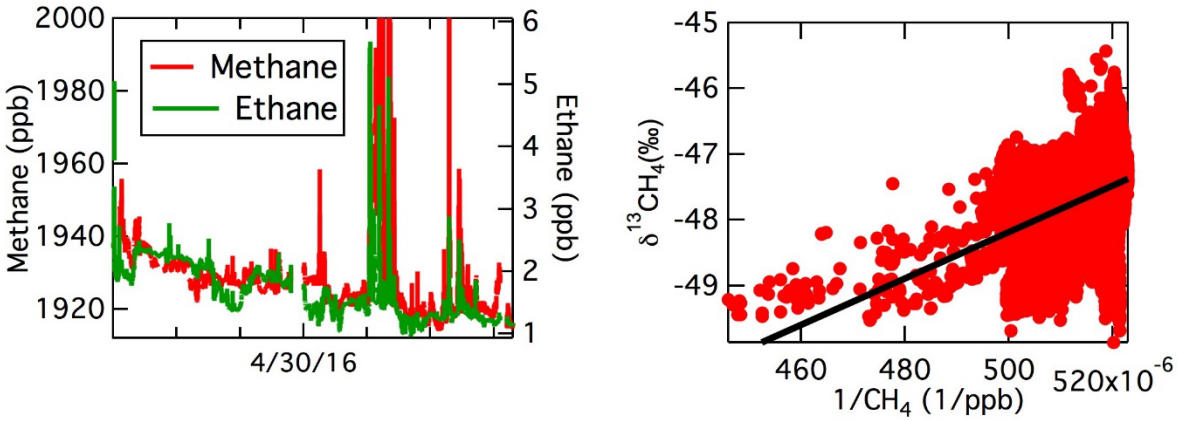

Figure 4. Time series of methane and ethane (left) and Keeling plot for methane (right). A portion of the observation period is shown in (A) for methane and ethane, highlighting a portion of the time sequence that demonstrated a strong correlation between methane and ethane. A plot of the isotopic shift as a function of the inverse of the total methane mixing ratio is shown in (B). This type of plot is known as a Keeling plot. With an intercept of -66 per mil, the results suggest a biogenic source.

The preliminary BC data demonstrate that BC mass was highly variable as a function of time during the winter and early spring in Barrow, as shown in Figure 5. These high-resolution BC measurements will allow detailed comparisons to be made for the first time between high-resolution atmospheric transport models and measurements over multiple months and seasons. These comparisons will provide a unique opportunity to refine models of the atmospheric processing of black carbon.

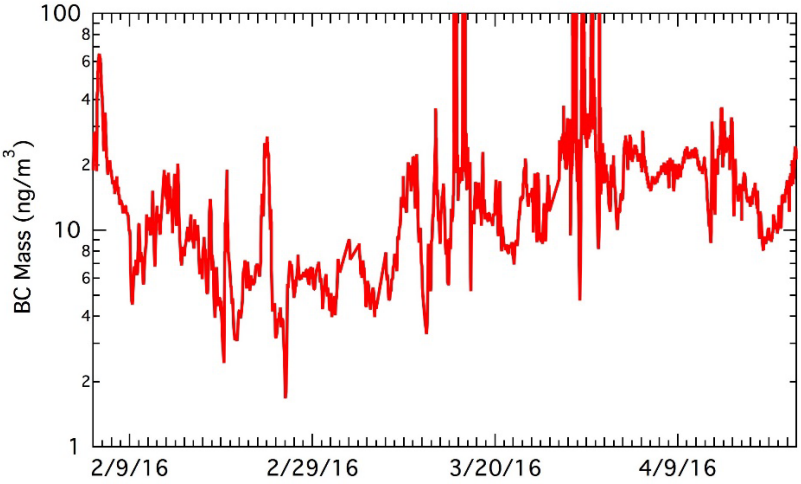

Figure 5. Time series of BC at the NOAA Barrow Observatory station. A time series of total black carbon mass measured by the SP2 is shown for a selected portion of the data set, emphasizing daily variability.

3.0 Publications and References

3.1 Presentations

Bambha, RP, BW LaFranchi, DA Lucero, MD Ivey, A Jefferson, R Burgener, B Thomas, and HA Michelsen. 2016. "The Arctic Methane, Carbon Aerosols, and Tracers Study", DOE BER ASR Science Team Meeting, Tysons Corner, Virginia.

3.2 References

Fisher, RE, S Sriskantharajah, D Lowry, M Lanoisellé, CMR Fowler, RH James, O Hermansen, C Lund Myhre, A Stohl, J Greinert , PBR Nisbet-Jones, J Mienert, and EG Nisbet. 2011. “Arctic methane sources: Isotopic evidence for atmospheric inputs.” *Geophysical Research Letters* 38(21), doi:10.1029/2011GL049319.

Quay, P, J Stutsman, D Wilbur, A Snover, E Dlugokencky, and T Brown. 1999. “The isotopic composition of atmospheric methane.” *Global Biogeochemical Cycles* 13(2) 445-461: 445-461, doi:10.1029/1998GB00006.


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