Vaios Moschos :: PhD student :: Paul Scherrer Institute (Switzerland)

Characterization of organic aerosol across the Arctic land surface

Imad El Haddad¹, Vaios Moschos¹, Julia Schmale¹,², Urs Baltensperger¹, André S.H. Prévôt¹, and the iCUPE collaboration

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¹Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, Villigen-PSI, Switzerland (vaios.moschos@psi.ch)
²EPFL Valais Wallis, Extreme Environments Research Laboratory, Switzerland
Ongoing (emission) changes in the Arctic

Arctic Haze
-35% since 1979 (!)

Arctic Sea Ice
1984: 6.79 million square kilometers (2.60 million square miles)
2012: 3.41 million square kilometers (1.32 million square miles)

Polar tourism, shipping?

Svalbard (Spitzbergen)

The Arctic is melting – but it’s also on fire

gas flaring (VOCs?) for oil/gas extraction
expanding vegetation, increasing wildfires

1. AMAP (2006)
2. Can declines in Arctic sea ice impact the weather over Europe? (viewed 12/12/19) petrieruth.wordpress.com
3. Expansion du tourisme de croisière dans l’Arctique canadien […] (viewed 12/12/19) corpus.ulaval.ca
4. Gas flaring and household stoves speed Arctic thaw (viewed 12/12/19) www.iiasa.ac.at
5. Why the Arctic is smouldering (viewed 12/12/19) www.bbc.com
6. The World’s Largest Forest Has Been on Fire for Months (viewed 12/12/19) www.bloomberg.com
Climate projections & (aerosol) Observations

Scarce (aerosol) observational data in climate-sensitive Arctic

In winter the sea ice extent is maximum!

Build a global Earth observatory

More «global brightening» in the future?

BUT: Uncertain evolution of OC in the Arctic!

1. KNMI Climate Change Atlas (accessed 12/12/19) climexp.knmi.nl
2. Wobus (2016) Earth’s Future
3. RCP Database, version 2.0 (generated 07/11/19)
Organic-containing aerosols in the Arctic

- Near-surface Arctic land stations: Aerosol transport pathways in winter vs summer[1]?
- Eurasia is the major lower atmospheric source region of transported Arctic air pollution[2,3]
- Strong eBC seasonality with winter high (Arctic Haze) and summer low, altitude sensitivity[4]
- Organic aerosol local production during/after polar sunrise[5] (open ocean, photochemistry)
- Abundant[6] Arctic OA interacts[7] with other aerosol components (soot[8], sulfate[9], metals[10])

Motivation

Organic aerosols (OA) both absorb and scatter light depending on the sources (anthropogenic/biogenic) & long-range transportation/atmos. processing\(^1\) and can alter the cloud properties.

Organic species are abundant (also in the Arctic) and can modulate, augment or offset the radiative forcing from other aerosol components\(^2\).

Multiple directions of future OA-climate interactions possible at different Arctic regions\(^3\).

Models have trouble capturing the seasonality of the observed aerosol mass, under(over)-prediction for winter (summer) months, poor representation of SOA & constraint of OA sources.

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**Short-term online AMS-PMF at Villum (NE Greenland)**

5. Shaw (2010) GRL
6. Fu (2013) Biogeosciences

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**FTIR organic functional groups & PMF factors at Barrow, Alaska**

AMS: Aerosol Mass Spectrometry; PMF: Positive Matrix Factorization; FTIR: Fourier-transform infrared spectroscopy

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**GC/MS-based Arctic Ocean-influenced (marine) OA**
Objectives of circum-Arctic offline campaign

1. Comprehensive observation of understudied Arctic OA, for **accurate representation in climate models** & realistic assessment of the effectiveness of potential climate mitigation (e.g., blend of emission sources to be targeted) or adaptation actions.

2. **Temporal & inter-annual evolution** of Arctic OA composition as documentation of **ongoing changes** (anthropogenic- and climate change-induced), providing a **reference point** for future comparisons.

3. Identification of **spatial variability** in OA composition and source emission strengths across the Arctic land surface.

4. Close huge gaps of aerosol (a) observational capacity during the **dark and cold winter** (polar night) and (b) spatial coverage in the vast **Russian Arctic**.

5. Provide link between quantitative AMS-PMF & **molecular fingerprinting**, for a deepened understanding of the atmospheric processing of Arctic organic species.
Spatial coverage of collected samples

Collaborative network for filter (station) collection including six Arctic Council nations, led by PSI
Both human-influenced & remote environments represented

Extension of offline HR-AMS technique coverage to the most climate change sensitive region

SNF scientific exchanges visit of Prof. Olga Popovicheva (Lomonosov Moscow State University) for Russian filters

[1] Adapted from: arcticportal.org/images/maps/small/1.8.jpg
# Temporal coverage & Data availability

<table>
<thead>
<tr>
<th>Station</th>
<th>Country</th>
<th>Coordinates/Altitude</th>
<th>Polar night</th>
<th>Midnight sun</th>
<th>Type of samples</th>
<th>Available data sets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrow</td>
<td>USA</td>
<td>71.4 N 156.8 W, 8 masl</td>
<td>19.11 to 23.01</td>
<td>11.05 to 01.08</td>
<td>HiVol, QF, TSP</td>
<td>OC/EC, major ions, 14C OC, LMW organic acids &amp; (selected) organic speciation by GC-MS</td>
</tr>
<tr>
<td>Alert</td>
<td>Canada</td>
<td>82.3 N 62.2 W, 210 masl</td>
<td>14.10 to 28.02</td>
<td>07.04 to 04.09</td>
<td>HiVol, QF, TSP</td>
<td>OC/EC, major ions, 14C/13C (Stockholm)</td>
</tr>
<tr>
<td>Villum</td>
<td>Denmark</td>
<td>81.4 N 16.4 W, 0 masl</td>
<td>16.10 to 25.02</td>
<td>-9.04 to 02.09</td>
<td>HiVol, QF, PM10</td>
<td>OC/EC, major ions (TSP), Aethalometer</td>
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<tr>
<td>Zeppelin</td>
<td>Norway</td>
<td>78.9 N 11.9 E, 475 masl</td>
<td>26.10 to 15.02</td>
<td>20.04 to 20.08</td>
<td>HiVol, QF, PM10</td>
<td>OC/EC, 14C OC (Bern), ice nuclei (Basel), cellulose (Vienna), org tracers, sugars, AE33</td>
</tr>
<tr>
<td>Gruvebadet</td>
<td>Norway</td>
<td>78.9 N 11.5 E, 10 masl</td>
<td>26.10 to 15.02</td>
<td>20.04 to 20.08</td>
<td>LowVol, QF, PM10</td>
<td>OC/EC, ACSM(?)</td>
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<tr>
<td>Pallas</td>
<td>Finland</td>
<td>68.0 N 24.1 E, 565 masl</td>
<td>10.12 to 02.01</td>
<td>27.05 to 17.07</td>
<td>HiVol, QF, PM10</td>
<td>OC/EC (semi-continuously), major ions (teflon/PM2.5), trace elements (teflon), PAHs (teflon), acidic gases</td>
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<tr>
<td>Baranova</td>
<td>Russia</td>
<td>79.2 N 101.5 E, 30 masl</td>
<td>22.10 to 22.02</td>
<td>22.04 to 22.08</td>
<td>n.a., QF, n.a.</td>
<td>OC/EC, elements (XRF), AE eBC, concentration-weighted trajectories</td>
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<tr>
<td>Tiksi</td>
<td>Russia</td>
<td>71.4 N 128.5 E, 1 masl</td>
<td>19.11 to 24.01</td>
<td>11.05 to 03.08</td>
<td>LowVol, QF, TSP</td>
<td>OC/EC, major ions (CE &amp; IC), AE eBC, trace elements (XRF)</td>
</tr>
</tbody>
</table>

More than 10yrs of filter-based cumulative data
First results on samples from 7 sites;
→ TOC analyser (WSOC)
→ HPLC-PAD (polyols & sugars)

WSOC:OC 62 ± 21% (blank-subtracted)
Levo in winter, biogenics in summer (PAL)

Remaining sample analyses ongoing,
also with HPLC-MS (organic acids)
& IC (inorganic anions/cations)
(for data not available already by Arctic collaborators)

<table>
<thead>
<tr>
<th>Sample ID (YYYY/MM/DD)</th>
<th>erythritol [ng/m^3]</th>
<th>xylitol [ng/m^3]</th>
<th>arabitol [ng/m^3]</th>
<th>sorbitol [ng/m^3]</th>
<th>mannitol [ng/m^3]</th>
<th>trehalose [ng/m^3]</th>
<th>levoglucosan [ng/m^3]</th>
<th>mannosan [ng/m^3]</th>
<th>galactosan [ng/m^3]</th>
<th>Rhamnose [ng/m^3]</th>
<th>glucose [ng/m^3]</th>
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<td>PAL_20190204 (winter)</td>
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<tr>
<td>PAL_20190624 (summer)</td>
<td>216.55</td>
<td>24.41</td>
<td>17.77</td>
<td>11.39</td>
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<td>29.06</td>
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</tbody>
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Offline AMS (organic) aerosol mass spectra

Typical measurement cycle (Russian Arctic filter samples)

Average UMR mass spectrum of the extracted aerosol fragments (all samples+water blanks)

Relative intensity of fitted UM-HR organic fragment groups (all samples+water blanks)

Feasibility check using ~50 samples (sample vs blank signal, variability in fragment ion composition among different sites/seasons)

Measurement of water extracts in Argon with Long-ToF-AMS (e⁻ impact, resolution ~7k avg)

UM(R): Unit Mass (Resolution); HR: High Resolution

UMR (Squirrel) & HR (Pika) preliminary analysis
Main fragment ion correlations

Individual (averaged) samples CO\(^+\) vs CO\(_2\)^+ assumed linear 1:1\(^{[1]}\) if measuring in N\(_2\)/O\(_2\) (N\(_2\) signal dominates m/z=28)

CO\(^+\):CO\(_2\)^+ ~ 0.40 ± 0.14,
No trend (yet) with season/station; lower limit for the ambient aerosol (only WS-OA fraction measured by the offline AMS technique)

Literature ratio ~ 0.59 ± 0.10\(^{[2]}\), season- (or T-) dependent

fCO\(_2\) (m/z=44) of 0.26 ± 0.08, more oxidized than continental OA fC\(_2\)H\(_3\)O (m/z=43) in the low range of previous observations

x5-10 lower levoglucosan fragment signal than at lower latitudes Expected due to degradation upon transportation to remote sites
Exception: Pallas winter (next to European Arctic Circle)

Fragment ion correlations & HR fitting
Significant spatial & temporal (bulk) variability despite using (bi-)weekly samples
More oxidized samples at the most remote sites (ALT, ZEP, BRW) during fall/winter

Fitted data: Slope = -0.55 & Intercept = 1.73 (r = 0.96),
consistent with OOA evolution\(^{[1,2]}\) (correlation of O:C with fCO\(_2\))

Primary OA-influenced samples (O:C < 0.55, H:C > 1.4)\(^{[1,3]}\) exhibit steeper slope (down to -2.0)\(^{[4]}\)

1. Hu (2013) ACP
2. Ng (2011a) ACP
3. Daellenbach (2017) ACP
4. Lambe (2012) ES&T
Variability in OA fragment composition

October 2015, Baranova
H:C = 1.53
O:C = 0.53

October 2015, Alert
H:C = 0.81
O:C = 1.64

Spatial variability in the OA fragment composition (functional groups)[1]

Pollution transport from mainland Russia, versus oxygenated fragment ions during transition to polar night

1. Petäjä (2020) ACPD
Summary & Ongoing work

Spatio-temporal dependence in OA fragment composition by offline L-ToF-AMS

Largely expected fragment ion correlations, enabling the application of AMS-PMF

No implications related to the low mass loadings in filter analyses performed so far

Finalization of supporting external measurements (WSOC/OC, ions, sugars, org. acids)

Offline data treatment & PMF analysis on full data set obtained from L-ToF-AMS

Long-term back-trajectory analysis on individual PMF-based OA source components

Molecular characterization of Arctic filter samples for AMS-PMF interpretation/validation
Acknowledgements
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- The European Union’s Horizon 2020 (H2020) research and innovation programme, under grant agreement No 689443 via project iCUPE (Integrative & Comprehensive Understanding on Polar Environments)
- The Swiss National Science Foundation (SNSF, grant no. 187566, “Source Apportionment of Russian Arctic Aerosol, SARAA“)
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• QUESTIONS ?