

Summertime Aerosol across the North Slope of Alaska Field Campaign Report

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Acronyms and Abbreviations

AMF	ARM Mobile Facility
AOS	aerosol observing system
APS	aerodynamic particle sizer
ARM	Atmospheric Radiation Measurement
ATOFMS	aerosol time-of-flight mass spectrometer
ATV	all-terrain vehicle
CCSEM-EDX	computer-controlled scanning electron microscopy with energy-dispersive x-ray spectroscopy
CPI	carbon preference index
DOE	U.S. Department of Energy
EC	elemental carbon
GC/MS	gas chromatography/mass spectrometry
IC	ion chromatography
IOP	intensive operational period
MOUDI	micro-orifice uniform deposition impactor
MPS	microanalysis particle sampler
MSA	methansulfonate
NOAA	National Oceanic and Atmospheric Administration
NSA	North Slope of Alaska
OC	organic carbon
PAH	polycyclic aromatic hydrocarbon
PI	principal investigator
PM	particulate matter
SMPS	scanning mobility particle sizer
SSA	sea spray aerosol
TSP	total suspended particulate matter
WSOC	water-soluble organic carbon

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1.0 Summary

The Summertime Aerosol across the North Slope of Alaska U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility field campaign, a collaborative effort between the University of Michigan and Baylor University, was focused on chemically characterizing sources of summertime aerosol impacting the Utqiagvik (Barrow, NSA) and the Oliktok Point (AMF3) ARM sites. This campaign was co-funded by a grant from the National Oceanic and Atmospheric Administration (NOAA, PI: Kerri Pratt, Co-I: Rebecca Sheesley) titled “Assessment of Atmospheric Aerosols Resulting from Oil and Gas Extraction Activities near the North Slope of Alaska”. The ARM field campaign took place on the North Slope of Alaska (NSA) from August 21 to September 30, 2015 and August 12 to September 20, 2016, with filter sampling occurring both years at both the NSA Barrow and AMF3 Oliktok Point sites. Online intensive measurements occurred at Barrow in 2015 and at Oliktok Point in 2016, coordinated with the arrival of the ARM Aerosol Observing System (AOS) in August 2016 at Oliktok Point.

During 2015, the University of Michigan deployed the newly constructed aerosol time-of-flight mass spectrometer (ATOFMS), as well as a microanalysis particle sampler (MPS) to collect particles for offline analysis by computer-controlled scanning electron microscopy with energy-dispersive x-ray spectroscopy (CCSEM-EDX). Unfortunately, an issue with the time-of-flight mass spectrometer on the ATOFMS limited the number of particles that produced mass spectra during the 2015 study. This issue was subsequently fixed for the 2016 deployment.

During 2016, the ATOFMS was deployed to the AMF3 at the Oliktok Point field site, in addition to a micro-orifice uniform deposition impactor (MOUDI) to collect particles for offline analysis by CCSEM-EDX. Notably, these measurements, to our knowledge, represent the first real-time, single-particle chemical characterization (aerosol mixing state) measurements at Utqiagvik and Oliktok Point. Online aerosol measurements also included: PM_{2.5} (particulate matter <2.5 μm) black carbon mass concentrations (aethalometer; Baylor) and size-resolved (0.013-20 μm) number concentrations (scanning mobility particle sizer, SMPS, and aerodynamic particle sizer, APS; Michigan).

Baylor conducted filter sampling at both the Utqiagvik and Oliktok Point locations during both intensive operational periods (IOPs). Baylor deployed a total suspended particulate matter (TSP) sampler to Oliktok Point, and continuous one-week samples were collected in 2015 for a total of seven samples; during 2016, continuous 3-7 day samples were collected, for a total of 13 filters. Baylor deployed a TSP sampler and a PM1.0 sampler at Utqiagvik, Alaska; continuous 4-7 day filter samples were collected in 2015 for a total of eight samples.

To supplement this campaign, PI Sheesley had a simultaneous DOE ARM field campaign at Utqiagvik and Oliktok Point (<https://www.arm.gov/research/campaigns/amf2016bbc>), the goal of which was to collect continuous one-week TSP samples at both sites from June 2016 to September 2017. These results provide better context in terms of annual trends and for year-to-year variability and a final report with data was already submitted by PI Sheesley for that project. Analysis by Baylor focuses on TSP samples because of the extremely low PM loading on the PM1.0 sampler. Michigan deployed a three-stage impactor (0.07-5 μm PM collection) at Utqiagvik and a 10-stage impactor (0.056-10 μm PM collection) at Oliktok Point, during the 2015 and 2016 campaigns, respectively. Baylor employed

multiple offline analytical techniques for analysis of the PM filters. Measured parameters included: elemental carbon/organic carbon mass concentrations (EC/OC analysis), water-soluble organic carbon mass concentrations (WSOC, total organic carbon analysis of water extracts), inorganic ion mass concentrations (ion chromatography, IC), organic molecular tracer mass concentrations (gas chromatography-mass spectrometry, GC/MS), and fossil/modern carbon speciation of total and elemental carbon (radiocarbon analysis). In addition, the ion chromatography capability for simultaneous analysis of inorganic anions and organic acids was established in the Sheesley Lab and applied to the collected samples. While WSOC analysis was completed for all 2015 samples, it was not found to provide enough additional information to compensate for the large fraction of filter required for its analysis; for 2016, the other analyses were given priority for filter aliquots.

During the 2015 intensive sampling, air masses influencing Utqiagvik were observed to be primarily from the Beaufort Sea, with time periods of Prudhoe Bay oil field and town (Utqiagvik) influence. During 2016 intensive sampling, it was observed that even ‘oil field background’ time periods were influenced by combustion emissions from the oil field, as described in the results.

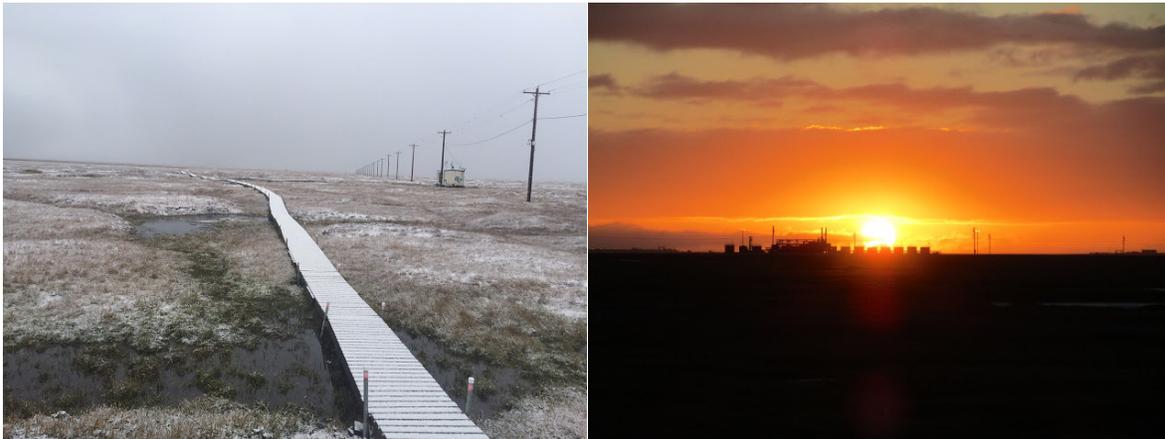


Figure 1. Photographs from the Barrow Environmental Observatory during the 2015 NSA field campaign (left) and at the Oliktok Point ARM site during the 2016 field campaign. Photo credit: Matt Gunsch.

2.0 Results

As described by Gunsch et al. (2017), during the August-September 2015 ARM field campaign, Utqiagvik was influenced by air masses from both the Arctic Ocean (Beaufort Sea) and the Prudhoe Bay oil fields, allowing a comparison of PM concentrations, chemical composition, and sources. The overall mode of the particle size number distribution shifted from 76 nm during Arctic Ocean influence to 27 nm during Prudhoe Bay influence with particle concentrations increasing from 130 cm⁻³ to 920 cm⁻³ due to transported particle emissions from the oil fields (Figure 2).

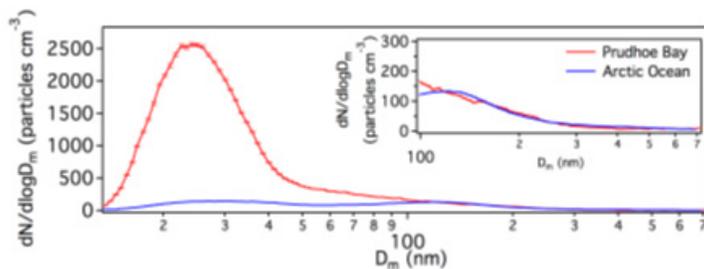


Figure 2. Average and standard error of the mean particle size (14-746 nm mobility diameter) distributions, with the >100 nm distributions inset, during air masses influenced by Prudhoe Bay and the Arctic Ocean at Utqiagvik (Gunsch et al., 2017).

During Arctic Ocean-influenced periods (70% of the study), fresh sea spray aerosol (SSA) contributed ~20%, by number, of particles between 0.13-0.4 μm , 40-70% between 0.4-1 μm , and 80-100% of 1-4 μm particles (Figure 3). In contrast, for periods influenced by emissions from Prudhoe Bay (10% of the study), the third-largest oil field in North America, there was a strong influence from submicron (0.13- 1 μm) combustion-derived particles (20-50% organic carbon (OC), by number, and 5-10% soot, by number). While sea spray aerosol still comprised a large fraction of particles (90% by number from 1- 4 μm) detected under Prudhoe Bay influence, these particles were internally mixed with sulfate and nitrate indicative of aging processes during atmospheric transport. The increased contributions of carbonaceous combustion products and partially aged sea spray aerosol should be considered in future arctic atmospheric composition and climate simulations.

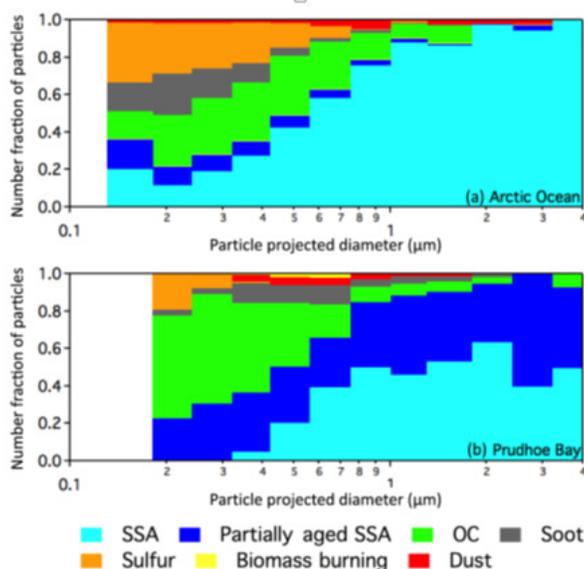


Figure 3. Size and chemical composition of individual particles measured by CCSEM-EDX during influence by (a) the Arctic Ocean and (b) Prudhoe Bay air masses at Utqiagvik (Gunsch et al., 2017).

During the August-September 2016 ARM field campaign at Oliktok Point, direct combustion plumes from local oil and gas extraction activities were characterized by fresh and aged soot particles and organic carbon particles, as measured by ATOFMS. PM_{2.5} concentrations averaged 1400 particles cm⁻³ and 2.6 $\mu\text{g}/\text{m}^3$ within the plumes. Nearly all 0.07-1.6 μm particles were internally mixed with sulfate. Sea

spray aerosol was observed throughout the study, with increased internal mixing with sulfate and nitrate during direct plume periods, consistent with multiphase reactions occurring in the local plumes from elevated NO_x and SO_2 . Non-plume periods were characterized by aged combustion aerosol, with no period of clean arctic air observed at Oliktok Point. During these oilfield background periods, $\text{PM}_{2.5}$ concentrations averaged 307 particles cm^{-3} and $1.2 \mu\text{g}/\text{m}^3$. Two ultrafine aerosol growth events were observed during oil field background periods. These single-particle chemical composition measurements provide insights into how increasing arctic development will impact arctic atmospheric composition and climate through local oil and gas extraction emissions. A manuscript describing these results is in preparation for submission to a peer-reviewed journal.

Overall, the 2015 campaign at Utqiagvik experienced very low OC and elemental carbon (EC) mass concentrations, with a general downward trend over the course of the campaign. This August-September period was also colder and rainier than the 2012 season. The 2016 campaign had some higher weeks for OC, but the EC was still very low. Low summertime EC is common for Utqiagvik. The lack of EC in Utqiagvik for this summer campaign indicates limited impact from biomass burning (in agreement with the ATOFMS measurements and low observed levoglucosan concentrations); this leaves the possibility of primary and secondary biogenic sources being important for summertime organic aerosol on the North Slope. The radiocarbon apportionment for Utqiagvik was very consistent across the 2015 and 2016 summer campaigns, ranging from 70-94% contemporary carbon for the total carbon (dominantly OC) (Figure 4). The radiocarbon apportionment in Oliktok Point was considerably more variable (Figure 5). The 2015 campaign showed a systematic decrease in contemporary carbon contributions from mid- August to the beginning of October. In 2016, the Oliktok Point carbon was similar to Utqiagvik, with very high contemporary contributions. However, the middle of September 2016 had similar fraction fossil as the previous year. Radiocarbon of EC for 2016 was 82-90% fossil for Oliktok, while the OC is dominantly contemporary for the August aerosol and split fossil and contemporary for mid-September. This indicates that in warmer seasons, the organic aerosol in Oliktok may see significant contribution from primary and secondary biogenic sources. In addition, the EC for Oliktok is likely from diesel, not gas flaring sources as the stable carbon, at -25.77 ‰ , was more enriched than would be expected for a natural gas source; this also agrees with the ATOFMS results.

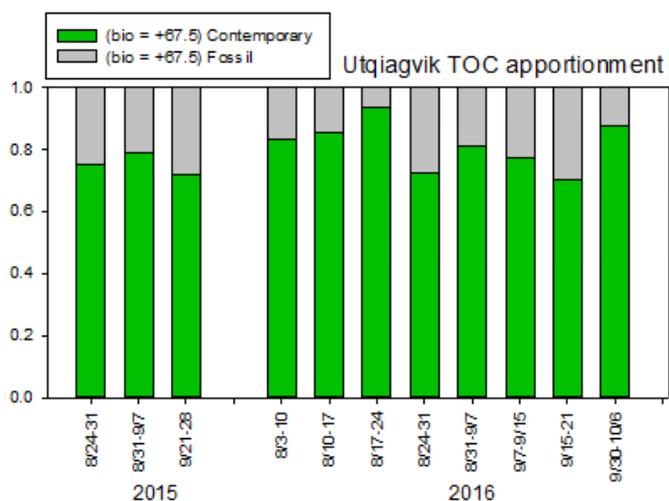


Figure 4. Utqiagvik radiocarbon apportionment of total organic carbon using a mixed biomass burning and biogenic endmember.

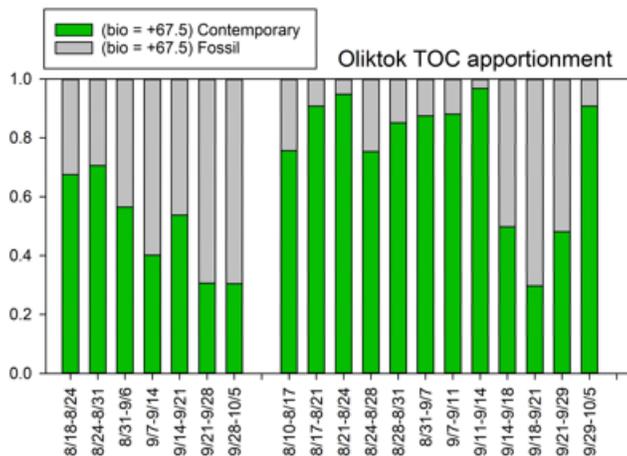


Figure 5. Oliktok Point radiocarbon apportionment of total organic carbon using a mixed biomass burning and biogenic endmember.

Utqiagvik and Oliktok were quite different in inorganic ion composition. Utqiagvik had a peak inorganic ion concentration, as measured by ion chromatography, near $5 \mu\text{g m}^{-3}$, while Oliktok remained below $3 \mu\text{g m}^{-3}$ in 2015. For Utqiagvik, sodium, sulfate, and chloride dominated the inorganic ion ambient concentration. The chloride concentration was the largest inorganic species measured in this TSP, consistent with the significant SSA influence observed by ATOFMS. Methanesulfonate (MSA) was consistently measured in most samples and fell within measured ranges reported previously for Utqiagvik. Summer 2016 had higher organic acid concentrations; however, malonate and oxalate were not measured in Oliktok. Small organic acids have recently been implicated in potential new particle formation and growth events when combined with MSA and organic amines.

The compound class results for Utqiagvik reveal a difference between 2015 and 2016 for hopanes, alkanes, and polycyclic aromatic hydrocarbon (PAHs). The highest summed concentration for n-alkanes (August 17-24, 2016) coincided with high concentrations of PAHs, a low CPI, and low hopanes; this would indicate significant contribution of a non-motor-vehicle combustion source. Results of organic tracer analysis reveal consistent motor vehicle contribution at Utqiagvik, as tracked by hopanes including norhopane. The norhopane concentration (campaign average of $1.05 \pm 0.76 \text{ pg m}^{-3}$) and hopane concentrations (campaign average of $1.35 \pm 0.96 \text{ pg m}^{-3}$) are over two orders of magnitude lower than a monthly average of hopane from Bakersfield, California ($290 \pm 11 \text{ pg m}^{-3}$). Potential local sources would include on-road gasoline-powered motor vehicles, heavy-duty diesel, and 4-stroke all-terrain vehicles (ATVs). Residences are heated by natural gas furnaces, which would be expected to have low PM emissions. The average norhopane concentration is a bit higher in Oliktok than Utqiagvik (1.79 versus 1.05 pg m^{-3}). It is in the CPI and low-molecular-weight PAHs that the difference is most apparent (Figures 6). The carbon preference index (CPI) measures the odd:even ratio of n-alkanes, in this case for C24-C33, to indicate the contribution of biogenic versus combustion sources. Biogenic emissions of n-alkanes have a reported CPI of at least 12, while the CPI of fossil fuel combustion is around 1.0. Biomass combustion is typically closer to fossil fuel combustion at around 1-3. For the samples with sufficient n-alkanes to calculate a CPI, the results were mixed, with periods of dominance from combustion sources ($\text{CPI} < 5$) and periods of dominance from biogenic sources ($\text{CPI} > 10$). Since the Utqiagvik CPI never went below 3, there is always considerable impact from biogenic sources (Figure 5). The CPI in Oliktok never rises above 6, which indicates that although there is always a mix between

biogenic and combustion, the combustion sources are more significant in Oliktok than Utqiagvik, as expected (Figure 6). The low-molecular-weight PAHs (202-252) are considerably higher in Oliktok ($0.64\text{--}28.6\text{ pg m}^{-3}$) than Utqiagvik ($0.66\text{--}3.8\text{ pg m}^{-3}$), with fluoranthene shown below as an example (Figure 6). The fluoranthene concentration in the weeklong samples for Oliktok peaked at 8.5 pg m^{-3} with high periods in both 2015 and 2016 and an average concentration of $2.4 \pm 2.5\text{ pg m}^{-3}$. For comparison, the average fluoranthene concentration for Utqiagvik was $0.19 \pm 0.20\text{ pg m}^{-3}$, an order of magnitude lower. This high contribution of low-molecular-weight PAHs is a local source in Oliktok that is not present in Utqiagvik, likely associated with natural gas processing.

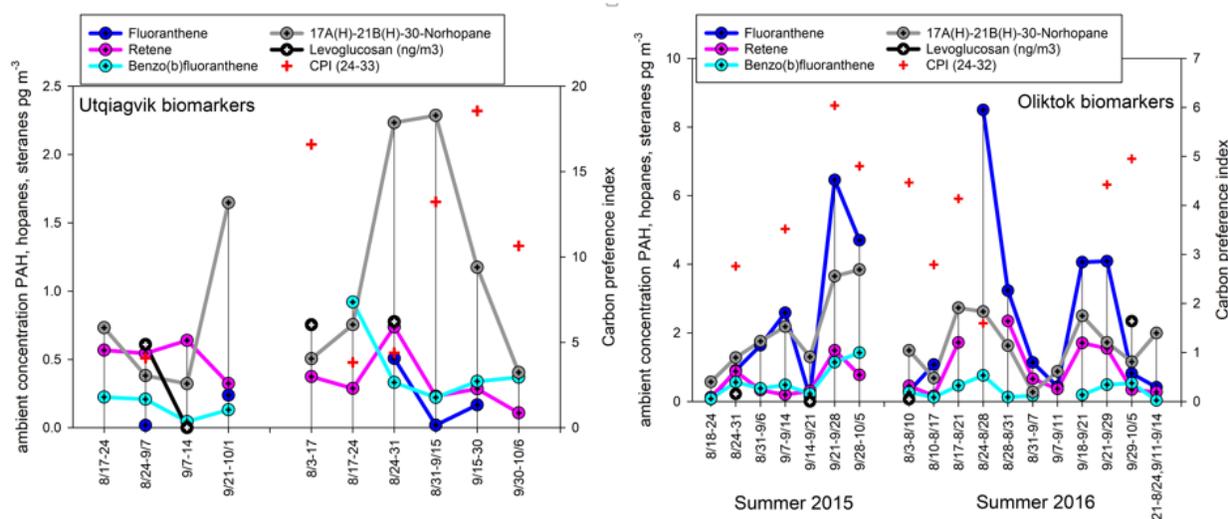


Figure 6. Ambient concentration of select biomarkers and carbon preference index (CPI) of n-alkanes for Utqiagvik and Oliktok Point, Alaska. The first four samples are 2015 (8/17-10/1) and the last six samples after the break are 2016 (8/3-10/6). Carbon preference index (CPI) is also reported on the right axis for n-alkanes of carbon length C24-33.

For biomass burning, only the late September 2016 sample had levoglucosan concentrations above 1 ng m^{-3} ; the 9/29 sample had levoglucosan over 2 ng m^{-3} and low concentrations for all other species, including retene (Figure 6). The summed compound class results for Utqiagvik and Oliktok reveal that both had consistent hopane sources. These would result from heavy oil combustion or the motor oil emissions associated with motor vehicle exhaust. In terms of ambient concentration, the n-alkanes were the dominant compound class measured in this study for TSP. Additional analysis of polar components including longer chain aliphatic acids and alcohols, as well as specific tracers for biogenic secondary organic aerosol, would be of interest to understand additional marine and terrestrial inputs.

3.0 Publications and References

3.1 Publications

Gunsch, MJ, RM Kirpes, KR Kolesar, TE Barrett, S China, RJ Sheesley, A Laskin, A Wiedensohler, T Tuch, and KA Pratt. 2017. "Contributions of transported Prudhoe Bay oilfield emissions to the aerosol population in Utqiagvik, Alaska." *Atmospheric Chemistry and Physics* 17(17): 10879-11892, [doi:10.5194/acp-17-10879-2017](https://doi.org/10.5194/acp-17-10879-2017).

3.2 Presentations

Pratt, KA. 2017. “Novel applications of mass spectrometry to atmospheric chemistry.” Triangle Area Mass Spectrometry Discussion Group Meeting. Raleigh, North Carolina. [Invited oral presentation]

Sheesley, R, C Moffett, T Barrett, M Gunsch, and K Pratt. 2017. “The relationship between organic carbon and methanesulfonic acid at two sites on the North Slope of Alaska over four summers.” American Geophysical Union National Meeting. New Orleans, Louisiana.

Pratt, KA. 2017. “Atmospheric aerosol sources and chemical composition in the changing Arctic.” University of Alaska, Fairbanks Department of Chemistry Seminar. Fairbanks, Alaska. [Invited oral presentation]

Pratt, KA, MJ Gunsch, RM Kirpes, K Kolesar, CE Moffett, TE Barrett, and RJ Sheesley. 2017. “Prudhoe Bay oilfield influences on atmospheric particulate matter (PM) on the North Slope of Alaska.” 2017 U.S.- Canada Northern Oil & Gas Research Forum. Anchorage, Alaska. [Invited oral presentation]

Pratt, KA, MJ Gunsch, RM Kirpes, K Kolesar, T Watson, CE Moffett, T Barrett, and RJ Sheesley. 2017. “Prudhoe Bay oilfield influences on atmospheric particles on the North Slope of Alaska.” 2017 International Global Atmospheric Chemistry Project (IGAC) Air Pollution in the Arctic: Climate, Environment and Societies (PACES) Workshop. Victoria, British Columbia. [Invited oral presentation]

Gunsch, MJ, R Kirpes, C Moffett, T Watson, R Sheesley, and K Pratt. 2017. “Atmospheric particulate matter within the Prudhoe Bay oilfields, Alaska.” 2017 Canadian Society for Chemistry National Meeting. Toronto, Ontario. [Oral presentation]

Sheesley, R, C Moffett, T Barrett, M Gunsch, and K Pratt. 2017. “Biogenic and fossil contributions to organic aerosol at two sites on the North Slope of Alaska.” European Geosciences Union Meeting. Vienna, Austria.

Sheesley, R, C Moffett, T Barrett, M Gunsch, and K Pratt. 2017. “Atmospheric aerosol sources and composition during summer at two Alaskan Arctic coastal sites.” 2017 joint meeting of the ARM Facility and ASR Program. Vienna, Virginia.

Sheesley, R. 2017. “Investigation of molecular and isotopic composition of aerosols from the Arctic to the Gulf of Mexico.” Department of Earth System Science. University of California-Irvine, Irvine, California. [Invited talk]

Gunsch, M, R Kirpes, C Moffett, R Sheesley, and K Pratt. 2016. “Chemical characterization of atmospheric particulate matter from Prudhoe Bay, Alaska.” 2016 American Geophysical Union Fall Meeting. San Francisco, California. [Poster]

Gunsch, M, R Kirpes, K Kolesar, J Cellini, T Barrett, R Sheesley, A Laskin, S China, and K Pratt. 2016. “Sources and chemical composition of individual atmospheric particles in the Alaskan Arctic.” 2016 NETCARE Workshop. Toronto, Ontario. [Invited oral presentation]

Pratt, KA. 2016. "Influence of the changing arctic surface on snow, aerosol, and gas chemistry." Michigan Technological University Earth Planetary & Space Sciences Institute Seminar. Houghton, Michigan. [Invited oral presentation]

Pratt, KA. 2016. "Novel applications of mass spectrometry to atmospheric chemistry." Delaware Valley Mass Spectrometry Discussion Group Meeting. Philadelphia, Pennsylvania. [Invited oral presentation]

Gunsch, M, R Kirpes, C Moffett, R Sheesley, and K Pratt. 2016. "Chemical characterization of atmospheric particulate matter from Prudhoe Bay, Alaska." 2016 Michigan Geophysical Union Symposium. Ann Arbor, Michigan. [Poster]

Moffett, CE, TE Barrett, M Gunsch, K Pratt, and RJ Sheesley. 2016. "Source apportionment of carbonaceous aerosols at two sites on the North Slope of Alaska." Society for Environmental Toxicology and Chemistry (SETAC) South Central Regional Meeting. Fort Worth, Texas.

Moffett, CE, TE Barrett, M Gunsch, K Pratt, and RJ Sheesley. "Source apportionment of carbonaceous aerosols at two sites on the North Slope of Alaska." American Geophysical Union National Meeting. San Francisco, California.

Gunsch, M, R Kirpes, A Ault, T Barrett, R Sheesley, and K Pratt. 2015. "Size-resolved chemical analysis of individual atmospheric aerosols near Barrow, AK." 2015 American Geophysical Union Fall Meeting. San Francisco, California. [Poster]

Gunsch, M, R Kirpes, A Ault, T Barrett, R Sheesley, and K Pratt. 2015. "Arctic Ocean and Prudhoe Bay influences of arctic aerosol chemistry." 35th Annual Meeting of the American Association for Aerosol Research. Portland, Oregon. [Oral presentation]

Gunsch, M, R Kirpes, A Ault, T Barrett, R Sheesley, and K Pratt. 2015. "Single particle analysis of transported Prudhoe Bay emissions in Barrow, AK." 2015 Karle Symposium. Ann Arbor, Michigan. [Poster]

Gunsch, M, R Kirpes, A Ault, T Barrett, R Sheesley, and K Pratt. 2015. "Single particle analysis of transported Prudhoe Bay emissions in Barrow, AK." 2015 Michigan Geophysical Union Symposium. Ann Arbor, Michigan. [Poster]

