Marine biogenic polysaccharides as a potential source of aerosol in the high Arctic
Towards a link between marine biology and cloud formation

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Abstract

Primary marine aerosol particles containing biogenic polymer microgels play a potential role for cloud formation in the pristine high Arctic summer. One of the major sources of the polymer gels in Arctic aerosol was suggested to be the surface water and more specifically, the surface microlayer (SML) of the open leads within the perennial sea ice as a result of bubble bursting at the air-sea interface. Phytoplankton and/or ice algae are believed to be the main origins of the polymer gels. In this thesis, we examine the chemical composition of biogenic polymers, with focus on polysaccharides, in seawater and airborne aerosol particles collected during the Arctic Summer Cloud Ocean Study (ASCOS) in the summer of 2008. The main results and findings include:

- A novel method using liquid chromatography coupling with tandem mass spectrometry was developed and applied for identification and quantification of polysaccharides.
- The enrichment of polysaccharides in the SML was shown to be a common feature of the Arctic open leads. Rising bubbles and surface coagulation of polymers are the likely mechanism for the accumulation of polysaccharides at the SML.
- The size dependencies of airborne polysaccharides on the travel-time since the last contact with the open sea are indicative of a submicron microgel source within the pack ice. The similarity of polysaccharides composition observed between the ambient aerosol particles and those generated by in situ bubbling experiments confines the microgel source to the open leads.

The demonstrated occurrence of polysaccharides in surface sea waters and in air, with surface-active and hygroscopic properties, has shown their potential to serve as cloud condensation nuclei and subsequently promote cloud-drop activation in the pristine high Arctic. Presumably this possibility may renew interest in the complex but fascinating interactions between marine biology, aerosol, clouds and climate.
List of Papers


Reprints are made with permission from the publishers. I made the following contributions to the papers presented here:

**Paper I**
I was responsible for the experimental work and authoring the paper in collaboration with Dr. Araia. Drs. Emmer and Leck gave supervision.

**Paper II**
I was responsible for the experimental work and authoring the paper in collaboration with Drs. Nilsson, Ilag and Leck.

**Paper III**
I was responsible for performing the monosaccharide measurements using LC/MS/MS, conducting the laboratory bubble experiment, and interpreting the results. Dr. Matrai’s group in Bigelow Laboratory performed the seawater sampling and measurements of total organic carbon and bulk carbohydrates. The text was developed through discussion with Drs. Leck and Matrai who also initiated the idea of this paper.

**Paper IV**
The idea underlying this paper was initiated by Dr. Leck. I was responsible for the novel analyses and the subsequent evaluation using LC/MS/MS, sampling of aerosol particles and the writing of the section concerning the analytical chemistry. Caroline Leck took the leading role in the interpretations of data and the discussion of the results as well as the construction of text.
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<td>ASCOS</td>
<td>Arctic Summer Cloud-Ocean study</td>
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<td>BCI</td>
<td>Berner cascade impactors</td>
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<td>CCN</td>
<td>Cloud condensation nuclei</td>
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<tr>
<td>CE</td>
<td>Capillary electrophoresis</td>
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<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
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<td>ESI</td>
<td>Electrospray ionization</td>
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<tr>
<td>EPS</td>
<td>Extracellular polymeric secretions</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>HILIC</td>
<td>Hydrophilic interaction liquid chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
</tr>
<tr>
<td>HMW-DOM</td>
<td>High molecular weight dissolved organic matter</td>
</tr>
<tr>
<td>MIZ</td>
<td>Marginal ice zone</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
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<tr>
<td>OW</td>
<td>Open water</td>
</tr>
<tr>
<td>PI</td>
<td>Pack ice</td>
</tr>
<tr>
<td>POM</td>
<td>Particulate organic matter</td>
</tr>
<tr>
<td>SCX</td>
<td>Strong cation exchange</td>
</tr>
<tr>
<td>SML</td>
<td>Surface microlayer</td>
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<tr>
<td>SPE</td>
<td>Solid phase extraction</td>
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<tr>
<td>SRM</td>
<td>Selected reaction monitoring</td>
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<tr>
<td>SSW</td>
<td>Subsurface water</td>
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<tr>
<td>TEP</td>
<td>Transparent exopolymer particles</td>
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<tr>
<td>TFA</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
<td>TFF</td>
<td>Tangential flow filtration</td>
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<tr>
<td>MS</td>
<td>Mass spectrometry</td>
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<td>MWCO</td>
<td>Molecular weight cutoff</td>
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1. Introduction

The potential of marine aerosol to serve as cloud condensation nuclei (CCN) and its role for forming clouds remains the largest uncertainty in projections of the Earth’s albedo and its effect on the climate (IPCC, 2007). In the pristine high Arctic north of 80°, a local source of aerosol particles is proposed to be surface water and more specifically, the surface microlayer (SML, uppermost 1 mm of the ocean surface) of the open water leads within pack ice region (Leck and Bigg, 2005a; Leck et al., 2002). The open-lead SML has been characterized as being enriched in biogenic microcolloids (denoted exopolymer secretions, EPS), shown to be polymer microgels or polymer gels resulting from biological activity including extracellular secretion, grazing and cell-lysis from microalgae and bacteria (Bigg et al., 2004; Matrai et al., 2008; Orellana et al., 2008). Polymer microgels are highly surface-active and hydrated (99% water) polysaccharide molecules spontaneously forming 3-dimensional networks inter-bridged with divalent ions, to which other organic compounds, such as proteins and lipids, are readily bound (Decho, 1990). Recent studies demonstrated that polymeric gels, due to their emergent properties, can constitute an important source of active CCN once they are ejected into air through bubble bursting (Orellana et al., 2011). These results verify past studies of the aerosol-cloud relationship over the Arctic pack ice area (Bigg and Leck, 2008; Leck and Bigg, 1999; Leck and Bigg, 2005b; Leck and Bigg, 2010; Leck et al., 2002). Yet, many aspects of the processes involved remain insufficiently investigated and verified. Knowledge of chemical characteristics of the biogenic polymers, essential for understanding the mechanisms whereby primary marine organic particulate matter affect CCN activation, is notably fragmentary.

The present thesis is centered on the chemical characterization of organic compounds over the central Arctic Ocean with focus on polysaccharides in seawater as well as atmosphere.

The overall objective is:

- To create prerequisites such as methodologies and instrumental techniques for determination of monosaccharide composition of organic matter in marine systems with emphasis on seawater and airborne aerosol particles (Papers I and II).

- To characterize the molecular composition of polysaccharides in the open-leads SML and to understand the chemical and physical processes taking place at the interface between the SML and the bulk water below. (Paper III).

- To elucidate possible pathways of the sea-to-air exchange of surface active organic matters by bubble bursting (Papers III and IV).

- To study the polysaccharides in size-resolved airborne aerosol particles and their source attribution (Paper IV).

The work was performed within the framework of the ASCOS program (Arctic Summer Cloud and Ocean Study, www.ascos.se) launched in the summer of 2008 as part of the International Polar Year 2007-2009.
1.1 Aerosol and its climatic relevance

Aerosol particles contribute to the Earth’s energy budget (cooling or warming) directly by scattering and absorbing radiation and indirectly by acting as CCN (Charlson and Pilat, 1969; McCormick and Ludwig, 1967). The aerosol indirect effect pertains to the mechanisms by which aerosol particles modify the microphysical properties of clouds and hence the radiative forcing of clouds. The reflectivity, lifetime and thickness of a cloud depend on the sizes of cloud droplets and the number concentration of the CCN on which cloud droplets form and grow (Twomey, 1977). The efficiency and effectiveness of an aerosol population for acting as CCN are determined by the size, chemical composition, morphology and state of mixing of the aerosol in addition to cloud dynamics (i.e., the water-vapor super saturation in the cloud). Typically, aerosol particles with sizes > 80 nm in diameter and with a hygroscopic component for promoting water vapor condensation will act as active CCN (Hoppel et al., 1994; Seinfeld and Pandis, 2006). The assessment of the Intergovernmental Panel on Climate Change (IPCC, 2007) reported that on a global average the sum of direct and indirect aerosol forcing is negative (cooling) and comparable in magnitude to the positive effect due to anthropogenic greenhouse gases of about 2.4 Wm$^{-2}$. These assessments of aerosol forcing have been based largely on model calculations and are, however, associated with the largest uncertainties (cf. Figure 1).

![Figure 1. Global average radiative forcing (RF) in 2005 (best estimates and 5 to 95% uncertainty ranges) for CO$_2$, CH$_4$, N$_2$O and other important agents and mechanisms, together with the typical geographical extent (spatial scale) of the forcing and the assessed level of scientific understanding (LOSU). Aerosol particles from explosive volcanic eruptions contribute an additional episodic cooling term for a few years following an eruption. The range for linear contrails does not include other possible effects of aviation on cloudiness (adapted from the fourth assessment report of the IPCC, Summary for policymakers 2007)](image_url)

The uncertainty of climate projections based on model calculations is particularly large for the Arctic region where the climate is changing faster than anywhere else on the earth, these at a
rate twice the global average (ACIA, 2004; Holland and Bitz, 2003). The major weakness in the simulations of future climate scenarios is due to insufficient understanding of the aerosol-cloud radiative processes and their feedback mechanisms involving the ocean, sea ice, snow cover and, not least, marine biological activity (e.g. Intrieri et al., 2002; Leck et al., 2004; Karlsson and Svensson, 2011; Tjernström et al., 2008). In the Arctic, the interactions between aerosol, cloud and radiation represent a warming factor for the regional climate due to the semi-permanent ice cover which increases the Earth’s albedo compared to the ocean surface (Mauritsen et al., 2010; Sedlar et al., 2010). Over the central Arctic Ocean during summer, the observed CCN number concentrations are usually extremely low (< 100 cm⁻³, occasionally < 1 cm⁻³) (Bigg and Leck, 2001; Bigg et al., 1996; 2001; Lannefors et al., 1983), which is typically orders of magnitude smaller than at low latitudes (100s-1000s cm⁻³) (Ramanathan et al., 2001). As a result, the cloud albedo is very sensitive to the both the temporal and spatial distribution of available aerosol particles in the air.

1.2 Marine biogenic organic aerosol particles over the ice

Marine aerosol particles over the remote ocean consist of a variety of chemical components including both inorganic (i.e., sea salts and non-sea-salt sulphates) - and organic compounds. These primary organic and inorganic aerosols can, upon bubble bursting at the air-sea interface, be ejected into the overlying atmosphere through both film drop and jet drop formation (Blanchard and Woodcock, 1957). The resulting particles could serve as sites for condensation of oxidation products such as dimethyl sulphide. (Clarke et al., 1998; O’Dowd et al., 1993; Facchini et al., 2008; O’Dowd et al., 2004; Leck and Bigg, 2005b; Leck et al., 2002).

More specifically, the SML of the open leads within the Arctic pack ice area was proposed (and very recently verified, cf. Orellana et al., 2011) as one of the major sources of the polymer microgels known to dominate the submicron aerosol population (Leck and Bigg, 1999; 2005a). These authors suggested that a bubble-induced mechanism was responsible for enrichment of organic matter in the SML (Bigg and Leck, 2008). The contribution of this biogenic organic matter to Arctic aerosol is enhanced in summer when sea-ice melting peaks and biological activity is high (Bigg et al., 2004; Matrai et al., 2008). The increasing fraction of organic aerosol during the period of high biological activity has also been documented at lower latitudes, e.g. over the North Atlantic Ocean (O’Dowd et al., 2004; Facchini et al., 2008) and the Southeast Pacific Ocean (Hawkins and Russell, 2010).

What past studies also have shown is that there is a potential for the polymer gels with their partially colloidal (extracellular) and granular (structural) structures (Leck and Bigg, 2005a; Leck and Bigg, 2010; Orellana et al., 2011) to separate into colloidal fragments having sizes within the sub-accumulation mode peaking in the Aitken mode at a diameter of around 40 nm (Figure 2). More than 80% of the observed gel particles were smaller than 100 nm, and nearly 100% were smaller than 200 nm. Gels in sizes as small as 2 nm could be quantified. The fragmentation process would be promoted by exposure to ultraviolet radiation (Orellana et al., 2011). Figure 2 shows examples of polymer microcolloids within sulphate and other particles containing a core microcolloid.
Figure 2. Transition electron micrographs of CCN in the Aitken mode (25-70nm; 1st column), the Accumulation mode (70-1000nm; 2nd column) and the Coarse mode (1-10 µm; 3rd column) sampled over the high Arctic leads. The Aitken-mode particles are organically derived, pentametric, virus-like particles (top left panel) or small microcolloid aggregates with EPS (centre left panel). As the submicron particles grow, we see particles resulting from the deposition of acids/organic vapours on a microcolloid aggregate (top and centre middle panels) or typical of a sulphur-containing particle in which any nucleus has become obscured by a surrounding of a sulphate-methane sulfonate-ammonium complex (bottom middle panel). Finally, the coarse mode includes single source particles such as sea salt, (which is only present on rare occasions of high winds >12 ms⁻¹, centre right) or a bacterium (top right) and particles of multiple-source origin, cf. the bottom right panel, showing sea salt and a bacterium coated with an organic film and characterized by the concentric rings typical of droplets of H₂SO₄. (Adapted from Leck et al., 2005c)

1.3 Polymer gels and extracellular polysaccharides

Marine polymer gels, also known as microcolloids, are, as briefly mentioned above, often used to denote a broadly defined group of extracellular polymeric secretions (EPS) produced by microorganisms such as bacteria and phytoplankton (Chin et al., 1998; Decho, 1990). Since polysaccharides constitute a substantial component of the polymers (which additionally include minor fractions of peptides and lipids), the abbreviation “EPS” is also employed to describe the extracellular polysaccharides or exopolysaccharides. Within the context of this thesis, both terms EPS and polysaccharide will be used, depending on whether focus is on the chemical or physical properties of the polymer microgels.
Microgels are three-dimensional (3-D) polymer networks inter-bridged with divalent ions (Ca$^{2+}$/Mg$^{2+}$) resulting from the spontaneous assembly/dispersion of dissolved organic matter (DOM). They are ubiquitous in marine environments ($10^6$-$10^9$ particles ml$^{-1}$) (Decho, 1990; Wells and Goldberg, 1993; Verdugo et al., 2004, Bigg et al., 2004) with a broad range of sizes from nanometers to several micrometers. They can exist in 'truly dissolved' form (< 1 kDa), as colloids and/or associated with particulate matter (i.e., bacteria, phytoplankton and their detritus etc.). Because of their high molecular weight, polymer gels predominantly belong to the colloidal fraction of DOM or high molecular-weight DOM (HMW-DOM) (Passow, 2002). Figure 3 shows the polymer gels over the full size range of organic matter from DOM, colloids (HMW-DOM) to traditional particulate organic matters (POM) (Azam and Malfatti, 2007). The freshly released polymers exist as fibrils with diameters from around 1 kDa to 10 kDa and lengths of hundreds of nanometers. The assembly of free macromolecules into 3-D microgels is a dynamic process in which macromolecules continuously redistribute themselves between bulk seawater and assembled microgels (Passow, 2002). Self-assembled polymer gels disperse under the influence of ultraviolet light (Orellana and Verdugo, 2003) and undergo volume-phase transitions upon acidification (Chin et al., 1998). EPS can be present as part of the tight capsular material surrounding the cell of an organism or released into the ambient environment as loosely dispersed slime free from any particular cell. The hydrated-layer EPS matrix provides a stable environment and is essential for the growth and survival of the embedded microbes. The matrix can act as physical buffering against sudden change in the adjacent environment (temperature, pH and salinity). In both the Arctic and Antarctic regions it was found that EPS together with the embedded microbial cells can be incorporated into new ice crystals during ice nucleation and float at the sea surface (Gleitz and Thomas, 1993).

**Figure 3.** The size range of organic matter in the ocean (adapted from Azam, 2007)
2. Characterization of marine biogenic polysaccharides and the analytical challenge

The monosaccharide composition of polysaccharides in marine microcolloids can help us to identify their sources (e.g., algae, bacteria or vascular plants) and understand their seawater-atmosphere exchange processes (chemical and physical). Chemical characterization of polysaccharides can also assist us in evaluating their lability (biological availability), diagenetic state and hygroscopic properties, which is essential for understanding their capability to serve as CCN. Polysaccharides of marine-biological origin represent a diverse mélange of macromolecules that are polyfunctional, heterogeneous, polyelectrolytic, polydisperse in molecular weight at marine environmental trace levels (typically picomolar). The chemical complexity of the marine polysaccharides and the enormous amount of information within their complex structure gives rise to truly analytical challenge which have led to the following words of wisdom from the renowned chemical oceanographer John Hedges:

--- The future of oceanographic research belongs in large part to those who can learn to read these molecular messages (Hedges and Carlson, 2001).

2.1 Chemical composition of marine polysaccharides

Most polysaccharides produced by marine microorganisms are heteropolysaccharides, i.e., complex carbohydrates composed of repeating unit of several types of monosaccharides in conjunction with glycosidic bonds. The monomers most commonly found in marine polysaccharides include hexose (glucose, galactose and mannose), pentose (arabinose, xylose and ribose) and deoxysugar (fucose and rhamnose), cf. Figure 4. These compounds make up the major building blocks of polysaccharides (Aspinall, 1970). The terms “neutral sugars” or neutral monosaccharides are also quite frequently used as synonyms in chemical oceanography when chromatographic techniques are employed for compositional analysis (Borch and Kirchmann, 1997; Rich et al., 1997). The relative abundance of different monomers in the total polysaccharide varies with the source or the specific phytoplankters /bacteria. E.g., polysaccharides from bacteria are generally rich in glucose and galactose (Sutherland, 1999), whereas polysaccharides from phytoplankton have a relatively higher content of rhamnose, xylose and mannose (Hoagland et al., 1993). Liebezeit(1984) found that large amounts of dissolved polysaccharides were released during phytoplankton blooms and that their composition changed during the bloom. A wide variety of functional groups (i.e., hydroxyl, amino, sulfate, phosphate groups) are often associated with the complex macromolecular structure in addition to the monomers mentioned above. The overall physicochemical characteristic of EPS is also governed by the abundance and type of other functional groups. E.g., uronic acids or sulfate, common functional groups in marine bacteria, give the polymers an overall negative charge, which results in a gel-like feature (high viscosity) for the biomolecules by binding to divalent cations (Ca$^{2+}$ and Mg$^{2+}$) (Chin et al.,
Removal of Ca$^{2+}$ and Mg$^{2+}$ will cause the network to collapse, whereas addition of Ca$^{2+}$ will restore the gel-like aggregation.

Figure 4. Some common monomers (aldohexoses, aldopentoses, amino sugars, deoxysugars and uronic acids) existing in marine polysaccharides (adapted from Panagiotopoulos, 2005)

2.2 Techniques for the determination of monosaccharide composition

In chemical oceanography, a chromatography-based method is often preferred for monosaccharide compositional studies while the colorimetric method is often used for studies of bulk carbohydrates, which have the most abundant isomers compared to any other group of chemical compounds. The high stereoisomeric diversity, the high hydrophilicity, the low volatility and the insufficient light-absorbing chromophore of monosaccharides pose a number of analytical challenges. It is thus desirable to develop a method with a low enough limit of detection and a sufficiently high resolution (separation capacity), especially for applications in the extremely pristine remote marine areas such as the inner Arctic during summer (Leck et al., 1996).
The following techniques have been developed in the past to characterize carbohydrates in various environmental samples:

- Spectrophotometric methods are used for bulk determination of carbohydrates and carbohydrate-analogues. However, it is prone to interferences and does not give information on molecular composition (Pakulski and Benner, 1992). The functional groups of carbohydrates (e.g., aldehyde and ketone groups) are not specific only to carbohydrates, especially in natural sample matrices.

- Gas-chromatography-based methods (Chen et al., 2002) require a derivatization step, since free sugars are insufficiently volatile for direct analysis. This time-consuming procedure may, to some extent, contribute to sample loss and potential contamination during sample preparation.

- High-performance anion-exchange liquid chromatography with pulsed amperometric detection is mostly used to determine liberated monosaccharides in marine environments (Johnson and LaCourse, 1990; Panagiotopoulos and Sempere, 2005). However, the delicate operation of the working electrode and the lengthy system-equilibration time (35–50min) limit its application. The ion-exchange conditions commonly used to achieve the monomer separation utilize high flow rates and a high salt content and are therefore not compatible with mass spectrometric analysis (Bruggink et al., 2005).

- High-performance liquid chromatography coupled to tandem mass spectrometry (HPLC/MS/MS) techniques, which is highly selective and sensitive is potentially advantageous and has recently attracted widespread interest. The limitation is that the retention of highly polar and hydrophilic carbohydrates on conventional reversed phase (RP) LC columns is not adequate for the separation of isomeric saccharides. The application of this technique has also been limited by the low ionization efficiency of neutral sugars using electrospray ionization.

- FTIR (Fourier transform infrared) scanning transmission X-ray microscopy and NMR (nuclear magnetic resonance spectroscopy) have recently been applied for the study of airborne organic matter chemically analogous to polysaccharides (Facchini et al., 2008; Hawkins and Russell, 2010; Russell et al., 2009). However, no quantitative information regarding molecular composition can be obtained by these methods.

- Capillary electrophoresis (CE) separates monosaccharides based on their different dissociation constants and provides extremely high resolution of even the positional isomers. The advantages are the small sample consumption (nL) and the need for minimal purification prior to analysis. However, the rather small volume required for injection is at the same time an obstacle for determining trace levels of saccharides in remote marine atmospheric samples, since it increases the detection limit.

2.3 Hydrophilic interaction liquid chromatography and tandem mass spectrometry

In marine colloids, as in any natural biological sample, the complexity of the sample matrix may lead to excessive baseline noise during the chromatographic analysis. Consequently, interferences between the matrix components and the target compounds can strongly affect
the results by hindering peak attribution and integration. From this point of view, tandem mass spectrometry is highly useful because of its high selectivity. However, one should be aware that very often in mass spectrometry, the matrix affects the signal strength by either enhancing or suppressing the signal.

**Hydrophilic interaction liquid chromatography (HILIC)** is a new separation technique which has greatly increased in popularity over the last few years due to the growing need for separation of polar and hydrophilic compounds in complex mixtures. In HILIC, the retention of the analytes on the LC column is achieved by a partitioning of the analytes between a water-enriched layer formed on the surface of the stationary phase and a relatively water-deficient mobile phase (usually 5–40% water in acetonitrile). Typical stationary phases of HILIC are silica or polymer particles carrying polar functional groups.

**Mass spectrometry (MS)** is an analytical technique that measures the mass-to-charge ratio (m/z) of charged particles. A mass spectrometer consists of three major modules: an ion source which ionizes the analyte molecules and transfers them into the gas phase; a mass analyzer that sorts the ions, *e.g.*, by applying electromagnetic fields, and a detector. In conjunction with LC, ionization can be achieved using electrospray ionization (ESI), atmospheric pressure chemical ionization or atmospheric pressure photoionization. ESI, as one of the most important ionization techniques, is the method of choice for labile biomolecules that hardly can be ionized by other techniques. The main problem of using ESI for monosaccharides is the low ionization efficiency achieved compared to other biomolecules. *E.g.*, peptides can be detected in the low femtomolar range, whereas monosaccharides require a picomolar concentrate (Harvey, 2001). Furthermore, ESI is highly prone to matrix effects, which either facilitate or hinder the ionization process. Efficient clean-up and chromatographic separation are important ways of minimizing the matrix interference, and use of isotope-labeled standards is advisable for reducing matrix effects on quantification. The higher fraction of volatile organic solvent in HILIC is beneficial, since the solvent evaporation becomes more efficient. This, in turn, decreases the ion suppression effect and enhances sensitivity.

**Tandem MS/MS**, also known as triple-quadrupole MS, consists of 3 quadrupole units arranged in sequence: a scanning Q1 quadrupole analyzer to separate the precursor ions; an non-scanning RF-only Q2 quadrupole that serves as a collision cell to fragment the ions transferred from Q1, and a scanning Q3 quadrupole that can separate the fragments produced in the Q2 unit (Figure 5). There are four possible scanning modes of operation: i) precursor ion scanning, ii) product ion scanning, iii) neutral loss scanning and iv) selected reaction monitoring (SRM). The Q1 and Q3 mass analyzers either scan within a defined m/z range or are fixed at a certain m/z. *E.g.*, in precursor-ion scanning, the Q1 scans all precursor ions of a fragment selected by the Q3. Conversely, in product-ion scanning mode the Q1 is fixed at one m/z and a full-mass spectrum of the fragment ions is produced after passing through the Q3.

**SRM scanning** is based on selection of ions originating from a fragmentation reaction. In SRM mode the Q1 is fixed at the m/z of a precursor and the Q3 at the m/z of a product, and thus the ions selected by Q1 are only detected if they produce a given fragment matching the selected reaction. SRM with a two-step mass filtering process provides very high selectivity, which is useful for complex samples. Even though the sensitivity (signal strength) is generally decreased compared to full-scan MS, the noise is reduced even more, leading to very high S/N ratios.
Figure 5. Triple quadrupole LC/MS/MS system
3. Experimental

3.1 Study area

This investigation was performed as part of the atmospheric program of the Arctic Summer Cloud Ocean Study (ASCOS, www.ascos.se) onboard the Swedish icebreaker Oden during the biologically most active period between the late-summer melt season and the transition to autumn freeze-up in 2008. The expedition was an interdisciplinary effort including meteorology, atmospheric chemistry, oceanography and, marine chemistry as well as biology aimed at understanding the process of low-level cloud formation over the central Arctic Ocean. The expedition started on August 2 from Svalbard, headed north to the inner Arctic and returned on September 9. After an open water (OW) station on August 3 and a marginal ice zone (MIZ) station on August 4 (both located in the Greenland Sea-Fram Strait area), Oden was moored to a large ice-floe (approximately 3×6km, Pack-ice-drift floe, PI) at 87.4°N; 1.5°W on August 12, and proceeded to drift for the following three weeks, until midnight between the 1st and 2nd of September (87.1°N; 12°W). One additional MIZ (September 6) and one OW (September 7) station were surveyed on the way back. Figure 6 illustrates the ASCOS cruise track. A photograph of the ice floe is included in Figure 6 with the open-lead station and the icebreaker Oden indicated. The majority of the collected seawater and atmospheric samples described below were obtained during the 3-week PI-drift operation and on the brief OW and MIZ stations.

Figure 6. Left: map of the ASCOS cruise track (pink) with ice-drift period highlighted (inset area marked in red). The ice edge (blue line) is shown for the start of the drift period on 12 August 2008. Right: The ice floe on which the ASCOS measurements took place with the icebreaker Oden and the Open Lead sampling site marked.

3.2 Sampling

- **SML samples** were collected from open leads by a small battery-powered, radio-controlled vessel equipped with a rotating drum (Figure 7, left panel). The microlayer water adhered to the surface of the rotating drum (which was partially submerged in the water) and subsequently dripped continuously into a glass bottle inside the
skimmer vessel. Corresponding subsurface water (SSW) was collected at the same locations at a depth of about 0.5 m. Knulst et al. (2003) reports full details on the operation of the sampling vessel.

- **Ambient aerosol particles** were collected onboard the icebreaker at a height of 23 m a.s.l. using multi-stage Berner cascade impactors (BCI) (Berner et al., 1979) controlled at 50% RH. Particles > 10 μm aerodynamic diameter (EAD) were excluded through a size-segregating inlet. Details about the sampling manifold and pollution the sensor are given by Leck et al. (2001) and references cited therein. The BCI used is a 5-stage, high sampling volume impactor that collects particles in the following size ranges (given in EAD): (1) <0.161 μm; (2) 0.161-0.665 μm; (3) 0.665-2.12 μm; (4) 2.12-5.0 μm; and (5) 5.0-10 μm with 50% cut-off efficiency. Converted to dry (20% RH) geometric mean diameters, the BCI size ranges corresponded to <0.113, 0.113-0.489, 0.489-1.58, 1.58-3.73 and 3.73-7.47 μm.

- **Bubble scavenge experiments** were conducted in the onboard wet laboratory using a pre-cleaned glass tower (10 cm inside diameter, 200 cm in height) (Figure 8). Seawater was fed directly into the tower. Bubbles were generated by purified zero air blown into the water from the bottom. The flow rate of zero air was controlled to provide sufficiently gentle bubbling at desired size. The uppermost layer (~3 cm) of seawater was taken to represent the substances enriched in the SML. Aerosol particles generated by bursting bubbles above the water layer were collected during the 1 h of bubbling.

- **Nascent spray particles** were generated in situ at the air-sea interface (Paper IV) by the generation of bubbles in order to study the processes whereby the dissolved organic matter is transported into the atmosphere. A sintered glass filter bubbling source was positioned 15 cm under the water surface and driven by a battery-operated pump. The spray particles were collected 10 cm above the water surface on nylon filters using a high-flow vacuum pump operating at 150 L min$^{-1}$. This set-up permits both generation of bubbles and collection of the spray particles and was clamped to a small floating catamaran (Figure 7, right panel).

- **Fresh sea ice** (newly formed) was collected at times when the lead was partly frozen.

- **Ice algal assemblage** loosely attached to the bottom of the ice floe was collected at the edge of the open lead.
3.3 Protocols for sample pretreatment

The characterization of polysaccharides in seawater was initiated with microfiltration of the particulate matter in seawater through membranes with nominal size of 0.22 µm in diameter.
under gravity or mild vacuum. The filtrated seawater was isolated and desalted by ultrafiltration using tangential flow filtration (TFF) and dialysis to extract that HMW-DOM fraction with a molecular weight above 5 kDa (1 kDa corresponds to 1 nm). Hydrolysis with trifluoroacetic acid (TFA) was performed after the ultrafiltration to yield a pool of monomers (monosaccharides). Further clean-up to remove residual salt or proteinaceous matter was accomplished using solid-phase extraction (SPE) technique. A schematic flowchart of the protocols used for the sample pretreatment is illustrated schematically in Figure 9. The size-resolved particulate matter collected by the BCIs was extracted with Milli-Q water followed by hydrolysis as described in Paper IV.

![Flowchart of sample pretreatment](image)

**Figure 9.** Schematic outline of the designed protocol for pretreatment of seawater sample.

**Desalting by ultrafiltration and SPE**

The dissolved chemicals in seawater are called "salts" by oceanographers, with NaCl being predominant. In this study TFF and dialysis were used to isolate the HMW-DOM fraction from the bulk seawater. Both techniques are based on physical size-separation, and low-molecular-weight DOM in the sample such as monosaccharides and amino acids are also removed during desalting. Dialysis was accomplished by further ultrafiltration with the addition of a large volume (usually 5L – 10L) of Milli-Q water to the retenate after concentration. Ion-exchange mixed-mode SPE (SCX and SAX, strong cation and anion exchange) was used for desalting of the sample. All monosaccharides to be determined were almost completely recovered (>93%).
Hydrolysis

The efficiency of both strong (HCl and H$_2$SO$_4$) and mild (TFA) hydrolysis was examined for carbohydrate polymers. Strong hydrolysis with H$_2$SO$_4$ was performed in two steps: samples were treated with concentrated H$_2$SO$_4$ (72 wt% --12 M) for 2 h at ambient temperature, followed by a treatment with 1 M H$_2$SO$_4$ (100°C for 4 h). Mild hydrolysis was performed without the pretreatment step using H$_2$SO$_4$ and TFA at a lower concentration (1 M or 2 M). Our results showed that the higher acid concentration gave only a slightly larger total monosaccharide yield than mild hydrolysis. However, the neutralization steps involving precipitation lead to a notable monosaccharide adsorption and subsequent loss of sample (about 40% loss). TFA was ultimately chosen due to its relatively high volatility and high yields of monosaccharides compared to HCl. Optimal hydrolysis was obtained at a temperature of 100 °C for 2 h with a concentration of 4 M TFA.

3.4 Determination of monosaccharides by LC/MS/MS

The analytical technique employed to analyze the polysaccharide samples collected during ASCOS was LC/MS/MS. Chromatographic separation was performed using an aminopropyl-silica column (150×2.1 mm, 5 μm, ZorbaxNH$_2$, Agilent) at room temperature. The mobile phase was composed of acetonitrile, methanol and water at an isocratic condition. The LC system was coupled to a triple-quadrupole mass spectrometer equipped with a heated ESI probe. The ionization interface was operated in a negative mode. Quantification was undertaken in the SRM mode with deprotonated monosaccharides as precursor ions ([M-H]$^-$, m/z 179, 163 and 149) and fragments (at 59 and 89 m/z) as product ions based on the examination described in Paper II.

Optimization of LC condition

Three types of LC stationary phases were examined for separation of 7 targeted monosaccharide isomers, including a Hypersil Gold column, a ZIC-HILIC column and an amino-based column. The ZIC-HILIC column employed initially has, according to the literature, been extensively used for sugar separation. However, peak-splitting of anomers for each monosaccharide could not be avoided under the optimized LC conditions unless the column temperature was increased to about 50°C. Consequently, this column was not selected due to the difficulties with interpreting the anomeric peaks. An RP-UHPLC (ultra HPLC) system with a Hypersil Gold column (50mm×1.9 μm, Thermo) was evaluated, aiming at taking advantage of the smaller stationary-phase particles (< 2μm), which in principle yield higher separation efficiency and in the UHPLC system increases the speed of the analysis. Results from the MS analyses showed that pentose, hexose and deoxysugars could be distinguished under the SRM mode based on their different MS/MS transitions. However, the retention of monosaccharides on the RP-LC column was not sufficient and the isomers with same mass-to-charge ratio could not be separated. Besides, the separation from interferences was insufficient, and thus this method was not further considered. The amino-based HILIC-column (150×2.1 mm, 5 μm, Zorbax NH$_2$, Agilent), on the contrary, eliminated the drawbacks mentioned above and the polar monosaccharides were retained sufficiently by using aqueous acetonitrile containing 20-30% water as mobile phase. A problem with this Zorbax NH$_2$ column is that the reducing monosaccharides to some extent react with amino groups on the stationary phase by a carbonyl-amine condensation, yielding Schiff bases. This reaction leads to a deterioration of column performance after prolonged use. The risk increases with the
water content in the mobile phase and consequently the column lifetime is rather limited. To increase the lifetime, water in the binary system (acetonitrile and water) was partially replaced with methanol.

**Optimization of MS/MS condition**

In the present study electrospray ionization (ESI) of monosaccharides in negative ion mode was chosen, since monosaccharides in positive ion mode give rise to formation of multiple adducts with alkali metals which are often difficult to fragment efficiently by collision-induced dissociation. Fragmentation patterns of each precursor ion \((M-H)\) were investigated and a typical MS/MS product ion spectrum of monosaccharides is shown in Figure 10. A proposed major fragmentation pathway was cross-ring cleavage and neutral losses, indicated by the structural formula in Figure 10.

![Figure 10](image)

*Figure 10. MS/MS product ion spectra of \((M-H)\) of glucose at a collision energy of 10 eV.*

The quadrupoles in the MS system can serve not only as the focusing device, but more importantly as the selection device itself. Therefore it is important to obtain sufficient transmission efficiency for a specific mass or mass range, which is a challenge for small molecules (<200 m/z) such as monosaccharides. To get an adequate ion transmission and a minimal loss of targeted ions, optimization of MS parameters was initially carried out for offset voltages in a series of ion optics. Noteworthy is the mass-dependent S-lens RF amplitude, which is a key parameter that can improve the detection limit for small molecules. What is known as the S-lens in the Thermo TSQ Vantage system is actually an implementation of a stacked-ring ion guide to confine ions, using radio frequency electric fields in the high-pressure inlet region of the mass spectrometer to transmit ions more efficiently. A mass-dependent potential (S-lens offset voltage) is applied to the S-lens to accelerate the ions into the background gas for collision, which helps desolvation of the ions and consequently increases the sensitivity. However, the S-lens offset voltage should not be set too high, otherwise fragmentation caused by in-source (or up-front) collision-induced dissociation will decrease the sensitivity. The S-lens offset voltage was tuned manually to obtain a maximum transmission of ions through the lens. Compared with a dynamic ramp of
S-lens offset voltages at different masses obtained from an automatic tuning (using polytyrosine-1,3,6 solution), an approximately 100-fold or greater increase in terms of absolute ion counts was observed for the analytes of interest versus the auto-tuned setting. The optimized MS conditions are summarized in Table 1. Figure 11 demonstrates the chromatographic performance for monosaccharide separation with the optimized LC/MS/MS condition. It is seen that a baseline separation of analytes with the identical m/z ratio (e.g., xylose vs fucose) is unnecessary due to the specificity of MS/MS.

**Table 1. Working parameters of HESI-MS/MS**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray voltage (v)</td>
<td>-3500</td>
</tr>
<tr>
<td>Capillary temperature (°C)</td>
<td>300</td>
</tr>
<tr>
<td>Vaporizer temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>Sheath gas pressure (arbitrary unit)</td>
<td>40</td>
</tr>
<tr>
<td>Auxiliary gas pressure (arbitrary unit)</td>
<td>5</td>
</tr>
<tr>
<td>Ion sweep gas pressure (arbitrary unit)</td>
<td>0</td>
</tr>
<tr>
<td>Declustering voltage (v)</td>
<td>10</td>
</tr>
<tr>
<td>Collision gas pressure (mTorr)</td>
<td>0.5</td>
</tr>
<tr>
<td>Mass resolution (Da)*</td>
<td>Q1: 0.7; Q3: 0.7</td>
</tr>
</tbody>
</table>

* Mass resolution at full width at half maximum (FWHM)

**Figure 11.** Reconstructed SRM chromatograms of monosaccharide standard mixture with optimized LC/MS/MS condition
4. Summary of papers

A novel method using HILC/MS/MS was developed in Paper II for characterization of monosaccharide compositions in seawater and airborne aerosol samples. The ultrafiltration protocol designed in Paper I is capable of concentrating marine HMW polysaccharides from a saline matrix by a factor of ~400. In Paper II we demonstrated that HILIC, with a high MS compatibility, is a powerful tool for simultaneous determination of diastereometric monosaccharides naturally occurring in marine organic matters. ESI involving cross-ring cleavage of deprotonated monosaccharides in negative ionization mode yields abundant fragment ions and provides a sufficient sensitivity in SRM mode. The instrumental and method limits of detection (LOD), limit of quantification (LOQ) and precision of this method are summarized in Table 2. The results imply the potential to detect carbohydrate in seawater, generally at low nanomolar level, without extensive preconcentration steps. By assuming a sampling volume of 100 m$^3$ of air (24 h sampling at the designated BCI flow rate of 77 L min$^{-1}$) the detection of monosaccharides at levels as low as 0.2-0.4 pmol m$^{-3}$ would be possible. The method developed permits the first measurements of neutral monosaccharides naturally occurring in marine biopolymers by HILIC/MS/MS without derivatization, postcolumn addition or adducts formation.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>LOD $^a$ (pg)</th>
<th>LOQ $^a$ (pg)</th>
<th>Method LOD (ng L$^{-1}$)</th>
<th>Method LOQ (ng L$^{-1}$)</th>
<th>Precision, % RSD</th>
<th>Accuracy, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylose</td>
<td>0.7</td>
<td>2.2</td>
<td>0.3</td>
<td>0.9</td>
<td>5</td>
<td>102</td>
</tr>
<tr>
<td>Arabinose</td>
<td>1.5</td>
<td>5.0</td>
<td>0.6</td>
<td>2</td>
<td>10</td>
<td>86</td>
</tr>
<tr>
<td>Rhamnose</td>
<td>1.0</td>
<td>3.4</td>
<td>0.4</td>
<td>1.4</td>
<td>10</td>
<td>97</td>
</tr>
<tr>
<td>Fucose</td>
<td>4.2</td>
<td>13.8</td>
<td>1.7</td>
<td>5.5</td>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>Glucose</td>
<td>1.3</td>
<td>4.3</td>
<td>0.5</td>
<td>1.7</td>
<td>12</td>
<td>95</td>
</tr>
<tr>
<td>Galactose</td>
<td>1.7</td>
<td>5.7</td>
<td>0.7</td>
<td>2.3</td>
<td>4</td>
<td>84</td>
</tr>
</tbody>
</table>

$^a$ Retention time

$^b$ Instrumental LOD and LOQ, indicated by the amount of analytes injected on column

In Papers III and IV, seawater as well as size-resolved aerosol samples were collected in the high Arctic (at approximately 87.5°N; 5°E) during ASCOS in the summer of 2008. Monosaccharide compositional analyses of the collected samples were carried out using the HILIC/MS/MS method developed in Paper II. The results of Paper III showed that the
central Arctic Ocean open leads in summer appeared to be a biologically productive community with high concentrations of total organic matter compared to the global average. Based on the examination of the monosaccharide signature, a significant proportion of the organic pool was found to be the result of extracellular secretion by sea-ice algae. High heterogeneity and surface activity was the common feature of the exopolysaccharides collected from the open lead. The SML samples were nearly identical to the SSW samples in terms of monosaccharide composition, suggesting \textit{in situ} production by microorganisms in the underlying seawater or adjacent sea ice as an important source for the SML polysaccharides (Figure 12). The enrichment of polysaccharides in the SML appeared to be a common feature, with enrichment factors ranging from 1.7 to 7.0 for particulate polysaccharides and 3.5 to 12.1 for those in the HMW-DOM fraction. The substantial measured enrichment of polysaccharides in the HMW-DOM class of our samples indicated that colloidal organic matter could be preferentially scavenged into the SML with respect to the POM pool. Bubble scavenging experiments demonstrated that rising bubbles and surface aggregation of bio-reactive microcolloids are among the main processes of importance for the formation of the SML. Highly enriched polysaccharides in the freshly formed sea ice samples (with an enrichment factor >10 compared to SSW) suggested that the preferred trapping of organic matter may have taken place during the initial freezing, which may also have contributed to the formation of SML in the course of melting of the open-lead fringes.

\textbf{Figure 12}. Relative mole percentage of monosaccharides (\% mol) in aerosols over pack ice, bubble-generated sea spray particles, surface-active foam samples, surface microlayer (SML), subsurface seawater (SSW), as well as newly formed sea ice and algal assemblage. Shown are xylose (Xyl), arabinose (Ara), rhamnose (Rha), fucose (Fuc), the sum of glucose (Glu) and manose (Man), and galactose (Gal) in the high-molecular-weight dissolved (HMW DOM) and particulate (POM) organic matter. Aerosols are shown in submicron (Aitken and accumulation mode) and supermicron (Coarse mode) particles.

In Paper IV, polysaccharides were detected in the size-resolved aerosol samples collected over the central Arctic Ocean. Total monosaccharide concentrations in the aerosol varied considerably from 13.2 to 736 pmol m$^{-3}$, with about 50\% apportioned in submicron size range. Surface-active polysaccharides containing deoxysugars showed a clear bimodal size
distribution (peaking at Aitken and coarse modes), whereas the bimodal structure in hexose and pentose was found to be less significant (Figure 13). The relative abundance of polysaccharides in submicron-mode particles was high (>80%) when air masses had spent more than 5 days over the pack ice. The dependencies of the mass size distribution of polysaccharides on the travel-time spent over the pack ice are indicative of particle sources in the inner Arctic being most pronounced in the submicron size range. The similarity in the biochemical fingerprint of the determined monosaccharides between the ambient aerosol and those generated in situ at the open lead (Figure 12) provides support for bubble bursting being capable of generating the Aitken particles with origin in the marine polymer microgels.

Figure 13. Size distribution of deoxysugar (yellow), pentose (green) and hexose (pink) of aerosol particles collected onboard during ASCOS.

It has been recognized historically that organic matter in seawater exists in a continuum of sizes with two distinct classes broadly categorized as suspended and sinking particles. The downward flux of sinking particles has long been of interest due to their importance for sequestration of ocean carbon. The prevalent suspended microcolloids or even nanogels, as precursors of particulate aggregates (demonstrated in Paper III) as well as their functional role in the exchange of organic matter between ocean and atmosphere have, however, been largely neglected until recently. With the highly associated concentration of colloid polysaccharides observed within the SML (Paper III) as well as in the atmospheric particles (Paper IV), bio-derived surface-active polymer microgels, due to their highly surface-active and hygroscopic nature, could potentially become important for cloud-droplet formation over the inner Arctic during summer. These finding are in agreement with the recent study by Orrelana et al. (2011) that strongly advocated that the marine microgels dominate the available cloud condensation nuclei number population in the high Arctic (north of 80°N) during summer. The chemical dynamics of biogenic polysaccharides has, to the best of our knowledge, to date not been specifically addressed at a molecular level in the context of interaction between surface water, SML, sea ice and atmosphere. The present study could thus open a new direction of research focused on the complex but fascinating interactions between marine microbiology, aerosol, clouds and climate as well as in the geochemical exchanges of organic matter between the ocean and the atmosphere seen in a global perspective.
5. Outlook

The LC-ESI/MS/MS technique is a powerful tool that allows for the monosaccharide composition in the DOM pool to be examined in detail. However, its application is restricted by the need of acidic hydrolysis, by which only up to 10 % of the organic carbon can be recovered as neutral monosaccharides. Other carbohydrates, including amino sugars, sugar alcohols and uronic acids, etc. (which constitute a considerable fraction, viz. up to 50%, of HMW-DOM) still remain outside the analytical window. In fact, the proportion of uronic acids in the polysaccharides has been reported to be important for the degree of cross-linking and the adsorption (or aggregation) properties of the biopolymers. Alternatively, information is lost on the secondary and tertiary structures of marine carbohydrates after the hydrolysis procedure. E.g., it is unclear whether the abundant glucose observed in DOM belongs to a β-1,3 glucan (storage polysaccharide), cellulose (structural polysaccharide), glycoprotein or glycolipid. The potential to directly identify the intact particles with little sample preparation might be a complementary future advance in that direction. This would include matrix-assisted laser desortion/ionization-time-of-flight (MALDI-ToF) or ToF-secondary ion mass spectrometry (TOF-SIMS), which have recently been reported in proteomics for rapid classification of intact bacteria species and in the study of size-resolved individual atmospheric particles (Lay and Liyanage, 2005; Peterson and Tyler, 2002).

The central Arctic Ocean with a minimum of interference from anthropogenic and continental influence provides a platform for the study of the contribution of marine biology on CCN. During ASCOS, as well as from the three previous expedition in the summers of 1991, 1996 and 2001, a tenuous cloud regime with limited CCN was observed (Bigg et al., 1996; 2001; Mauritsen et al., 2010). The time resolution of aerosol sampling for polysaccharides in the present study was about 24 to 48 h and consequently air masses of different geographic origin could be collected as a mixture in one sample. The importance of polysaccharides for the real-time new-particle formation or subsequent growth can hardly be reflected and highlighted by the current time-resolved data. It can, however, be judged from the discrepancy between the size distribution of polysaccharides and the observed particle number concentration. With the highly sensitive LC/MS/MS method developed in the course of the present thesis, it would be possible to shorten the sampling time to 12 h or less using current impactor techniques. With the improved LC/MS/MS capability for analysis of smaller or less concentrated samples and higher measurement resolution, the potential exists to investigate biogenic organics in various environmental contexts at an unprecedented level of detail. E.g., characterization of polysaccharides preserved in deep-sea sediments or even ice cores might provide an instructive history of the Earth’s state or how the biosphere responded to global change in the past.

Arctic warming leads to an increasing area of ice-free water in the central Arctic, as suggested by most coupled atmosphere-ocean models as well as from satellite-data analysis (Johannesen et al., 2004; Walsh et al., 2002; Wang and Key, 2005). This will be intimately connected to an overall prolonged biologically productive season and rising level of bio-derived organic matter in the surface euphotic layer and subsequently in the marine airborne aerosol. This requires more comprehensive climate modeling involving marine biota in order to include the effects of the abundant biogenic-driven organic aerosol particles observed in the Arctic.
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