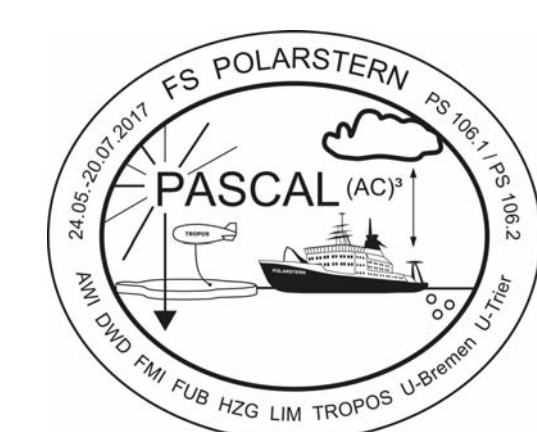
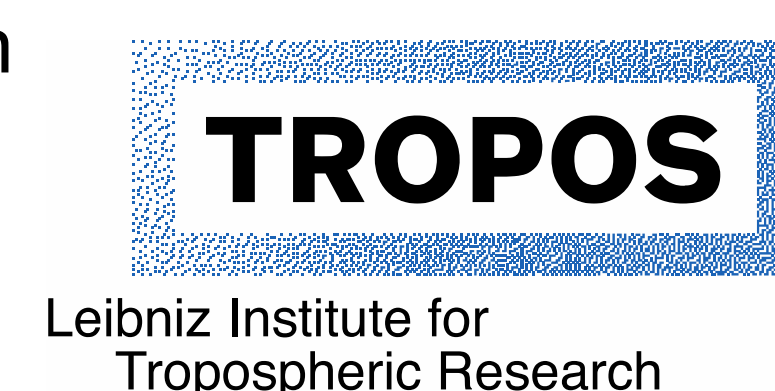


Sea-air transfer measurements of marine carbohydrates in the Arctic

Sebastian Zeppenfeld, Markus Hartmann, Manuela van Pinxteren, Frank Stratmann, and Hartmut Herrmann

Leibniz Institute for Tropospheric Research (TROPOS), Permoserstraße 15, 04318 Leipzig, Germany
Contact: zeppenfeld@tropos.de



Introduction

Marine polysaccharides as potential ice nucleating particles (INP)

Arctic ice and mixed-phase clouds play an important role in Arctic net cloud forcing. However, their microphysics (e.g. formation and glaciation) are currently not well understood and require further investigations.

Heterogeneous freezing of droplets requires the presence of **ice nucleating particles (INP)**. So far there is little knowledge about sources of INP and chemical composition available, especially for the Arctic.

Recent studies discuss the **sea surface microlayer (SML)** and **sea spray aerosol (SSA)** as important sources of INP.^{[1],[2]} So far, this ice nucleating activity has been attributed to proteins and carbohydrates. These large biomolecules offer a lot of active sites for structuring water molecules and supporting the formation of ice embryos at temperatures higher than -38°C.

However, detailed chemical characterizations of INP within SML and SSA do not exist so far.

By performing concerted measurements of Arctic bulk water, SML and aerosol samples we aim to identify relations between chemical information (e.g. the presence of marine carbohydrates) and their physical properties (e.g. IN activity). Furthermore we study the sea-air transfer of marine carbohydrates for evaluating their relevance in the Arctic planetary boundary layer.

The following results were acquired during the field campaign PS 106 (PASCAL/ SiPCA) aboard the German research vessel *Polarstern* from May to July 2017.

Sampling in the Arctic

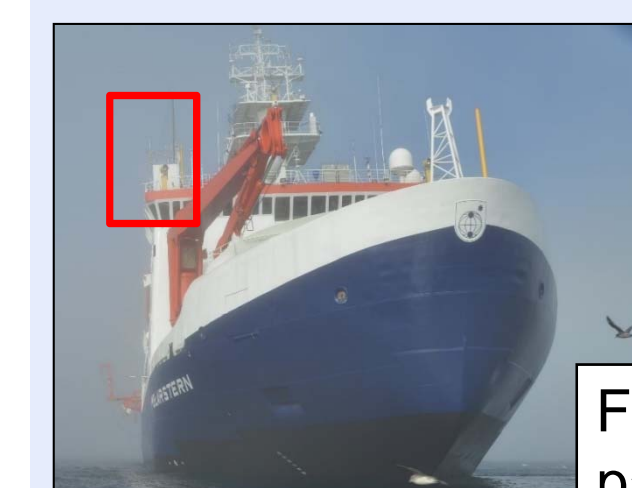


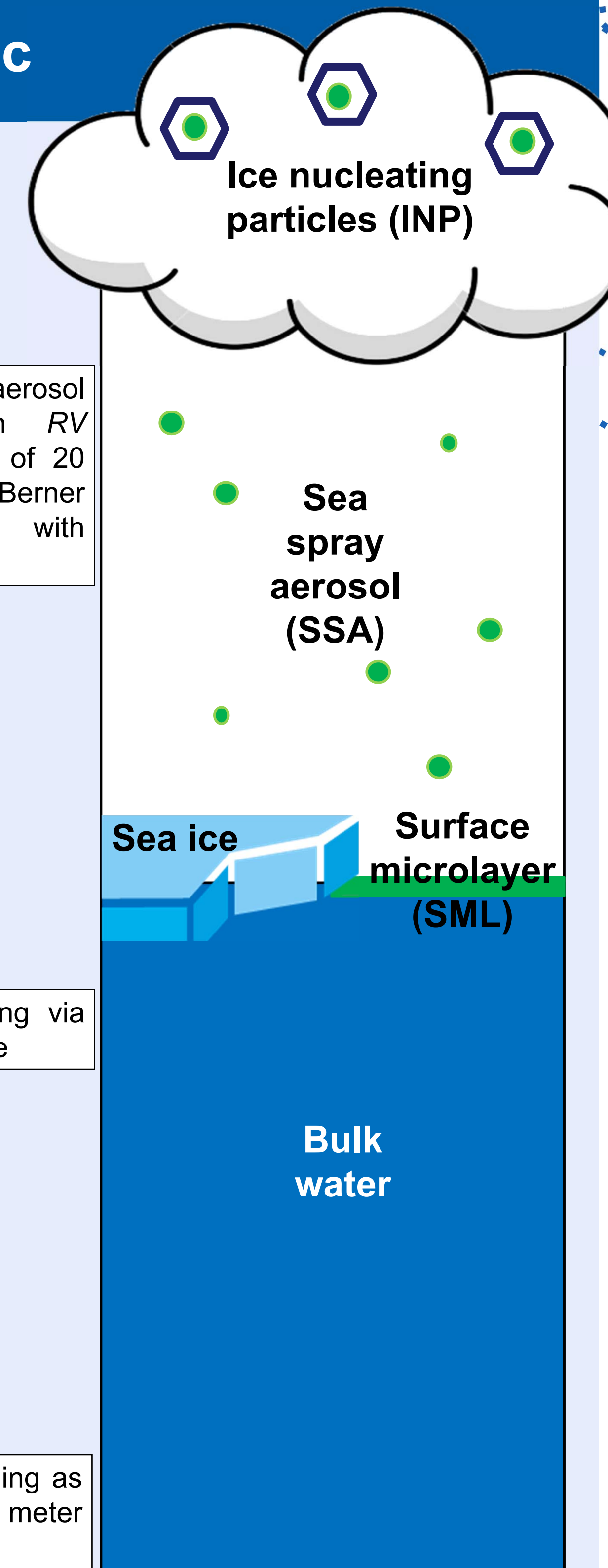
Fig 1: Size resolved aerosol particle sampling on RV *Polarstern* at a height of 20 meter over sea level by Berner impactor (5 stages) with conditioning system



Fig 2: SML sampling via glass plate technique



Fig 3: Bulk water sampling as reference water at 1 meter depth



Method for sugar analysis in sea water

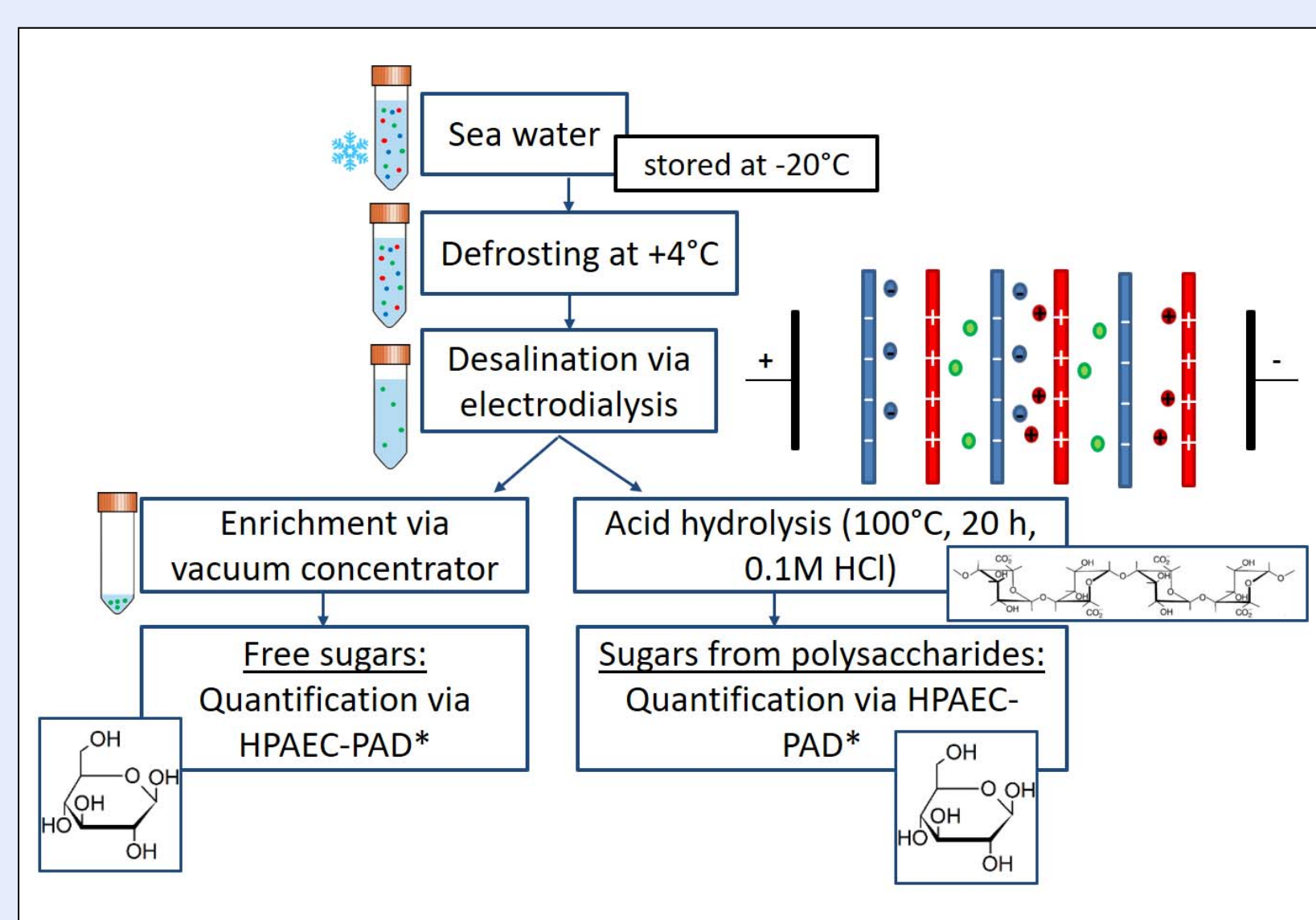


Fig 4: Scheme about carbohydrate measurements in sea water

- High Performance Anionic Exchange Chromatography coupled to Pulsed Amperometric Detection (HPAEC-PAD) for the quantification of free monosaccharides and combined sugars (polysaccharides) in aerosol particles and sea water
- Removal of sea salt via electro dialysis (high recovery for neutral sugars and large biomolecules)
- Enrichment procedure via vacuum concentrator for samples with low concentrations (Limit of detection for glucose=500 ng/L)

Results: Carbohydrates in sea water

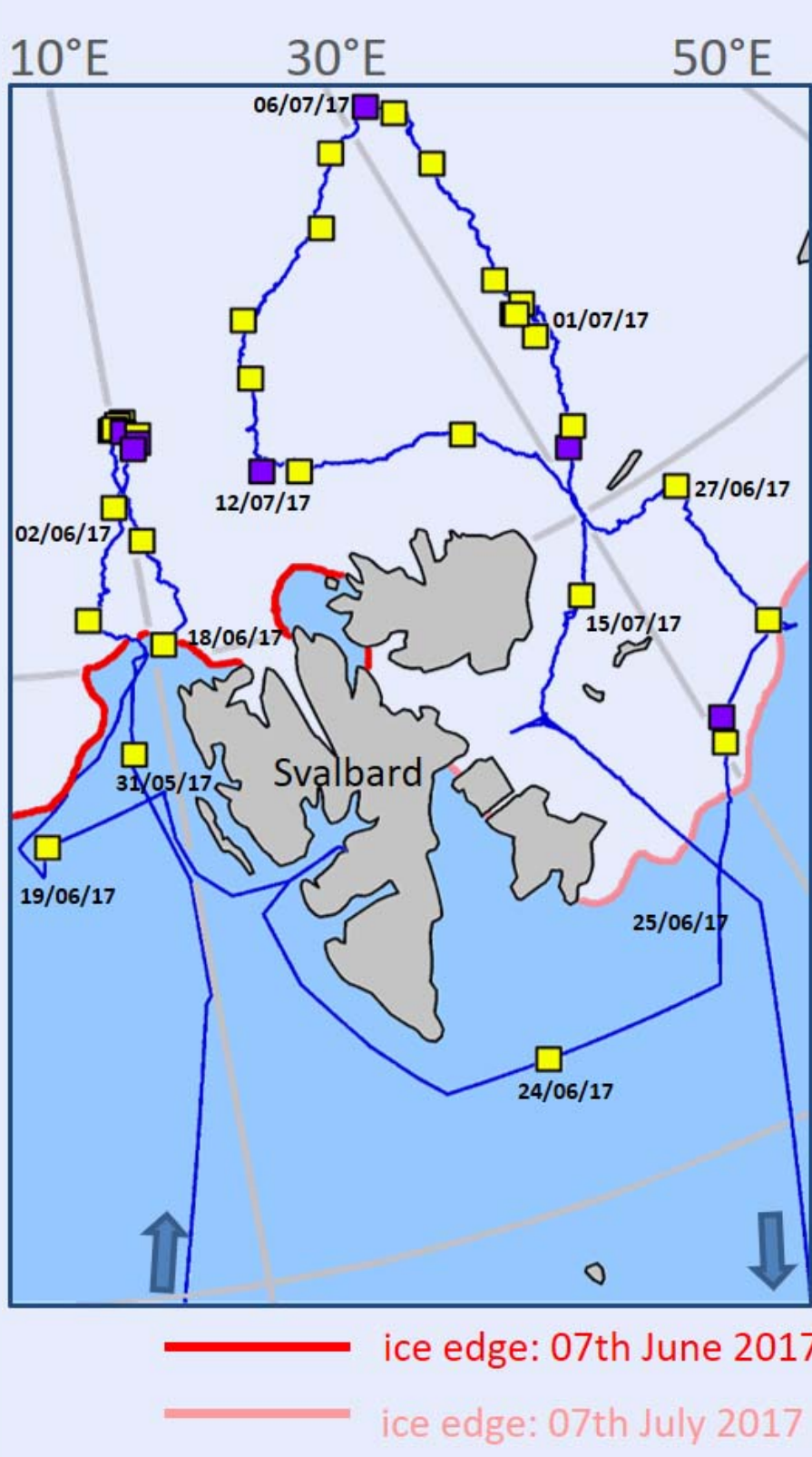


Fig 5: Sampling locations during PS 106. Yellow squares: open ocean samples, purple squares: melt ponds

- High enrichment of combined sugars in SML in open ocean polynyas and melt ponds (enrichment up to a factor of 4) → **potential sources of polysaccharides in aerosols**
- Higher concentrations of carbohydrates in Arctic SML compared to samples from a tropical region (Cape Verde), very likely due to factors like availability of nutrients or wind speed

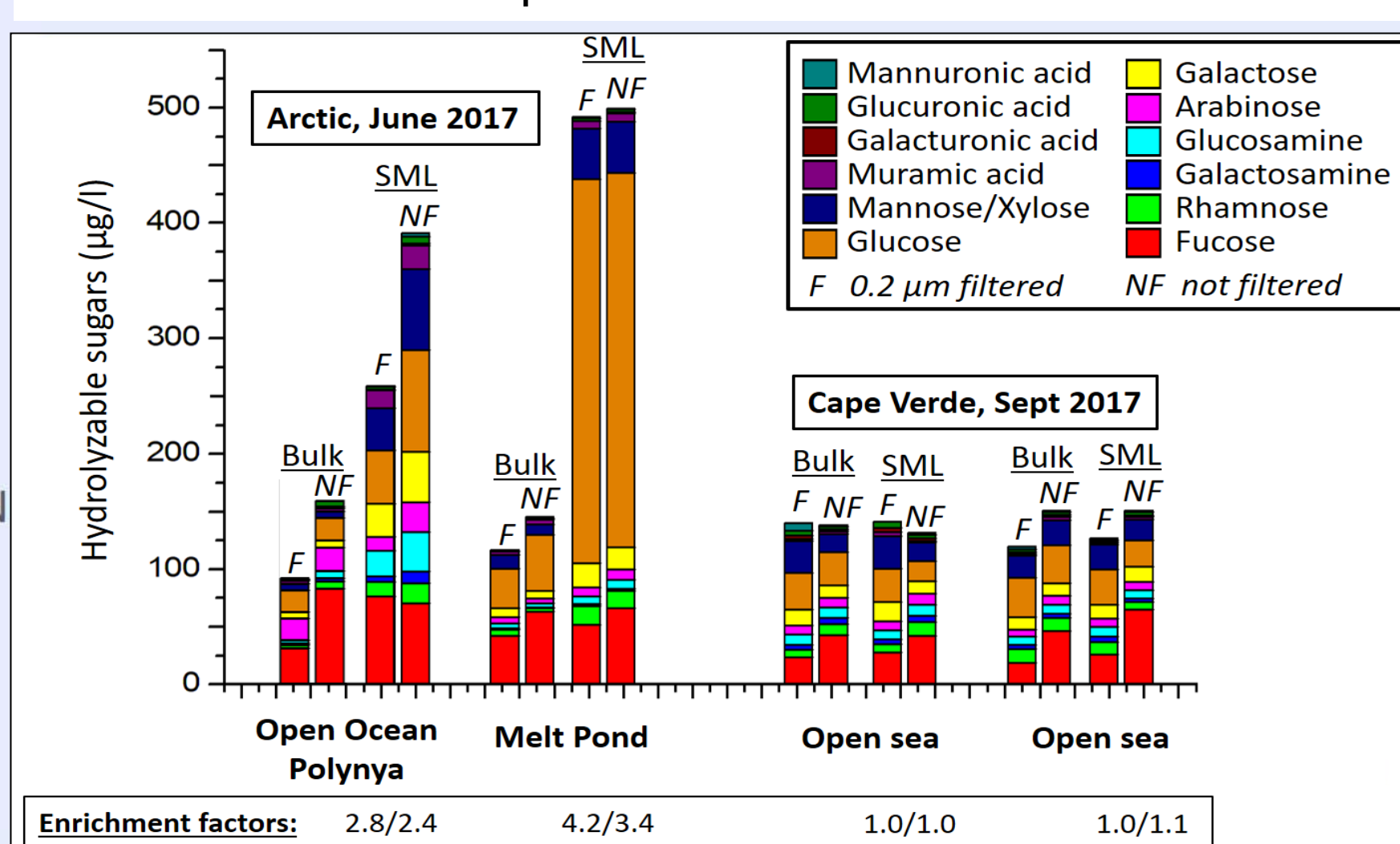


Fig 6: Monosaccharide composition of marine polysaccharides in sea water after acid hydrolysis

Results: Measurements of aerosol particles

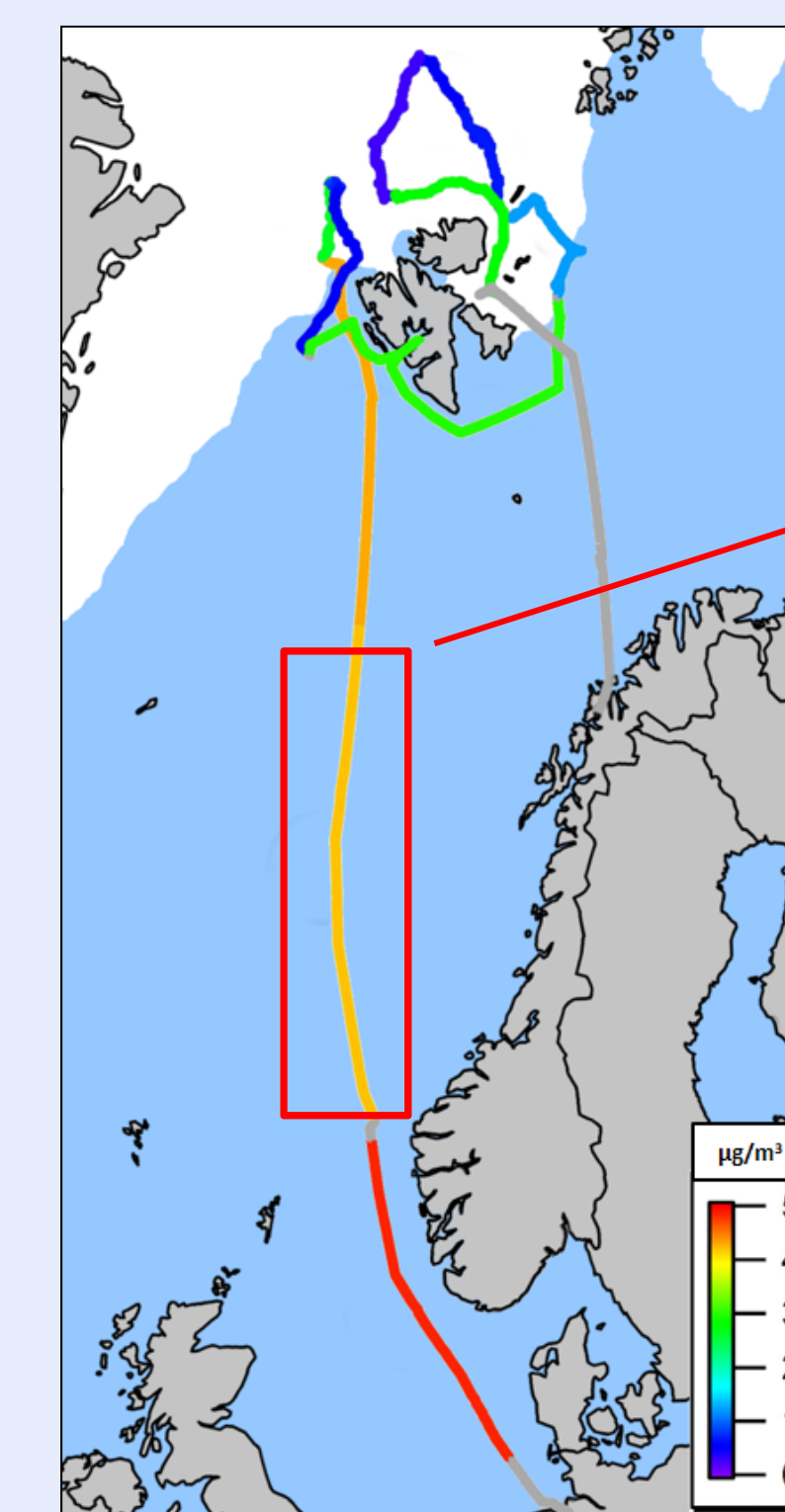


Fig 7: PM 10 mass concentration measured during PS 106 (sum of all Berner impactor stages (0.05-10 µm in diameter))

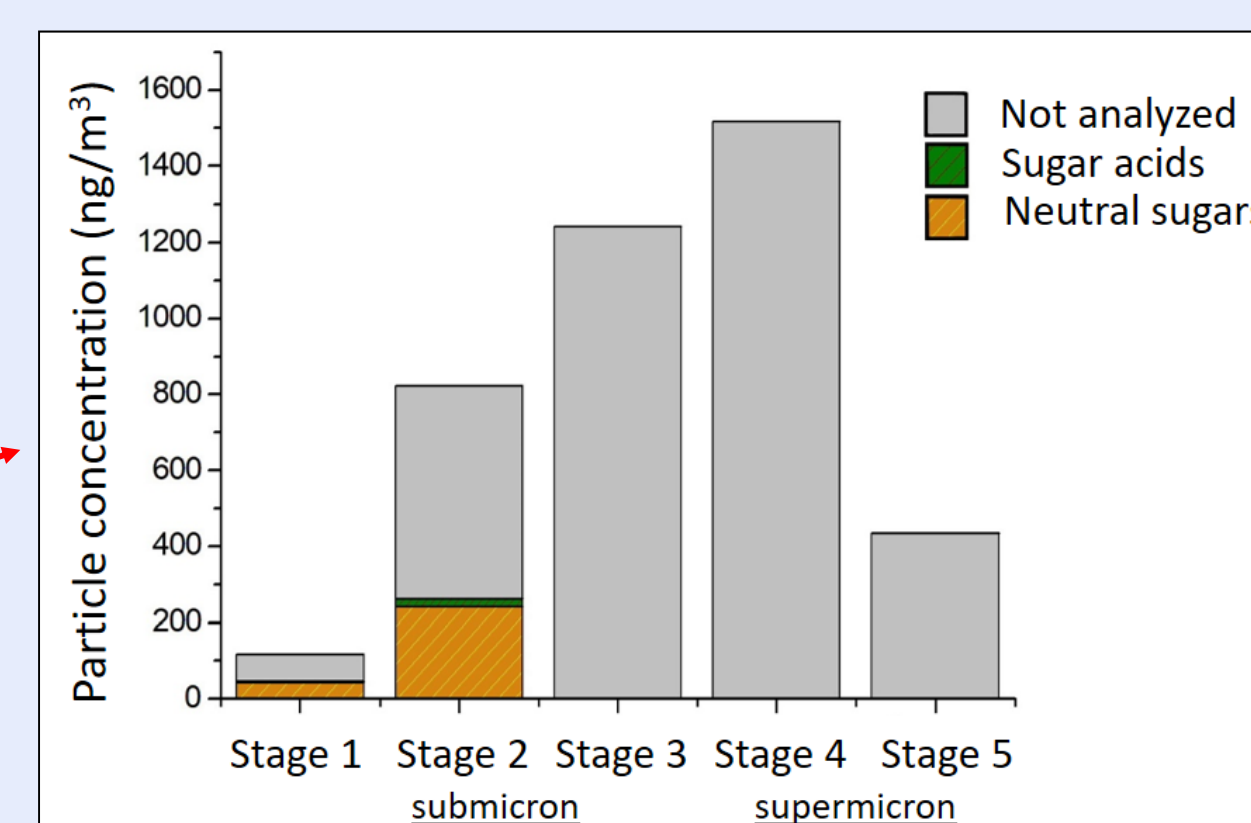


Fig 8: Size-resolved carbohydrate measurements in marine aerosols

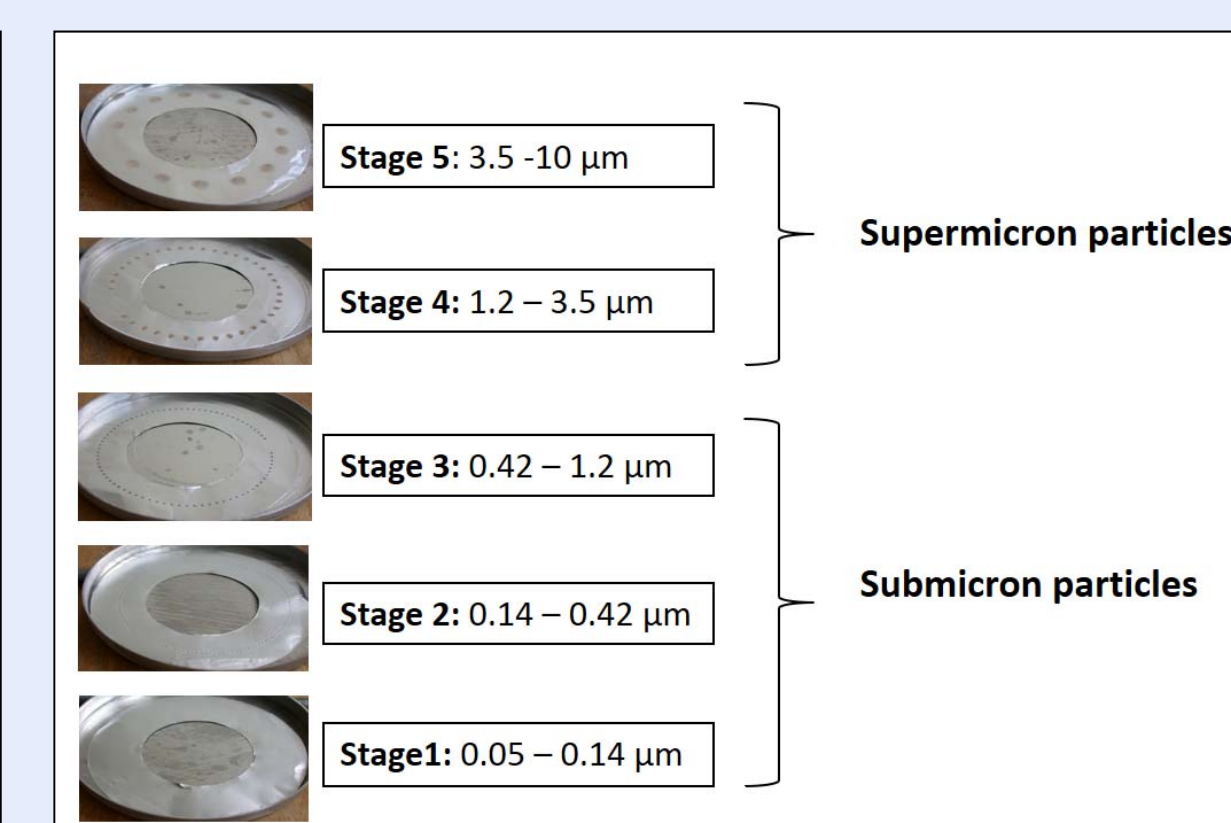


Fig 9: Range of particle diameters on each stage of the Berner impactor

- PM10 aerosol mass concentrations varied during PS 106: **3-5 µg/m³ (over ice-free ocean)** and **0.3-1 µg/m³ (over sea ice)** (in agreement with previous studies: 0.6 – 1.0 µg/m³ [3],[4])
- Marine carbohydrates can be found in submicron particles up to a total mass ratio of 38% over ice-free ocean → very likely from film droplets produced by bubble bursting processes

→ Measurements of aerosol samples over sea ice are in progress

Freezing activity and chemical parameters

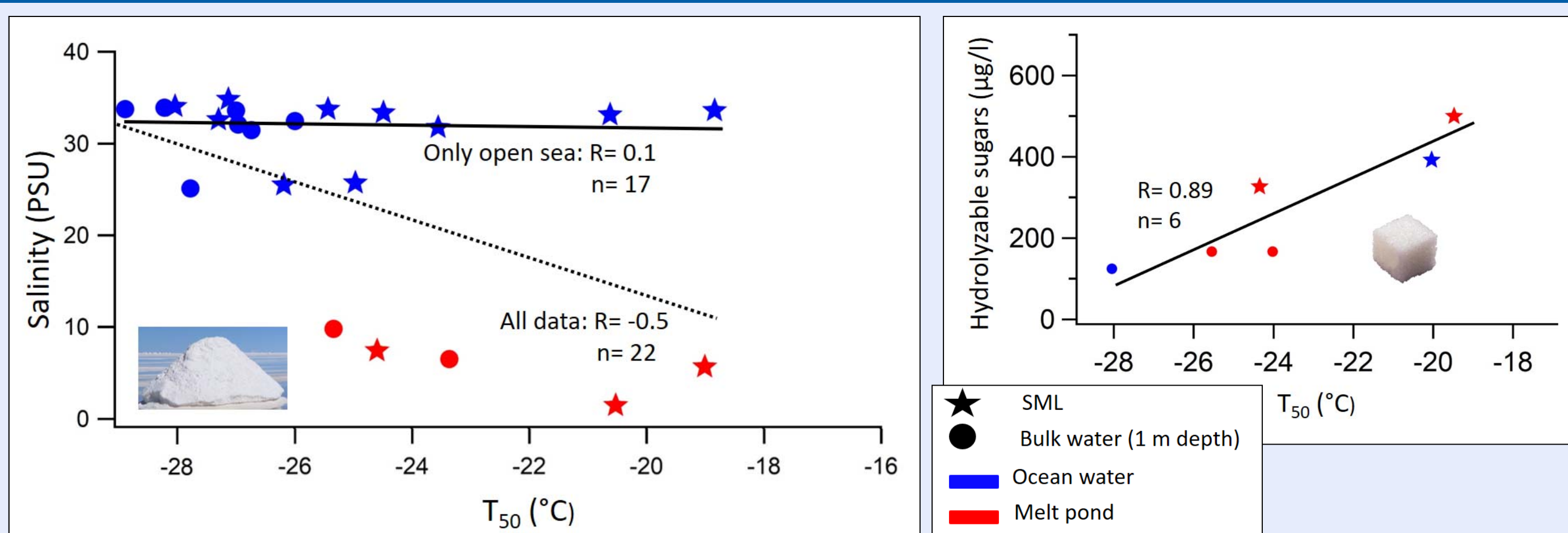


Fig 10: Correlation tests between freezing temperature (50% of all wells frozen in Leipzig Ice Nucleation Array) and salinity (left) or concentration of combined sugar (right) in Arctic sea water

- Correlation between salinity of sea water and its freezing activity could not be observed
 - Strong correlation seem to exist between the concentration of marine combined sugars in sea water and its freezing activity → Source of INP in Arctic sea water seems to be biological (algae, bacteria)
 - It is still unclear if polysaccharides are INP themselves or if they are released together with efficient INP by cells (active emission or passively by cell damage/lysis)
- More measurements needed for supporting first observations statistically

References and Funding

- [1] Wilson et al. (2015) *Nature* 525(7568), 234-238
- [2] DeMott et al. (2016) *PNAS* 113(21), 5797-5803
- [3] Leck and Perrson. (1996) *Tellus B* 48, 156-177
- [4] Nguyen et al. (2014) *J. Geophys. Res.* 119, 5011-5027
- [5] Leck et al. (2013) *Atmos. Chem. Phys.*, 13, 12573-12588
- [6] Irish et al. (2017) *Atmos. Chem. Phys.*, 17, 10583-10595

This study is supported by the DFG funded Transregio project TR 172 „Arctic amplification (AC)³“

Summary and Outlook

- SML of Arctic melt ponds and open ocean polynyas were identified as potential sources of polysaccharides in Arctic aerosols
- Polysaccharides can be found in submicrometer aerosol particles over open ocean up to 38% of total aerosol particle mass concentration
- Strong correlation between freezing activity and combined sugars found

→ More measurements needed for supporting observations statistically
→ Stronger investigation of biological species as producers of INP
→ Participation on MOSAiC campaign 2019/2020 for a higher spatial and temporal resolution