PAUL SCHERRER INSTITUT

LABOR FÜR ATMOSPHÄREN-CHEMIE

[Abstract]


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# Characterization of organic aerosol across the Arctic land surface

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European Geosciences Union, General Assembly 2020 (Display), May 2020

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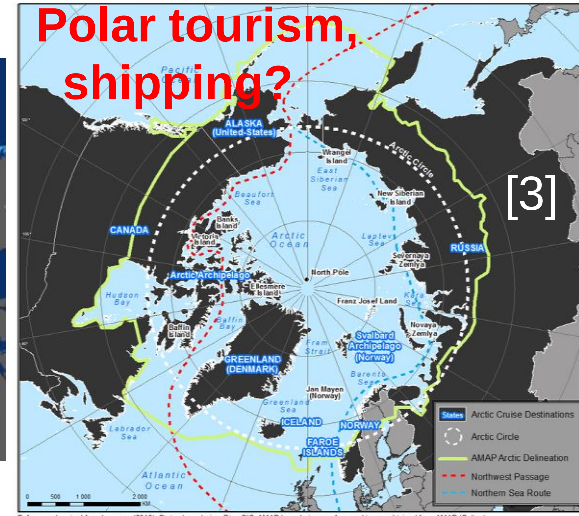
[2]*EPFL Valais Wallis, Extreme Environments Research Laboratory, Switzerland*

# Ongoing (emission) changes in the Arctic

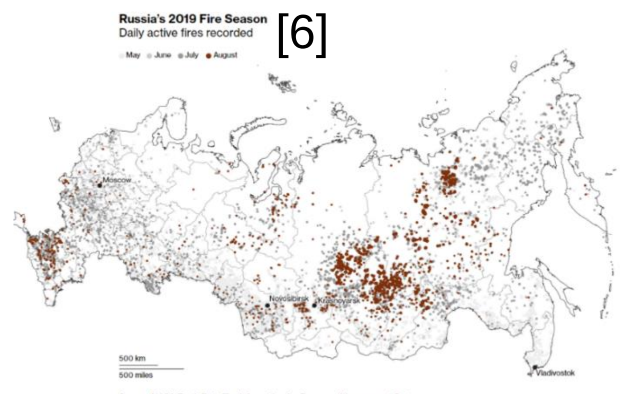

**-35% since 1979 (!)**

Reference: Inspired from Lasserre (2010); States boundaries: Diva-GIS; AMAP boundaries: georeferenced image obtained from AMAP (Online)

The Arctic is **melting** – but it's also **on fire**


*gas flaring (VOCs?) for oil/gas extraction*

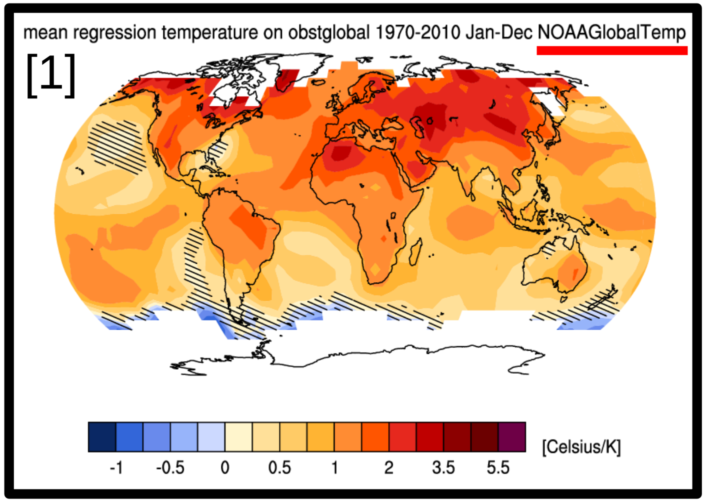



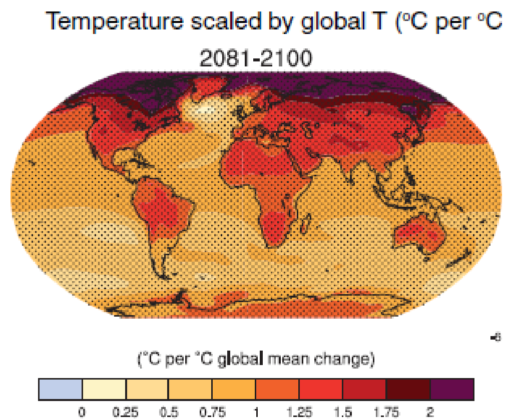

*expanding vegetation, increasing wildfires*


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

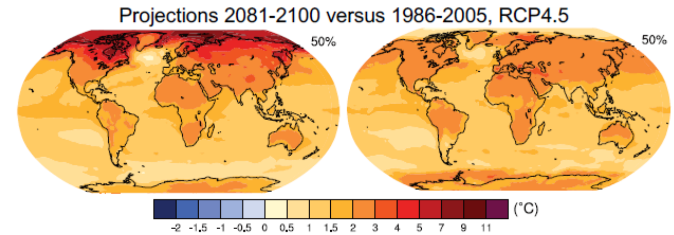


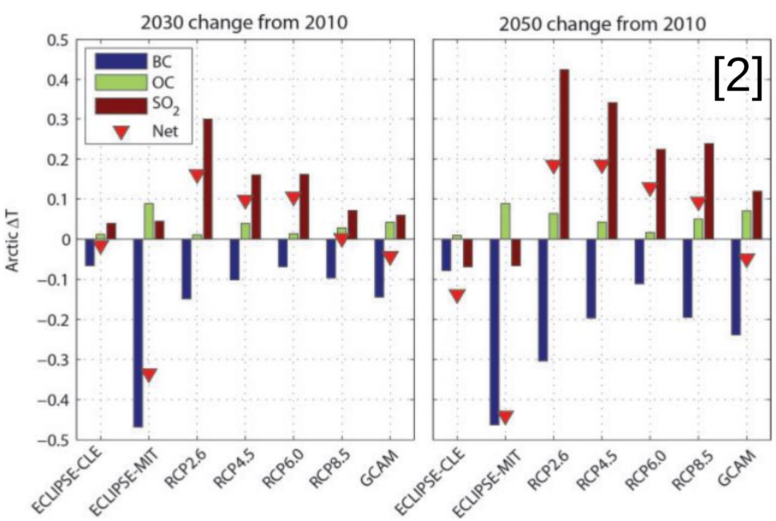

(IPCC, AR5, Ch12)

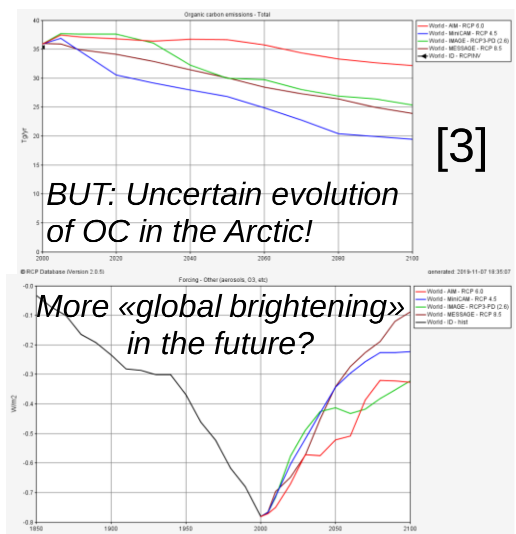
**Seasonal cycle** (IPCC, AR5, App1)

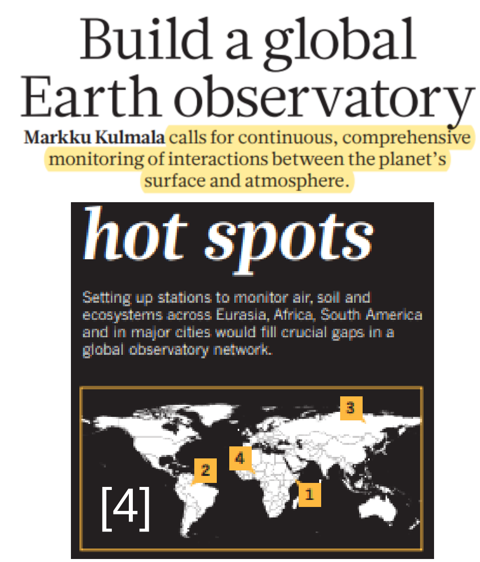
**DJF** **JJA**




*In winter the sea ice extent is maximum!*



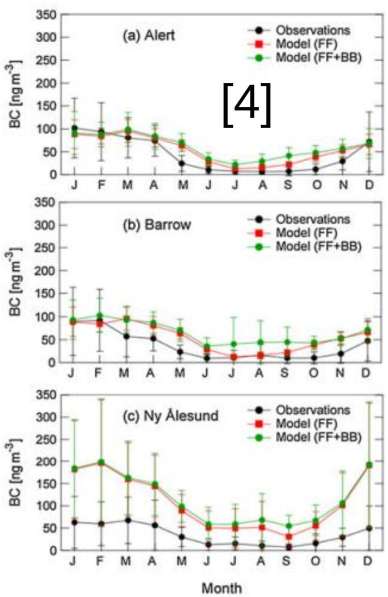



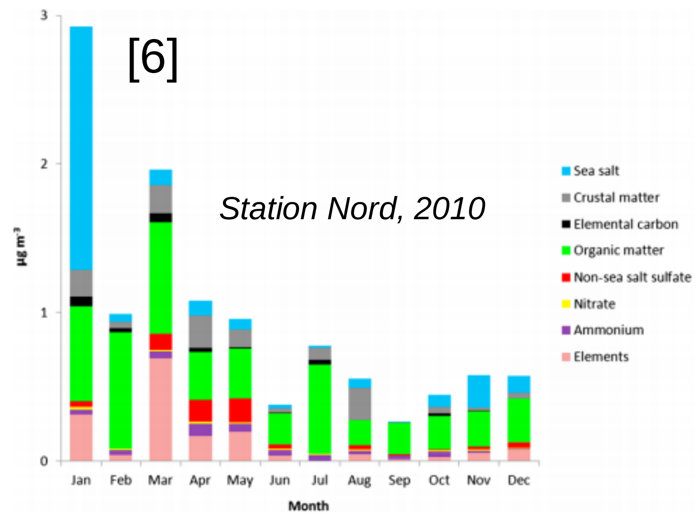


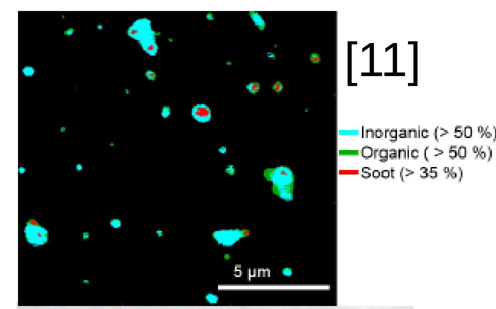
1. KNMI Climate Change Atlas (accessed 12/12/19) climexp.knmi.nl
2. Wobus (2016) Earth's Future
3. RCP Database, version 2.0 (generated 07/11/19)
4. Kulmala (2018) Nature

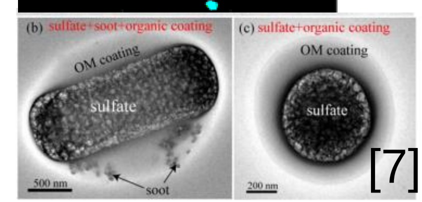
# Organic-containing aerosols in the Arctic

- 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])




1. Willis (2018) Rev. Geophys. 2. Sharma (2019) JGR Atmos. 3. Law (2007) Science
4. Sharma (2013) JGR Atmos. 5. Kawamura (1996) Atmos. Environ. 6. Nguyen (2014) JGR Atmos.
7. Yu (2019) ACP 8. AMAP (2015) 9. Kirpes (2018) ACP 10. Shaw (2010) GRL 11. Kirpes (2018) ACP

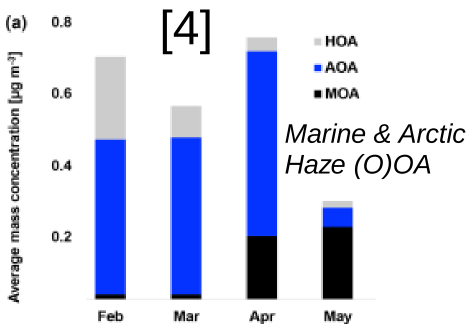
# Motivation

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.

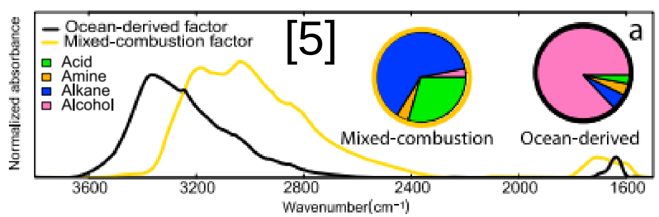
Organic species are abundant (also in the Arctic) and can modulate, augment or offset the radiative forcing from other aerosol components[2].

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.



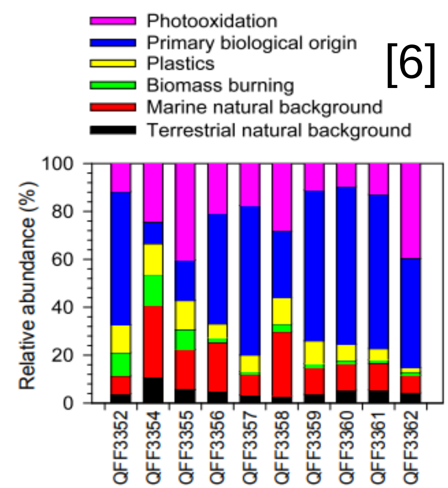

*Short-term online AMS-PMF at Villum (NE Greenland)*




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

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

*GC/MS-based Arctic Ocean-influenced (marine) OA*





1. Moschos (2018) ES&T Lett.
2. Schmale (2018) Earth's Future
3. Scott (2018) Nat. Geosci.
4. Nielsen (2019) ACP
5. Shaw (2010) GRL
6. Fu (2013) Biogeosciences

# 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.

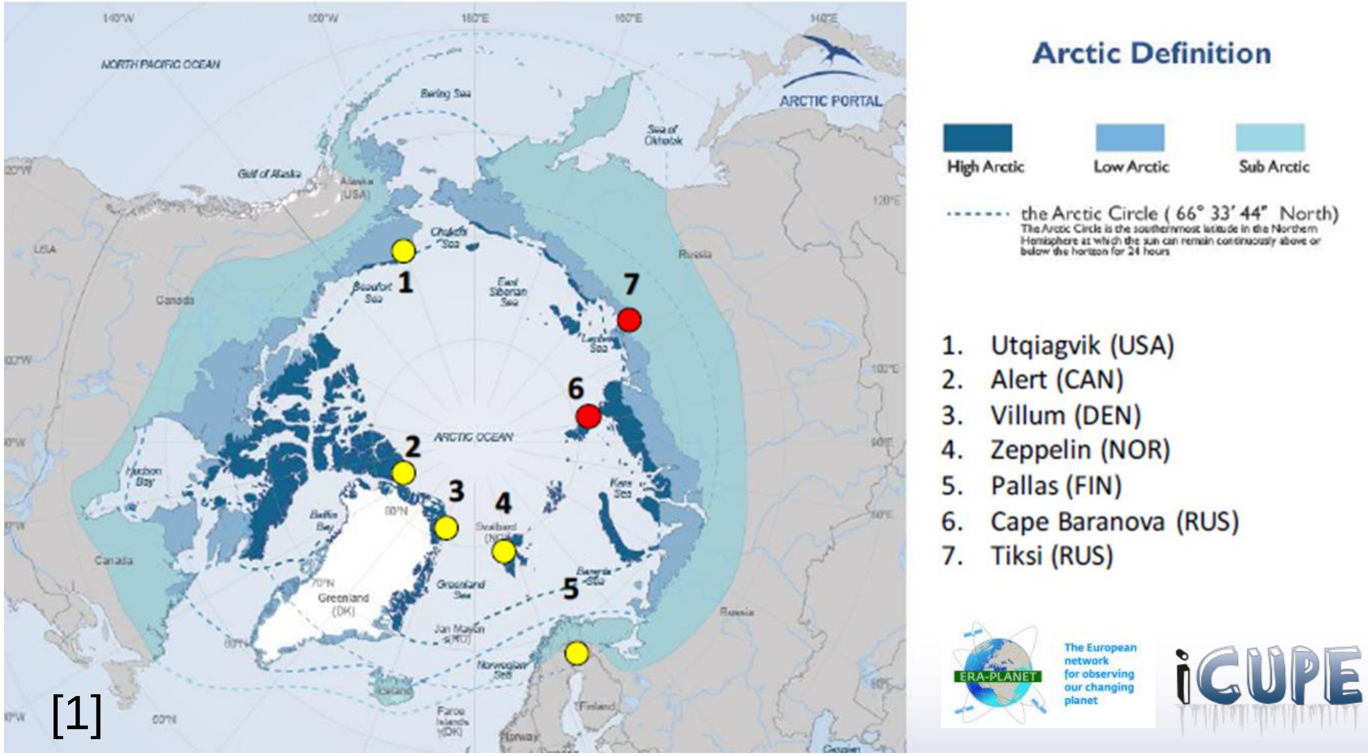
2. **Temporal & inter-annual evolution** of Arctic OA composition as documentation of **ongoing changes** (anthropogenic- and climate change-induced), providing a **reference point** for future comparisons.

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




## Collaborators

FINNISH METEOROLOGICAL INSTITUTE

NILU Norsk institutt for luftforskning Norwegian Institute for Air Research

Lomonosov Moscow State University

INFN Istituto Nazionale di Fisica Nucleare

BAYLOR UNIVERSITY

AARHUS UNIVERSITY

Environment and Climate Change Canada

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

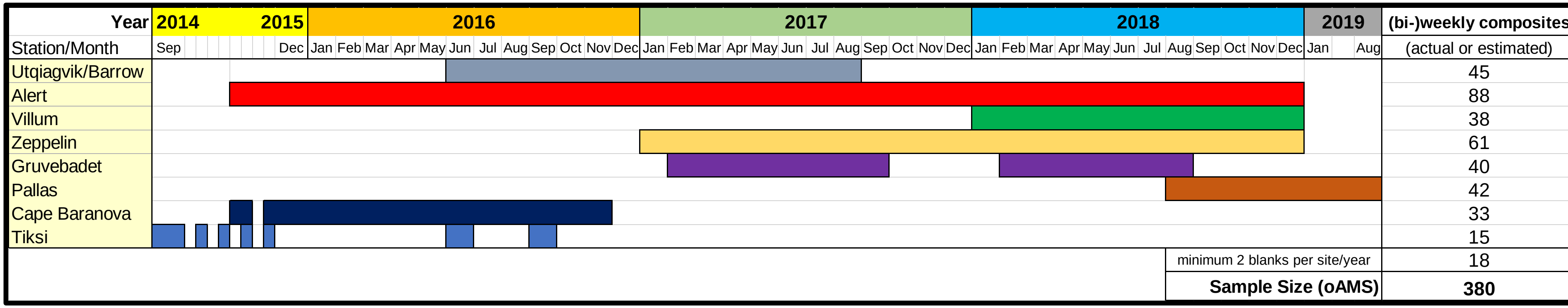
Extension of offline HR-AMS technique coverage to the most climate change sensitive region

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

*Own aerosol sampling in Pallas (Matorova)*

[1] Adapted from: arcticportal.org/images/maps/small/1.8.jpg

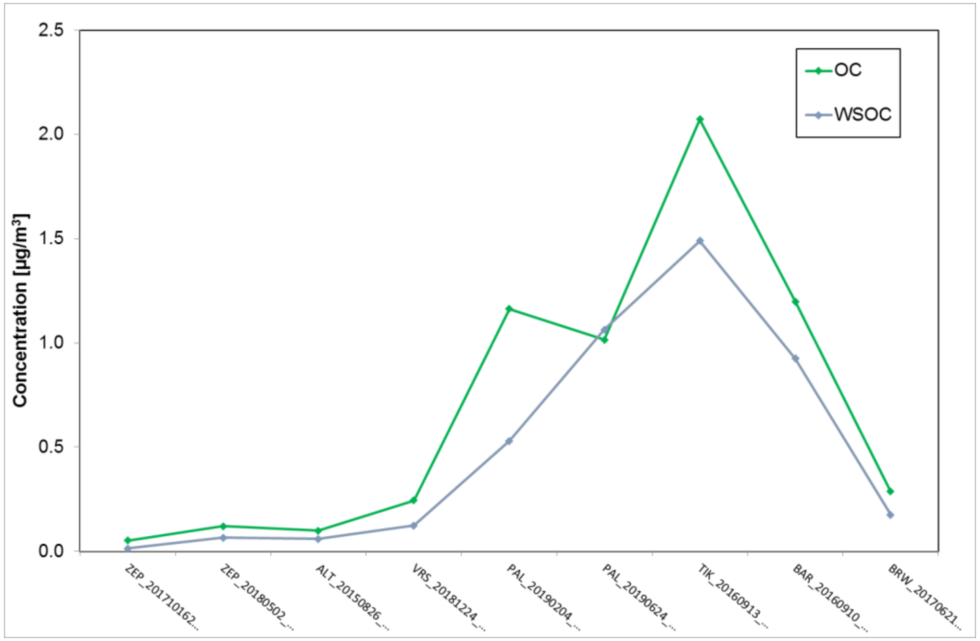
# Temporal coverage & Data availability




More than 10yrs of filter-based cumulative data

| Station | Country | Coordinates/Altitude | Polar night | Midnight sun | Type of samples | Available data sets |
|---|---|---|---|---|---|---|
| Barrow | USA | 71.4 N 156.8 W, 8 masl | 19.11 to 23.01 | 11.05 to 01.08 | HiVol, QF, TSP | OC/EC, major ions, 14C OC, LMW organic acids & (selected) organic speciation by GC-MS |
| Alert | Canada | 82.3 N 62.2 W, 210 masl | 14.10 to 28.02 | 07.04 to 04.09 | HiVol, QF, TSP | OC/EC, major ions, 14C/13C (Stockholm) |
| Villum | Denmark | 81.4 N 16.4 W, 0 masl | 16.10 to 25.02 | ~09.04 to 02.09 | HiVol, QF, PM10 | OC/EC, major ions (TSP), Aethalometer |
| Zeppelin | Norway | 78.9 N 11.9 E, 475 masl | 26.10 to 15.02 | 20.04 to 20.08 | HiVol, QF, PM10 | OC/EC, 14C OC (Bern), ice nuclei (Basel), cellulose (Vienna), org tracers, sugars, AE33 |
| Gruvebadet | Norway | 78.9 N 11.5 E, 10 masl | 26.10 to 15.02 | 20.04 to 20.08 | LowVol, QF, PM10 | OC/EC, ACSM(?) |
| Pallas | Finland | 68.0 N 24.1 E, 565 masl | 10.12 to 02.01 | 27.05 to 17.07 | HiVol, QF, PM10 | OC/EC (semi-continuously), major ions (teflon/PM2.5), trace elements (teflon), PAHs (teflon), acidic gases |
| Baranova | Russia | 79.2 N 101.5 E, 30 masl | 22.10 to 22.02 | 22.04 to 22.08 | n.a., QF, n.a. | OC/EC, elements (XRF), AE eBC, concentration-weighted trajectories |
| Tiksi | Russia | 71.4 N 128.5 E, 1 masl | 19.11 to 24.01 | 11.05 to 03.08 | LowVol, QF, TSP | OC/EC, major ions (CE & IC), AE eBC, trace elements (XRF) |

# External measurements




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)

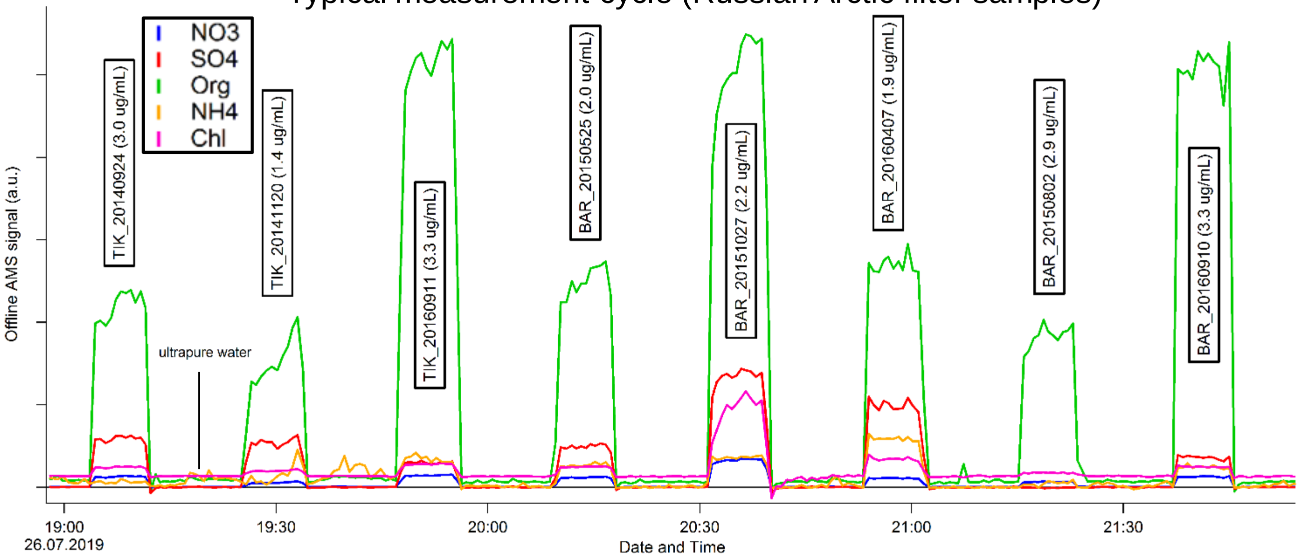
Remaining sample analyses ongoing,
also with HPLC-MS (organic acids)
& IC (inorganic anions/cations)
(for data not available already by Arctic collaborators)

| | erythritol | xylitol | arabitol | sorbitol | mannitol | trehalose | levoglucosan | mannosan | galactosan | Rhamnose | glucose |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample ID (YYYY/MM/DD)** | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] | [ng/m^3] |
| **BAR_BR16QIFieldBlank** | - | - | - | - | - | - | - | - | - | - | - |
| **ZEP_2017101624** | | | | | | | 0.23 | | | | |
| **ZEP_20180502** | | | | | | | | | | | |
| **ALT_20150826** | | | 0.15 | | | | | | | | |
| **VRS_20181224** | | | | | | | 2.13 | 0.37 | | | |
| **PAL_20190204** *(winter)* | 6.82 | | | | | | 29.06 | 3.35 | | | 3.02 |
| **PAL_20190624** *(summer)* | 216.55 | | 24.41 | | 17.77 | 11.39 | | | | | 30.34 |
| **TIK_20160913** | 7.41 | | 3.31 | | 4.17 | | 12.33 | 3.36 | 0.97 | | 2.93 |
| **BAR_20160910** | 5.79 | | | | | | 10.79 | 1.24 | | | |
| **BRW_20170621** | | | 1.39 | | 1.18 | | | | | | 2.65 |

*empty cells: below LOD*

# Offline AMS (organic) aerosol mass spectra

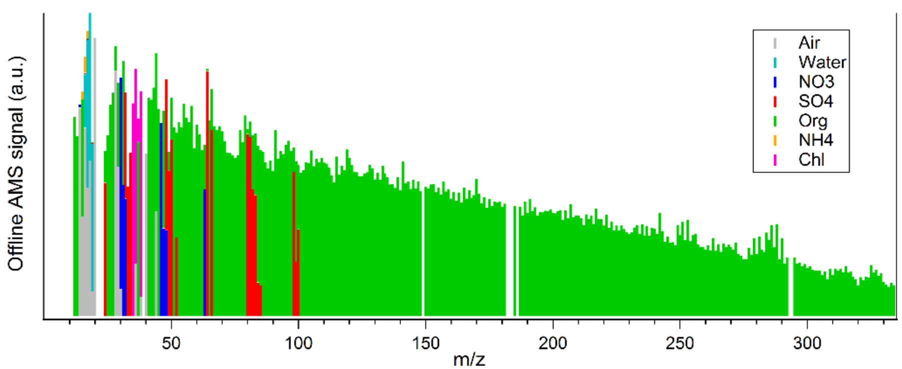
Typical measurement cycle (Russian Arctic filter samples)



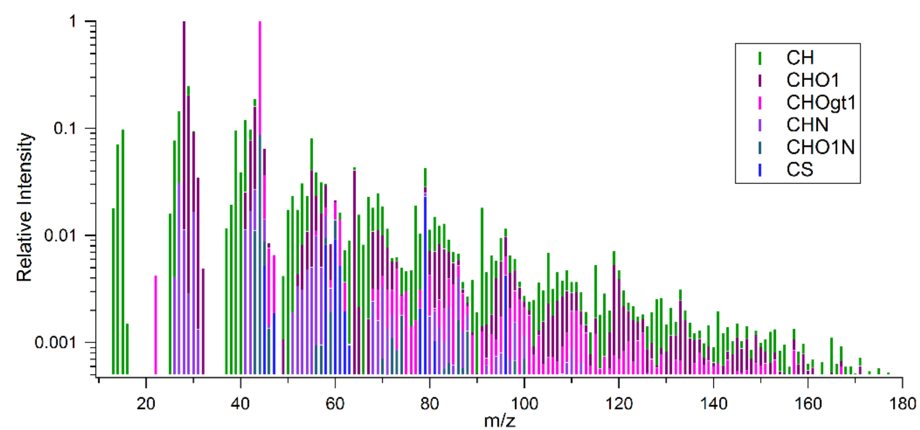

UMR (Squirrel) & HR (Pika) preliminary analysis

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

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



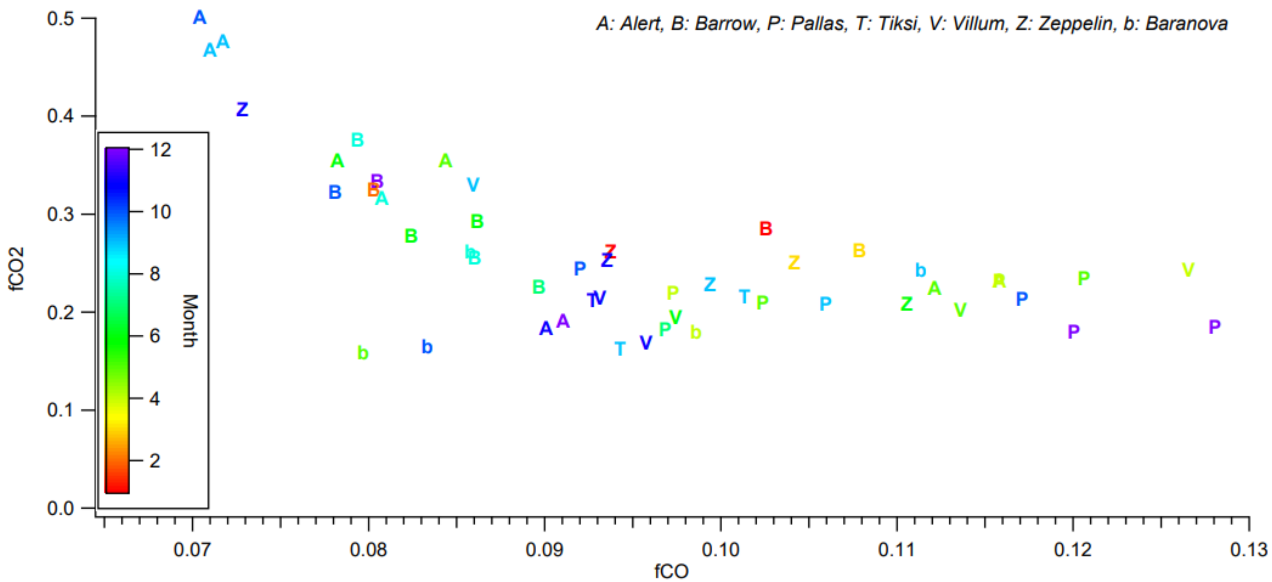

Relative intensity of fitted UM-HR organic fragment groups (all samples+water blanks)




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

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

# Main fragment ion correlations

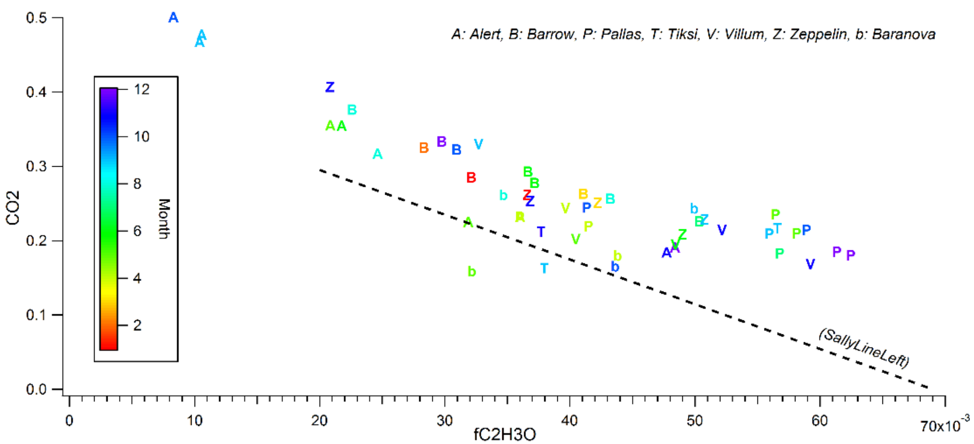


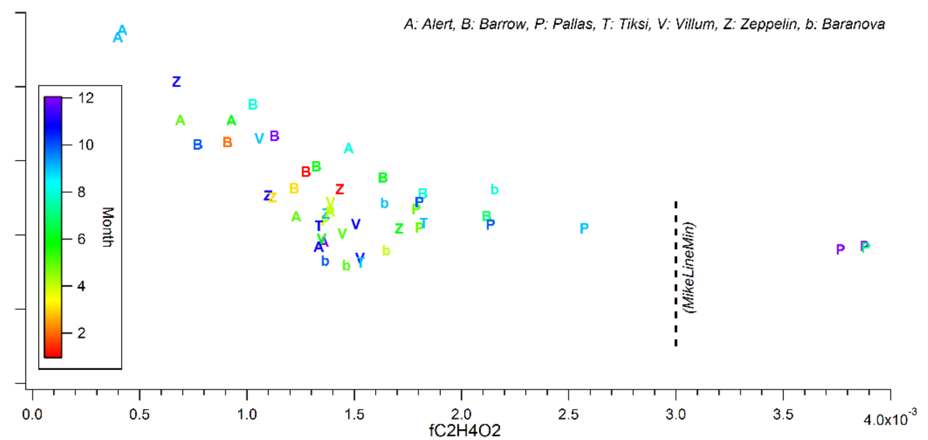

Individual (averaged) samples

$CO^+$ 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



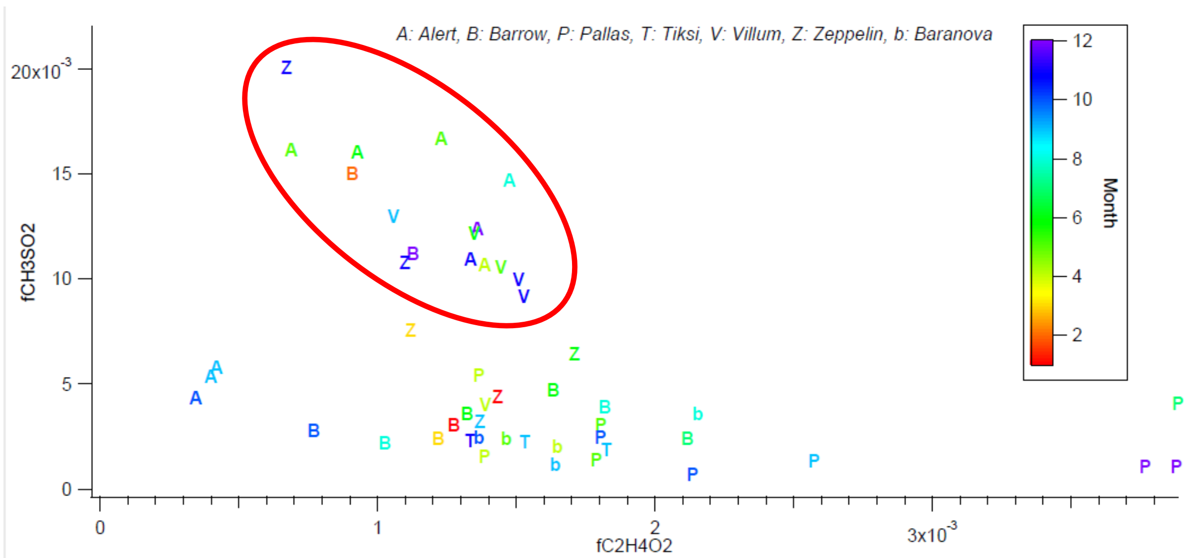

$fCO_2$ (m/z=44) of 0.26 ± 0.08, more oxidized than continental OA
$fC_2H_3O$ (@m/z=43) in the low range of previous observations

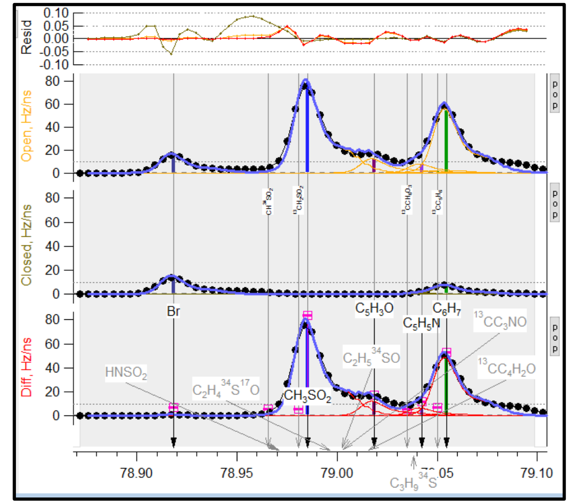
x5-10 lower levoglucosan fragment signal than at lower latitudes
Expected due to degradation upon transportation to remote sites
Exception: Pallas winter (next to European Arctic Circle)

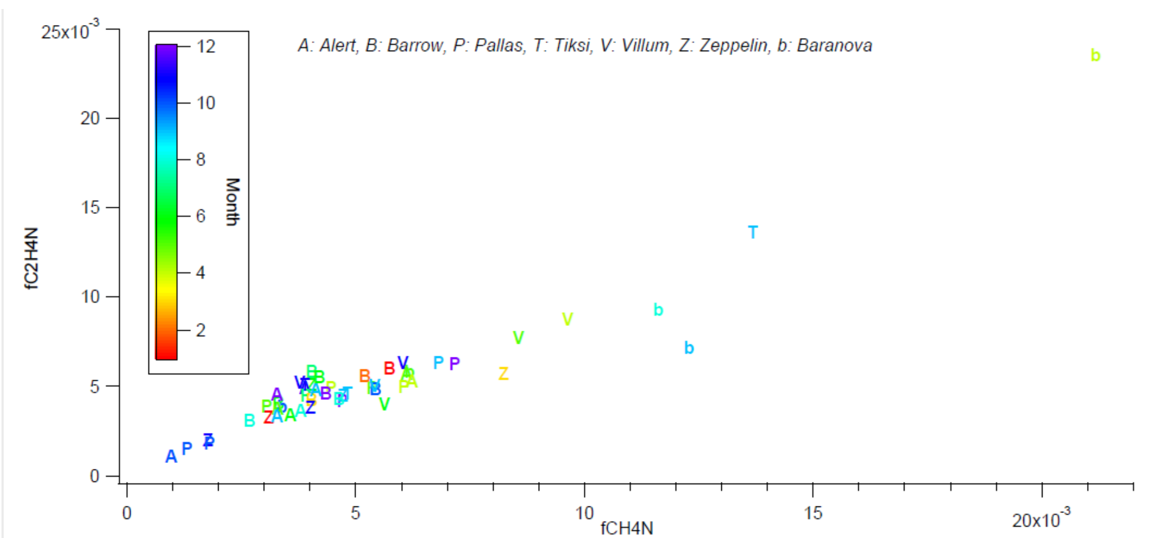


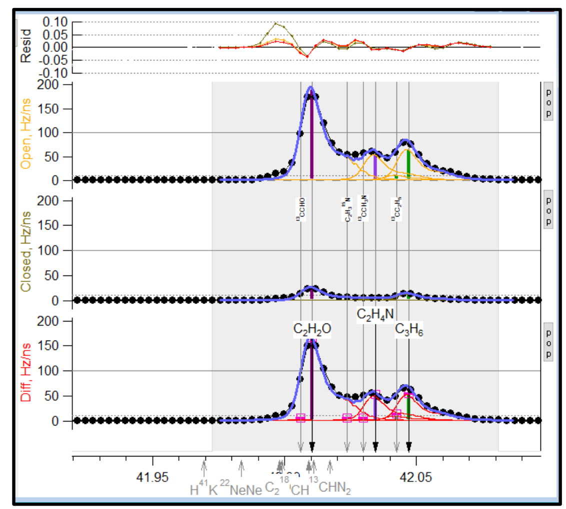
1. Aiken (2008) ES&T 2. Bozzetti (2017) ACP

# Fragment ion correlations & HR fitting

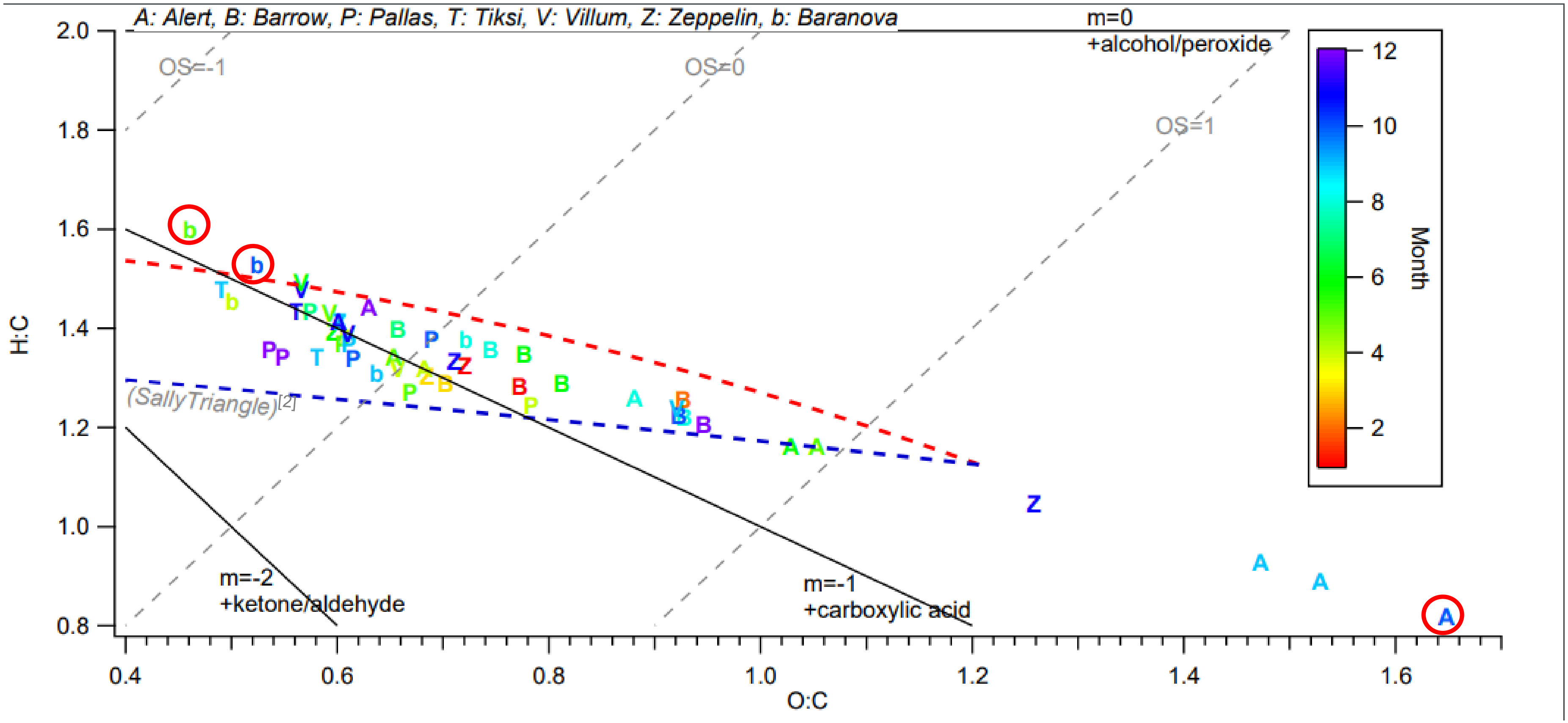


# Van Krevelen diagram for Arctic filters




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

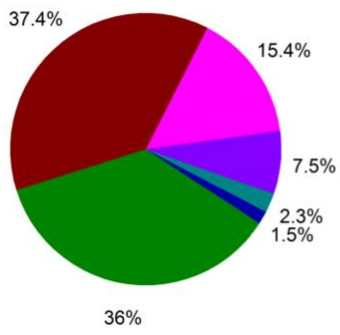
Fitted data: Slope = -0.55 & Intercept = 1.73 (r = 0.96),
consistent with OOA evolution[1,2] (correlation of O:C with $fCO_2$)

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

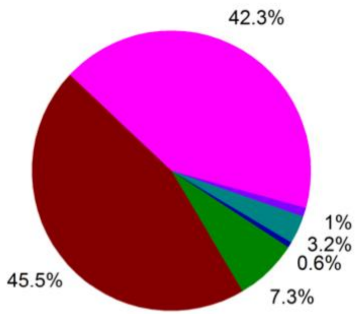

1. Hu (2013) ACP
2. Ng (2011a) ACP
3. Daellenbach (2017) ACP
4. Lambe (2012) ES&T

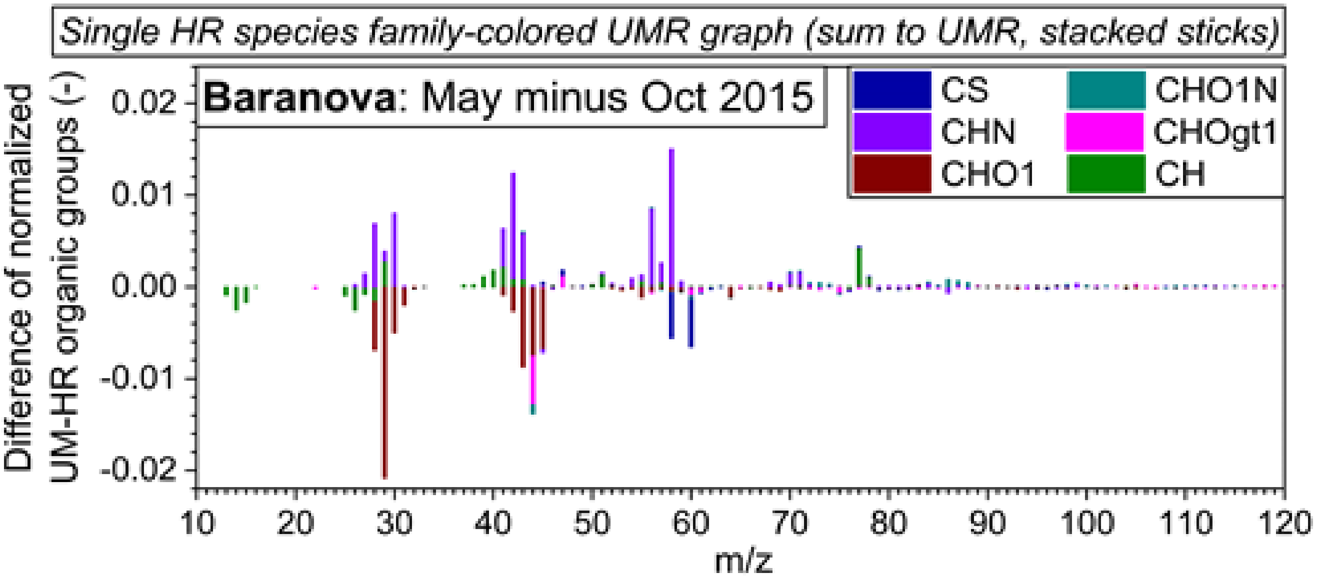
# Variability in OA fragment composition

October 2015,
<u>Baranova</u>
H:C = 1.53
O:C = 0.53




October 2015,
<u>Alert</u>
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

# Wir schaffen Wissen – heute für morgen


## Acknowledgements

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- The Swiss National Science Foundation (SNSF, grant no. 187566, “Source Apportionment of Russian Arctic Aerosol, SARAA”)

VM acknowledges the A.G.Leventis Foundation for a doctoral student Educational Grant


- QUESTIONS ?