The relationship between organic carbon and methanesulfonic acid at two sites on the North Slope of Alaska

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Abstract

Aerosols in the Arctic have large potential impacts on the radiative balance via direct and indirect effect such as scattering solar radiation and acting as cloud condensation nuclei (CCN). Marine aerosols, consisting of both inorganic particles and organic carbon (OC) contribute to these effects greatly. There are many sources of OC in the atmosphere such as oil and gas emissions, fossil fuel combustion, biomass burning, and biogenic sources, which includes marine aerosols. Dimethyl sulfide (DMS), a gas produced by phytoplankton, is photo oxidized in the atmosphere to form methanesulfonic acid (MSA). MSA can be important in forming cloud condensation nuclei, especially in remote regions such as the Arctic. While MSA has been studied in the Arctic, its relationship to particulate OC is not well understood. Total suspended particulate matter samples were collected at two sites, Utqiaġvik, AK, and Oliktok Point, AK, from June 2016 to August 2017 (ARM Field Campaign: 2014-6694). Utqiaġvik, AK, is located on the northern most point of the United States with a population of 4,581. The site is 7.4 km north of the village of Utqiaġvik. Oliktok Point, AK, is 300 km south east of Utqiaġvik in a region of intense petroleum development. Potential marine biogenic inputs to gas and particle phase organics include phytoplankton and algae in the Arctic Ocean. Terrestrial sources may also impact biogenic OC for these North Slope sites. For this study our primary focus is the relationship between MSA and OC. In addition, we are investigating the variability in summertime organic acid concentrations and relationship with OC and MSA. Samples were analyzed for OC and organic and inorganic ions including MSA. MSA may exist primarily in the smaller size fraction so the method was modified to measure it in the presence of high chloride. Measurements of MSA were also completed using an aerosol time-of-flight mass spectrometer (ATOFMS). Preliminary results show that MSA concentrations follow previously reported results (Quinn et. al., 2009). The ambient concentrations of MSA range from 0.34 to 35 ng/m^3 at Utqiaġvik and 1.4 to 25 ng/m^3 at Oliktok Point. Other organic acids detected include formic acid, acetic acid, and malonic acid. The data collected from this campaign can also be compared to results collected in 2012 and 2015.

Figure 1. The ARM NSA sampling sites in Utqiaġvik, AK and Oliktok Point, AK.

Sampling Sites and Sampling Description

- Total suspended particulate matter (TSP) samples collected at the North Slope of Alaska (NSA) Atmospheric Radiation Measurement (ARM) Climate Research Facility in Utqiaġvik, AK (71˚19'23.73" N, 156˚36'56.70" W), 7.4 km NE of the village of Utqiaġvik.
- TSP samples were collected at the NSA ARM extended mobile facility deployment site at Oliktok Point, ~300 km southeast of Utqiaġvik and west of Prudhoe Bay, AK.
- TSP samplers were from Hi-Q Environmental Products, customized with digital flow measurement, data logger, cold weather insulation and operator messaging.
- Additional instrumentation included an aethalometer and an aerosol time-of-flight mass spectrometer (ATOFMS) set up in Utqiaġvik, AK at the Barrow Artic Science Consortium (BASC) Cakeater Lab, 3 km from the ARM site.

Acknowledgments

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- Fred Helsel, Dan Lucero, and Jeffry Zirzow of the Sandia National Laboratory for site access and preparation.

Summertime OC, EC and radiocarbon apportionment

Filters were analyzed for OC and EC using the NIOSH 5040 method (Sunset Lab OCEC Aerosol Analyzer). Radiocarbon abundance was performed at NOSAMS at the Woods Hole Oceanographic Institution for total organic carbon (TOC). The radiocarbon abundance for Utqiaġvik, AK, in 2012 was analyzed as a composite of three weeks.

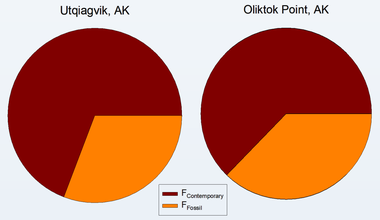

Figure 2. The TOC $F_{contemporary}$ and F_{fossil} for both sites, averaged over 2012-2016 for Utqiaġvik and 2015-2016 for Oliktok.

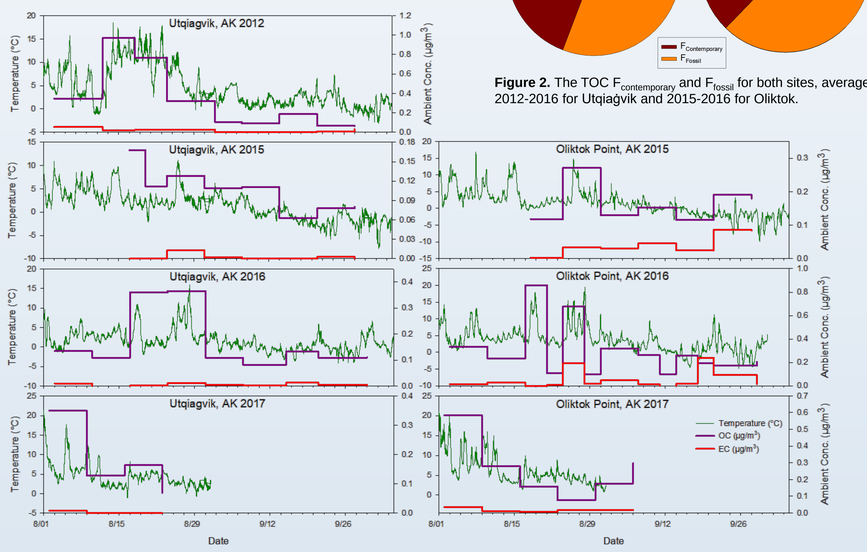

Figure 3. The ambient concentrations of OC and EC plotted with the ambient temperature at both sites.

Summertime inorganic ions and organic acids

An aliquot of the filter was extracted in water, sonicated and centrifuged. Analysis was performed with a Dionex ICS-2100 Integrated Reagent Free Ion Chromatography System and a Dionex Aquion Ion Chromatography System.

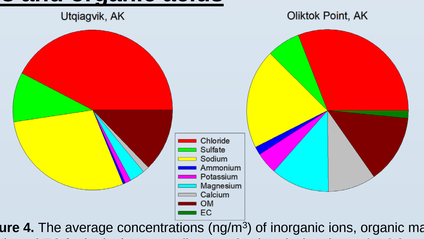

Figure 4. The average concentrations (ng/m^3) of inorganic ions, organic mass (OM), and EC for both sites over all years. OM is calculated as 1.6 * OC.

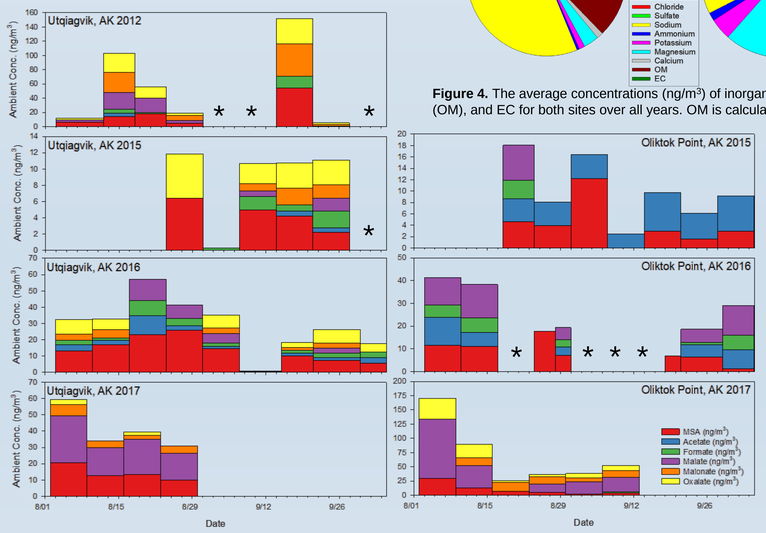

Figure 5. The ambient concentrations of organic acids (OA) at both sites over all years. The average MSA ambient concentration is displayed for each year by site. Differences between sites may be driven by differences in back trajectories with more marine influence at Utqiaġvik. Black asterisks represent samples for which IC analysis has not yet been completed.

References

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[3] Xu, J., B.J. Finlayson-Pitts, R.B. Gerber, *Proton transfer in mixed clusters of methanesulfonic acid, methylamine, and oxalic acid: Implications for atmospheric particle formation.* The Journal of Physical Chemistry, 2017. **121**(12), p. 2377-2385

What is the relationship between MSA and OC on the NSA?

Sources of organic acids in the atmosphere vary greatly. Primary sources include vegetation, soils, and marine microorganisms such as phytoplankton, while secondary sources include the photooxidation of organic compounds from these sources.[1]

Organic acids and MSA show similar trends with temperature as OC does in early through mid August, but does not appear to follow those trends in September. ATOFMS data indicated that MSA was present in 7% of measured particles (0.07-1.6 µm) by number for 2016 in Oliktok.

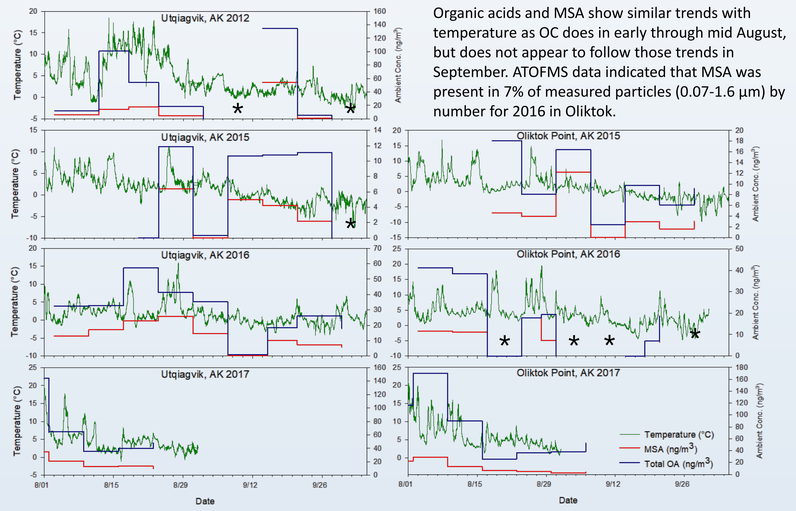

Figure 6. The total ambient concentration of organic acids and the ambient concentration of MSA plotted with the temperature at each site. Black asterisks represent samples that have not yet been analyzed.

MSA ambient concentrations correlate with OC ambient concentrations. Concentrations of MSA may indicate high contributions of biogenic marine sources to OC. Quinn et. al. found that sea ice extent was a good predictor of MSA ambient concentrations in the month of June, but not July - September. Oxalic acid which has been identified in both urban and marine particles has been shown to influence new particle formation when present with MSA and methylamine in the atmosphere.

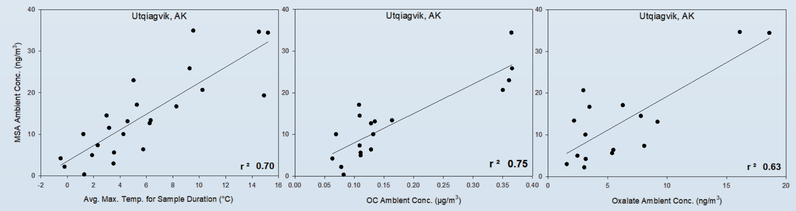

Figure 7. The ambient concentrations of MSA plotted against the average maximum temperature for the sample duration, the OC ambient concentration, and the oxalate ambient concentration at Utqiaġvik, AK.

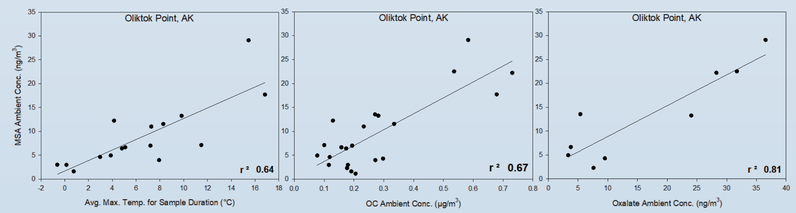

Figure 8. The ambient concentrations of MSA plotted against the average maximum temperature for the sample duration, the OC ambient concentration, and the oxalate ambient concentration at Oliktok Point, AK.

Table 1. The average ratio of Organic Acids to Organic Mass for each year at each site.

Year	Utqiaġvik Organic Acid: Organic Mass	Oliktok Point Organic Acid: Organic Mass
2012	0.105	---
2015	0.059	0.041
2016	0.111	0.051
2017	0.211	0.145

Conclusions

- Organic carbon is dominated by contemporary carbon sources in the summertime NSA, despite differences in local activity.
- A major fraction of that organic carbon is organic acids, including MSA, which are implicated in new particle formation in Arctic marine regions.
- Temperature appears to be a major driver in biogenic carbonaceous aerosol during the summer on the North Slope. This may impact both marine and terrestrial emissions.

Future Work

- Additional investigation is planned to understand how these marine and biogenic emissions impact aerosol processes in the Arctic.