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Methods for biogeochemical studies of sea ice: The state of the art, caveats, and recommendations

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Abstract

Over the past two decades, with recognition that the ocean's sea-ice cover is neither insensitive to climate change nor a barrier to light and matter, research in sea-ice biogeochemistry has accelerated significantly, bringing together a multi-disciplinary community from a variety of fields. This disciplinary diversity has contributed a wide range of methodological techniques and approaches to sea-ice studies, complicating comparisons of the results and the development of conceptual and numerical models to describe the important biogeochemical processes occurring in sea ice. Almost all chemical elements, compounds, and biogeochemical processes relevant to Earth system science are measured in sea ice, with published methods available for determining

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biomass, pigments, net community production, primary production, bacterial activity, macronutrients, numerous natural and anthropogenic organic compounds, trace elements, reactive and inert gases, sulfur species, the carbon dioxide system parameters, stable isotopes, and water-ice-atmosphere fluxes of gases, liquids, and solids. For most of these measurements, multiple sampling and processing techniques are available, but to date there has been little intercomparison or intercalibration between methods. In addition, researchers collect different types of ancillary data and document their samples differently, further confounding comparisons between studies. These problems are compounded by the heterogeneity of sea ice, in which even adjacent cores can have dramatically different biogeochemical compositions. We recommend that, in future investigations, researchers design their programs based on nested sampling patterns, collect a core suite of ancillary measurements, and employ a standard approach for sample identification and documentation. In addition, intercalibration exercises are most critically needed for measurements of biomass, primary production, nutrients, dissolved and particulate organic matter (including exopolymers), the CO_2 system, air-ice gas fluxes, and aerosol production. We also encourage the development of *in situ* probes robust enough for long-term deployment in sea ice, particularly for biological parameters, the CO_2 system, and other gases.

1. The rise of sea-ice biogeochemical studies

Sea ice covers up to 8% of the Earth's ocean surface (Steele et al., 2001), and despite global warming trends, both polar oceans are still mainly covered by sea ice in winter (Comiso, 2010) and likely will continue to be for the foreseeable future. The changes in sea-ice extent and physical structure associated with a warming climate (Perovich and Richter-Menge, 2009; Massom and Stammerjohn, 2010) are causing dramatic shifts in sea-ice ecosystems and the interactions between sea ice and both the atmosphere and the underlying waters. Long assumed to be a passive barrier to both light and matter, sea ice was relatively neglected in biogeochemical studies until the early 1990s. Since then, intensive research in the Arctic and Southern Oceans, as well as in subpolar seas, has shown that, in reality, sea ice is an active player in biogeochemical processes, making significant contributions to regional and possibly global cycles of many elements (*e.g.*, Arrigo et al., 2010; Deming, 2010; Thomas et al., 2010; Loose et al., 2011; Rysgaard et al., 2011; Vancoppenolle et al., 2013). Future changes in the sea-ice environment will be accompanied by changes to these biogeochemical cycles, generating an urgent need to better understand the chemical-physical-biological function of the ocean-ice-atmosphere system.

Although this review is focused on recent methodological developments in sea-ice biogeochemistry, the first formal biological studies of sea ice date back to the mid-19th century (Horner, 1985), and chemical studies extend back to the early 20th century (*e.g.*, Ringer, 1928; Wiese, 1930). Post-war studies of sea-ice chemistry were mainly motivated by efforts to understand sea-ice structural properties in support of cold-war military operations and potential industrial development in the polar regions (*e.g.*, Nelson and Thompson, 1954; Assur, 1958; Bennington, 1963; Tsurikov, 1965), but that work also provided extremely useful information on the geochemistry of ice brines. Incremental work continued at a slow pace for several decades, but with recent increases in access to polar regions and technological developments, as well as with the growing urgency in climate-change research (*e.g.*, Post et al., 2013) and a need to improve representation of sea-ice processes in numerical models at all spatial and temporal scales, the study of sea-ice biogeochemistry has expanded rapidly. Scientists have come to this field from a variety of disciplines, including glaciology, oceanography, sedimentology, and even tundra ecology; as we attempt to understand the complex biogeochemical processes occurring in sea ice, many creative modifications have been applied to methods not originally designed for sea-ice applications.

Sea ice presents a particularly challenging environment for biogeochemical studies (see Petrich and Eicken, 2010, for a comprehensive description of sea-ice types, characteristics, and life-cycles). Perhaps most significantly, the sea-ice environment is cold. Standard seawater with a salinity of 35 g kg^{-1} freezes at –1.9 °C (Petrich and Eicken, 2010). Sea-ice temperatures below -30 °C have been measured (*e.g.*, Miller et al., 2011b), while the air temperatures above the ice, where people and instruments must operate, can drop to – 60 °C or even lower. Standard oceanographic equipment, however, has been built to operate at temperatures only as low as 0 °C, while most chemical analyses and instrumentation are designed to operate between 20 and 25 °C. If it is not cold, *i.e.*, if the temperatures are around 0 °C, as occurs during the spring and autumn transition seasons, the sea ice is often very thin or deteriorating, making sampling dangerous. Additional difficulties arise from the heterogeneity of sea ice, which is a complex mixture of pure ice, solid salts and particulate organic matter, liquid brines, and gas bubbles. Even the boundary conditions are variable, with snow, frost flowers, and melt ponds at the top and skeletal ice, platelet ice, and algal mats at the bottom. In many ways, soils or sediments are a better conceptual model than seawater for describing sea-ice spatial variability, for multi-phase theories are required to describe sea-ice physical-chemical properties (*i.e.*, a "mushy layer"; Vancoppenolle et al., 2010; Hunke et al., 2011). Finally, the high and variable salinities of sea-ice brines compromise chemical analyses by complicating calibrations and corroding delicate instrument components.

Comprehensive guides for biological and physical methods in sea-ice research have already been published (Horner et al., 1992; Eicken et al., 2009; Michel and Niemi, 2009); we will not attempt to reiterate them

here. Rather, we are accepting the challenge issued by Eicken et al. (2009) in their preface, wherein they hoped their book would "spark broader collaboration among sea-ice researchers to document and refine the best-practice approaches to sea-ice field studies." We discuss not only some remaining ambiguities in determining biomass, nutrient concentrations, and the rates of biological processes in sea ice, but also the challenges of quantifying gas concentrations and fluxes, aerosol emissions, trace metals and their chemical speciation, the complex inorganic carbon and organic sulfur systems, and the sticky problem of organic matter in sea ice, including the difficulties in defining and distinguishing between the dissolved, colloidal, and particulate fractions. We also make concrete recommendations for what ancillary physical data should be collected in conjunction with biogeochemical measurements, to allow effective interpretation of the resulting data sets, as well as for the most critical and potentially useful directions for future methodological developments. We do not intend this paper to be a stand-alone methods manual. Rather, we direct readers to the sources in which individual methods are described.

2. General considerations

Each element, compound, or process has a unique set of sampling and analytical requirements for accurate, precise, and useful results. The bulk of this paper addresses the specialized procedures for sampling and analyzing a wide range of parameters in sea ice. However, there are several generalities in sampling ice and its components that are worth discussing before tackling the specifics.

2.1. Patchiness and scaling

Sea-ice physical, chemical, and biological properties are highly variable, both temporally and spatially. During most seasons, sea ice is characterized by strong vertical gradients in temperature, brine salinity, habitable pore space, and permeability (Eicken, 1992; Petrich and Eicken, 2010; Vancoppenolle et al., 2013). Particularly during spring and, possibly, autumn, those gradients can change rapidly on daily or even hourly timescales (*e.g.*, Mundy et al., 2005; Nomura et al., 2010a). Horizontal variability is also extremely high; for example, biomass can vary by an order of magnitude on the sub-meter scale (Spindler and Dieckmann, 1986; Steffens et al., 2006). Horizontal patchiness of ice algae has been mainly attributed to the spatial variability in physical sea-ice properties (Eicken et al., 1991) and light exposure (Raymond et al., 2009), which are affected by ice formation processes, parent seawater salinity, and meteorological events, among other factors (Gosselin et al., 1986; Rysgaard et al., 2001; Granskog et al., 2005a; Fritsen et al., 2011). This sea-ice heterogeneity has consequences for sampling design: not only do the goals of the project dictate the type of ice that should be sampled (*i.e.*, first-year, multi-year, smooth, ridged, young, melting, *etc.*), but the most appropriate sampling scheme and the minimum number of samples required will depend on the representativeness of any single sample.

The scales of horizontal spatial variability in biological parameters in different sea-ice regimes have been investigated using transects and nested equilateral triangle sampling patterns combined with parametric and non-parametric statistical analysis techniques (*e.g.*, Gosselin et al., 1986; Swadling et al., 1997; Granskog et al., 2005a; Steffens et al., 2006; Søgaard et al., 2010, 2013). We recommend that, to the extent possible and relevant to the specific study, researchers design their sampling using a nested approach that facilitates extrapolation of detailed information to larger scales by distinguishing hierarchical layers of detail (Figure 1). In a nested sampling regime, the primary scale defines the study area, in all its variation, and the secondary scale serves to determine the representativeness of each site within the study area. The tertiary scale (*i.e.*, the number of individual sampling sites), along with the number of replicates (the quaternary scale), defines the accuracy of a parameter.

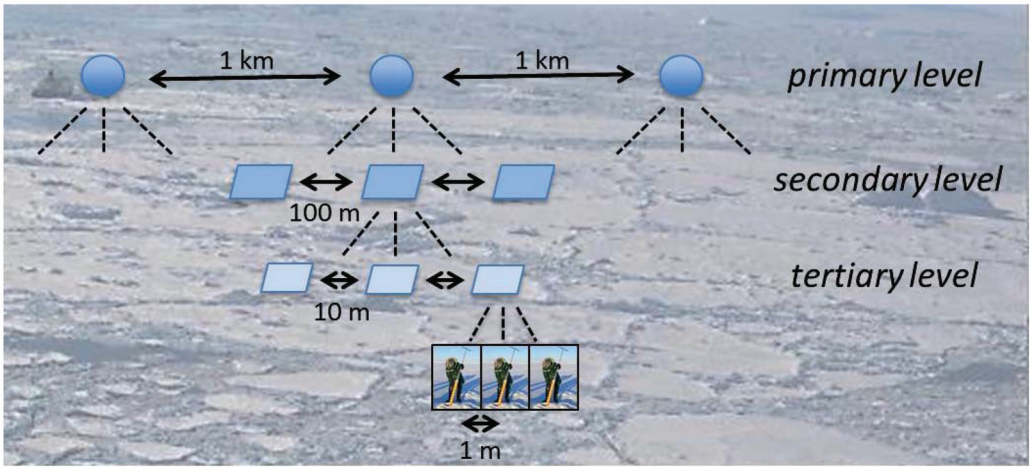

Figure 1
Hierarchical sea-ice sampling design.

Photos: J. Stefels; D. Leitch.

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Designing a nested sampling program begins with a visual survey of the sampling area to establish the various spatial scales of the variability and determine how many sites and samples are required at each hierarchical level. There is no simple, universal algorithm that can be used; every sampling site must be assessed in relation to the goals and resources of the project. For example, Sturm (2009) provides recommendations for sampling densities required to minimize errors in mean snow depth (see his Figure 3.1.13), but the ease of snow-depth measurements allows for a large number of data points that are not always practical for studies of biogeochemical properties.

In addition, the practical and safety requirements associated with ice coring unavoidably produce a bias towards stable ice floes with low levels of deformation. The true scale of the horizontal variability can be determined more accurately by combining methods that provide information on varying scales (*e.g.*, ice coring surveys combined with optical investigations from underwater platforms; Williams et al., 2013). State-of-the-art methods to determine floe-scale sea-ice physical properties, such as sea-ice surface elevation, snow thickness, freeboard, and sea-ice draft, need to be linked with new methods in sea-ice ecology (*e.g.*, determination of ice algal biomass from transmitted under-ice irradiance spectra; Mundy et al., 2007) to evaluate coupled physical-biological sea-ice processes on relevant scales. Developing ice buoy networks and autonomous underwater vehicle technology, combined with improved physical (*e.g.*, CTDs, upward looking sonars), chemical (*e.g.*, oxygen and pH sensors), and bio-optical (*e.g.*, hyperspectral radiometers, fluorometers) sensors, is an active field of research and promises a step-change in our understanding of horizontal patchiness and physical-chemical controls over biological properties in sea ice.

2.2 Sampling techniques and considerations

In general, because sea ice is highly heterogeneous (section 2.1), collecting different samples for analyses of different parameters makes it difficult to confidently link the biogeochemistry of those parameters. Therefore, to the extent possible, each individual sample should be analyzed for as many parameters as is feasible. However, this ideal goal is severely constrained by realities of required sample volumes for analyses, incompatible sample processing requirements, and vulnerabilities to different contamination sources. Here we summarize the basic techniques to collect samples from sea-ice environments, noting that the best approach may vary depending on the project goals and the sea-ice conditions. With this in mind, we have also included what we feel are important considerations to take into account when sampling each particular medium.

2.2.1 Bulk ice

A standard approach to processing sea-ice samples is to collect a core and divide it into sections using a clean stainless steel saw, depending on the scientific question and the demands of analytical sample volume and of collaborative cooperation between researchers (Figure 2). The core sections are then melted and analyzed as any other aquatic samples. The thickness of the core sections may vary, according to the needs of the project, but parameters to be compared should be analyzed on sections of comparable thickness. Cores are usually sectioned from the bottom, to limit brine loss from more permeable parts of the ice (the vertical extent of

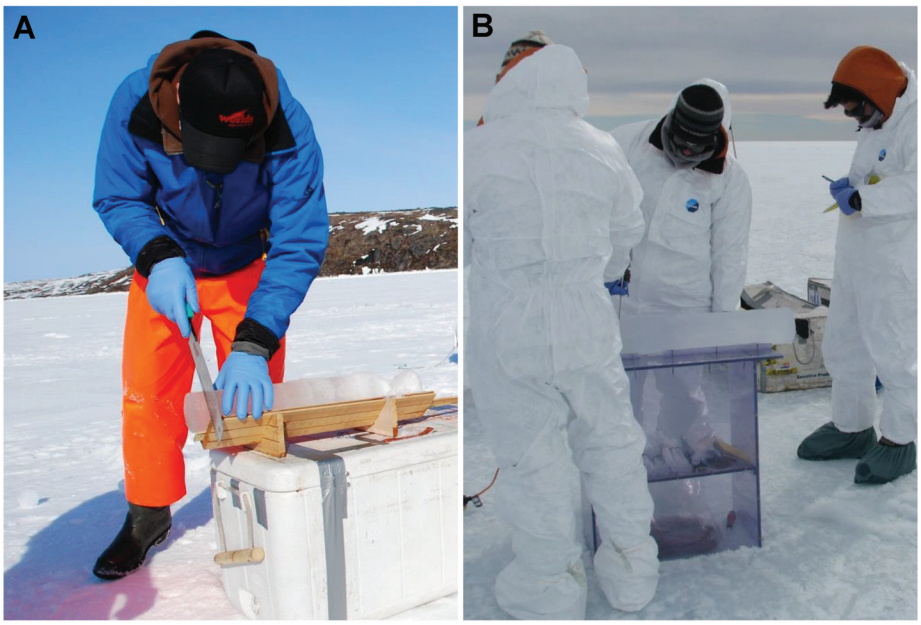

Figure 2

Sectioning ice cores in the field.

(a) Organic-clean methods off Nuuk, Greenland, April 2013. Photo: N.-X. Geilfus. (b) Trace metal-clean methods on McMurdo Sound, November 2012. Photo: T. Goossens.

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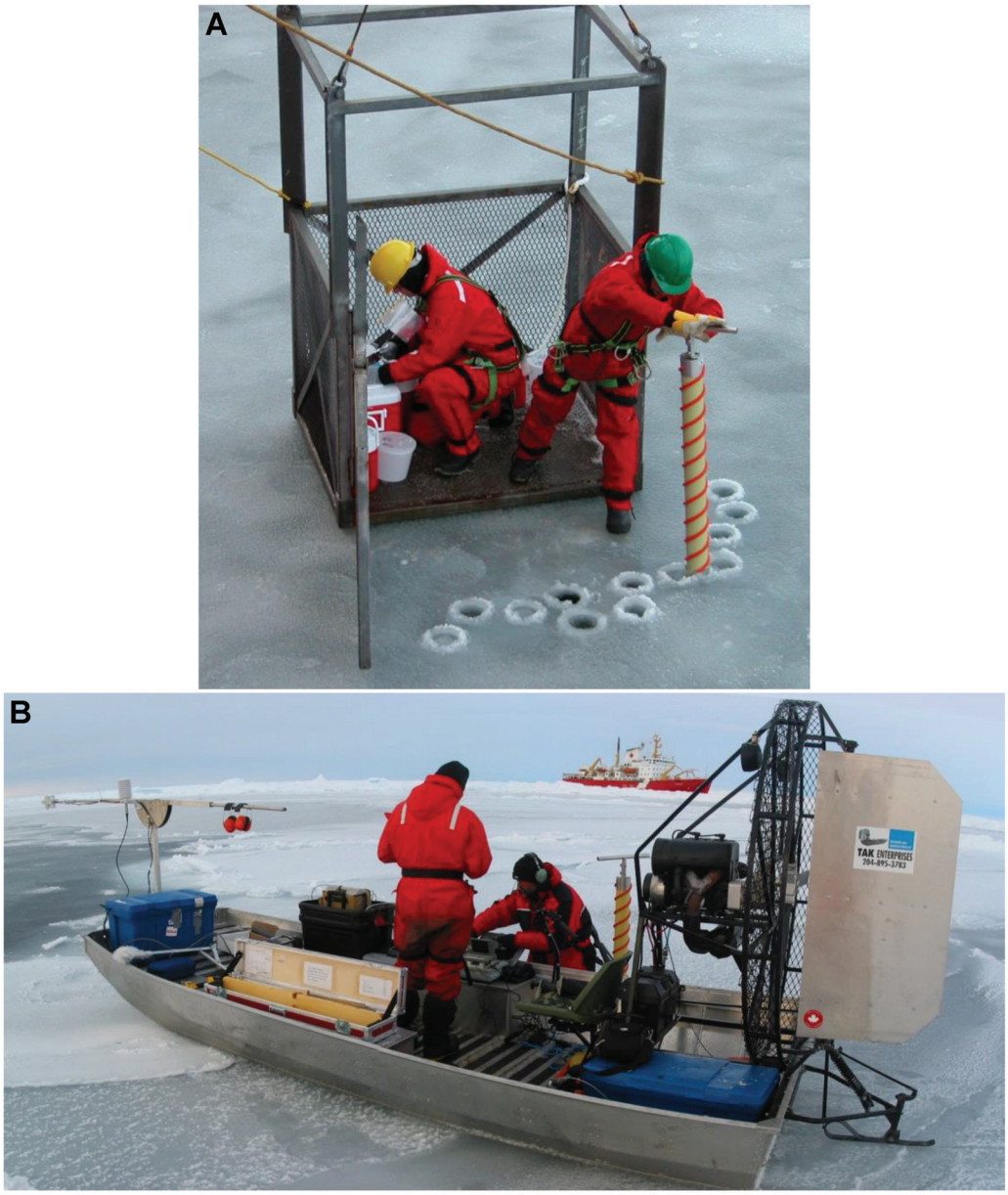

Figure 3
Sampling young ice.

Using a ship's basket (a) and a flat-bottomed boat (b) in the Beaufort Sea, October 2003. Photos: M. Poulin, J. Ehn.

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which depends on ice temperature, salinity, and texture), although the individual sections should be identified according to their depth from the top of the ice (see section 2.3). Core extraction invariably results in at least some brine loss (*e.g.*, Notz et al., 2005), contributing to losses of both dissolved and particulate matter, and therefore, cores must be sampled and processed quickly, preferably sectioned into melt containers in the field. Divers have collected sea ice from below in attempts to more quantitatively recover the components of bottom ice (*e.g.*, Welch et al., 1988; Horner et al., 1992; McMinn and Hegseth, 2007). In addition, although analyses of melted ice cores are most common, many interesting analytes and processes (such as microorganism abundances and species compositions, metabolic rates, gas partitioning, salt precipitation and dissolution, *etc.*) are strongly affected by the drastic changes in temperature and salinity that result when sea ice melts (see section 3.2, below); more complex sampling and analysis methods are often required to avoid melting samples.

The early stages of ice formation play a fundamental role in partitioning material and organisms between the atmosphere, ice, and underlying water (*e.g.*, Giannelli et al., 2001; Notz and Worster, 2009; Müller et al., 2013), but sampling young ice that cannot bear a load (*i.e.*, frazil, grease, nilas, or pancake ice) requires special safety considerations. Thin, broken ice (brash ice and small pancakes) can be sampled from a dinghy (*e.g.*, Grossmann and Dieckmann, 1994) or with a bucket or basket lowered from the side of the ship (*e.g.*, Gradinger and Ikävalko, 1998). Intact, young ice sheets can be cored or cut directly by researchers from a ship's basket (Figure 3a) or using a flat-bottomed boat (Figure 3b). Young, poorly consolidated ice samples contain high quantities of interstitial water and brines that are easily lost, which makes it important to record

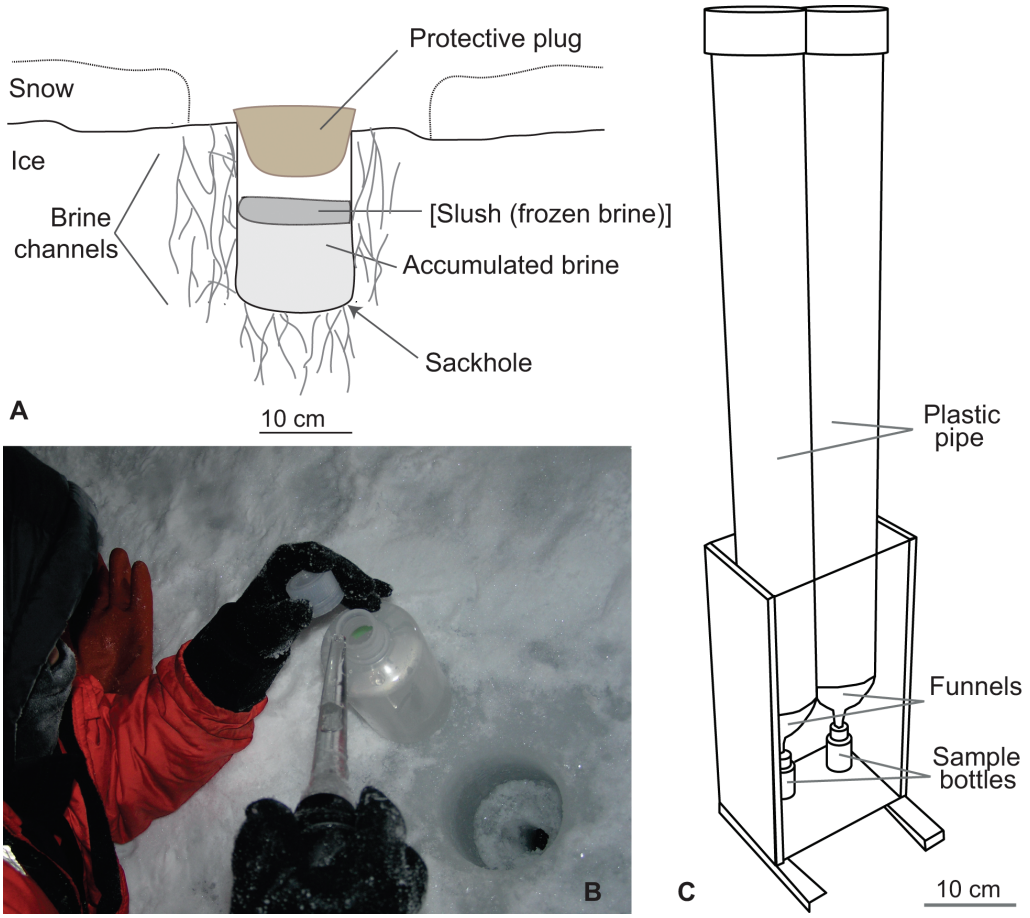

Figure 4
Sampling sea-ice brines.

(a) Schematic diagram of a sackhole for sampling sea-ice brines (slush on top of collected brine not always present). (b) Sampling sea-ice brines accumulated overnight in a sackhole using a clean baster to reach the bottom of the hole. Photo: M. Ewert. (c) Apparatus for collecting brines from whole cores by gravity drainage.

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whether young ice samples were drained to separate the pore water or if special care was taken to retain the brines (Grossmann and Dieckmann, 1994). Cottier et al. (1999) and Smedsrud and Skogseth (2006) described specialized tools for collecting frazil and young sea ice. High-salinity brine waters surrounding frazil and brash ice as it is forming can also be collected using open-mouth jars covered with mesh (Miller et al., 2011a). Similarly, Kristiansen et al. (1998) sampled the infiltration community at the snow-ice interface of flooded ice floes by immediately filtering the slush, at low temperature, through a 200 µm net to remove ice crystals.

Thick, ridged sea ice is even more severely undersampled than young, thin ice, due to a number of significant difficulties with travelling over and through ridged ice, accessing ridge keels and sails, and collecting representative samples from such a varied environment (see section 2.1). However, ridged ice constitutes a large fraction of the total area and volume of sea ice and, according to the limited data available, represents an important biomass pool (Gradinger et al., 2010; Meiners et al., 2012). The methods used for sampling thick, deformed ice have been largely *ad hoc*; standardized approaches are needed.

2.2.2 Brines

The fractionation between the solid (ice and particulates) and liquid (brine) phases of the ice is often important to understanding sea-ice biogeochemical cycles, but effectively collecting and accurately analyzing representative brine samples from mature sea ice has been an exceptional challenge. Traditionally, sea-ice brines have been collected by drilling sackholes (partial core holes) to a desired depth within the ice and then allowing brines from the surrounding ice to drain into the hole (Figure 4a). The most obvious problem with this approach is that, because of the three-dimensional structure and variable connectivity of the brine network, the sackhole brine integrates the geochemical properties of numerous individual brine channels from an undefined volume of the sea ice surrounding the hole. Therefore, sackhole brines provide data on the vertical and horizontal macro-scale (over several tens of centimeters, depending on the depth of the sackhole); our ability to obtain data on the brines at the micro-scale level (a few centimeters or less) in sea ice is still limited for the majority of solutes of biogeochemical interest. Also, if the ice is warm and highly permeable, the collected brines can be contaminated with upward seeping seawater or draining snowmelt and meltpond water; the significance of this problem can be assessed by comparing the measured brine salinity to that estimated from the *in situ* temperature profile. Conversely, the colder the ice, the less brine it contains, the less connected the brine network is, and the longer it takes for a sufficient volume of brine to accumulate in the sackhole. At very

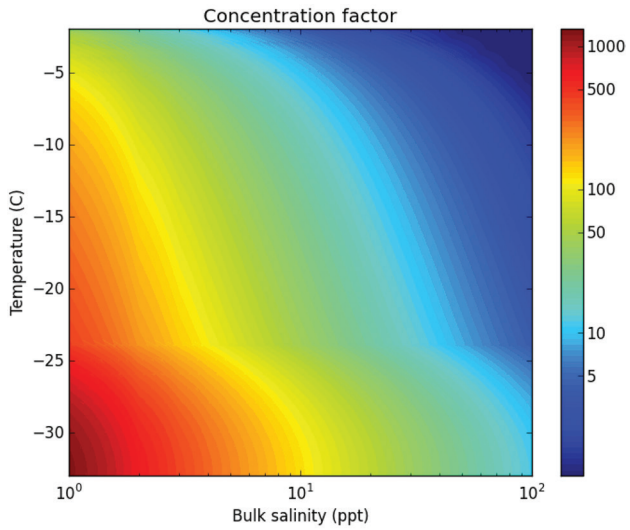

Figure 5

Theoretical concentration factors in sea-ice brines.

Concentration factors (equivalent to S_B:S_I; Equation 1) modelled as the inverse of the brine volume fraction for temperatures between –2 and –35 °C and brine salinities between 1 and 200, encompassing the range observed in sea-ice environments, including frost flowers. Brine volume fraction was calculated according to Equation 2.6 of Petrich and Eicken (2010). This calculation represents the ideal case, where the solute is entirely partitioned into the brine phase and does not precipitate. Experimental measurements of brine salinity between -2 and -23 °C show a similar concentration factor for salts, although measured brine salinities deviate from the ideal case at the lowest temperatures, due to salt precipitation.

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cold temperatures, it may not be possible to collect enough brine within a suitable timeframe. Furthermore, the longer it takes for the brines to accumulate, the greater the risk that the sample will be compromised by interaction with the air, which is likely at a different temperature (often much lower) than the ice interior, causing the brines to freeze further within the sackhole. Potential brine-air exchange is a particular problem for analyses of insoluble gases (section 4.4). To minimize such air-brine interactions, the sackhole can be capped with plugs made from thick insulated material. When sampling sackholes, any snow needs to be removed from the sampling site before coring, and care is required to prevent ice core shavings from entering the hole and contaminating the brines. The accumulated brine can be extracted from the sackhole with a large pipette (a "turkey baster"; Figure 4b), with tubing attached to a syringe or a peristaltic pump, or simply by dipping a bottle into the brine.

Other methods used to collect sea-ice brines include gravity-draining full cores into containers (Figure 4c; Nomura et al., 2009) or crushing and/or centrifuging ice samples (*e.g.*, Grossmann and Dieckmann, 1994; McMinn et al., 2009; Munro et al., 2010). However, both of those approaches generally deliver relatively small volumes that are suitable for only a limited number of analyses and may not be statistically representative (see section 2.1). Also, the pressure generated by centrifugation can melt some of the ice, diluting the extracted brines (Papadimitriou et al., 2004), apparently by as much as 15%.

Particulates (including organisms) and organic matter appear to be under-represented in brines collected in sackholes (*e.g.*, Weissenberger, 1992; Sime-Ngando et al., 1997; Lannuzel et al., 2008) by up to 98% (Becquevort et al., 2009). Likely explanations include preferential adsorption onto the ice walls, "filtration" by the brine channel network, and impeded transport by sticky, gelatinous exopolymeric substances (EPS) or aggregates of ice algae (Meiners et al., 2004; Krembs et al., 2011).

Concentrations of dissolved materials in brines can also be estimated from calculated brine salinity (based on *in situ* temperature; Cox and Weeks, 1983; Petrich and Eicken, 2010) and measured bulk ice concentrations (Figure 5), using the equation

$$C_B = C_I\left(\frac{S_B}{S_I}\right), \quad (1)$$

where C indicates analyte concentration, S is salinity, and the subscripts B and I represent brine and bulk ice (*e.g.*, Dieckmann et al., 1991a; Norman et al., 2011). This calculation assumes that none of the analyte is in solid or gaseous form and that, therefore, the concentration of the analyte in the brine is directly proportional to salinity, an assumption that is probably only valid for highly soluble substances. Not only do supersaturated brines precipitate salts (even the highly soluble ions Cl^- and Na^+ precipitate from sea-ice brine solutions to a significant extent at temperatures below –24 °C; Assur, 1958) and release gas bubbles, but both dissolved and particulate organic matter can adsorb onto the surface of the brine channels. In addition, high concentrations of organic matter, particularly EPS (section 4.2.3), can impact sea-ice microstructure (Krembs et al., 2011), with hypothesized (Ewert and Deming, 2013) but still unknown implications for the sea-ice equations of state (Cox and Weeks, 1983).

2.2.3 Gases

The third phase in sea ice, gas bubbles, are particularly important in carbon, oxygen, and sulfur cycling, but gas inclusions are even more challenging to recover and analyze than brines. The methods that have been developed to tackle this problem are summarized in section 4.4.

Figure 6
Sampling frost-flowers with a clean spatula.

Beaufort Sea, January 2008. Note that this sampling method does not separate frost flowers from the underlying brine skim layer. Photo: M. Ewert.

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2.2.4 Snow and frost flowers

On top of sea ice, the snow cover thermally insulates the ice, limits the penetration of visible and UV radiation, and exchanges brines and gases with the underlying ice (*e.g.*, Kelley and Gosink, 1985; Massom et al., 2001; Zemmelink et al., 2008; Ewert et al., 2013). The snow cover is generally sampled in layers by excavating snow pits, as described by Sturm (2009). Established sampling methods for other environments can usually be adapted to snow over sea ice. For example, clean methods used for sampling trace elements in snow over land have been successfully implemented for sampling of halogens and trace elements in snow over sea ice (Simpson et al., 2005, Poulain et al., 2007).

Frost flowers are usually collected by simply scraping or scooping them into sample containers (Figure 6; Obbard et al., 2009; Bowman and Deming, 2010; Miller et al., 2011a; Aslam et al., 2012; Douglas et al., 2012; Bowman et al., 2013; Fransson et al., 2013; Granfors et al., 2013a), although Alvarez-Aviles et al. (2008) used tweezers. Brine skims on the top of the ice (often associated with frost flowers) can be collected with a scooped spatula (Bowman and Deming, 2010; Roscoe et al., 2011) or an eyedropper (Alvarez-Aviles et al., 2008). However, exclusive sampling of frost flowers separately from brine skims remains a challenge, nor do current approaches likely adequately capture volatile components. Effective study of these sea-ice micro-environments can benefit from application of non-invasive techniques, such as infrared imaging (Barber et al., 2014), and from development of sensitive but robust microsensors for *in situ* analyses.

2.3. Record-keeping

Sea-ice scientists still use non-standardized, *ad hoc* systems for identifying samples, but if we are to establish comprehensive, accessible, and useful sea-ice biogeochemical databases, then instituting basic standards to classify samples will be necessary. These metadata requirements apply not only to observations at the time of sampling, but also to sample processing and preparing data sets for archiving. In an effort to begin to meet the need for standardized record-keeping, we encourage researchers to always identify their samples with the following information:

- latitude and longitude;
- date and time (preferably UTC, but if local time is used, clearly identify the time zone and whether it is under Summer, or Daylight Savings, Time);
- weather conditions, including air temperature, cloud fraction, wind speed and direction, and contact information for complete meteorological data from a nearby ship or station;
- water depth, particularly in coastal waters;
- ice description, including approximate age (*i.e.*, whether it is multi-year or first-year ice, and for young ice, estimates of time since initial ice formation), thickness, freeboard, and texture (according to Eicken et al., 2009);
- if applicable, depth in the ice core, measured from the top, in cm; and
- if applicable, estimates of snow or melt-pond coverage and measurements of their depths on the surface of the ice.

For each core, a standard data sheet should be prepared, giving the important metadata, information on how the core was processed, and what subsamples were taken for what analyses (Figure 7); eventually these sheets should be also populated with the analysis results for archiving. As it is usually best to collect several ice samples or cores, the distance between samples or the approximate total area from which the samples originated must also be specified in the metadata. If possible, replicates should be collected according to the guidelines for nested sampling design in section 2.1.

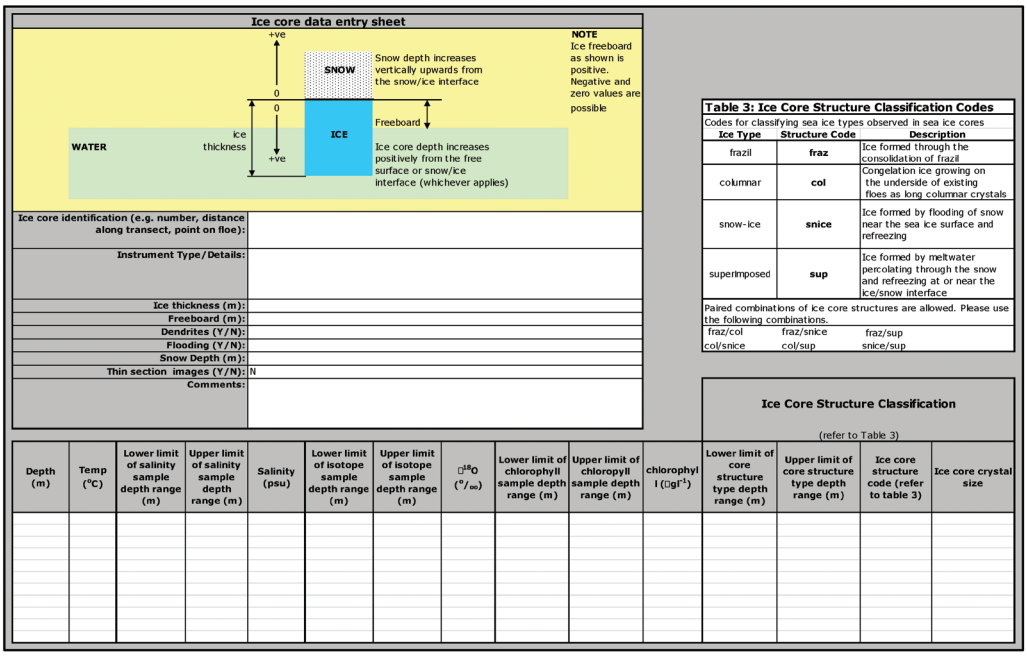

Figure 7

Example ice core data sheet.

Developed by the Antarctic Sea Ice Processes & Climate (ASPeCt) program. Additional data columns should be added for all project-specific parameters. This and other standardized sea-ice data entry templates are available for download via the sea-ice physical data portal of the Australian Antarctic Data Centre.

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To facilitate data archiving and retrieval, we suggest that each sample be identified (at least in data files, if not also on the samples themselves) by an expedition code, followed by the date in YYYYMMDD format (with a lower-case letter for each sampling 'event' on a given day, associated with a unique time and location), followed by an identifier of the sample type (*i.e.*, "ice" for sea-ice cores, "br" for sackhole brines, "ff" for frost flowers, "sn" for snow, "gap" for gap layers, and "pond" for melt ponds), with each replicate core or sample receiving a different sequential number. Individual core sections should then be identified by the depth from the air-ice or snow-ice interface. For example, a specific core section from an Antarctic sea-ice camp in the year 2015 might be identified as BS2015-20150409b-ice-03-20-30, where BS2015 would be the expedition code, followed by the date (April 9th) and "b" indicating that it was the second location sampled that day, the 3rd replicate core from that location, and the 20–30 cm section down in that core.

2.4. Ancillary measurements

Any biogeochemical study of sea ice should include a number of ancillary measurements (Table 1). Beyond the needs for working up and interpreting our own results, when archived data are used by later researchers investigating questions we have not yet conceived, the ancillary data may prove critical.

Table 1. Ancillary measurements for sea-ice biogeochemical studies

Importance	Parameter
Required	Temperature[a]
	Bulk salinity[a]
Strongly recommended	Brine salinity[a]
	Ice texture[a]
	$\delta^{18}O$[b]
	Snow thickness[a]
Recommended	Macronutrients[b]
	Chlorophyll *a*[b]
	Brine volume[a]
	Snow biogeochemistry[b]
	Radiative forcing fluxes (light and heat)[a]

[a]Methods given by Eicken et al., 2009.
[b]Methods reviewed in this paper.

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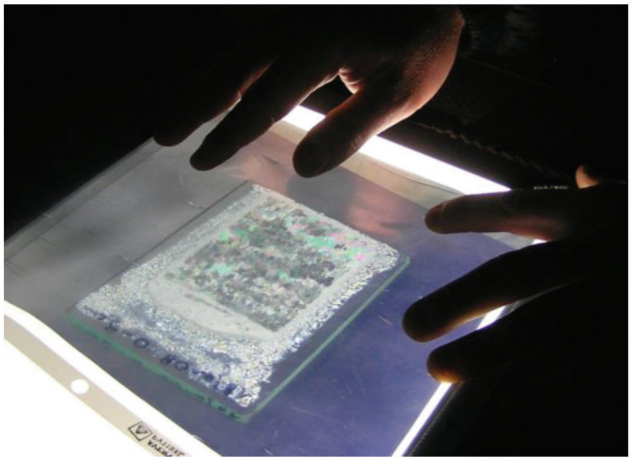

Figure 8

Sea-ice texture observed under a polarized filter in a thin slice of ice.

Cut lengthwise from an ice core section in a -20 °C cold room. Photo: M. Ewert.

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Most importantly, the physical properties of the ice should be described in as much detail as possible (see Eicken et al., 2009, for standard methods). At a minimum, the *in situ* ice temperature and bulk salinity should be determined and reported, preferably in 5-cm vertical increments throughout the depth of the ice. Indeed, bulk salinity is sufficiently important (and simple enough to measure) that it should be determined on all sections analyzed for any biogeochemical parameter.

We also encourage sea-ice investigators to report brine salinity, which can be calculated from temperature (assuming thermodynamic equilibrium; Petrich and Eicken, 2010), and the brine volume as a fraction of the bulk sea-ice volume, which provides insight into the connectivity of the brine channel network (Golden et al., 1998). Estimating the brine volume fraction (Cox and Weeks, 1983, for $T < -2$°C; Leppäranta and Manninen, 1988, for $T > -2$°C) requires that in addition to temperature and bulk salinity, the ice density be measured (Eicken, 2009) or estimated based on an assumed air volume content. It is also helpful to describe the ice texture throughout the full profile (Eicken, 2009), at least based on a direct visual inspection of the thicknesses and sequence of granular and columnar layers (which can be recorded with photographs). A polarized light source, if available, can provide more detailed information (Figure 8). The $\delta^{18}O$ ratio of the sea ice (section 4.8) helps identify its meteoric versus marine origins (*e.g.*, Macdonald et al., 1999; Tison et al., 2008). Finally, macronutrient (nitrate, nitrite, phosphate, silicic acid, ammonium; section 4.1) and chlorophyll *a* (Chl *a*; section 3.3.2) measurements, in combination, allow us to assess the overall status of the biological community in the ice (*i.e.*, bloom versus non-bloom states; degree of nutrient limitation, *etc.*).

At a minimum, the presence of a snow cover and its thickness need to be reported. If resources allow, the snow cover should be fully characterized, as described by Sturm (2009), including basic stratigraphic analysis, with measurements of thickness, temperature, density, hardness, and grain properties (shape and size) for each layer. Snow samples from different strata should be also collected and analyzed for $\delta^{18}O$ (for insight into brine exchange with the underlying sea ice), as well as for the same analyses as those planned for the ice samples. More specialized information on atmospheric forcing, both light and heat, is also valuable, and standard methods are given by Perovich (2009).

3. Biological factors

Sea ice contains an abundant and taxonomically diverse community, including Bacteria and Archaea (hereafter referred to jointly as bacteria), autotrophic algae, hetero- and mixo-trophic protists, fungi, and metazoans. Algal cell concentrations in bulk sea ice range over six orders of magnitude (from 10^1 to 10^6 cells/mL; Arrigo et al., 2010), whereas those of bacteria range over four orders of magnitude (from 10^3 to 10^7 cells/mL; Deming, 2010) and those of viruses over three orders of magnitude (from 10^5 to 10^8 viral particles/mL; Deming, 2010). In order to understand and budget the exchanges of matter and energy within this rich sea-ice microbial community and between it and the surrounding environment, including the atmosphere, the water column, and sediments (*i.e.*, the paleorecord), it is essential to have good measurements of biomass, its chemical composition (C, N, P, Si, *etc.*), taxonomic composition, and metabolic functions and transformation rates. Such measurements are challenging in any environment, and particularly so in sea ice.

3.1. Sampling

Sampling considerations for determining the biological properties of sea ice depend on the parameter, organism of interest, and type of ice sampled. When sampling for microorganisms, especially bacteria, application of sterile aseptic technique, to the extent possible in the field, is needed; *e.g.,* the use of ethanol-sterilized tools

for coring, cutting or otherwise collecting the samples, and sterile receptacles (*e.g.*, Bowman et al., 2012). Tools must be ethanol-cleaned between samples to prevent cross-contamination. Samples should be kept as close to the *in situ* temperature as possible, to prevent thermal or osmotic shock to the microorganisms, and light exposure needs to be minimized during transport and storage to limit growth, light shock, and photochemical degradation.

When the planned analysis requires full, intact ice cores, the cores should be placed into sterilized, black plastic sleeves, to retain brines and protect organisms from light stress, immediately after extraction from the core barrel (*e.g.*, Maas et al., 2012). Typically, however, the core is divided into sections to determine detailed vertical profiles (section 2.2.1). When cutting ice cores into sections, contamination may be prevented by placing them on autoclaved foil (Bowman et al., 2012) or, as when sampling for organic compounds (section 4.2.1), removing the outer layers of the cores (Song et al., 2011; Fripiat et al., 2014a). If the bottom ice community is of interest, the core must be handled gently to preserve the lower skeletal layer. Dieckmann et al. (1992) developed an apparatus for sampling unconsolidated platelet layers that can be deployed through a hole in the ice only 5 cm in diameter and was successfully deployed by Arrigo et al. (1995) and Robinson et al. (1998) to study the biogeochemistry and photophysiology of the platelet ice community. When large sample volumes are required, sections from different cores can be pooled during melting, although information on the horizontal heterogeneity (section 2.1) is lost.

3.2. Sample processing

Ideally, we would study the sea-ice biological community *in situ* in order to fully understand the relationship between the organisms and their environment (Junge et al., 2001; Krembs et al., 2002). However, most standard methods for evaluating biomass and activity are unable to accommodate the bulk ice matrix; investigators usually melt ice samples before examining the biological community. Unfortunately, large temperature changes or osmotic stress, as the salinity drops during ice melt, can cause sympagic cells to burst, a significant concern in biological sea-ice studies. In addition, even if cells remain intact, photosynthetic stress has been observed in sea-ice algae subjected to dramatic salinity decreases (Ralph et al., 2007). Therefore, samples should generally be processed in the cold (*i.e.*, at or only slightly above the freezing point of the final melt solution) to limit temperature changes (Deming, 2010; Mikkelsen and Witkowski, 2010), but limiting osmotic shock is more difficult. A variety of methods are used to melt sea ice, with a range of potential impacts on the sea-ice community. Available protocols include simply melting the ice (direct melt), melting in filtered or artificial seawater (seawater melt), and melting in concentrated brine to give a final salinity similar to the *in situ* brine salinity (brine, or isohaline, melt). Use of direct and seawater melts in samples collected for analyses of nutrients, organics, extracellular polysaccharides, and sulfur species is discussed in sections 4.1, 4.2.1, 4.2.3, and 4.5, respectively.

Although some studies have observed no difference between direct and seawater melts for Chl *a* measurements (Dieckmann et al., 1998; Kaartokallio, 2004) or diatom counts (Mikkelsen and Witkowski, 2010), or for the culturable fraction of sea-ice bacteria (Helmke and Weyland, 1995), direct melting can cause loss of anywhere from 13 to 97% of eukaryotic cells, with ciliates and flagellates most susceptible to bursting (Garrison and Buck, 1986; Mikkelsen and Witkowski, 2010). However, Mikkelsen and Witkowski (2010) found that slow, direct melting under refrigerated conditions appeared to be suitable for most of the eukaryotic cells, with no significant differences from seawater-buffered melts, except for one flagellate group. Winter ice, which can contain sharp vertical gradients in brine salinity, varying from salinities similar to seawater (approximately 35 g kg^{-1}) at the bottom to over 200 g kg^{-1} near the upper surface, requires particular care in melting. In a comparison of direct and brine melts for different sections of the winter ice column, Ewert et al. (2013) found that direct melts resulted in a significant loss of up to 55% of bacterial cells in the upper ice column but no difference in the lower sections, indicating that *in situ* brine salinity is a key factor in selecting the appropriate melting method. An important caveat to melting under refrigerated or buffered conditions is that it can take several days (Mikkelsen and Witkowski, 2010), during which ongoing biological processes can modify the sample and its community structure in ways that are still difficult to assess.

As a general recommendation, the choice of melt protocol should be based on the target measurement and the expected change in salinity resulting from the melting process. Although isohaline melts often appear to be the best approach to melting sea-ice samples for analyses of biological parameters, isohaline melting at low temperature is time consuming, which may introduce artifacts into the analyses (even while protecting against others). In addition, adding seawater or brines (either natural or artificial) can dilute or contaminate the sample, both in terms of organisms and analytes. Therefore, usually the concentrations of relevant analytes (such as macronutrients) need to be quantified in those seawater or brine solutions, which in turn must be pretreated to remove or inactivate contaminants (*e.g.*, by filtration or UV oxidation). Finally, whereas the loss of a specific group of organisms can unacceptably bias the community composition, it may not necessarily impact total biomass determinations (POC, PON, $bSiO_2$, Chl *a*) to a significant extent, particularly if the community is dominated by diatoms.

3.3. Biomass and community structure

3.3.1. Particulate organic matter and biominerals in sea ice

Particulate organic matter, which includes both living and non-living material, has been measured in sea-ice melts at concentrations up to 10^3 μmol C L^{-1} (*e.g.*, Gradinger, 1999; Kennedy et al., 2002). Such maximum concentrations are up to two orders of magnitude higher than in the surface open ocean (Martiny et al., 2013), confirming that sea ice is an important pool of biogenic organic matter in the polar oceans.

The differentiation between the particulate and dissolved phases in sea-ice melts and brines is arbitrary and based on the filters used, a problem in all aquatic biogeochemical studies (see Hilmer and Bate, 1989; Knefelkamp et al., 2007, and Wang et al., 2007, for reviews of the best practices for filtration in aquatic science). At the molecular level, the distinction between dissolved, colloidal, and particulate material is physically ambiguous and variable, particularly at high concentrations, such as in sea-ice brines. Also, the filtration process, itself, can cause particulate organic matter to break apart, while dissolved macromolecules can adsorb onto the filters (*e.g.*, Wangersky, 1993). This latter effect can be a particular problem for sea-ice samples with high concentrations of EPS that might clog the filters and reduce their effective pore size. Most but not all bacteria are captured by 0.2 μm pore-size filters; capturing viruses requires filters of even smaller pore size (0.02 μm; *e.g.,* Wells and Deming, 2006). In practice, many researchers rely on the convenience of glass and quartz fiber filters (*e.g.*, GF/F, 0.7 μm nominal pore-size, pre-combusted at high temperatures to remove organic contamination), although they, of course, are not suitable for analyses of biogenic silica (see below).

After melting (section 3.2) and filtration, the C and N contents of the particulate organic matter (particulate organic carbon, POC, and nitrogen, PON) in sea-ice samples are generally analyzed by combustion to CO_2 and N_2, the standard method used in seawater (*e.g.*, Ehrhardt and Koeve, 1999). Although studies of Chl *a* in sea ice have found no difference between cores melted with or without filtered seawater (section 3.2), to our knowledge, similar confirmation that melt procedures do not impact POC and PON analyses has not yet been published.

Measurements of cellular abundance in sea ice can be reported in different units for different purposes (Horner et al., 1992). For bulk macroscale analyses important in biogeochemical modelling, depth-integrated abundances (*i.e.*, cells m^{-2}) can be useful, as can further converting cellular abundance to biomass (typically in mmol C m^{-2}), either by direct measurement of elemental composition or by using a published conversion factor (*e.g.*, Miller et al., 2011b). For insight into the ecology of the organisms, results are sometimes scaled to the *in situ* brine volume (*e.g.*, cells mL^{-1} brine; Junge et al., 2004; Wells and Deming, 2006; Collins et al., 2008).

Diatoms are the only ecologically significant group in sea ice producing biogenic silica ($bSiO_2$), which is filtered from ice melts using polycarbonate membranes (Fripiat et al., 2007). Analysis generally follows a double/single wet-alkaline digestion method (Ragueneau et al., 2005) to also assess lithogenic contamination, which could be an issue in landfast sea ice. Biogenic calcium carbonate ($CaCO_3$), in the form of foraminifera, has been observed and quantified by visual counting in Southern Ocean sea ice (Spindler and Dieckmann, 1986; Dieckmann et al., 1991b; Eicken et al., 1991; Thomas et al., 1998). The analysis of abiotic $CaCO_3$ minerals is discussed in section 4.6.5.

3.3.2. Ice algal pigments and absorption spectra

Algal pigments provide both quantitative and qualitative information on the composition of the sea-ice community over a variety of temporal and spatial scales; Chl *a*, a ubiquitous pigment in algae and phytoplankton, is the most commonly used proxy of viable algal biomass in sea ice (*e.g.*, Dieckmann et al., 1998; Meiners et al., 2012). Pigments are collected by filtering melted ice core sections in the dark using either GF/F or polycarbonate membrane filters; in general, GF/F filters capture nearly all of the algae and are compatible with standard pigment extraction methods (Mantoura et al., 1997; Roy et al., 2011). Investigators usually melt the ice in filtered seawater to prevent cell rupture (*e.g.*, Garrison and Buck, 1986; Becquevort et al., 2009), although some have found no significant difference in Chl *a* concentrations between samples melted with and without filtered seawater (section 3.2). Exposure to light can affect the algal pigment composition; therefore, melting should always take place in the dark.

Chlorophyll *a* is usually determined by fluorometric detection following an acetone/methanol extraction (*e.g.*, Arar and Collins, 1997; Gosselin et al., 1997). Many investigators apply a constant ratio to convert Chl *a* to carbon biomass, but in sea ice (as well as in other environments), this ratio is highly variable among photosynthetic organisms, as well as with changes in light, temperature, and nutrient concentrations (*e.g.*, Arrigo et al., 2010). Therefore, although POC is a more expensive analysis than Chl *a*, sea-ice investigations benefit from parallel measurements of POC and Chl *a*.

High Performance Liquid Chromatography (HPLC) allows simultaneous analyses of a number of other pigments, in addition to Chl *a*. Standard methods are presented by Bidigare et al. (2005) and Roy et al. (2011). The large variations in light conditions throughout the sea-ice column and horizontal heterogeneity (section 2.1) strongly affect cellular pigment contents, so that special care is required in implementing the

Table 2. Extraction of nucleic acids (DNA or RNA) from sea ice for sequencing

DNA or RNA	Extraction method[a]	Season	Sea ice types[b]	References
DNA	PC	Spring/summer	FYI and MYI	Brown and Bowman, 2001
DNA	DNeasy	Summer/autumn/winter	FYI and MYI	Brinkmeyer et al., 2003
DNA	DNeasy	Summer	MYI	Gerdes et al., 2005
DNA	PC	Winter/spring	FYI	Brakstad et al., 2008
DNA	PC	Winter/spring	FYI	Kaartokallio et al., 2008
DNA	PC	Winter	FYI	Collins et al., 2010
Both	PC, RNeasy	Summer	MYI	Koh et al., 2010
Both	DN-, RNeasy	Summer	MYI	Cowie, 2011
DNA	PC	Summer	MYI	Martin et al., 2011
DNA	PC	Summer	MYI	Bowman et al., 2012
DNA	PC	Spring	FYI	Maas et al., 2012
DNA	PC	Spring	YI and FF	Bowman et al., 2013
DNA	PC	Winter	FYI, YI, FF	Barber et al., 2014

[a]PC = phenol chloroform; DNeasy and RNeasy available from Qiagen.
[b]FYI = first year sea ice, MYI = multiyear sea ice, YI = young sea ice, FF = frost flowers.
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complex algorithms used to process HPLC data (Wright and Jeffrey, 2006; Latasa, 2007; Alou-Font et al., 2013). In particular, different layers of an ice core may have to be treated as separate community groups.

3.3.3. Bacteria and viruses

Bacteria and viruses contribute directly to the particulate nutrient and carbon pools in sea ice, participate in the still poorly understood sympagic food web, and mediate changes in the chemical composition of the ice brines. Knowing the abundance of bacteria and viruses is the first step in assimilating these microorganisms into conceptual and mathematical models of biogeochemical cycling in sea ice. Additional information on microbial metabolic rates (section 3.4.3) and diversity (sections 3.3.2 and 3.3.4) further facilitate the conceptual integration of biological and chemical perspectives on sea-ice processes.

Epifluorescence microscopy of melted ice samples (subject to the limitations and ambiguities discussed in section 3.2) is the principal technique by which bacterial and viral abundances are determined in sea ice. The methods have not changed substantially since they were first introduced in the late 1970s (*e.g.*, Hobbie et al., 1977; Porter and Feig, 1980; Noble and Fuhrman, 1998; Kaartokallio et al., 2008). Challenges faced by users of this method in sea-ice samples include the difficulty of microscopic observations aboard moving vessels, high background fluorescence (attributed to non-specific staining or staining of nucleic acids in EPS), and extremely low or high cellular or viral abundances in some melted ice samples. Flow cytometry, with its high sample throughput, is commonly used for measurements of bacterial and viral abundance in marine systems and can also be useful in sea-ice biology (Riedel et al., 2007a; Kaartokallio et al., 2013; Piwosz et al., 2013), although high EPS concentrations could interfere with the analysis in some sea-ice samples.

3.3.4. Genetic community assessments

Since 2001, investigators have extracted environmental DNA from sea ice for various sequencing or prokaryotic community fingerprinting applications, enabling determination of prokaryotic community composition, structure, and metabolic potential within sea-ice samples (Table 2). In a few cases, RNA has been extracted with DNA to determine the structure and function of the active prokaryotic community.

Samples are often size-fractionated with filters of different pore sizes to separate major components of the community before nucleic acid extraction. To facilitate intercomparison with the GOS (Global Ocean Sampling Expedition) dataset, we recommend standard pore sizes of 0.1, 0.8, and 3.0 μm (Rusch et al., 2007), although there is little evidence that these cutoffs correspond to natural ecological boundaries in sea ice. For accurate DNA extraction from cells, free from background contamination, it is essential that cells not be lysed until after capture on the filter, making the sample melting conditions critical (section 3.2). Low biomass samples, such as winter sea ice and some multi-year sea ice, require large melt volumes (greater than 1 L), while higher biomass samples can have an overabundance of eukaryotic DNA, along with interfering compounds such as EPS and non-specific humics. Because these compounds are chemically similar to nucleic acids, they often co-extract and interfere with downstream applications, such as the polymerase chain reaction (*e.g.*, Tebbe and Vahen, 1993). An ideal nucleic acid extraction protocol for sea ice would produce a high

yield of the target molecule, reducing the bias toward or against any member of the microbial community and minimizing the co-extraction of EPS, humics, and other interfering compounds.

The available extraction methods fall into three broad categories: phenol chloroform (PC), kit-based, and electrophoretic methods. Although electrophoretic extraction is a promising new technology that may overcome some of the challenges regarding biomass and interfering compounds (*e.g.*, So et al., 2010), to date, only PC and kit-based methods have been applied to sea-ice samples. Cowie (2011) evaluated PC and kit-based methods in Antarctic sea ice and found that PC (using the methods of Moeseneder et al., 2001) is suitable for sea-ice samples. The same study also found that the RNA extraction kit RNeasy (Qiagen) in combination with bead beating was the most effective RNA extraction method, when samples were preserved with RNAlater (Qiagen). Although this and other studies show that nucleic acids can be extracted from sea ice, we encourage more comprehensive intercomparisons. In the meantime, investigators should carefully test their methods on the specific ice types they are studying.

3.4 Metabolic processes

Numerous studies have attempted to adapt methods for determining community metabolic rates in aquatic systems to the sea-ice environment (Table 3). None of these methods has been entirely satisfactory. Intercalibration experiments and further method development are high priorities in sea-ice biogeochemistry.

3.4.1. Primary production and elemental uptake rates

The term "primary production" largely refers to organic matter synthesis by photosynthetic organisms, harvesting light to convert inorganic to organic carbon. The conversion of inorganic to organic carbon by chemosynthetic microorganisms in sea ice, in particular by nitrifying bacteria (which are also chemosynthetic), has been implicated in studies using stable isotopes (*e.g.*, Fripiat et al., 2014a) and DNA sequencing (Barber et al., 2014), but chemosynthesis is generally considered a minor contribution to overall primary production in sea ice. Several methods exist to directly estimate photosynthesis-based primary production (gross and net) in aquatic systems (*e.g.*, Falkowski and Raven, 2007); each method has its own assumptions, ambiguities, and biases, which have been extensively discussed in the oceanographic literature (*e.g.*, Bender et al., 1987; Laws et al., 2002). However, the complexity of the sea-ice/brine matrix presents particular problems in quantifying metabolic rates.

Incubations for determining primary production in sea ice, usually based on the incorporation of a tracer into particulate organic matter over a known amount of time, can be conducted either *in vitro*, in refrigerated incubators with spectral filters to mimic natural light conditions, or *in situ*, by embedding inoculated samples back into the sea-ice environment (*e.g.*, Horner and Schrader, 1982; Mock and Gradinger, 1999; McMinn and Hegseth, 2007; Gradinger, 2009). *In vitro* incubations remove the *in situ* variability, allowing

Table 3. Methods used for estimating metabolic rates in sea ice

Approach	Method	Targeted processes	Timeframe	Spatial scale (m^2)	Location in ice cover	Comments[a]	Example references
Incubations	^{14}C,^{13}C	Gross-net primary production[b]	days	0.01	Interior	Invasive	Arrigo et al., 2003; Gradinger, 2009
	^{15}N	Nutrient uptake, remineralization	days	0.01	Interior	Invasive	Kristiansen et al., 1992; 1998
	^{3}H-leucine, ^{3}H-thymidine	Bacterial production	days	0.01	Interior	Invasive; requires tracer-to-carbon conversion factors	Kaartokallio, 2004
	Dissolved O_2	Gross primary production + respiration	days	0.01	Interior[c]	Invasive	Satoh and Watanabe, 1988
Oxygen fluxes	O_2:Ar ratio	Net community production	vegetative season	0.01	Interior	Non-invasive; physical biases	Zhou et al., 2014b
	Optodes	Gross primary production	days	0.01	Interior	Non-invasive; physical biases; placement unknown	Mock et al., 2003
	Microelectrodes	Gross primary production	days	1	Bottom	Non-invasive; physical biases	McMinn et al., 2000; 2007
	Under-ice eddy covariance	Net community production	days	100	Bottom	Non-invasive; spatial integration; physical biases	Long et al., 2012

[a]Physical biases include bubble formation, sea ice-atmosphere exchange, and solubility changes.
[b]Rate depends on the incubation time, with shorter incubation times more closely approximating gross primary production (*e.g.*, Laws et al., 2002).
[c]Satoh and Watanabe (1988) incubated algae scraped off the bottom of ice cores, but the method should be applicable to any depth in the ice core.
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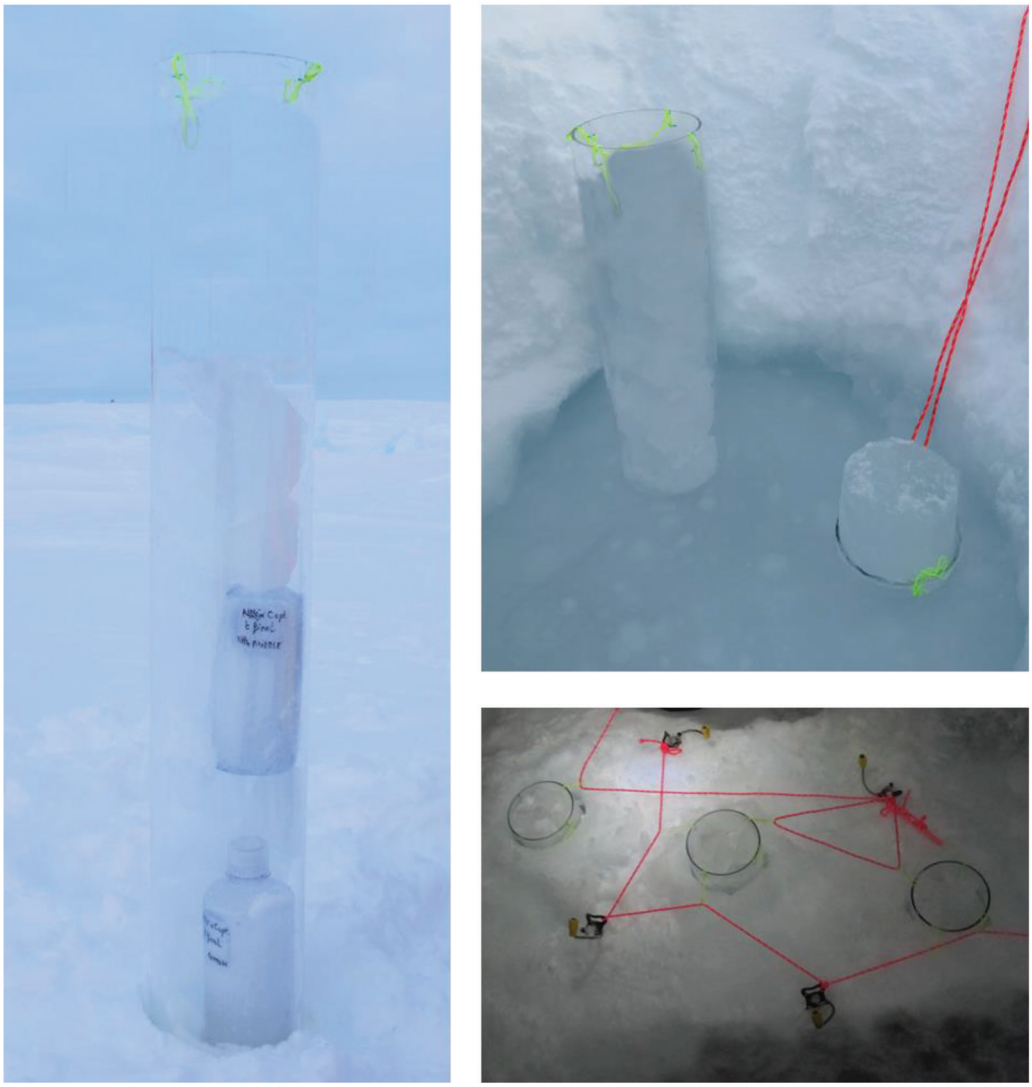

Figure 9

***In situ* incubations for determining metabolic rates in sea-ice communities.**

Ice sections were crushed, placed in polycarbonate bottles, and spiked with enriched isotopes (^{15}N and ^{13}C). Bottles were then incubated *in situ* using Plexiglas tubes (filled with untreated ice sections and incubation bottles) re-inserted into the core holes. Antarctic pack ice, the Sea Ice Physics and Ecosystem eXperiment (SIPEX2). Photos: A. Roukaerts.

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easier comparison between different experiments, and are still the best method to determine maximum photosynthetic rates and efficiencies as functions of light intensity (*e.g.*, Burkholder and Mandelli, 1965; Arrigo and Sullivan, 1992). By combining these parameters with measurements of Chl *a* and light in the field, primary production can be derived (Arrigo et al., 2010). On the other hand, *in situ* incubations more directly assess primary production under the specific conditions to which the natural community is exposed.

For an incubation to be informative, the sample needs to represent the *in situ* community and environment as well as possible. Although brines collected from sackholes or by centrifugation are convenient to handle and provide a solution that represents the environment experienced by sea-ice algae, the biomass collected with such brines is not representative of the sea-ice community (section 2.2.2). On the other hand, while bulk sea-ice melts seem to provide representative biomass of some taxonomic groups, the dramatic changes in temperature and salinity associated with melting, even if the ice samples are melted in seawater, destroy the natural habitat, as well as often rupturing cells (particularly the flagellated taxa; section 3.2). In addition, the melting process at low temperature can take some time (often more than a day), further alienating the community from *in situ* conditions. The cost-benefit balance of the length of time required for melting (longest for isohaline melts if also isothermal; Junge et al., 2004) versus the modification of the samples (greatest for direct melts) is unknown.

Some investigators have incubated whole ice sections in closed containers filled with seawater bearing the relevant isotopic tracer either *in vitro* (*e.g.*, Grossi et al., 1987) or *in situ* by replacing the inoculated ice samples, sealed in transparent containers, into the core holes from which the ice had been extracted (Figure 9; Mock and Gradinger, 1999; Mock, 2002). These methods using unmelted ice sections have the advantage of maintaining a representative sample, but questions remain as to whether the tracer is adequately distributed within the

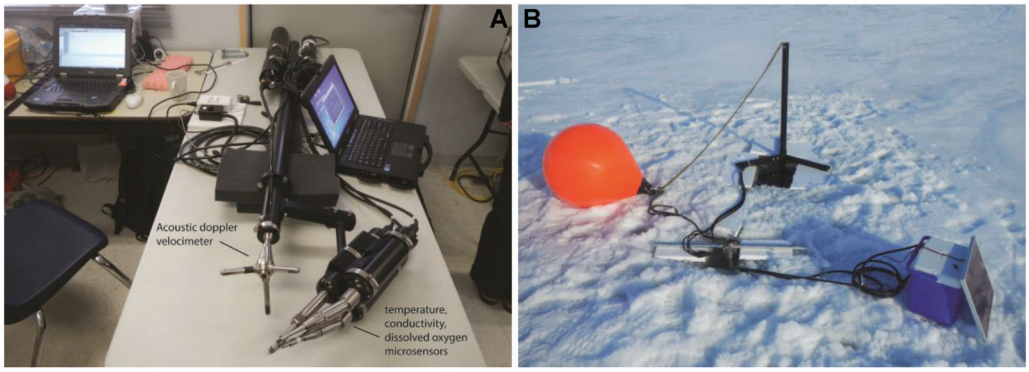

Figure 10

An underwater eddy covariance system for measuring fluxes of dissolved oxygen, salt, heat, and momentum.

In the laboratory prior to deployment (a) and deployed through 60-cm thick sea ice in southeast Greenland (b), March 2013. Photos: B. Else.

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brine network. If the tracer preferentially remains in the surrounding seawater or brines, primary production could be severely underestimated. Crushing the ice (Rysgaard et al., 2007) should improve homogenization.

Changes in O_2 concentration can be used to estimate net community production (NCP), defined as primary production minus respiration. This method has been applied to sea-ice communities using *in situ* oxygen optodes (Mock et al., 2003) and microelectrodes (McMinn and Ashworth, 1998; McMinn et al., 2000; 2007; McMinn and Hegseth, 2007). Determining NCP solely from O_2 dynamics in sea ice is complicated by exchange with the atmosphere arising from solubility changes, as temperature and salinity vary with ice formation and melt (Glud et al., 2002). In seawater, Ar measurements are used to correct for such physical contributions to the O_2 concentration changes (*e.g.*, Craig and Hayward, 1987); Zhou et al. (2014b) have used O_2/Ar ratio measurements to estimate NCP in winter and spring sea ice.

With recent technological advances, underwater eddy covariance (EC) has potential for investigating sea-ice primary production (Long et al., 2012). The technique (which is analogous to the atmospheric technique described in section 5.1.3) requires the under-ice deployment of a three-dimensional current velocimeter in conjunction with a fast-response oxygen electrode (Figure 10). The instruments can be deployed through a hole in the ice and are usually positioned within 1 m of the ice-seawater interface. By correlating oxygen concentrations with vertical current velocity, oxygen fluxes representative of conditions in an area upstream of the instruments (typically on the order of 100 m^2) can be calculated. The technique is thus a true *in situ* measurement, it does not disturb the ice under investigation, and it avoids some of the small-scale patchiness issues associated with other techniques. However, at best, EC only provides a measurement of net productivity (as respiration cannot be separated from photosynthesis). At worst, EC may be strongly influenced by abiotic processes, such as gas rejection (during ice growth) and dilution (during melt), which need to be accounted for in certain cases. The technique is also only useful for measuring production in the bottom-most layers of the ice (*i.e.*, those that are freely exchanging with the underlying seawater).

Incubations with other isotopic tracers, such as ^{15}N (Harrison et al., 1990; Kristiansen et al., 1992; 1998), can be used to assess the nature of primary production (*e.g.*, new versus regenerated; Dugdale and Goering, 1967) and concomitant biogeochemical dynamics (such as N-uptake and nitrification). Because diatoms are important members of sea-ice communities, the information on Si uptake and $bSiO_2$ dissolution that could be generated by adapting methods for incubations with ^{30}Si and ^{32}Si (Fripiat et al., 2009) to sea-ice samples would be particularly valuable. Such incubations depend on many of the same assumptions as carbon-based primary production incubations and, therefore, suffer from the same challenges and limitations. In addition, because these macronutrients occur in sea-ice brines at much smaller concentrations than inorganic carbon, labelled N and Si substrates are added to the incubations in 'trace' quantities (generally, 10% of the ambient level is recommended; Dudgale and Goering, 1967).

3.4.2. Variable fluorescence methods to determine ice algal photosynthetic parameters

Over the last 20 years, chlorophyll *a* variable fluorescence methods have proven to be useful tools for understanding photophysiological properties of marine algae. The application of pulse amplitude modulated (PAM) fluorometry to study sea-ice algae was pioneered by Kühl et al. (2001) in the Arctic and McMinn et al. (2003) in Antarctica. This approach measures the energy conversion efficiency of photosystem II (the quantum efficiency) to derive maximum relative electron transport rates and estimate photosynthetic efficiency and the photoadaptive index of the algae (Ralph and Gademann, 2005). In general, because PAM fluorometers do not provide a direct measurement of carbon fixation, the overall value in PAM fluorescence techniques lies more in their ability to measure ice algal photophysiological responses to varying physicochemical conditions, particularly on small scales relevant to the sea-ice skeletal layer and brine channels (*e.g.*, Hawes et al., 2012).

The most widely used PAM methods in sea-ice research involve ice shavings, brines, and melted ice samples that are analyzed *in vitro* (McMinn et al., 2007; Ralph et al., 2007; Manes and Gradinger, 2009; Meiners et al., 2009; Hawes et al., 2012; Granfors et al., 2013a); these methods are thus biased by sea-ice sampling procedures (sections 2.2 and 3.2). To bypass sample extraction artifacts, divers have successfully deployed

non-invasive PAM fluorometers under sea ice to measure the spatial variability of bottom ice algal biomass and algal photosynthetic parameters in Greenland fast ice (Kühl et al., 2001). Detailed studies utilizing PAM techniques have also confirmed vertical variability in ice algal distributions and photosynthetic properties (Manes and Gradinger, 2009; Hawes et al., 2012).

A second type of variable fluorescence instruments, so-called Fast Repetition Rate (FRR) fluorometers, are increasingly used in phytoplankton research but have not yet been employed widely in sea-ice research. In contrast to PAM fluorometers, FRR fluorometers provide measurements of quantum efficiency, absorption cross section, and turnover times of photosystem II and can, therefore, be used to estimate primary production (Robinson et al., 1998; Suggett et al., 2003).

3.4.3. Bacterial production

Marine bacterial biomass production is usually estimated from incubations with radioisotope-labelled precursors of DNA or proteins (*e.g.*, Ducklow, 2000). As with primary production measurements (section 3.4.1), incubations of melted ice samples are of limited utility, and methods that attempt to maintain the *in situ* conditions during the incubations are preferred. Tritiated-thymidine incorporation (TTI) into DNA (*e.g.*, Smith and Clement, 1990; Deming, 2010) and ^{3}H-leucine (LEU) incorporation into protein (*e.g.*, Kaartokallio, 2004; Paterson and Laybourn-Parry, 2012) are the most common techniques applied to sea-ice samples. While TTI and LEU incorporation often co-vary in the marine environment, suggesting that both methods address bacterial production-related processes, the two methods measure distinctly separate physiological processes; a range of ratios of LEU incorporation to TTI has been reported, with very high ratios in some sea-ice habitats (Mock et al., 1997; Kaartokallio et al., 2008; 2013). High ratios have been attributed to unbalanced growth (*e.g.*, investment in cell growth, measured by LEU incorporation, versus cell division, measured by TTI), but also to incorporation of the radiolabeled LEU tracer into other, non-protein components of sea-ice organisms. Bacterial activity in sea ice has also been estimated from transformations of ^{15}N-labelled nitrogen substrates (Rysgaard and Glud, 2004) and from uptake and reduction of the dye 5-cyano-2,3-ditolyl tetrazolium chloride (CTC; Junge et al., 2004; Meiners et al., 2008).

Estimating bacterial biomass production from the uptake of labelled substrates requires tracer-to-carbon conversion factors, but such conversion factors are not easy to measure routinely; conversion factor determination usually involves incubating natural samples for several days. Therefore, literature values from open-water studies are often applied to sea-ice data, although the accuracy of the conversion factor is strongly affected by community composition and physiology. In order to accurately estimate sea-ice bacterial carbon production, conversion factors for both the LEU incorporation and TTI methods need to be determined for a variety of sea-ice communities in different habitats and regions. In addition, bacterial processes can be particularly sensitive to temperature (*e.g.*, Rivkin and Legendre, 2001); the impact of incubation temperature on measured metabolic rates specifically for sympagic organisms warrants further investigation.

4. Chemical components

Methods for analyzing the major seawater ions (Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+) in sea ice, its overlying snow, and frost flowers are well established and uncontroversial (*e.g.*, Nelson and Thompson, 1954; Domine et al., 2004; Granskog et al., 2004; Douglas et al., 2012). Modern methods almost universally utilize ion chromatography. However, the analyses of nearly all other chemical parameters in sea ice are still subject to debate. Our focus here is on those methods in which we have less confidence.

Our lack of confidence in most chemical analyses in sea ice stems from difficulties in sampling, handling, and processing the samples, and rarely from the actual analyses of the aqueous samples. An important exception is analyses of undiluted brine samples, in which the high salinities often reduce precision and complicate calibrations.

4.1. Inorganic macronutrients

Fundamental information on the nutritional state of the sympagic biological community can be derived from the distributions of the inorganic macronutrients (phosphate, PO_4^{3-}; silicic acid, $Si(OH)_4$; and the nitrogen species: nitrate, NO_3^-; nitrite, NO_2^-; and ammonium, NH_4^+) in sea ice (*e.g.*, Dieckmann et al., 1992; Kaartokallio, 2001). Variations in their concentrations throughout the ice column and with time indicate biological activity and exchange with the underlying water. Most sea-ice nutrient analyses are based on spectrophotometric analysis, using a continuous flow analyzer (*e.g.*, Hydes et al., 2010). A large range of nutrient concentrations occurs in sea ice (Thomas et al., 2010), from depleted to replete conditions, and sampling requires the usual precautions against contamination. To the extent possible, equipment preparation and analyses should follow standard repeat hydrography protocols (*e.g.*, Granskog et al., 2005b; Hydes et al., 2010).

Nutrients are often measured in melted bulk sea-ice samples, but brines for nutrient analyses have also been collected both by centrifuging ice samples (*e.g.*, McMinn et al., 2009; Munro et al., 2010) and from

sackholes (*e.g.*, Gleitz et al., 1995; Papadimitriou et al., 2007). The costs versus benefits of filtering ice melts before nutrient analysis are unclear. Particulate (intracellular) nutrient concentrations can be quite high in sea ice, because of high biomass accumulation, particularly near the ice-water interface (*e.g.*, Arrigo et al., 2010). On the other hand, particle-bound nutrients can be released to solution during melting (section 3.2), although Thomas et al. (1998) found no evidence during their spring-time study that cell lysis significantly impacted dissolved nutrient measurements of bulk ice samples melted without adding seawater (direct melt). Large cells generally would have higher intracellular nutrient contents to release upon lysis than small cells, but large diatoms, which often dominate sea-ice communities, appear to have reduced susceptibility to lysis during melting (section 3.2; Mikkelsen and Witkowski, 2010), minimizing the effect of cell lysis on nutrient concentration estimates for diatom-rich ice. Additional intercalibration exercises are needed to more thoroughly assess the effects of core melting protocols and filtration on measured nutrient concentrations with different microbial communities and in different seasons.

Ideally, nutrient samples, particularly those for ammonium, should be analyzed immediately after sampling to avoid artifacts associated with biological growth or decay during sample storage (Holmes et al., 1999; Hydes et al., 2010). When analysis cannot be completed within hours, the samples generally should be stored frozen (< -20°C) in the dark. However, silicic acid in seawater polymerizes when it freezes and only very slowly redissolves when the sample is thawed for analysis, possibly resulting in underestimation of the original dissolved silicic acid concentration (*e.g.*, Hydes et al., 2010). The impacts of this phenomenon on estimates of *in situ* concentrations of biologically available silicic acid in sea-ice brines is unknown. Therefore, filtration to remove Si-bearing diatoms and storage at room temperature in the dark are more suitable procedures for silicic acid analyses of sea-ice samples (Fripiat et al., 2014b). Alternatively, filtered samples for nutrient analyses can be poisoned with agents such as mercuric chloride and stored refrigerated but unfrozen until analysis (*e.g.*, Kattner, 1999).

4.2. Organic compounds

Sea ice acquires organic matter from seawater during ice formation and through *in situ* biological production (Thomas et al., 1998; 2001a; Giannelli et al., 2001; Granskog et al., 2004; Riedel et al., 2007a; Stedmon et al., 2007; 2011; Müller et al., 2013). Extremely high concentrations of dissolved organic carbon, several thousand μmol L^{-1} (up to two orders of magnitude higher than seawater values; Hansell et al., 2009), have been reported in sea-ice samples (*e.g.*, Thomas et al., 2001a; Junge et al., 2004; Riedel et al., 2008). The resulting sea-ice organic pool is a complex mixture of living and non-living particulate material and dissolved compounds. Operational definitions of dissolved, colloidal, and particulate carbon are particularly tenuous in sea ice, as the temperature and salinity changes associated with melting can cause phase changes in the organic matter. In addition, we do not know how well sampled brines represent the organic content of brine pockets and channels within the undisturbed ice; even if not rigorously particulate, the colloidal and dissolved organic matter may still be "sticky" and adhere to brine channel walls.

In most cases, concentrations should be measured and reported in units of moles of carbon (or nitrogen or phosphorous) and not grams of bulk organic matter. This approach allows the data to be used in biogeochemical cycling studies, including incorporation into numerical models, without unverified assumptions about carbon content and the C:N:P ratios of the organic matter.

Most studies of organic biogeochemistry in sea ice to date have focused on the bulk parameters of total, dissolved, and particulate organic matter. Methods for determining the particulate fractions are detailed in section 3.3.1. Here we address sample collection for the total (unfiltered) and dissolved (filtered) aqueous fractions. Photochemically active colored dissolved organic matter (CDOM) is discussed in section 4.7; halocarbons are discussed in section 5.2.

4.2.1. Sample handling

Organic matter concentrations in sea ice vary over an order of magnitude, from low values similar to those observed in the deep ocean to high values in spring brines and gap layers (*e.g.*, Thomas et al., 1995; Song et al., 2011). When dissolved organic matter (DOM) is present in high concentrations in sea-ice samples, some of the stringent protocols required to successfully sample seawater for DOM are eased. In low-DOM sea-ice samples, however, care is required to avoid not only environmental contamination during sampling and processing, but also cross-contamination between samples during both processing and analyses. Therefore, the exact requirements for preventing contamination of sea-ice DOM samples have not yet been established and probably depend on the samples; that is, upper levels of multiyear ice probably need to be handled more rigorously than gap-layer slush samples. To eliminate potential contamination during core extraction and manipulation, the outer layers of cores can be removed before subsampling for organic matter (Granskog et al., 2004; Song et al., 2011; Fripiat et al., 2014a). In addition, although glass equipment that has been combusted at high temperatures is preferred, plastics are being used more often and may be acceptable under some conditions (*e.g.*, Thomas et al., 1998; Miller et al., 2011b), particularly if contact times are kept short. Rigorous experiments are still required to confirm the conditions under which plastics can be used.

The question of whether or not to filter samples for organic analysis can only be answered within the context of each specific study. Particularly in concentrated brines, the physical and behavioral distinction between "dissolved" and "particulate" organic matter may have little relationship with the operational definition based on the type of filter used. Filtration also introduces artifacts, as dissolved organic matter can stick to filters and turbulence or pressure gradients associated with the filtration process can break apart particles (section 3.3.1).

Furthermore, the salinity changes associated with melting ice can cause coagulation and disaggregation of organic matter, as well as cell lysis (section 3.2). On the other hand, while melting the ice in artificial or filtered seawater will minimize artifacts associated with salinity changes, it is almost impossible to generate truly "organic-free" seawater and thus avoid contributing to the analysis in ways that are difficult to quantify.

4.2.2. Total organic carbon and nitrogen (TOC and TON)

The generic, undifferentiated pool of organic matter has been analyzed in melted bulk ice (*e.g.*, Thomas et al., 2001a; Cozzi, 2008; Dumont et al., 2009) and in brines collected from sackholes (*e.g.*, Papadimitriou et al., 2007; Meiners et al., 2009). In parallel to seawater methods, the samples are often passed through precombusted glass fiber filters, in which case the resulting analytical results are termed "dissolved" organic carbon or nitrogen (DOC, DON), although this pool also includes some bacteria and viruses (Deming, 2010).

High temperature catalytic oxidation is generally used for TOC and DOC analyses (Qian and Mopper, 1996; Spyres et al., 2000), while DON is often inferred from the difference between total dissolved nitrogen (TDN; Bronk et al., 2000) and the inorganic nitrogen species (NO_3^-, NO_2^-, NH_4^+; section 4.1). Sea-ice studies have generally measured TDN using UV oxidation (Thomas et al., 2001a; Papadimitriou et al., 2007; Cozzi, 2008), although other methods may also be suitable (*e.g.*, chemical oxidation with persulfate; Bronk et al., 2000; Fripiat et al., 2014a). Less common are studies of urea in sea ice (Harrison et al., 1990; Kristiansen et al., 1998; Conover et al., 1999; Garrison et al., 2003; Papadimitriou et al., 2009), generally measured using the urease or diacetyl monoxime methods (*e.g.*, Price and Harrison, 1987).

4.2.3. Exopolymeric substances (EPS)

Over the past decade, extracellular or exopolymeric substances (EPS) have been recognized as extremely important components of sea ice. This high-C, low-N material, similar to the transparent exopolymeric particles (TEP) found in seawater, may act as a cryoprotectant for sympagic biota and has a measurable effect on the microstructure and salinity of sea ice (Krembs et al., 2011). Also present in surface sea-ice environments, such as frost flowers and snow, EPS has additional implications for air-ice interactions (Bowman and Deming, 2010; Ewert et al., 2013).

Ice core samples for EPS analysis have been melted (section 3.2) directly (*e.g.*, Krembs et al., 2002; Juhl et al., 2011), in seawater (*e.g.*, Meiners et al., 2003; Riedel et al., 2006), and in concentrated brines (*e.g.*, Collins et al., 2008; Ewert et al., 2013). Direct melts are convenient, because lower salinities simplify further chemical analyses, but additional studies are required to confirm whether the melting protocol has an effect on measured EPS content or on the physical and chemical properties of this complex material.

After melting, EPS is separated into dissolved (dEPS) and particulate (pEPS) fractions by filtration through different types of filters (Table 4). Additional size fractionation can be achieved with sequential precipitation of dEPS fractions of varying solubility across an ethanol gradient (Underwood *et al.* 2010; 2013; Aslam et al., 2012). Three methods are commonly used to quantify particulate and dissolved EPS in sea-ice research (Table 4): the standard colorimetric Alcian blue method developed for TEP analysis of seawater (Passow, 2002), the colorimetric TPTZ (2,4,6-tripyridyl-*s*-triazine) method of Myklestad et al. (1997), and the phenol-sulfuric acid assay (PSA) of Dubois et al. (1956), modified for small sample volumes. In a direct comparison, van der Merwe et al. (2009) found that results from analyses of Antarctic sea ice using the Alcian blue and PSA methods agreed at high but not at low EPS concentrations near the detection limits. More such intercomparisons are needed to confirm the validity and comparability of results from the Alcian blue, TPTZ, and PSA methods under varying conditions. Some investigators have quantified specific components of EPS using a carbazole assay for uronic acids (Bitter and Muir, 1962) and hydrolysis followed by gas chromatography for the neutral monosaccharide composition (Table 4). Methods need to be developed to more thoroughly characterize EPS in sea ice, including: polymer composition, structure and molecular size in different EPS types; interactions between EPS and other components of the sea-ice biogeochemical system (salts, trace metals, other forms of organic matter); and the potential for EPS to interfere with other chemical analyses.

Filters stained with Alcian blue can also be analyzed microscopically to determine particle abundance, size distribution, and the number of EPS-associated bacteria (Meiners et al., 2003; 2004; 2008). Krembs et al. (2002; 2011) also used *in situ* visualization of EPS distribution within brine pockets and channels to directly examine the association between EPS and ice biota.

Table 4. EPS analyses in sea ice

Approach	Method	Comments	References
Size fractionation	GF/F filters (nominally 0.7 μm)	Consistent with POC/DOC methods	Dumont et al., 2009
	Polycarbonate membranes (0.4 μm)	Compatible with microscopic observation and PSA assay	Krembs et al., 2002; 2011
			Meiners et al., 2003
			Riedel et al., 2006; 2007a;b; 2008
			Collins et al., 2008
			van der Merwe et al., 2009
			Bowman and Deming, 2010
			Juhl et al., 2011
			Ewert et al., 2013
			Barber et al., 2014
	Polycarbonate membranes (0.2 μm)	Compatible with bacterial capture	van der Merwe et al., 2009
	Consecutive filtration	Multiple size fractions	Ewert et al., 2013
	Ethanol gradient precipitation	Recovery of higher quantities of EPS	Underwood et al., 2010; 2013
			Krembs et al., 2011
			Aslam et al., 2012
Chemical analysis	TPTZ	High sensitivity	Herborg et al., 2001
	Alcian blue	Consistent with seawater TEP methods and microscopic analysis	Krembs et al., 2002; 2011
			Riedel et al., 2006; 2007a;b; 2008
			Collins et al., 2008
			Dumont et al., 2009
			van der Merwe et al., 2009
	Phenol sulfuric acid (PSA) assay	Commonly used	van der Merwe et al., 2009
			Bowman and Deming, 2010
			Underwood et al., 2010; 2013
			Juhl et al., 2011
			Krembs et al., 2011
			Aslam et al., 2012
			Ewert et al., 2013
	Carbazole assay w/gas chromatography	Acidic component, neutral monosaccharides	Underwood et al., 2010
			Aslam et al., 2012
Microscopic/visual observation	Alcian blue on filters	Size distribution	Meiners *et al*., 2003; 2004; 2008
	Alcian blue in sea ice	Observations of unmelted/melting ice	Krembs et al., 2002; 2011
			Juhl et al., 2011

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4.2.4. Specific organic compounds

Very few studies have attempted to measure specific organic classes or compounds, either natural or anthropogenic, in sea ice. The steps required to limit contamination, gas exchange, or brine loss strongly depend on the nature of the compounds of interest: their concentration ranges, sources, volatility, and particle affinity.

Herborg et al. (2001) and Dumont et al. (2009) distinguished between the mono- and polycarbohydrate fractions of the DOC pool in sea ice. Belt et al. (2013) measured the lipid paleo-biomarker IP25, sterols, and fatty acids in filtered bulk sea-ice melts. Mycosporine-like amino acids (MAAs), which may serve as photoprotectants under some circumstances, have been determined in both Arctic and Antarctic sea ice (Ryan et al., 2002; Uusikivi et al., 2010; Mundy et al., 2011). Stedmon et al. (2007; 2011) and Granskog et al. (2015) used fluorescence to quantify humics and "amino acid-like" organic matter in sea-ice melts and brines. A number of organic anthropogenic contaminants have been measured in sea-ice melts (Rahm et al., 1995; Pućko et al., 2010a;b), in brines (Pućko et al., 2010b), and in snow (Garbarino et al., 2002), frost flowers, and brine skims (Douglas et al., 2012) over sea ice.

Table 5. Trace metal analyses in sea ice

Element	Samples	Fractions	Reference
Al	Bulk ice	Particulate	Hölemann et al., 1999
	Bulk ice	Total	Granskog and Virkanen, 2001
	Bulk ice	Total	Granskog et al., 2004
	Snow	Dissolved	Garbarino et al., 2002
	Brine	Dissolved, particulate	Hendry et al., 2010a
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
	Snow, bulk ice	Particulate	de Jong et al., 2013
	Bulk ice	Dissolved, particulate, colloidal	Lannuzel et al., 2014
Ti	Bulk ice	Particulate	Hölemann et al., 1999
V	Bulk ice	Particulate	Hölemann et al., 1999
	Bulk ice	Total	Tovar-Sánchez et al., 2010
Cr	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
Mn	Bulk ice	Total, dissolved	Campbell and Yeats, 1982
	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Dissolved, particulate	Grotti et al., 2005
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
	Bulk ice	Dissolved, particulate, colloidal	Lannuzel et al., 2014
Fe	Bulk ice	Total, dissolved	Campbell and Yeats, 1982
	Snow	Total	Westerlund and Öhman, 1991
	Snow, bulk ice, brine	Total dissolvable	Löscher et al., 1997
	Bulk ice	Particulate	Hölemann et al., 1999
	Bulk ice	Organic complexes	Boye et al., 2001
	Snow	Total dissolvable	Edwards and Sedwick, 2001
	Bulk ice	Total, dissolved	Granskog and Virkanen, 2001
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Total	Granskog et al., 2004
	Bulk ice	Dissolved, particulate	Grotti et al., 2005
	Snow, bulk ice, brine	Total dissolvable, dissolved	Lannuzel et al., 2006; 2007
	Bulk ice	Dissolved	Aguilar-Islas et al., 2008
	Snow, bulk ice, brine	Total dissolvable, dissolved, particulate	Lannuzel et al., 2008
	Snow, bulk ice, brine	Dissolved	van der Merwe et al., 2009
	Bulk ice	Dissolved	Lannuzel et al., 2010
	Bulk ice	Total	Tovar-Sánchez et al., 2010
	Snow, bulk ice, brine	Total dissolvable, dissolved, particulate	van der Merwe et al., 2011a;b
	Snow, bulk ice	Dissolved, particulate	de Jong et al., 2013
	Bulk ice	Dissolved, particulate, colloidal	Lannuzel et al., 2014
	Snow	Dissolved	Winton et al., 2014
Co	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Total	Tovar-Sánchez et al., 2010
Ni	Bulk ice	Total, dissolved	Campbell and Yeats, 1982
	Bulk ice	Particulate	Hölemann et al., 1999
	Bulk ice	Total	Granskog and Virkanen, 2001
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Total	Tovar-Sánchez et al., 2010

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Element	Samples	Fractions	Reference
Cu	Bulk ice	Total, dissolved	Campbell and Yeats, 1982
	Bulk ice	Particulate	Hölemann et al., 1999
	Bulk ice	Particulate	Frache et al., 2001
	Bulk ice	Total, dissolved	Granskog and Virkanen, 2001
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Total	Granskog et al., 2004
	Bulk ice	Dissolved, particulate	Grotti et al., 2005
	Bulk ice	Total	Tovar-Sánchez et al., 2010
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
Zn	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Total	Granskog et al., 2004
	Bulk ice	Total	Tovar-Sánchez et al., 2010
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
As	Bulk ice	Particulate	Hölemann et al., 1999
Rb	Bulk ice	Particulate	Tütken et al., 2002
Sr	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Particulate	Tütken et al., 2002
Mo	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice	Total	Tovar-Sánchez et al., 2010
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
Cd	Bulk ice	Total, dissolved	Campbell and Yeats, 1982
	Bulk ice	Particulate	Hölemann et al., 1999
	Bulk ice	Particulate	Frache et al., 2001
	Snow	Dissolved	Garbarino et al., 2002
	Snow, bulk ice	Dissolved	Nedashkovskii, 2002
	Snow, bulk ice	Total	Granskog and Kaartokallio, 2004
	Bulk ice	Total	Granskog et al., 2004
	Bulk ice	Dissolved, particulate	Grotti et al., 2005
	Brine	Dissolved	Hendry et al., 2010b
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
Sn	Bulk ice	Particulate	Hölemann et al., 1999
Sb	Bulk ice	Particulate	Hölemann et al., 1999
Cs	Bulk ice	Particulate	Hölemann et al., 1999
Ba	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Snow, bulk ice	Dissolved, particulate	Lannuzel et al., 2011
Nd	Bulk ice	Particulate	Tütken et al., 2002
Hg	Snow	Total, dissolved	Garbarino et al., 2002
	Snow, frost flowers	Total[a]	Douglas et al., 2005
	Snow	Total, particulate	Poulain et al., 2007
	Snow	Total	Douglas et al., 2008
	Snow, bulk ice, brine	Total	Chaulk et al., 2011
	Snow, bulk ice, brine	Dissolved	Cossa et al., 2011
	Snow, frost flowers	Total, stable isotopes	Sherman et al., 2012
	Bulk ice	Dissolved, particulate	Burt et al., 2013

Element	Samples	Fractions	Reference
Tl	Snow	Dissolved	Garbarino et al., 2002
Pb	Bulk ice	Particulate	Hölemann et al., 1999
	Bulk ice	Particulate	Frache et al., 2001
	Bulk ice	Total	Granskog and Virkanen, 2001
	Snow	Dissolved	Garbarino et al., 2002
	Snow, bulk ice	Total, particulate	Nedashkovskii, 2002
	Snow, bulk ice	Total	Granskog and Kaartokallio, 2004
	Bulk ice	Total	Granskog et al., 2004
	Bulk ice	Dissolved, particulate	Grotti et al., 2005
Th	Bulk ice	Particulate	Hölemann et al., 1999
U	Bulk ice	Particulate	Hölemann et al., 1999
	Snow	Dissolved	Garbarino et al., 2002
	Bulk ice, brine	Total	Not et al., 2012

[a]Methods not specified

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4.3. Trace metals

The seasonal ice cover represents a key reservoir, storing and transporting potentially bio-active trace metals and thus likely playing major roles in not only trace metal cycles but also the carbon cycle in polar and subpolar oceans (*e.g.*, Lannuzel et al., 2010). However, trace metal research in sea ice is subject to the same draconian restrictions required in seawater to avoid contamination (Figure 11; *e.g.*, Bruland and Rue, 2001; Cutter et al., 2010). In general, all equipment, preparations, and analyses should follow standard GEOTRACES protocols (Cutter et al., 2010). Several studies have successfully developed sampling and measurement techniques for trace metals in the cryospheric environment and have reported data for numerous elements in sea ice, snow, and brines in the Arctic and Southern Oceans (Table 5).

Samples for trace metal analyses need to be recovered from a dedicated sampling site, upwind from all other operations, and specific sampling procedures must be performed against the wind. Clean-room garments and plastic gloves should be worn over cold-weather clothing. While trace metal-clean sampling is relatively straightforward for snow above sea ice (*e.g.*, Edwards and Sedwick, 2001; Lannuzel et al., 2006), ice core sampling carries a greater risk of contamination. Ideally, a titanium or an electropolished stainless steel corer (Lannuzel et al., 2006) should be used, although standard corers can also be used, if the outer layer of the core can be removed without contamination or substantial brine loss (Figure 11b; Hölemann et al., 1999; Granskog and Kaartokallio, 2004; Granskog et al., 2004; Grotti et al., 2005; Aguilar-Islas et al., 2008). The ice should be cored by hand, although electric auger motors have also been used with the generators downwind (*e.g.*, de Jong et al., 2013). A number of investigators have collected brine samples from sackholes for trace metal analyses (Lannuzel et al., 2006; 2007; van der Merwe et al., 2009; 2011a; Chaulk et al., 2011; Cossa et al., 2011).

Changes to the *in situ* chemical speciation and fractionation between oxidation states and particulate/colloidal/soluble phases during sample collection and processing are exceptionally problematic in sea-ice studies of trace metals. In particular, iron speciation is very poorly understood in sea ice, and the definitions of what is actually measured are highly operational (*e.g.*, Bruland and Rue, 2001). To date, trace metal speciation

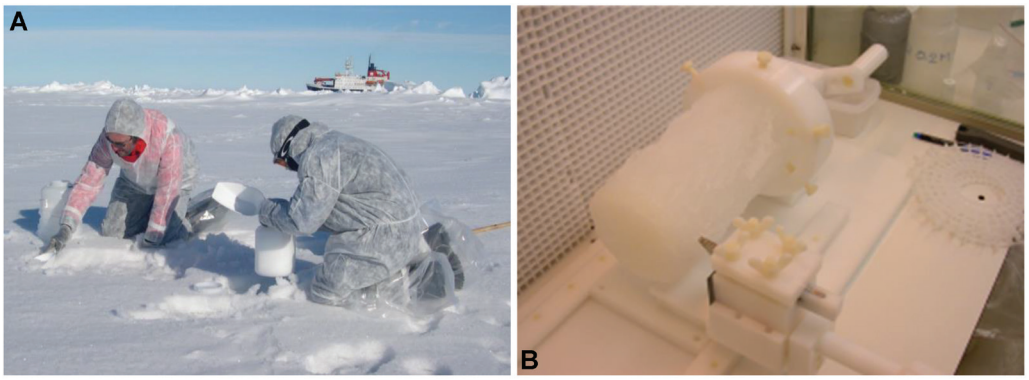

Figure 11

Trace metal-clean sample handling.

(a) Collecting snow on top of sea ice. Weddell Sea, January, 2005. Photo: J-L. Tison. (b) A trace metal-clean lathe (polypropylene, with titanium blade and ceramic handle) for removing contaminated outer layers of cores (with a core section), mounted in a laminar flow bench in a cold lab. Photo: D. Lannuzel

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measurements in sea ice and brines have been limited mainly to separations between operationally-defined particulate and dissolved fractions, separated by filtration and varying dissolution procedures (*e.g.*, Grotti et al., 2005; Lannuzel et al., 2006; 2007; 2011; van der Merwe et al., 2011a; Hendry et al., 2010a). Boye et al. (2001) analyzed iron-organic complexation in one sea-ice sample and confirmed that a large fraction of the iron in sea ice can be complexed by organic matter, indicating that organic complexation may be as important in sea ice as in seawater.

Mercury is another special case, involving not only a highly contamination-prone metal in solution, but also gaseous and organic phases. Most studies of Hg in the marine cryosphere have been focused above the ice, analyzing snow, frost flower, or surface brine skim samples (Garbarino et al., 2002; Douglas et al., 2005; 2008; Poulain et al., 2007; Sherman et al., 2012). The analyses utilize either standard cold vapor atomic fluorescence spectroscopy (EPA, 2002) or atomic absorption spectroscopy methods. Chaulk et al. (2011) and Cossa et al. (2011) measured total Hg and dissolved Hg chemical speciation, respectively, within sea ice. Sherman et al. (2012) also used stable mercury isotopes (Δ^{199}Hg, analyzed by inductively coupled plasma mass spectrometry) to investigate air-ice mercury fluxes.

4.4. Gases

With the realization that sea ice is porous comes an understanding that it could serve as a source or sink of climatically active gases. Most of the gases measured in sea ice, to date, have been found at relatively high concentrations; in general, the precision of the analyses has been a greater challenge than detection limits. The

Table 6. Gas analyses in sea ice

Gas	Samples	Extraction method	Analysis	References
Total gas content	Bulk ice	Thaw/freeze cycling	Toepler pump	Tison et al., 2002
		Melting in artificial seawater	Tygon burette	Rysgaard and Glud, 2004
O_2	Bulk ice	Thaw/freeze cycling	GC[a]	Matsuo and Miyake, 1966
		In situ	Optodes	Mock et al., 2002; 2003
				Rysgaard et al., 2008
		Dry crushing	GC[a]	Tison et al., 2002
		Melting in artificial seawater	Winkler titration, GC[a]	Rysgaard and Glud, 2004
		Direct melting	Winkler titration	Søgaard et al., 2010
	Brine	Sackholes	Winkler titration	Gleitz et al., 1995
				Delille et al., 2007
				Papadimitriou et al., 2007
		Gravity drainage	Winkler titration	Nomura et al., 2009
	Bubbles	Melting in artificial seawater	GC[a]	Søgaard et al., 2010
CO_2	Bulk ice	Thaw/freeze cycling	GC[a]	Matsuo and Miyake, 1966
		Dry head-space equilibration	GC[a]	Gosink, 1978
				Geilfus et al., 2012b; 2014a;b
		Dry crushing	GC[a]	Tison et al., 2002
		In situ	NDIR[b]	Miller et al., 2011a
			GC[a]	Miller et al., 2011b
	Brine	Sackholes	NDIR[b]	Geilfus et al., 2012a;b; 2014a;b
	Snow	Syringe	GC[a]	Gosink and Kelley, 1985[c]
CH_4	Bulk ice	Purge and trap	GC[a]	Gosink, 1980[c]
		Thaw/freeze cycling	GC[a]	Zhou et al., 2014a
CO	Bulk ice	Melt head-space equilibration	GC[a]	Gosink, 1980[c]
				Xie and Gosselin, 2005
				Song et al., 2011
N_2	Bulk ice	Dry crushing	GC[a]	Tison et al., 2002
Ar	Bulk ice	Dry crushing	GC[a]	Zhou et al., 2013
N_2O	Bulk ice	Purge and trap	GC[a]	Kelley and Gosink, 1979
				Gosink, 1980[c]
				Randall et al., 2012

Gas	Samples	Extraction method	Analysis	References
DMS	Bulk ice	Melting in base[d]	GC[a]	Turner et al., 1995
		Melting in acid	GC[a]	Trevena and Jones, 2006
		Melting in brine	GC[a]; PTR-MS[e]	Stefels et al., 2012
		Dry crushing	GC[a]; PTR-MS[e]	Tison et al., 2010
				Stefels et al., 2012
	Brine	Sackholes	GC[a]	Delille et al., 2007
				Asher et al., 2011
Halocarbons	Bulk ice	Purge and trap	GC[a]	Kelley and Gosink, 1979[c]
				Sturges et al., 1997
				Granfors et al., 2013a
	Brine	Purge and trap	GC[a]	Mattson et al., 2012
				Granfors et al., 2013a;b
	Snow/Frost flowers	Purge and trap	GC[a]	Sturges et al., 1997
				Granfors et al., 2013a;b

[a]GC: Gas Chromatography with suitable detectors
[b]NDIR: Non-dispersive infrared spectroscopy
[c]Methods not specified
[d]Determined total DMS+DMSP
[e]Proton-transfer-reaction mass spectrometry
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most obvious difficulty in sampling sea ice for gases is the potential for exchange with the air. In most cases, gases are lost from the ice to the atmosphere, but ice samples can also be contaminated by contact with air, particularly by pollutant volatile organics and hydrocarbons. In addition, gases occur in sea ice both as solutes and as bubbles; some methods will extract both fractions, while others collect only the fraction dissolved in the brines. In this section, we discuss general concerns with analyzing gases in sea ice and summarize the specific methods used to date (Table 6). The details of measuring dimethylsulfide and carbon dioxide are discussed in respective sections 4.5 and 4.6, elemental mercury is covered in section 4.3, halocarbons are discussed in section 5.2, and studies of other volatile organic compounds are included in section 4.2.4.

The oldest methods for extracting gases from sea ice are wet extractions, involving sequential melting and refreezing of ice samples (Matsuo and Miyake, 1966). For insoluble gases at high concentrations in the ice or for which analyses with low detection limits exist, the refreezing step is not required. With knowledge of the gas partitioning coefficient between the aqueous melt and air, the initial melt can simply be equilibrated with a volume of ambient air, which is then analyzed. This approach has been used successfully for analyses of total gas content (Tison et al., 2002), CO (Xie and Gosselin, 2005; Song et al., 2011), N_2O (Kelley and Gosink, 1979; Randall et al., 2012), methane (Zhou et al., 2014a), and organohalides (section 5.2).

Dry-extraction (or dry crushing), involving crushing an ice sample with steel balls in a vacuum chamber, has proven effective for determining O_2, N_2 (Tison et al., 2002), and Ar (Zhou et al., 2013) in sea ice. The size of the crushed ice sample mainly depends on the concentration of the target gas in the ice and the sensitivity of the gas chromatography detector. For trace gases (such as DMS, section 4.5), the gas may need to be preconcentrated before injection into the gas chromatograph. Crushing the ice has one intrinsic problem: contamination by methane released by the metal-metal friction between the stainless steel balls and the container during the crushing process (Higaki et al., 2006). Therefore, other extraction methods are used for analyses of carbon-containing species.

Sea-ice brines for gas analyses are usually collected from sackholes, although Nomura et al. (2009) used full-core gravity drainage (Figure 4c) to collect brines for O_2 analysis. In general, extracting brines for gas analyses is only satisfactory for relatively soluble gases, such as O_2 and CO_2, and even so, only if temperatures are high enough for the brines to accumulate quickly and the sackhole is capped (Papadimitriou et al., 2007). In contrast, the bulk of the insoluble gases in sea ice is probably located in bubbles within brine pockets and channels; when only the brines are analyzed, such gas bubbles within the ice are lost. Zhou et al. (2014a) found that brine CH_4 concentrations deduced from measurements in bulk ice can be up to 10 times higher than the concentrations directly measured in brine samples, a difference almost certainly due to exchange with the atmosphere during brine percolation.

In situ probes hold great potential for determining gas concentrations in sea ice (McMinn et al., 2009). Probes based on photochemical detection (*i.e.*, optodes) are particularly promising for sea-ice applications; oxygen has been measured successfully in sea ice using commercially available optodes (Figure 12a; Mock

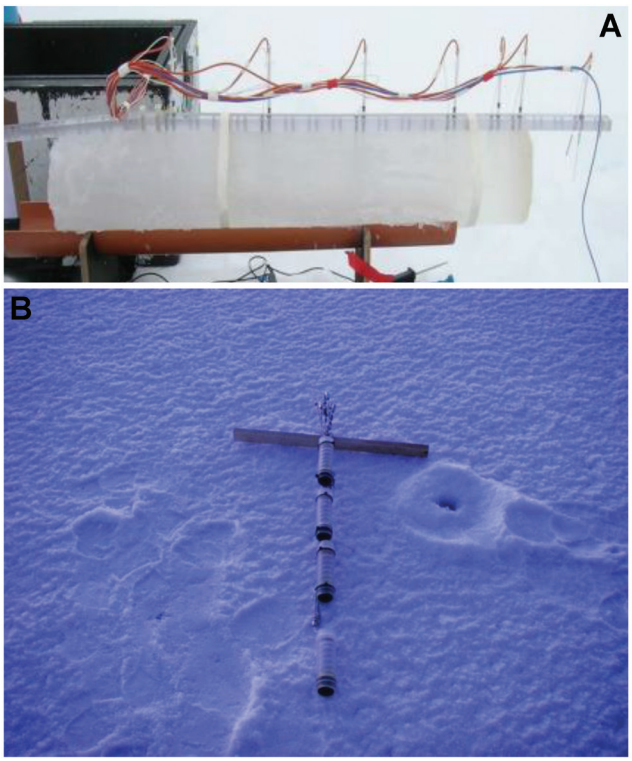

Figure 12

***In situ* probes for measuring gases in sea ice.**

(a) Oxygen optodes deployed in an ice core, prior to being replaced into the original core hole. Photo: A. Krell. (b) Silicone chamber 'peeper' array ready for deployment through the adjacent hole in the sea ice. Amundsen Gulf, December 2007. Photo: N. Sutherland.

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et al., 2002; Rysgaard et al., 2008), although reaction times are slow and calibrations are potentially complicated by both high salinities and organic matter concentrations. Another potential drawback of microprobe measurements is uncertainty in the specific microenvironment sampled. For example, an oxygen optode might only sense the liquid phase, missing the (often dominant) gas phase. In addition, any *in situ* probe will change the thermodynamic environment of the ice to at least some extent; particularly under sunny conditions, objects frozen into the ice absorb heat, causing localized excess melt. Gas-permeable silicone chambers developed by the soil science community have been deployed for measuring *in situ* CO_2 mole fractions in sea ice (Figure 12b; section 4.6.4; Miller et al., 2011a;b) and theoretically could be used for analyses of other gases, including O_2, CH_4, and N_2O (*e.g.*, Holter, 1990; Kammann et al., 2001). Electrochemical probes are generally unsuitable for sea-ice applications, because their internal electrolyte solutions freeze, but have potential for further development. The primary drawbacks to *in situ* sensors, in general, are that the study site must be occupied for an extended period and, unless the sensors can be deployed at freeze-up, their installation requires disturbing the ice cover.

4.5. Sulfur species

Dimethylsulfide (DMS) is one of the most abundant volatile sulfur compounds in the ocean and accounts for more than half of the global biogenic sulfur flux to the atmosphere (*e.g.*, Liss et al., 1997). Sea ice usually contains larger amounts of DMS and its precursor dimethylsulfoniopropionate (DMSP) than does the under-ice water (up to two orders of magnitude higher), although the amounts in sea ice are highly variable (*e.g.*, Trevena and Jones, 2006). Therefore, seasonal ice melting introduces elevated DMS concentrations to surface waters from the release of sea-ice DMS and DMSP (*e.g.*, Tison et al., 2010). The sulfur compounds studied in sea ice to date are DMS, DMSP (which occurs in both particulate and dissolved fractions), and dimethylsulfoxide (DMSO). Other sulfur species important in the sulfur cycle that have not yet been investigated in sea ice include sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2).

Total and dissolved DMSP have been measured in ice brines recovered from sackholes (Trevena and Jones, 2006; Asher et al., 2011), although it is not clear how well dissolved DMSP measurements from brines distinguish the *in situ* partitioning between dissolved and particulate fractions within the brine network of undisturbed ice (sections 2.2.2, 4.2.1). Total DMSP is often analyzed in bulk ice melts (Levasseur et al., 1994; Curran and Jones, 2000; Trevena et al., 2000; Trevena and Jones, 2006), whether obtained by melting in filtered seawater (Levasseur et al., 1994), in acidified filtered seawater (Trevena et al., 2000; Trevena and Jones, 2006), or in concentrated brine (Stefels et al., 2012). However, in a direct comparison of DMSP analyses

from twin cores, one melted in concentrated filtered seawater and one dry-crushed (section 4.4), Stefels et al. (2012) found that large amounts of DMSP can be converted to DMS during the melting process.

Because of its very low solubility, accurately measuring DMS concentrations in ice samples has been a challenge. Although brines have been analyzed for DMS (Table 6), it is generally considered too insoluble to be recovered confidently from brines collected from sackholes. Trevena and Jones (2006) melted ice samples directly into acid within purge chambers. Small ice samples have also been directly crushed to recover and

Table 7. CO_2 system analyses in sea ice

Parameter[a]	Samples	Processing	References
DIC and TIC	Bulk ice	Melting in distilled water	Rysgaard et al., 2007
			Søgaard et al., 2013
		Direct melting	Fransson et al., 2011; 2013
			Miller et al., 2011a;b
			Geilfus et al., 2012a; 2014a
			Hawes et al., 2012
	Brine	Sackholes	Garrison et al., 2003
			Papadimitriou et al., 2004; 2007; 2009; 2012
			Munro et al., 2010
			Fransson et al., 2011; 2013
			Miller et al., 2011a
			Geilfus et al., 2012a; 2014a
			Nomura et al., 2010b; 2013b
		Gravity drainage	Nomura et al., 2009
		Centrifugation	Munro et al., 2010
	Frost flowers	Direct melting	Miller et al., 2011a
			Fransson et al., 2013
A_T	Bulk ice	Direct melting	Lyakhin, 1970
			Anderson and Jones, 1985
			Nedashkovsky et al., 2009
			Fransson et al., 2011; 2013
			Miller et al., 2011a;b
			Geilfus et al., 2012a;b; 2013; 2014a
			Hare et al., 2013
			Nomura et al., 2013a
		Melting in distilled water	Ryssgaard et al., 2007
			Søgaard et al., 2013
		Melting in seawater	Nedashkovsky and Shvetsova, 2010
	Brine	Sackholes	Gleitz et al., 1995
			Kennedy et al., 2002
			Delille et al., 2007
			Papadimitriou et al., 2007; 2009; 2012
			Fransson et al., 2011; 2013
			Geilfus et al., 2012a;b; 2014a;b
			Nomura et al., 2010b; 2013a
		Gravity drainage	Nomura et al., 2009
	Snow	Melting in seawater	Nedashkovsky and Shvetsova, 2010
	Frost flowers	Direct melting	Miller et al., 2011a
			Douglas et al., 2012
			Fransson et al., 2013
			Geilfus et al., 2013

Parameter[a]	Samples	Processing	References
pH	Brine	Sackholes	Gleitz et al., 1995
			Kennedy et al., 2002
			Papadimitriou et al., 2004
			Delille et al., 2007
			Miller et al., 2011a
			Hare et al., 2013
			Geilfus et al., 2014b
PIC	Brine	Centrifugation	Tison et al., 2002
	Bulk ice	Pipetting from melts	Dieckmann et al., 2008
			Miller et al., 2011b
			Fischer et al., 2012
			Geilfus et al., 2013
			Nomura et al., 2013a
		Melt filtration	Dieckmann et al., 2010
			Fischer et al., 2012
			Søgaard et al., 2013
		Microscopy	Rysgaard et al., 2013
			Geilfus et al., 2014a
	Frost flowers	Pipetting from melts	Geilfus et al., 2013

[a]See Table 6 for pCO_2 analyses.

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analyze DMS (Tison et al., 2010; Stefels et al., 2012). Fluxes of DMS out of sea ice have been estimated using both chamber (section 5.1.1; Nomura et al., 2012) and micrometeorological (section 5.1.4; Zemmelink et al., 2008) techniques. The analyses generally use gas chromatography with either flame photometric or mass spectrometric detection.

Analyses of DMSO in sea ice are still scarce and complicated by the need to eliminate interference from DMSP (Brabant et al., 2011). Lee et al. (2001) measured DMSO associated with the particulate (algal) fraction in sea ice, Brabant et al. (2011) determined total DMSO in bulk ice, and Asher et al. (2011) measured dissolved DMSO in sea-ice brines. All of these studies analyzed DMSO as DMS, after purging and reduction.

The rates at which sulfur species are formed and degraded is one of the largest uncertainties in the global sulfur cycle (*e.g.*, Ayers and Cainey, 2007); in only one study have natural rates of interconversion between the various sulfur compounds in sea ice brines been determined directly (using short-term incubations with ^{2}H- and ^{13}C-labelled DMS, DMSP, and DMSO tracers; Asher et al., 2011). Stefels et al. (2012) described a method for spiking samples with deuterated DMS and DMSP before melting, in order to document and then correct for DMSP degradation. Although used to examine sample storage and processing artifacts (Stefels et al., 2012), this tracer method also has potential for investigating conversion rates by the *in situ* community. As for primary production and bacterial production (sections 3.4.1 and 3.4.3), a satisfactory method for determining sulfur cycling rates in undisturbed ice environments has not been reported, making continued method development a high priority. In general, we encourage immediate processing and analysis of sea-ice samples for sulfur cycle studies to limit interconversion between sulfur species and loss of insoluble DMS.

4.6. The carbon dioxide system

The inorganic carbon system in sea ice is controlled by complex biogeochemical processes that transform carbon between phases (gas bubbles, brine, and particles) and between inorganic and organic forms, while also exchanging with the atmosphere and the underlying water (*e.g.*, Thomas et al., 2010; Loose et al., 2011). A number of methods have been used to collect and process samples for determining CO_2 system parameters in sea ice (Table 7), but sample storage and analyses have generally followed standard protocols for seawater (Dickson et al., 2007); methodological intercalibrations are desperately needed. For example, in the one study that determined pCO_2 within sea ice by multiple methods (calculated from TIC and alkalinity in brines, section 4.6.1; calculated from TIC and alkalinity in bulk ice melts, section 4.6.3; and with *in situ* peepers, section 4.6.4), poor agreement was found between them (Miller et al., 2011a).

Interpretations of inorganic carbon data from sea ice have also been heavily influenced by our understanding of the seawater inorganic carbon system (*e.g.*, Zeebe and Wolf-Gladrow, 2001). This reliance on the seawater model is perilous, because the seawater methods have been optimized for seawater and thus calibrated for very narrow concentration and salinity ranges; both sea-ice brines and bulk melt samples almost always fall

outside those ranges. In addition, pH is defined analytically on a number of different scales (*e.g.*, Dickson, 1993). The standard scale used for seawater (the total hydrogen ion scale, pH_T), and standard buffers certified on that scale, cannot be applied rigorously to sea-ice brines (*e.g.*, Miller et al., 2011a). Finally, the conditional stability constants used to convert between CO_2 partial pressure (pCO_2), dissolved inorganic carbon (DIC), total alkalinity (A_T), and pH in seawater are only rigorously valid for temperatures above 0 °C and salinities between 5 and 50 g kg^{-1}. Studies in spring ice (Delille et al., 2007) indicated that seawater thermodynamic relationships may be acceptable in warm, low-salinity sea ice, but in sea-ice brines at even moderate brine salinities of 80 g kg^{-1}, Brown et al. (2014) found that measured and calculated values of the CO_2 system parameters can differ by as much as 40%. On the other hand, because the CO_2 system parameters are much more variable in sea ice than in seawater, sea-ice measurements demand less precision than those in seawater.

As indicated by Tables 6 and 7, most carbonate system parameters have been measured in both bulk ice and brines. Attempts to use those data to understand sea-ice biogeochemistry always involves uncomfortable assumptions about the validity of the sample handling and the *in situ* behavior of the CO_2 system. For example, whereas brine samples are compromised by gas exchange during sampling, interpreting measurements in bulk sea ice requires assumptions about the presence of gaseous and solid inorganic carbon. Therefore, the best way to sample the ice and the best parameters to measure depend on both the conditions and specific questions targeted by the study.

Nonetheless, we can make some recommendations. In general, samples for CO_2 system analyses in sea ice should be collected upwind from any ship, camp, or generator to avoid contamination by CO_2 or soot from fossil fuel combustion. Hand-coring is preferable, although electric auger motors can be used, as long as the generator is located a substantial distance downwind. Some investigators have filtered their samples for DIC analyses (Papadimitriou et al., 2004; 2007; 2012) using specialized techniques to avoid significant gas exchange (McCorkle et al., 1985), but vacuum filtration is not recommended. Because the concentration of particulate inorganic carbon (PIC) can be high in sea ice (Dieckmann et al., 2008; 2010; Rysgaard et al., 2013), the results from DIC analyses of unfiltered sea-ice samples are properly termed total inorganic carbon (TIC).

4.6.1. Brines

Samples for pCO_2, TIC, and pH are sensitive to gas exchange and need to be isolated from the atmosphere during sampling. Therefore, analyses of these parameters in brines, which are difficult to sample without exposing them to the air, can be problematic (see also sections 2.2.2 and 4.4).

Electrochemical pH measurements are particularly challenging in ice brines, because the high sample salinities result in large liquid junction potentials and severely slow electrode response times. In addition, stable, certified standard buffers are not available for brine solutions, compromising electrode calibration. Although the first sea-ice brine pH measurements were made electrochemically (Gleitz et al., 1995), spectrophotometric measurements are becoming more common (Miller et al., 2011a; Hare et al., 2013). Wren and Donaldson (2012) have developed a spectrophotometric method for analyzing pH in surface brine films that may have potential for *in situ* applications. Particular care is needed in spectrophotometric analyses to use optical and thermodynamic parameters for the dyes that have been defined for appropriate temperature and salinity ranges (*e.g.*, Millero et al., 2009).

4.6.2. Gas bubbles

The standard method of crushing ice under vacuum to retrieve gases trapped in bubbles within an ice sample, as developed for glacial ice, may give artificially high pCO_2 values when applied to sea ice (*e.g.*, Tison et al., 2002). The vacuum likely disrupts the CO_2 system equilibria within the brines, causing CO_2 outgassing from the brine solution and possibly also precipitating $CaCO_3$ (Geilfus et al., 2012b). Therefore, Geilfus et al. (2012b) developed a method to accurately measure CO_2 in gas bubbles and brines in sea ice by equilibration with a headspace of known volume and CO_2 mole fraction (dry head-space equilibration). The headspace must be as small as possible to assure that the $CO_{2(g)}$ released from the ice dominates the CO_2 signal, with only a small contribution from the standard headspace gas. Gosink (1978) described an *in situ* head-space equilibration technique that involved sealing sampling cuvettes to the ice surface.

4.6.3. Bulk ice melts

Total alkalinity of bulk ice melts is a relatively uncomplicated analysis that has been performed for decades (*e.g.*, Lyakhin, 1970; Anderson and Jones, 1985; Nedashkovsky et al., 2009). In a standard potentiometric titration (*i.e.*, Dickson et al., 2007), the measured A_T will include not only that which was in the brines *in situ*, but also a contribution from any particulate inorganic carbon (*e.g.*, $CaCO_{3(s)}$) that dissolves as the ice melts or when the sample is acidified during the titration.

On the other hand, because TIC is impacted by gas exchange, its analysis in bulk ice is more complicated; a method for confidently melting ice samples without allowing interaction with ambient CO_2 has not yet been devised. In the field, ice cores need to be retrieved, sectioned, and isolated from the atmosphere as quickly as possible. The most common approach to melting ice samples for TIC analysis is to use gas-impermeable

bags (made from fluoropolymers such as ALTEF® or Kynar®; Rysgaard et al., 2009; Fransson et al., 2011; 2013; Miller et al., 2011a). After sealing the sample in the bag, the headspace should be removed using a hand pump, to assure that the sample is not exposed to an excessive vacuum. As long as the container in which the sample is melted is sealed and the headspace (after melting) is less than 2% of the total volume, the TIC concentration in the solution should be correct to within 0.01% (Dickson et al., 2007); in fact, because the pCO_2 of ice melts is generally low, the melt solution should also absorb essentially all of the gaseous CO_2 initially present as bubbles trapped in the ice. Alternatively, the ice sample can be melted without a headspace in water of known TIC concentration (Rysgaard et al., 2007; 2009).

Unless A_T and TIC samples can be analyzed within 1–2 hours of collection, they generally should be poisoned with small quantities of $HgCl_2$ (Dickson et al., 2007). Although straightforward and relatively safe for samples that are initially aqueous, like seawater and brines, poisoning is more complicated for sea-ice melts, which cannot be bottled for long-term storage until after melting is complete. Some researchers have added the $HgCl_2$ directly to the bag with the melting sample (Rysgaard et al., 2009; Fransson et al., 2013). However, because ice melts are poorly buffered, the $Hg(OH)_2$ complexes formed from the added mercury may impact the carbonate system chemistry (Fransson et al., 2013). In addition, it is difficult to completely contain the mercury when working with gas-impermeable bags (during cleaning between samples, but also because the bags can fail at low temperatures, developing small holes and leaking), creating an exposure risk for all personnel using the core-processing laboratory. Therefore, $HgCl_2$ is often added to samples only after they are transferred from the bags into bottles for long-term storage. We still lack a satisfactory method for safely preserving sea-ice samples for carbonate system analyses during melting.

Unlike TIC and A_T (in units of mol kg^{-1}), which are total quantities unaffected by the temperature and salinity changes associated with melting, pH and pCO_2 are potentials; their values measured in sea-ice melts cannot be directly converted to the original conditions in the solid ice/brine matrix. Therefore, pCO_2 and pH measurements in ice melts do not provide information about the initial, *in situ* conditions of the ice, although the measurements can be used to calculate other CO_2 system parameters or to derive the theoretical characteristics of the melt that will influence the surface waters in summer (Nedashkovsky and Shvetsova, 2010, Fransson et al., 2011; Geilfus et al., 2013). Samples for pCO_2 and pH analyses have the same issues with potential degradation during melt as TIC and A_T samples: standard seawater protocols (*e.g.*, Dickson et al., 2007) indicate that pCO_2 samples that cannot be analyzed within a couple of hours should be poisoned with $HgCl_2$; and, presently, pH samples cannot be stored for they change significantly within hours of collection (*i.e.*, within the time it takes for an ice sample to melt).

4.6.4. *In situ* sensors

Ideally, *in situ* sensors would provide the most meaningful pCO_2 and pH measurements in sea ice, particularly if the sensors could be deployed at freeze-up, so that installation would not disrupt an established ice cover. To date, available pH microelectrodes are still unsuitable for deployment in sea ice, because their electrolyte solutions freeze at low temperatures, in addition to the calibration and response-time issues discussed in section 4.6.1. Although *in situ* silicone gas exchange chambers ("peepers") have been used for pCO_2 measurements (section 4.4; Miller et al., 2011a;b), gas diffusion rates in silicone decrease dramatically with temperature, and peepers require long equilibration times, limiting deployments to extended occupations of a single site. In addition, peepers have not yet been fully tested or calibrated under controlled conditions. As noted in section 4.4, *in situ* CO_2 or pH probes will modify their local thermodynamic environment within the ice to at least some extent.

4.6.5. Particulate inorganic carbon (PIC)

A number of carbonate salts are known to precipitate from brines in sea ice, including calcium carbonate (generally in the form of ikaite, $CaCO_3{\cdot}6H_2O$; *e.g.*, Dieckmann et al., 2008) and magnesium- and mixed magnesium-calcium-carbonates (*e.g.*, Assur, 1958). Precipitation of any of these minerals likely has a strong influence on pCO_2 and the entire CO_2 system within the ice. Ikaite has been identified in both Antarctic and Arctic sea ice (Delille, 2006; Dieckmann et al., 2008; 2010; Rysgaard et al. 2012; 2013; Geilfus et al., 2013; Nomura et al., 2013a), but solid salts are not recovered from all samples (*e.g.*, Nomura et al., 2013a). The lack of observable PIC in some samples is likely due to natural variability in sea ice (possibly related to phosphate concentrations, thermal history of the ice, and/or sea-ice permeability; Nomura et al., 2013a; Rysgaard et al., 2013; Papadimitriou et al., 2013; 2014) and not methodological differences, as the presence and absence of precipitates are observed by the same groups. Recent laboratory studies have defined the thermodynamics and kinetics of ikaite precipitation in abiotic ice brines (Papadimitriou et al., 2013; 2014), but the conditions controlling the formation and preservation of solid $CaCO_3$ in natural sea ice are still largely unknown.

Because carbonate salts are water soluble to varying extents at temperatures above freezing, the ice samples must be melted at a low temperature and processed as soon as melting is completed. Although the melted samples can be filtered to collect the solid precipitate (Dieckmann et al., 2010; Fischer et al., 2012; Søgaard et al., 2013), the quantity of particulate organic matter present in the sea ice can interfere with subsequent visualization and analysis of the inorganic salts, so the precipitate is often collected from sea-ice melt samples

using a pipette (Dieckmann et al., 2008; Miller et al., 2011b; Geilfus et al., 2013; Nomura et al., 2013a). Rysgaard et al. (2013) have developed a microscopic method to visually identify and quantify ikaite crystals from the ice as it melts. Even when dry, ikaite is unstable at temperatures above 4 °C; if confirmation of the specific calcium carbonate mineralogy (*i.e.*, ikaite versus calcite, aragonite, or vaterite) is required, the sample must be kept below 4 °C throughout sample recovery, melting, storage, transport, and analysis. Analysis is usually by x-ray diffraction spectrometry, but facilities able to keep a sample cold throughout the analysis are rare. If the specific mineralogy of the salt is not required, the precipitate sample can be stored indefinitely at room temperature and analyzed on any x-ray diffraction instrument (Dieckmann et al., 2008; Miller et al., 2011b) or with a standard calcium assay (Fischer et al., 2012).

The question of whether carbonate minerals that precipitate within sea ice are mobile with the brines has not been completely resolved. Despite observations that particulates are under-represented in percolating sea-ice brines (section 2.2.2), solid $CaCO_3$ has been recovered from centrifuged brines (Tison et al., 2002), and circumstantial evidence from the Sea of Okhotsk (Lyakhin, 1970) and the Beaufort Sea (Fransson et al., 2013) has indicated that abiotic $CaCO_3$ precipitates from sea ice may be released to the water column.

4.7. Photochemistry: CDOM, hydrogen peroxide, and ozone

Photochemical processes are likely to be very important in many sea-ice biogeochemical cycles, but while numerous studies have examined the transmission of electromagnetic radiation through sea ice (*e.g.*, Perovich, 2009), there has been little research on photochemistry within the ice (Belzile et al., 2000). Colored dissolved organic matter (CDOM, usually measured spectrophotometrically and reported as absorption coefficients, in units of m^{-1}) likely represents the most photochemically active fraction of the non-living sea-ice components and has been measured in sea ice by a number of investigators (Belzile et al., 2000; Scully and Miller, 2000; Granskog et al., 2005b; 2015; Uusikivi et al., 2010; Norman et al., 2011). Fluorescence has also been used to measure and differentiate the components of CDOM in natural and laboratory sea ice and in frost flowers (Stedmon et al., 2007; 2011; Müller et al., 2013; Granskog et al., 2015). Although generally assumed to be less prone to contamination than bulk DOC, samples of CDOM, particularly those measured by fluorescence, can easily be contaminated. In addition, the effects of melting protocols on the absorbance of organic matter from sea ice has not been investigated explicitly. Hydrogen peroxide and other photochemically produced oxidizers, such as ozone, are likely important players in any photochemical reactions occurring in sea ice (Klánová et al., 2003; King et al., 2005), but no one has reported direct sea-ice measurements of these compounds.

4.8. Stable isotopes: ^{18}O, ^{2}H, ^{13}C, ^{15}N, ^{30}Si

The stable oxygen isotope ratio (^{18}O relative to ^{16}O) in the water molecules of a sea-ice sample is controlled by many of the processes that influence sea-ice biogeochemistry, including freezing, melting, flooding, and snowfall, making $\delta^{18}O$ a powerful tool for sea-ice studies (*e.g.*, Eicken, 1998; Granskog et al., 2003; Tison et al., 2008; Nomura et al., 2009; 2011). Particularly in the Arctic Ocean, where $\delta^{18}O$ measurements can also help distinguish between riverine versus sea-ice melt sources of freshwater in the surface ocean (*e.g.*, Macdonald et al., 1989), $\delta^{18}O$ is often considered a mandatory parameter, along with salinity.

Sampling $\delta^{18}O$ is simple and inexpensive; the main concern is evaporation during sample storage. Although evaporation during melting could also be an issue, if the container is open or the headspace is large, evaporation is no more of a problem for $\delta^{18}O$ than for salinity. Mass spectrometric analyses of $\delta^{18}O$ require as little as a few milliliters of sample; both bulk sea-ice melts and brines have been analyzed for $\delta^{18}O$ (*e.g.*, Zhou et al., 2013). Glass containers with caps forming a tight seal are preferred, particularly if the samples are likely to be stored for more than a few months before analysis (*e.g.*, McLaughlin et al., 2012). Parafilm can also be wrapped around the outside of the cap, to further protect against leakage (Miller et al., 2011b).

Sea-ice measurements of the stable isotopes of other elements are summarized in Table 8. Deuterium fractionation in the water molecules in sea ice is greater than that of ^{18}O, providing additional information on brine convection and ice melt. Sampling and handling of ^{2}H samples for mass spectrometric analysis should follow those for ^{18}O samples (Zhou et al., 2013). Stable isotope ratios of carbon (^{13}C relative to ^{12}C), nitrogen (^{15}N relative to ^{14}N), and silicon (^{30}Si relative to ^{28}Si) are proving to be useful tools in investigations of sea-ice biogeochemical cycles, including interpretations of sedimentary records in the polar oceans. In sea ice, stable isotope measurements can potentially help distinguish between the origins (*i.e.*, land, seawater, or sea ice) of the particulate organic matter, as well as between biogeochemical cycling pathways. Samples for stable isotope analyses are typically collected from bulk sea ice and sackhole brines following the methodologies for POC, PON, $bSiO_2$ (section 3.3.1), NO_3-, $Si(OH)_4$ (section 4.1), TDN (section 4.2.2), and TIC (section 4.6); the analyses have used standard mass-spectrometric techniques (*e.g.*, McCorkle et al., 1985; Kennedy and Robertson, 1995; Sigman et al., 2001; Cardinal et al., 2003).

Table 8. Stable isotope measurements in sea ice[a]

Element	Isotope measured	Samples	References
Hydrogen	δ^2H-H_2O	Snow	Zhou et al., 2013
		Bulk ice	Zhou et al., 2013
			Geilfus et al., 2014a
		Brine	Zhou et al., 2013
			Geilfus et al., 2014a
Carbon	δ^{13}C-DIC	Platelet ice/interstitial waters	Thomas et al., 2001b
		Gap Layer Water	Kennedy et al., 2002
			Papadimitriou et al., 2009
		Brine	Papadimitriou et al., 2004; 2007
			Munro et al., 2010
	δ^{13}C-POC	Bulk ice	Gibson et al., 1999
			Schubert and Calvert, 2001
			Arrigo et al., 2003
			Tremblay et al., 2006
			Pineault et al., 2013
		Platelet ice/ interstitial waters	Thomas et al., 2001b
		Gap layer water	Kennedy et al., 2002
			Papadimitriou et al., 2009
Nitrogen	δ^{15}N-PON	Bulk ice	Rau et al., 1991
			Schubert and Calvert, 2001
			Tremblay et al., 2006
			Pineault et al., 2013
			Fripiat et al., 2014a
	δ^{15}N-NO_3^-	Bulk ice	Fripiat et al., 2014a
	δ^{15}N-TDN[b]	Bulk ice	Fripiat et al., 2014a
Silicon	δ^{30}Si-$Si(OH)_4$	Brine	Fripiat et al., 2007
			Fripiat et al., 2014b
	δ^{30}Si-bSiO_2	Bulk ice	Fripiat et al., 2007

[a]δ^{18}O analyses are routine and, therefore, not included.
[b]TDN = NO_3^- + NO_2^- + NH_4^+ + DON and DON = dissolved organic N.
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5. Ice-atmosphere and ice-ocean fluxes

Because sea ice is porous, it exchanges material with both the overlying atmosphere and the underlying water. Brine rejection from sea ice has long been recognized as a primary driver of oceanic deepwater formation and global circulation (*e.g.*, Chu and Gascard, 1991), with likely implications for the biogeochemical cycles of many elements. Likewise, the atmosphere, both in the boundary layer directly above the sea ice and at higher altitudes (*e.g.*, Begoin et al., 2010), is strongly influenced by sea-ice biogeochemistry.

Qualitative information about the direction of fluxes can be derived from measurements of concentration gradients between the ice and the atmosphere or the water: the larger the gradient, the larger the flux might be. However, confirming and quantifying those presumed fluxes requires more sophisticated methods. In particular, when material fluxes above sea ice are measured directly, the fluxes estimated from the measured ice-air gradients can be wrong both in magnitude and direction, because of reactions occurring at the interface, in the surface brines, frost flowers, and snow cover, that produce or consume gases and aerosols.

5.1. Air-ice gas fluxes

A number of methods have been developed to estimate gas fluxes above sea ice, but no systematic intercomparisons between various gas flux techniques over ice surfaces have been published. In particular, micrometeorological (sections 5.1.2–5.1.6) and chamber (section 5.1.1) methods measure fluxes on very different temporal and spatial scales, which has confounded efforts to compare the resulting flux estimates. Comparisons between eddy covariance and chamber methods have been carried out over terrestrial surfaces

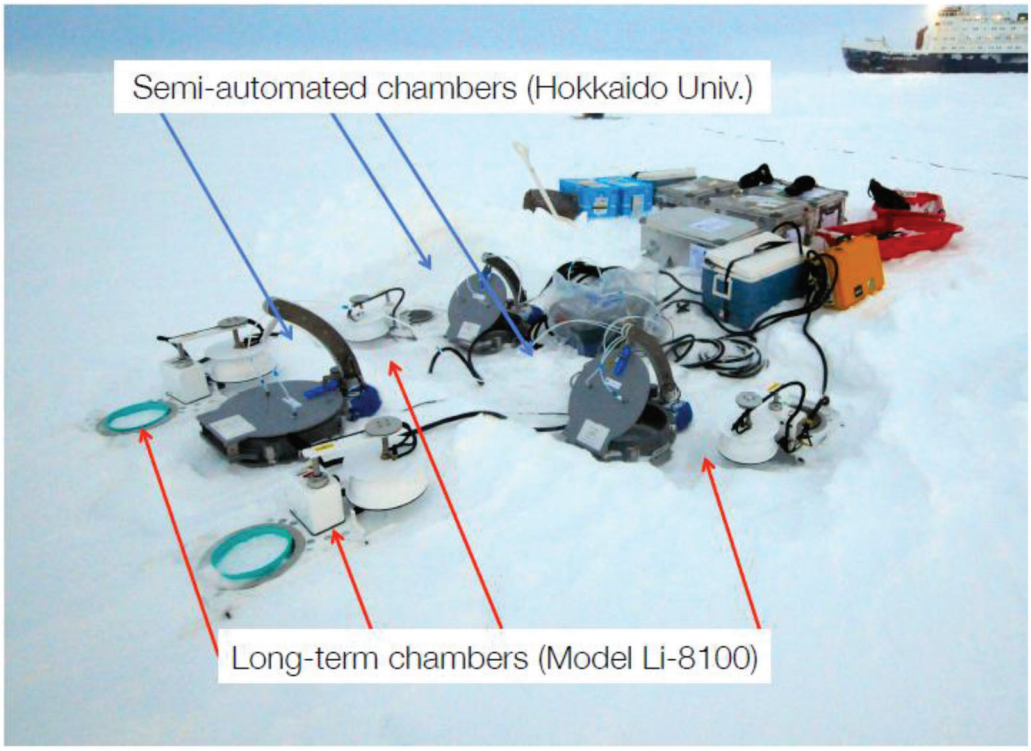

Figure 13

Gas flux chambers deployed to measure air-sea ice CO_2 exchange.

Configured for an intercalibration experiment between two types of chamber systems: 1) semi-automated CO_2 chambers originally developed at Hokkaido University for soil CO_2 flux measurements; and 2) long-term chambers (Li-8100) manufactured by LI-COR Biosciences, USA. Weddell Sea, July 2013. Photo: D. Nomura.

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Table 9. Sea ice-air flux measurements

Gas	Method	References
CO_2	Enclosure	Gosink, 1978
		Semiletov et al., 2004
		Delille, 2006
		Nomura et al., 2010a;b; 2013b
		Sejr et al., 2011
		Geilfus et al., 2012a; 2013; 2014a;b
		Fischer, 2013
	Eddy covariance	Semiletov et al., 2004
		Zemmelink et al., 2006
		Else et al., 2011
		Miller et al., 2011b
		Papakyriakou & Miller, 2011
DMS	Eddy accumulation	Zemmelink et al., 2008
	Enclosure	Nomura et al., 2012
CO	Mass balance	Gosink and Kelley, 1979
		Kelley and Gosink, 1979
O_3	Eddy covariance	Muller et al., 2012
Iodated organics	Mass balance	Shaw et al., 2011

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(Wang et al., 2013; Riederer et al., 2014), but carefully designed intercalibration experiments over sea ice are still needed to resolve remaining important questions about how each type of flux measurement performs in the sea-ice environment.

5.1.1. Flux chambers

Enclosure methods, which were widely used in early biosphere-atmosphere exchange studies (*e.g.*, Mosier, 1989), are still common for some applications, including sea-ice biogeochemistry (Figure 13; Table 9). The

method is based on the rate of increase (or decrease) of the trace gas concentration with time within a chamber placed directly on the ice (or snow) surface providing the flux (McMinn et al., 2009).

All enclosure methods are subject to potential artifacts in the measured flux (*e.g.*, Winston et al., 1995; Fowler et al., 2001; Nomura et al., 2012), because the enclosure itself introduces:

- changes in the radiation balance (both short and long wave);
- changes in the temperatures of the air and the surface (*i.e.*, the ice or snow);
- changes in turbulence, wind speed, and the vertical density profile;
- a pressure gradient between inside and outside the chamber; and
- a surface-atmosphere gas concentration gradient, including changes in the gas concentration inside the chamber resulting from the flux.

To overcome these issues, flux measurements should be completed quickly, before changing conditions introduce artifacts. Although the optimum length of time for a measurement is dependent on the situation (*e.g.*, weather, gas concentration gradient), 20 to 30 minutes is generally recommended. However, over snow, even a perfect chamber deployment may underestimate the flux, because in an undisturbed system, wind-driven pressure pumping within a snow cover can enhance the transport beyond molecular diffusion by up to 40% (Bowling and Massman, 2011).

Two fundamentally different types of chamber systems are available (Mosier, 1989; Luo and Zhou, 2006): in closed systems, the change in the gas concentration inside the chamber is measured directly, usually by connecting the interior to an on-line gas analyzer in a closed loop; in open systems, ambient air is pumped through the chamber, and the flux is calculated from the air flow rate and the difference in gas concentrations between the inlet and outlet. Changes in the trace gas concentration within the enclosure are a larger concern with a closed system, but open chamber methods are more susceptible to artifacts arising from interior-to-exterior pressure gradients. To date, only closed-chamber systems have been used to measure gas fluxes above sea ice; because of the difficulty in controlling the pressure differential in open systems, we recommend using closed systems, particularly if they incorporate dampening to equalize the pressure (as described by Xu et al., 2006). Current generation closed-chamber systems (*e.g.*, the Li-COR 8100-104) include such dampening mechanisms, making them probably the best chambers for measuring gas fluxes over sea ice (Fischer, 2013).

The greatest advantages and disadvantages to using enclosure methods are both due to spatial variability. Chamber enclosures only integrate the signal from the area they cover (generally, a few hundred cm^2); if the exchange is governed by factors that vary on larger horizontal scales (*i.e.*, the thickness and wetness of the snow cover, melt ponds, leads, under-ice hydrology, *etc.*), a prohibitive number of individual chamber measurements over a large area may be required to estimate the flux accurately (section 2.1). On the other hand, the method is ideal for studying specific, small-scale processes influencing variations in the flux (*i.e.*, brine channel distributions, ice algae respiration, *etc.*), and enclosure methods are the only technique available to determine fluxes on the same scale as most sea-ice biogeochemical measurements. In contrast, the micrometeorological techniques (sections 5.1.2–5.1.6) cover areas several orders of magnitude larger than chambers, integrating fluxes from different ice types and any open water in the footprint; micrometeorological results can, therefore, be difficult to interpret over heterogeneous surfaces.

5.1.2. Micrometeorological methods: general

Micrometeorological techniques, such as eddy covariance (EC), can be used to measure fluxes of gases, as well as of momentum, sensible heat, and latent heat (*e.g.*, Vihma et al., 2009) above sea ice. Unlike enclosure techniques, micrometeorological methods do not modify the observed environment, and they integrate processes occurring over relatively large spatial areas (up to several hundred m^2). This integration can be a problem if the surface is heterogeneous (*i.e.*, sea ice, leads, or other open water features may contribute to the observed fluxes), but typically the issue can be addressed by calculating the "footprint" of the flux measurement (*e.g.*, Vesala et al., 2008). The EC method has been used widely to examine CO_2 fluxes over all types of surfaces, but its application to many other chemical compounds has been hampered by a lack of fast-response sensors and by small signal levels. These limitations have led to development of a variety of alternative methods, including eddy accumulation (Businger and Oncley, 1990) and gradient techniques (*e.g.*, Businger et al., 1971). However, EC is, by definition, a direct flux measurement method (*e.g.*, Swinbank, 1951), while the others are based on several assumptions that break down over heterogeneous surfaces and in stably stratified atmospheres, such as often occur over sea ice.

The basic framework for measuring and interpreting micrometeorological flux data, including those from EC systems, is based on simultaneous measurements of the gas concentration and vertical, turbulent motion in the atmosphere (Figure 14). Ideal conditions for micrometeorological flux measurements include a horizontal and homogeneous surface, no source or sink in the atmosphere that can alter the concentration above the surface, and consistent atmospheric conditions (*i.e.*, air temperature, wind velocity, and mean gas concentration).

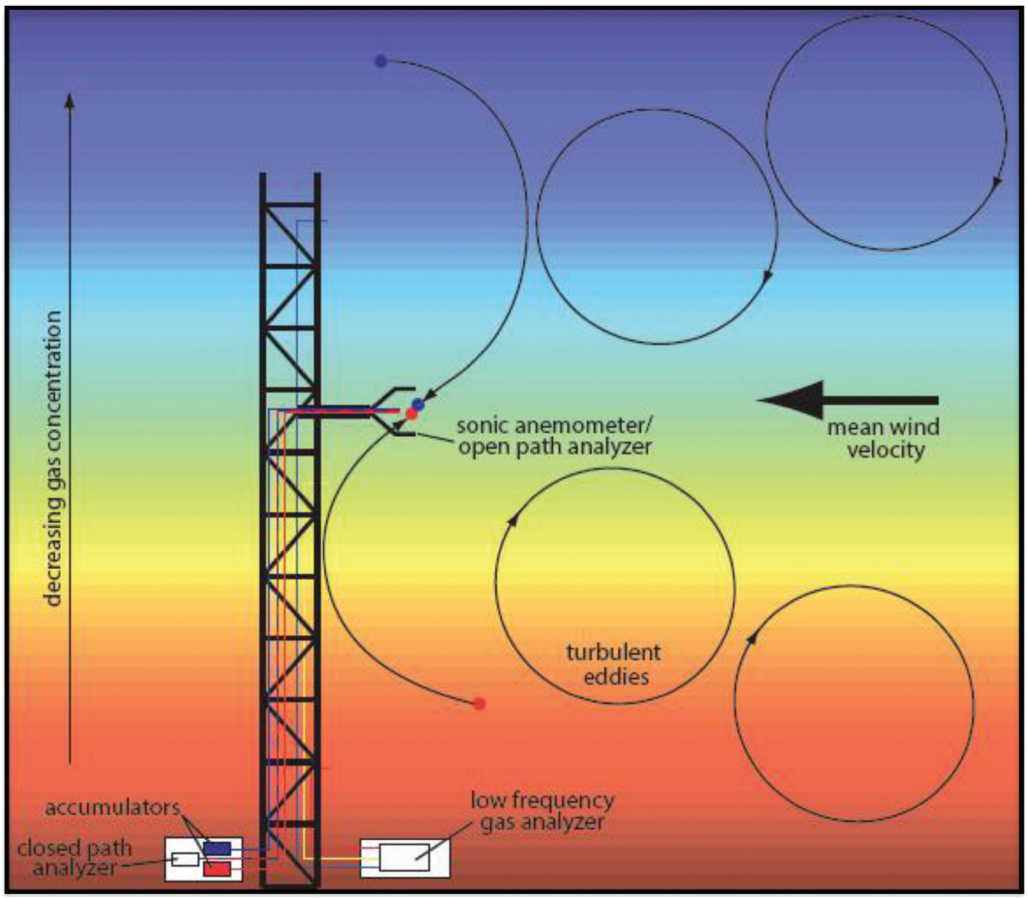

Figure 14

Principles behind micrometeorological methods for measuring gas exchange.

In this example, the surface is releasing a gas to the atmosphere, resulting in a vertical concentration gradient, with higher concentrations (red colors) near the surface, and lower concentrations (blue colors) away from the surface. Upward moving eddies will have higher gas concentrations than downward moving eddies, and by sampling these concentrations (either *in situ* or with a sampling tube) along with the vertical wind velocity, fluxes can be calculated via eddy covariance. For eddy accumulation, the samples are collected conditionally, depending on whether the eddy is moving upwards or downwards, and the samples accumulate in a bag or chamber for later laboratory analyses. The gradient method measures the vertical concentration gradient (usually by transporting sample air to a low-frequency gas analyzer), and then estimates the rate of transport across that gradient by parameterization or comparison to measured transport rates of heat or momentum.

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5.1.3. Eddy covariance

A general description of EC methods is given by Lee et al. (2004), but briefly, both the three-dimensional motion field and the analyte must be measured at the same place and at the same high frequency. Sonic anemometers are used for the motion field, while the analyte can either be measured *in situ* by an instrument exposed to the atmosphere (an "open path" system) or by transporting air in a constant stream to an analyzer (a "closed path" system). Non-dispersive infrared (NDIR) analyzers are generally used to measure CO_2 fluxes in EC systems (*e.g.,* Baldocchi, 2003), but other types of detectors are also available for CO_2 and CH_4 (Crosson, 2008; Detto et al., 2011) and for volatile organic compounds (VOCs; Müller et al., 2010). Fluxes are derived from the covariance between the vertical velocity and the concentration of the species of interest (Figure 14); the EC approach is, of course, only valid when the fluctuations in the concentration are caused by the vertical turbulence, not by sources or sinks within the boundary layer. In order to resolve the turbulence and measure a sufficient fraction of the vertical transport, the sampling frequency must be higher than 10 Hz.

Over sea ice, the EC method has primarily been used to measure CO_2 exchanges (Table 9) through deployments either on ships or directly on the ice (Figure 15). All published studies, with the possible exception of Semiletov et al. (2004) who did not specify their instrumentation, have used the LI-7500 open-path CO_2/H_2O analyzer, manufactured by LI-COR Biosciences. This instrument has been used widely at lower latitudes, but it suffers from some biases under cold conditions and in the marine environment. In cold weather, the instrument may significantly heat the column of air it is sampling, which lowers the measured gas concentration and biases flux measurements towards CO_2 uptake (Burba et al., 2008). In addition, salt deposited on the lens of the instrument interferes with the infrared absorption measurement, resulting in flux overestimations (Prytherch et al., 2010). In most cases, researchers have taken steps to minimize or correct for these biases, but results obtained using these open-path sensors should still be interpreted with a healthy dose of skepticism.

Closed-path EC systems potentially avoid many of these problems associated with the open-path sensors, because the temperature of the air sample can be controlled and instrument lenses can be protected by filters. However, the closed-path systems also suffer from their own shortcomings. Most importantly, closed-path systems inevitably attenuate gas concentration fluctuations and thus degrade the flux signal (Leuning and King, 1992; Lee et al., 2004), making it difficult to confidently identify gas exchanges between sea ice and the atmosphere, which are often much smaller than those observed over terrestrial or open-water surfaces.

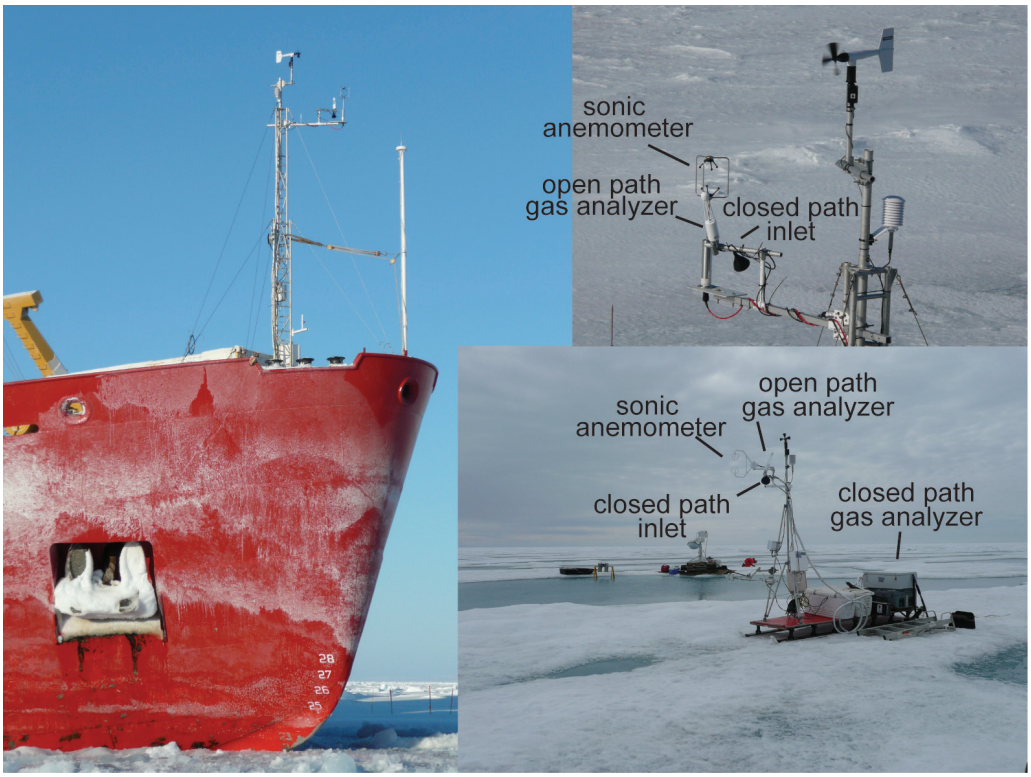

Figure 15

Eddy covariance systems for measuring CO_2 exchange over sea ice.

Clockwise from left: a micrometeorological tower installed on the CCGS *Amundsen*; a close-up view of the flux instrumentation on the *Amundsen*; and a portable micrometeorological tower deployed on a sled directly on the sea ice. Amundsen Gulf, March–June, 2008. Photos: B. Else.

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This difficulty may be why no sea ice-air CO_2 flux measurements using closed-path EC systems have yet been reported, despite several attempted deployments. However, Muller et al. (2012) have reported ozone fluxes over sea ice measured using a closed-path EC system.

Eddy covariance measurements can be subject to significant biases and random errors (Businger, 1986; Finkelstein and Sims, 2001), but there are no straightforward ways to calibrate or validate EC flux measurements in the field. These errors are exacerbated over sea ice, where the observed fluxes are often small. Particularly when temperatures and, therefore, sea-ice permeability are low, the fluxes are likely to be close to eddy covariance detection limits (estimated to be 1 μg C m^{-2} s^{-1} for CO_2; Wang et al., 2013), and the uncertainty in the measured flux can be over 200% in some cases (Sørensen et al., 2014). However, evaluating the frequency spectra of the sampled EC data can eliminate some sources of error (*e.g.*, advection, noise), and coupling fluxes estimated from EC and by spectral techniques gives more robust results (Kaimal et al., 1972; Sørensen and Larsen, 2010; Norman et al., 2012; Sørensen et al., 2014). Flux estimations based on the spectral methods use the same instrumental configuration as EC, but corrections for atmospheric stability are also required.

5.1.4. Eddy accumulation

For many trace gases, fast-response sensors, as required for EC flux measurements, are not available; relaxed eddy accumulation (REA) provides an alternate method for estimating the fluxes of these gases. Measurements by REA rely on conditional sampling (Hicks and McMillen, 1984; Businger and Oncley, 1990) of the gas into separate reservoirs depending on whether the bulk air movement is upward or downward. The "relaxation" refers to the fact that samples are taken with a constant flow rate and are not weighted according to the vertical wind speed; the data consequently lack information on the vertical wind speed. To date, only DMS fluxes have been measured over sea ice by REA (Zemmelink et al., 2008), but the method has potential for application to fluxes of other gases.

5.1.5. Gradient techniques

Gradient techniques provide another alternative for measuring fluxes of trace species for which no fast response sensor is available. Basically, the gradient technique requires measurements of gas concentrations from at least two levels (one typically within 1 m of the air-ice surface, the other 1–10 m from the surface), along with some estimate of how rapidly the gas is transported between those levels. This transport rate estimate is generally based on observations or parameterizations of atmospheric turbulence, which are usually derived from wind velocity and temperature measurements (preferably made at the same two levels). The method is indirect, can require a number of empirical functions to account for thermal stratification of the atmosphere, and is based on the assumption that turbulent transfer is analogous to molecular diffusion. The most common

gradient technique is the aerodynamic method, which is based on the momentum flux equation and the wind speed-gradient relationship (Businger et al., 1971; Businger, 1986; Baldocchi et al., 1988; Sørensen et al., 2005). To date, the gradient technique has only been applied to measure nitric acid (Beine et al., 2003) and ozone (Bocquet et al., 2011) fluxes over terrestrial snow, but the method has potential for applications over sea ice.

5.1.6. Best practices for micrometeorological techniques

Several textbooks and review articles (we recommend Lee et al., 2004) have dealt extensively with issues of best practice for micrometeorological techniques, particularly with respect to eddy covariance. The interested reader should consult those texts, but we address several points here that are unique to the sea-ice environment.

The first important consideration is the installation of the meteorological tower, especially if the measurements are to last through a portion of the melt season. A melting sea-ice surface is inherently unstable; towers can tilt and even topple in such conditions. We recommend one of two approaches to combat such tower instability. First, the tower can be mounted on a qamutiq (sled), which can be periodically moved or repositioned to keep the tower level (Figure 15). Alternatively, the tower should be frozen into the ice by drilling holes (to a depth of about 50 cm), in which the ends of the tower posts are anchored with frozen fresh water. This system can be improved by also passing the tower posts through a plywood base on the ice surface, as this will shade the posts and prevent localized melt. The tower can also be directly fixed to a sheet of plywood (preferably with rigid insulation underneath), but freezing the tower legs into the ice is preferred.

The orientation of the tower is also important. Even a low-profile lattice-style tower can create significant snow drifts; it is best to place the meteorological equipment on the side of the tower that faces the prevailing wind direction, so that it will measure fluxes predominately over an undisturbed, upwind surface. Most eddy covariance installations over sea ice are by necessity close to the ground (less than 5 m above the surface), leading us to recommend sampling at a rate of 20 Hz to capture the small-scale eddies that exist near the surface. Finally, it is important to choose instruments that have low-temperature ratings and are well sealed against blowing snow. As discussed previously, particular attention should be paid to the choice of infrared gas analyzer to ensure that it operates properly in cold environments.

5.2. Aerosols, frost flowers, and saline snow

The formation of atmospheric particulate aerosols is another important interface flux in the sea-ice system. The polar regions frequently receive aerosols from lower latitudes, but wintertime sea-ice formation is also associated with vertical particle fluxes. Whereas under open-water conditions, the sea-to-air transport of both solid and liquid aerosols is controlled by breaking waves, in polar regions brine-wetted saline snow and frost flowers formed on new sea ice provide additional sources of atmospheric aerosols. In particular, frost flowers may be broken up by blowing wind, and the submicron fraction may have lifetimes up to a week. Both frost flowers and saline snow contain NaCl, other ocean salts from sea-ice brines, and organic components, including both organisms and their products (Alvarez-Aviles et al., 2008; Bowman and Deming, 2010; Douglas et al., 2012; Ewert et al., 2013). Particles from frost flowers and saline snow can be lofted into the atmosphere and transported long distances by wind, eventually deposited in new places under dry or wet conditions. Therefore, the size and composition of such particles should be characterized in studies of atmospheric aerosols in polar regions (Yang et al., 2008; Obbard et al., 2009; Roscoe et al., 2011).

Several methods exist to measure aerosols: in-line with mass spectrometers and ion chromatographs, as well as off-line by gas chromatography-mass spectrometry and Fourier transform infrared spectroscopy (*e.g.,* Russell, 2014). Each of these recommended methods characterizes different, complementary chemical qualities. However, comparability between methods requires well-characterized inlets and careful techniques for minimizing artifacts during collection and storage. New advances in quantifying aerosol fluxes require simultaneous analyses of sea-ice components, with careful attention to the local meteorology, so that the measured aerosols can be linked to their upwind source regions.

Of particular interest is the role of halogens in atmospheric chemistry of the polar regions (Simpson et al., 2007; Abbatt et al., 2012), including the function of Br in tropospheric ozone and mercury depletion and the possible importance of iodine in new particle formation. High concentrations of BrO observed in satellite datasets during the polar spring, in particular, suggest that halogens originate at the sea-ice surface; the available studies of halocarbons in sea ice, to date, have confirmed variable and often high concentrations of biogenic halocarbons in ice, brines, and overlying snow (Sturges et al., 1997; Simpson et al., 2005; Atkinson et al., 2012; Mattson et al., 2012; Granfors et al., 2013a;b). Inorganic halides are easily sampled and analyzed (after melting and filtering) by, for example, ion chromatography for bromide, cyclic voltammetry for iodide, and spectrophotometry for iodate (*e.g.*, Atkinson et al., 2012). On the other hand, sampling sea ice for halocarbons, which are volatile, should follow methods to limit gas exchange (section 4.4), including melting samples in gas-impermeable bags with minimal headspace (as for inorganic carbon species, section 4.6.3). Halocarbon samples are usually analyzed by gas chromatography, requiring aqueous (*i.e.*, melted, see section 3.2) or gas samples. Shaw et al. (2011) measured iodated organics in artificial sea ice

from laboratory tank studies by melting ice samples directly in sealed syringes to limit gas exchange. New methods to confidently analyze the halogen chemistry of frost flowers are particularly needed.

5.3. Ice-water fluxes

Most efforts to quantify biogeochemical exchanges at the ice-water interface have used mass balance and budgeting tactics. This approach has been most successful in identifying water-to-ice fluxes of nutrients (Cota et al., 1987; 1990; Rahm et al., 1995; Nishi and Tabeta, 2008) and of trace metals (Granskog and Kaartokallio, 2004; Lannuzel et al., 2010; 2011; van der Merwe et al., 2011a). Recent models of ice-brine dynamics have confirmed that seawater pumping into the brine network of growing sea ice could cycle enough surface seawater through the lower parts of the ice cover to account for observations of the nutrient and iron distributions in the ice (Vancoppenolle et al., 2010). On the other hand, efforts to estimate inorganic carbon fluxes from sea ice into the underlying surface waters have been confounded by the need to identify small changes in large, variable concentrations (*e.g.*, Miller et al., 2011b; Fransson et al., 2013).

Attempts to use the gradient method to derive sea ice-water chemical fluxes have been limited by the difficulty of collecting high-vertical resolution water samples from under the undisturbed ice sheet. Although Dieckmann et al. (1992) developed a promising device for detailed under-ice sampling, it has not been utilized widely, and efforts by divers to collect biogeochemical samples from under the ice have not produced consistent results. *In situ* microsensors, such as those deployed for measuring oxygen by Rysgaard et al. (2001) and McMinn et al. (2000), show some promise for measuring gradients near the ocean-ice interface, but deployment of such instruments (usually by divers) remains difficult.

Eddy covariance shows promise for measuring ice-water, as well as ice-air, fluxes. Although to date only oxygen fluxes have been determined (section 3.4.1; Long et al., 2012), the method should be applicable to any analyte for which an *in situ* sensor is available with a response time less than 1 second. Sensors for measuring fluxes of nitrate (Johnson et al., 2011) and hydrogen sulfide (McGinnis et al., 2011) have been employed in benthic studies and could be adapted to the sea-ice environment.

Sinking particle fluxes from the sea ice can be measured using particle interceptor traps tethered below the ice (Michel et al., 1996; Fortier et al., 2002; Juul-Pedersen et al., 2008; Nishi and Tabeta, 2008); time series from such "sediment" traps have proven to be a valuable tool in estimating carbon budgets of sea-ice primary production, export, and transfers to pelagic and benthic grazers (*e.g.,* Michel et al., 2002; Renaud et al., 2007). The traps are typically deployed at shallow depths specifically to capture particles exported from the ice (as opposed to produced within the water column) and to avoid excessive drag on the trap line. However, the traps can also be deployed at deeper depths, thereby providing insights into sea ice-pelagic-benthic coupling (Fortier et al., 2002). The extensive literature pertaining to sediment trap methodology does not deal specifically with under-ice deployments, although standard protocols for particle trap deployments should be followed as much as possible (*i.e.,* Gardner, 2000). Particular challenges associated with under-ice deployments include over- and under-trapping if the traps are deployed under moving ice floes or under fast ice in high current regimes.

6. The future

Biogeochemists working in the sea-ice environment have made tremendous strides over recent years in learning how to measure and then understand the biogeochemical processes occurring in sea ice. Nonetheless, we still have much work ahead of us to resolve the uncertainties in the measurements we are making and identify which of the methods we are using are most suitable under various conditions (Table 10).

Dedicated, collaborative, field and laboratory studies are required to compare and intercalibrate a number of methods, most notably those for primary production and the CO_2 system, but also for nutrients, biomass, cell abundance, and size fractionation of organic matter. Time on icebreakers and in ice camps is expensive; it is often difficult to rationalize, within interdisciplinary process studies, the kind of redundant sampling and analyses that are required for rigorous intercalibrations. Therefore, to resolve methodological discrepancies, we will need expeditions and experiments that are focused first on methods. This kind of approach is difficult for many sea-ice scientists, as well as our funding agencies, who are motivated to use every opportunity in remote polar environments to address questions on how sea ice impacts the functioning of our planet. However, in the end, the confidence in our measurements provided by focused methodological studies will make these efforts worthwhile. In the meantime, to the extent possible, we encourage interdisciplinary process studies to include methodological intercalibrations.

For the most part, large icebreakers are not essential (and may be overkill) for the intercalibration and method validation experiments required (Table 10). Rather, a number of coastal laboratory facilities with ready access to fast ice, such as those in Barrow (Alaska, USA), Svalbard (Norway), McMurdo Sound (Antarctica), Saroma-ko (Hokkaido, Japan), and Tvärminne (Hanko, Finland), could be very useful sites for this work. Laboratory studies, including those in large-scale ice-tank facilities, will also be a critical component of our efforts to understand our methods and their limitations. The spatial and temporal variability in natural sea ice

Table 10. Priorities for sea-ice biogeochemical method development, validation, and intercalibration[a]

Method development	*In situ* probes for CO_2 system parameters and gases
	Analyses of small-volume and high-salinity samples
	Sampling and studying ridged and deformed ice
	Sulfur cycling rates in undisturbed ice environments
	Net community production using O_2: Ar ratios
	Gross primary production using stable oxygen isotope ratios
	Halogen chemistry in frost flowers
	Inoculation of laboratory sea ice with representative sympagic communities
	Sea ice-seawater exchange processes
	Characterization of EPS polymer composition, structure, and molecular size
	Sampling and studying surface brine skims and frost flowers
	Rates of biogenic silica cycling using Si isotope methods
	Preserving bulk ice samples for CO_2 system parameters during melting
	Improving precision of gas extraction procedures
Validation	Errors in sackhole brine measurements of particulates and soluble versus insoluble gases
	Tracer-to-carbon conversion ratios for bacterial production measurements
	CO_2 system thermodynamics in ice brines
	Sensitivity of sea-ice TOC samples to contamination
	Accuracy of flow cytometric analyses in sea-ice samples with high organic matter content
	Impact of high EPS concentrations on nominal pore sizes of different filters
	EPS interference in analyses of salts, trace metals, and other organic compounds
	Certified reference materials over sea-ice concentration and salinity ranges for DOC, macro-nutrients, salinity, A_T, and DIC
	Incubation temperature impacts on measured microbial metabolic rates
	Accuracy of sea-ice equations of state in the presence of high organic matter concentrations
	Effects of melting method on measurements of macronutrients, EPS, and other organic compounds
	Precision of fluxes determined by eddy covariance
Intercalibration	Melting methods for determining biomass and community composition
	Primary and secondary production measurements
	Melting and filtration methods for macronutrient and organic matter analyses
	pCO_2 analysis
	Chamber and micrometeorological methods for determining ice-air CO_2 fluxes
	Aerosol production
	PIC extraction and analyses
	Nucleic acid extraction
	EPS analyses

[a]The order in which items are listed does not necessarily imply priority.

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often prevents us from accurately constraining our methods; in controlled laboratory tanks can we determine the true methodological precision and accuracy of chemical measurements in sea ice. On the other hand, to date, laboratory tanks have not been successfully inoculated with a natural sea-ice community, which, when coupled with universal challenges to laboratory-based biological experiments (*i.e.*, maintaining nutrient supply, *etc.*), severely limits the utility of laboratory experiments for studying the complexity of biological processes in sea ice.

The field of sea-ice biogeochemistry is also ripe for new technological developments; we have only begun by trying to adapt methods we know from other disciplines. As the field matures, we hope that entirely new approaches and methods will be developed. These efforts could be facilitated by recruiting more students with degrees in analytical chemistry, biotechnology, bioengineering, and electronics, as well as through new collaborations. In particular, *in situ* probes are critically needed to answer many of our questions effectively. Electrochemical and optical technologies show the most promise; throughout this paper, we have highlighted

a number of biogeochemical parameters that we believe are particularly well-suited for sensor development, but there will certainly also be others. Robust ice buoys on which such chemical sensors could be deployed received a substantial boost from the 2007–08 International Polar Year (*e.g.,* Knepp et al., 2010) but require additional development to recover data dependably throughout the entire cycle of freeze-up and melt. Recent advances in under-water vehicle technology, including successful under-ice deployments of instrumented remotely operated vehicles (ROVs) and autonomous underwater vehicles (AUVs) also promise new tools to study sea-ice physical-ecological-biogeochemical interactions on scales from meters to kilometers (Wadhams and Doble, 2008; Williams et al., 2013).

Finally, a key challenge for the future is integrating interdisciplinary measurements on different scales to tell a more complete story of sea-ice biogeochemistry. For example, measurements of biogenic gas fluxes paired with analyses of bacterial gene expression and *in situ* nutrient concentrations are far more valuable than any of these observations, alone.

In closing, we have described many of the problems with existing methods for studying sea-ice biogeochemistry, while also noting the successes, which have been significant. This important and exciting research field is now beginning to mature. We hope that the insights presented here will provide inspiration for new scientists to boldly tackle some of these challenging methodological problems, because we must solve these problems, if we are to understand how sea ice impacts the Earth's biogeochemical cycles.

References

Abbatt JPD, Thomas JL, Abrahamsson K, Boxe C, Granfors A, et al. 2012. Halogen activation via interactions with environmental ice and snow in the polar lower troposphere and other regions. *Atmos Chem Phys* **12**: 6237–6271. doi: 10.5194/acp-12-6237-2012.

Aguilar-Islas AM, Rember RD, Mordy CW, Wu J. 2008. Sea ice-derived dissolved iron and its potential influence on the spring algal bloom in the Bering Sea. *Geophys Res Lett* **35**: L24601. doi: 10.1029/2008GL035736.

Alou-Font E, Mundy C-J, Roy S, Gosselin M, Agustí S. 2013. Snow cover affects ice algal pigment composition in the coastal Arctic Ocean during spring. *Mar Ecol-Prog Ser* **474**: 89–104. doi: 10.3354/meps10107.

Alvarez-Aviles L, Simpson WR, Douglas TA, Sturm M, Perovich D, et al. 2008. Frost flower chemical composition during growth and its implications for aerosol production and bromine activation. *J Geophys Res* **113**: D21304. doi: 10.1029/2008JD010277.

Anderson LG, Jones EP. 1985. Sea ice melt water, a source of alkalinity, calcium and sulfate? Results from the CESAR Ice Station. *Rit Fiskideildar* **9**: 90–96.

Arar EJ, Collins GB. 1997. Method 445.0: In Vitro Determination of Chlorophyll *a* and Pheophytin *a* in Marine and Freshwater Algae by Fluorescence. Cincinnati: Office of Research and Development, U.S. Environmental Protection Agency. #445.0.

Arrigo KR, Dieckmann G, Gosselin M, Robinson DH, Fritsen CH, et al. 1995. High resolution study of the platelet ice ecosystem in McMurdo Sound, Antarctica: Biomass, nutrient, and production profiles within a dense microalgal bloom. *Mar Ecol-Prog Ser* **127**: 255–268.

Arrigo KR, Mock T, Lizotte MP. 2010. Primary producers in sea ice, in Thomas DN, Dieckmann GS, eds., *Sea Ice*. 2nd ed. Oxford: Wiley-Blackwell. pp. 283–325.

Arrigo KR, Robinson DH, Dunbar RB, Leventer AR, Lizotte MP. 2003. Physical control of chlorophyll *a*, POC, and TPN distributions in the pack ice of the Ross Sea, Antarctica. *J Geophys Res* **108**: 3316. doi:10.1029/2001JC001138.

Arrigo KR, Sullivan CW. 1992. The influence of salinity and temperature covariation on the photophysiological characteristics of Antarctic sea ice microalgae. *J Phycol* **28**: 746–756.

Asher EC, Dacey JWH, Mills MM, Arrigo KR, Tortell PD. 2011. High concentrations and turnover rates of DMS, DMSP and DMSO in Antarctic sea ice. *Geophys Res Lett* **38**: L23609. doi: 10.1029/2011GL049712.

Aslam SN, Underwood GJC, Kaartokallio H, Norman L, Autio R, et al. 2012. Dissolved extracellular polymeric substances (dEPS) dynamics and bacterial growth during sea ice formation in an ice tank study. *Polar Biol* **35**: 661–676. doi: 10.1007/s00300-011-1112-0.

Assur A. 1958. Composition of sea ice and its tensile strength, in, *Arctic Sea Ice*. Easton, Maryland: National Academy of Sciences, National Research Council: pp. 106–138.

Atkinson HM, Huang R-J, Chance R, Roscoe HK, Hughes C, et al. 2012. Iodine emissions from the sea ice of the Weddell Sea. *Atmos Chem Phys* **12**: 11,229–11,244. doi: 10.5194/acp-12-11229-2012.

Ayers GP, Cainey JM. 2007. The CLAW hypothesis: a review of the major developments. *Environ Chem* **4**: 366–374. doi: 10.1071/EN07080.

Baldocchi DD. 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: Past, present and future. *Glob Change Biol* **9**: 479–492.

Baldocchi DD, Hicks BB, Meyers TP. 1988. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometerological methods. *Ecology* **69**(5): 1331–1340.

Barber DG, Ehn JK, Pućko M, Rysgaard S, Deming JW, et al. 2014. Frost flowers on young Arctic sea ice: The climatic, chemical and microbial significance of an emerging ice type. *J Geophys Res-Atmos*. doi: 10.1002/2014JD021736.

Becquevort S, Dumont I, Tison J-L, Lannuzel D, Sauvée M-L, et al. 2009. Biogeochemistry and microbial community composition in sea ice and underlying seawater off East Antarctica during early spring. *Polar Biol* **32**: 879–895. doi: 10.1007/s00300-009-0589-2.

Begoin M, Richter A, Weber M, Kaleschke L, Tian-Kunze X, et al. 2010. Satellite observations of long range transport of a large BrO plume in the Arctic. *Atmos Chem Phys* **10**: 6515–6526. doi: 10.5194/acp-10-6515-2010.

Beine HJ, Dominé F, Ianniello A, Nardino M, Allegrini I, et al. 2003. Fluxes of nitrates between snow surfaces and the atmosphere in the European high Arctic. *Atmos Chem Phys* **3**: 335–346.

Belt ST, Brown TA, Ringrose AE, Cabedo-Sanz P, Mundy CJ, et al. 2013. Quantitative measurement of the sea ice diatom biomarker IP_{25} and sterols in Arctic sea ice and underlying sediments: Further considerations for palaeo sea ice reconstruction. *Org Geochem* **62**: 33–45. doi: 10.1016/j.orggeochem.2013.07.002.

Belzile C, Johannessen SC, Gosselin M, Demers S, Miller WL. 2000. Ultraviolet attenuation by dissolved and particulate constituents of first-year ice during late spring in an Arctic polynya. *Limnol Oceanogr* **45**: 1265–1273.

Bender M, Grande K, Johnson K, Marra J, Williams PJL, et al. 1987. A comparison of four methods for determining planktonic community production. *Limnol Oceanogr* **32**: 1085–1098.

Bennington KO. 1963. Some chemical composition studies on Arctic sea ice, in Kingery WD, ed, *Ice and Snow: Properties, Processes, and Applications*. Cambridge, Massachusetts: MIT Press: pp. 248–257.

Bidigare RR, Van Heukelem L, Trees CC. 2005. Analysis of algal pigments by high-performance liquid chromatography, in Andersen RA, ed, *Algal Culturing Techniques*. Burlington: Elsevier Academic Press: pp 327–345.

Bitter T, Muir HM. 1962. A modified uronic acid carbazole reaction. *Anal Biochem* **4**: 330–334.

Bocquet F, Helmig D, Van Dam BA, Fairall CW. 2011. Evaluation of the flux gradient technique for measurement of ozone surface fluxes over snowpack at Summit, Greenland. *Atmos Meas Tech* **4**: 2305–2321. doi: 10.5194/amt-4-2305-2011.

Bowling DR, Massman WJ. 2011. Persistent wind-induced enhancement of diffusive CO_2 transport in a mountain forest snowpack. *J Geophys Res* **116**: G04006. doi: 10.1029/2011JG001722.

Bowman JS, Deming JW. 2010. Elevated bacterial abundance and exopolymers in saline frost flowers and implications for atmospheric chemistry and microbial dispersal. *Geophys Res Lett* **37**: L13501. doi: 10.1029/2010GL043020.

Bowman JS, Larose C, Vogel TM, Deming JW. 2013. Selective occurrence of *Rhizobiales* in frost flowers on the surface of young sea ice near Barrow, Alaska and distribution in the polar marine rare biosphere. *Environ Microbiol Rep* **5**: 575–582. doi: 10.1111/1758-2229.12047.

Bowman JS, Rasmussen S, Blom N, Deming JW, Rysgaard S, et al. 2012. Microbial community structure of Arctic multiyear sea ice and surface seawater by 454 sequencing of the 16S RNA gene. *ISME J* **6**: 11–20. doi: 10.1038/ismej.2011.76.

Boye M, van den Berg CMG, de Jong JTM, Leach H, Croot P, et al. 2001. Organic complexation of iron in the Southern Ocean. *Deep-Sea Res Pt I* **48**: 1477–1497.

Brabant F, El Amri S, Tison J-L. 2011. A robust approach for the determination of dimethylsulfoxide in sea ice. *Limnol Oceanogr Methods* **9**: 261–274. doi: 10:4319/lom.2011.9.261.

Brakstad OG, Nonstad I, Faksness L-G, Brandvik PJ. 2008. Responses of microbial communities in Arctic sea ice after contamination by crude petroleum oil. *Microb Ecol* **55**: 540–552. doi: 10.1007/s00248-007-9299-x.

Brinkmeyer R, Knittel K, Jürgens J, Weyland H, Amann R, et al. 2003. Diversity and structure of bacterial communities in Arctic versus Antarctic pack ice. *Appl Environ Microb* **69**: 6610–6619. doi: 10.1128/AEM.69.11.6610-6619.2003.

Bronk DA, Lomas MW, Glibert PM, Schukert KJ, Sanderson MP. 2000. Total dissolved nitrogen analysis: comparisons between the persulfate, UV and high temperature oxidation methods. *Mar Chem* **69**: 163–178.

Brown KA, Miller LA, Davelaar M, Francois R, Tortell PD. 2014. Over-determination of the carbonate system in natural sea ice brine and assessment of carbonic acid dissociation constants under low temperature, high salinity conditions. *Mar Chem* **165**: 36–45. doi: 10.1016/j.marchem.2014.07.005.

Brown MV, Bowman JP. 2001. A molecular phylogenetic survey of sea-ice microbial communities (SIMCO). *FEMS Microbiol Ecol* **35**: 267–275.

Bruland KW, Rue EL. 2001. Analytical methods for the determination of concentrations and speciation of iron, in Turner DR, Hunter KA, eds., *The Biogeochemistry of Iron in Seawater*. West Sussex: John Wiley & Sons Ltd.: pp 255–289.

Burba GG, McDermitt DK, Grelle A, Anderson DJ, Xu L. 2008. Addressing the influence of instrument surface heat exchange on the measurements of CO_2 flux from open-path gas analyzers. *Glob Change Biol* **14**: 1854–1876. doi: 10.1111/j.1365-2486.2008.01606.x.

Burkholder PR, Mandelli EF. 1965. Productivity of microalgae in Antarctic sea ice. *Science* **149**: 872–874.

Burt A, Wang F, Pućko M, Mundy C-J, Gosselin M, et al. 2013. Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice. *J Geophys Res-Oceans* **118**: 4746–4754. doi: 10.1002/jgrc.20380.

Businger JA. 1986. Evaluation of the accuracy with which dry deposition can be measured with current micrometeorological techniques. *J Clim Appl Meteorol* **25**: 1100–1124.

Businger JA, Oncley SP. 1990. Flux measurement with conditional sampling. *J Atmos Ocean Tech* **7**: 349–352.

Businger JA, Wyngaard JC, Isumi Y, Bradley EF. 1971. Flux-profile relationships in the atmospheric surface layer. *J Atmos Sci* **28**: 181–189.

Campbell JA, Yeats PA. 1982. The distribution of manganese, iron, nickel, copper and cadmium in the waters of Baffin Bay and the Canadian Arctic Archipelago. *Oceanol Acta* **5**(2): 161–168.

Cardinal D, Alleman LY, de Jong J, Ziegler K, André L. 2003. Isotopic composition of silicon measured by multicollector plasma source mass spectrometry in dry plasma mode. *J Anal Atom Spectrom* **18**: 213–218. doi: 10.1039/b210109b.

Chaulk A, Stern GA, Armstrong D, Barber DG, Wang F. 2011. Mercury distribution and transport across the ocean-sea-ice-atmosphere interface in the Arctic Ocean. *Environ Sci Technol* **45**: 1866–1872. doi: 10.1021/es103434c.

Chu PC, Gascard GC, eds. 1991. *Deep Convection and Deep Water Formation in the Oceans*. Amsterdam: Elsevier.

Collins RE, Carpenter SD, Deming JW. 2008. Spatial heterogeneity and temporal dynamics of particles, bacteria, and pEPS in Arctic winter sea ice. *J Marine Syst* **74**: 902–917. doi: 10.1016/j.jmarsys.2007.09.005.

Collins RE, Rocap G, Deming JW. 2010. Persistence of bacterial and archaeal communities in sea ice through an Arctic winter. *Environ Microbiol* **12**: 1828–1841. doi: 10.1111/j.1462-2920.2010.02179.x.

Comiso JC. 2010. Variability and trends of the global sea ice cover, in Thomas DN, Dieckmann GS, eds., *Sea Ice*. 2nd ed. Oxford: Wiley-Blackwell: pp. 205–246.

Conover RJ, Mumm N, Bruecker P, MacKenzie S. 1999. Sources of urea in arctic seas: seasonal fast ice? *Mar Ecol-Prog Ser* **179**: 55–69.

Cossa D, Heimbürger L-E, Lannuzel D, Rintoul SR, Butler ECV, et al. 2011. Mercury in the Southern Ocean. *Geochim Cosmochim Acta* **75**: 4037–4052. doi: 10.1016/j.gca.2011.05.001.

Cota GF, Anning JL, Harris LR, Harrison WG, Smith REH. 1990. Impact of ice algae on inorganic nutrients in seawater and sea ice in Barrow Strait, NWT, Canada, during spring. *Can J Fish Aquat Sci* **47**: 1402–1415.

Cota GF, Prinsenberg SJ, Bennett EB, Loder JW, Lewis MR, et al. 1987. Nutrient fluxes during extended blooms of Arctic ice algae. *J Geophys Res* **92**: 1951–1962.

Cottier F, Eicken H, Wadhams P. 1999. Linkages between salinity and brine channel distribution in young sea ice. *J Geophys Res* **104**(C7): 15,859–15,871.

Cowie ROM. 2011. Bacterial Community Structure, Function and Diversity in Antarctic Sea Ice [Ph.D. thesis], Wellington: Victoria University of Wellington, Ecology and Biodiversity.

Cox GFN, Weeks WF. 1983. Equations for determining the gas and brine volumes in sea-ice samples. *J Glaciol* **29**: 306–316.

Cozzi S. 2008. High-resolution trends of nutrients, DOM and nitrogen uptake in the annual sea ice at Terra Nova Bay, Ross Sea. *Antarct Sci* **20**: 441–454. doi: 10.1017/S0954102008001247.

Craig H, Hayward T. 1987. Oxygen supersaturation in the ocean: Biological versus physical contributions. *Science* **235**: 199–202.

Crosson ER. 2008. A cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor. *Appl Phys B* **92**: 403–408. doi: 10.1007/s00340-008-3135-y.

Curran MAJ, Jones GB. 2000. Dimethyl sulfide in the Southern Ocean: Seasonality and flux. *J Geophys Res* **105**(D16): 20,451–20,459.

Cutter G, Andersson P, Codispoti L, Croot P, Francois R, et al. 2010. Sampling and Sample-handling Protocols for GEOTRACES Cruises.

de Jong J, Schoemann V, Maricq N, Mattielli N, Langhorne P, et al. 2013. Iron in land-fast sea ice of McMurdo Sound derived from sediment resuspension and wind-blown dust attributes to primary productivity in the Ross Sea, Antarctica. *Mar Chem* **157**: 24–40. doi: 10.1016/j.marchem.2013.07.001.

Delille B. 2006. Inorganic carbon dynamics and air-ice-sea CO_2 fluxes in the open and coastal waters of the Southern ocean [thesis], Liège: Université de Liège, Faculté des Sciences.

Delille B, Jourdain B, Borges AV, Tison J-L, Delille D. 2007. Biogas (CO_2, O_2, dimethylsulfide) dynamics in spring Antarctic fast ice. *Limnol Oceanogr* **52**: 1367–1379.

Deming JW. 2010. Sea ice bacteria and viruses, in Thomas DN, Dieckmann GS, eds., *Sea Ice*. 2nd ed. Oxford: Wiley-Blackwell: pp. 247–282.

Detto M, Verfaillie J, Anderson F, Xu L, Baldocchi D. 2011. Comparing laser-based open- and closed-path gas analyzers to measure methane fluxes using the eddy covariance method. *Agr Forest Meteorol* **151**: 1312–1324. doi: 10.1016/j.agrformet.2011.05.014.

Dickson AG. 1993. The measurement of sea water pH. *Mar Chem* **44**: 131–142.

Dickson AG, Sabine CL, Christian JR. 2007. Guide to Best Practices for Ocean CO_2 Measurements. Sidney: North Pacific Marine Science Organization. PICES Special Publication 3.

Dieckmann GS, Arrigo K, Sullivan CW. 1992. A high-resolution sampler for nutrient and chlorophyll a profiles of the sea ice platelet layer and underlying water column below fast ice in polar oceans: Preliminary results. *Mar Ecol-Prog Ser* **80**: 291–300.

Dieckmann GS, Eicken H, Haas C, Garrison DL, Gleitz M, et al. 1998. A compilation of data on sea ice algal standing crop from the Bellingshausen, Amundsen and Weddell Seas from 1983 to 1994, in Lizotte MP, Arrigo KR, eds., *Antarctic Sea Ice: Biological Processes, Interactions and Variability*. Washington: American Geophysical Union: pp. 85–92.

Dieckmann GS, Lange MA, Ackley SF, Jennings Jr JC. 1991a. The nutrient status in sea ice of the Weddell Sea during winter: Effects of sea ice texture and algae. *Polar Biol* **11**: 449–456.

Dieckmann GS, Nehrke G, Papadimitriou S, Göttlicher J, Steininger R, et al. 2008. Calcium carbonate as ikaite crystals in Antarctic sea ice. *Geophys Res Lett* **35**: L08501. doi: 10.1029/2008GL033540.

Dieckmann GS, Nehrke G, Uhlig C, Göttlicher J, Gerland S, et al. 2010. Ikaite ($CaCO_3{\cdot}6H_2O$) discovered in Arctic sea ice. *The Cryosphere* **4**: 227–230. doi: 10.5194/tc-4-227-2010.

Dieckmann GS, Spindler M, Lange MA, Ackley SF, Eicken H. 1991b. Antarctic sea ice: A habitat for the foraminifer *Neogloboquadrina pachyderma*. *J Foramineferal Res* **21**: 182–189.

Domine F, Sparapani R, Ianniello A, Beine HJ. 2004. The origin of sea salt in snow on Arctic sea ice and in coastal regions. *Atmos Chem Phys* **4**: 2259–2271.

Douglas TA, Domine F, Barret M, Anastasio C, Beine HJ, et al. 2012. Frost flowers growing in the Arctic ocean-atmosphere-sea ice-snow interface: 1. Chemical composition. *J Geophys Res* **117**: D00R09. doi:10.1029/2011JD016460.

Douglas TA, Sturm M, Simpson WR, Blum JD, Alvarez-Aviles L, et al. 2008. Influence of snow and ice crystal formation and accumulation on mercury deposition to the Arctic. *Environ Sci Technol* **42**: 1542–1551. doi: 10.1021/es070502d.

Douglas TA, Sturm M, Simpson WR, Brooks S, Lindberg SE, et al. 2005. Elevated mercury measured in snow and frost flowers near Arctic sea ice leads. *Geophys Res Lett* **32**: L04502. doi: 10.1029/2004GL022132.

Dubois M, Gilles KA, Hamilton JK, Rebers PA, Smith F. 1956. Colorimetric method for determination of sugars and related substances. *Anal Chem* **28**: 350–356.

Ducklow H. 2000. Bacterial production and biomass in the oceans, in Kirchman DL, ed., *Microbial Ecology of the Oceans*. Toronto: John Wiley & Sons, Inc.: pp. 85–120.

Dugdale RC, Goering JJ. 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnol Oceanogr* **12**: 196–206.

Dumont I, Schoemann V, Lannuzel D, Chou L, Tison J-L, et al. 2009. Distribution and characterization of dissolved and particulate organic matter in Antarctic pack ice. *Polar Biol* **32**: 733–750. doi: 10.1007/s00300-008-0577-y.

Edwards R, Sedwick P. 2001. Iron in East Antarctic snow: Implications for atmospheric iron deposition and algal production in Antarctic waters. *Geophys Res Lett* **28**(20): 3907–3910.

Ehrhardt M, Koeve W. 1999. Determination of particulate organic carbon and nitrogen, in Grasshoff K, Kremling K, Ehrhardt M, eds., *Methods of Seawater Analysis*. Toronto: Wiley-VCH: pp. 437–444.

Eicken H. 1992. The role of sea ice in structuring Antarctic ecosystems. *Polar Biol* **12**: 3–13.
Eicken H. 1998. Deriving modes and rates of ice growth in the Weddell Sea from microstructural, salinity and stable-isotope data, in Jeffries MO, ed., *Antarctic Sea Ice: Physical Processes, Interactions and Variability*. Washington: American Geophysical Union: pp. 89–122.
Eicken H. 2009. Chapter 3.3, Ice sampling and basic sea ice core analysis, in Eicken H, Gradinger R, Salganek M, Shirasawa K, Perovich D, Leppäranta M, eds., *Field Techniques for Sea Ice Research*. Fairbanks: University of Alaska Press: pp. 117–140.
Eicken H, Gradinger R, Salganek M, Shirasawa K, Perovich D, et al. eds. 2009. *Field Techniques for Sea Ice Research*. Fairbanks: University of Alaska Press.
Eicken H, Lange MA, Dieckmann GS. 1991. Spatial variability of sea-ice properties in the northwestern Weddell Sea. *J Geophys Res* **96**(C6): 10,603–10,615.
Else BGT, Papakyriakou TN, Galley RJ, Drennan WM, Miller LA, et al. 2011. Wintertime CO_2 fluxes in an Arctic polynya using eddy covariance: Evidence for enhanced air-sea gas transfer during ice formation. *J Geophys Res* **116**: C00G03. doi:10.1029/2010JC006760.
EPA. 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. Washington, DC: Environmental Protection Agency.
Ewert M, Carpenter SD, Colangelo-Lillis J, Deming JW. 2013. Bacterial and extracellular polysaccharide content of brine-wetted snow over Arctic winter first-year sea ice. *J Geophys Res-Oceans* **118**: 726–735. doi:10.1002/jgrc.20055.
Ewert M, Deming JW. 2013. Sea ice microorganisms: Environmental constraints and extracellular responses. *Biology* **2**(2): 603–628.
Falkowski PG, Raven JA. 2007. Photosynthesis and primary production in nature, in, *Aquatic Photosynthesis*. Princeton: Princeton University Press: pp. 319–363.
Finkelstein PL, Sims PF. 2001. Sampling error in eddy correlation flux measurements. *J Geophys Res* **106**(D4): 3503–3509.
Fischer M. 2013. Sea ice and the air-sea exchange of CO_2 [thesis], Bremen: Universität Bremen, Biologie/Chemie.
Fischer M, Thomas DN, Krell A, Nehrke G, Göttlicher J, et al. 2012. Quantification of ikaite in Antarctic sea ice. *Antarct Sci*. doi:10.1017/S0954102012001150.
Fortier M, Fortier L, Michel C, Legendre L. 2002. Climatic and biological forcing of the vertical flux of biogenic particles under seasonal Arctic sea ice. *Mar Ecol-Prog Ser* **225**: 1–16.
Fowler D, Coyle M, Flechard C, Hargreaves K, Nemitz E, et al. 2001. Advances in micrometeorological methods for the measurement and interpretation of gas and particle nitogen fluxes. *Plant Soil* **228**: 117–129.
Frache R, Abelmoschi ML, Grotti M, Ianni C, Magi E, et al. 2001. Effects of ice melting on Cu, Cd and Pb profiles in Ross Sea waters (Antarctica). *Int J Environ An Ch* **79**: 301–313.
Fransson A, Chierici M, Miller LA, Carnat G, Shadwick E, et al. 2013. Impact of sea-ice processes on the carbonate system and ocean acidification at the ice-water interface of the Amundsen Gulf, Arctic Ocean. *J Geophys Res-Oceans* **118**: 7001–7023. doi: 10.1002/2013JC009164.
Fransson A, Chierici M, Yager PL, Smith Jr WO. 2011. Antarctic sea ice carbon dioxide system and controls. *J Geophys Res* **116**: C12035. doi:10.1029/2010JC006844.
Fripiat F, Cardinal D, Tison J-L, Worby A, André L. 2007. Diatom-induced silicon isotopic fractionation in Antarctic sea ice. *J Geophys Res* **112**: G02001. doi: 10.1029/2006JG000244.
Fripiat F, Corvaisier R, Navez J, Elskens M, Schoemann V, et al. 2009. Measuring production-dissolution rates of marine biogenic silica by ^{30}Si-isotope dilution using a high-resolution sector field inductively coupled plasma mass spectrometer. *Limnol Oceanogr Methods* **7**: 470–478.
Fripiat F, Sigman DM, Fawcett SE, Rafter PA, Weigand MA, et al. 2014a. New insights into sea ice nitrogen biogeochemical dynamics from the nitrogen isotopes. *Glob Biogeochem Cy* **28**: 115–130. doi: 10.1002/2013GB004729.
Fripiat F, Tison J-L, André L, Notz D, Delille B. 2014b. Biogenic silica recycling in sea ice inferred from Si-isotopes: constraints from Arctic winter first-year sea ice. *Biogeochemistry* **119**: 25–33. doi: 10.1007/s10533-013-9911-8.
Fritsen CH, Memmott JC, Ross RM, Quetin LB, Vernet M, et al. 2011. The timing of sea ice formation and exposure to photosynthetically active radiation along the Western Antarctic Peninsula. *Polar Biol* **34**: 683–692. doi: 10.1007/s00300-010-0924-7.
Garbarino JR, Snyder-Conn E, Leiker TJ, Hoffman GL. 2002. Contaminants in Arctic snow collected over Northwest Alaskan sea ice. *Water Air Soil Poll* **139**: 183–214.
Gardner WD. 2000. Sediment trap sampling in surface waters, in Hanson RB, Ducklow HW, Field JG, eds., *The Changing Ocean Carbon Cycle: A Midterm Synthesis of the Joint Global Ocean Flux Study*. Cambridge: Cambridge University Press: pp. 240–281.
Garrison DL, Buck KR. 1986. Organism losses during ice melting: A serious bias in sea ice community studies. *Polar Biol* **6**: 237–239.
Garrison DL, Jeffries MO, Gibson A, Coale SL, Neenan D, et al. 2003. Development of sea ice microbial communities during autumn ice formation in the Ross Sea. *Mar Ecol-Prog Ser* **259**: 1–15.
Geilfus N-X, Carnat G, Dieckmann GS, Halden N, Nehrke G, et al. 2013. First estimates of the contribution of $CaCO_3$ precipitation to the release of CO_2 to the atmosphere during young sea ice growth. *J Geophys Res-Oceans* **118**: 244–255. doi: 10.1029/2012JC007980.
Geilfus N-X, Carnat G, Papakyriakou T, Tison J-L, Else B, et al. 2012a. Dynamics of pCO_2 and related air-ice CO_2 fluxes in the Arctic coastal zone (Amundsen Gulf, Beaufort Sea). *J Geophys Res* **117**: C00G10. doi:10.1029/2011JC007118.
Geilfus N-X, Delille B, Verbeke V, Tison J-L. 2012b. Towards a method for high vertical resolution measurements of the partial pressure of CO_2 within bulk sea ice. *J Glaciol* **58**: 287–300. doi: 10.3189/2012JoG11J071.
Geilfus N-X, Galley RJ, Crabeck O, Papakyriakou T, Landy J, et al. 2014a. Inorganic carbon dynamics of melt pond-covered first year sea ice in the Canadian Arctic. *Biogeosciences Discuss* **11**: 7485–7519. doi: 10.5194/bgd-11-7485-2014.
Geilfus N-X, Tison J-L, Ackley SF, Galley RJ, Rysgaard S, et al., 2014b. Sea ice pCO_2 dynamics and air-ice CO_2 fluxes during the Sea Ice Mass Balance in the Antarctic (SIMBA) experiment – Bellingshausen Sea, Antarctica. *The Cryosphere* **8**: 2395–2407. doi: 10.5194/tc-8-2395-2014.

Gerdes B, Brinkmeyer R, Dieckmann G, Helmke E. 2005. Influence of crude oil on changes of bacterial communities in Arctic sea-ice. *FEMS Microbiol Ecol* **53**: 129–139. doi: 10.1016/j.femsec.2004.11.010.

Giannelli V, Thomas DN, Haas C, Kattner G, Kennedy H, et al. 2001. Behaviour of dissolved organic matter and inorganic nutrients during experimental sea-ice formation. *Ann Glaciol* **33**: 317–321.

Gibson JAE, Trull T, Nichols PD, Summons RE, McMinn A. 1999. Sedimentation of ^{13}C-rich organic matter from Antarctic sea-ice algae: A potential indicator of past sea-ice extent. *Geology* **27**: 331–334.

Gleitz M, Rutgers vd Loeff M, Thomas DN, Dieckmann GS, Millero FJ. 1995. Comparison of summer and winter inorganic carbon, oxygen and nutrient concentrations in Antarctic sea ice brine. *Mar Chem* **51**: 81–91.

Glud RN, Rysgaard S, Kühl M. 2002. A laboratory study on O_2 dynamics and photosynthesis in ice algal communities: quantification by microsensors, O_2 exchange rates, ^{14}C incubations and a PAM fluorometer. *Aquat Microb Ecol* **27**: 301–311.

Golden KM, Ackley SF, Lytle VI. 1998. The percolation phase transition in sea ice. *Science* **282**: 2238–2241.

Gosink T. 1978. The Arctic: A significant source-sink of carbon dioxide, in Gosink TA, Kelley JJ, eds., *Gases in the Sea Ice*. Fairbanks, AK: Institute of Marine Science, University of Alaska: pp. 79–91.

Gosink TA. 1980. Atmospheric trace gases in association with sea ice. *Antarct J US* **15**: 82–83.

Gosink TA, Kelley JJ. 1979. Carbon monoxide evolution from Arctic surfaces during spring thaw. *J Geophys Res* **84**: 7041.

Gosink T, Kelley JJ. 1985. Final Report: Carbon Dioxide in Arctic and Subarctic Regions. University of Alaska, 215 pp.

Gosselin M, Legendre L, Therriault J-C, Demers S, Rochet M. 1986. Physical control of the horizontal patchiness of sea-ice microalgae. *Mar Ecol-Prog Ser* **29**: 289–298.

Gosselin M, Levasseur M, Wheeler PA, Horner RA, Booth BC. 1997. New measurements of phytoplankton and ice algal production in the Arctic Ocean. *Deep-Sea Res Pt II* **44**: 1623–1644.

Gradinger R. 1999. Vertical fine structure of the biomass and composition of algal communities in Arctic pack ice. *Mar Biol* **133**: 745–754.

Gradinger R. 2009. Sea-ice algae: Major contributors to primary production and algal biomass in the Chukchi and Beaufort Seas during May/June 2002. *Deep-Sea Res Pt II* **56**: 1201–1212.

Gradinger R, Bluhm B, Iken K. 2010. Arctic sea-ice ridges — Safe heavens for sea-ice fauna during periods of extreme ice melt? *Deep-Sea Res Pt II* **57**: 86–95. doi: 10.1016/j.dsr2.2009.08.008.

Gradinger R, Ikävalko J. 1998. Organism incorporation into newly forming Arctic sea ice in the Greenland Sea. *J Plankton Res* **20**: 871–886.

Granfors A, Andersson M, Chierici M, Fransson A, Gårdfeldt K, et al. 2013a. Biogenic halocarbons in young Arctic sea ice and frost flowers. *Mar Chem* **155**: 124–134. doi: 10.1016/j.marchem.2013.06.002.

Granfors A, Karlsson A, Mattsson E, Smith Jr. WO, Abrahamsson K. 2013b. Contribution of sea ice in the Southern Ocean to the cycling of volatile halogenated organic compounds. *Geophys Res Lett* **40**: 3950–3955. doi: 10.1002/grl.50777.

Granskog MA, Kaartokallio H. 2004. An estimation of the potential fluxes of nitrogen, phosphorus, cadmium and lead from sea ice and snow in the northern Baltic Sea. *Water Air Soil Poll* **154**: 331–347.

Granskog MA, Kaartokallio H, Kuosa H, Thomas DN, Ehn J, et al. 2005a. Scales of horizontal patchiness in chlorophyll *a*, chemical and physical properties of landfast sea ice in the Gulf of Finland (Baltic Sea). *Polar Biol* **28**: 276–283. doi: 10.1007/s00300-004-0690-5.

Granskog MA, Kaartokallio H, Shirasawa K. 2003. Nutrient status of Baltic Sea ice: Evidence for control by snow-ice formation, ice permeability, and ice algae. *J Geophys Res* **108**(C8). doi: 10.1029/2002JC001386.

Granskog MA, Kaartokallio H, Thomas DN, Kuosa H. 2005b. Influence of freshwater inflow on the inorganic nutrient and dissolved organic matter within coastal sea ice and underlying waters in the Gulf of Finland (Baltic Sea). *Estuar Coast Shelf S* **65**: 109–122. doi: 10.1016/j.ecss.2005.05.011.

Granskog MA, Nomura D, Müller S, Krell A, Toyota T, et al. 2015. Evidence for significant protein-like dissolved organic matter accumulation in Sea of Okhotsk sea ice. *Ann Glaciol* **56**(69): 1–8. doi: 10.3189/2015AoG69A002.

Granskog MA, Virkanen J. 2001. Observations on sea-ice and surface-water geochemistry — Implications for importance of sea ice in geochemical cycles in the northern Baltic Sea. *Ann Glaciol* **33**: 311–316.

Granskog MA, Virkkunen K, Thomas DN, Ehn J, Kola H, et al. 2004. Chemical properties of brackish water ice in the Bothnian Bay, the Baltic Sea. *J Glaciol* **50**: 292–302.

Grossi SM, Kottmeier ST, Moe RL, Taylor GT, Sullivan CW. 1987. Sea ice microbial communities. VI. Growth and primary production in bottom ice under graded snow cover. *Mar Ecol-Prog Ser* **35**: 153–164.

Grossmann S, Dieckmann GS. 1994. Bacterial standing stock, activity, and carbon production during formation and growth of sea ice in the Weddell Sea, Antarctica. *Appl Environ Microbiol* **60**(8): 2746–2753.

Grotti M, Soggia F, Ianni C, Frache R. 2005. Trace metals distributions in coastal sea ice of Terra Nova Bay, Ross Sea, Antarctica. *Antarct Sci* **17**(2): 289–300. doi: 10.1017/S0954102005002695.

Hansell DA, Carlson CA, Repeta DJ, Schlitzer R. 2009. Dissolved organic matter in the ocean: A controversy stimulates new insights. *Oceanography* **22**: 202–211.

Hare AA, Wang F, Barber D, Geilfus N-X, Galley RJ, et al. 2013. pH evolution in sea ice grown at an outdoor experimental facility. *Mar Chem* **154**: 46–54. doi: 10.1016/j.marchem.2013.04.007.

Harrison WG, Cota GF, Smith REH. 1990. Nitrogen utilization in ice algal communities of Barrow Strait, Northwest Territories, Canada. *Mar Ecol-Prog Ser* **67**: 275–283.

Hawes I, Lund-Hansen LC, Sorrell BK, Nielsen MH, Borzák R, et al. 2012. Photobiology of sea ice algae during initial spring growth in Kangerlussuaq, West Greenland: insights from imaging variable chlorophyll fluorescence of ice cores. *Photosynth Res* **112**: 103–115. doi: 10.1007/s11120-012-9736-7.

Helmke E, Weyland H. 1995. Bacteria in sea ice and underlying water of the eastern Weddell Sea in midwinter. *Mar Ecol-Prog Ser* **117**: 269–287.

Hendry KR, Meredith MP, Measures CI, Carson DS, Rickaby REM. 2010a. The role of sea ice formation in cycling of aluminium in northern Marguerite Bay, Antarctica. *Estuar Coast Shelf S* **87**: 103–113. doi: 10.1016/j.ecss.2009.12.017.

Hendry KR, Rickaby REM, de Hoog JCM, Weston K, Rehkamper M. 2010b. The cadmium-phosphate relationship in brine: biological versus physical control over micronutrients in sea ice environments. *Antarct Sci* **22**(1): 11–18. doi:10.1017/S0954102009990381.

Herborg L-M, Thomas DN, Kennedy H, Haas C, Dieckmann GS. 2001. Dissolved carbohydrates in Antarctic sea ice. *Antarct Sci* **13**: 119–125.

Hicks BB, McMillen RT. 1984. A simulation of the eddy accumulation method for measuring pollutant fluxes. *J Clim Appl Meteorol* **23**: 637–643.

Higaki S, Oya Y, Makide Y. 2006. Emission of methane from stainless steel surface investigated by using tritium as a radioactive tracer. *Chem Lett* **35**: 292–293. doi: 10.1246/cl.2006.292.

Hilmer T, Bate GC. 1989. Filter types, filtration and post-filtration treatment in phytoplankton production studies. *J Plankton Res* **11**(1): 49–63.

Hobbie JE, Daley RJ, Jasper S. 1977. Use of Nuclepore filters for counting bacteria by fluorescence microscopy. *Appl Environ Microbiol* **33**: 1225–1228.

Hölemann JA, Schirmacher M, Kassens H, Prange A. 1999. Geochemistry of surficial and ice-rafted sediments from the Laptev Sea (Siberia). *Estuar Coast Shelf S* **49**: 45–59.

Holmes RM, Aminot A, Kérouel R, Hooker BA, Peterson BJ. 1999. A simple and precise method for measuring ammonium in marine and freshwater ecosystems. *Can J Fish Aquat Sci*. **56**: 1801–1808.

Holter P. 1990. Sampling air from dung pats by silicone rubber diffusion chambers. *Soil Biol Biochem* **22**: 995–997.

Horner R. 1985. History of ice algal investigations, in Horner RA ed., *Sea Ice Biota*. Boca Raton, Florida: CRC Press. pp. 1–19.

Horner R, Ackley SF, Dieckmann GS, Gulliksen B, Hoshiai T, et al. 1992. Ecology of sea ice biota: 1. Habitat, terminology, and methodology. *Polar Biol* **12**: 417–427.

Horner R, Schrader GC. 1982. Relative contributions of ice algae, phytoplankton, and benthic microalgae to primary production in nearshore regions of the Beaufort Sea. *Arctic* **35**: 485–503.

Hunke EC, Notz D, Turner AK, Vancoppenolle M. 2011. The mulitphase physics of sea ice: a review for model developers. *The Cryosphere* **5**: 989–1009. doi: 10.5194/tc-5-989-2011.

Hydes DJ, Aoyama M, Aminot A, Bakker K, Becker S, et al. 2010. Determination of dissolved nutrients (N, P, Si) in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers. *The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines*.

Johnson KS, Barry JP, Coletti LJ, Fitzwater SE, Jannasch HW, et al. 2011. Nitrate and oxygen flux across the sediment-water interface observed by eddy correlation measurements on the open continental shelf. *Limnol Oceanogr Methods* **9**: 543–553. doi: 10.4319/lom.2011.9.543.

Juhl AR, Krembs C, Meiners KM. 2011. Seasonal development and differential retention of ice algae and other organic fractions in first-year Arctic sea ice. *Mar Ecol-Prog Ser* **436**: 1–16. doi: 10.3354/meps09277.

Junge K, Eicken H, Deming JW. 2004. Bacterial activity at -2 to -20°C in Arctic wintertime sea ice. *Appl Environ Microbiol* **70**(1): 550–557.

Junge K, Krembs C, Deming J, Stierle A, Eicken H. 2001. A microscopic approach to investigate bacteria under in situ conditions in sea-ice samples. *Ann Glaciol* **33**: 304–310.

Juul-Pedersen T, Michel C, Gosselin M, Seuthe L. 2008. Seasonal changes in the sinking export of particulate material under first-year sea ice on the Mackenzie Shelf (western Canadian Arctic). *Mar Ecol-Prog Ser* **353**: 13–25. doi: 10.3354/meps07165.

Kaartokallio H. 2001. Evidence for active microbial nitrogen transformation in sea ice (Gulf of Bothnia, Baltic Sea) in midwinter. *Polar Biol* **24**: 21–28.

Kaartokallio H. 2004. Food web components, and physical and chemical properties of Baltic Sea ice. *Mar Ecol-Prog Ser* **273**: 49–63.

Kaartokallio H, Søgaard DH, Norman L, Rysgaard S, Tison J-L, et al. 2013. Short-term variability in bacterial abundance, cell properties, and incorporation of leucine and thymidine in subarctic sea ice. *Aquat Microb Ecol* **71**: 57–73. doi: 10.3354/ame01667.

Kaartokallio H, Tuomainen J, Kuosa H, Kuparinen J, Martikainen PJ, et al. 2008. Succession of sea-ice bacterial communities in the Baltic Sea fast ice. *Polar Biol* **31**: 783–793. doi: 10.1007/s00300-008-0416-1.

Kaimal JC, Wyngaard JC, Izumi Y, Coté OR. 1972. Spectral characteristics of surface-layer turbulence. *Q J Roy Meteor Soc* **98**: 563–589.

Kammann C, Grünhage L, Jäger H-J. 2001. A new sampling technique to monitor concentrations of CH_4, N_2O and CO_2 in air at well-defined depths in soils with varied water potential. *Eur J Soil Sci* **52**: 297–303.

Kattner G. 1999. Storage of dissolved inorganic nutrients in seawater: poisoning with mercuric chloride. *Mar Chem* **67**: 61–66.

Kelley JJ, Gosink TA. 1979. Gases in Sea Ice: 1975–1979. Fairbanks, Alaska: University of Alaska, Fairbanks. Final report to ONR N000 14-76C-0331.

Kelley JJ, Gosink TA. 1985. Sources and sinks of carbon dioxide in the Arctic regions, in *Final Report: Carbon Dioxide in Arctic and Subarctic Regions*. Fairbanks: University of Alaska: 131–165.

Kennedy H, Robertson J. 1995. Variations in the isotopic composition of particulate organic carbon in surface waters along an 88°W transect from 67°S to 54°S. *Deep-Sea Res Pt II* **42**: 1109–1122.

Kennedy H, Thomas DN, Kattner G, Haas C, Dieckmann GS. 2002. Particulate organic matter in Antarctic summer sea ice: concentration and stable isotopic composition. *Mar Ecol-Prog Ser* **238**: 1–13.

King MD, France JL, Fisher FN, Beine HJ. 2005. Measurement and modelling of UV radiation penetration and photolysis rates of nitrate and hydrogen peroxide in Antarctic sea ice: An estimate of the production rate of hydroxyl radicals in first-year sea ice. *J Photochem Photobiol A* **176**: 39–49. doi: 10.1016/j.jphotochem.2005.08.032.

Klánová J, Klán P, Heger D, Holoubek I. 2003. Comparison of the effects of UV, H_2O_2/UV and γ-irradiation processes on frozen and liquid water solutions of monochlorophenols. *Photochem Photobiol Sci* **2**: 1023–1031. doi: 10.1039/b303483f.

Knefelkamp B, Carstens K, Wiltshire KH. 2007. Comparison of different filter types on *chlorophyll-a* retention and nutrient measurements. *J Exp Mar Biol Ecol* **345**: 61–70. doi: 10.1016/j.jembe.2007.01.008.

Knepp TN, Bottenheim J, Carlsen M, Carlson D, Donohoue D, et al. 2010. Development of an autonomous sea ice tethered buoy for the study of ocean-atmosphere-sea ice-snow pack interactions: the O-buoy. *Atmos Meas Tech* **3**: 249–261.

Koh EY, Atamna-Ismaeel N, Martin A, Cowie ROM, Beja O, et al. 2010. Proteorhodopsin-bearing bacteria in Antarctic sea ice. *Appl Environ Microbiol* **76**: 5918–5925. doi: 10.1128/AEM.00562-10.

Krembs C, Eicken H, Deming JW. 2011. Exopolymer alteration of physical properties of sea ice and implications for ice habitability and biogeochemistry in a warmer Arctic. *Proc Natl Acad Sci* **108**: 3653–3658.

Krembs C, Eicken H, Junge K, Deming JW. 2002. High concentrations of exopolymeric substances in Arctic winter sea ice: implications for the polar ocean carbon cycle and cryoprotection of diatoms. *Deep-Sea Res Pt I* **49**: 2163–2181.

Kristiansen S, Farbrot T, Kuosa H, Myklestad S, Quillfeldt CHv. 1998. Nitrogen uptake in the infiltration community, and ice algal community in Antarctic pack-ice. *Polar Biol* **19**: 307–315.

Kristiansen S, Syvertsen EE, Farbrot T. 1992. Nitrogen uptake in the Weddell Sea during late winter and spring. *Polar Biol* **12**: 245–251.

Kühl M, Glud RN, Borum J, Roberts R, Rysgaard S. 2001. Photosynthetic performance of surface-associated algae below sea ice as measured with a pulse-amplitude-modulated (PAM) fluorometer and O_2 microsensors. *Mar Ecol-Prog Ser* **223**: 1–14.

Lannuzel D, Bowie AR, van der Merwe PC, Townsend AT, Schoemann V. 2011. Distribution of dissolved and particulate metals in Antarctic sea ice. *Mar Chem* **124**: 134–146. doi:10.1016/j.marchem.2011.01.004.

Lannuzel D, de Jong J, Schoemann V, Trevena A, Tison J-L, et al. 2006. Development of a sampling and flow injection analysis technique for iron determination in the sea ice environment. *Anal Chim Acta* **556**: 476–483. doi:10.1016/j.aca.2005.09.059.

Lannuzel D, Schoemann V, de Jong J, Chou L, Delille B, et al. 2008. Iron study during a time series in the western Weddell pack ice. *Mar Chem* **108**(1–2): 85–95. doi: 10.1016/j.marchem.2007.10.006.

Lannuzel D, Schoemann V, de Jong J, Pasquer B, van der Merwe P, et al. 2010. Distribution of dissolved iron in Antarctic sea ice: Spatial, seasonal, and inter-annual variability. *J Geophys Res*. **115**: G03022. doi: 10.1029/2009JG001031.

Lannuzel D, Schoemann V, de Jong J, Tison J-L, Chou L. 2007. Distribution and biogeochemical behaviour of iron in the East Antarctic sea ice. *Mar Chem* **106**: 18–32. doi:10.1016/j.marchem.2006.06.010.

Lannuzel D, van der Merwe PC, Townsend AT, Bowie AR. 2014. Size fractionation of iron, manganese and aluminium in Antarctic fast ice reveals a lithogenic origin and low iron solubility. *Mar Chem* 161: 47–56. doi: 10.1016/j.marchem.2014.02.006.

Latasa M. 2007. Improving estimations of phytoplankton class abundances using CHEMTAX. *Mar Ecol-Prog Ser* **329**: 13–21.

Laws E, Sakshaug E, Babin M, Dandonneau Y, Falkowski P, et al. 2002. Photosynthesis and Primary Productivity in Marine Ecosystems: Practical Aspects and Application of Techniques. Bergen: Joint Global Ocean Flux Study. JGOFS Report No. 36.

Lee PA, de Mora SJ, Gosselin M, Levasseur M, Bouillon R-C, et al. 2001. Particulate dimethylsulfoxide in Arctic sea-ice algal communities: The cryoprotectant hypothesis revisited. *J Phycol* **37**: 488–499.

Lee X, Massman W, Law B, eds. 2004. *Handbook of Micrometeorology: A Guide for Surface Flux Measurement and Analysis*. Boston: Kluwer Academic Publishers.

Leppäranta M, Manninen T. 1988. *The Brine and Gas Content of Sea Ice with Attention to Low Salinities and High Temperatures*. Helsinki: Finnish Institute of Marine Research.

Leuning R, King KM. 1992. Comparison of eddy-covariance measurements of CO_2 fluxes by open- and closed-path CO_2 analysers. *Bound-Lay Meteorol* **59**: 297–311.

Levasseur M, Gosselin M, Michaud S. 1994. A new source of dimethylsulfide (DMS) for the arctic atmosphere: Ice diatoms. *Mar Biol* **121**: 381–387.

Liss PS, Hatton AD, Malin G, Nightingale PD, Turner SM. 1997. Marine sulphur emissions. *Philos T Roy Soc B* **352**: 159–169.

Long MH, Koopmans D, Berg P, Rysgaard S, Glud RN, et al. 2012. Oxygen exchange and ice melt measured at the ice-water interface by eddy correlation. *Biogeosciences* **9**: 1957–1967. doi: 10.5194/bg-9-1957-2012.

Loose B, Miller LA, Elliott S, Papakyriakou T. 2011. Sea ice biogeochemistry and material transport across the frozen interface. *Oceanography* **24**: 202–218. doi: 10.5670/oceanog.2011.72.

Löscher BM, deBaar HJW, de Jong JTM, Veth C, Dehairs F. 1997. The distribution of Fe in the Antarctic Circumpolar current. *Deep-Sea Res Pt II* **44**(1–2): 143–187.

Luo Y, Zhou X. 2006. *Soil Respiration and the Environment*. San Francisco: Academic Press.

Lyakhin YI. 1970. Saturation of water of the Sea of Okhotsk with calcium carbonate. *Oceanology* **10**: 789–795.

Maas EW, Simpson AM, Martin A, Thompson S, Koh EY, et al. 2012. Phylogenetic analyses of bacteria in sea ice at Cape Hallett, Antarctica. *New Zeal J Mar Fresh* **46**: 3–12.

Macdonald RW, Carmack EC, McLaughlin FA, Iseki K, Macdonald DM, et al. 1989. Composition and modification of water masses in the Mackenzie shelf estuary. *J Geophys Res* **94**(C12): 18,057–18,070.

Macdonald RW, Carmack EC, Paton DW. 1999. Using the $\delta^{18}O$ composition in landfast ice as a record of arctic estuarine processes. *Mar Chem* **65**: 3–24.

Manes SS, Gradinger R. 2009. Small scale vertical gradients of Arctic ice algal photophysiological properties. *Photosynth Res* **102**: 53–66. doi: 10.1007/s11120-009-9489-0.

Mantoura RFC, Wright SW, Jeffrey SW, Barlow RG, Cummings DE. 1997. Filtration and storage of pigments from microalgae, in Jeffrey SW, Mantoura RFC, Wright SW, eds., *Phytoplankton Pigments in Oceanography*. UNESCO Publishing: 283–305.

Martin A, Anderson MJ, Thorn C, Davy SK, Ryan KG. 2011. Response of sea-ice microbial communities to environmental disturbance: an *in situ* transplant experiment in the Antarctic. *Mar Ecol-Prog Ser* **424**: 25–37. doi: 10.3354/meps08977.

Martiny AC, Vrugt JA, Primeau FW, Lomas MW. 2013. Regional variation in the particulate organic carbon to nitrogen ratio in the surface ocean. *Glob Biogeochem Cy* **27**: 723–731. doi: 10.1002/gbc.20061.

Massom RA, Eicken H, Haas C, Jeffries MO, Drinkwater MR, et al. 2001. Snow on Antarctic sea ice. *Rev Geophys* **39**: 413–445. doi: 10.1029/2000RG000085.

Massom RA, Stammerjohn SE. 2010. Antarctic sea ice change and variability - Physical and ecological implications. *Polar Sci* **4**: 149–186. doi: 10.1016/j.polar.2010.05.001.

Matsuo S, Miyake Y. 1966. Gas composition in ice samples from Antarctica. *J Geophys Res* **71**: 5235–5241.

Mattson E, Karlsson A, Smith Jr. WO, Abrahamsson K. 2012. The relationship between biophysical variables and halocarbon distributions in the waters of the Amundsen and Ross Seas, Antarctica. *Mar Chem* **140–1**: 1–9. doi: 10.1016/j.marchem.2012.07.002.

McCorkle DC, Emerson SR, Quay PD. 1985. Stable carbon isotopes in marine porewaters. *Earth Planet Sc Lett* **74**: 13–26.

McGinnis DF, Cherednichenko S, Sommer S, Berg P, Rovelli L, et al. 2011. Simple, robust eddy correlation amplifier for aquatic dissolved oxygen and hydrogen sulfide flux measurements. *Limnol Oceanogr Methods* **9**: 340–347. doi:10.4319/lom.2011.9.340.

McLaughlin F, Proshutinsky A, Carmack EC, Shimada K, Brown K, et al. 2012. Physical, Chemical and Zooplankton Data from the Canada Basin and Canadian Arctic Archipelago, July 20 to September 14, 2006. Sidney: Institute of Ocean Sciences. Canadian Data Report of Hydrography and Ocean Sciences 186.

McMinn A, Ashworth C. 1998. The use of oxygen microelectrodes to determine the net production by an Arctic sea ice algal community. *Antarct Sci* **10**: 39–44.

McMinn A, Ashworth C, Ryan KG. 2000. *In situ* net primary productivity of an Antarctic fast ice bottom algal community. *Aquat Microb Ecol* **21**: 177–185.

McMinn A, Gradinger R, Nomura D. 2009. Chapter 3.8, Biogeochemical properties of sea ice, in Eicken H, Gradinger R, Salganek M, Shirasawa K, Perovich D, et al., eds., *Field Techniques for Sea Ice Research*. Fairbanks: University of Alaska Press: pp. 259–82.

McMinn A, Hegseth EN. 2007. Sea ice primary productivity in the northern Barents Sea, spring 2004. *Polar Biol* **30**: 289–294. doi: 10.1007/s00300-006-0182-x.

McMinn A, Ryan K, Gademann R. 2003. Diurnal changes in photosynthesis of Antarctic fast ice algal communities determined by pulse amplitude modulation fluorometry. *Mar Biol* **143**: 359–367. doi: 10.1007/s00227-003-1052-5.

McMinn A, Ryan KG, Ralph PJ, Pankowski A. 2007. Spring sea ice photosynthesis, primary productivity and biomass distribution in eastern Antarctica, 2002–2004. *Mar Biol* **151**: 985–995. doi: 10.1007/s00227-006-0533-8.

Meiners K, Brinkmeyer R, Granskog MA, Lindfors A. 2004. Abundance, size distribution and bacterial colonization of exopolymer particles in Antarctic sea ice (Bellingshausen Sea). *Aquat Microb Ecol* **35**: 283–296.

Meiners K, Gradinger R, Fehling J, Civitarese G, Spindler M. 2003. Vertical distribution of exopolymer particles in sea ice of the Fram Strait (Arctic) during autumn. *Mar Ecol-Prog Ser* **248**: 1–13.

Meiners K, Krembs C, Gradinger R. 2008. Exopolymer particles: microbial hotspots of enhanced bacterial activity in Arctic fast ice (Chukchi Sea). *Aquat Microb Ecol* **52**: 195–207. doi: 10.3354/ame01214.

Meiners KM, Papadimitriou S, Thomas DN, Norman L, Dieckmann GS. 2009. Biogeochemical conditions and ice algal photosynthetic parameters in Weddell Sea ice during early spring. *Polar Biol* **32**: 1055–1065. doi: 10.1007/s00300-009-0605-6.

Meiners KM, Vancoppenolle M, Thanassekos S, Dieckmann GS, Thomas DN, et al. 2012. Chlorophyll *a* in Antarctic sea ice from historical ice core data. *Geophys Res Lett* **39**: L21602. doi: 10.1029/2012GL053478.

Michel C, Legendre L, Ingram RG, Gosselin M, Levasseur M. 1996. Carbon budget of sea-ice algae in spring: Evidence of a significant transfer to zooplankton grazers. *J Geophys Res* **101**(C8): 18,345–18,360.

Michel C, Nielsen TG, Nozais C, Gosselin M. 2002. Significance of sedimentation and grazing by ice micro- and meiofauna for carbon cycling in annual sea ice (northern Baffin Bay). *Aquat Microb Ecol* **30**: 57–68.

Michel C, Niemi A. 2009. Field and laboratory methods for biogeochemical analyses of sea ice, seawater and particle interceptor trap samples. Winnipeg: Fisheries and Oceans Canada. Canadian Technical Report of Fisheries and Aquatic Sciences # 2852.

Mikkelsen DM, Witkowski A. 2010. Melting sea ice for taxonomic analysis: a comparison of four melting procedures. *Polar Res* **29**: 451–454.

Miller LA, Carnat G, Else BGT, Sutherland N, Papakyriakou TN. 2011a. Carbonate system evolution at the Arctic Ocean surface during autumn freeze-up. *J Geophys Res* **116**: C00G04. doi: 10.1029/2011JC007143.

Miller LA, Papakyriakou TN, Collins RE, Deming JW, Ehn JK, et al. 2011b. Carbon dynamics in sea ice: A winter flux time series. *J Geophys Res* **116**: C02028. doi: 10.1029/2009JC006058.

Millero FJ, DiTrolio B, Suarez AF, Lando G. 2009. Spectroscopic measurements of the pH in NaCl brines. *Geochim Cosmochim Acta* **73**: 3109–3114. doi: 10.1016/j.gca.2009.01.037.

Mock T. 2002. *In situ* primary production in young Antarctic sea ice. *Hydrobiologia* **470**: 127–132.

Mock T, Dieckmann GS, Haas C, Krell A, Tison J-L, et al. 2002. Micro-optodes in sea ice: A new approach to investigate oxygen dynamics during sea ice formation. *Aquat Microb Ecol* **29**: 297–306.

Mock T, Gradinger R. 1999. Determination of Arctic ice algal production with a new *in situ* incubation technique. *Mar Ecol-Prog Ser* **177**: 15–26.

Mock T, Kruse M, Dieckmann GS. 2003. A new microcosm to investigate oxygen dynamics at the sea ice water interface. *Aquat Microb Ecol* **30**: 197–205.

Mock T, Meiners KM, Giesenhagen HC. 1997. Bacteria in sea ice and underlying brackish water at 54° 26′50″ N (Baltic Sea, Kiel Bight). *Mar Ecol-Prog Ser* **158**: 23–40.

Moeseneder MM, Winter C, Herndl GJ. 2001. Horizontal and vertical complexity of attached and free-living bacteria of the eastern Mediterranean Sea, determined by 16S rDNA and 16S rRNA fingerprints. *Limnol Oceanogr* **46**: 95–107.

Mosier AR. 1989. Chamber and isotope techniques, in Andreae MO, Schimel DS, eds., *Exchange of Trace Gases between Terrestrial Ecosytems and the Atmosphere*. Toronto: John Wiley & Sons: pp. 175–187.

Muller JBA, Dorsey JR, Flynn M, Gallagher MW, Percival CJ, et al. 2012. Energy and ozone fluxes over sea ice. *Atmos Environ* **47**: 218–225. doi: 10.1016/j.atmosenv.2011.11.013.

Müller M, Graus M, Ruuskanen TM, Schnitzhofer R, Bamberger I, et al. 2010.First eddy covariance flux measurements by PTR-TOF. *Atmos Meas Tech* **3**: 387–395.

Müller S, Vähätalo AV, Stedmon CA, Granskog MA, Norman L, et al. 2013. Selective incorporation of dissolved organic matter (DOM) during sea ice formation. *Mar Chem* **155**: 148–157. doi: 10.1016/j.marchem.2013.06.008.

Mundy CJ, Barber DG, Michel C. 2005. Variability of snow and ice thermal, physical and optical properties pertinent to sea ice algae biomass during spring. *J Marine Syst* **58**: 107–120.

Mundy CJ, Ehn JK, Barber DG, Michel C. 2007. Influence of snow cover and algae on the spectral dependence of transmitted irradiance through Arctic landfast first-year sea ice. *J Geophys Res* **112**: C03007. doi: 10.1029/2006JC003683.

Mundy CJ, Gosselin M, Ehn JK, Belzile C, Poulin M, et al. 2011. Characteristics of two distinct high-light acclimated algal communities during advanced stages of sea ice melt. *Polar Biol* **34**: 1869–1886. doi: 10.1007/s00300-011-0998-x.

Munro DR, Dunbar RB, Mucciarone DA, Arrigo KR, Long MC. 2010. Stable isotope composition of dissolved inorganic carbon and particulate organic carbon in sea ice from the Ross Sea, Antarctica. *J Geophys Res* **115**: C09005. doi: 10.1029/2009JC005661.

Myklestad SM, Skånøy E, Hestmann S. 1997. A sensitive and rapid method for analysis of dissolved mono- and polysaccharides in seawater. *Mar Chem*. **56**: 279–286.

Nedashkovskii AP. 2002. Cadmium and lead in the ice of Amur Bay (Sea of Japan). *Oceanology* **42**: 344–349.

Nedashkovsky AP, Khvedynich SV, Petrovsky TV. 2009. Alkalinity of sea ice in the high-latitudinal Arctic according to the surveys performed at North Pole Drifting Station 34 and characterization of the role of the Arctic ice in the CO_2 exchange. *Oceanology* **49**: 55–63. doi: 10.1134/S000143700901007X.

Nedashkovsky AP, Shvetsova MG. 2010. Total inorganic carbon in sea ice. *Oceanology* **50**: 861–868. doi: 10.1134/S0001437010060056.

Nelson KH, Thompson TG. 1954. Deposition of salts from sea water by frigid concentration. *J Mar Res* **13**: 166–182.

Nishi Y, Tabeta S. 2008. Relation of material exchange between sea ice and water to a coupled ice-ocean ecosystem at the Hokkaido coastal region of the Okhotsk Sea. *J Geophys Res* **113**: C01003. doi: 10.1029/2006JC004077.

Noble RT, Fuhrman JA. 1998. Use of SYBR Green I for rapid epifluorescence counts of marine viruses and bacteria. *Aquat Microb Ecol* **14**: 113–118.

Nomura D, Assmy P, Nehrke G, Granskog MA, Fischer M, et al. 2013a. Characterization of ikaite ($CaCO_3{\cdot}6H_2O$) crystals in first-year Arctic sea ice north of Svalbard. *Ann Glaciol* **54**: 125–131. doi: 10.3189/2013AoG62A034.

Nomura D, Eicken H, Gradinger R, Shirasawa K. 2010a. Rapid physically driven inversion of the air-sea ice CO_2 flux in the seasonal landfast ice off Barrow, Alaska after onset of surface melt. *Cont Shelf Res* **30**: 1998–2004. doi: 10.1016/j.csr.2010.09.014.

Nomura D, Granskog MA, Assmy P, Simizu D, Hashida G. 2013b. Arctic and Antarctic sea ice acts as a sink for atmospheric CO_2 during periods of snowmelt and surface flooding. *J Geophys Res-Oceans* **118**: 6511–6524. doi: 10.1002/2013JC009048.

Nomura D, Koga S, Kasamatsu N, Shinagawa H, Simizu D, et al. 2012. Direct measurements of DMS flux from Antarctic fast sea ice to the atmosphere by a chamber technique. *J Geophys Res* **117**: C04011. doi:10.1029/2010JC006755.

Nomura D, McMinn A, Hattori H, Aoki S, Fukuchi M. 2011. Incorporation of nitrogen compounds into sea ice from atmospheric deposition. *Mar Chem* **127**: 90–99. doi: 10.1016/j.marchem.2011.08.002.

Nomura D, Takatsuka T, Ishikawa M, Kawamura T, Shirasawa K, et al. 2009. Transport of chemical components in sea ice and under-ice water during melting in the seasonally ice-covered Saroma-ko Lagoon, Hokkaido, Japan. *Estuar Coast Shelf S* **81**: 201–209. doi: 10.1016/j.ecss.2008.10.012.

Nomura D, Yoshikawa-Inoue H, Toyota T, Shirasawa K. 2010b. Effects of snow, snowmelting and refreezing processes on air-sea-ice CO_2 flux. *J Glaciol* **56**: 262–270.

Norman L, Thomas DN, Stedmon CA, Granskog MA, Papadimitriou S, et al. 2011. The characteristics of dissolved organic matter (DOM) and chromophoric dissolved organic matter (CDOM) in Antarctic sea ice. *Deep-Sea Res Pt II* **58**: 1075–1091. doi: 10.1016/j.dsr2.2010.10.030.

Norman M, Rutgersson A, Sørensen LL, Sahlée E. 2012. Methods for estimating air-sea fluxes of CO_2 using high-frequency measurements. *Bound-Lay Meteorol* **144**: 379–400. doi: 10.1007/s10546-012-9730-9.

Not C, Brown K, Ghaleb B, Hillaire-Marcel C. 2012. Conservative behavior of uranium vs. salinity in Arctic sea ice and brine. *Mar Chem* **130–1**: 33–39. doi:10.1016/j.marchem.2011.12.005.

Notz D, Wettlaufer JS, Worster MG. 2005. A non-destructive method for measuring the salinity and solid fraction of growing sea ice in situ. *J Glaciol* **51**(172): 159–166.

Notz D, Worster MG. 2009. Desalination processes of sea ice revisited. *J Geophys Res* **114**: C05006. doi: 10.1029/2008JC004885.

Obbard RW, Roscoe HK, Wolff EW, Atkinson HM. 2009. Frost flower surface area and chemistry as a function of salinity and temperature. *J Geophys Res* **114**: D20305. doi: 10.1029/2009JD012481.

Papadimitriou S, Kennedy H, Kattner G, Dieckmann GS, Thomas DN. 2004. Experimental evidence for carbonate precipitation and CO_2 degassing during sea ice formation. *Geochim Cosmochim Acta* **68**: 1749–1761. doi: 10.1016/j.gca.2003.07.004.

Papadimitriou S, Kennedy H, Kennedy P, Thomas DN. 2013. Ikaite solubility in seawater-derived brines at 1 atm and sub-zero temperatures to 265 K. *Geochim Cosmochim Acta* **109**: 241–253. doi:10.1016/j.gca.2013.01.044.

Papadimitriou S, Kennedy H, Kennedy P, Thomas DN. 2014. Kinetics of ikaite precipitation and dissolution in seawater-derived brines at sub-zero temperatures to 265 K. *Geochim Cosmochim Acta* **140**: 199–211. doi: 10.1016/j.gca.2014.05.031.

Papadimitriou S, Kennedy H, Norman L, Kennedy DP, Dieckmann GS, et al. 2012. The effect of biological activity, $CaCO_3$ mineral dynamics, and CO_2 degassing in the inorganic carbon cycle in sea ice in late winter-early spring in the Weddell Sea, Antarctica. *J Geophys Res* **117**: C08011. doi:10.1029/2012JC008058.

Papadimitriou S, Thomas DN, Kennedy H, Haas C, Kuosa H, et al. 2007. Biogeochemical composition of natural sea ice brines from the Weddell Sea during early austral summer. *Limnol Oceanogr* **52**: 1809–1823.

Papadimitriou S, Thomas DN, Kennedy H, Kuosa H, Dieckmann GS. 2009. Inorganic carbon removal and isotopic enrichment in Antarctic sea ice gap layers during early austral summer. *Mar Ecol-Prog Ser* **386**: 15–27. doi: 10.3354/meps08049.

Papakyriakou T, Miller L. 2011. Springtime CO_2 exchange over seasonal sea ice in the Canadian Arctic Archipelago. *Ann Glaciol* **52**: 215–224.

Passow U. 2002. Transparent exopolymer particles (TEP) in aquatic environments. *Prog Oceanogr* **55**: 287–333.

Paterson H, Laybourn-Parry J. 2012. Sea ice microbial dynamics over an annual ice cycle in Prydz Bay, Antarctica. *Polar Biol* **35**: 993–1002. doi: 10.1007/s00300-011-1146-3.

Perovich D. 2009. Chapter 3.6, Sea ice optics measurements, in Eicken H, Gradinger R, Salganek M, Shirasawa K, Perovich D, et al., eds., *Field Techniques for Sea Ice Research*. Fairbanks: University of Alaska Press: pp. 215–229.

Perovich DK, Richter-Menge JA. 2009. Loss of sea ice in the Arctic. *Annu Rev Mar Sci* **1**: 417–441. doi: 10.1146/annurev.marine.010908.163805.

Petrich C, Eicken H. 2010. Growth, structure and properties of sea ice, in Thomas DN, Dieckmann GS, eds., *Sea Ice*. 2nd ed., Oxford: Wiley-Blackwell: 23–77.

Pineault S, Tremblay J-É, Gosselin M, Thomas H, Shadwick E. 2013. The isotopic signature of particulate organic C and N in bottom ice: Key influencing factors and applications for tracing the fate of ice-algae in the Arctic Ocean. *J Geophys Res-Oceans* **118**: 287–300. doi:10.1029/2012JC008331.

Piwosz K, Wiktor JM, Niemi A, Tatarek A, Michel C. 2013. Mesoscale distribution and functional diversity of picoeukaryotes in the first-year sea ice of the Canadian Arctic. *ISME J* **7**: 1461–1471. doi: 10.1038/ismej.2013.39.

Porter KG, Feig YS. 1980. The use of DAPI for identifying and counting aquatic microflora. *Limnol Oceanogr* **25**: 943–948.

Post E, Bhatt US, Bitz CM, Brodie JF, Fulton TL, et al. 2013. Ecological consequences of sea-ice decline. *Science* **341**: 519–524. doi: 10.1126/science.1235225.

Poulain AJ, Garcia E, Amyot M, Campbell PGC, Ariya PA. 2007. Mercury distribution, partitioning and speciation in coastal vs. inland high Arctic snow. *Geochim Cosmochim Acta* **71**: 3419–3431. doi: 10.1016/j.gca.2007.05.006.

Price NM, Harrison PJ. 1987. Comparison of methods for the analysis of dissolved urea in seawater. *Mar Biol* **94**: 307–317.

Prytherch J, Yelland MJ, Pascal RW, Moat BI, Skjelvan I, et al. 2010. Direct measurements of the CO_2 flux over the ocean: Development of a novel method. *Geophys Res Lett* **37**: L03607. doi:10.1029/2009GL041482.

Pućko M, Stern GA, Barber DG, Macdonald RW, Rosenberg B. 2010a. The International Polar Year (IPY) Circumpolar Flaw Lead (CFL) System Study: The importance of brine processes for α- and γ-hexachlorocyclohexane (HCH) accumulation or rejection in sea ice. *Atmos Ocean* **48**: 244–262. doi: 10.3137/OC318.2010.

Pućko M, Stern GA, Macdonald RW, Barber DG. 2010b. α- and γ-hexachlorocyclohexane measurements in the brine fraction of sea ice in the Canadian high Arctic using a sump-hole technique. *Environ Sci Technol* **44**: 9258–9264. doi: 10.1021/es102275b.

Qian J, Mopper K. 1996. Automated high-performance, high-temperature combustion total organic carbon analyzer. *Anal Chem* **68**: 3090–3097.

Ragueneau O, Savoye N, Del Amo Y, Cotten J, Tardiveau B, et al. 2005. A new method for the measurement of biogenic silica in suspended matter of coastal waters: using Si:Al ratios to correct for the mineral interference. *Cont Shelf Res* **25**: 697–710. doi: 10.1016/j.csr.2004.09.017.

Rahm L, Håkansson B, Larsson P, Fogelqvist E, Bremle G, et al. 1995. Nutrient and persistent pollutant deposition on the Bothnian Bay ice and snow fields. *Water Air Soil Poll* **84**: 187–201.

Ralph PJ, Gademann R. 2005. Rapid light curves: A powerful tool to assess photosynthetic activity. *Aquat Bot* **82**: 222–237. doi: 10.1016/j.aquabot.2005.02.006.

Ralph PJ, Ryan KG, Martin A, Fenton G. 2007. Melting out of sea ice causes greater photosynthetic stress in algae than freezing in. *J Phycol* **43**: 948–956. doi: 10.1111/j.1529-8817.2007.00382.x.

Randall K, Scarratt M, Levasseur M, Michaud S, Xie H, et al. 2012. First measurements of nitrous oxide in Arctic sea ice. *J Geophys Res* **117**: C00G15. doi: 10.1029/2011JC007340.

Rau GH, Sullivan CW, Gordon LI. 1991. $\delta^{13}C$ and $\delta^{15}N$ variations in Weddell Sea particulate organic matter. *Mar Chem* **35**: 355–369.

Raymond B, Meiners K, Fowler CW, Pasquer B, Williams GD, et al. 2009. Cumulative solar irradiance and potential large-scale sea ice algae distribution off East Antarctica (30°E–150°E). *Polar Biol* **32**: 443–452. doi: 10.1007/s00300-008-0538-5.

Renaud PE, Riedel A, Michel C, Morata N, Gosselin M, et al. 2007. Seasonal variation in benthic community oxygen demand: A response to an ice algal bloom in the Beaufort Sea, Canadian Arctic? *J Marine Syst* **67**: 1–12. doi: 10.1016/j.jmarsys.2006.07.006.

Riedel A, Michel C, Gosselin M. 2006. Seasonal study of sea-ice exopolymeric substances on the Mackenzie shelf: Implications for transport of sea-ice bacteria and algae. *Aquat Microb Ecol* **45**: 195–206.

Riedel A, Michel C, Gosselin M. 2007a. Grazing of large-sized bacteria by sea-ice heterotrophic protists on the Mackenzie Shelf during the winter-spring transition. *Aquat Microb Ecol* **50**: 25–38. doi:10.3354/ame01155.

Riedel A, Michel C, Gosselin M, LeBlanc B. 2007b. Enrichment of nutrients, exopolymeric substances and microorganisms in newly formed sea ice on the Mackenzie shelf. *Mar Ecol-Prog Ser* **342**: 55–67.

Riedel A, Michel C, Gosselin M, LeBlanc B. 2008. Winter-spring dynamics in sea-ice carbon cycling in the coastal Arctic Ocean. *J Marine Syst* **74**: 918–932. doi: 10.1016/j.jmarsys.2008.01.003.

Riederer M, Serafimovich A, Foken T. 2014. Net ecosystem CO_2 exchange measurements by the closed chamber method and the eddy covariance technique and their dependence on atmospheric conditions. *Atmos Meas Tech* **7**: 1057–1064. doi:10.5194/amt-7-1057-2014.

Ringer WE. 1928. Ueber die Veränderungen in der Zusammensetzung des Meereswassersalzes beim Ausfrieren. Copenhagen: Conseil Permanent International Pour L'Exploration de la Mer. Volume 47.

Rivkin RB, Legendre L. 2001. Biogenic carbon cycling in the upper ocean: Effects of microbial respiration. *Science* **291**: 2398–2400.

Robinson DH, Arrigo KR, Kolber Z, Gosselin M, Sullivan CW. 1998. Photophysiological evidence of nutrient limitation of platelet ice algae in McMurdo Sound, Antarctica. *J Phycol* **34**: 788–797.

Roscoe HK, Brooks B, Jackson AV, Smith MH, Walker SJ, et al. 2011. Frost flowers in the laboratory: Growth, characteristics, aerosol, and the underlying sea ice. *J Geophys Res* **116**: D12301. doi:10.1029/2010JD015144.

Roy S, Llewellyn CA, Egeland ES, Johnsen G. 2011. *Phytoplankton Pigments: Characterization, Chemotaxonomy and Applications in Oceanography*. Cambridge: Cambridge University Press.

Rusch DB, Halpern AL, Sutton G, Heidelberg KB, Williamson S, et al. 2007. The *Sorcerer II* global ocean sampling expedition: Northwest Atlantic through eastern Tropical Pacific. *PLoS Biology* **5**(3): e77. doi: 10.1371/journal.pbio.0050077.

Russell LM. 2014. Carbonaceous particles: Source-based characterization of their formation, composition, and structures, in Holland HD and Turekian KK, eds., *Treatise on Geochemistry*. Second ed. Oxford: Elsevier: pp. 291–316.

Ryan KG, McMinn A, Mitchell KA, Trenerry L. 2002. Mycosporine-like amino acids in Antarctic sea ice algae, and their response to UVB radiation. *Z Naturforsch* **54c**: 471–477.

Rysgaard S, Bendtsen J, Delille B, Dieckmann GS, Glud RN, et al. 2011. Sea ice contribution to the air-sea CO_2 exchange in the Arctic and Southern Oceans. *Tellus B* **63**: 823–830. doi: 10.1111/j.1600-0889.2011.00571.x.

Rysgaard S, Bendtsen J, Pedersen LT, Ramløv H, Glud RN. 2009. Increased CO_2 uptake due to sea ice growth and decay in the Nordic Seas. *J Geophys Res* **114**: C09011. doi:10.1029/2008JC005088.

Rysgaard S, Glud RN. 2004. Anaerobic N_2 production in Arctic sea ice. *Limnol Oceanogr* **49**: 86–94.

Rysgaard S, Glud RN, Lennert K, Cooper M, Halden N, et al. 2012. Ikaite crystals in melting sea ice - implications for pCO_2 and pH levels in Arctic surface waters. *The Cryosphere* **6**: 901–908. doi:10.5194/tc-6-901-2012.

Rysgaard S, Glud RN, Sejr MK, Bendtsen J, Christensen PB. 2007. Inorganic carbon transport during sea ice growth and decay: A carbon pump in polar seas. *J Geophys Res* **112**: C03016. doi:10.1029/2006JC003572.

Rysgaard S, Glud RN, Sejr MK, Blicher ME, Stahl HJ. 2008. Denitrification activity and oxygen dynamics in Arctic sea ice. *Polar Biol* **31**: 527–537. doi: 10.1007/s00300-007-0384-x.

Rysgaard S, Kühl M, Glud RN, Hansen JW. 2001. Biomass, production and horizontal patchiness of sea ice algae in a high-Arctic fjord (Young Sound, NE Greenland). *Mar Ecol-Prog Ser* **223**: 15–26.

Rysgaard S, Søgaard DH, Cooper M, Pućko M, Lennert K, et al. 2013. Ikaite crystal distribution in winter sea ice and implications for CO_2 system dynamics. *The Cryosphere* **7**: 707–718. doi: 10.5194/tc-7-707-2013.

Satoh H, Watanabe K. 1988. Primary productivity in the fast ice area near Syowa Station, Antarctica, during spring and summer 1983/84. *J Oceanogr Soc Japan* **44**: 287–292.

Schubert CJ, Calvert SE. 2001. Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition. *Deep-Sea Res Pt I* **48**: 789–810.

Scully NM, Miller WL. 2000. Spatial and temporal dynamics of colored dissolved organic matter in the North Water Polynya. *Geophys Res Lett* **27**: 1009–1011.

Sejr MK, Krause-Jensen D, Rysgaard S, Sørensen LL, Christensen PB, et al. 2011. Air-sea flux of CO_2 in arctic coastal waters influenced by glacial melt water and sea ice. *Tellus B* **63**: 815–822. doi: 10.1111/j.1600-0889.2011.00540.x.

Semiletov I, Makshtas A, Akasofu S-I, Andreas EL. 2004. Atmospheric CO_2 balance: The role of Arctic sea ice. *Geophys Res Lett* **31**: L05121. doi:10.1029/2003GL017996.

Shaw MD, Carpenter LJ, Baeza-Romero MT, Jackson AV. 2011. Thermal evolution of diffusive transport of atmospheric halocarbons through artificial sea-ice. *Atmos Environ* **45**: 6393–6402. doi: 10.1016/j.atmosenv.2011.08.023.

Sherman LS, Blum JD, Douglas TA, Steffen A. 2012. Frost flowers growing in the Arctic ocean-atmosphere-sea ice-snow interface: 2. Mercury exchange between the atmosphere, snow, and frost flowers. *J Geophys Res* **117**: D00R10. doi: 10.1029/2011JD016186.

Sigman DM, Casciotti KL, Andreani M, Barford C, Galanter M, et al. 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal Chem* **73**: 4145–4153.

Sime-Ngando T, Juniper SK, Demers S. 1997. Ice-brine and planktonic microheterotrophs from Saroma-ko Lagoon, Hokkaido (Japan): quantitative importance and trophodynamics. *J Marine Syst* **11**: 149–161.

Simpson WR, Alvarez-Aviles L, Douglas TA, Sturm M, Domine F. 2005. Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime. *Geophys Res Lett* **32**: L04811. doi: 10.1029/2004GL021748.

Simpson WR, von Glasow R, Riedel K, Anderson P, Ariya P, et al. 2007. Halogens and their role in polar boundary-layer ozone depletion. *Atmos Chem Phys* **7**: 4375–4418.

Smedsrud LH, Skogseth R. 2006. Field measurements of Arctic grease ice properties and processes. *Cold Reg Sci Technol* **44**: 171–183. doi: 10.1016/j.coldregions.2005.11.002.

Smith REH, Clement P. 1990. Heterotrophic activity and bacterial productivity in assemblages of microbes from sea ice in the high Arctic. *Polar Biol* **10**: 351–357.

So A, Pel J, Rajan S, Marziali A. 2010. Efficient genomic DNA extraction from low target concentration bacterial cultures using SCODA DNA extraction technology. *Cold Spring Harb Protoc* **2010**: 1150–1153, 1185–1198. doi:10.1101/pdb.prot5506.

Søgaard DH, Kristensen M, Rysgaard S, Glud RN, Hansen PJ, et al. 2010. Autotrophic and heterotrophic activity in Arctic first-year sea ice: seasonal study from Malene Bight, SW Greenland. *Mar Ecol-Prog Ser* **419**: 31–45. doi: 10.3354/meps08845.

Søgaard DH, Thomas DN, Rysgaard S, Glud RN, Norman L, et al. 2013. The relative contributions of biological and abiotic processes to carbon dynamics in subarctic sea ice. *Polar Biol* **36**: 1761–1777. doi:10.1007/s00300-013-1396-3.

Song G, Xie H, Aubry C, Zhang Y, Gosselin M, et al. 2011. Spatiotemporal variations of dissolved organic carbon and carbon monoxide in first-year sea ice in the western Canadian Arctic. *J Geophys Res* **116**: C00G05. doi: 10.1029/2010JC006867.

Sørensen LL, Jensen B, Glud RN, McGinnis DF, Sejr MK, et al. 2014. Parameterization of atmosphere-surface exchange of CO_2 over sea ice. *The Cryosphere* **8**: 853–866. doi:10.5194/tc-8-853-2014.

Sørensen LL, Larsen SE. 2010. Atmosphere-surface fluxes of CO_2 using spectral techniques. *Bound-Layer Meteorol* **136**: 59–81. doi: 10.1007/s10546-010-9499-7.

Sørensen LL, Pryor SC, de Leeuw G, Schulz M. 2005. Flux divergence of nitric acid in the marine atmospheric surface layer. *J Geophys Res* **110**: D15306. doi: 10.1029/2004JD005403.

Spindler M, Dieckmann GS. 1986. Distribution and abundance of the planktic foraminifer *Neogloboquadrina pachyderma* in sea ice of the Weddell Sea (Antarctica). *Polar Biol* **5**: 185–191.

Spyres G, Nimmo M, Worsfold PJ, Achterberg EP, Miller AEJ. 2000. Determination of dissolved organic carbon in seawater using high temperature catalytic oxidation techniques. *TrAC Trends Anal Chem* **19**(8): 498–506.

Stedmon CA, Thomas DN, Granskog M, Kaartokallio H, Papadimitriou S, et al. 2007. Characteristics of dissolved organic matter in Baltic coastal sea ice: Allochthonous or autochthonous origins? *Environ Sci Technol* **41**: 7273–7279. doi: 10.1021/es071210f.

Stedmon CA, Thomas DN, Papadimitriou S, Granskog MA, Dieckmann GS. 2011. Using fluorescence to characterize dissolved organic matter in Antarctic sea ice brines. *J Geophys Res* **116**: G03027. doi: 10.1029/2011JG001716.

Steele JH, Turekian KK, Thorpe SA, eds. 2001. Appendix 2, Useful Values, in, *Encyclopedia of Ocean Sciences*. 2nd ed. Oxford: Academic Press: 376.

Stefels J, Carnat G, Dacey JWH, Goossens T, Elzenga JTM, et al. 2012. The analysis of dimethylsulfide and dimethylsulfoniopropionate in sea ice: Dry-crushing and melting using stable isotope additions. *Mar Chem* **128–129**: 34–43. doi: 10.1016/j.marchem.2011.09.007.

Steffens M, Granskog MA, Kaartokallio H, Kuosa H, Luodekari K, et al. 2006. Spatial variation of biogeochemical properties of landfast sea ice in the Gulf of Bothnia, Baltic Sea. *Ann Glaciol* **44**: 80–87.

Sturges WT, Cota GF, Buckley PT. 1997. Vertical profiles of bromoform in snow, sea ice, and seawater in the Canadian Arctic. *J Geophys Res* **102**(C11): 25,073–25,083.

Sturm M. 2009. Field techniques for snow observations on sea ice, in Eicken H, Gradinger R, Salganek M, Shirasawa K, Perovich D, et al., eds., *Field Techniques for Sea Ice Research*. Fairbanks: University of Alaska Press: pp. 25–47.

Suggett DJ, Oxborough K, Baker NR, Macintyre HL, Kana TM, et al. 2003. Fast repetition rate and pulse amplitude modulation chlorophyll *a* fluorescence measurements for assessment of photosynthetic electron transport in marine phytoplankton. *Eur J Phycol* **38**: 371–384. doi: 10.1080/0967026031000161265 5.

Swadling KM, Gibson JAE, Ritz DA, Nichols PD. 1997. Horizontal patchiness in sympagic organisms of the Antarctic fast ice. *Antarct Sci* **9**: 399–406.

Swinbank WC. 1951. The measurement of vertical transfer of heat and water vapor by eddies in the lower atmosphere. *J Meteorol* **8**: 135–145.

Tebbe CC, Vahjen W. 1993. Interference of humic acids and DNA extracted directly from soil in detection and transformation of recombinant DNA from bacteria and a yeast. *Appl Environ Microb* **59**: 2657–2665.

Thomas DN, Lara RJ, Eicken H, Kattner G, Skoog A. 1995. Dissolved organic matter in Arctic multi-year sea ice during winter: Major components and relationship to ice characteristics. *Polar Biol* **15**: 477–483.

Thomas DN, Lara RJ, Haas C, Schnack-Schiel SB, Dieckmann GS, et al. 1998. Biological soup within decaying summer sea ice in the Amundsen Sea, Antarctica, in Lizotte MP, Arrigo KR, eds., *Antarctic Sea Ice: Biological Processes, Interactions and Variability*. Washington: American Geophysical Union: pp. 161–171.

Thomas DN, Kattner G, Engbrodt R, Giannelli V, Kennedy H, et al. 2001a. Dissolved organic matter in Antarctic sea ice. *Ann Glaciol* **33**: 297–303.

Thomas DN, Kennedy H, Kattner G, Gerdes D, Gough C, et al. 2001b. Biogeochemistry of platelet ice: Its influence on particle flux under fast ice in the Weddell Sea, Antarctica. *Polar Biol* **24**: 486–496.

Thomas DN, Papadimitriou S, Michel C. 2010. Biogeochemistry of sea ice, in Thomas DN, Dieckmann GS, eds., *Sea Ice*. 2nd ed., Chichester: Wiley-Blackwell: pp. 425–467.

Tison J-L, Brabant F, Dumont I, Stefels J. 2010. High-resolution dimethyl sulfide and dimethylsulfoniopropionate time series profiles in decaying summer first-year sea ice at Ice Station Polarstern, western Weddell Sea, Antarctica. *J Geophys Res* **115**: G04044. doi: 10.1029/2010JG001427.

Tison J-L, Haas C, Gowing MM, Sleewaegen S, Bernard A. 2002. Tank study of physico-chemical controls on gas content and composition during growth of young sea ice. *J Glaciol* **48**: 177–191.

Tison J-L, Worby A, Delille B, Brabant F, Papdimitriou S, et al. 2008. Temporal evolution of decaying summer first-year sea ice in the Western Weddell Sea, Antarctica. *Deep-Sea Res Pt II* **55**: 975–987. doi: 10.1016/j.dsr2.2007.12.021.

Tovar-Sánchez A, Duarte CM, Alonso JC, Lacorte S, Tauler R, et al. 2010. Impacts of metals and nutrients released from melting multiyear Arctic sea ice. *J Geophys Res* **115**: C07003. doi: 10.1029/2009JC005685.

Tremblay J-É, Michel C, Hobson KA, Gosselin M, Price NM. 2006. Bloom dynamics in early opening waters of the Arctic Ocean. *Limnol Oceanogr* **51**(2): 900–912.

Trevena AJ, Jones GB. 2006. Dimethylsulphide and dimethylsulphoniopropionate in Antarctic sea ice and their release during sea ice melting. *Mar Chem* **98**: 210–222. doi: 10.1016/j.marchem.2005.09.005.

Trevena AJ, Jones GB, Wright SW, van den Enden RL. 2000. Profiles of DMSP, algal pigments, nutrients and salinity in pack ice from eastern Antarctica. *J Sea Res* **43**: 265–273.

Tsurikov VL. 1965. Formation of the ionic composition and salinity of sea ice. *Oceanology* **5**: 59–66.

Turner SM, Nightingale PD, Broadgate W, Liss PS. 1995. The distribution of dimethyl sulphide and dimethylsulphoniopropionate in Antarctic waters and sea ice. *Deep-Sea Res Pt II* **42**: 1059–1080.

Tütken T, Eisenhauer A, Wiegand B, Hansen BT. 2002. Glacial-interglacial cycles in Sr and Nd isotopic composition of Arctic marine sediments triggered by the Svalbard/Barents Sea ice sheet. *Mar Geol* **182**: 351–372.

Underwood GJC, Aslam SN, Michel C, Niemi A, Norman L, et al. 2013. Broad-scale predictability of carbohydrates and exopolymers in Antarctic and Arctic sea ice. *P Natl Acad Sci* **100**(39): 15734–15739. doi:10.1073/pnas.1302870110.

Underwood GJC, Fietz S, Papadimitriou S, Thomas DN, Dieckmann GS. 2010. Distribution and composition of dissolved extracellular polymeric substances (EPS) in Antarctic sea ice. *Mar Ecol-Prog Ser* **404**: 1–19. doi:10.3354/meps08557.

Uusikivi J, Vähätalo AV, Granskog MA, Sommaruga R. 2010. Contribution of mycosporine-like amino acids and colored dissolved and particulate matter to sea ice optical properties and ultraviolet attenuation. *Limnol Oceanogr* **55**: 703–713.

van der Merwe P, Lannuzel D, Bowie AR, Mancuso Nichols CA, Meiners KM. 2011a. Iron fractionation in pack and fast ice in East Antarctica: Temporal decoupling between the release of dissolved and particulate iron during spring melt. *Deep-Sea Res Pt II* **58**: 1222–1236. doi: 10.1016/j.dsr2.2010.10.036.

van der Merwe P, Lannuzel D, Bowie AR, Meiners KM. 2011b. High temporal resolution observations of spring fast ice melt and seawater iron enrichment in East Antarctica. *J Geophys Res* **116**: G03017. doi:10.1029/2010JG001628.

van der Merwe P, Lannuzel D, Mancuso Nichols CA, Meiners K, Heil P, et al. 2009. Biogeochemical observations during the winter-spring transition in East Antarctic sea ice: Evidence of iron and exopolysaccharide controls. *Mar Chem* **115**: 163–175. doi:10.1016/j.marchem.2009.08.001.

Vancoppenolle M, Goosse H, de Montety A, Fichefet T, Tremblay B, et al. 2010. Modeling brine and nutrient dynamics in Antarctic sea ice: The case of dissolved silica. *J Geophys Res* **115**: C02005. doi:10.1029/2009JC005369.

Vancoppenolle M, Meiners KM, Michel C, Bopp L, Brabant F, et al. 2013. Role of sea ice in global biogeochemical cycles: emerging views and challenges. *Quat Sci Rev* **79**: 207–230. doi: 10.1016/j.quascirev.2013.04.011.

Vesala T, Kljun N, Rannik U, Rinne J, Sogachev A, et al. 2008. Flux and concentration footprint modelling: State of the art. *Environ Pollut* **152**(3): 653–666. doi:10.1016/j.envpol.2007.06.070.

Vihma T, Johansson MM, Launiainen J. 2009. Radiative and turbulent surface heat fluxes over sea ice in the western Weddell Sea in early summer. *J Geophys Res* **114**: C04019. doi:10.1029/2008JC004995.

Wadhams P, Doble MJ. 2008. Digital terrain mapping of the underside of sea ice from a small AUV. *Geophys Res Lett* **35**: L01501. doi:10.1029/2007GL031921.

Wang K, Liu C, Zheng X, Pihlatie M, Li B, et al. 2013. Comparison between eddy covariance and automatic chamber techniques for measuring net ecosystem exchange of carbon dioxide in cotton and wheat fields. *Biogeosciences* **10**: 6865–6877. doi: 10.5194/bg-10-6865-2013.

Wang Y, Hammes F, Boon N, Egli T. 2007. Quantification of the filterability of freshwater bacteria through 0.45, 0.22, and 0.1 µm pore size filters and shape-dependent enrichment of filterable bacterial communities. *Environ Sci Technol* **41**: 7080–7086. doi: 10.1021/es0707198.

Wangersky PJ. 1993. Dissolved organic carbon methods: a critical review. *Mar Chem* **41**: 61–74.

Weissenberger J. 1992. The environmental conditions in the brine channels of Antarctic sea-ice. *Ber Polarfosch* **111**: 1–159.

Welch HE, Bergmann MA, Jorgenson JK, Burton W. 1988. A subice suction corer for sampling epontic ice algae. *Can J Fish Aquat Sci* **45**: 562–568.

Wells LE, Deming JW. 2006. Modelled and measured dynamics of viruses in Arctic winter sea-ice brines. *Environ. Microbiol* **8**: 1115–1121. doi: 10.1111/j.1462-2920.2005.00984.x.

Westerlund S, Öhman P. 1991. Iron in the water column of the Weddell Sea. *Mar Chem* **35**: 199–217.

Wiese W. 1930. Zur Kenntnis der Salze des Meereises. *Annalen der Hydrographie und Maritimen Meteorologie* **58**: 282–286.

Williams GD, Maksym T, Kunz C, Kimball P, Singh H, et al. 2013. Beyond point measurements: Sea ice floes characterized in 3-D. *EOS* **94**: 69–70. doi:10.1002/2013EO070002.

Winston GC, Stephens BB, Sundquist ET, Hardy JP, Davis RE. 1995. Seasonal variability in CO_2 transport through snow in a boreal forest, in Tonnessen KA, Williams MW, Tranter M, eds., *Biogeochemistry of Seasonally Snow-Covered Catchments*. Boulder: IAHS: pp. 61–70.

Winton VHL, Dunbar GB, Bertler NAN, Millet M-A, Delmonte B, et al. 2014. The contribution of aeolian sand and dust to iron fertilization of phytoplankton blooms in southwestern Ross Sea, Antarctica. *Glob Biogeochem Cy* **28**: 423–436. doi: 10.1002/2013GB004574.

Wren SN, Donaldson DJ. 2012. Laboratory study of pH at the air-ice interface. *J Phys Chem C* **116**: 10,171–10,180. doi: 10.1021/jp3021936.

Wright SW, Jeffrey SW. 2006. Pigment markers for phytoplankton production, in Volkman JK, ed., *Marine Organic Matter: Biomarkers, Isotopes and DNA*. Heidelberg: Springer-Verlag: pp. 71–104.

Xie H, Gosselin M. 2005. Photoproduction of carbon monoxide in first-year sea ice in Franklin Bay, southeastern Beaufort Sea. *Geophys Res Lett* **32**: L12606. doi: 10.1029/2005GL022803.

Xu L, Furtaw MD, Madsen RA, Garcia RL, Anderson DJ, et al. 2006. On maintaining pressure equilibrium between a soil CO_2 flux chamber and the ambient air. *J Geophys Res* **111**: C08S10. doi: 10.1029/2005JD006435.

Yang X, Pyle JA, Cox RA. 2008. Sea salt aerosol production and bromine release: Role of snow on sea ice. *Geophys Res Lett* **35**: L16815. doi: 10.1029/2008GL034536.

Zeebe RE, Wolf-Gladrow D. 2001. *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes*. San Francisco: Elsevier.

Zemmelink HJ, Dacey JWH, Houghton L, Hintsa EJ, Liss PS. 2008. Dimethylsulfide emissions over the multi-year ice of the western Weddell Sea. *Geophys Res Lett* **35**: L06603. doi: 10.1029/2007GL031847.

Zemmelink HJ, Delille B, Tison JL, Hintsa EJ, Houghton L, et al. 2006. CO_2 deposition over the multi-year ice of the western Weddell Sea. *Geophys Res Lett* **33**: L13606. doi: 10.1029/2006GL026320.

Zhou J, Delille B, Brabant F, Tison J-L. 2014b. Insights into oxygen transport and net community production in sea ice from oxygen, nitrogen and argon concentrations. *Biogeosciences* **11**: 5007–5020. doi: 10.5194/bg-11-5007-2014.

Zhou J, Delille B, Eicken H, Vancoppenolle M, Brabant F, et al. 2013. Physical and biogeochemical properties in landfast sea ice (Barrow, Alaska): Insights on brine and gas dynamics across seasons. *J Geophys Res-Oceans* **118**: 3172–3189. doi: 10.1002/jgrc.20232.

Zhou J, Tison J-L, Carnat G, Geilfus N-X, Delille B. 2014a. Physical controls on the storage of methane in landfast sea ice. *The Cryosphere* **8**: 1019–1029. doi: 10.5194/tc-8-1-2014.

Contributions

- LAM wrote the first draft and coordinated and synthesized the contributions from the other authors.
- FF and BGTE contributed material and coordinated and synthesized contributions for sections 3 and 5, respectively.
- All other authors contributed material.

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Competing interest

To the best of our knowledge, none of the authors have a competing interest in the publication of this manuscript.

Data accessibility statement

This manuscript does not present original data.