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Glucose as a Potential Chemical Marker for Ice Nucleating Activity in Arctic Seawater and Melt Pond Samples

Sebastian Zeppenfeld,[†] Manuela van Pinxteren,[†] Markus Hartmann,[‡] Astrid Bracher,[§,∥] Frank Stratmann,[‡] and Hartmut Herrmann*[,†]

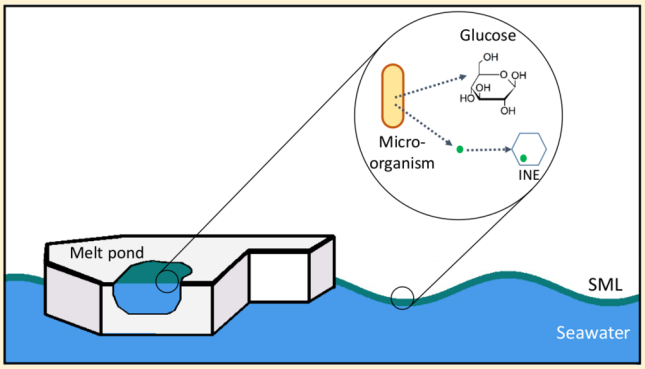
[†]Atmospheric Chemistry Department (ACD) and [‡]Experimental Aerosol and Cloud Microphysics Department, Leibniz-Institute for Tropospheric Research (TROPOS), Leipzig, Germany

[§]Alfred-Wegener-Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany

[∥]Institute of Environmental Physics, University of Bremen, Bremen, Germany

Supporting Information

ABSTRACT: Recent studies pointed to a high ice nucleating activity (INA) in the Arctic sea surface microlayer (SML). However, related chemical information is still sparse. In the present study, INA and free glucose concentrations were quantified in Arctic SML and bulk water samples from the marginal ice zone, the ice-free ocean, melt ponds, and open waters within the ice pack. T_{50} (defining INA) ranged from −17.4 to −26.8 °C. Glucose concentrations varied from 0.6 to 51 μg/L with highest values in the SML from the marginal ice zone and melt ponds (median 16.3 and 13.5 μg/L) and lower values in the SML from the ice pack and the ice-free ocean (median 3.9 and 4.0 μg/L). Enrichment factors between the SML and the bulk ranged from 0.4 to 17. A positive correlation was observed between free glucose concentration and INA in Arctic water samples (T_{50}(°C) = (−25.6 ± 0.6) + (0.15 ± 0.04)·Glucose(μg/L), R_P = 0.66, n = 74). Clustering water samples based on phytoplankton pigment composition resulted in robust but different correlations within the four clusters (R_P between 0.67 and 0.96), indicating a strong link to phytoplankton-related processes. Since glucose did not show significant INA itself, free glucose may serve as a potential tracer for INA in Arctic water samples.



INTRODUCTION

In the Arctic, ice and mixed-phase clouds affect the Earth's energy budget and hence the regional climate as well as the full climate system.[1,2] Arctic clouds scatter solar radiation back to space (cooling effect) and re-emit and absorb terrestrial radiation (warming effect). The transition of positive to negative net cloud forcing of clouds depends on the cloud phase (liquid, mixed phase, ice), microphysics, the cloud's thickness and formation mechanisms.[3−6] Since clouds are known to play an important role on Arctic Amplification, a detailed understanding of these cloud-related parameters and formation processes is crucial.[2,7]

At temperatures below −38 °C, the formation of ice in clouds occurs via homogeneous ice nucleation within seconds for ∼10 μm sized droplets.[3,8] Between 0 and −38 °C, freezing of water droplets is thermodynamically favored but kinetically hindered.[9] Impurities with certain catalytic surfaces allow a structured arrangement of water molecules and facilitate the transition from the liquid to the solid phase.[9] These impurities with ice nucleating activity (INA) are addressed as ice nucleating entities (INEs) or more specific for the aerosol phase as ice nucleating particles (INPs).[10]

Several complex biological structures in bacteria,[11−15] birch and pine pollen,[16,17] lichen,[18] fungi,[19,20] and the organic matter of soil[21] have been identified as efficient INPs. Besides terrestrial sources, marine INEs in bulk seawater and sea spray aerosol have been the focus of intensive investigations in the last decades.[22−26] The latest studies pointed to a high INA in the Arctic sea surface microlayer (SML).[27,28] The SML describes the uppermost layer of the oceanic water column with a typical thickness ranging between 1 and 1000 μm.[29−33] Especially for particulate organic matter and surface-active molecules within dissolved organic matter (DOM), the SML can be highly enriched compared to the underlying bulk with reported enrichment factors (the ratio between the concentrations in the SML and the bulk) higher than 10 for gel particles[34] and up to 50 for amino acids (free dissolved and combined).[35] Organic substances found in the SML are transferred to the atmosphere during the generation of sea

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spray aerosol,[30] which implicates the SML as a potential source of INPs for the formation of ice in clouds, especially in the Arctic.

Dissolved organic carbon (DOC) has been suggested as an important pool for marine INPs.[24−27,36] Studies of the INA in the Arctic SML indicate their origin from bacterio- or phytoplankton in the open ocean[27] or organisms associated with sea ice.[37] Complex biological structures, like marine diatom cells and fragments, are known for their ability to induce heterogeneous ice freezing.[38] Strong correlations between the INA of Arctic SML samples and several algal exudates, such as polyunsaturated aldehydes (e.g., octadienal) and unsaturated hydrocarbons (e.g., hormosirene), proposing these compounds as INA tracers, have been described before.[28] Recent mesocosm experiments revealed a link between increased INP generation in sea spray aerosol and the decay of phytoplankton blooms and the degradation of algal exudates by bacterial enzymes.[24,26] However, more detailed chemical information about the INE or correlations with related molecules in field samples is sparse.

The INA of environmental samples is often attributed to proteins or lipids.[9,15,21,36] Very high INA is suspected when certain repeated hydrophilic−hydrophobic patterns appear in the chemical structure of the INE as it has been demonstrated for the membrane protein inaZ of the bacterium *Pseudomonas syringae*.[12] However, the molecular structure of carbohydrates provides many important features of an efficient INE as well: Long molecules with hydrophilic side groups forming hydrogen bonds with water (e.g., hydroxyl groups, aldehyde groups), which could facilitate structuring water to an ice embryo.[9] Several studies already confirmed that the INA in birch pollen and in the fluid reservoirs of some succulent plants is derived from robust polysaccharides and not proteins.[16,39] In seawater, marine carbohydrates and carbohydrate-like compounds are considered a major fraction of DOM. In surface seawater, the carbon contained in the total amount of carbohydrates (TCHO) accounts for around 15−35% of DOC.[40] The majority of marine carbohydrates is found as long chains of various monosaccharides connected via glycosidic bonds, which are called polysaccharides or combined sugars. A small fraction of TCHO is the group of dissolved free monosaccharides (DFCHO), which is assumed to be breakdown products of polysaccharides or directly released after the lysis of phytoplankton cells.[41−43] As the main compound of DFCHO,[44] free glucose may indicate the decay of phytoplankton or polysaccharide exudates in seawater. Hence, it could be related to the release of INEs. Since water-soluble free glucose is neither surface active nor particulate, its enrichment in the SML is expected to be quite low, as it has been shown previously.[45] Typical concentrations in seawater from the middle latitudes, tropics, and the polar regions have been found in the lower microgram per liter range or below the limit of detection (LOD) since it is utilized by marine microorganisms quite quickly.[41,42,46−48]

As discussed above, previous work indicates biogenic sources to be relevant for the INA in Arctic seawater. Therefore, we were testing this hypothesis over a range of different environments (ice-free ocean, marginal ice zone, ice pack, melt ponds) in the Arctic Ocean. In the present study, we focused on relating INA to biological parameters and free glucose concentrations, possibly released together during biological stress or decay. In order to quantify reliably the content of free glucose, we applied a HPAEC-PAD method with prior desalination by electrodialysis, which followed from the successful method development and application for the determination of sugars and anhydrosugars in tropospheric particles in our group.[49]

EXPERIMENTAL SECTION

Sample Collection. Water samples (SML and bulk water) were collected from the Fram Strait and Barents Sea during cruise PS 106.1 ("PASCAL") and PS 106.2 ("SiPCA") onboard the German icebreaker RV *Polarstern* in May−July 2017.[7] Samples were acquired from the ice-free ocean, the marginal ice zone, the ice pack (open leads and polynyas), and melt ponds. Water sampling locations are visualized in Figure S1, while Table S3 summarizes sampling date and geographic coordinates of these stations. For minimizing the contamination of water samples by exhausts and wastewater, sampling close to the ship was avoided. Seawater was collected either from a rubber boat or from an ice edge. Melt ponds on ice floes were sampled with elevated care to prevent anthropogenic contaminations. SML samples were collected using the glass plate technique:[31] For SML samples, a glass plate (sampling area 2000 cm^2) was immersed vertically into the surface water and removed slowly. The SML film stuck to the glass surface and was drawn off by a framed Teflon wiper. The SML thickness was calculated as a ratio between the collected sample volume and the sampling area of the glass plate[50] and resulted in an average thickness of 76 ± 10 μm. The bulk water was sampled in LDPE bottles (500 mL) mounted on a telescopic rod at a defined depth of 1 m,[50] except at the melt ponds where it was taken from the bottom at 20−40 cm depth. Out of six sampled melt ponds, five were closed at the bottom and, therefore, isolated from oceanic water. One melt pond was open at the bottom.

Sample Preparation. A small aliquot of the water samples was used to determine the salinity by using a conductivity meter (pH/Cond 3320, WTW).

All sampling bottles were rinsed with dilute hydrochloric acid (10% v/v) prior to the campaign. Bulk and SML samples were immediately frozen at −20 °C for INA analysis in 15 mL centrifuge tubes (Labsolute, PP, conical, sterile) and for free glucose analysis in 500 mL wide mouth bottles (Labsolute, LDPE). The samples stayed onboard of RV *Polarstern* at these conditions until the ship's return to Bremerhaven (Germany) in October 2017. After a fast transport to our laboratories in Leipzig in plastic thermoboxes filled with dry ice, samples were kept frozen at −20 °C until analysis. Previous work showed that freezing of seawater does not significantly modify their INA.[22]

For pigment analysis, bulk water was filtered onto GF/F filters (Whatman). Depending on the intensity of the color of the water, volumes of 30−2500 mL per sample were filtered. However, filtering time was never exceeding 1 h in order to avoid degradation of pigments during filtration. After shock freezing in liquid nitrogen, these filters were stored at −80 °C until analysis.

Analysis of Freezing Temperature. For measurement of the INA of water samples, a device called LINA (Leipzig Ice Nucleation Array) was used. LINA is an optical freezing array for measuring INA by immersion freezing, which has been described elsewhere.[51,52] It is a further development of the BINARY, which was explained in detail by Budke and Koop (2015).[53] In short, 90 sample droplets of 1 μL volume are placed onto a hydrophobic glass slide. These droplets are

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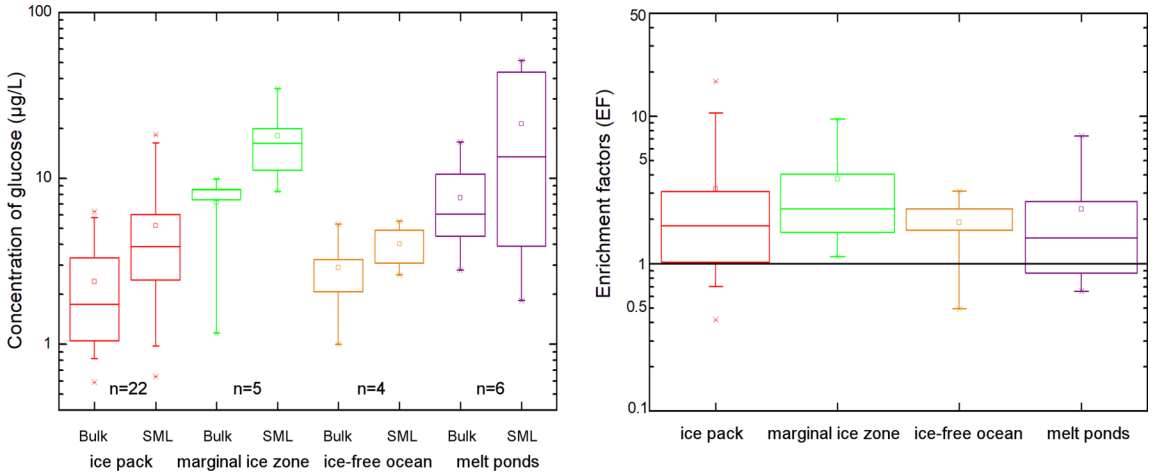

Figure 1. Box-whisker plots of (a) free glucose concentrations in Arctic water samples and (b) enrichment factors between SML and bulk water. (Red) Open leads or polynya within the ice pack, (green) marginal ice zone, (orange) ice-free ocean including two samples from the North Atlantic, (purple) melt ponds. Black horizontal line: EF = 1 as reference.

cooled down with a continuous rate of 1 K/min, while a camera takes a picture of the array every 6 s. Frozen droplets acquire a darker color than liquid droplets and can be counted as a function of temperature.

For the correction for freezing temperature depression caused by sea salt, the water activity was calculated according to Pruppacher and Klett (2010)[54] using measured salinities under the assumption that the total amount of salt consists of NaCl. Then the approach by Koop and Zobrist (2009)[55] was applied to adjust freezing temperatures. The value T_{50} describes the corrected freezing temperature where 50% of all droplets in this array was frozen.

Pigment Analysis. For pigment analysis via high-performance liquid chromatography (HPLC) we followed the method of Barlow et al. (1997),[56] which was adjusted to our temperature-controlled instruments as detailed in Taylor et al. (2011).[57] The following pigments were determined: monovinyl-chlorophyll a, divinyl-chlorophyll a, chlorophyllide a, chlorophyll b, chlorophyll c1+c2, chlorophyll c3, phaeophorbide a, phaeophytin a, alpha-carotene, beta-carotene, 19-but-fucoxanthin, 19-hex-fucoxanthin, alloxanthin, antheraxanthin, diadinoxanthin, diatoxanthin, dinoxanthin, fucoxanthin, lutein, neoxanthin, peridinin, prasinoxanthin, violaxanthin, and zeaxanthin. The total chlorophyll a (TChl-a) concentration is defined as the sum of the concentrations of chlorophyllide a, monovinyl-chlorophyll a, and divinyl-chlorophyll a[57,58] (the later pigment was not present in our samples).

Since this procedure requires a large sample volume (generally 2500 mL), pigment analysis was only performed for bulk samples. Pigment results of all samples passed the quality control described in Aiken et al. (2009),[59] besides sample Bulk 17- accordingly- this sample was marked in all graphs.

The fractional composition of the main phytoplankton groups (diatoms, dinoflagellates, haptophytes, cyanobacteria, chlorophytes, cryptophytes, chrysophytes) was calculated following the approach by Losa et al. (2017, Supporting Information)[58] using diagnostic pigment-specific coefficients derived from a large in situ pigment database excluding the Southern Ocean to convert each diagnostic pigment concentration into a group specific chlorophyll a concentration. As it is used for global assessments, zeaxanthin was applied as a diagnostic pigment for cyanobacteria. However, although zeaxanthin is mainly present in this group, it can also be contained in some types of chlorophytes. Recent measurements using molecular or flowcytometric techniques have verified the appearance of cyanobacteria in the Arctic Ocean.[60−62]

Analysis of Free Glucose. For the analysis of the free glucose, an analytical method was applied using a desalination step via electrodialysis and a quantification using high-performance anion-exchange chromatography coupled to pulsed amperometric detection (HPAEC-PAD). An extensive description for the analysis of free glucose is given in the SI.

Statistics. For performing statistical analysis, OriginPro software was used. In the presented box-whisker plots, each box encloses the interquartile range. The median value is illustrated as a line and the mean value as an open square. The ends of the whiskers show the 5% and 95% percentiles within the data set. The asterisks indicate the minimum and maximum values of each data set. Pearson correlation coefficients R_P and Spearman correlation coefficients R_S were calculated to characterize the relationship between the chemical and physical information on seawater. The errors for the slope and the y intercept were calculated for an interval of confidence of 95%. The significance of the correlation coefficients is given through their respective P values. Water samples were grouped in clusters according to the results of hierarchical cluster analysis (HCA) using the Manhattan distance as the distance measure and Ward's method for linking clusters.[63−65] As input data, all 24 pigment concentrations were used.

Data Availability. All data are available on the public repository PANGAEA; https://doi.pangaea.de/10.1594/PANGAEA.899258 and https://doi.pangaea.de/10.1594/PANGAEA.899284.

RESULTS AND DISCUSSION

Measurements of Free Glucose in Ocean and Melt Pond Samples. For the present study, water samples from four different ice-related environmental settings were investigated for the free glucose concentration in the SML and the corresponding bulk water. This includes samples from the open water areas within the ice pack (open leads and

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polynyas), the marginal ice zone, and the ice-free water in the Arctic Ocean and the North Atlantic. To our knowledge, free glucose concentrations were measured in melt ponds for the first time.

Determined concentrations ranged between 0.6 and 51 μg/L in all water samples (Figure 1a). The median concentration of free glucose in SML samples was the highest in the marginal ice zone (16.3 μg/L) and in melt ponds (13.5 μg/L), reaching up to 10−50 μg/L for individual samples. Glucose concentrations were much lower in SML samples from the ice pack (3.9 μg/L) and from the ice-free ocean (4.0 μg/L). With a few exceptions, glucose concentrations in SML samples were either similar to or much higher than in the bulk for all settings. However, the majority (85%) of all analyzed water samples contained less than 10 μg glucose/L.

DFCHO is considered to be utilized by marine microbial communities with high turnover rates, which explains the very low amounts of DFCHO generally found in seawater.[41,46,66] In previous studies, concentrations of free glucose have been reported ranging from below LOD to 121 μg/L in seawater from various depths and several coastal and open ocean sites.[42,46,67] Free glucose of surface seawater typically ranged between 5 and 40 μg/L in the North Sea, Bering Sea, and Central Arctic Ocean.[41,47,48] These values fit well into the concentrations of our study. Previously, a negative correlation between DFCHO and salinity has been observed in seawater samples from the western Arctic Ocean, which indicates the potential role of freshwater input (melt ponds and marginal ice zone) as a source of carbohydrates to the Arctic Ocean.[68]

To quantify the enrichment or depletion of free glucose in the SML in comparison to the corresponding bulk water, the enrichment factor (EF) was calculated[32]

$$\mathrm{EF} = x(\mathrm{SML})/x(\mathrm{Bulk}) \quad (1)$$

with x being the determined free glucose concentration in the SML or bulk water. EF's higher than 1 represent an enrichment, while values below 1 indicate a depletion. In this study, we observed EF's varying between 0.4 and 17 (Figure 1b). In 80% of all samples, the glucose concentration was higher in the SML than in the bulk (EF > 1), and in 45% of all samples, an enrichment with EF > 2 could be observed. A significant difference between the EF's within these four sample groups (ice pack, marginal ice zone, ice-free ocean, melt ponds) was not found (ANOVA, one-way, 0.05 significance level).

Free glucose, as a part of the DFCHO, belongs to the low molecular, less surface-active fraction of DOM. Hence, it is quite surprising that this enrichment occurred in some SML samples, since an enrichment by bubble scavenging in the underlying water column and Gibbs adsorption at the air−water boundary surface seems to be unlikely. Coadsorption of these highly soluble carbohydrates to surface-active molecules, e.g., lipids and proteins, in marine films could explain this enrichment in the SML.[69] Since this enriching interaction is found to be mainly based on Coulombic forces between charged groups at the surfactant molecules and the carbohydrates,[69] this process appears to be less probable for neutral glucose under environmental conditions.

An in situ production of free glucose may be another possibility for the elevated amounts of glucose in the SML. A previous study in the northern North Sea showed that DFCHO increases toward the end of a phytoplankton bloom, which may result from extracellular hydrolysis of excreted polysaccharides, most likely cleft and utilized by heterotrophic bacteria.[41,42] Another study found a negative correlation between monosaccharides and polysaccharides at depths above the oxygen minimum, which supports the hypothesis that microbes degrade macromolecules into small monosaccharides.[43] In SML samples from the eastern Pacific Ocean, Thornton et al. (2016) observed enrichment factors of DFCHO between 1.2 and 1.8, while no enrichment of polysaccharides was found, which could be an indication for degradation processes like hydrolysis and photolysis.[45] However, as a comparable issue, an extracellular hydrolysis of proteins has been disproved as a reason for the elevated enrichment factors of free amino acids within the SML.[35]

A direct release of DFCHO from an intracellular pool during the lysis of phytoplankton in the SML might be another reason for this enrichment.[41] Cell death and cell lysis could be caused by viral infection,[70] nutrient deficiency,[71] grazing,[72] or physical stress.[73] Frost damage as a driver for a high release of free glucose may explain the high concentrations in the SML, especially in areas within the Arctic, which are permanently exposed to freezing and melting (melt ponds and marginal ice zone).

In summary, an enrichment of free glucose in the SML could have occurred by a transport from the bulk water via coadsorption at surface-active substances, an in situ production via extracellular hydrolysis of polysaccharides, or a direct release of free glucose in the SML caused by cell lysis. On the basis of previous studies, the last both mechanisms seem to be most likely for explaining the enrichment. However, further experiments are required.

INA of Arctic Water Samples and Correlating Trend with Free Glucose Concentration. The presence of salt in seawater is known to cause a depression of the freezing point up to 3 K.[37] For performing an adequate correction of raw INA data,[54,55] we measured the salinity of all water samples. Depending on the contribution of melting ice, seawater samples exhibited salinities between 25.7 and 34.5. Closed melt ponds consisted of much fresher water with lower and more variable salinities ranging between 5.6 and 19.5, since they are formed by melting snow and surface sea ice.[74] An open melt pond contained a salinity of 4 in the SML and 30 in the bulk.

The determined T_{50} values of surface water from the ice pack, the marginal ice zone, the ice-free ocean, and the melt ponds ranged between −17.4 and −26.8 °C (Figure 2) and are hence all higher than the blank value for ultrapure water (T_{50} = −27.5 °C). T_{50} of most samples (90%) was below −23 °C and hence not very high. The median T_{50} of the bulk samples did not differ much from each other within the four sample groups with values between −24.8 and −25.8 °C.

Comparing SML with bulk water samples, the SML T_{50} values were either higher or at least similar. In particular, SML samples from the marginal ice zone and melt ponds stood out with much higher T_{50}. We observed the trend that melt ponds sampled in the end of June showed much higher INA than the freshly formed melt ponds (age of 2−3 days) sampled in the beginning of June. SML samples from the ice-free ocean and from the ice pack showed a rather low INA, except for two open spaces within the ice pack where a visibly strong biological film covered the surface.

The fact that the Arctic SML studied here showed a strong INA is in good agreement with previous studies[27,28,75] (Table S2). Even though we acquired several Arctic SML samples with

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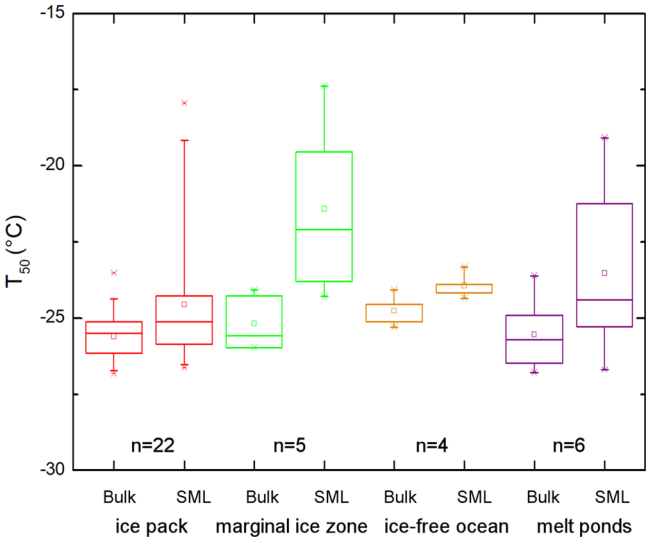

Figure 2. Box-whisker plots of T_{50} of Arctic water samples (SML and bulk). (Red) Open leads or polynya within the ice pack, (green) marginal ice zone, (orange) ice-free ocean including two samples from the North Atlantic, (purple) melt ponds.

elevated INA, none of the samples was comparable to the higher T_{50} for SML samples, which had been measured before with T_{50} reaching −10[27] or −6.9 °C[75] while using the same droplet volumes as in our study. This could be explained by the different seasons of SML sampling. Wilson et al. (2015) and Irish et al. (2019) sampled in July/August, when the growing season of the phytoplankton was already more advanced than in the end of May until July when samples of this work were taken. Apparently, this calls for a better temporal resolution of such INA measurements in the Arctic. Furthermore, Wilson et al. (2015) focused on sampling within the marginal ice zone (which was found to show higher INA), while our study also included samples from the ice pack. In our study, clear bi- or trimodal INA could not be observed (Figure S3), which is in agreement with previous work.[27,75] This indicates that INA was dominated by only one type of INEs.

Previous studies already identified the marginal ice zone as a source of efficient marine INP.[27,28] Recently, Creamean et al. (2018) observed highest concentrations of warm-temperature INPs on aerosol samples collected in Alaska when air masses had traveled over the marginal ice zone most of the time.[76] To the authors' knowledge, our study for the first time determines the INA of Arctic melt pond samples. The SML of biologically active melt ponds exhibited a very strong INA, as well as in the marginal ice zone. The areal coverage of melt ponds can reach in summer up to 80% of the Arctic sea ice[74] with an estimated total carbon production of about 2.6 Tg C/yr in all melt ponds in the Arctic Ocean.[77] Even though this production seems to be small in comparison to the recent total organic carbon production in the Arctic Ocean (400−500 Tg C/yr),[78,79] organic material from aged, biologically active melt ponds may contain a high amount of efficient INEs. These findings highlight melt ponds as potential sources of atmospheric INP, especially under the "polar dome", which is known as a transport barrier preventing the penetration of midlatitude air masses into the high Arctic lower troposphere.[80−82] Therefore, the biochemical and microphysical processes in Arctic marine environments with elaborated biological activity (melt ponds, marginal ice zone) should be the focus of further studies.

Comparing the results of INA and free glucose analysis of all analyzed water samples, we observed a significant correlation between these two characteristics with a Pearson correlation coefficient of $R_P = 0.66$ ($P < 0.001$) (Figure S2). Samples with a high INA also contained an elevated amount of free glucose. This suggests a link between biological processes creating free glucose and efficient INEs.

To test whether free glucose itself possesses a significant INA, freezing experiments were performed with glucose standard solutions (Figure S3). We could not find a significant contribution of glucose to the INA, even with extremely high glucose concentration of 10 mg/L. That means that free glucose obviously does not serve as an INE itself but appears to be closely linked to the release of INEs. We conclude that free glucose may serve as a tracer for INA in Arctic water.

Cluster Analysis for Glucose/INA Source Factor Separation. The species composition and the physiological status of phytoplankton affects its response to environmental conditions.[83,84] Phytoplankton pigments in seawater serve as biomarkers for the composition of phytoplankton communities and the level of exposed stress caused by grazing activities, bacterial decay, or photo-oxidative stress (e.g., xanthophyll cycle).[85,86] Our acquired seawater samples showed a very variate and complex pigment composition, making a direct comparison difficult. Therefore, we applied hierarchical cluster analysis[57,63−65]—a statistical algorithm that groups samples into clusters based on similarities in all their characterizing data. As input data, the concentrations of all 24 determined pigments of the bulk water samples were used. Several studies have suggested that microorganisms in the SML are mainly seeded by bulk water communities.[87−89] On this basis, we used the approach that the relative phytoplankton composition of the bulk water may be comparable to the SML.

Hierarchical cluster analysis identified the Atlantic water samples to be separated from the other samples. Therefore, we excluded those from further considerations. From the remaining, all Arctic, water samples, four different clusters with similar pigment composition could be distinguished (Figure S4). Cluster 1 comprises one melt pond sample and several ice pack samples. Interestingly, cluster 2 contains 5 of 6 melt pond samples and 2 of 5 samples from the marginal ice zone, which implies that the environmental conditions in both of these Arctic habitats may have been quite similar. Cluster 3 covers both ice-free ocean samples and many of the open lead samples from the ice pack. Only one sample from cluster 3 stood out with elevated glucose concentration and INA. Cluster 4 contained two samples from the marginal ice zone and several ice pack samples.

In summary, phytoplankton pigments allowed a clustering of all these heterogeneous water samples. It may support a later identification of important species for the production of INE and INA tracers.

Free Glucose in Correlation with T_{50} within the Four Clusters. Within the four clusters based on pigment composition, free glucose concentrations were correlated against T_{50}. A strong positive linear correlation was found within three out of four clusters (Figure 3). The Pearson correlation coefficient R_P in clusters 1, 2, and 4 varied from 0.83 to 0.96 ($P < 0.001$). These strong correlations between the INA and free glucose indicate that INA is strongly linked with biochemical processes, the phytoplankton composition, and physiological state in Arctic waters. The correlation of cluster 3 was with $R_P = 0.67$ ($P < 0.001$), much lower, which is

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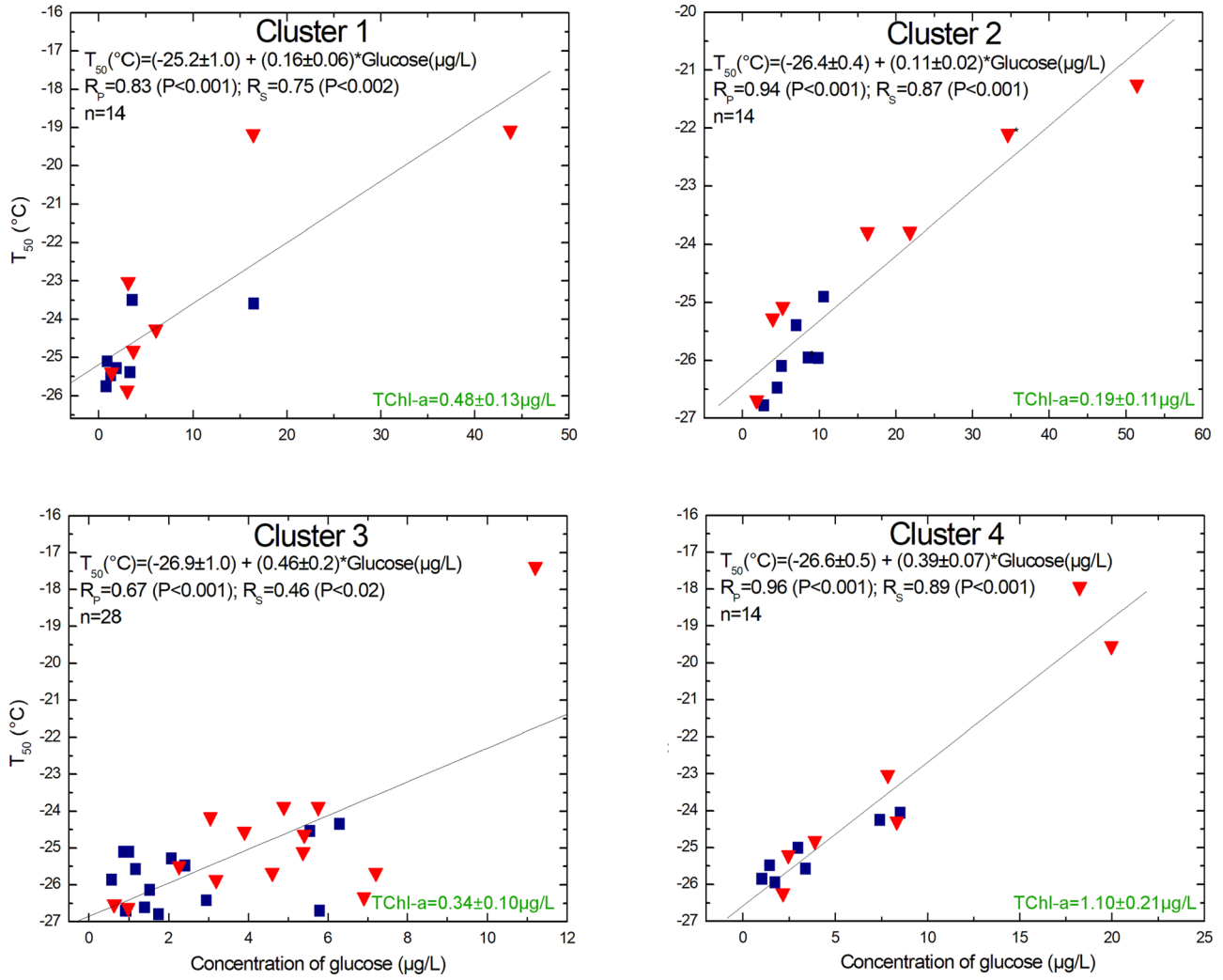

Figure 3. T_{50} plotted against free glucose concentration for each cluster including the average TChl-a concentration and standard deviation of all bulk samples within each cluster. (Red triangles) SML samples, (blue) bulk water samples. Black line represents the linear fit. Clustering of water samples was performed using hierarchical cluster analysis based on phytoplankton pigments.

due to small scattering values within this cluster, except for one higher one strongly impacting the overall correlation. In clusters 1, 2, and 4, the ranked Spearman correlation coefficients R_S were similar to R_P. Only in cluster 3, R_s was much lower than R_P, since a lot of scattering low values dominated this cluster.

The slopes of these linear correlations varied between 0.11 and 0.46 among the different clusters. TChl-a as an indicator of the total phytoplankton biomass[90] averaged 0.49 ± 0.34 μg/L for the Arctic bulk samples (all values shown in Figure S4a). As already published before, a direct correlation between TChl-a in bulk samples and INA could not be observed.[24,75,91] However, average TChl-a for each cluster showed a positively correlating trend with the slopes of the glucose/T_{50} correlation for clusters 1, 2, and 4 (Figure 3). This indicates that TChl-a as a marker for total phytoplankton biomass and free glucose possibly describes the release of INEs in Arctic water together.

Regarding the fractional composition of the phytoplankton groups based on diagnostic pigment analysis (Figure S5b), cluster 1 samples were dominated by the group of chlorophytes (average 62%) and almost no haptophytes and dinoflagellates appeared. The fractional phytoplankton composition of cluster 2, comprising samples from melt ponds and the marginal ice zone, was more inhomogeneous for the contributing groups among the respective samples than that of the other clusters. However, the highest fractional amounts of dinoflagellates (average 33%) and cyanobacteria (average 17%) were found in cluster 2. Clusters 3 and 4 showed similar phytoplankton patterns containing mostly diatoms (average 33−39%) and chlorophytes (average 26−30%) and a certain amount of haptophytes (average 15−17%). However, TChl-a concentration was much higher in cluster 4 than in cluster 3. With some few exceptions, diatoms, chryptophytes, and chrysophytes seemed to be distributed within all clusters in comparable amounts. A concrete assignment of INA to a certain phytoplankton group was difficult due to the biological complexity of these samples. However, a more detailed investigation of the phytoplankton and bacterial composition was beyond of the scope of this work, which only enabled pigment samples for the bulk waters. This needs to be investigated in further studies.

Possible Biochemical Links between Free Glucose and INA in Arctic Seawater. Previous studies have already demonstrated that the INA of Arctic seawater seems to be connected to the presence of marine microorganisms.[27,28,76] Recently, Irish et al. (2017) found a strong negative correlation

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between INA and salinity in Canadian Arctic open ocean samples,[37] as it had been reported for DFCHO and salinity in Arctic seawater samples.[68] These authors concluded that melting sea ice might release microorganisms and exudates with high INA. In our study, we observed that high INA/free glucose concentrations occurred in locations that are exposed to persistent melting processes, as it happens at the marginal ice zone and in melt ponds. Thereby, INEs could directly be released from the sea ice or INEs are actively produced due to stress caused by the permanent exposure to freezing and melting at the freezing point of seawater. Slow freezing of water could cause the uncontrolled crystallization of intracellular ice, which may perforate the cell walls and cell membranes of prokaryotes and algal cells. An adaption of these microorganisms to these challenging environmental conditions could be either the availability of intracellular cryoprotective substances, as free glucose, or the controlled freezing by excreting INEs.

Such processes were already described for some terrestrial phytopathogenic bacteria (e.g., *Pantoea agglomerance* or *Pseudomonas syringae*). They are known for their capability to induce the nucleation of ice in supercooled water from −1.5 to −3 °C[92] and drive frost damage on leaves of many plants, especially during cool spring mornings. For minimizing harm on their own cells by aggregation of proteins or changed membrane fluidity, they contain several low molecular cryoprotective substances. Glucose as an intracellular cryoprotectant has been found in some bacteria strains of *Pseudomonas lurida* and P*antoea ananas*.[93,94] Therefore, it seems to be likely that marine phytopathogenic bacteria do also contain such cryoprotectant substances as glucose for their own protection while they are causing freezing damage at algal cells. In accordance with Chance et al. (2018), glucose as an INA tracer may be released at the same time as the INE itself after microbiological cell damage caused by stress situations.

As a survival strategy, diatoms and other algae exude exopolymeric substances (EPS), mainly from exopolysaccharides, in environments of low or fluctuating water potential.[85] These biofilms play important buffering and cryoprotectant roles for microorganisms against high salinity and ice crystal damage and even allow the survival in subzero brine in the Arctic winter.[95,96] Potentially, these carbohydrate-containing microgels allow a structuring of water molecules and may act as INEs. An enzymatical degradation of these gels to free glucose might explain the simultaneous occurrence of INA and free glucose. However, following controlled lab experiments should elucidate the biochemical link of free glucose with the INA in more detail.

In conclusion, the SML of melt ponds and the marginal ice zone has been identified as a potential source for Arctic INP. Positive correlations between the abundance of free glucose and the INA in Arctic water samples could be shown, especially under consideration of phytoplankton pigment compositions. Possibly, the formation of free glucose is connected to the release of INEs in Arctic seawater, e.g., by the decay of phytoplankton or exuded polysaccharides with INA. Therefore, free glucose may have the potential to serve as a tracer for INEs in Arctic water, particularly when biological parameters (e.g., phytoplankton and bacteria characterization) are available for the aqueous samples. Further investigations are needed to understand the biochemical role of free glucose within the process of the generation of INEs by phyto- and bacterioplankton, including the analysis of polysaccharides as likely precursors and potential INEs. Dedicated lab experiments under controlled conditions may help to understand enriching processes of free glucose/INEs in the SML. For testing the temporal and spatial applicability of the found correlation, long-term observations of glucose, INA, phytoplankton, and bacterial information in the different habitats such as the marginal ice zone and melt ponds as well in entirely other regions on Earth, e.g., in the Tropics or Antarctica, should be performed. To this end, the development of a quick test for glucose (e.g., based on enzymatic reactions) might help to identify interesting samples with high INA directly during future field campaigns. Further studies should focus on selective transfer mechanisms of free glucose and INPs into Arctic aerosol, cloudwater and precipitation samples. Understanding the (bio)-chemical links to INA inside the potential pools for atmospheric INP will help to understand the formation of mixed-phase and ice clouds in the Arctic and get a better understanding of biochemical processes contributing to the Arctic Amplification.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01469.

> Locations of water sampling (SML and bulk) during cruise PASCAL/SiPCA; T_{50} plotted against free glucose concentration including all collected Arctic and Atlantic seawater samples; fraction frozen curves of glucose standard solutions; dendrogramm derived from hierarchical cluster analysis; TChl-a concentration and fractional phytoplankton composition in Arctic water samples; previous studies of INA in Arctic SML and bulk water samples; detailed sample information; details about the analysis of free glucose (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: herrmann@tropos.de.

ORCID

Hartmut Herrmann: 0000-0001-7044-2101

Notes

The authors declare no competing financial interest.

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