

## Secondary Aerosol Formation in an Arctic Oil Field Campaign Report

KA Pratt  
K Kulju  
D Jeong  
JE Krechmer  
F Maljuf

AT Lambe  
N Perkins  
BM Lerner  
MS Claflin  
ES Cross

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# **Secondary Aerosol Formation in an Arctic Oil Field Campaign Report**

KA Pratt, University of Michigan (UM)  
Principal Investigator

AT Lambe, Aerodyne Research (AR)  
Co-Investigator

K Kulju, UM  
N Perkins, UM  
D Jeong, UM  
BM Lerner, AR  
JE Krechmer, AR  
MS Claflin, AR  
F Maljuf, AR  
ES Cross, Quant AQ

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## Acronyms and Abbreviations

AMF3	third ARM Mobile Facility
ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
CCSEM-EDX	computer-controlled scanning electron microscopy with energy-dispersive X-ray spectroscopy
Cl	chlorine
FIGAERO-ToF-CIMS	filter inlet for gases and aerosols coupled to time-of-flight chemical ionization mass spectrometer
IOP	intensive operational period
MOUDI	micro-orifice uniform deposition impactor
NSA	North Slope of Alaska
NSF	National Science Foundation
OVOC	oxygenated volatile organic compound
PI	principal investigator
PTR-ToFMS	proton transfer reaction time-of-flight mass spectrometer
SMPS	scanning mobility particle sizer
SOA	secondary organic aerosol
UTC	Coordinated Universal Time
VOC	volatile organic compound

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## 1.0 Summary

Atmospheric aerosols contribute significantly to arctic warming, yet significant differences in aerosol concentration levels and seasonal cycles often exist between models and observations. Recent studies of cloud properties across the North Slope of Alaska show the significant, regional influence of oil field emissions.<sup>1-4</sup> Development across the Arctic motivates the need to characterize these oilfield emissions to further predict their roles in changing future arctic climate.<sup>5</sup> Our previous August-September 2016 Atmospheric Radiation Measurement (ARM) user facility field campaign resulted in improved understanding of atmospheric particles emitted within the North Slope of Alaska (NSA) oil fields, as well as the aging of sea spray aerosol.<sup>6</sup> Following Polar Sunrise during arctic spring, chlorine chemistry is active,<sup>7,8</sup> and we hypothesize that oxidation of oil field hydrocarbons by chlorine atoms (Cl) generates oxygenated volatile organic compounds (OVOCs) leading to springtime arctic secondary organic aerosol (SOA) formation.

The overarching scientific goals of this ARM field campaign at Oliktok Point, Alaska (third ARM Mobile Facility [AMF3]) were to: 1) characterize the molecular composition of volatile organic compounds (VOCs), OVOCs, and SOA present in the NSA oil fields, 2) characterize the molecular composition of OVOCs and additional SOA generated from the oxidation of VOCs exposed to Cl generated in an oxidation flow reactor, and 3) measure the size distributions and mixing states of individual atmospheric particles. These intensive measurements were complemented by routine aerosol and meteorological measurements at the AMF3. This field campaign addresses the key U.S. Department of Energy Atmospheric System Research (ASR) research areas of 'Aerosol Processes' and 'High-Latitude Processes'. Prevailing winds are easterly, transporting combustion emissions up to ~75 km across the oil fields, thereby enabling measurements of both fresh and aged combustion emissions.

The field campaign at Oliktok Point, Alaska (Figure 1) was conducted from February to March 2020 (before the field campaign ended early due to COVID-19). This coincided with the period of diel solar cycles and snowpack cover associated with active Cl chemistry.<sup>9</sup> The list of online instruments, corresponding parameters measured, sampling for off-line analysis, and sampling dates are provided in Table 1. On March 14, 2020, site access was not possible due to phase three conditions. During this time, the intensive operational period (IOP) gas-phase inlet became impacted with snow and ice, so ~24 h of data is not usable from March 14-15 (UTC).



**Figure 1.** Oliktok Point (AMF3) site photographs taken by the University of Michigan during the ARM field campaign.

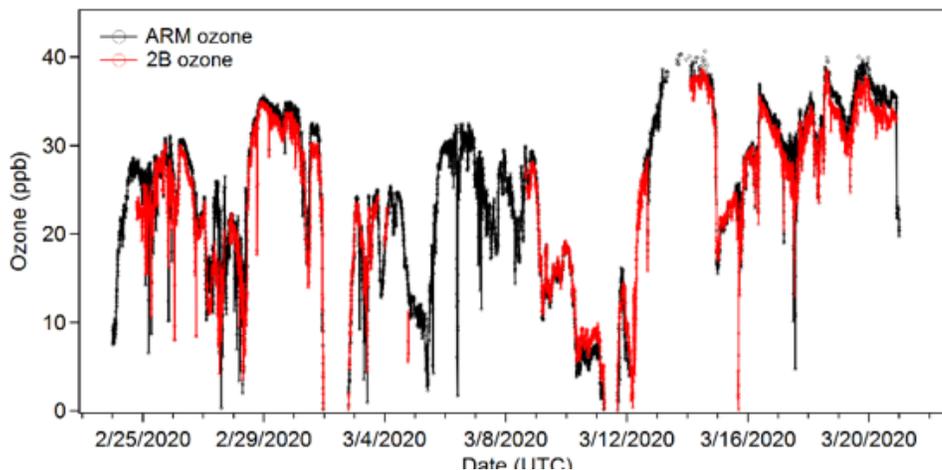
**Table 1.** February-March 2020 ARM field campaign measurements at Oliktok Point, Alaska (AMF3).

Instrument/Sample	Parameter	Measurement/ Sampling Dates
TSI micro-orifice uniform deposition impactor (MOUDI) – Collection of particle samples	Off-line individual particle morphology and elemental composition using computer-controlled scanning electron microscopy with energy-dispersive X-ray spectroscopy (CCSEM-EDX)	March 5-24, 2020
2B Technol. ozone monitor	O <sub>3</sub>	February 25-March 20, 2020
TSI Scanning mobility particle sizer spectrometer (SMPS)	Size-resolved particle number concentrations from 12-594 nm	March 1-23, 2020
Aerodyne FIGAERO-ToF-CIMS (Filter inlet for gases and aerosols coupled to a time-of-flight chemical ionization mass spectrometer)	OVOC and SOA molecular composition	February 26-March 24, 2020
Aerodyne GC-Vocus-PTR-ToFMS (Gas chromatograph coupled to a NO <sup>+</sup> chemical ionization Vocus proton transfer reaction time-of-flight mass spectrometer)	VOC molecular composition	March 6-24, 2020
QuantAQ electrochemical sensor package	O <sub>3</sub> , CO, CO <sub>2</sub> , NO, NO <sub>2</sub>	March 3-19, 2020
Aerodyne oxidation flow reactor	Controlled real-time exposure of ambient air to Cl radicals to investigate OVOC and SOA formation	March 19-24, 2020
Snow sampling	Inorganic ion concentrations using ion chromatography	March 6-23, 2020
Baseline AMF3 measurements		

## 2.0 Results

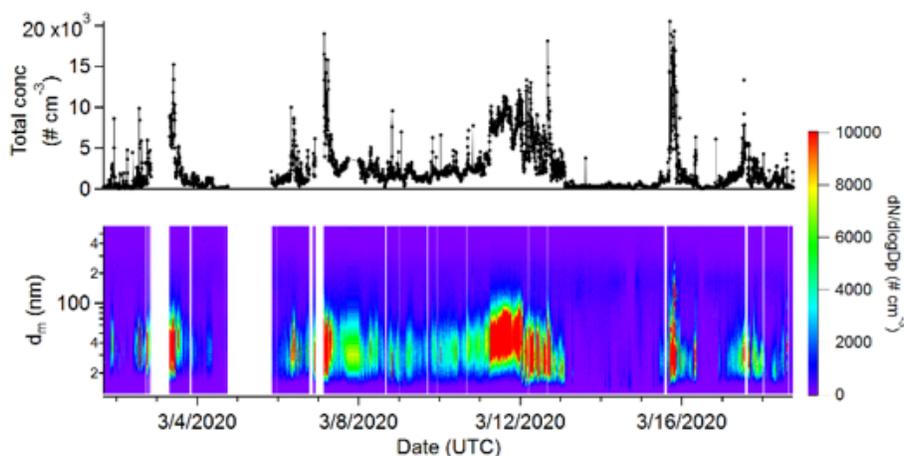
This ARM field campaign was associated with National Science Foundation (NSF) RAPID grants AGS-2002695 (University of Michigan) and AGS-2002696 (Aerodyne Research, Inc.). A collaborative proposal to NSF is planned in the near future to fund additional data and sample analysis. Select preliminary results are presented here.

Figure 2 shows time series of ozone (O<sub>3</sub>) mole ratios measured by ARM (Thermo Fisher Scientific model 49i) and the University of Michigan (2B Technologies model 205). Ozone depletion, due to reactive bromine chemistry,<sup>10</sup> was observed, with two sustained periods observed with levels below 15 ppb. This shows that the elevated NO<sub>x</sub> levels within the NSA oil fields<sup>11</sup> are not sufficient to either completely replenish O<sub>3</sub>-depleted air (via O<sub>3</sub> production from reaction of combustion-derived hydrocarbons and NO<sub>x</sub>) or completely inhibit local bromine chemistry.<sup>12</sup> Analysis of FIGAERO-ToF-CIMS and GC-Vocus-PTR-ToFMS data is ongoing to investigate novel molecular tracers that may be associated with these explanations.



**Figure 2.** 5 min.-averaged ozone mole ratios from ARM (black) and the 2B ozone monitor operated by the University of Michigan during the intensive operational period (IOP; red).

Figure 3 shows the time series of total number concentrations and size-resolved number concentrations measured by the scanning mobility particle sizer spectrometer deployed during the IOP by the University of Michigan. The total number concentrations are similar to those measured by a condensation particle counter during our previous March 2017 ARM field campaign at Oliktok Point.<sup>13</sup>



**Figure 3.** Total number concentrations (top) and aerosol size distributions (bottom) from 12-594 nm electrical mobility diameter ( $d_m$ ) measured by the University of Michigan SMPS during the IOP.

### 3.0 Publications and References

The analysis of real-time data and collected samples is ongoing and has been slowed to due to COVID-19 and limited personnel resources. Presentations and publications are expected in the future. Thus far, one presentation has been made:

Lerner, B, M Claflin, J Krechmer, F Maljuf, A Lambe, K Pratt, N Perkins, D Jeong, and K Kulju. Gas chromatography coupled with NO<sup>+</sup> Vocus-TOFMS for ambient VOC measurements. 2020 Aerodyne ToF-CIMS Users' Meeting. Virtual. May 2020.

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## 4.0 Lessons Learned

The Sandia National Laboratory staff and ARM technicians were excellent to work with, especially given the challenging circumstances of COVID-19 that became problematic part-way through the study. Quick and creative thinking by all staff involved was critical to the success of our measurements and field campaign. It was clear that the staff valued the success of our field campaign and the safety of the University of Michigan students, which is extremely appreciated. Near-daily principal investigator (PI) communication with Joe Hardesty, Ben Bishop, and Fred Helsel from mid- to late March was critical to the success of the latter half of our field campaign, which ended early due to COVID-19. They worked with the PIs to determine the best course of action to maintain safety while continuing the field campaign as long as safely possible. Sandia and ARM staff were also extremely helpful in facilitating new lodging solutions when our students lost access to ENI corporate staff housing and then Air Force housing at the beginning of the COVID-19 pandemic. Lori Parrot and Valerie Sparks provided logistical assistance that was critical to returning the instrumentation to our institutions so that it did not get inadvertently left at Oliktok Point during the COVID-19 shutdown.

Fred Helsel played a critical and creative role in working with us to determine the best sampling location for our system to minimize transmission losses in atmospheric trace gas sampling. This ended up requiring drilling a new hole in the guest container and was critical to the success of our sampling. Valerie Sparks was instrumental in the success of the logistics of our study, facilitating our shipments of hazardous materials (<sup>210</sup>Po source necessary to run the ToF-CIMS, and gas cylinders required for the GC-Vocus and ToF-CIMS instruments) and facilitating the last minute return shipment when the study ended early. The quick delivery of new gas cylinders was paramount to the success of the study when we learned that use of our N<sub>2</sub> generator led to measurement complications. Ben Bishop was extremely helpful during our field site setup and orientation, including to the lodging.

Lastly, the technicians that we worked with (Justin, Wyatt, Michael, and Billy) were very helpful during our IOP. For example, when we needed a frame for the ToF-CIMS to elevate it off the guest container floor, Wyatt built one. At the end of the campaign, when the students had to commute to and from the Deadhorse Aviation Center, Justin and Wyatt commuted in two trucks to ensure that the students were safe traveling under the hazardous conditions and did not get hung up at security checkpoints. Overall, our field campaign greatly benefited from the knowledge and expertise of the technicians.



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