

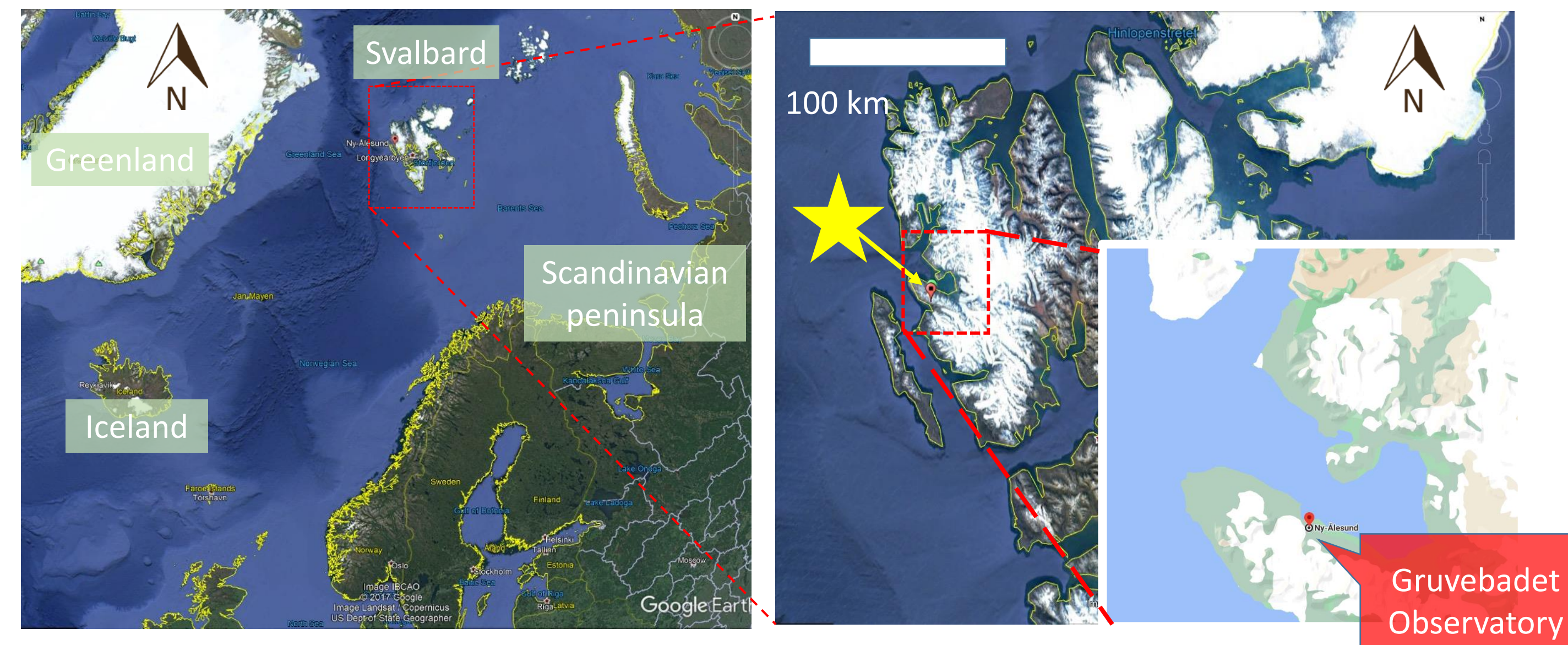
Abundance of ice-nucleating particles (INPs) from the Gruebadet observatory in Svalbard during 2017-2019

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Goals

- ❖ Generating new immersion mode INP concentration (n_{INP}) data from Ny-Ålesund (Spitsbergen, Svalbard) during 2017-2019.
- ❖ Comparing atmospheric n_{INP} to the concentrations of aerosol particle tracers.
- ❖ Complement our knowledge of INPs – would ambient n_{INP} increase in the Arctic region in response to warming^[1]?



n_{INP} Derivation & Detection Limit (DL)

The $C_{INP}(T)$ value, which is the nucleus concentration in pure water suspension (L^{-1} water) at a given T ^[5], was calculated as a function of unfrozen fraction, $f_{unfrozen}(T)$ (i.e., the ratio of number of droplets unfrozen to the total number of droplets) as:

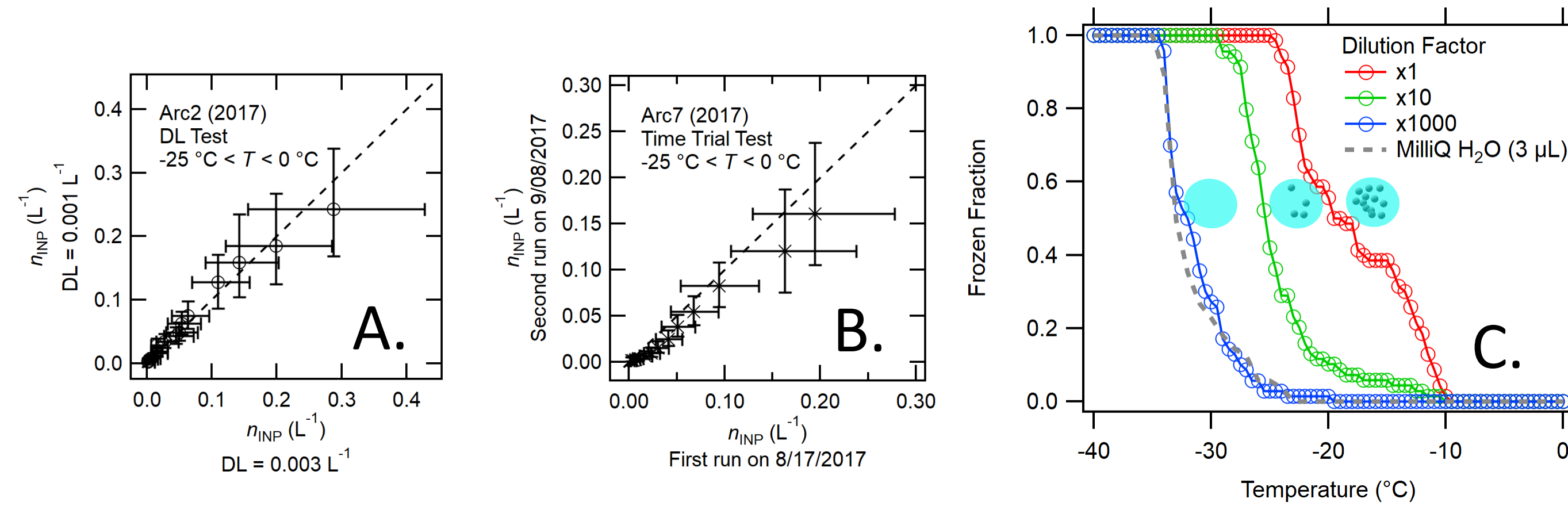
$$C_{INP}(T) = -\frac{\ln(f_{unfrozen}(T))}{V_d} \quad (1)$$

in which, V_d is the volume of individual droplets ($3 \mu L$). Next, we converted $C_{INP}(T)$ to $nINP(T)$. The cumulative n_{INP} per unit volume of sample air (L^{-1} air) was estimated as:

$$nINP(T) = C_{INP}(T) \times DF \times \frac{V_i}{V_{air}} \quad (2)$$

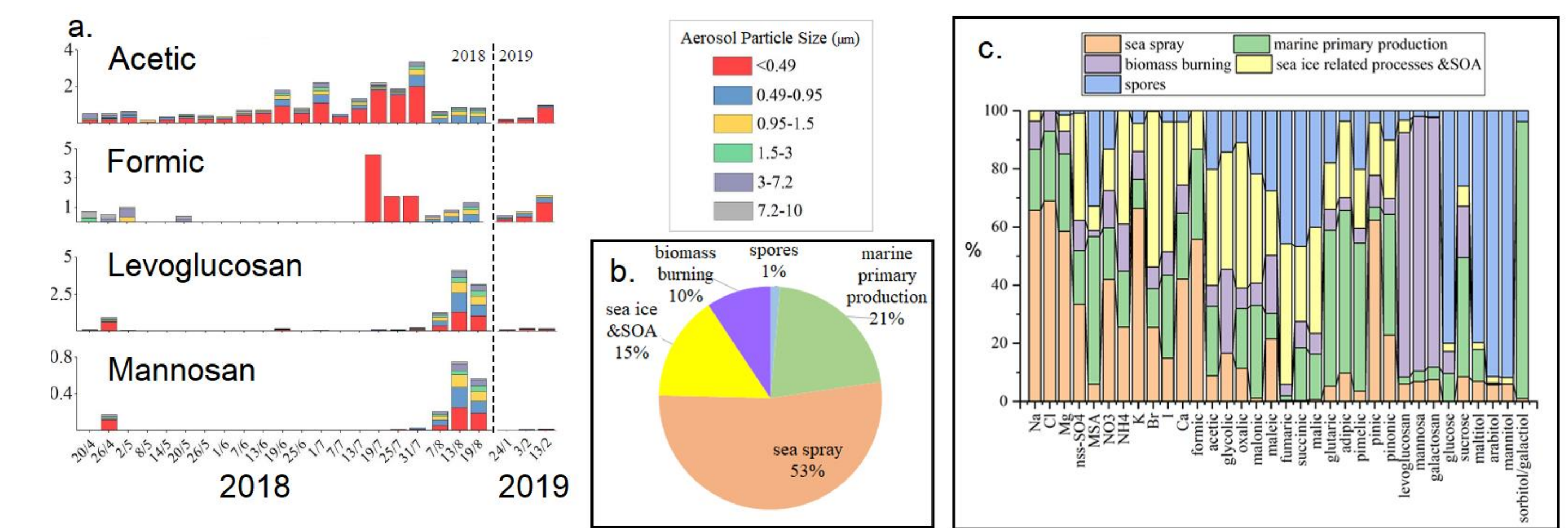
where DF is a serial dilution factor (e.g., DF = 1 or 10 or 100 and so on). The sampled air volume (V_{air}) and the suspension volume (V_i) are computed to optimize the detection limit ($0.0005 - 0.001 L^{-1}$) for each sample.

▼ Our detection limit variation and time trial tests verified that [A] varying DL for a factor of three did not impact measured n_{INP} at T_s below $-25^\circ C$ and [B] storing a sample for ~ 3 weeks at $4^\circ C$ did not alter n_{INP} beyond the 95% confidence interval with our DL. From [C], we also demonstrated that our method is reasonable to estimate n_{INP} down to $-25^\circ C$ without substantial artifacts, and the sample could be diluted until frozen fraction collapsed onto the water background spectrum.



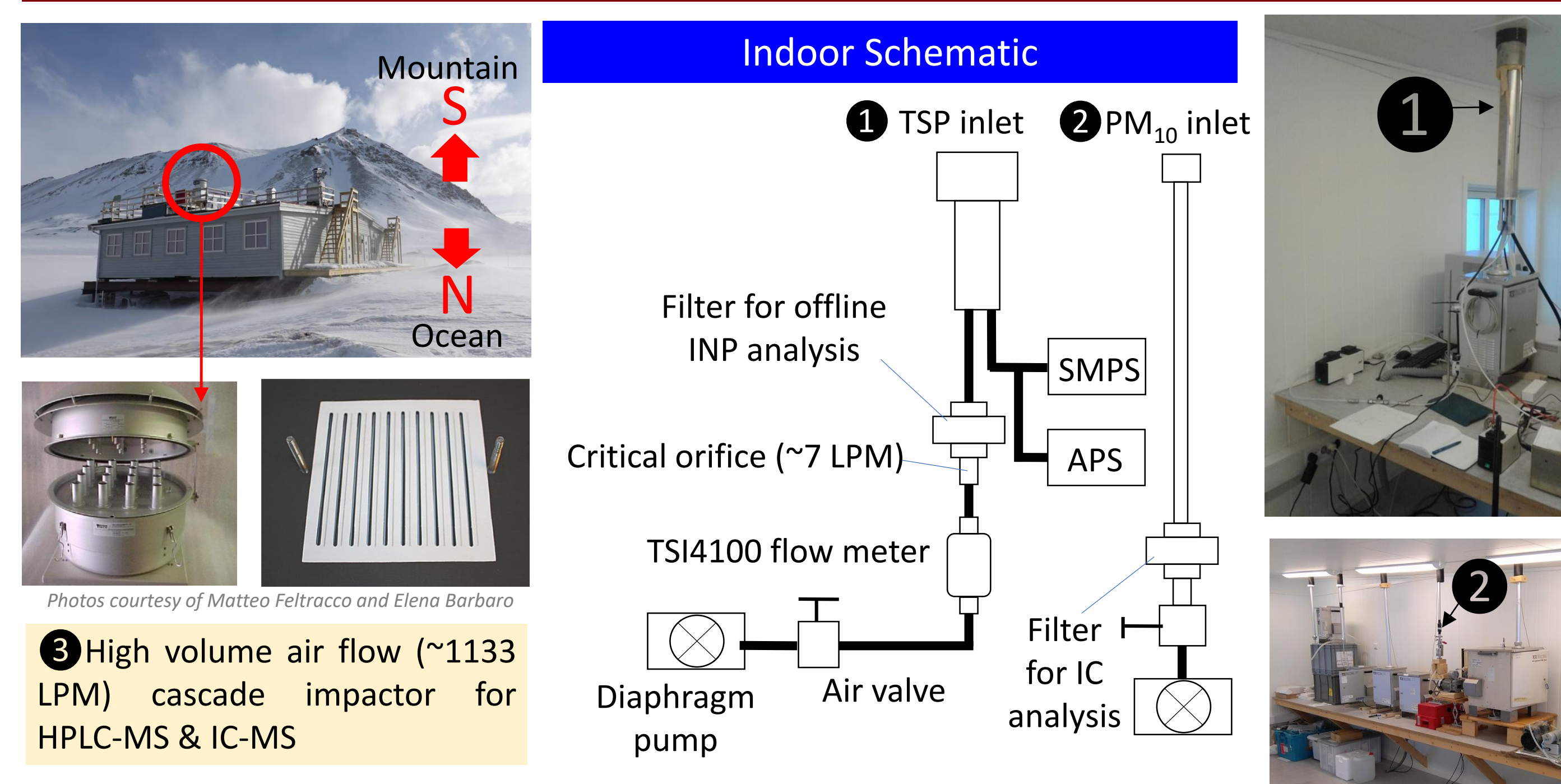
Preliminary Results *Cont'd*

▼ Size-resolved aerosol particle compositions and concentrations over 2018 – 2019 measured by HPLC-MS and IC-MS^[6,7]: time series of a subset of organics in aerosol particles (a), positive matrix factorization-based sources (b) and fraction of individual species from each source (c).



- ❖ Increase in coarse acetic and formic acids containing aerosol particles towards summer.
- ❖ Notable biomass burning episodes in July – August, 2018.
- ❖ Predominant sea spray/ice source of detected ions and organics.

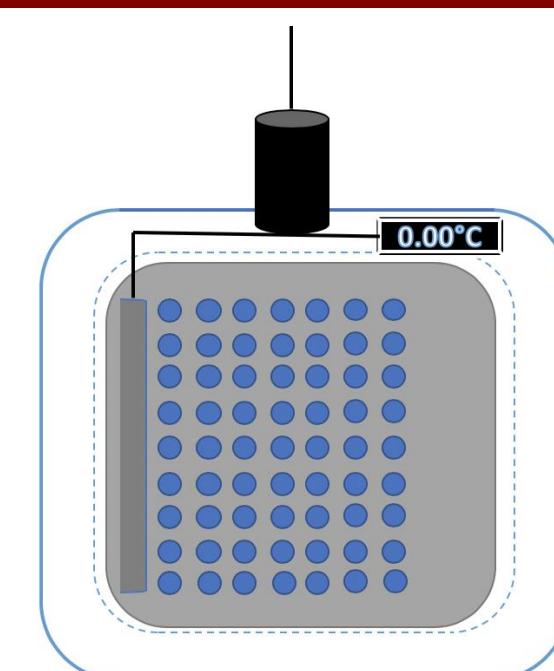
Field Sampling Activities^[2,3]



1. A total of 67 aerosol particle samples for offline n_{INP} analysis were collected using 47 mm Nuclepore filters ($0.2 \mu m$ pore) at the Gruebadet observatory ($\sim 40 m$ above sea level) over 2017 – 2019: March 2 – 30, 2017, April 16 – August 15, 2018, January 31 – February 11, 2019, April 12 – July 16, 2019 and October 3 – 30, 2019. A typical sampling interval was 4 days with sampled air volume of $>10^4 L$.
 2. A TECORA Skypost sequential sampler equipped with a PM_{10} sampling head was operated with a flow rate of $\sim 38 LPM$ to sample aerosol particles on 47 mm PTFE filters for ion chromatography (IC) analysis of major and trace ion species. A typical sampling interval was a day.
 3. An Andersen TE-6000 impactor (6 stages) collected aerosol particles of $\sim 10 \mu m$, $7.2 \mu m$, $3.0 \mu m$, $1.5 \mu m$, $0.95 \mu m$ and $<0.49 \mu m$ for high performance liquid chromatography – mass spectrometry (HPLC-MS) and IC-MS. Typical sampling intervals were 6 days (summer) and 10 days (winter).
- In addition, a combination of a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer (APS) through the total suspended particle (TSP) inlet measured aerosol particle size distribution in $0.01-20 \mu m$.

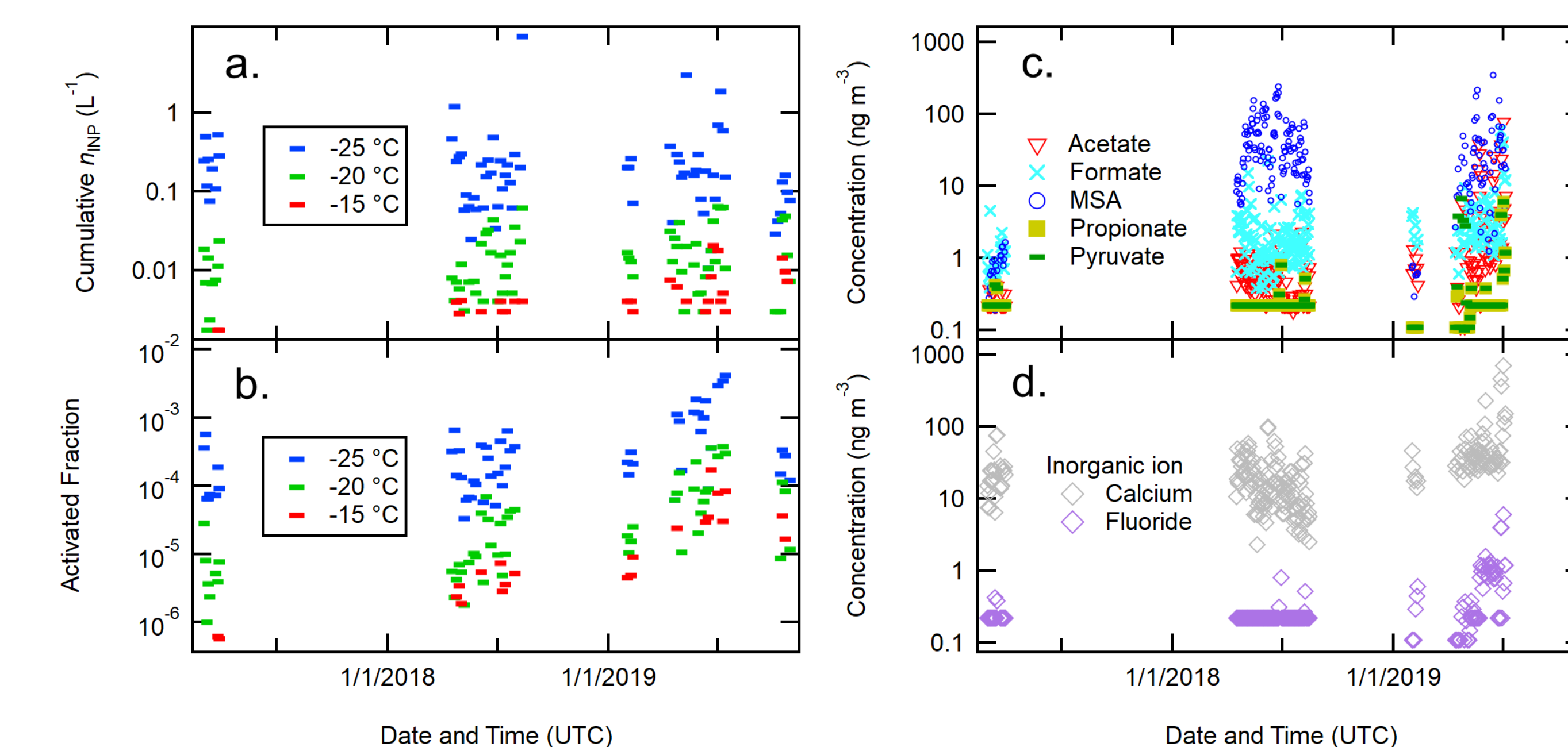
Immersion Freezing Experiment^[4]

Immersion freezing experiments were performed using the West Texas - Cryogenic Refrigerator Applied to Freezing Test (WT-CRAFT) system^[4]. 70 solution droplets ($3 \mu L$ each) placed on a hydrophobic Vaseline layer were analyzed per experiment. The freezing ability of super-microliter-sized droplets containing our samples at a set weight percent were examined at a cooling rate of $1^\circ C min^{-1}$. Frozen fraction and n_{INP} were measured as a function of temperature (T) for every $0.5^\circ C$ based on the phase transition visually observed in each system.



Preliminary Results

▼ Time series of cumulative n_{INP} at -15 , -20 and $-25^\circ C$ (a), activated fraction given by $n_{INP}/n_{aerosol,0.5-10 \mu m}$ at the same three T points (b), IC-measured carboxylic ion mass concentration (c), inorganic ion concentration (d), and n_{INP} spectra (e).



- ❖ Constant n_{INP} at measured T_s for the investigated periods.
- ❖ Substantial inter-annual variability of activated fraction.
- ❖ High activated fraction towards summertime.
- ❖ Slight correlation between some ions associated with carboxylic acids and activated fraction: Acetate ($r = 0.37$) and Propionate ($r = 0.46$).
- ❖ The highest correlation between Fluoride and activated fraction ($r = 0.49$)
- ❖ Our n_{INP} spectra for $-25^\circ C < T < -10^\circ C$ show reasonable agreement with previously studied Arctic n_{INP} range.

Summary & Outlook

- ✓ Stable n_{INP} and seasonally/inter-annually variable activated fraction were observed for T_s below $-25^\circ C$ for our samples analyzed for this study.
- ✓ The increase in coarse aerosol particles containing anthropogenic carboxylic acids and associated ions (e.g., acetic acid/acetate formic acid/formate) correlated (coincided?) with high activated fraction of INPs.
- ✓ These acids/ions persisted during winter in the size range of $<0.49 \mu m$.
- ✓ Organic biomass burning tracers were detected in summer, but no notable influence in INP propensity.
- ✓ Fluoride may have derived from multiple sources: anthropogenic, marine aerosols, combustion and industrial processes and/or mineral weathering.
- ✓ Propionate concentration slightly correlated with INP activated fraction ($r = 0.46$).
- ✓ Propionate or propionic acid could derive from marine biological activity (produced as dimethylsulfoniopropionate, DMSP), produced by phytoplankton, especially dinoflagellates and prymnesiophytes, as an antioxidant and osmolyte^[8]. They can also have minor sources from green algae and some higher plants and potentially bacteria^[9].
- ❑ Heat treatment (boiling suspension at $100^\circ C$ for 20 min) has been conducted for our 2019 samples. A comparison to the result pre-treated samples will be carried out.
- ❑ INP, IC, IC-MS and HPLC-MS analysis for our samples from 2020 may constrain our findings.
- ❑ Fractions of individual carboxylic acid should be compared to INP activated fraction.
- ❑ Ice nucleation ability/efficiency of DMSP, other carboxylic acids and amino acids will be assessed.

References

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