Carbohydrates from sea spray aerosol as a potential source of ice nucleating particles (INP) in the Arctic

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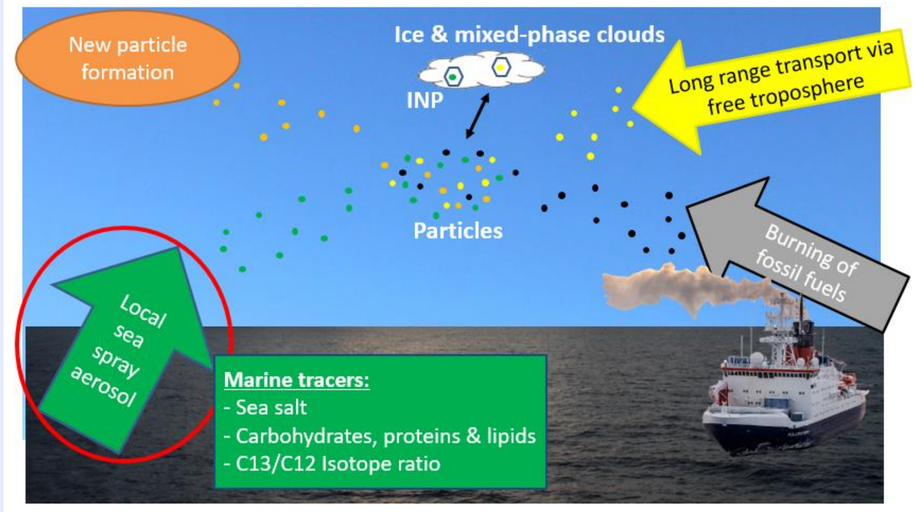
Motivation

Marine biopolymers as potential ice nucleating particles (INP)

The Arctic is a particularly sensitive region to global warming. The term **arctic amplification** describes the observed phenomenon of the striking increase of the arctic surface air temperature exceeding the global average over the past three decades.
For improving currently used models and predictions for the future of the arctic climate we urgently need to learn more about relevant atmospheric processes and feedback mechanisms.
Arctic clouds play an important role on arctic net cloud forcing. However, their microphysics and formation mechanisms are so far not well understood and need further investigations.
Freezing of water, an elemental step for the formation of ice and mixed-phase clouds, requires the presence of **ice nucleating particles (INP)** under heterogeneous conditions. But so far there is very few knowledge about sources of INP and the chemical composition of their active sites available, especially for the Arctic.

Recently, the **sea surface microlayer (SML) and sea spray aerosol (SSA)** are being discussed as an important source of INP.[1], [2] So far, this ice nucleating activity has been attributed to proteins and carbohydrates produced by phyto- and bacterioplankton. However, detailed chemical characterizations of INP within SML and SSA do not exist so far.
Transparent exopolymer particles (TEP), a special group of polysaccharides, are gelatinous, stainable exudates from marine microorganisms in seawater. They may enter the planetary boundary layer by sea-air phase transfer processes such as breaking waves and bubble bursting. To date, there are only very few analytical measurements for TEP available, especially in arctic marine aerosol particles. The chemical structure of TEP might allow a structured arrangement of water molecules and could therefore act as a potential INP.

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 biopolymers) and their physical properties (e.g. IN activity). Theses samples will be collected during the field campaign PASCAL aboard the German research vessel Polarstern from May to July 2017.

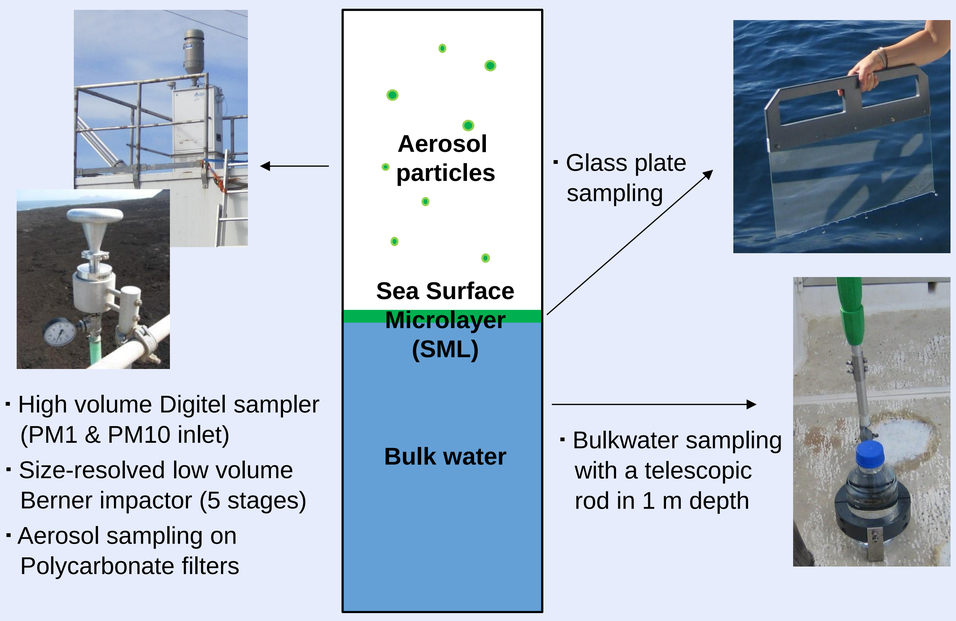


Potential sources of INP in the Arctic

Experimental

Concerted field sampling in the Arctic:

Collection of samples during field campaign PASCAL aboard the German research vessel Polarstern from May to July 2017

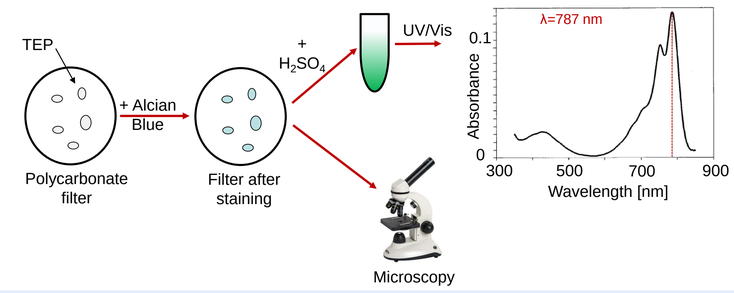


- High volume Digitel sampler (PM1 & PM10 inlet)
- Size-resolved low volume Berner impactor (5 stages)
- Aerosol sampling on Polycarbonate filters

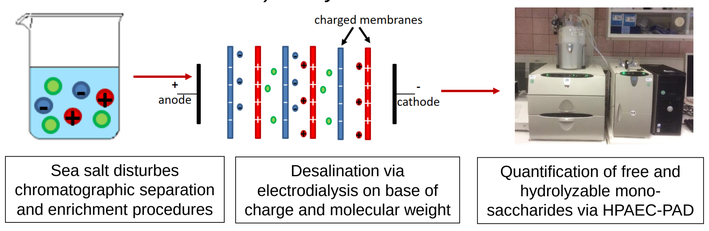
Analysis of chemical composition and physical properties:

Chemical analysis:

- Alcian blue staining coupled to photometric analysis for the quantification of **TEP in water and aerosol** samples



- Quantification of individual monosaccharides via High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD) analysis after desalination

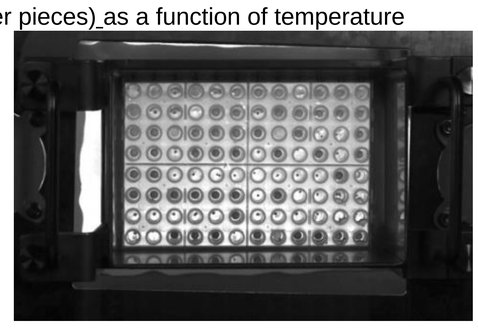


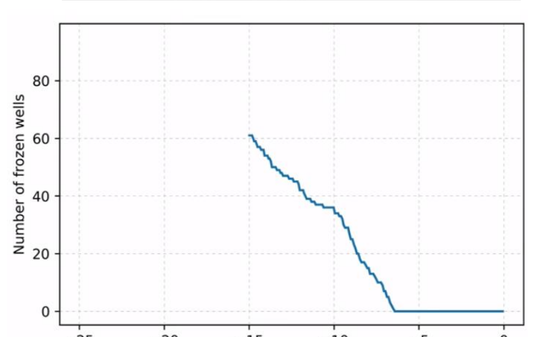
Sea salt disturbes chromatographic separation and enrichment procedures	Desalination via electrodialysis on base of charge and molecular weight	Quantification of free and hydrolyzable mono-saccharides via HPAEC-PAD

anions (e.g. Cl^-, SO_4^{2-})
cations (e.g. Na^+, Ca^{2+})
neutral substances (e.g. glucose)

Physical analysis:

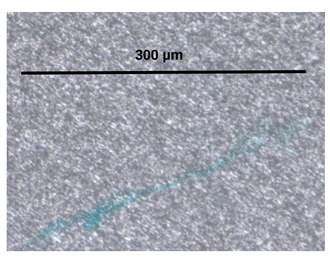
- Ice Nucleation Droplet Array (INDA) for the characterization of the ice nucleating activity of aqueous samples (bulk water, SML, filter extracts, immersed filter pieces) as a function of temperature

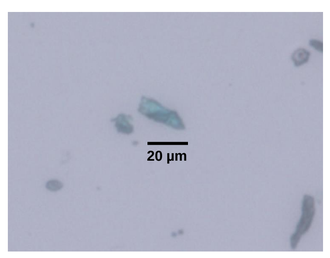




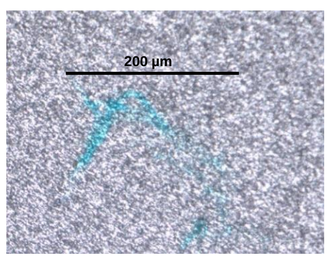
Method Development and First Results

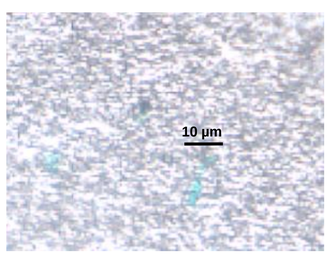
TEP in bulk water





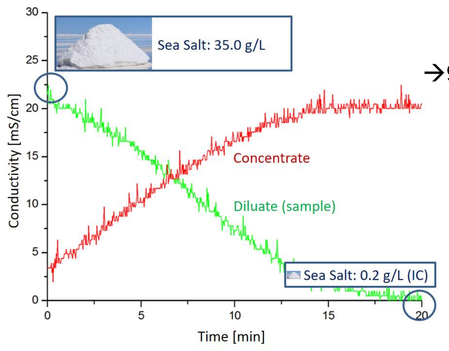
TEP in aerosol



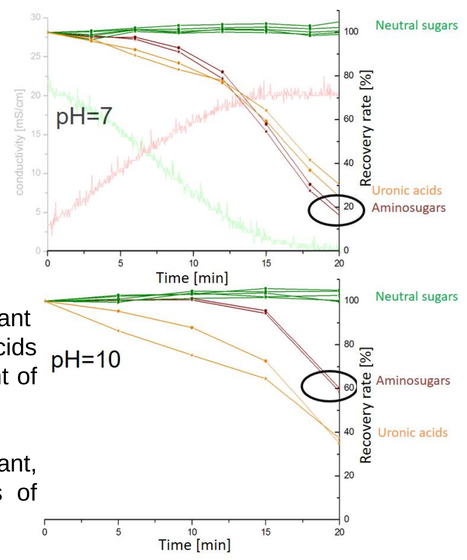


→TEP could be found in water and aerosol samples microscopically (samples from METEOR campaign 2015, research area: Baltic sea)
→ size range from 10-300 µm length

Desalination of aqueous samples for sugar analysis



→99.4% sea salt reduction by electrodialysis

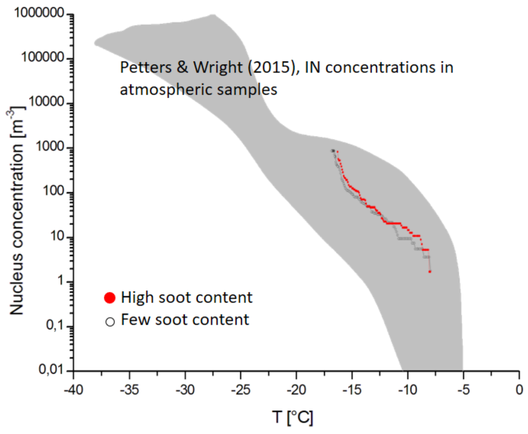


Recovery of free monosaccharides:
→ Neutral sugar concentrations stay constant
→ Loss of free amino sugars and uronic acids under neutral conditions, but adjustment of pH improves recovery rates

Charged polysaccharides stay constant, since they cannot pass the membranes of electrodialysis

Influence of soot on IN activity

- Research vessel Polarstern may emit ice nucleating soot
- IN activity of soot in literature highly controversial [3], [4], [5]



· PM 2.5 filter samples from Beijing (collected in Nov 2016) with different soot content analyzed on IN activity
→ High soot concentrations do not lead to shifts in INP concentration
→ Ship emissions may not influence the INP measurement

References and Funding

[1] Wilson et al. (2015) *Nature* 525(7568), 234-238.
[2] DeMott et al. (2016) *PNAS* 113(21), 5797-5803
[3] Brooks et al. (2014) *J. Phys. Chem.* 118(43), 10036-10047
[4] Koehler et al. (2009) *Phys. Chem. Chem. Phys.* 11(36), 7906-7920
[5] Popovicheva et al. (2008) *Atmos. Res.* 90(2),326-337

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Summary and Outlook

→ TEP can be found in water and aerosol samples by Alcian blue staining
→ Carbohydrate composition can be quantified by HPAEC-PAD after a prior desalination step by electrodialysis
→ Ship soot may not influence the INP measurement in the Arctic

Next steps: → Analysis of arctic bulk water, SML and aerosol samples
→ Correlation of chemical and physical properties