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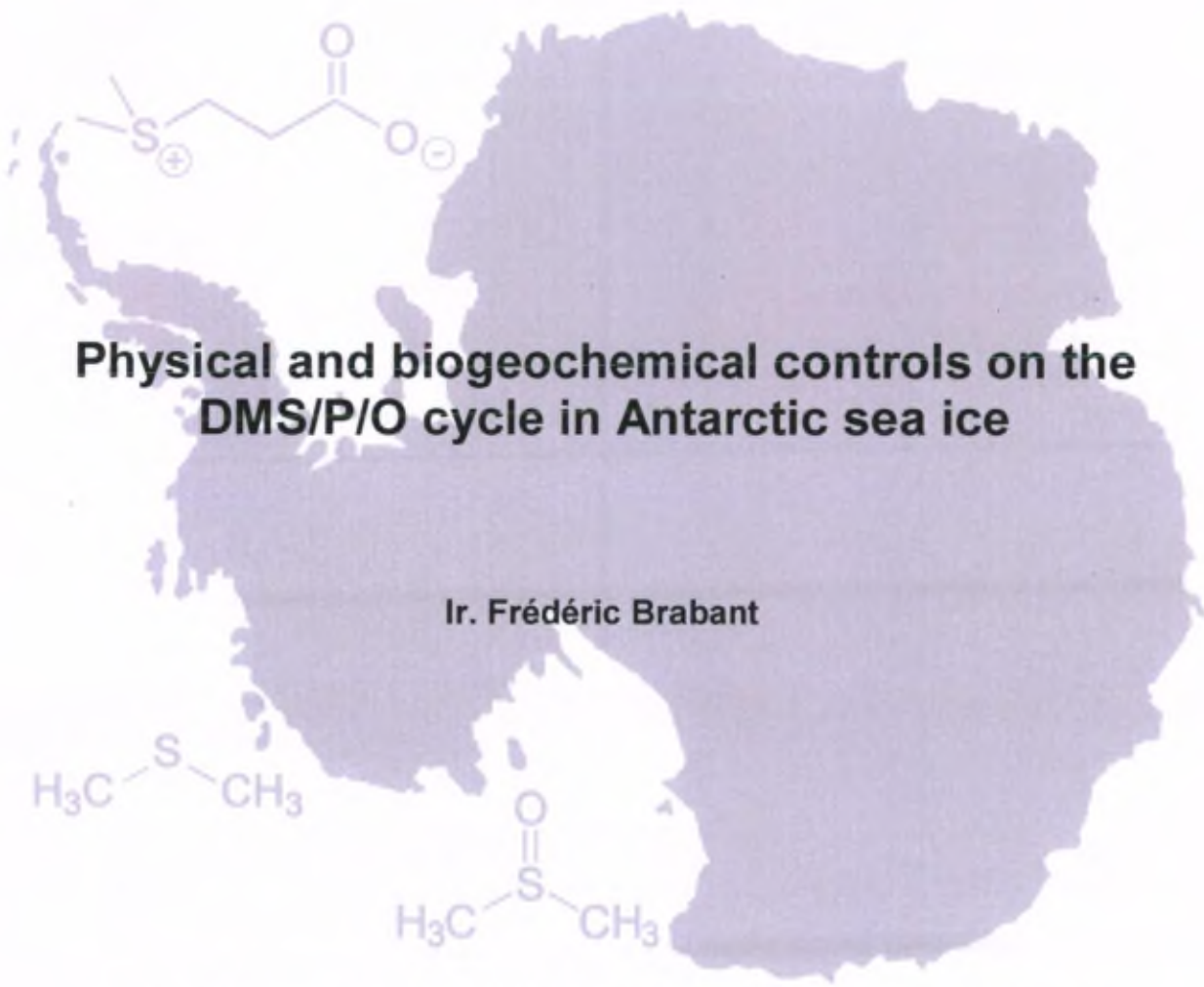


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Université Libre de Bruxelles

Faculté des Sciences – Ecole Interfacultaire de Bioingénieurs

Laboratoire de Glaciologie



Physical and biogeochemical controls on the DMS/P/O cycle in Antarctic sea ice

Ir. Frédéric Brabant

Thèse de doctorat présentée en vue de l'obtention du grade de
Docteur en Sciences agronomiques et Ingénierie biologique

Juillet 2012

Promoteur : Prof. J.-L. TISON

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CHAPTER I: Introduction

Sea ice as a material

As material, sea ice is a semi-solid matrix of nearly pure ice crystals that incorporates bubbles of gas and brine inclusions in the form of pockets, tubes or as a network of brine channels [e.g., Weeks and Ackley 1986; Trodahl et al. 2001]. Depending on the conditions prevailing during its growth, various texture profiles can be encountered. The stratigraphy of a 'typical' ice cover generally comprises layers of different texture and usually consists of a sequence of granular ice, transitional layer and columnar ice [Petrich and Eicken, 2010 and references therein]. Granular texture, whose formation generally initiates that of the sea ice cover, originates from the consolidation of millimetric individual platelet-, spicule- or needle-shaped frazil ice crystals growing in the turbulent uppermost metres of the water column agitated by the combined effect of mixed layer and wind stress [Petrich and Eicken, 2010]. This texture class generally dominates in the Antarctic. Quiescent conditions, generally favoured by the presence of an ice slush layer which mitigates mixing by wind, are necessary for columnar ice (a.k.a. congelation ice) to start its growth. Columnar ice is composed of vertically elongated prismatic crystals whose dimensions can be as large as several centimetres in diameter and tens of centimetres in length [Weeks and Ackley, 1986; Petrich and Eicken, 2010]. When loose frazil ice crystals consolidate into a solid granular ice layer or when columnar ice forms, voids in the ice crystal lattice are reduced and do not allow the incorporation of the major ions present in seawater, that are rejected ahead the advancing freezing front. While the larger fraction of impurities and salts is rejected into the underlying water column, part of the salt is retained in the solid ice matrix and contributes to maintain a significant liquid fraction in the form of brine inclusions [Petrich et al., 2010]. The presence of a brine microstructure in sea ice has profound implications on its ability to host life forms and exchange material (particulate, dissolved or gaseous) with its environment and distinguishes sea ice from ice grown in freshwater bodies like lakes.

Sea ice significance

Areal extent – Depending on the season, sea ice in Polar Regions covers from 3 to 6% of the total surface area of the globe with an extent ranging between $16.6 \times 10^6 \text{ km}^2$ and $27.5 \times 10^6 \text{ km}^2$, making of the sea ice cover one of the most expansive and most seasonal geophysical

parameters on the earth's surface [Comiso, 2010]. With an areal extent ranging between $3.6 \times 10^6 \text{ km}^2$ in winter and $18.8 \times 10^6 \text{ km}^2$ in summer [Comiso, 2010], Antarctic sea ice is the main contributor to the oceanic component of the cryosphere and might maintain this status in the future in the view of the trend towards a global increase of the sea ice extent in the Southern Ocean [Zhang et al., 2007] compared with the observed accelerating decline of sea ice in the Arctic [Stroeve et al., 2007] (see comparative trends in sea ice extent in Figure 1). The vast majority of Antarctic sea ice is pack ice that is offshore sea ice submitted to drifting under the action of winds and current (as opposed to land fast sea ice anchored to the shore or the ocean bottom). With a maximum extent of $0.8 \times 10^6 \text{ km}^2$, land fast sea ice would only account for ~5% of the total Antarctic sea ice extent [Fedotov et al., 1998 and references therein].

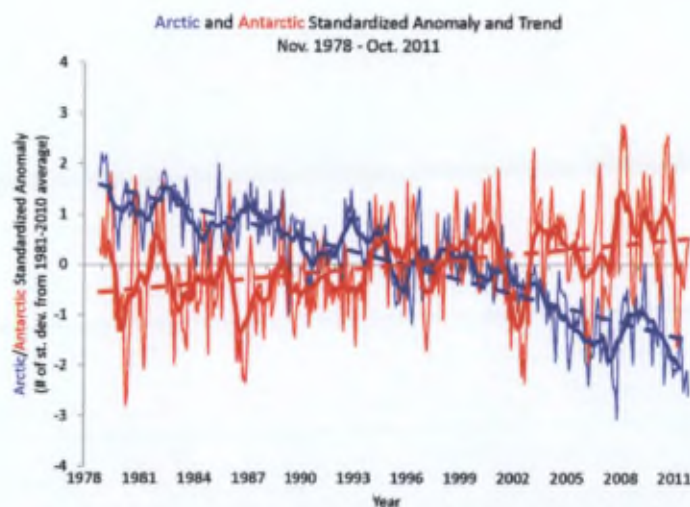


Figure 1 Arctic and Antarctic Sea Ice Extent Anomalies, 1979-2011: Arctic sea ice extent underwent a strong decline from 1979 to 2011, but Antarctic sea ice underwent a slight increase, although some regions of the Antarctic experienced strong declining trends in sea ice extent. Thick lines indicate 12-month running means, and thin lines indicate monthly anomalies. Graph courtesy of the National Snow and Ice Data Center, University of Colorado, Boulder, 2011.

Recent studies confirm that the observed decline of Arctic sea ice is well faster than what is generally predicted by general circulation models [Kay et al., 2011]. The overall trend towards increasing sea ice extent in the Antarctic is however very likely to hide marked regional trends to decrease (e.g. around the Antarctic Peninsula) that could have consequences at a larger scale [Stammerjohn et al., 2008]. In their modeling effort to assess the influence of increased loading of greenhouse gases in the atmosphere through the 21st century, Liu and Curry [2010] suggested that Antarctic sea ice could soon initiate a global decline in response

to increased ocean and air temperatures and increased liquid precipitation associated with the enhanced hydrological cycle.

Climate regulation - As sea ice is subject to climate change, it is also an actor of the earth's climate regulation. Through its seasonal mediation on the exchanges of heat, momentum, moisture and gas between the ocean and the atmosphere in Polar Regions, sea ice exerts an influence on the climate at global scale. With significantly higher albedo values than open water [Perovich, 2003], sea ice exposes a large reflective surface to incoming solar radiation and avoids a substantial portion of it to heat the upper layers of the ocean. Existence of feedback mechanisms like the ice-albedo feedback [Massom and Stammerjohn, 2010 and references therein] further supports the increasing importance attached to sea ice in the perspective of a change in the climate. Cold and dense brine rejection from sea ice during its growth is acknowledged as the driver of the global thermohaline circulation, which is also influenced by the freshening of the upper layers of the ocean on sea ice melting [Lubin and Massom, 2006 and references therein; cited by Massom and Stammerjohn, 2010].

Sea ice was until recently still considered as an impermeable barrier to gas exchanges between the ocean and the atmosphere [Tréguer and Pondaven, 2002] despite Gosink et al. [1976] already demonstrated, almost three decades ago, that sea ice above -15 °C was permeable to gas. Emerging work suggests that sea ice exerts a control on the atmospheric CO₂ of Polar Regions through physical and biogeochemical processes [Rysgaard et al., 2011]. Those recent findings should encourage the scientific community to now consider the biogeochemical aspect of the earth's climate regulation by sea ice (mediation of climatically significant gases) besides its already acknowledged physical aspect (surface radiative budget and thermohaline circulation) and include it into numerical models. Those findings could indeed worsen the prediction produced by global circulation models, which presently evade such a control of sea ice on the atmospheric CO₂ in Polar Regions, by racing the already existing physical ice-albedo feedback.

Sea ice and polar waters biota – Formation of granular or columnar ice layers (see above) leads to the incorporation of dissolved and particulate biological material including microalgae, heterotrophic protists and bacteria [Ackley and Sullivan, 1994; Rozanska et al., 2008]. The persistence of a liquid brine microstructure even at low temperatures allows autotrophic organisms to survive in the ice where they can develop substantial standing stocks

[see Arrigo et al., 2010, for an extensive review of algal biomass in the Arctic and in the Antarctic], representing thereby the only source of fixed carbon for higher trophic levels (e.g. Antarctic krill [Quetin and Ross, 2009]) in ice covered waters. Ice algal production would account for up to 10 to 28% of primary production in Antarctic ice covered waters [Arrigo, 2004 and references therein]. Sea ice also plays a crucial role for polar oceans biota on its decay. When sea ice melts, it inoculates the upper ocean with the release of biological material and essential (micro-) nutrients accumulated in the ice and snow cover during winter and spring, amongst which Fe, known to be limiting for algal growth in Southern Ocean waters [Lannuzel et al., 2006; 2007]. By the combined effects of stabilisation of the ocean mixed layer by the meltwater, which maintains autotrophic organisms exposed to elevated light levels, and favourable timing in the release of biogeochemical tracers from melting [Dumont, 2009], sea ice contributes to trigger development of large algal blooms in the Southern Ocean [Arrigo et al., 2008; Vernet et al., 2008].

Sea ice algae and habitat – Within ice assemblages, diatoms are generally the dominant taxa and would have the most of the sea ice photosynthetic production to its credit [Lizotte, 2003]. Other commonly encountered taxa like dinoflagellates, chlorophytes, prymnesiophytes, prasinophytes and chrysophytes may become dominant later in the season or in particular sea-ice habitats (e.g. *Phaeocystis* sp. proliferates in summer ice surface assemblages) [Mock and Thomas, 2005]. Although generally flourishing at the bottom of the ice cover where environmental conditions are generally stable (temperature, salinity, light level) and access to nutrients warranted, ice algal assemblages can develop elsewhere in the ice cover, generally ensuing invasion of the ice cover by seawater. Development of infiltration communities at the surface and freeboard (or gap layer) communities are common features in Antarctic sea ice, generally associated with high biomass and high values of dissolved organic substances thanks to both sustained supply of nutrients and little light limitation [Brierley and Thomas, 2002; Kattner et al., 2004].

Physiological adaptations – While living in the ice provides advantages to microalgae like access to sufficient light levels by the maintain at the sea surface [Arrigo et al., 2010] and protection against large grazers due to the geometry of the brine microstructure, it also necessitates that ice algae have developed the capability of responding to salinity, light, temperature, pH, nutrients and gas fluxes stresses encountered within the sea ice medium [Mock and Thomas, 2005]. In previous studies, acclimation ability of sea ice algae to the aforementioned environmental factors has generally been assessed by measuring the alteration

of photosynthetic performances compared to optimal conditions (reviewed by Arrigo et al. [2010]). The ability to compensate the decrease in physiological processes rate related to low temperatures prevailing in the sea ice habitat is a widespread feature of polar microalgae [Mock and Hoch, 2005]. A critical adverse effect of low temperatures is the decrease in membrane fluidity. Although also influenced by nutrient availability, salinity and light levels, the increased synthesis of lipids with prevalence of polyunsaturated fatty acids (PUFAs) observed at low temperatures with sympagic organisms is mainly attributed to the maintenance of functional phospholipid membranes whose fluidity is altered in those conditions [Arrigo and Thomas, 2004 and references therein]. Synthesis and exsudation of cryoprotectant compounds, like ice-binding proteins or exopolymeric substances (EPS) able to interfere with the growth of ice crystals is also a strategy used by some sea ice algae to create microenvironments favourable to their growth in the sea ice matrix [Janech et al., 2006; Krembs et al., 2011; Raymond, 2011]. Thriving at the bottom of the ice cover beneath a few meters of snow and ice necessitates adaptation to low-light conditions which can be accomplished by the increased synthesis of accessory pigments (e.g. fucoxanthin, chlorophyll *c*), enhancing utilisation of wavelengths of light penetrating the snow and ice cover, relative to chlorophyll *a* [Arrigo et al., 2010]. High levels of ultraviolet radiations (especially UVB), such as those witnessed by the organisms living beneath the ozone hole in the Southern Ocean, can inhibit photosynthesis in sea ice diatoms and increase DNA damage [Karentz and Spero, 1995]. Synthesis of elevated amounts of compound like mycosporine-like amino acids (MAAs) acting as chemical sunscreens has been proposed as a strategy developed by microalgae to counteract deleterious effects of ultraviolet radiations on photosynthesis and genetic material but still has to be clearly demonstrated [Ryan et al., 2002]. Abrupt changes in ambient salt concentrations can induce an osmotic stress with ice algae. Ralph et al. [2007] demonstrated that the hypo-osmotic conditions resulting from sea ice melting caused higher photosynthetic stress with Antarctic sea ice algae than the hyperosmotic conditions prevailing during freezing up. In their experiment with Antarctic bottom algae, Ryan et al [2004] suggested that some diatoms species could acclimate to salinity down-shock by recovering photosynthetic efficiency over a few days. One way for sea ice algae to acclimate to changes in ambient salinity consists in modifying their intracellular concentrations of osmolytes. Dimethylsulphoniopropionate (DMSP), recognised as a compatible solute [Stefels, 2000], may play such a role with sea ice algae, in the view of the elevated concentrations of this compounds often found in various sea ice environments [reviewed by Trevena et al., 2003].

DMS/P/O in the marine environment

Climatic role – DMSP is the main precursor of dimethylsulphide (DMS), a climatically active volatile organic compound. Oceanic emissions of DMS account for almost all the natural flux of reduced sulphur compounds to the atmosphere [Kettle and Andreae, 2000]. Once emitted to the atmosphere, DMS can successively be oxidised to sulphur dioxide and then sulphate which can affect the radiative budget of the atmosphere directly by backscattering part of the incoming solar radiation and indirectly by acting as condensation nuclei favouring the formation of clouds (cloud condensation nuclei or CCN). In their famous study which stimulated two decades of intense research dedicated to the production of DMS in the marine environment, Charlson et al. [1987] hypothesised that an increase of atmospheric CO₂, hence temperature, would result in an increase of algal primary production which in turn could drive increased DMS production that would compensate the greenhouse effect of CO₂. This hypothesis (known as the CLAW hypothesis) seems to definitely have to be retired, because of the combined effect of the low sensitivity between DMS emissions and CCN, between CCN and cloud albedo and the low sensitivity of seawater DMS concentrations to a global warming scenario [Quinn and Bates, 2011]. Although the CLAW climate feedback loop has been invalidated in the view of recent advances in the understanding of the DMS cycle, influence of phytoplankton emissions of DMS and on the regional climate, notably in the Southern Ocean, would still be significant [Krüger and Grassl, 2011] and certainly still warrants further investigation.

DMS/P/O cycle – The DMS cycle is intricate with numerous pathways linking DMS, DMSP and dimethylsulphoxide (DMSO) governed by factors of different natures (abiotic, algal, bacterial,...) (see Figure 2). As main source of DMS, DMSP is produced by some planktonic groups in response to environmental stimuli inducing a cellular stress like salinity, light, temperature and nutrient availability. The ability to produce DMSP would be limited to a reduced number of species. Amongst the algal DMSP-producers, the levels produced can vary by up to 4 orders of magnitude between algal groups, with dinoflagellates and haptophytes being acknowledged to be major DMSP-producers [reviewed by Stefels et al., 2007], revealing taxonomic composition as the most determining factor in the ability of an algal community to produce DMSP. Although increase in salinity of the medium is bound to induce an increase of intracellular DMSP [Stefels, 2000], mechanisms regulating its concentration upon short-term salinity shifts are still obscure.

Despite its acknowledged function of compatible solute at low temperatures [Stefels, 2000 and references therein], assessment of intracellular levels of DMSP under cold conditions has rarely been investigated. Increased DMSP:C ratio reported for *Emiliana huxleyi* and *Phaeocystis* at low temperatures (but still positive temperature ranges) suggest that DMSP could play a metabolic role in mitigating the deleterious effects of low temperatures [Stefels et al., 2007 and references therein]. As elevated DMSP levels were observed in algal cultures submitted to various oxidative stressors amongst which visible light and ultraviolet radiations, Sunda et al. [2002] suggested that DMSP, in combination with DMS and DMSO notably, could exhibit an antioxidant function. Given its structural analogy with glycine betaine [Challenger, 1951], acknowledged for its osmoregulation function, it has been proposed that DMSP could be produced as an alternative to this compound under nitrogen-limited conditions. This hypothesis has ever since hardly been demonstrated [Stefels, 2000]. As limited access to nutrients can generate imbalance in carbon and nitrogen metabolic pathways, Stefels [2000] proposed that DMSP would be produced in the frame of an overflow mechanism allowing the maintenance of cellular metabolic processes by the release of excess reduced sulphur, dissipation of excess energy and saving of nitrogen for amino acids synthesis.

Once produced in the algal cell, DMSP can be released into the ambient medium either directly following active exudation, cell rupture through autolysis or viral lysis, or indirectly following the action of zooplankton grazers (all mechanisms reviewed by Stefels et al. [2007]). Part of DMSP released in seawater (dissolved DMSP or DMSPd) can be converted into DMS and acrylate following enzymatic cleavage by algal or bacterial DMSP-lyases. Contribution of DMSPd to the marine DMS pool has to date not been constrained. Simo et al. [2000] estimated that 5 – 100% of DMSP turnover can yield DMS. Other studies report values in the lower range of those estimates (e.g. ~30% [Bates, 1994], 24% [Simo and Pedros-Alio, 1999], 1% [Archer et al., 2002]). Finally, it is acknowledged that only 10% of the marine DMS would ultimately be vented to the atmosphere [Archer et al., 2002].

Besides its supposed physiological roles [Lee and de Mora, 1999; Sunda et al, 2002], DMSO can act as a sink for DMS through photochemical or bacterial oxidation of DMS or as a source following its biosynthesis by microalgae and further reduction by some bacteria [reviewed by Hatton, 2005]. A recent study demonstrated that the ability to reduce DMSO into DMS is a widespread feature with marine phytoplankton, unlike the ability to produce DMS from DMSP which is restricted to a limited number of algal species, DMSO

ice environment than in open water due to the peculiar nature of the sea ice material (e.g. limited access to nutrients [e.g. Fripiat et al., 2007], sensitivity to photochemical reactions owing to the presence of elevated levels of coloured dissolved organic material [Belzile et al., 2002],...). Kirst et al. [1991] were the first to validate this hypothesis by observing sea ice

Table 1 Literature sea ice DMS and DMSP data. ^a Sp, spring; Su, summer; Wi, winter; NA, not available; SO, Southern Ocean; ^b Mean is given in bold, followed by the range in parentheses; ^c DMSP only; ^d DMSPd + DMS; ^e Calculated for ice categories with ice thickness <1.20 m; ^f Number of cores weighted average.

Location	Ice type	Season ^a	DMSP ^b (nM)	DMS ^b (nM)	DMS+DMSP ^b (nM)	Source
Weddell Sea	Pack ice	Sp	322 (4–1664)	NA	NA	Kirst et al. [1991]
Resolute Passage	Pack ice	Sp	325c (0–6014) ^c	NA	950 ^d (nd–15051) ^d	Levasseur et al. [1994]
Bellingshausen Sea	Pack ice	Sp - Su	200 (17–546)	NA	NA	Turner et al. [1995]
Prydz Bay	Pack ice	Sp	144 (8–725)	NA	NA	Curran et al. [2003]
Dumont D'Urville	Sea Pack	Wi	40 (nd - 193)	NA	NA	Curran et al. [2003]
Ross Sea	Pack ice	Sp - Su	212 (5–980)	NA	NA	DiTullio et al. [1998]
Ross Sea	Fast ice	Sp	150 (81–219)	NA	NA	DiTullio et al. [1998]
Offshore Prydz	Bay Pack	Sp	107 (6–787)	NA	NA	Trevena et al. [2003]
Baffin Bay	Pack ice	Sp - Su	126 ^e (8.66–987) ^e	NA	NA	Lee et al. [2001]
Prydz Bay	Fast ice	Sp - Su	112 (9–1478)	NA	NA	Trevena et al. [2003]
Gerlache Inlet	Fast ice	Su	NA (4.4–450)	NA	NA	Gambaro et al. [2004]
Indian sector of SO	Pack/Fast ice	Sp	185 ^f (45–796) ^e	12 (<0.3–75)	NA	Trevena and Jones [2006]
Dumont D'Urville Sea	Fast ice	Sp	NA	NA (4–74)	NA	Delille et al. [2007]

DMSP levels up to 56 times higher than those observed in open water. Although all studies conducted over Antarctic sea ice to date agree in terms of range of DMSP levels observed [Trevena et al., 2003], they hardly contribute to give a clear picture of existing seasonal or regional patterns (see also Table 1). Particularly winter and time series studies are lacking. An attempt is made below to briefly summarise the main findings of sea ice studies conducted in both hemispheres about factors controlling the observed levels of DMS, DMSP and DMSO.

Relationships to biomass and ice assemblages – There is a broad consensus to state that the distribution of DMSP in sea ice is related to that of the algal biomass usually inferred from chlorophyll *a*. Attempts to investigate the existence of a functional and statistically significant relationship between those two variables were however not always successful. Reasons invoked to explain the absence or the poor nature of the relationship between DMSP and chlorophyll *a* are various: sampling bias [Kirst et al., 1991], spatial decoupling between DMSP and chlorophyll *a* due to algal mortality [Trevena et al., 2003], non relevance to use chlorophyll *a* as a proxy for algal biomass as algae can adjust their chlorophyll *a* content in response to light intensity [Lee et al., 2001] or complex nature of multispecies samples

analysed [Lee et al., 2001]. Significant relationships are sometimes revealed following a more or less rigorous selection of the data or reduction of the dataset to particular cases [Trevena and Jones, 2012]. Some particular ice algal assemblages like slush communities in interior ice of rafted sea ice or surface slush communities, generally exhibiting high levels of algal biomass, demonstrated to be hotspots in terms of DMSP [Trevena et al., 2006] and DMS [Zemmelink et al., 2008] production. The taxonomic composition of algal assemblages seems to exert a major role on the observed DMSP levels. Already acknowledged as important DMSP-producers in open water studies [Stefels et al., 2007], haptophytes/ prymnesiophytes (amongst which *Phaeocystis* sp.) [Kirst et al., 1991; Turner et al., 1995; di Tullio et al., 1998; Trevena et al., 2000] and dinoflagellates [Kirst et al., 1991; Trevena et al., 2000] maintain their status in the sea ice environment. Unlike in sea water where they are acknowledged to be low DMSP-producers [Stefels et al., 2007], there is a broad consensus between authors to state that diatoms are important contributors to the sea ice DMSP pool due to the generally high biomass levels they exhibit in the sea ice environment [Levasseur et al., 1994; Turner et al., 1995; di Tullio et al., 1998; Trevena et al., 2000; 2003].

Dependency on ice thickness and season – Trevena and Jones [2006] identified a relationship between DMSP and ice thickness and stated that the higher levels of DMSP encountered in thinner ice covers resulted from exposure of newly incorporated sea ice algae to higher light levels (compared with light conditions encountered in mixed layer seawater) enhancing algal productivity and DMSP synthesis. These authors state, however that such a relationship may not apply to other seasons, notably winter. DMSP production in sea ice is indeed very likely to be season-dependent in the view of the unique low mean concentration of DMSP (40 nM) reported in Antarctic winter sea ice off Dumont d'Urville station [Curran and Jones, 1998].

Role of nutrients – Although expected, nutrient availability in sea ice was not reported to exert a strong influence on the observed DMSP levels. Trevena et al. [2000] detected no relationship between nitrate and DMSP and attributed it to the fact that it is difficult to isolate such kind of trend from field data. Trevena et al. [2003] suggested silicate exerted an indirect influence on DMSP production by controlling the ice algal biomass.

Response to various environmental stresses – Attempts to demonstrate that DMSO could act as cryoprotectant or accessory pigment with Arctic ice algal communities were not successful [Lee et al., 2001], this failure being attributed to the complex nature of the multispecies samples analysed. The likely osmotic shock undergone by sea ice algae during melting is

thought to favour the release of intracellular DMSP into the dissolved phase and its further transformation into DMS [Trevena et al., 2006]. In this view of a potential control of ambient salinity on DMS/P cycling, Delille et al. [2007] observed that the increase of brine DMS was inversely related to the decrease in salinity. Those authors also stated that the increase of DMS could result from increasing grazing pressure which may coincide with the widening of brine channels during melting [see also Archer et al., 1996]. Hyperoxic conditions encountered in sea ice brine would also enhance DMS production from the perspective that DMS would be part of a consortium of free radical scavenger molecules [Delille et al., 2007]. In a recent tracer experiment conducted on Antarctic sea ice brines, Asher et al. [2011] demonstrated the intense DMS/P/O cycling that can take place in this environment and identified DMSO reduction as a major pathway of DMS production in Antarctic sea ice.

Fluxes – It is acknowledged that sea ice contributes to increase the DMS/P pool of the Southern Ocean on melting [e.g. Trevena et al., 2012 and references therein]. Recent studies have also confirmed the assumption that sea ice could emit substantial amounts of DMS into the atmosphere measuring significant DMS flux over highly productive surface slush communities in Weddell Sea multiyear pack ice [Zemmelink et al., 2008] and in East Antarctic fast ice [Nomura et al., 2012], stressing the major role played by the snow cover in determining the timing and amplitude of the DMS fluxes. Those two studies are the only ones to date to address temporal evolution of either DMS, DMSP or DMSO in sea ice.

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THESIS OUTLINE

This thesis was a contribution to the ARC project n°02/07-287 entitled “Sea Ice Biogeochemistry in a Climate Change Perspective” (SIBCLim) funded by the Communauté française de Belgique (now called Fédération Wallonie – Bruxelles) which main objective was the study of carbon, iron and sulphur biogeochemical interactions between sea-ice, ocean and atmosphere and their controlling mechanisms in the perspective of the role played by ice-covered regions of the northern and southern polar oceans in regulating the earth’s climate.

In this context, the aims of this work were multiple:

1. Develop a reliable analytical method for the determination of dimethylsulphoxide (DMSO) in sea ice taking into account the specificity of the sea ice material (bulk ice measurements, impact of sea ice melting on the sympagic organisms);
2. Characterise the evolution of the physicochemical properties of the spring and summer first year sea ice cover during ISPOL (Ice Station Polarstern, Western Weddell Sea, Antarctica, November – December 2004) and SIMBA (Sea Ice Mass Balance in Antarctica, Bellingshausen Sea, Antarctica, September – October 2007), respectively, providing thereby the necessary framework to assist with interpretation of biological and biogeochemical datasets acquired in parallel;
3. Acquire sea ice DMS, DMSP and DMSO datasets by the routine use of robust methods (developed in the frame or in parallel of the present work) to characterise the temporal evolution of those compounds in spring (SIMBA) and summer (ISPOL) Antarctic sea ice in relation to the previously described physicochemical frame and to a series of ancillary biological and biogeochemical variables with an emphasis on the exchanges processes (inferred fluxes) with the Atmosphere and the Ocean;
4. Assess the impact of physicochemical properties of a growing ice cover on the evolution of the gas properties (gas content and composition (O_2 and N_2)) and test the validity of the boundary-layer model to describe the evolution of such gas properties, which could be applied to other gas (notably DMS) and taken into account for further modelling efforts.

In the perspective of providing the scientific community, especially ecosystem modellers, with useful datasets, the general philosophy of this work could be summarized as following: 1) the physicochemical characterisation of the ice cover, generally deficient in many sea ice biogeochemical studies, must precede any other analysis; 2) choice of textbook case studies (e.g. level ice) is encouraged in order to emphasise the evolution of the monitored variables in a time series perspective; 3) the use and development of robust analytical procedures is encouraged to produce reliable data.

THESIS FORMAT

This thesis takes the form of an article thesis, with each chapter consisting of one or two peer-reviewed publications in international scientific journals (four published one in review and one in preparation).

After the introduction, Chapter II outlines the challenges posed by the sampling and preparation of sea ice samples for biogeochemical analyses and recommends a robust method for the sequential analysis of DMS, DMSP and DMSO in sea ice.

Chapter III describes the evolution of physicochemical properties of the sea ice cover that would constitute the context into which the evolution of biogeochemical variables (notably DMS, DMSP and DMSO) will be discussed.

Chapter IV describes the temporal evolution of DMS and DMSP in first-year summer sea ice and the comparative temporal evolution at two contrasting sites of DMS, DMSP and DMSO in first-year spring sea ice.

Chapter V describes the temporal evolution of the gas properties of laboratory prepared sea ice and illustrates the relevance to use a boundary layer model to describe the evolution of the gas concentration profiles in growing sea ice under the sole influence of physicochemical processes

Chapter VI finally draws the general conclusions of the present research work.

CHAPTER II: Towards better practices for the determination of biogeochemical compounds in sea ice: the case of dimethylsulfoxide (DMSO).

Paper 1 :

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

Contribution of F. Brabant: Experimental design, samples preparation, laboratory measurements, analysis of the results, writing of the paper.

A robust approach for the determination of dimethylsulfoxide in sea ice

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Abstract

The melting of sea ice samples is acknowledged to be deleterious to sympagic microorganisms due to the hypo-osmotic shock undergone by the organism when released from high salinity brine inclusions into the sample melt. Because melting of sea ice samples was also anticipated to modify the initial proportions of dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP), and dimethylsulfoxide (DMSO), three sample treatments were tested on an Antarctic sea ice sample, with the aim of identifying an efficient procedure that could routinely be applied for the determination of DMSO in sea ice. Herein, it was demonstrated that purging the melted sample before the determination of DMSO in the sample via an enzyme-linked method produced reliable DMSO results ($215.8 \pm 8.9 \text{ nmol L}^{-1}$, precision 4.1%). However, analysis revealed that the unintentional enzymatic cleavage of DMSP through the subsequent production of interfering DMS during melting caused an overestimation of the DMSO content in the sample by more than 59% and concurrently an underestimation of the DMSP content by approximately 9%. The sequential determination of DMSP after the DMSO determination by the enzyme-linked method was shown to be problematic. To circumvent all of these issues, we recommend an analytical procedure for the sequential determination of DMS, DMSP, and DMSO in sea ice. Ultimately, the first depth profile of DMSO at high resolution in sea ice was produced. The depth-integrated DMSO concentration in sea ice was determined to be $718 \text{ } \mu\text{mol m}^{-2}$, which indicated that Antarctic sea ice is a potentially important source of DMSO for the Southern Ocean.

Dimethylsulfoxide (DMSO) is a widespread nonvolatile dimethylated sulfur species that is present in a wide variety of aquatic environments. Ubiquitous in the marine environment, DMSO originates from a series of biotic and abiotic processes; on occasion, it is found at levels exceeding those of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) (Simó 1998; Lee and de Mora 1999a). Interest in studying DMSO in the marine environment lies in its link with DMS, a biogenic trace gas, which might play an impor-

tant role in climate control by mitigating global warming (Charlson et al. 1987; Andreae 1990; Bates et al. 1999). DMSO may either act as a source of DMS, through the production of DMSO by phytoplankton and its subsequent reduction into DMS, or as a sink through the formation of DMSO by photochemical or bacterial oxidation of DMS (Hatton et al. 2005). DMSO can be a polyvalent protective compound at the cellular level. Lee and de Mora (1999b) have proposed three major roles for DMSO: it can act as a specialist osmoregulator in extreme environments (cryo-osmoregulator), as a free radical scavenger and as an intracellular electrolyte modifier. Sunda et al. (2002) suggested that DMSO might take part in a chain of free radical scavengers (along with DMSP, DMS, and methane sulfinic acid) initiated by the lysis of DMSP. The levels and distribution of DMS and DMSP in the marine environment have been largely reported for approximately thirty years; however, the emergence of studies dedicated to DMSO is more recent. In the last decade, the development of analytical techniques with sufficient sensitivity and selectivity to quantify trace amounts of DMSO has provided a better understanding of the distribution of DMSO in the ocean (Simó 1998). Most of those techniques encompass a reduction step of DMSO to DMS and

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the subsequent gas phase analysis of the produced DMS via a gas chromatography procedure. Depending on the reduction method used, interference with DMSP in the sample may occur, leading to an overestimation of DMSO content (reviewed by Simó 1998).

Elimination of DMSP prior to DMSO analysis (Simó et al. 1996; Simó et al. 1998) or the use of a specific reducing agent, such as DMSO reductase (DMSOr) (Hatton et al. 1994), can prevent this bias. The main motivation of studying DMSO in sea ice is that DMSO can be produced in high concentrations by ice algae, because of the potential role of DMSO in osmoregulation and cryoprotection (Lee et al. 2001). A good correlation between intracellular levels of DMSO (particulate DMSO or DMSOp) and DMSP (particulate DMSP or DMSPp) has been shown in data collected in various marine biomes and during different seasons. The data suggest that both compounds have a common origin in phytoplankton and that DMSP may be the precursor of DMSO (Simó and Vila-Costa 2006; Hatton and Wilson 2007). If the same correlation applies to sea ice, high levels of DMSO are expected to be found in sea ice because high levels of DMSP (up to three orders of magnitude higher than background sub-nanomolar values in seawater) are commonly observed in that environment (e.g., Kirst et al. 1991; Levasseur et al. 1994; DiTullio et al. 1998; Trevena and Jones 2006). Only two studies have reported sea ice DMSO concentrations, which were measured in the bottom 2 cm of the ice cover in the Arctic (Lee et al. 2001; Bouillon et al. 2002). The levels of DMSO measured in these studies, with DMSOp concentrations ranging between 1.35 and 102 nmol L⁻¹ (average 13.7 nmol L⁻¹), were much higher than those usually found in the water column. Bouillon et al. (2002) attributed these high values to the higher biomass of ice algae found in the ice samples. In their study, Lee et al. (2001) tested the hypothesis that DMSO would be biosynthesized by sea ice algae as a cryoprotectant and as an accessory pigment, which would enhance the harvesting of blue light by the algae, as proposed by Horne and McEwan (1998); however, those presumed roles could not be demonstrated. Lee et al. (2001) attributed the lack of clear trends or relationships involving DMSO to the complex nature of the multispecies samples analyzed.

Impacts of sea ice sample melting

Effects on sympagic organisms

Sea ice is a semi-solid matrix of nearly pure ice crystals that incorporates bubbles of gas and brine inclusions in the form of pockets, tubes or as a network of brine channels (e.g., Weeks and Ackley 1986; Trodahl et al. 2001). This labyrinth of brine inclusions constitutes the habitat of sympagic (sea-ice associated) organisms (including DMSP and DMSO producers), which live embedded in the viscous gel phase of the exopolymeric substances (EPS) produced by diatoms (Krembs et al. 2002a). Because of its complex nature, sampling sea ice and preparing samples for further biogeochemical analysis with little distur-

bance to the sample is a challenge (Brierley and Thomas 2002). To apply the methods developed for measuring DMSO in aqueous solutions to sea ice, it is necessary either to melt the sea ice sample or to sample the liquid phase of sea ice (sea ice brines), assuming all of the analytes of interest occur exclusively within that phase. Both procedures have advantages and limitations. In their review, Brierley and Thomas (2002) reported three methods routinely used to sample the organisms living in sea ice. The sackhole sampling technique (Garrison and Buck 1986; Stoecker et al. 1992, 1993; Gleitz et al. 1995; Papadimitriou et al. 2007) and the centrifugation of ice core sections at in situ temperatures (Weissenberger et al. 1992; Krembs et al. 2000, 2001, 2002b) are two methods dedicated to the collection of sea ice brine, assuming that most sympagic organisms live within the brine inclusions. The main limitation of both of these methods, however, is that they fail to recover all the particulate matter within the ice (Brierley and Thomas 2002). This failing might be explained by the viscous gel phase of EPS filling the pore space that would retain a substantial fraction of the particulate matter anchored to the ice crystals and would also partly retain dissolved material, such as dissolved organic carbon (DOC), as demonstrated by Iecquevort et al. (2009). A recent time series study of first-year sea ice in the Weddell Sea demonstrates that the same explanation would also hold for DMSP, which has been found to be predominantly linked to the solid phase of sea ice rather than dissolved in the sea ice brine (Tison et al. 2010). The melting of sea ice core sections, conversely, ensures the recovery of both the particulate and dissolved phases; however, the main drawback with this method is that it requires the sympagic organisms to undergo hypo-osmotic shock when released from the highly saline brine inclusions into a hypotonic solution. The hypo-osmotic shock is believed to alter the biogeochemical properties of the sample. Thus, the rapid decrease in salinity of the medium (potentially above 200 when melting winter sea ice) can result in a wide range of physiological impacts at the cellular level, including cell rupture, reduced photosynthesis and damage to enzymes (Ralph et al. 2007). Garrison and Buck (1986) demonstrated that the rapid and extreme changes in salinity undergone by sympagic organisms during the melting of a sea ice sample resulted in a substantial loss of fragile organisms, such as flagellates and ciliates, whereas diatoms and other silicified organisms were slightly affected. These authors showed that more than 70% of those fragile organisms were lost due to cell lysis in response to the osmotic stress compared with an osmotically buffered melted control. Thomas et al. (1998) showed that the contribution of the dissolved chemicals in the sample (like nutrients, DOC) from cell disruption or release of intracellular osmolytes during the melting process would be insignificant to the concentrations of the main nutrients and chemicals usually measured in sea ice, considering the internal cellular pools of these main compounds (Thomas et al. 2010). It has also been demonstrated that exposing the samples to hyposaline conditions affects the rate of photosynthesis for sea ice algae (Arrigo and Sullivan

1992; Ralph et al. 2007). Deming (2010) reported that melting the sample would also drastically affect the abundance of sea ice bacteria unless a procedure was used to reproduce the in situ salinity and temperature of the brine inclusion within the sample melt (Junge et al. 2004).

Physiological response of algae to the hypo-osmotic shock and potential effects on the initial sea ice DMS and DMSP pools

To date, the most common practice used to release DMS, DMSP, or DMSO from the sea ice matrix before analysis is to melt the sample in filtered seawater to at least partly mitigate the hypo-osmotic shock. When on-field analysis of the compounds is impossible, additional preservation techniques can be applied to preserve either the DMS or DMSP, such as the acidification technique (Curran et al. 1998; Curran and Jones 2000). Trevena et al. (2003) used this technique but concluded their study by mentioning some limitations of the method for the determination of DMS-related compounds. They observed that nearly all DMSP was found in the dissolved fraction and suggested that this DMSP could have partly originated from damage to the cell caused by salinity stress undergone during thawing. A physiological response to a hypo-osmotic shock involving DMS and related molecules has been observed with some algal species. Additionally, the rapid release of intracellular DMSP into the medium has already been observed for a benthic diatom *Cylindrotheca closterium* (Van Bergeijk et al. 2002; Van Bergeijk et al. 2003) and for the DMSP-producing prasinophyte *Tetraselmis subcordiformis* (Dickson and Kirst 1986) following a salinity down-shock. Dickson and Kirst (1986) suggested that the rapid excretion of DMSP (and the subsequent production of dissolved DMSP or DMSPd) could be an osmotic acclimatization process because DMSP is a compatible solute (Welsh 2000) and well-known for its role in cellular osmoregulation (Stefels 2000; Van Alstyne 2008). A recent laboratory experiment (Barbara R. Lyon, Marine Biomedicine and Environmental Science, Medical University of South Carolina, pers. comm.) was designed to assess the impact of changes in the salinity of medium on both the intracellular and extracellular DMSP concentrations with *Fragilariopsis cylindrica* (a sea ice diatom ubiquitous in Antarctic sea ice algal assemblages). A drastic increase in DMSPd concentration was observed after lowering the salinity of the medium from 35 to 10 in 24 h. This observation was thought to be the result of the passive release of DMSP into the dissolved fraction because of a change in membrane permeability; further experiments using a Sytox stain demonstrated that algal cells exposed to an abrupt salinity shift showed compromised membrane integrity without evidence of massive cell lysis (Barbara R. Lyon, pers. comm.). In another laboratory experiment with the dinophyte *Heterocapsa triquetra*, Nikl et al. (2007) showed that hypo-osmotic shock was likely to enhance algal DMS production. According to these authors, the low-salinity shock undergone by the algae stimulated the release of DMSP (as DMSPd). The DMSP was then proposed to be converted to DMS by the DMSP-lyase of *Heterocapsa*

triquetra whose enzymatic activity did not seem to be inhibited by the salinity drop. To quantify the importance of the entire DMSO pool (dissolved and particulate) in sea ice, melting the sample is mandatory, provided that neither the sackhole nor centrifugation methods ensured the full collection of the particulate fraction of the organic matter, including sea ice algae (Brierley and Thomas 2002). Collection of the particulate matter is crucial because this fraction has already been shown to contain substantial levels of DMSO in sea ice (Lee et al. 2001; Bouillon et al. 2002). As observed for seawater samples in response to hypo-osmotic shock, similar perturbations of the dimethylated sulfur pool are very likely to occur with the melting of a sea ice sample. These considerations seem to indicate that the initial proportions of DMSP and DMS within a sea ice sample might be significantly modified during its melt. An unintentional enzymatic cleavage of natural DMSP and the subsequent production of DMS are anticipated for the following reasons: first, sea ice is well known to contain elevated algal standing stocks (see Arrigo et al. 2010, for a thorough review of the literature), including DMSP producers (e.g., Kirst et al. 1991; Levasseur et al. 1994; DiTullio et al. 1998; Trevena and Jones 2006). Second, among those sympagic DMSP producers, a few species commonly observed in sea ice algal assemblages, like *Phaeocystis antarctica*, are known to have DMSP-lyase activity (Rellinger et al. 2009 and references therein). Finally, the important hypo-osmotic shock caused by the melt of the sample is likely to induce the release of intracellular DMSP into the medium by excretion or cell lysis, which can then be enzymatically cleaved into DMS. DMS produced by this process of unintentional enzymatic cleavage of DMSP (referred to hereafter as "interfering DMS") is then expected to interfere with DMS stemming from DMSO reduction, which can consequently lead to an overestimation of the DMSO content in the sea ice sample. In this article, we first test the hypothesis that the direct application of an existing method for the determination of DMSO in aqueous solutions on melted sea ice samples produces overestimated results, and the associated error is quantified. We then propose a simple and fast procedure for the non-biased DMSO determination in sea ice using the reliable enzyme-linked method (Hatton et al. 1994). The most suitable order or sequence for the determination of DMS, DMSP, and DMSO is also discussed.

Material and procedures

Analytical approach

To assess the influence of melting sea ice samples on measured DMSO levels, replicates of a natural sea ice samples were submitted to three different treatments in which DMSO, DMSP, and interfering DMS were analyzed sequentially by a gas chromatography procedure as described below.

Materials

Sample

Experiments were performed on a sample of summer first-year sea ice collected in the western Weddell Sea during the

ISPOL drift experiment (see Tison et al. 2008, for a full description of the temporal evolution of physical parameters at the different stations of the time series). To ensure that significant levels of DMSO could be measured, a sample of approximately 60 g was taken from the bottom-most 5 cm of the ice cover from station 04.12.04 for which a full set of biogeochemical data are available elsewhere (Tison et al. 2008; Dumont et al. 2009; Dumont 2009).

Sample preparation

The selected sea ice sample was reduced into a fine powder following the procedure described below for the analysis of DMS in a nonmelted sea ice sample. This process involved a dry crushing step inspired from a dry-phase gas extraction procedure designed for polar ice cores (Raynaud et al. 1982). This method has been developed to measure DMS (and potentially other volatile compounds) in nonmelted sea ice samples because melting the sample before the measurement of DMS proved to produce biased results for DMS concentrations. A comparative study of the melting and dry crushing extraction methods conducted on an Antarctic sea ice core showed that although the features of the total DMS+DMSP profile were conserved, the melting method resulted in a six-fold increase of the mean DMS:DMSP ratio compared with the crushing method with a DMS concentration exceeding the DMSP by a factor nine on occasion (Stefels et al. unpub. data). For the purpose of the analysis by gas chromatography, the complete conversion of either DMSO or DMSP to DMS was performed in 20 mL glass vials hermetically sealed with a butyl/PTFE septum cap. After conversion, the vial was connected to a simple purge-and-trap system similar to the one described by Stefels (2009) to be used as a purge chamber, with the exception that an acid scrubber for DMSO analysis was not installed because the reduction method used did not produce acidic vapors. Using a small disposable vial as purge chamber has many advantages. First, it allows the analysis of small volumes, which is particularly suitable to analyze sea ice samples that are expected to contain high levels of DMS, DMSP, and DMSO. Second, there is no risk of interference with remnants of particulate matter from previous analysis in the purge chamber, which can produce persistent elevated blank values and artificially increase the DMS concentration of the samples via an unintentional release of DMS (Uher 1999 and references therein). Minimal maintenance of the system is therefore required. Finally, the portability of the equipment, except for the gas chromatograph (GC), is also an undeniable advantage of the system, making it particularly suitable for field measurements.

Sulfur quantitation

DMSO and DMSP were analyzed as DMS using an Inter-science (Thermo Finnigan) Trace GC gas chromatograph equipped with a six-port switching valve, a 1 m $\times$ 0.75 mm (i.d.) Restek Rt-XLSulfur packed column and a flame photometric detector (FPD). Gas flow rates at the flame were 90 mL min⁻¹ of H₂, 115 mL min⁻¹ of dry air and 20 mL min⁻¹ of He,

as the carrier gas. The GC oven was operated using a temperature program (60–180°C) and the detector temperature was set at 230°C. In this configuration, the DMS eluted at approximately 4.3 min. The detector output was recorded using an EZChrom Elite (Scientific Software Inc., Agilent) interface. The GC was calibrated against dilutions of pure DMSO (>99.7%) for gas chromatography (Merck) in ultra-pure water, which were reduced to DMS following the enzyme-linked method described by Hatton et al. (1994). Because the FPD response is proportional to the n power of the amount of sulfur and may vary depending on the analytical set-up (n is generally in the range 1.5 < n < 2.5 (Farwell and Barinaga 1986), a linear regression of $\log(\text{area})$ vs. $\log(\text{mass of DMSO})$ was applied, as recommended by Simó (1998). The analytical precision achieved with the standards was approximately 5%. Using this analytical set-up, a detection limit of 0.006 nmol sulfur was obtained, which corresponded to a concentration of 0.622 nmol L⁻¹ for a 10 mL sample. Although this concentration level was higher than the concentration of 0.156 nmol DMSO dm⁻³ obtained by Hatton et al. (1994) for a seawater sample with a maximum volume of 100 cm³, it was sufficiently low in view of the high levels of DMSO expected to occur in sea ice samples. To estimate the very high DMSP levels in samples of treatment C (see below), the GC was calibrated against dilutions of pure DMSP (Research Plus Inc.) at a very high concentration after hydrolysis with NaOH, as described below, and it was then analyzed as DMS using the analytical set-up described above. Because the FPD response was prone to change at high sulfur masses due to an autoquenching phenomenon in the detector flame, Sola et al. (1997) suggested evaluation of the relative error generated as a consequence of applying one single linear fit to the whole mass range interval; this would establish the need to decompose the $\log(\text{area})$ vs. $\log(\text{mass of DMSO})$ curve in a series of linear sectors. Using the same approach, the analysis of the calibration dataset revealed that the determination of two different linear equations corresponding to a part of the whole mass range was required to capture the data at its best and to minimize the relative error, especially in the high mass range (1.86–3.11 nmol). Results are expressed in nmol per liter of ice (nmol L⁻¹). The sample density (0.92 Mg/m³) used to compute the sample volume was calculated according to Cox and Weeks (1983) using the bulk ice salinity (8.86) and ice temperature (−1.8°C) measured on the field on a twin ice core (Tison et al. 2008); a value of 9% was determined for the relative air volume, which was measured as described by Tison et al. (2002) on another sample at the same depth from the same core.

Procedures

Sample preparation

In a cold room (−30°C), the sea ice sample was placed together with two stainless-steel marbles into a stainless-steel vessel specifically designed for the analysis of DMS in sea ice samples (Stefels et al. unpub. data). After hermetical sealing,

the vessel was fixed onto a crushing device and mechanically shaken (several hundred cycles min^{-1}) for 4 cycles of 45 s each to produce a fine ice powder and to ensure that all gas bubbles and brine inclusions were released from the ice matrix. The vessel was then connected to a standard purge and trap line and a GC as described by Stefels (2009) and purged with He to quantify DMS from the nonmelted sea ice sample. DMS from the dry crushed ice sample was purged from the vessel, maintained at approximately -30°C to avoid melting of the sample, but not quantified in the framework of this study. However, this procedure ensured that all the DMS was removed from the sample at this stage, thus preventing any interference with the determination of DMSO and DMSP. The fine ice powder was recovered and divided (by weighing) into 15 vials of 20 mL. The vials were hermetically sealed with a butyl/PTFE septum cap, and samples were stored at -30°C in the dark for further DMSO and DMSP analysis.

DMSP analysis

For the quantitation of total DMSP, NaOH was added to the vial containing the ice powder to bring the OH^{-} concentration above 2 N and to induce the hydroxide decomposition of DMSP in DMS and acrylic acid (Dacey and Blough 1987); this procedure proved to be 100% efficient (Turner et al. 1990). The vial was then immediately crimp-sealed with a butyl/PTFE septum cap, and the sample was left to melt and react at $+4^{\circ}\text{C}$ in the dark for at least 24 h until analysis. The vial was then connected to the purge and trap system, and the sample was purged for 30 min with ultrahigh purity (UHP) grade He (Air Liquide, Alphagaz 2, 99.99999%) at a flow rate of 25 mL min^{-1} ; DMSP was quantitated as DMS by the GC apparatus described above.

DMSO analysis

Once the ice powder had melted, DMSO was reduced into DMS for GC quantitation according to the enzyme-linked reduction method developed by Hatton et al. (1994), except that the sample was bubbled for 25 min with UHP grade He at a flow rate of 25 mL min^{-1} . This reduction of DMSO using the DMSO reductase (DMSOr) (Glycomar Ltd.) is known to be the most precise and reproducible among the different existing reduction methods (reviewed by Simó 1998).

Assessment

Experiments

Three different treatments, in which DMSP and DMSO concentrations were determined in different orders, were applied to the sample for the following reasons: a) to demonstrate that the direct application of an existing DMSO determination method on a melted sea ice sample, even a specific method, such as the enzyme-linked method used in the present study leads to an overestimation of the DMSO content; b) to test a fast and simple procedure expected to produce reliable DMSO results and c) to validate the results produced by the latter procedure (see Fig. 1 for an overview of the whole analytical sequence). For further statistical analysis, five replicates were analyzed for each treatment. In treatment A, the ice powder

was melted in a crimp-sealed vial at $+4^{\circ}\text{C}$ in the dark. Once the sample had completely melted, the reducing solution containing DMSOr was added to the sample through the septum. The vial was then connected to the purge and trap system, and the DMSO content was analyzed as DMS as described above. After the analysis of DMSO, NaOH was added to the sample for the analysis of DMSP as DMS as described above. The aim of treatment A was to establish whether the direct determination of DMSO on a melted sea ice sample might lead to the overestimation of DMSO in the sample. For treatment B, the ice powder was melted as in treatment A. The vial was connected to the purge and trap system, and the sample was bubbled for 30 min with UHP grade He at a flow rate of 25 mL min^{-1} for the analysis of interfering DMS.

After the analysis of interfering DMS, the reducing solution containing DMSOr was added to the sample, and DMSO was analyzed using the same procedure as treatment A. After DMSO analysis, NaOH was added to the sample for the analysis of DMSP as in treatment A. Treatment B was designed to investigate whether a simple purge step applied to the sample prior to DMSO determination might produce nonbiased results. In treatment C, NaOH was added to the ice powder before the vial was crimp sealed. The sample was then melted and left to react at $+4^{\circ}\text{C}$ in the dark for at least 24 h, then DMSP was analyzed as described above. The sample was then neutralized with HCl and a $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ buffer to bring the pH back to a working range for DMSOr, which is ideally between 6.5 and 7.3 (Dr. Derek Thomson, Glycomar Ltd., pers. comm.). The DMSOr reducing solution was then added to the sample, and the DMSO content was analyzed as described previously for treatments A and B. Because all DMSP should have been removed from the sample through the alkaline hydrolysis before the determination of DMSO, treatment C was intended as a control. This treatment was also intended to validate the DMSO results obtained after treatment B and, therefore, to assess whether treatment B could be applied routinely.

Statistical analysis

Results of the experiment are summarized in Table 1. A one-way analysis of variance (ANOVA) was performed on the results of the total DMSO concentration. The ANOVA (level of significance $\alpha = 0.05$) indicated a significant difference ($P < 0.001$) among the mean DMSO concentrations measured for the three treatments (see Fig. 2). To investigate the origin of the differences between the treatments, a Holm-Sidak pairwise multiple comparison procedure (level of significance $\alpha = 0.05$) was performed. Both the ANOVA procedure and the Holm-Sidak procedure were performed using Sigmaplot 11 (Systat Software). Results of the Holm-Sidak procedure revealed that the DMSO concentrations measured in treatment A were significantly higher ($P < 0.001$) than those measured in treatments B and C, as anticipated. No difference was found in DMSO concentration between treatments B and C ($P = 0.067$). A systematic overestimation of the DMSO content in the sea ice samples was, therefore, proven when the DMSO determi-

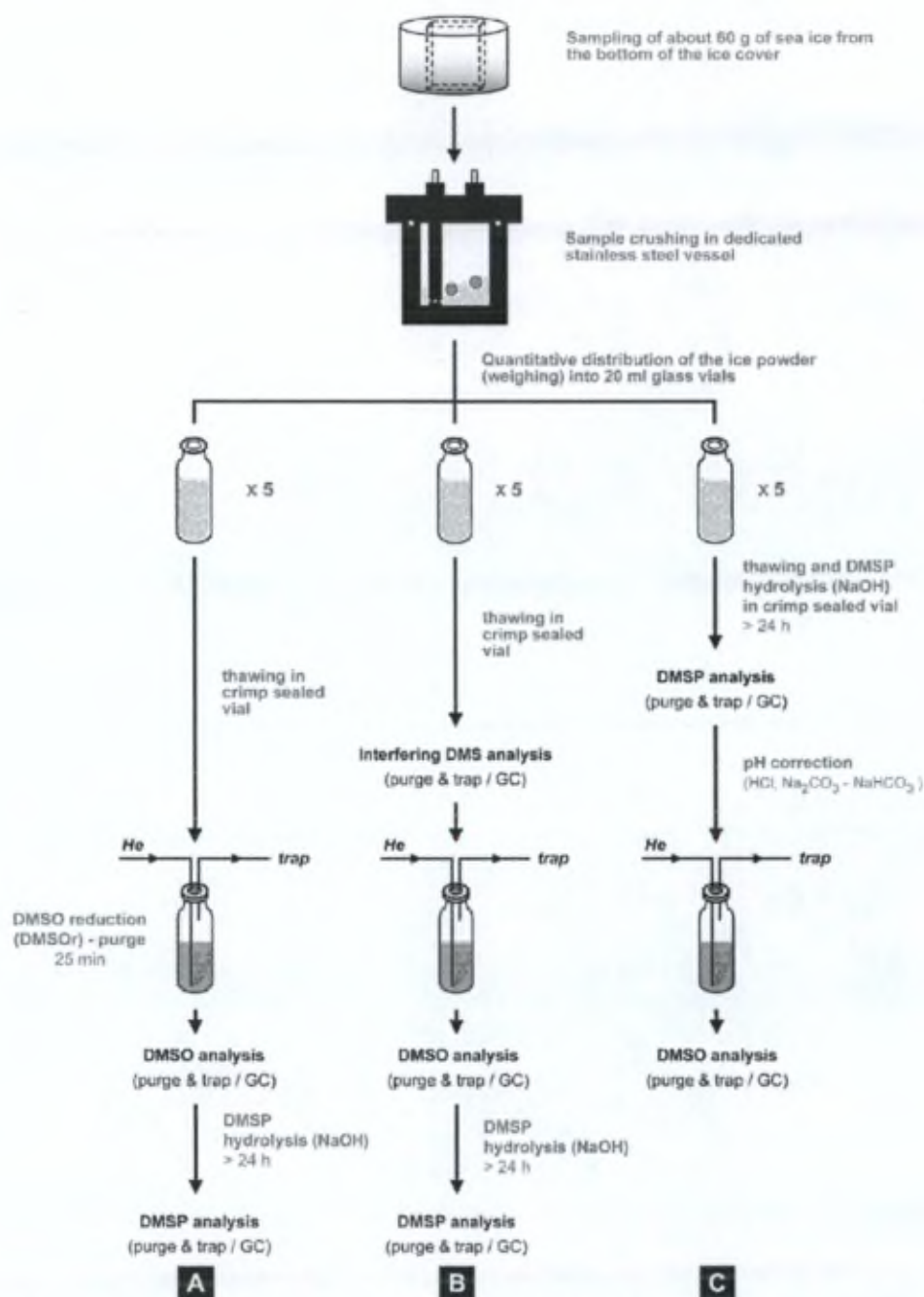


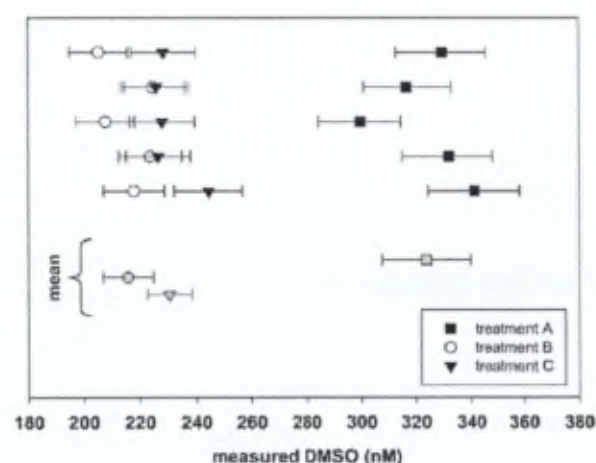
Fig. 1. Analytical procedure designed to compare the mean DMSO levels measured in a melted sea ice sample when the DMSO determination is performed directly (treatment A), the DMSO determination is performed after the removal of interfering DMS (treatment B), and the DMSO determination is performed after the removal of DMSP (treatment C). See text for details.

Table 1. Concentrations of DMSO, interfering DMS and DMSP (in nmol L⁻¹) obtained for the different treatments of the sample.

Analyte	Treatment		
	A	B	C
DMSO	323.7 ± 16.1	215.8 ± 8.9	230.6 ± 7.8
int. DMS	—	128.5* ± 3.9	—
DMSP	424.6 ± 39.6	443.3* ± 33.0	978.9† ± 122.1

*Mean and standard deviation for *n* = 4 due to operator error.

†Estimate of the real value due to detector saturation.

**Fig. 2.** DMSO concentration for the three treatments (black and white symbols represented with 5% analytical error bar). Gray symbols represent the mean DMSO concentration values represented along with total reproducibility for each method.

nation was applied directly on the melted sample. DMSO determination by the enzyme-linked method produced, on average, the same results irrespective of whether the sea ice sample was purged (treatment B) or all DMSP was removed before DMSO analysis (treatment C). Therefore, treatment B or C can be applied indiscriminately for the determination of DMSO on sea ice. The total accuracy and reproducibility for the DMSO determination was 4.1% for treatment B and 3.4% for treatment C. Treatment B was faster (15 min for the removal of interfering DMS and 25 min for the DMSO determination) and required less manipulation compared to treatment C (which required at least 24 h for the hydroxide hydrolysis of DMSP and neutralization of the sample prior to DMSO determination) at a similar performance level. Levels of interfering DMS, which is thought to result from the unintentional enzymatic cleavage of DMSP during melting, were measured in treatment B (128.5 ± 3.9 nmol L⁻¹) and were significant, especially compared with DMSO levels measured in treatment B (see Table 1).

To assess whether the interfering DMS levels might account for the differences observed in the DMSO content for treatments A and B, we reconstructed the DMSO levels that would have been measured following treatment A, i.e., by summing the DMSO value and the interfering DMS value for the samples for which both values were available in treatment B (*n* = 4). The reconstructed DMSO levels were compared with the DMSO results obtained for treatment A using a *t* test ($\alpha = 0.05$). The *t* test revealed a significant difference ($P = 0.046$) between the mean DMSO levels from treatment A and the mean reconstructed DMSO levels from treatment B (346.9 ± 11.4). Given that the *P* value of the *t* test (0.046) was very close to the level of significance chosen ($\alpha = 0.05$), it was reasonable to think that most of the difference observed between treatment A and treatments B and C was due to interfering DMS.

DMSP results were analyzed following the same approach used for DMSO analysis. As mentioned in the legend of Table 1, DMSP levels for treatment C were estimates. High DMSP levels present in the bottom sea ice sample chosen for the present study led to a change in the response of the FPD. The GC was calibrated accordingly, as mentioned above. The mean DMSP level measured in treatment C was bound to be an underestimate because the results obtained from other areas at the same depth range (bottom 5 cm) of the ice cover produced substantially higher values. Analysis on another sample from the same ice core with the analytical set-up used in the present study (hydroxide hydrolysis of DMSP after crushing for the dry extraction of DMS) revealed a DMSP level of 1395.6 nmol L⁻¹ (unpubl. data). The determination of DMSP from a sample taken from a twin ice core sample collected on the same day but using a different analytical apparatus (PTRMS), produced a value of 1536.4 nmol L⁻¹ (Tison et al. 2010). ANOVA studies on DMSP levels measured for the three treatments revealed a significant difference ($P < 0.001$) between the mean DMSP levels of the treatments. A Holm-Sidak procedure run on the ANOVA results revealed that treatments A and B gave, on average, the same results, but those results were lower than those measured in treatment C (significant difference, $P < 0.001$). These results were expected because a portion of the initial DMSP content gave rise to interfering DMS and was measured as-is (treatment B) or was measured along with DMS stemming from the reduction of DMSO (treatment A) before the DMSP determination. To assess whether the DMSP determination performed after the DMSO determination produced quantitative results, initial DMSP levels were reconstructed by summing the levels of interfering DMS and DMSP measured in treatment B and compared with the DMSP levels measured in treatments A and C. ANOVA results revealed a significant difference ($P < 0.001$) between the mean DMSP levels measured for each treatment. A Holm-Sidak procedure applied to these results revealed a significant difference between treatments A and C, B and C ($P < 0.001$) and between A and B ($P = 0.048$). Thus, on average, treatment A produced lower DMSP levels than treatment B, which in turn produced lower DMSP levels

than treatment C. In the present case, the DMSP levels measured after the determination of DMSO via the enzyme-linked method (as in treatment A and B) were on average underestimated by more than 70% compared with the mean for the DMSP levels measured on two other independent samples ($1466.0 \text{ nmol L}^{-1}$ DMSP); this result suggested that the determination of the compounds in that order using the enzyme-linked method was problematic. The significantly lower yields of DMSP hydrolysis observed for both treatments A and B compared with the levels measured in treatment C suggested that one of the reagents present in the DMSO cocktail (DMSO itself, ethylenediaminetetraacetic acid [EDTA] or flavine mononucleotide [FMN]) might have hampered the reaction of DMSP hydrolysis by OH^- . Because DMSO is a zwitterion (i.e., an electrically neutral molecule bearing formal unit electrical charges of opposite sign on different atoms), interaction with EDTA, which is a well-known chelating agent (Zaitoun and Lin 1997) was plausible. EDTA could make DMSP partially unavailable for hydrolysis by OH^- by interacting with DMSP at the level of the sulfur atom bearing a positive charge. In a reducing solution placed in semianaerobic conditions and illuminated by incandescent light bulbs, EDTA forms radicals which reduce FMN to FMNH_2 , and the latter acts as an electron donor to DMSO catalyzing the reduction of DMSO to DMS (Hatton et al. 1994). As EDTA and FMN are in excess concentrations in the reducing solution, radicals produced by EDTA are available to potentially react with other compounds in the sample. Superoxide ions ($\text{O}_2^{\cdot-}$) produced by the rapid spontaneous oxidation of FMNH_2 (Massey et al. 1969; Michelson 1973) might have also initiated secondary reactions (Vigny and Michelson 1974). To assess the influence of EDTA alone or in combination with FMN on the DMSP hydroxide hydrolysis yield, a standard solution of pure DMSP (of approximately 60 nM) was prepared, treated with NaOH and analyzed as described above. Two other batches of the standard DMSP solution were prepared. Two milliliters EDTA solution were added to the vials of the first batch while 2 mL of a mixture of EDTA+FMN were added to the vials of the second batch; these solutions were submitted to the same analytical procedure as treatment A. Both reagents were prepared in the same concentration as was present in the DMSO reducing solution, i.e., 30 mM EDTA and $540 \text{ }\mu\text{M}$ FMN (Hatton et al. 1994). The results of the DMSP analysis performed on those two batches were compared with the results obtained for the pure DMSP solution (Table 2). The ANOVA ($\alpha = 0.05$) performed on the DMSP analysis results revealed that there was a significant difference between the mean levels of DMSP measured for each batch (Table 2). The Holm-Sidak procedure applied to the results indicated that there were no differences among the samples from the EDTA/FMN batch, the pure DMSP batch and the EDTA batch. Conversely, there was a significant difference between samples from the EDTA batch and samples from the pure DMSP batch. It is noteworthy that the unadjusted p value of this individual pairwise comparison

Table 2. Results of the comparison of the hydroxide hydrolysis of a standard solution of pure DMSP or in presence of EDTA or EDTA + FMN ($n = 5$ for each batch). Results are expressed as relative yields and were computed in comparison to the results obtained for the hydroxide hydrolysis of the standard DMSP solution.

	Pure DMSP	EDTA	EDTA/FMN
DMSP (nmol)	0.56 ± 0.04	0.61 ± 0.01	0.58 ± 0.03
Relative yield (%)	100 ± 6	109 ± 8	104 ± 9

Error on DMSP analysis measurement has been propagated for the computation of the relative yield.

(0.017) was close to the critical level (0.010). The relative yields of the hydroxide hydrolysis of DMSP, either in the presence of EDTA alone or in combination with FMN, were close to the yield obtained for the pure DMSP solution and never led to an underestimate of DMSP levels, as anticipated.

Although no influence of EDTA or EDTA/FMN could be demonstrated through assessment of a standard solution of pure DMSP, the assessment performed on the natural sample might have led to a different conclusion. In the case of the analyzed melted sea ice samples, the radicals formed by EDTA or $\text{O}_2^{\cdot-}$ generated by the spontaneous oxidation of FMNH_2 , might have reacted with compounds occurring in natural samples of sea ice to create compounds that would have hampered the hydrolysis of DMSP by OH^- . Additional tests would be required to further support this hypothesis and identify the compounds liable to react with the radicals formed by EDTA or with $\text{O}_2^{\cdot-}$. However, this issue is beyond the scope of the present study.

Discussion

It has been demonstrated that the direct application of an existing DMSO determination method on a melted sea ice sample leads to an overestimation of the DMSO content in the sample (see results of treatment A vs. treatments B and C in Table 1). It appeared crucial to either remove all the DMSP from the sample before analysis (as in treatment C) or purge interfering DMS before analysis (as for treatment B). Reliable DMSO concentration results were obtained by applying either treatment indiscriminately. The levels of interfering DMS measured in treatment B were substantial and likely originated from a process similar to the one proposed by Niki et al. (2007) to explain the increased DMS production by *Heterocapsa triquetra* observed in their experiment as a result of a hypo-osmotic shock. In the present experiment, the rapid salinity drop undergone by the sympagic organisms rapidly released from the sea ice brine environment (brine salinity of 32.2; computed based on the ice temperature according to Eicken [2003] and Petrich and Eicken [2010]) into the hypo-osmotic melted sample (bulk ice salinity of 8.86) was estimated to be about 24 in only a few minutes. Data on the microbial community of the ice bottom horizon of station 04.12.04 reported

by Dumont et al. (2009) might provide an argument to support the hypothesis of an important production of interfering DMS. Data were collected on a twin ice core taken no further than a few decimeters away from the place where the ice core used in the present study was extracted. Analysis of the algal assemblage revealed that it was largely dominated by diatoms (*Cylindrotheca* sp., *Nitzschia* sp., *Amphiprora* sp., *Fragilariopsis* sp.), which contributed up to 99% of the total autotrophic biomass ($2299 \mu\text{g C L}^{-1}$), whereas dinoflagellates made up the remaining 1%. The total biomass of the heterotrophic organisms ($28 \mu\text{g C L}^{-1}$) was divided into the following composition: 62% protozoa (50% dinoflagellates, 50% other flagellates) and 38% bacteria (Dumont 2009). In view of the biogeochemical properties of the analyzed sample, a combination of several factors may have provided favorable conditions for the production of Interfering DMS: a) an important hypo-osmotic shock (salinity drop of 24 in a few minutes); b) a high DMSP level in the sample (around $1466.0 \text{ nmol L}^{-1}$); c) the occurrence in the sample of an ice algal species (*Fragilariopsis* sp.), which was recently proven to release DMSP in response to a hypo-osmotic shock (Barbara R. Lyon, pers. comm.), and d) the occurrence in the sample of dinoflagellates, a phytoplankton group well known for its DMSP-lyase activity (Steinke et al. 2002; Stefels et al. 2007). In these conditions, the proportion of the total DMSP concentration in the sample that would have been enzymatically cleaved to interfere with DMS, accounted for approximately 9% (provided the total DMSP concentration in the sample was $1466.0 \text{ nmol L}^{-1}$, i.e., the mean of the two measurements performed on other samples, see above). This unintentional production of DMS likely resulted in an overestimation of the total DMSO content of the sample by more than 59% (Table 1). These results undoubtedly raised the question of the reliability of measurements of DMSP or dissolved DMS performed on melted sea ice samples. Currently, only two studies have reported measurements of dissolved DMS in sea ice (Trevena and Jones 2006; Delille et al. 2007). Trevena and Jones (2006) reported dissolved DMS concentrations in 81 sea ice core sections ($<0.3\text{--}75 \text{ nmol L}^{-1}$). DMS chemisorption for further analysis was performed on melted samples after the addition of HCl to bring the pH of the melted sample down to 1 and to preserve the total DMSP (DMSPt). The activity of algal DMSP-lyase was known to be drastically reduced at low pH values (Stefels and Dijkhuizen 1996). Given this property of DMSP-lyase, the acidification technique was commonly used to preserve DMSP in seawater samples (Smith et al. 1999). However, this technique appears to be unsuitable for preserving DMSPt in sea ice samples. As sea ice is a composite material, it is expected to melt sequentially depending on the melting point of the different phases (Fripiat et al. 2007). Because the melting of the sample is not homogeneous, it is very likely that unintentional enzymatic cleavage of DMSP occurs locally well before HCl penetrates the whole ice matrix. Important salinity shifts are expected to take place in the brine inclusions because of the dilution of the

brine medium by the melting of pure ice crystals. The contact between DMSP that is freshly released from algal cells in response to the hypo-osmotic shock and DMSP-lyase can then produce DMS within the ice matrix. In addition to this issue, Kiene et al. (2007) recently reported that the acidification technique failed to preserve DMSP in seawater samples in presence of *Phaeocystis* sp., which is often found in Antarctic sea ice algal assemblages. DMSP-lyases in *Phaeocystis* sp. would remain active up to several minutes after acid addition. It is impossible to state whether the sea ice DMS and DMSP concentrations reported by Trevena and Jones (2006) were actually affected by such a bias, even if it was likely. No melting artifact is thought to have influenced the values reported by Delille et al. (2007) ($4\text{--}74 \text{ nmol L}^{-1}$) because they directly measured dissolved DMS in the sea ice brine. Junge et al. (2004) recently developed an isothermal-isohaline melting approach that involved the thawing of a sea ice sample into a laboratory prepared solution of brine with a higher salinity than the sea ice brine. The salinity of the laboratory prepared brine solution was adjusted so that the final melted sample had a salinity equal to that of the original brine inclusions, calculated according to Cox and Weeks (1983). This approach proved to be successful in preserving the bacteria on melts (Deming 2010) and could have been applied to our samples to potentially circumvent the bias due to the melting of the sample. However, this is a time- and labor-intensive procedure that hardly seemed feasible in the framework of the present study because only small sample volumes were processed for the DMSP and DMSO analysis; in addition, this procedure would be difficult to apply when a large number of samples must be analyzed. Depth profiles of DMSO concentrations were measured, as in treatment II, with a vertical resolution of 5 cm on the whole ice cover thickness of station 04.12.04 (Fig. 3). DMS and DMSP concentrations were determined on a twin ice core

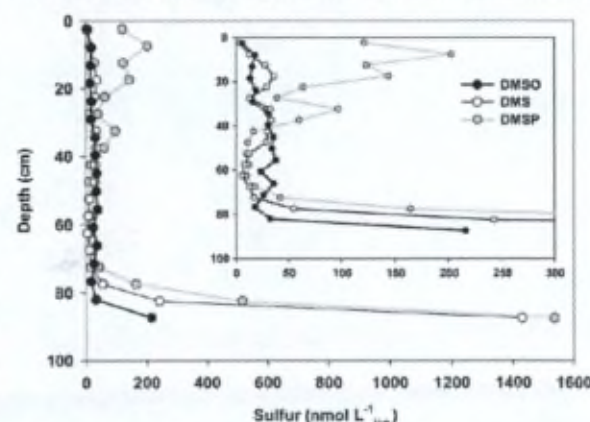


Fig. 3. Depth profile for DMSO (black), DMS (white), and DMSP (gray) in summer, first-year sea ice taken in the Weddell Sea, Antarctica. The inset is a close-up for the range $0\text{--}300 \text{ nmol L}^{-1}$ ice.

sampled the same day, using a different analytical apparatus (PTRMS) from the one used to determine DMSO; however, the same crushing procedure for the dry extraction of DMS was utilized (Tison et al. 2010). DMSO concentrations ranged from 6.1 to 215.8 nmol L⁻¹ over the whole profile, with the highest levels observed near the bottom, likewise DMS and DMSP. The changes in DMSO concentrations along the profile were close to values obtained for DMS, which occurred in the same concentration range (3.4–242.7 nmol L⁻¹), with the exception of the bottom value, which peaked at higher than 1400 nmol L⁻¹, likewise DMSP. The DMSO concentrations measured in this profile of summer, first-year Antarctic sea ice are higher than the DMSO concentrations Lee et al. (2001) and Bouillon et al. (2002) observed in the bottom-most 2 cm of Arctic sea ice. Determination of DMSO on the whole ice cover revealed significant levels above the bottom layer. DMSO concentrations integrated on the whole ice thickness of station 04.12.04 (0.85 m) gave results of 718 $\mu\text{mol m}^{-2}$. This is an important value when compared with the mixed-layer integrated DMSO concentrations of 927–2574 $\mu\text{mol m}^{-2}$ measured by del Valle et al. (2009) during the summer in the Ross Sea and calculated over a mixed-layer depth ranging between about 25 and 65 m (i.e., 30 to 75 % the sea ice thickness). These data make Antarctic sea ice a potentially important source of DMSO for the Southern Ocean. Processes governing the evolution of DMS and DMSP profiles in decaying Antarctic summer sea ice are discussed elsewhere (Tison et al. 2010). A thorough analysis of the temporal evolution of the DMSO profiles in the same context will appear elsewhere.

Comments and recommendations

The melting of sea ice appears to be the only sampling technique that allows the collection of both particulate and dissolved phases for further analysis of compounds that need to be performed in aqueous solutions. Sharp salinity shifts that occur during the melting process of the sample may, however, result in an important bias at the time of biogenic compound determination in sea ice. As far as DMS, DMSP, and DMSO are concerned, the production of interfering DMS from DMSP during the melting process can result in inaccurate estimations of the initial proportions of those compounds in the dimethylated sulfur pool if a suitable procedure is not followed. The sequential analysis of DMS, DMSP, and DMSO in the field should be performed following the procedure proposed in Fig. 4, which is rapid and exempt from analytical artifacts. DMS should be analyzed immediately after ice core sampling, as substantial losses of this volatile compound (more than 50%) have been observed after a storage period of several months (Stefels et al. unpub. data). In the recommended procedure, DMSO is determined from some of the melted ice powder resulting from DMS analysis and was analyzed following the enzyme-linked method (Hatton et al. 1994), which is unprecedented in terms of precision and rapidity. It is recommended that DMSP is analyzed on another subsample drawn

from the same initial crushed sample due to the following reasons: a) the determination of DMSP prior to DMSO involves more manipulations to prepare the sample for subsequent DMSO determination by the enzyme-linked method and b) the determination of DMSP after DMSO proved to be problematic. This procedure should be followed for the determination of DMS, DMSP, and DMSO in future sea ice studies and should contribute to the production of a larger dataset of sulfur compound concentrations in sea ice. These data can provide a better overview of their distribution in sea ice and a better estimate of the contribution of sea ice to the sulfur budget of Polar Regions.

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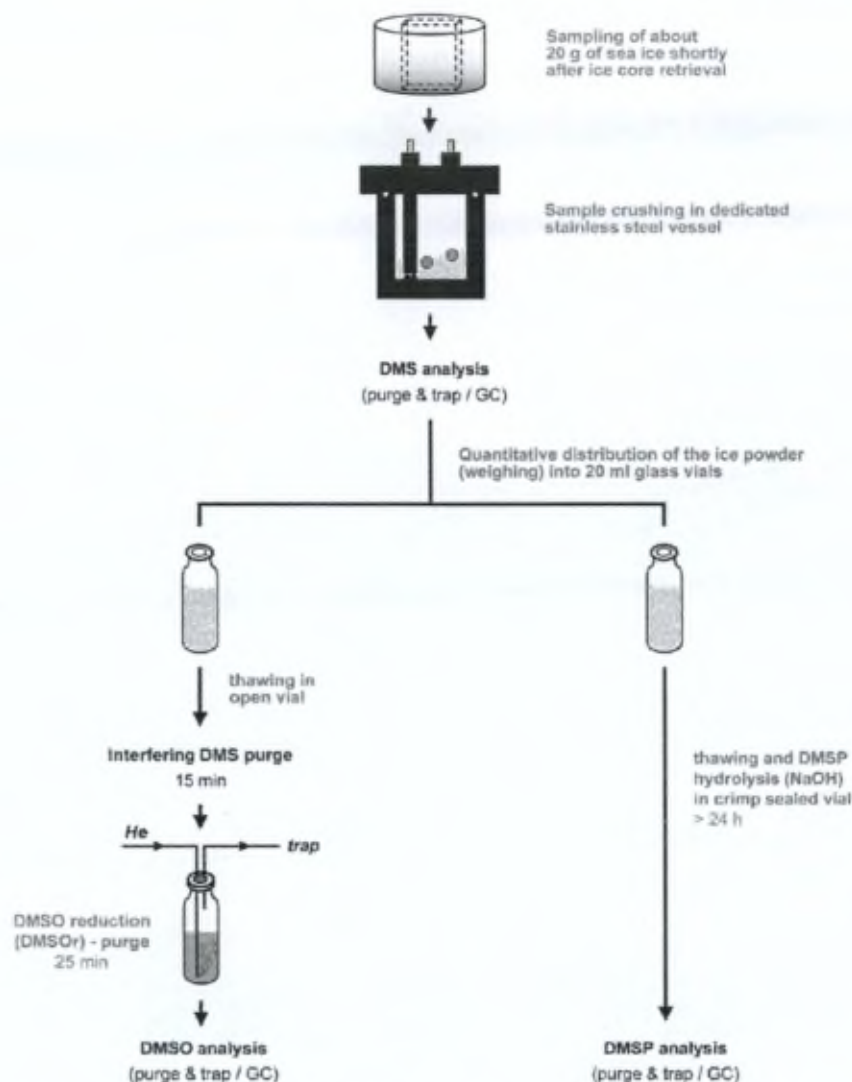


Fig. 4. Recommended analytical procedure for the sequential analysis of DMS, DMSP, and DMSO in sea ice. See text for details.

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CHAPTER III: Characterisation of the physicochemical properties of the sea ice cover: a necessary step prior to biogeochemical analyses

Paper 2 :

Temporal evolution of decaying summer first-year sea ice in the Western Weddell Sea, Antarctica, 2008. *Deep-Sea Res II*, 55, 975 – 987. by Tison J.-L., A. Worby, B. Delille, F. Brabant, S. Papadimitriou, D. Thomas, J. De Jong, D. Lannuzel and C. Haas.

Contribution of F. Brabant: Preparation of thin sections and montage of the pictures. Processing of the “laboratory” sea ice samples and salinity measurements. Analysis of data and discussion of the observed differences between field and laboratory salinity measurements. Statistical analysis of the ice thickness dataset.



Temporal evolution of decaying summer first-year sea ice in the Western Weddell Sea, Antarctica

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Abstract

The evolution of the main physico-chemical properties of the unflooded 90-cm-thick first-year sea-ice cover at the Ice Station POLarstern (ISPOL) “clean site” is described. ISPOL was an international experiment of the German research icebreaker R.V. *Polarstern*. The vessel was anchored to an ice floe for an observation period of 5 weeks, during the early summer melt onset in the Western Weddell Sea. The “clean site” was specially designed and accessed so as to prevent any trace metal contamination of the sampling area. Observations were made at 5-day intervals during December 2004 in the central part of the main floe. Results show the succession of two contrasting phases in the behavior of the brine network (brine channels, pockets, and tubes). Initially, brine salinity was higher than that of sea-water, leading to brine migration and a decrease in the mean bulk salinity of the ice cover. This process is highly favored by the already high bulk porosity (14%), which ensures full connectivity of the brine network. Gravity drainage rather than convection seems to be the dominant brine transfer process.

Half-way through the observation period, the brine salinity became lower than that of the sea-water throughout the ice column. The brine network therefore switched to a “stratified” regime in which exchange with sea-water was limited to molecular diffusion, strongly stabilizing the bulk mean sea-ice salinity. During the transition between the two regimes, and in areas closer to ridges, slush water (resulting from a mixture of snow meltwater and sea water accumulated at the snow-ice interface) penetrated through the growing “honeycomb-like structure” and replaced the downward draining brines. This resulted in a slight local replenishment of nutrients (as indicated by dissolved silicic acid). However, as a whole, the described decaying regime in this globally unflooded location with limited snow cover should be unfavorable to the development of healthy and active surface and internal microbial communities.

The switch from gravity to diffusion controlled transport mechanisms within the ice column also should affect the efficiency of gas exchange across the sea-ice cover. The observed late build-up of a continuous, impermeable, superimposed ice layer should further significantly hamper gas exchange.

Statistical estimates of the evolution of the ice thickness during the observation period and salinity trends of the under-ice water salinity down to 30 m corroborate model predictions of a moderate bottom melting (5–10 cm) from ocean heat fluxes.

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1. Introduction

Sea ice in both hemispheres covers between 18 and 28 millions km² in the course of a single year, an area range that compares with the largest biomes on Earth (IPCC, 2001). Because of its peculiar properties and large

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variations in seasonal extent, sea ice influences the global climate system through a suite of large-scale processes, including albedo fluctuations, insulation between the ocean and the atmosphere, production of deep-water, stratification of the surface waters during spring melting and seeding primary production in the marginal ice zone (e.g., Jacobs and Weiss, 1998; Jeffries, 1998; Lizotte and Arrigo, 1998; Thomas and Dieckmann, 2003). Further, recent work (Semiletov et al., 2004; Delille, 2006) has demonstrated the usual assumption that the sea-ice cover is a barrier to gas exchange between the upper ocean and the atmosphere might need to be reconsidered for ice temperatures greater than -10°C (Gosink et al., 1976). This impinges on the fluxes of climatically important gases (CO_2 , DMS, CH_4).

Sea ice hosts a complex web of microorganisms, which have adapted to its specific physico-chemical constraints. The resident biological community consumes and produces biogases, which gives sea ice a controlling role in gas exchange between the ocean and the atmosphere. The impact of these potentially important processes is unknown and has led to an increasing number of studies on the biogeochemistry of sea ice in the past two decades (Thomas and Dieckmann, 2003), with initiation of dedicated interdisciplinary research programs aiming at improving our understanding of the physical and biogeochemical properties of growing and decaying sea ice, and their potential impact on the air–ice–ocean fluxes of climatically significant gases in the polar seas. A further objective is to model these processes and scale them up to a global level.

This paper focuses on the time series of the main physico-chemical properties of an 80–90 cm thick first-year sea-ice cover section of the ISPOL floe. Understanding better the processes that govern the decay of Antarctic first-year sea ice is of primary importance to biogeochemical studies, because they profoundly affect the environment in which the spring/summer sea ice and surface sea-water microbial activity occurs. Sea-ice decay has been best studied in the Arctic (Untersteiner, 1968; Weeks and Ackley, 1986; Eicken et al., 2000; Johnston, 2006) but only described in terms of salinity and stable isotopes ($\delta^{18}\text{O}$) in the Antarctic (e.g. Eicken, 1998). More work is needed to help develop a conceptual and, ultimately, a numerical model of meltwater and brine transport through sea ice (Eicken, 2003). It has been shown that the most effective desalination process in the Arctic is “meltwater flushing”, a process in which the hydraulic head created by snow and ice meltwater produced at the top surface flushes downwards the resident brine. How much of this process is active in the Antarctic, where summer melting is generally less extensive than in the Arctic, is not known. Clearly, surface snow melting is large enough to produce layers of superimposed ice at intermediate levels in the snow cover, where the temperature is still below the melting point and meltwater refreezes (e.g., Haas et al., 2001; Kawamura et al., 2004). A more developed situation occurs when the amount of melting is large enough for the meltwater to

reach the snow–sea ice interface, where superimposed ice will then eventually form under a double-diffusion process. In the latter, snow melt at the temperature of the melting point will lose heat an order of magnitude faster than it gains salt from the underlying sea ice brine (also at its melting point), and therefore freeze at the interface (Morris and Jeffries, 2001; Haas et al., 2001; Kawamura et al., 2004). Snow thickness and wetness also will play an important role in controlling the sea-ice decay process. Thick snow will favor negative freeboard (snow–sea ice interface below sea level) and induce sea-water flooding of the floe surface. Contrary to winter conditions, when the low temperature of the snow will induce sea-water freezing and snow-ice formation, the sea-water will remain liquid in the summer and mix with surface snow at the snow–sea ice interface to form “slush”. Although tracer studies in the Arctic have shown that both vertical and lateral transport of meltwater occur in the sea-ice cover (Eicken et al., 2002), yet it is not clear which process dominates flooding in permeable summer Antarctic ice (i.e. lateral flow from ridged areas or leads nearby vs. vertical transfer of sea water from below). Reduced snow thickness and/or water occurrence at the ice surface will reduce the albedo and favor heat absorption in the upper ice layers. Eventually, as the season progresses, upper ice temperatures and related fractional brine volumes ($V_{\text{brine}}/V_{\text{bulk ice}}$) will increase to reach the connectivity threshold of about 5% (Buckley and Trodahl, 1987; Golden et al., 1998). In the early stages of decay, brine salinity should still be above sea-water value, inducing density instability within the brine network. The aim of this ISPOL early summer time-series study is to understand how the density instability will be resolved (gravity-driven brine drainage and convection with underlying sea-water, or, brine flushing under hydraulic head), how will the brine network then evolve with further warming as summer proceeds, and what the consequences should be for the biogeochemical evolution of the sea-ice cover.

2. Study site, material and methods

2.1. Choice of the site

ISPOL took place in the Western Weddell Sea, at approximately 68°S and 55°W . During the 5-week observation period, the floe drifted about 100 km northward and 20 km to the west. The ISPOL floe was located at the boundary between a band of second-year ice in the East and a band of thick first-year ice originating from the Ronne polynya in the West (Fig. 1, Hellmer et al., 2006).

A major concern for this study was the selection of an unflooded (positive freeboard), level first-year sea-ice section, in order to keep processes as simple as possible. Extensive surveys of ice and snow thickness revealed that the majority of the ISPOL floe consisted of thick second-year ice, with ice and snow thicknesses between 1.8 and 2.3 m, and 0.6 and 0.9 m, respectively (Haas et al., 2008).

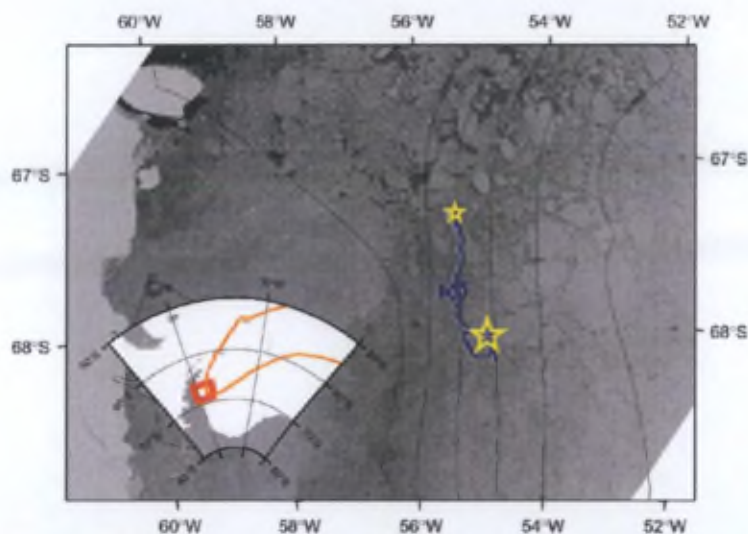


Fig. 1. Envisat synthetic aperture radar image acquired on 30 November 2005, showing the Ice Station Polarstern (ISPOL) study area in the Western Weddell Sea (inset, plus cruise track) and the start (27 November 2004, large yellow star) and end points (2 January 2005, small yellow star) of the drift. The western border coincides with the Larsen-C ice front; the northern boundary is close to the sea ice edge. Black contours show water depth in meters. Note the north-south extent of a dark appearing band of first-year sea ice at about 56°W (from Hellmer et al., 2006).

Consequently, most ice had negative freeboard and was partially flooded. However, between areas of second-year ice, a network of refrozen leads and cracks extended with ice thicknesses of 0.8–0.9 and 0.1–0.25 m of snow, which resulted in a clear secondary mode in the thickness distribution.

A 70 × 30 m area ("clean site" in Fig. 2A and B) was selected in this first-year ice, with a positive freeboard of a few centimeters, for the duration of the experiment. Its perimeter was naturally delimited by ridges. Within the area, smaller adjacent 5 × 5 m units were chosen for regular sampling at about 5-day intervals (number and color scheme in Fig. 3A). On each sampling day, a first half of the unit was dedicated to ice-core sampling and the other half to brine sampling from holes drilled in the ice and in-situ measurements (Fig. 3B). Usually, the hole from the first ice-core retrieval was used for sea-water sampling.

2.2. Working procedure at the clean site

All operations were conducted wearing clean garments (Tyvek overalls, overshoes and polyethylene gloves). First, snow was collected in polyethylene containers using polypropylene shovels. Then ice cores were retrieved using a specially designed electropolished stainless-steel corer that has been shown to allow trace metal clean sampling (Lannuzel et al., 2006). Cores were immediately wrapped in PE bags and stored on the sampling site in an insulated box filled with individual cooling bags, pre-cooled at −30 °C, in order to limit brine drainage from samples as much as possible. Holes were drilled into the ice cover at 20 and

60 cm depth, to allow gravity-driven brine collection (the sackholes sampling technique, Thomas and Dieckmann, 2003). Brine from the ice core was collected as well as under ice sea-water at interface, 1 and 30 m depth using a portable peristaltic pump (Cole-Palmer, Masterflex E/P).

Sampling was carried out on seven occasions, between 29.11.04 and 30.12.04, at regular intervals (usually every five days). On each sampling day, about 14 ice cores were retrieved, about 20 cm apart from each other, and 24 sackholes drilled. These allowed the measurement of a full range of physical and biogeochemical variables among which only temperature, crystal fabric, bulk salinity, and water stable isotopes will be discussed here.

2.3. Methods

Ice temperature was measured in-situ directly after extraction of the cores, using a calibrated probe (TESTO 720) inserted in pre-drilled holes (perpendicular to core sides) at the exact diameter of the probe and with a depth resolution of 5–10 cm. Precision of the measurements was ±0.1 °C (not including potential bias from heat transfer on drilling).

Bulk ice-salinity measurements were done on two different kinds of samples, to investigate the dependence of the measured salinity on sample size. On board, melted ice samples were usually collected from successive 5-cm-thick slices of a dedicated ice core, with a diameter of 14 cm, and were measured with a portable salinometer with a precision of ±0.1. Bulk ice-salinity measurements also were performed back in the home laboratory, on "twin"

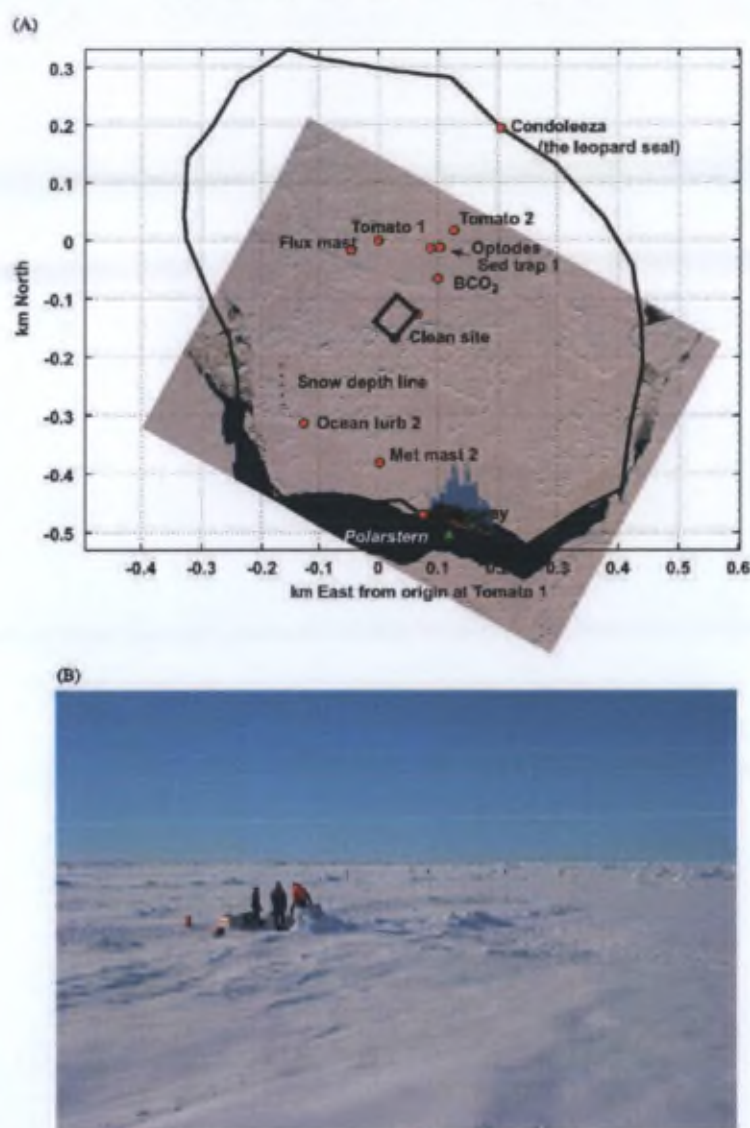


Fig. 2. (A) Clean site location on the ISPOL floe and (B) general view from the loading area. Note the prominent ridges surrounding the sampling site. GPS referenced location map courtesy M. McPhee.

cores from the same sampling day. These were kept below -25°C at all times during transport and storage, therefore preventing post-sampling brine drainage. Two datasets were recovered: one from successive thin vertical samples at 5 cm resolution (about 20 ml), and the other from regularly spaced discontinuous (4 cm apart) 1-cm-thick horizontal slices (about 100 ml). In both cases, salinity was determined using a Radiometer Titralab TIM 870 conductimeter and a calibration curve from diluted aliquots of an IAPSO (10

salinity standard. Comparison of the "on-board" vs. "laboratory" salinity measurements provides insights into the required minimum amount of sample to ensure reliable bulk salinity values. Fig. 4A shows the ranges of salinity profiles on 29.11.04, obtained from the three different sample volumes. Clearly, large amounts such as those collected in the field, on a dedicated ice core, are necessary to ensure the reliability of the measurements. Note also that the vertical cuts show less variability than the

horizontal ones, probably because the first have less probability to include large, horizontally discrete, porosity features such as brine channels.

In order to gain accuracy in the measurements, under-ice sea-water salinity was measured on samples stored in sealed bottles and brought back to the University of Liège. Salinity was then determined with a Guildline—Autosal induction salinometer with an accuracy of ± 0.003 .

Ice thick sections were cut on board the R.V. *Polarstern* for ice texture observations such as, banding, brine channels, holes and bubble density. Thin sections also were studied in the home cold room laboratory (-30°C) on another nearby core, using the standard procedure developed by Langway (1958).

One-way analysis of variance (ANOVA) was performed on the ice-core length dataset for testing the equality of the

population means at different time. The method of orthogonal contrast (Dagnelie, 1998) was then used to look for a possible temporal trend in the mean sea-ice cover thickness.

Water aliquots (10 ml) were collected from the melted ice samples dedicated to the bulk salinity measurements to perform for $\delta^{18}\text{O}$ measurements at the Australian Antarctic CRC. Isotope ratios were measured with a dual-inlet VG SIRA mass spectrometer using the conventional water– CO_2 equilibration method. Accuracy with respect to VSMOW is $\pm 0.12\text{‰}$.

Major nutrients, including dissolved silica, which is shown in this paper, were measured on board. Silicic acid was determined using standard colorimetric methodology (Grasshoff et al., 1983) as adapted for flow injection analysis (FIA) on a LACHAT Instruments Quick-Chem 8000 autoanalyzer (Hales et al., 2004) with a precision better than 5%.

3. Results

Fig. 5 gives an overview of ice texture at the ISPOL clean site between 29.11.04 and 30.12.04. All cores had a top 6- to 14-cm layer of granular ice underlain by columnar ice down to the bottom of the ice column. Examination of the upper 10 cm of the cores from the second half of the period (Fig. 5B—14.12.04 to 30.12.04) showed the occurrence of layers of coarser, elongated, bubble-free ice crystals. Large-scale porosity features are clearly becoming dominant in the upper 40 cm of the sea-ice cover as time goes by. Freeboard was always positive, although generally small ($+5$ to $+1$ cm, red numbers in Fig. 5A). Snow thickness ranged from 6 to 25 cm, and was generally lower than values observed in other sections of the ISPOL floe (0.6–0.9 m, Haas et al., 2008). There was no clear sign of

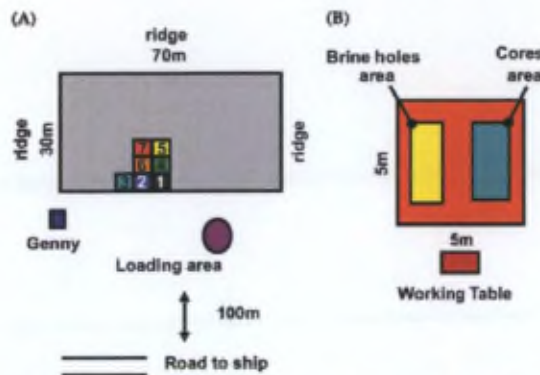


Fig. 3. Clean site-sampling strategy: (A) overall sampling strategy and (B) daily sampling scheme. Numbers and color schemes in (A) refer to the time series.

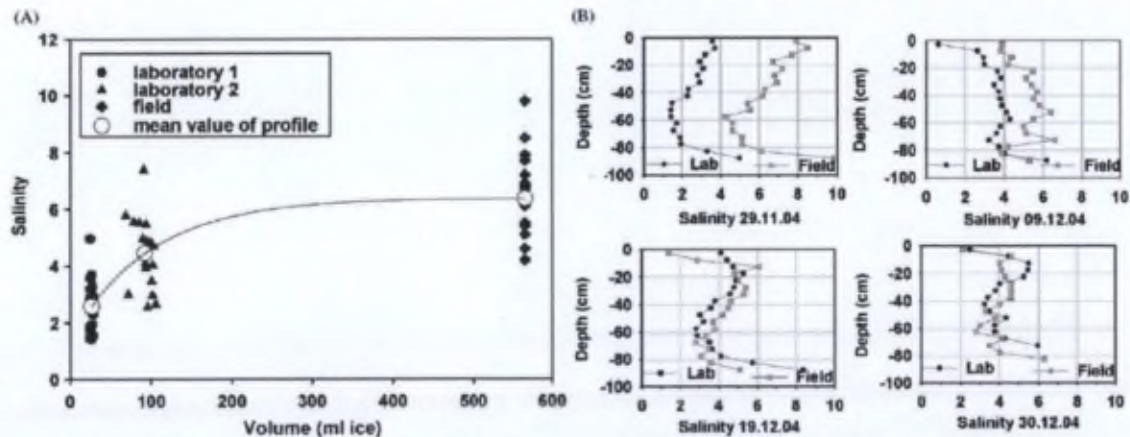


Fig. 4. (A) Bulk ice salinity profiles obtained with increasing sample volume and different sample orientation for ISPOL station 1 (29.11.04—"laboratory 1" = continuous vertical samples, "laboratory 2" = discontinuous horizontal sampling, "field" = continuous horizontal sampling) and (B) comparison between laboratory (vertical, 20 ml) and field (continuous horizontal, 575 ml) bulk ice salinity measurements at four illustrative sampling times. See text for details.

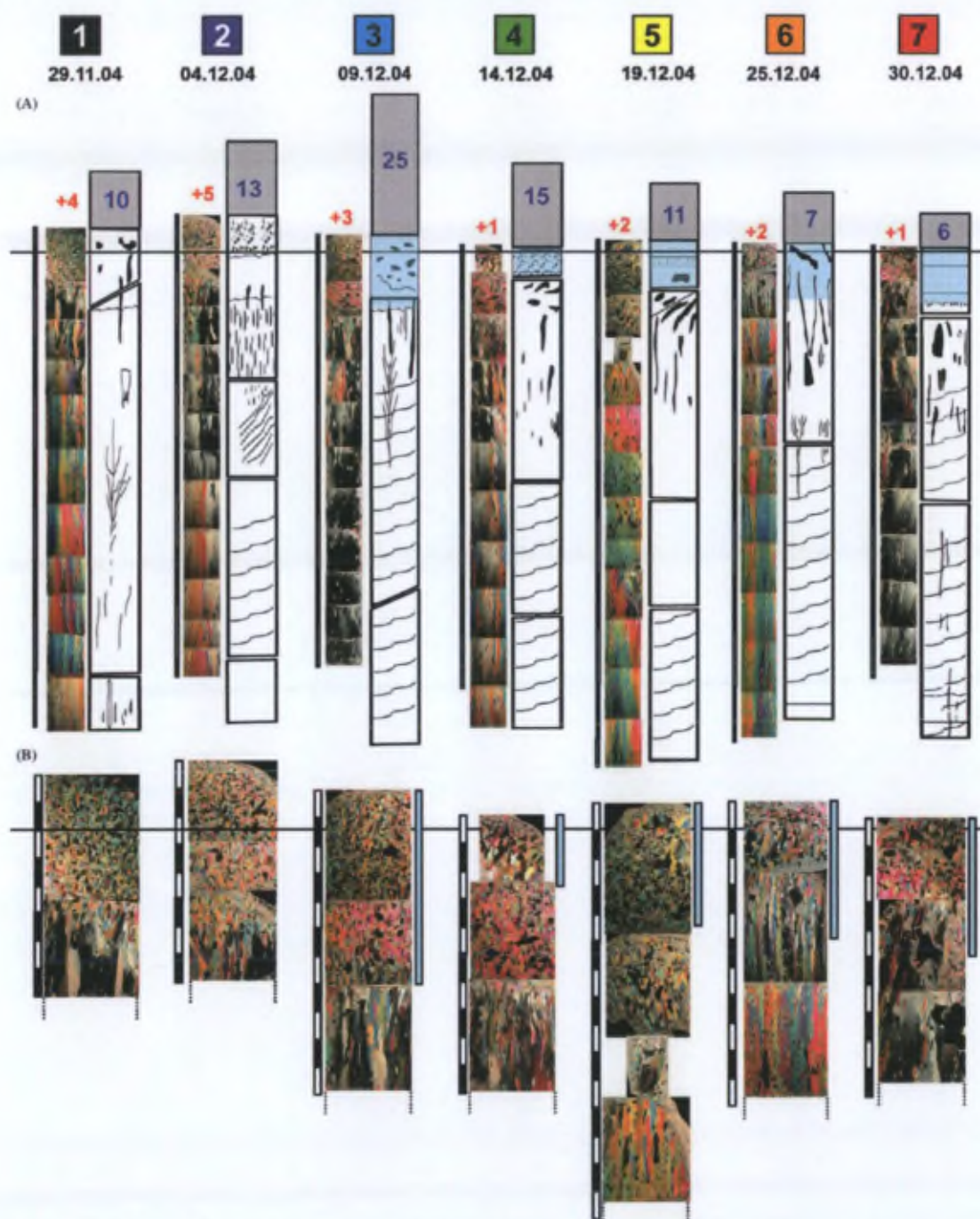


Fig. 5. Textural properties of the ice-core time series at the ISPOL clean site: (A) overview in vertical thin sections under crossed polarizers (texture core) and half core description on-board R.V. *Polarstern* (DMS core), (B) enlargement of the top part of the cores showing the development of superimposed ice and of the "honeycomb structure". Upper scale unit = 10 cm, lower scale unit = 2 cm. Blue shading shows areas with $\delta^{18}\text{O}$ lower than sea-water value, indicating a snow contribution. Red numbers are freeboard (cm) and blue numbers, snow thickness (cm). Black horizontal line is sea level (see text for details).

flooding, although the ice surface appeared occasionally “wetted”.

Ice temperature was on the whole quite warm, ranging from -3.1 to -0.2 °C (Fig. 6A). Times series of the temperature depth profiles showed that the ice cover was warming up with time, with increasing amplitude of changes observed closer to the surface. The temperature trend with depth reverted on 09.12.04, with the occurrence of a temperature minimum at 55 cm depth on that date.

Bulk “on-board” salinity at the ISPOL “clean site” (Fig. 6B) switched from the typical C-shape to a Z-shape profile in the course of time, with the strongest decrease in the upper half of the ice cover. Although great care was taken to limit brine drainage during sampling (see above), we cannot rule out brine losses, especially from the very porous surface layers, at the end of the experiment. Again, the salinity profile observed on 09.12.04 is somewhat peculiar, with a steadily increasing salinity with depth and a saltier 45–80 cm section.

Calculated brine salinity and brine volumes, hypothesizing thermodynamic equilibrium of the brine (Cox and Weeks, 1983; Leppäranta and Manninen, 1988; Eicken, 2003), are illustrated in Fig. 6C and D, respectively. Brine salinity ranged from 48 to 8 for the whole experiment. As expected from the temperature and salinity trends described above, it was regularly decreasing with time, with the largest changes occurring in the upper half of the sea-ice cover. The two first sampling days showed brine salinity higher or equal to the sea-water value (34.20–34.40) while profiles from the last four sampling days were below it, with record minimum salinity values of 8 in the surface layer. The 09.12.04 profile was transitional, with a brine salinity maximum of 37 at 55 cm depth, similar to the value observed in the layers above on the previous sampling event (04.12.04).

Fig. 6C also shows, as open triangles, brine salinity observed in the sackholes for the 0–20 and 0–60 cm integrated depth ranges.

Calculated brine volumes (Fig. 6D) ranged from 9% to 32%. It is noted that these are likely to be minimal estimates, since the bulk ice salinity might have been biased by brine loss on sampling, especially in the top and bottom sections. The highest values were observed in the upper half of the ice cover, which also exhibited the highest level of changes, corroborating the visual observations of gradually increasing voids in the ice textures. The brine volume was more stable with time, at 10–15%, in the lower half of the ice cover, to the expected exception of the very bottom layer showing much higher values. Another exception is again sampling day 09.12.04, with no depth trend, and consistently higher values in the lower 50 cm.

Fig. 6E and F (detail) shows the $\delta^{18}\text{O}_{\text{bulk ice}}$ depth profiles. Surface snow had an isotopic composition range from -13‰ to -17‰ while the $\delta^{18}\text{O}$ of slush (with a salinity of 27), collected on the flanks of a ridge nearby, was about -7.5‰ . Bottom water fluctuates slightly around -0.5‰ (mean: -0.47‰ , sd: $\pm 0.06\text{‰}$). Bulk ice values are

generally consistent between sampling days, increasing from $+0.7\text{‰}$ at the surface to -1.9 at the bottom, with, however, two noticeable exceptions. Firstly, more negative values in the top 15 cm of the ice cover and, secondly, sampling day 09.12.04, which shows significantly more negative $\delta^{18}\text{O}_{\text{bulk ice}}$ values at all depths, except for the very bottom.

4. Discussion

Despite the fact that we have paid attention to (a) study a level ice floe with a homogeneous surface and (b) sample small contiguous areas, we must acknowledge here that a time series such as this one may be affected by spatial variability that could not be assessed. This should therefore be kept in mind when we discuss the evolutionary processes of the sea-ice cover. On similar grounds, one might wonder if, despite the reasonable distances kept between areas dedicated to consecutive sampling days, previous ice-core sampling operations could have affected results from the subsequent sampling days. Although this is difficult to assess, neither temperature, nor calculated or observed brine salinities indicated detectable effects of disturbed heat fluxes or sea-water infiltration processes.

All cores show a typical textural sequence of first-year pack ice: surface granular ice underlain by dominant columnar ice. Isotopic $\delta^{18}\text{O}$ composition of the ice (Fig. 6E and F) shows that part of the granular ice is actually “snow-ice” resulting from refrozen sea-water infiltration in snow (blue shading in Fig. 5), with an isotopic signature below the mean sea-water value (Lange et al., 1990; Eicken et al., 1994; Jeffries et al., 1994, 1997; Eicken, 1998). Furthermore, the occurrence of coarser, elongated, bubble-free ice crystal embedded in the granular ice is typical of “superimposed ice” formed by refrozen snow melt (Morris and Jeffries, 2001; Haas et al., 2001; Kawamura et al., 2004).

Ice thickness evolution as seen in Fig. 5A does not indicate a clear trend of basal melting, as would be expected from heat flux measurements at the ice–ocean interface at other locations on the floe (McPhee, 2008). The spatial variability at a given observation time (comparing the thin sections textural core to the half-core description of the DMS core on board *Polarstern*) is indeed apparently as large as the temporal variability, and in the range of the calculated thickness reduction from basal melting (9–15 cm for the whole period, MCPhee, 2008). However, the availability of a large number of cores for each of the sampling days (between 10 and 14) allows us to plot a mean thickness of the sea-ice cover as a function of time (Fig. 7, squares) and to use a statistical approach to test for a significant trend in these values. The result of the ANOVA test (level of significance $\alpha = 0.05$) leads to the conclusion that there is a highly significant difference amongst the means of the ice-core lengths for the different time steps. Since the p -value related to the ANOVA ($p = 0.003$) is lower than the threshold of 0.01 in the present case, we can

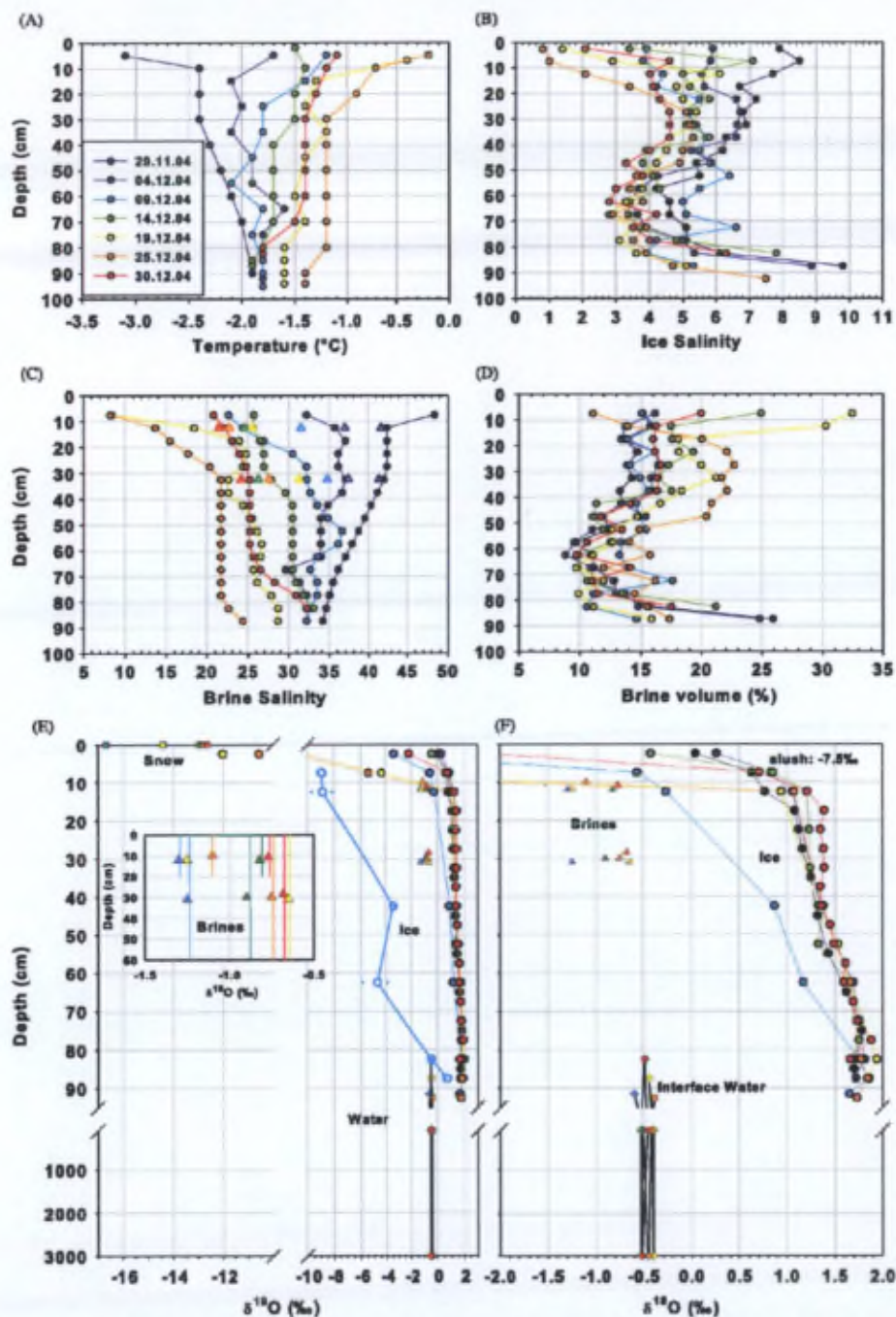


Fig. 6. Ice temperature (A), bulk ice salinity (B), theoretical (dots) and measurements within sackholes (open triangles at middle of depth range) brine salinities (C), theoretical brine volumes (D) and snow, ice, slush, brine and water $\delta^{18}\text{O}$ (E) and (F, detail) of the ice cores time series at the TSPOL clean site. Open circles and crosses in (E) are calculated $\Delta\delta^{18}\text{O}$ brine, see text for details.

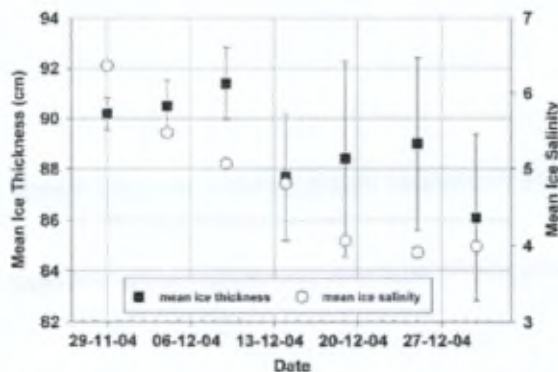


Fig. 7. Evolutions of mean ice thickness (black squares) and mean bulk ice salinity (open circles) for all ice cores of the ISPOL time series. Error bars on mean ice thickness are drawn at $\pm 1\sigma$.

conclude the existence of a highly significant difference for one or more means. The method of orthogonal contrast was then applied to investigate a possible temporal trend in the means. The p -value related to the test ($p < 0.001$) for a linear decreasing trend of the mean sea-ice cover thickness with time reveals that the ice-core lengths data fit in a very highly significant way to the linear decreasing model. Finally, 1σ error bars on ice thickness are clearly increasing with time, supporting the idea that basal melting increases the ice–water interface roughness.

Melting does not only affect the ice–ocean interface. Both thin sections and thick sections show a clear degradation of the cores structure in their upper half (0–40 cm), with an increasing proportion of large pores and holes in the ice texture over the course of the survey.

The temperature profile at the start of the experiment (Fig. 6A, 29.11.04) was inherited from typical winter conditions, with lower temperatures in the upper parts of the ice column, but all temperatures were already well above the reference temperature of -5°C , that would indicate restored connectivity (5% relative brine volume) for bulk ice salinity above 5 (the so-called “law of fives”, Buckley and Trodahl, 1987; Golden et al., 1998). As indicated above, relative brine volume (Fig. 6D) was always above 9% and reached more than 30% within the surface layers.

The temperature and salinity trends observed at our ISPOL “clean site” were very similar to those recently described for first-year ice in the Arctic during the first months of decay (May–June, Johnston, 2006). Meltwater flushing during ice warming and decay and resultant drastic changes in the temperature and salinity profiles over the entire ice column are a common feature in Arctic sea ice. However Eicken (1992) reported that this process is not important in Antarctic sea ice from the Weddell Sea, and usually restricted to second-year and multi-year ice, but nevertheless depending on the time of the year and on the distance from the ice edge. Our observations show that

Antarctic first-year sea ice can be affected by important changes in temperature and salinity profiles during its decay process. It is also interesting to note that, as shown in Fig. 4B, where profiles from 20- and 575-ml samples are compared for the various time slices, the bias from reduced salinity sample volume decreases as the ice decays. This is in accordance with experimental observations in tank ice (Interice experiment 1) from Cottier et al. (1999) who have demonstrated the decoupling between zones of high salinity and brine location as impurities relocate in warming sea ice, smoothing out the initial heterogeneity.

The mean ice-core salinity is plotted in Fig. 7 (open circles). It shows a clear decrease during the first half of the experiment and a stable value at about 4 for the last three sampling days.

Calculated brine salinity (Fig. 6C) decreased with time to values below sea-water salinity about halfway through the experiment, suggesting a transition from unstable to stable density profiles in the brine network. Since calculated brine volumes were all well above the threshold value of 5% for impermeable ice (Buckley and Trodahl, 1987; Golden et al., 1998) from the very beginning of the survey, connectivity is ensured within the brine network and helps explaining the trend of the mean ice salinity in Fig. 7. Brine drainage under the unstable density profile leads to desalination in the first half of the observation period while density stratification limits further brine loss in the second half of the study period.

It is also worth comparing the calculated brine salinities to those observed in the sackholes for the 0–20 and 0–60 cm depth ranges (triangles in Fig. 6C). There is a good agreement between the two values for the first two sampling days, in the shallower holes. Discrepancies tend to increase during the observation period, suggesting either a potential limitation of the accuracy of the ice temperature measurements (used in the calculation) in a porous ice medium or that the system is not in thermodynamic equilibrium. The values of the lower sackholes are clearly not representative, most likely because these holes are integrating brines drained from the upper layers.

The lower $\delta^{18}\text{O}$ values in the upper 15 cm of ice column indicate variable contribution of snow ice or superimposed ice, as also seen in the textures in Fig. 5.

Since the ice cover is in a general state of decay and since there is no fractionation on pure-ice melting (Jouzel and Souchez, 1982; Souchez and Jouzel, 1984), the peculiar isotopic profile at sampling day 09.12.04 can only be related to changes in the isotopic composition of brine in an open system (brine migration or brine loss). A first order estimate of the differences in brine isotopic composition ($\Delta\delta^{18}\text{O}_{\text{brine}}$) between sampling day 09.12.04 and the other sampling occasions/locations can be deduced from the differences in $\delta^{18}\text{O}_{\text{bulk ice}}$, considering that the $\delta^{18}\text{O}_{\text{pure ice}}$ did not change in the course of time and neither did the relative brine volume. The latter assertion is clearly not true, but since the relative change in relative brine volume is reasonably small, especially in the early stages of the

experiment, we can use it for a first estimate of the $\Delta\delta^{18}\text{O}_{\text{brine}}$, e.g., by comparing profiles of 04.12.04 and 09.12.04. The result is shown in Fig. 6E as open circles (using mean brine volume for the 04.12.04–09.12.04 period at a given depth) and crosses (using either of relative brine volumes on 04.12.04 and 09.12.04). This gives a $\Delta\delta^{18}\text{O}_{\text{brine}}$ profile ranging between -9‰ and $+0.5\text{‰}$, with a clear decrease of its absolute value with depth. Such a lowering of the isotopic composition of brine can only result from infiltration of water contaminated by snow or snow ice meltwater. Three potential candidates can be pointed at: (a) internal melting of the snow ice layer ($-3.5\text{‰} < \delta^{18}\text{O} < -0.5\text{‰}$), which is present at the site location (Figs. 5 and 6E), (b) snow melt from the surface ($-17\text{‰} < \delta^{18}\text{O} < -13\text{‰}$), and (c) lateral infiltration of the slush that forms in the areas closer to the ridges ($\delta^{18}\text{O}_{\text{slush}} = -7.5\text{‰}$). It also should be noted that, although within the range of two error bars, the interface sea-water value is the lowest on 09.12.04 (Fig. 6F).

Note that the calculated differences in brine isotopic values clearly imply much lower $\delta^{18}\text{O}_{\text{brine}}$ values than those observed in the sackhole brines (triangles in Fig. 6E and F). This could be explained by the fact that the sackhole sampling procedure biases $\delta^{18}\text{O}_{\text{brine}}$ toward less negative values because of surface melting and increased contribution from the crystal melt. The 09.12.04 sackhole brine $\delta^{18}\text{O}$ is, however, the lowest in the range.

Finally, comparing the initial (29.11.04, black line) and final (30.12.04, red line) $\delta^{18}\text{O}_{\text{bulk ice}}$ profiles above 60 cm depth, it is interesting to note that the final bulk ice signature is always higher than the initial. Following the same rationale as above, i.e. that these changes can only be related to changes in the isotopic composition of the brine, suggests that, in areas not influenced by surface slush infiltration, the initially lighter brine (resulting from interface isotopic fractionation on freezing that enriches the solid phase in the heavier isotope and the interface liquid in the lighter one (e.g., Souchez and Jouzel, 1984; Tison and Haren, 1989; Souchez et al., 1989; Eicken, 1998))

is progressively replaced by pure-ice melt, with a heavier signature.

4.1. A model for the temporal evolution of the sea-ice cover

We are now able to describe the temporal evolution of the first-year sea-ice cover at the ISPOL “clean site”, using the dataset described above, as sketched in Fig. 8. At the beginning of the observation period, the brine network is unstable in terms of density and already largely interconnected. This should favor downward brine migration, either through convection (where downward brine movement in some areas is counterbalanced by upward sea-water movement in others) or brine drainage (where downward brine movement is compensated by melting/infiltration in the upper layers), and results in the observed regular mean ice salinity drop for the three first sampling days. The isotopic record at sampling day 09.12.04 does not support a convective process. Indeed, because of the isotopic fractionation occurring on ice growth (Jouzel and Souchez, 1982; Souchez and Jouzel, 1984; Tison and Haren, 1989; Souchez et al., 1989; Eicken, 1998), the brine isotopic signal will always be more negative than (or equal to) the mean sea-water signature (-0.5‰). Therefore, replacing part of the initial brine with sea-water would inevitably shift the bulk ice $\delta^{18}\text{O}$ towards less negative values. This is the reverse of the observed trend from 04.12.04 to 09.12.04. As surface brine travels downward, it is progressively replaced by either sea water/snow slush from the flooded ridges flanks nearby (sampling day 09.12.04 is the closest to the ridges bordering the “clean site” patch—Figs. 2B and 3A, and show the thickest snow layer, inherited from previous snow fall and wind drift accumulation—Fig. 5) or by in-situ melting as the temperature increases, particularly in the upper layers. Direct snow-melt contribution to brine channel infiltration, away from the ridges, is probably a very limited source since below-zero temperatures at the snow-ice interface

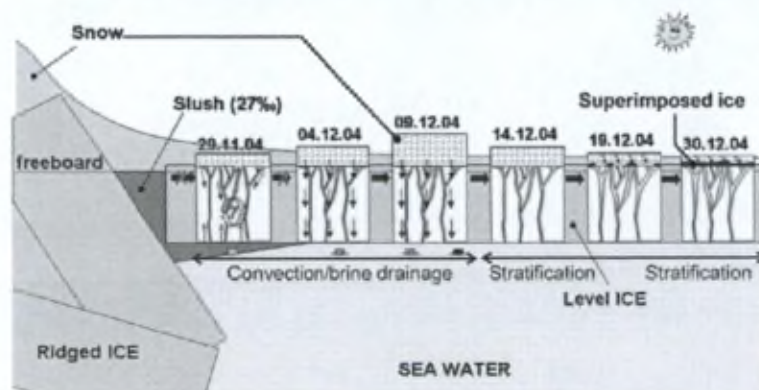


Fig. 8. A simple model for the degradation of the first-year level sea-ice cover at the ISPOL clean site.

were the rule, as shown by the superimposed ice formation at the end of the period (Fig. 5B) and by extensive direct temperature measurements at other locations on the ice floe. The already large porosity of about 14% greatly favors brine transfer, not only vertically, but also potentially laterally from the ridges nearby, through the building “honeycomb-like” structure. Indeed, the snow cover at sampling day 09.12.04 (with its clear infiltration signature) did not show any sign of slush build up at the snow-ice interface. Note that, in that case, the profile at sampling day 09.12.04 would typically illustrate interference of spatial variability within a time-series study. As discussed above, we cannot preclude, however, that the more negative $\delta^{18}\text{O}$ value observed in the brine is a contribution from in situ melting of the upper part of the snow-ice layer. Considering a mean brine volume of 15% on the 09.12.04, 13 cm snow ice melt would be required to fully “refill” the existing brine network. Observed snow-ice thicknesses are compatible with this value, though rather on the high side. However, since reduction in snow-ice thickness has not been observed prior to 09.12.04, snow-ice melt is probably not the only contributor. Finally, one could argue that snow ice is also present at sampling days 4–7 (Fig. 5) and that no sign of infiltration of brines with lower $\delta^{18}\text{O}$ is seen there (Fig. 6E and F). As we have seen, brine dynamics has undergone major changes halfway through the experiment and the initiation of brine stratification would have hampered downwards infiltration of snow ice-melt, making sampling day 09.12.04 a singular case.

Of particular importance, from a biogeochemical perspective, is the actual process of brine migration. Brine convection or sea-water/snow-slush invasion from the surface layer (a first step towards flooding) will favor nutrient replenishment and potentially boost the development of the surface and/or internal microbial community. Internal melting of channel walls will, on the contrary, dilute nutrients and eventually destroy algae anchoring sites. Nutrients records, as illustrated for dissolved silica in Fig. 9, did not indicate replenishment during the first half of the observation period (29.11.04, black symbols; 04.12.04, dark blue symbols). Apart from those in the skeletal layer (samples shown with crosses in Fig. 9A), all data points were below the conservative sea-water dilution curve (Fig. 9A), with a clear trend of decreasing concentrations between 29.11.04 and 04.12.04 (Fig. 9B). Only at sampling day 09.12.04 was the concentration slightly higher in the upper half of the ice cover, probably reflecting the surface slush infiltration, without, however, recovering the sea-water dilution curve silica concentration within the brine. This example, and the behavior of a suite of other variables (including other nutrients) that will be described elsewhere, suggest that brine drainage (as opposed to brine convection with sea-water upwards movement within the sea-ice cover) was the dominant process of desalination in the early stages of decay. Since no obvious flooding occurred on site (before and apart from the local event on 09.12.04) and the freeboard was

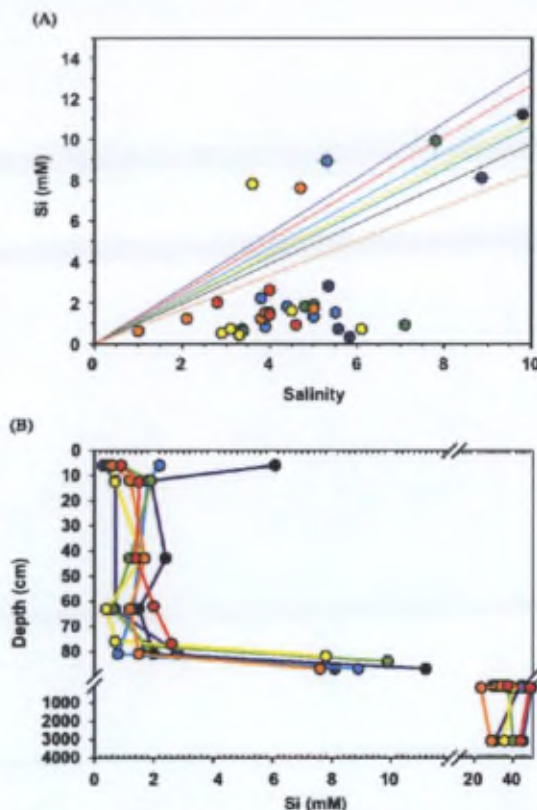


Fig. 9. Evolution of the dissolved silica concentration in all ice cores for the ISPOL time series: (A) samples position vs. conservative dilution curves of sea-water, (B) depth profiles in ice and underlying water. Each dilution curve describes the theoretical evolution of the Si concentration in sea-water when it is progressively diluted by melting pure ice. To draw the dilution lines, the mean Si value of the underlying water has been used at each sampling occurrence. If Si behaves conservatively, bulk ice samples should lie on the dilution curve. Any consumption process (such as biological uptake of nutrients) would bring the bulk ice samples below the dilution curve and vice versa. Note the dominant pattern of substantial undersaturation, apart for the ice-water interface samples (crosses).

positive (+5 to +3 cm in the first half of the period), one has to attribute the brine drainage process to the slight hydraulic head that must have resulted from increased melting in the surface layers above the freeboard.

As brine salinity dropped below the sea-water value, stratification of the brine network occurred, and solute exchange should now be mainly controlled by molecular diffusion along concentration gradients, especially as the freeboard level was getting close to zero. Fig. 10 shows a clear trend of decreasing salinity in the surface sea-waters, and, if this is attributable to exchange with the regional decaying sea ice drifting north, the dilution must have resulted from basal or lateral melting of the sea-ice cover (eventually increased in areas of brash and floe/lead

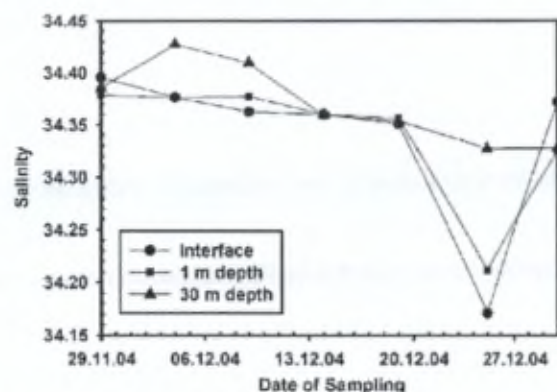


Fig. 10. Evolution of the salinity of the underlying water at the "clean site" in the course of the ISPOL experiment. Note that the measurements were only made at three discrete depths (ice–water interface, 1 and 30 m). See text for details.

edges—see, e.g., 25.12.04 at interface and 1 m depth), since no further desalination is observed in the mean ice-core salinity record. This melting process resulted in the observed diminishing trend of the sea-ice thickness (Fig. 7). Finally, textural observations (Fig. 5B) indicate that superimposed ice formation started in the second half of the study period, as melting surface snow infiltrated and refroze at the top of the more saline and colder granular ice. This process is also of interest from a biogeochemical perspective, because it will impede gas exchange with the atmosphere, by giving rise to an impermeable layer of superimposed ice. A pause in the downward flux of CO_2 into the ice was observed on the site for the last two sampling days whereas breaking the existing superimposed ice crust immediately re-established the flux (Delille and Tison, unpubl. data).

5. Conclusions

Regular five-day sampling of the main physico-chemical properties of an unflooded 90-cm-thick first-year sea-ice cover at ISPOL during spring/early summer 2004 has provided insights into the changing character of sea ice during the summer decay season, and the processes involved. Progressive melting occurs both in the top layers and at the ice–ocean interface. In the first case, internal melting largely dominates resulting in a strong increase of the ice porosity, while interface melting dominates in the latter.

In the early stages of decay, brine salinity in the upper layers is higher than sea-water resulting in density instability. This favors downward brine migration, as attested by the steady decrease of the mean bulk-ice salinity. Bulk-ice salinity depth profiles and brine salinity measurements during the first three sampling days clearly showed downward salt transfer, with replacement by fresher brine in the upper layers. The driver of the brine

migration was likely brine drainage under the hydraulic head resulting from increased melting in the upper sea-ice layers, as well as enhanced horizontal and vertical brine transfer favored by the large porosity. Closer to the ridged areas, local events of downward slush infiltration were detected, although there were no signs of flooding at the surface, suggesting sub-surface transfer occurs through the building up of a "honeycomb-like" structure (Haas et al., 2001). Convection processes involving the underlying sea-water were less likely, as indicated by the $\delta^{18}\text{O}$ values of the brine and because nutrient replenishment of the internal layers was not observed.

Further surface and internal melting leads to brine salinity that is lower than sea-water throughout the sea-ice cover, which stratifies the brine medium and ends the drainage process, limiting the exchange of solutes via molecular diffusion. As a result, and since the freeboard is close to zero (and therefore strongly limiting the potential for an efficient hydraulic head), the bulk ice salinity and the salinity profiles stabilized. The contribution of sea-ice melting to the underlying sea-water is then mainly limited to the ice–ocean interface.

In a way, this second phase of internal sea-ice cover decay is a preliminary stage of the more extensive case of melt ponds conditions in the Arctic.

This overall process of decay, in the (near) absence of flooding, is of utmost importance for the ice biogeochemical evolution since it would limit nutrient replenishment and compromise brine channel wall stability, therefore impeding the development of surface and internal algal communities. The situation is likely to be very different in areas where a thicker snow cover would favor flooding by depressing the freeboard to below sea-water level (i.e. negative freeboard). The observation of an infiltration event at sampling day 09.12.04 suggests that, if flooding occurred during this early summer stage in the evolution of the sea ice, it would mainly result from lateral sources, rather than bottom-up water transfer. The latter case would indeed be restricted to the cases where ice submergence from snow fall events or bottom melting would induce upward brine/water movement by the amount of submergence.

The switch from a brine drainage to a diffusion controlled transfer of solutes within the ice column, together with the late build-up of a continuous superimposed ice layer, should also considerably affect gas exchange in this generally highly porous medium, but this is outside the scope of the present paper.

Although the thickness of the snow cover and local meteorological conditions will undoubtedly control the timing of the decay process and the potential for flooding, we believe that the processes described here should apply to a large number of other locations around Antarctica since more than 80% of the Antarctic sea ice cover is made of level first-year pack ice. It is, however, clear that future work should focus on both the effects of flooding and the evolution of multiyear floes. Increased surface and internal

melting as summer progresses should further reduce brine and bulk ice salinity profiles. Should the ice survive the summer, the resulting second-year ice would display low salinity "T"-shaped profiles, as documented by Eicken (1992) in the Weddell Sea or Remy et al. (in press) in McMurdo Sound during the B-15 iceberg stranding event.

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Paper 3 :

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Contribution of F. Brabant: Field sampling. Compilation of temperature and salinity data and computation of brine salinity and brine volume fraction profiles.



Sea ice and snow cover characteristics during the winter–spring transition in the Bellingshausen Sea: An overview of SIMBA 2007

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ABSTRACT

The Sea Ice Mass Balance in the Antarctic (SIMBA) experiment was conducted from the RVIB *N.B. Palmer* in September and October 2007 in the Bellingshausen Sea in an area recently experiencing considerable changes in both climate and sea ice cover. Snow and ice properties were observed at 3 short-term stations and a 27-day drift station (Ice Station Belgica, ISB) during the winter–spring transition. Repeat measurements were performed on sea ice and snow cover at 5 ISB sites, each having different physical characteristics, with mean ice (snow) thicknesses varying from 0.6 m (0.1 m) to 2.3 m (0.7 m). Ice cores retrieved every five days from 2 sites and measured for physical, biological, and chemical properties. Three ice mass-balance buoys (IMBs) provided continuous records of snow and ice thickness and temperature. Meteorological conditions changed from warm fronts with high winds and precipitation followed by cold and calm periods through four cycles during ISB. The snow cover regulated temperature flux and controlled the physical regime in which sea ice morphology changed. Level thin ice areas had little snow accumulation and experienced greater thermal fluctuations resulting in brine salinity and volume changes, and winter maximum thermodynamic growth of ~ 0.6 m in this region. Flooding and snow–ice formation occurred during cold spells in ice and snow of intermediate thickness. In contrast, little snow–ice formed in flooded areas with thicker ice and snow cover, instead nearly isothermal, highly permeable ice persisted. In spring, short-lived cold air episodes did not effectively penetrate the sea ice nor overcome the effect of ocean heat flux, thus favoring net ice thinning from bottom melt over ice thickening from snow–ice growth, in all cases. These warm ice conditions were consistent with regional remote sensing observations of earlier ice breakup and a shorter sea ice season, more recently observed in the Bellingshausen Sea.

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1. Introduction

The Sea Ice Mass Balance in Antarctic (SIMBA) research program conducted in September and October 2007 provided an excellent opportunity to observe sea ice and snow cover characteristics of the Bellingshausen Sea sector of the Antarctic during the winter–spring transition of the International Polar Year. The Bellingshausen Sea is a region that is experiencing significant recent changes both in climate and sea ice cover (Jacobs and Comiso, 1997; Massom et al., 2008; Parkinson, 2004; Stammerjohn et al., 2008). The near 30-year record of passive microwave (PM) remote sensing data has shown the Bellingshausen–Amundsen Seas sector and the Ross Sea sector to have the greatest reported change, although with opposing trends

(Zwally et al., 2002; Comiso and Nishio, 2008). The overall trend in sea ice extent is decreasing for the Bellingshausen–Amundsen sector at $-5.7 \pm 1.0\%$ per decade, whereas sea ice extent in the Ross Sea sector increased by $4.2 \pm 0.7\%$ per decade (Comiso and Nishio, 2008). Additional analysis of PM data by Stammerjohn et al. (2008) indicates that overall trends of sea ice extent not only decrease in the Bellingshausen Sea, but also that the timing of advance and retreat of the seasonal sea ice cover changes with an overall reduction in ice duration of 85 ± 20 days per year. This decrease in the extent and relative duration of the sea ice cover has been attributed in part to coincident occurrence of La Niña in the southern Pacific Ocean and positive anomalies of the Southern Annular Mode (SAM) (Stammerjohn et al., 2008), and changes in atmospheric circulation patterns due to stratospheric ozone depletion (Turner et al., 2008).

Recent studies (Stammerjohn et al., 2011) indicate similar atmospheric and sea ice anomalies occurred in the Bellingshausen Sea during 2007. The atmospheric circulation and strong westerly winds attributed to decreasing sea ice extent in the Bellingshausen Sea also

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suggest changes in the mechanisms of sea ice formation and accumulation in this region (Massom et al., 2008). The use of passive microwave remote sensing data to assess the changes in the sea ice zone does not address potential changes in the ice thickness distribution that may result from rafting and ridging in the ice pack, or snow-ice formation from interface flooding. Such occurrences are expected to increase sea ice thickness by consolidation in the former and by accretion in the latter, although linkages between the two have been shown to contribute to regional homogeneity (Sturm et al., 1998). Previous sea ice studies performed in the Bellingshausen Sea have identified recurring cyclic patterns of meteorological conditions that influence the growth and evolution of the sea ice and snow cover characteristics (Jeffries et al., 1998, 2001; Sturm et al., 1998). Warm atmospheric fronts are accompanied by high northerly winds and precipitation that increase snow loading on sea ice (Sturm et al., 1998); however, the mobility of snow cover under high wind conditions suggests not only snow accretion in some areas, but significant snow redistribution and also snow loss in open leads within the ice pack (Eicken et al., 1994; Massom et al., 2001). Thus, warmer and/or fresher localized ocean conditions are anticipated to affect heat transfer and sea ice growth (Lytle and Ackley, 2001).

The redistribution of snow cover on the ice pack directly affects isostatic balance (buoyancy) and the presence of thick snow cover results in negative freeboard (snow/ice interface submerged below sea level). In warmer conditions, generally relating to a brine volume above approximately 5%, sea ice becomes increasingly permeable (Cox and Weeks, 1975; Golden et al., 1998, 2007) and negative freeboard allows flooding of the snow/ice interface, either vertically through open brine channels or laterally from fractures associated with deformation features or open leads, forming a mixed layer of snow and sea water (slush) (Maksym and Jeffries, 2000). Subsequent freezing of the slush layer forms granular snow-ice, an extremely important component of Antarctic sea ice, which contributes to thermodynamic growth on a circumpolar scale (Eicken et al., 1994; Lytle and Ackley, 1996; Jeffries et al., 1998; Worby et al., 1998). The presence of thick snow cover not only gives rise to flooding, but also provides thermal insulation from cold air temperatures above, affecting the thermal evolution of sea ice (Massom et al., 2001).

The overall objectives of SIMBA were to establish a baseline data set in an under-sampled region of the Antarctic from which to study sea ice processes and monitor future change. These include: (1) physical processes of snow and ice growth/accumulation, physical properties, heat flux and energy balance; (2) biogeochemical processes of gas exchange, nutrient flux, biological growth, inorganic and trace metals; and (3) the evaluation of various satellite remote sensing instruments for sea ice assessment. While the results of these studies may be found in a number of papers within this volume, our paper specifically provides an overview of SIMBA and the physical setting. We present results of recurrent measurements of sea ice and snow characteristics as obtained during the winter-spring transition in 2007. These observations show how sea ice structure and snow cover of the region change in response to a cyclical pattern of atmospheric warming-cooling events. The effects of changing snow thickness, evolution of sea ice brine volume and salinity, and the effects of flooding are also discussed in the paper.

2. SIMBA study area

The SIMBA research program (NBP 0709) consisted of an international contingent with a range of scientific objectives related to both physical and biological interactions between the ocean, sea ice, snow cover, and atmosphere. The R/V *B. Nathaniel B. Palmer* (NBP) reached the marginal ice zone (MIZ) near Peter I

Island in the Bellingshausen Sea on 25 September 2007. During the inbound passage, ice observations were performed from the ship's bridge using the ASPeCt protocol (Worby and Allison, 1999). Ice types and concentration, snow and ice thickness, and weather conditions were classified at hourly intervals. The ice edge along the inbound track was noted in ASPeCt observations to be 0.1 concentration (frazil ice), and transitioned to open water at 67.333°S. The area of open water extended south to Peter I Island, where ice was again encountered at 0.3 concentration (shuga and frazil) at 68.767°S. The ice showed a southward transition to brash ice and then first year floes. The ship track for the SIMBA cruise from the Chilean 200-mile territorial limit, short-term ice stations (Stations 1–3), and long-term drift station (Ice Station Belgica), are given in Fig. 1. Relevant position and timing information are given in Table 1.

2.1. Stations 1–3

Three 3 to 4 hour long ice stations were performed on sea ice floes to measure snow and ice properties and obtain ice cores. These stations varied in characteristic ice type, overall ice and snow cover thickness representing a transition from the MIZ to larger sea ice floes toward the interior of the ice pack. Station 1 consisted of a Type Y first year sea ice floe (Jeffries et al., 1998; Perovich et al., 2004) with 1 m mean ice thickness, thick snow cover and a flooded snow-ice interface. Station 2 consisted of a thicker Type Z floe with mean ice thickness of 1.7 m, deformation ridges and evidence of rafting, thick snow cover and flooded snow-ice interface. Station 3 consisted of thin level first year Type X floe with thinner snow cover and neutral to slightly positive freeboard. At the short-term stations, measurement transect lines were established to obtain snow, slush and ice thickness and snow/ice interface temperature. Separate snowpits were excavated adjacent to transect lines, and ice cores were obtained in a "clean" area separate from the snow and ice measurement transects. The weather during transit into the ice pack was generally inclement with varying snowfall, fog and overcast skies with high cloud cover. Air temperatures varied from approximately -1 to -4 °C and northerly and easterly winds ranged from about 5 to 10 gusting to 22 m s⁻¹.

2.2. Ice Station Belgica

The long-term drift station, Ice Station Belgica (ISB), was established south of Peter I Island for 27 days as shown in Fig. 2. The ISB floe was selected based on the presence of a variety of ice types and snow cover that are characteristic of the greater region and the relative floe size which was likely to survive the duration of the field experiments. Five specific sites (Brussels, Liège, Fabra, Patria, and Frost Flower) characterized different snow and ice regimes suitable for the different objectives of the sampling programs. Biogeochemical sampling "clean areas" at Brussels and Liège were selected based on a number of factors including: (1) homogeneity of surface properties to reduce spatial variability; (2) contrast in ice and snow properties between sites emphasizing difference in processes; (3) minimized area to reduce logistic constraints; and (4) distance from the ship suitable to prevent sample contamination. Snow and ice measurements performed at Brussels, Fabra and Patria focused on snow and ice elevation, snow and ice thickness by direct measurement and electromagnetic induction, and snow properties from representative snowpits (Weissling et al., 2011). By necessity, these activities were kept distinctly separate from the biogeochemical sampling to avoid cross contamination issues. The Frost Flower site was used to observe and sample frost flowers.

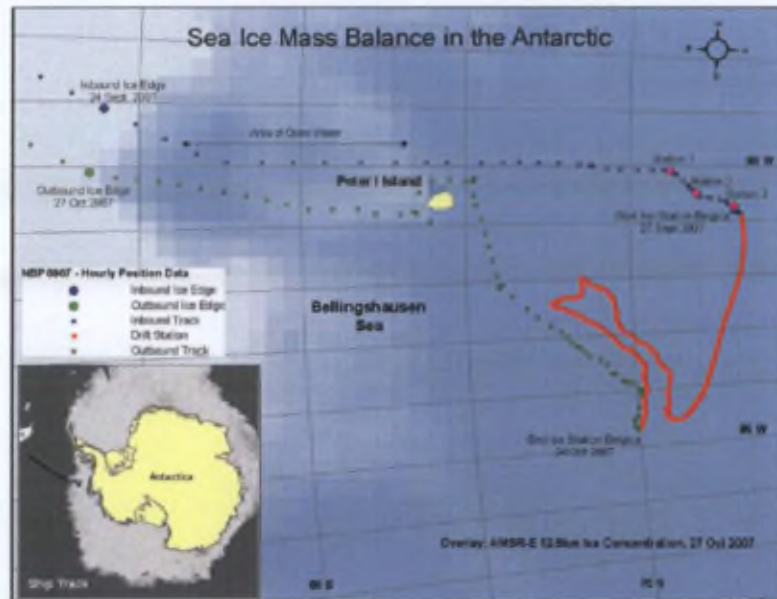


Fig. 1. Hourly position data for the Sea Ice Mass Balance in the Antarctic (SIMBA) research program aboard the RVIB Nathaniel B. Palmer (NBP0907) during the 2007 winter-spring transition in the Bellingshausen Sea, Antarctica. The location of the inbound ice edge, outbound ice edge, inbound short-term ice stations, and 27-day drift station (Ice Station Belgica) are noted. Along the inbound track, a stretch of open water was encountered between the ice edge and Peter I Island as indicated above.

Table 1
SIMBA positions.

Location	Date	Day of year	Time (GMT)	Latitude	Longitude
Inbound Ice Edge	24 September 2007	267	17:00	–66.783	–89.083
Station 1	25 September 2007	268	18:35	–70.245	–90.071
Station 2	26 September 2007	269	16:52	–70.408	–90.483
Station 3	27 September 2007	270	4:55	–70.635	–90.736
Start Ice Station Belgica	27 September 2007	270	18:35	–70.55	–90.905
End Ice Station Belgica	24 October 2007	297	11:00	–69.995	–94.706
Outbound Ice Edge	24 October 2007	300	8:00	–66.710	–90.692

The Brussels site (Fig. 2) was utilized for both biogeochemical sampling and ice and snow thickness profiles. Brussels may be generally characterized as level first year sea ice of 0.5–0.7 m thickness with little deformation, minimal snow accumulation and overall positive freeboard. The Liège site was utilized primarily for biogeochemical sampling and may be generally characterized as deformed first year sea ice of 0.9–1.2 m thickness, thick snow cover, and some flooding at the snow/ice interface. Liège was not used for ice thickness transects, however, snowpits were excavated in characteristic areas away from the “clean area”. The Fabra site consisted of multi-year sea ice of mean thickness exceeding 2 m that was highly deformed with numerous pressure ridges and ice blocks at the surface. The snow cover at Fabra exceeded 1 m thickness in places with extensive flooding encountered at the snow/ice interface. Snow and ice measurements were conducted along the same transect lines at Fabra, including snowpits excavated to assess snow properties. The Patria site consisted of deformed first year sea ice similar in snow and ice thickness to Liège with overall slightly negative freeboard. Snow and ice thickness measurements were performed on two different occasions along the same transect line. The Frost Flower site

consisted of newly formed nilas (0.07 m) along a lead near the ship where frost flower formation was observed on 4 October at the ice surface. There the sea ice thickened to 0.27 m on 17 October when additional sampling was performed. The results from the Frost Flower site will be specifically addressed elsewhere (Tison, in preparation).

3. Data collection and methods

Meteorological and the vessel's position data, as well as other standard oceanographic parameters, were collected on a near continuous basis from shipboard sensors on the NBP. These data were provided by Raytheon Polar Services for the US Antarctic Program (Grant and Acha, 2007).

3.1. Thickness transects of snow and ice

Transects varying between 100 and 300 m length were established at Fabra, Brussels and Patria. At ISB, repeat measurements along the transect lines were carried out at varying frequency. The endpoints of

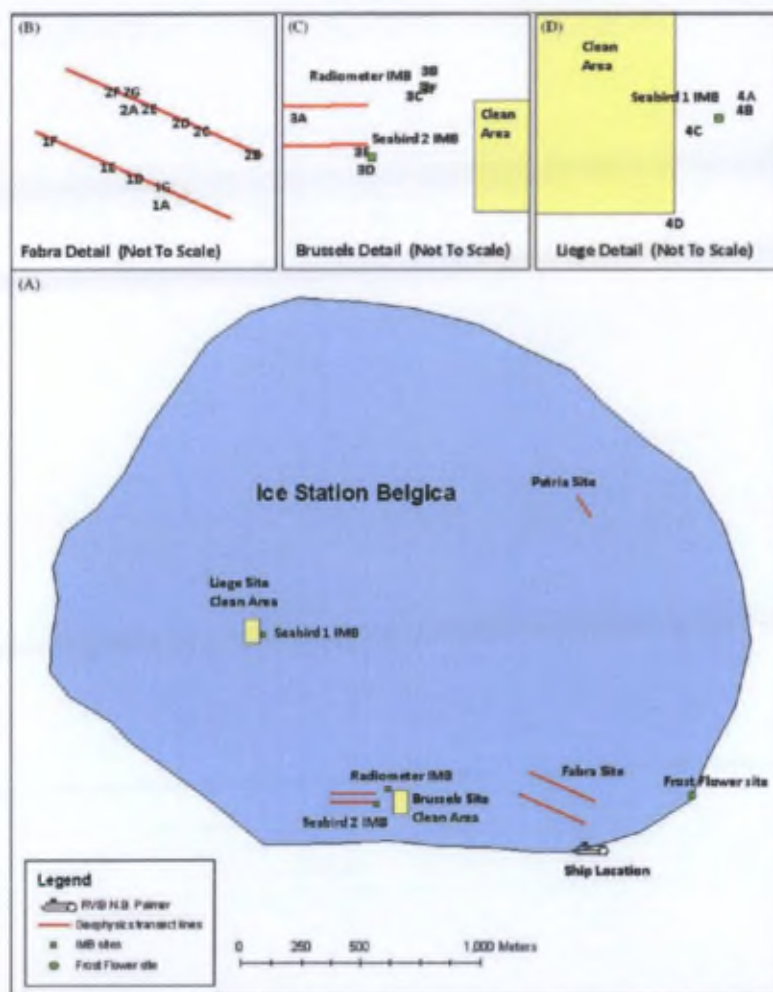


Fig. 2. (A) Layout of the drift station Ice Station Belgica. The various study sites, snow and ice thickness transect lines, IMB locations, sampling clean areas and Ship location are shown. Detail inset maps show (B) the Fabra site, (C) the Brussels site, and (D) the Liège site, including locations of snow pits (1A through 4D) relative to other site features.

each line were staked and intermediate stakes were set at 50 m intervals. Level surveys of the surface topography were performed using an optical beam level and stadia rod at 1 m intervals along each transect. The measurements were referenced to a sea level benchmark established by drilling auger holes between instrument stations. Snow thickness measurements were obtained from the surface of the snow pack using a meter-long ruler. Ice freeboard (sea ice surface relative to sea level) was calculated as the difference between surface elevation and snow thickness at each location. Ice thickness was measured by two methods: (1) electromagnetic induction (EMI), and (2) drilling of auger holes and manual gauging of the ice thickness. The measured freeboard was recorded for each drill hole location, including thickness of slush layers. At Stations 1–3, snow and ice thickness measurements were performed manually by similar methods, however, no level surveys or EMI measurements were performed.

3.2. Snowpits

Snowpits were excavated in representative areas closely aligned with thickness transects or ice mass-balance buoys Fabra, Brussels, Liège, and Patria (Fig. 2) and at Stations 1–3. Stratigraphic layers of the snow profiles were assessed and described following the International Classification System (Colbeck et al., 1990). Temperature measurements were obtained in vertical profile using a digital thermometer (Fisher Scientific Pt-100, accuracy ± 0.1 °C). Snow samples were extracted from the vertical profile using tapered 0.05 m diameter cylindrical aluminum tubes of measured volume and weight. Snow sample tubes were inserted into the snowpit profile at various intervals and then excavated, capped, and brought aboard the NBP for further analysis. Snow samples were weighed for density determination. Meltwater was tested on the ship for salinity and for oxygen isotopes.

Snowpit 2G was excavated on 16 October to perform temperature, density and salinity measurements and to observe the stratigraphy and texture in profile. A 0.05 m auger hole was drilled approximately 0.10 m adjacent to the cut wall and temperature “button” data loggers (Onset HOBO TidBitv2) were installed in the snow pack. The data loggers were placed into the slush layer, at the snow/slush interface, and at increments above the interface in the snow pack. The snowpit was backfilled and data loggers left in place until 22 October, prior to departure from ISB. The data loggers operated throughout a warming event that peaked in temperature on 19 October, during which additional flooding (increase in slush layer thickness) occurred.

3.3. Ice mass-balance buoys

Three ice mass-balance buoys (IMBs) were deployed on 2, 4 and 12 October 2007 at Brussels and Liège (Fig. 2) at locations close to the clean sampling sites. IMBs were designed and constructed by the Cold Regions Research and Engineering Laboratory (Perovich and Elder, 2001; Perovich et al., 2004; Richter-Menge et al., 2006) and equipped with data acquisition systems mounted on steel framed tables anchored to the sea ice. Instrumentation on each buoy consisted of a common suite of sensors including thermistors in the upper ocean, sea ice, snow and air at 0.05 or 0.10 m interval;

acoustic range-finder sounders to record the ice bottom and snow surface elevation. Additional sensors included an underwater radiometer (1 buoy) and Seabird conductivity–temperature–depth (CTD) sensors (2 buoys). The buoys were equipped with global positioning system (GPS) receivers and communications equipment that utilized Iridium satellite uplink to transmit data. The Seabird 1 buoy installed at Liège was recovered prior to departure from ISB due to problems with its CTD sensor, while the other two IMBs operated for 55 and 73 days (Table 2). During ISB the IMBs drifted eastward with the floe (Fig. 3), changing directions midway to a westward track. After departing ISB, the surviving IMBs (radiometer and Seabird 2) drifted primarily in a northeast direction, extending northward beyond Peter I Island until 23 November, at which time, the GPS position records diverged and the IMB trajectories separated near 69.001°S, 91.453°W (see Fig. 3, inset). The buoy sensors provided two-hourly data for the duration of the drift. However, premature loss of thermistors, snow pinger and air temperature sensors occurred on the radiometer buoy on 1 November and the radiometer stopped operating around 26 November. The Seabird 2 IMB maintained thermistor data transmissions until 6 December, at which time the buoy ceased to operate at approximately 67.717°S, 89.244°W. On 14 December (67.295°S, 85.665°W), the radiometer buoy ceased transmission of barometric pressure and GPS location.

Table 2
IMB deployment.

IMB	Buoy ID	Location	Start date (DoY)	End date (DoY)	End status
Radiometer	29834	Brussels	2 October 2007 (275)	14 December 2007 (348)	Transmission lost
Seabird 1	29837	Liège	4 October 2007 (277)	22 October 2007 (295)	Recovered by science team
Seabird 2	29846	Brussels	12 October 2007 (285)	6 December 2007 (340)	Transmission lost

Note: DoY = Day of Year.

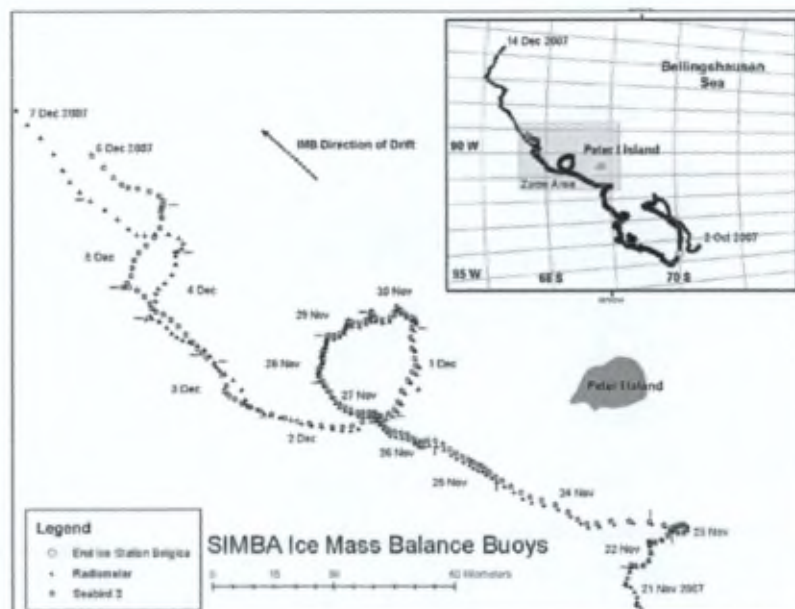


Fig. 3. Drift track for ice mass-balance buoys (IMB) installed during SIMBA. The IMB installed at the Liège site was removed prior to leaving Ice Station Belgica. The two IMBs installed at the Brussels site continued to operate into December, with the Radiometer buoy losing transmission on 14 December. Zoom detail shows the later stages of the drift track. Daily drift segments are noted between hash marks. The floe breaks apart on 23 November and the IMB drift tracks separate (see text for details).

3.4. Ice cores

Ice cores at ISB were obtained at designated “clean areas” comprising a 100 m by 60 m footprint that was subdivided into small work sub-areas approximately 5 m by 5 m. The 25 m² sub-areas (see Fig. 4) were located adjacent to each other to minimize spatial variability. The integrity of the site was controlled by clearly marking the boundaries and limiting entry to essential personnel with Tyvek® coveralls, plastic boot covers and gloves and only essential equipment. The power supply generator (for coring equipment) was excluded from the clean area and a long power cord was used to supply the electric drill. Similarly, staging and supply areas were established at least 100 m from the clean areas. Each site was revisited on alternating intervals, with a five day period between sampling events. Brussels cores were obtained on the following dates (Day of Year, [DoY]): 1 October [274], 6 October [279], 11 October [284], 16 October [289], and 21 October [294]. Similarly, Liège cores were obtained on the following dates: 3 October [276], 8 October [281], 13 October [286], 18 October [291], and 23 October [296].

The sampling protocol is illustrated in Fig. 4. The initial core (TS) was dedicated to “in situ” temperature and salinity measurements at 0.05 m intervals using a drill to bore small holes into which the fast-response temperature probe (TESTO 720, accuracy ± 0.1 °C) was inserted. 0.05-m-thick slices of the ice cores were later melted and tested for salinity using a portable salinometer with accuracy to 0.1. The brine volume and brine salinity were calculated for each “in situ” core using relationships from Cox and Weeks (1983). The brine reflects relative changes in temperature, while brine volume integrates both temperature and bulk salinity. Therefore the “in situ” core was utilized for this purpose due to contemporaneous

sampling for both on the same core. Additional cores were obtained at 0.20 m adjacent locations, frozen with cold packs (cooling bags at -25 °C) and transported to the ship for a suite of measurements, including chlorophyll, “frozen” salinity and nutrients (Sbio), atmospheric gas content (G1 and G2), dimethylsulfide and pre-cursors (DS), calcium (Ca), organic matter (Bio3), bacteria (Bio4), carbonate chemistry (KJ), bulk biological parameters (TB), and iron chemistry (I1–I3). The core hole from TS was used for sea water sampling using a peristaltic pump and silicone tubing at two depths: the water interface at sea level and 1 meter below the water surface. A 30 m depth water sample was obtained using the pump and transparent braided PVC tubing. The sea water samples were analyzed for the same suite of parameters as ice cores. Additional measurements included: (1) snow sampling for trace metal concentrations, (2) bell method CO₂ flux measurements (Frankignoulle et al., 2001) performed randomly both at the snow and ice surfaces, (3) brine sampling from sackholes (incomplete cores within the sea ice) at various depths to allow gravity drainage of internal brine (Thomas and Dieckmann, 2003), and (4) in situ pCO₂ measurements from sea ice at varying depth intervals.

Special attention was given to sampling procedure in order to prevent contamination due to the presence of trace metals, especially iron. Nitrile gloves were used in handling samples and equipment was cleaned by acid wash and stored in sealed plastic bags. A specially designed 0.14 m diameter electropolished stainless core barrel was used (Tison et al., 2008). Snow samples were obtained using a polyethylene shovel and 10 l polyethylene containers. Once collected, snow, ice core, brine, and sea water samples were transferred to the NBP for further processing, preservation/cold storage, and analysis. Sections of 0.002 m thickness were cut from ice cores to provide visual

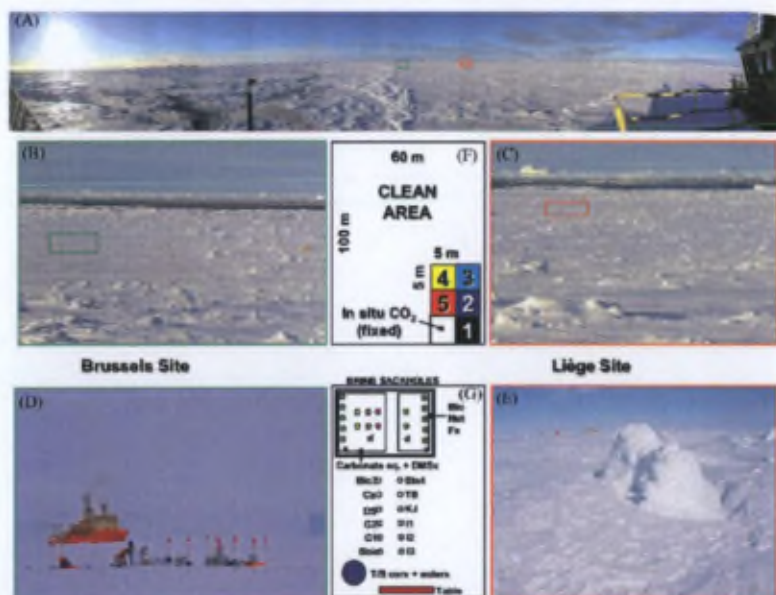


Fig. 4. Overview of Brussels and Liège: (A) composite panoramic view of the northern section of Ice Station Belgica from the bridge of the N.B. Palmer. The middle views are enlargements of Brussels (B) and Liège (C) sampling sites. Bottom view shows the working areas at Brussels (D) and Liège (E). On the latter, a ridge is at the foreground, the flags delimiting the station area are seen on extreme left and right at mid-distance and the ship in the far background. The centre-top sketch (F) illustrates the location of the areas chosen for the five successive sampling events at each clean area. The centre-bottom sketch shows the (idealized) setting of a given sampling site. The working table was installed in the lower part of the area, and the T/S (temperature/bulk salinity) core drilled nearby. The drill hole was used for sea water access and sampling. The central area was dedicated to drilling of the suite of multiparametric ice cores (Bio – complementary biological parameters, Ca – collection of calcium carbonate precipitates, TB – top half/bottom half bulk biological parameters, DS – DMS (P,O), KJ – CO₂ calibration, G – gas measurements, I – iron measurements, Sbio – basic biological measurements + nutrients). The top section of the area was used for “shallow” (s – ice with temperature below -5 °C) and “deep” (d – ice with temperature above -5 °C) sackhole drilling dedicated to brine studies (see text for details).

examination of sea ice texture and crystallographic structure, and document the presence of brine, gas, or other inclusions using transmitted light and cross-polarizing filters. Additionally, ice cores were cut, crushed, and/or melted to perform various chemical analyses. Additional on-board experiments were conducted on a limited basis using cores from Brussels to assess factors affecting biological growth.

Sampling procedures at Stations 1–3 were similar to the procedures described for ISB above and shown in Fig. 4. Differences in core lengths between in situ and frozen cores are noted and indicate the amount of spatial variability present at the various coring sites. The core profiles and data are presented based on the depth from ice surface and cross-correlation of individual layers between cores is not presented.

4. Results

4.1. Inbound stations

The inbound ice stations represented a typical cross section of floes transitioning from a highly dynamic environment in the MIZ, affected by ocean wave energy, to a more stable environment within

the pack ice. Ice observations along the inbound track show frazil and shuga encountered at the ice edge, changing to brash ice near Peter I Island. South of Peter I Island, the sea ice transitions to first year ice floes. The three inbound stations show contrasting structure as indicated in Fig. 5. Stations 1 and 2 consist of predominantly granular ice, reflecting the dynamic environment of the MIZ, however, the ice thickness at station 2 is greater than twice the thickness of station 1 and has a different growth history based on differences in layered sequence of ice type and textural features. Station 3 is more typical of level first year sea ice growing in calm conditions with a dominance of columnar texture (Weeks and Ackley, 1986). An overview of snow and ice thickness measurements and snow properties for the three stations is given in Table 3. The snow–ice interface at the first two stations was extensively flooded as indicated by the largely negative freeboard conditions and the presence of slush identified at 95% (station 1), and 82% (station 2) of the measured locations. These two stations had significantly greater snow thickness and greater mean snow density than station 3, which had slightly positive freeboard and little or no flooding.

The ice core from station 1 (Fig. 5) indicates a thin layer of columnar ice sandwiched by layers of granular ice above and below. The presence of a thick snow cover (0.40 m) and flooded snow–ice interface (0.09 m slush), along with negative $\delta^{18}\text{O}$ values in the upper

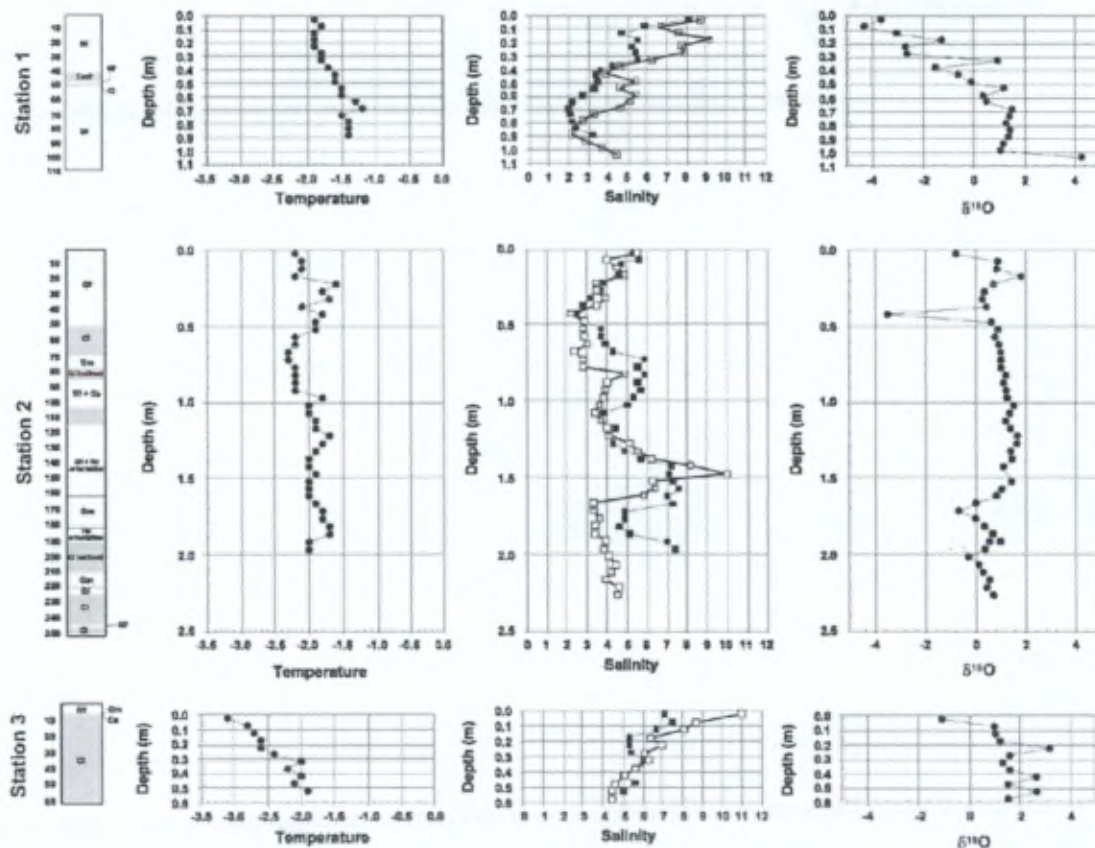


Fig. 5. Short-term ice stations core textural and physical properties. Station 1 (top) through Station 3 (bottom) contains core textural properties (left) in situ temperature (left center), both "in situ" (■) salinity and "frozen" (□) salinity (right center) $\delta^{18}\text{O}$ isotope values (right). Texture codes: granular ice (G), columnar ice (C), (FS) frozen snow, very fine (vf), fine (f), medium (m), coarse (c) or large (l). Differences in thickness between core texture profiles and measurements are based on the assemblage of data from multiple cores during each sampling event, showing the spatial variability at the site.

part of the ice profile indicate the presence of snow-ice formed by freezing of flooded snow pack. It is estimated from the station 1 core that 42% of the profile contains snow-ice and 7% columnar ice. Higher salinity in the upper layer is attributed to freezing of saline slush and

slow diffusion through the columnar ice layer. The remaining 51% of the profile consists of granular ice, indicative of frazil ice accumulation as shown by positive $\delta^{18}\text{O}$ values (Fig. 5). The ice core profile of station 2 is illustrative of a rafted floe as indicated by the greater overall thickness and presence of inclined layers, oblique columnar inclusions and aligned layers of frazil. The fluctuating profiles of temperature, salinity and $\delta^{18}\text{O}$ shown in Fig. 5 also support the interpretation of rafted structure. The presence of these fluctuations in the profile measurements indicate the rafting process occurred in the very recent past. Similarly, station 2 has mean snow thickness of 0.53 m with significant percentage of the interface flooded by sea water (0.05 m slush). The presence of snow-ice (12% of the profile) further indicates by low $\delta^{18}\text{O}$ values, even at depth, which further supports the hypothesis of rafting events. The station 2 core has a larger percentage of columnar ice (34%) that is sandwiched in layers of granular ice (remaining 54%). The station 3 core profile shows a dominance of columnar ice (92%) with thin snow cover and largely positive freeboard. The temperature, salinity, and $\delta^{18}\text{O}$ profiles indicate the thin layer of granular ice at the surface (remaining 8%) of the column to be snow-ice or consolidated snow. The sea ice at all three stations is relatively warm (above -5°C), with the greatest negative gradient at station 3 where air temperature was colder.

Table 3

Snow and ice measurements for inbound short-term stations.

Parameter	n	Minimum	Maximum	Mean	Std. dev.
Station 1					
Ice thickness (m)	21	0.50	2.38	1.02	0.38
Snow thickness (m)	62	0.19	0.84	0.40	0.12
Freeboard (m)	61	-0.20	0.00	-0.09	0.05
3-h air temp at 15 m ($^\circ\text{C}$)	10,657	-1.80	-0.20	-1.11	0.35
Snow temp ($^\circ\text{C}$)	19	-1.58	-0.88	-1.33	0.24
S/I interface temp ($^\circ\text{C}$)	64	-2.40	-1.62	-1.97	0.19
Snow density (kg/m^3)	14	316	417	370	34.78
Station 2					
Ice thickness (m)	17	0.80	4.20	1.70	0.74
Snow thickness (m)	81	0.18	0.87	0.53	0.11
Freeboard (m)	73	-0.17	0.00	-0.08	0.05
3-h air temp at 15 m ($^\circ\text{C}$)	10,652	-2.90	-0.60	-1.93	0.58
Snow temp ($^\circ\text{C}$)	25	-3.55	-1.53	-2.06	0.49
S/I interface temp ($^\circ\text{C}$)	17	-2.70	-1.80	-2.69	0.21
Snow density (kg/m^3)	16	290	459	375	50.05
Station 3					
Ice thickness (m)	21	0.52	0.91	0.67	0.12
Snow thickness (m)	101	0.08	0.35	0.17	0.05
Freeboard (m)	25	-0.08	0.00	-0.03	0.02
3-h air temp at 15 m ($^\circ\text{C}$)	10,650	-4.20	-3.30	-3.80	0.10
Snow temp ($^\circ\text{C}$)	16	-4.49	-1.49	-2.87	0.96
S/I interface temp ($^\circ\text{C}$)	21	-3.50	-2.80	-3.10	0.22
Snow density (kg/m^3)	6	266	384	300	43.71

4.2. Brussels site

Brussels (Fig. 6) was first year sea ice composed primarily of columnar sea ice (~75%), with a variable number of thin granular ice inclusions (~10%) and a 0.1–0.15 m layer of fine granular snow-ice at the top (~15%). Brussels had moderately thin snow cover that is influenced by the lack of surface ice features to retain windblown snow drifts. The mean snow thickness based on

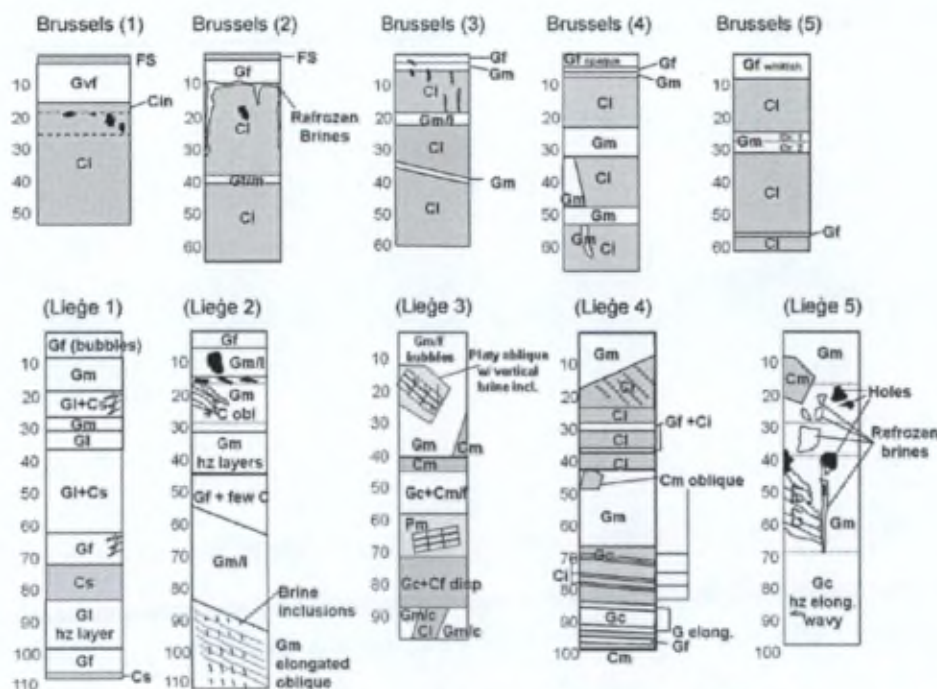


Fig. 6. Time series of ice cores from Brussels (top) and Liege (bottom) sampling sites showing textural properties determined from 2 mm backlit thick sections. Texture codes: granular ice (G), columnar ice (C), (P) "platy" crystals, (FS) frozen snow, very fine (vf), fine (f), medium (m), coarse (c) or large (l).

measurements along the transect lines adjacent to the clean area (Table 4) varied from 0.08 ± 0.03 m on 3 October to 0.14 ± 0.08 m on 22 October, with an overall thickness range 0.01–0.425 m. The snow thickness at Brussels ice core locations varied from 0.08 to 0.25 m, which is within the range of other snow measurements at Brussels. Ice thickness measurements at Brussels gave a range 0.47–0.69 m with a mean value, of 0.57 ± 0.06 m. Time-series snow and ice thickness measurements from IMB stations at Brussels give a range of snow thickness from 0.02 to 0.16 m and a range of ice thickness from 0.51 to 0.66 m. During the period of ISB, the ice thickness at Brussels decreased at an approximate rate of -0.004 m/day (average of 2 IMBs) indicating dominance of basal melting. The sea ice retained an overall positive freeboard for the duration of Ice Station Belgica as indicated by the time series of

measurements in ice cores. The ice freeboard relative to sea level as calculated from the elevation survey shows a mean value of 0.054 ± 0.027 m, while direct measurements from core and auger holes give a mean of about 0.03 m.

The texture and structure of the time series of ice cores is given in Fig. 6 and salinity, temperature, and oxygen isotope data for all cores are given in Fig. 7. Examination of thick sections and cuttings processed from the cores did not show a singular brine channel structure in the columnar ice. Instead, large tubes of refrozen brine inclusions were observed to initiate at the top of the columnar ice structure and infiltrate through a network of smaller interconnected channels to the bottom of the core. This is illustrated in the Brussels 2 and Brussels 3 core structure diagrams and transmitted light photograph through a 0.01-m-thick cut section of Brussels 4 core in Fig. 8. The lower portions of the cores, below 0.40 m, show limited temperature change over time, although not isothermal. The two sets of salinity measurements generally show similar trend and range, decreasing with depth and temperature. Discrepancies occur mainly in the upper 0.20 m of the cores (e.g. Brussels 3) probably reflecting spatial variability due to enclosure (or not) of refrozen brine tubes. The upper layer of granular sea ice present in all five cores varies in thickness from a few centimeters to ~ 0.15 m. The negative $\delta^{18}\text{O}$ values present in this upper layer of granular ice indicate the presence of snow-ice.

Brussels 1, the warmest of the recorded conditions, has brine salinities comparable to ocean water values. It is noted that all of the cores, except for Brussels 4, are above the critical brine volume threshold ($\approx 5\%$) at which permeability for columnar sea ice is significantly reduced (Cox and Weeks, 1975; Golden et al., 1998, 2007). The time series of measurements from Brussels IMBs, given in Fig. 9A, B, show at least 3 successive cycles of atmospheric cooling at ISB during which ice cores were obtained. Brussels 1 was cored on 1 October during the warm interval before the first recorded cold cycle. Under-ice photographs obtained on 2 October, during the subsequent cool-down period, clearly show brine drainage (clouded plumes) at the ice bottom (Fig. 11). Brussels 2 and 3 (6 and 11 October, respectively) were cored during mid-cycle as the thermal gradient decreased within the sea ice. Brussels 4 was cored on 16 October at the end of the 3rd (and longest) cooling cycle and Brussels 5 was cored on 21 October during the final warming trend at the end of ISB. One additional cold cycle occurred after station departure and the 1st of November marked the end of the cold-warm cycling period in the early spring period. After 1 November, temperatures in the ice remained warm (Fig. 9B) until the buoy lost transmission (Fig. 3) on 6 December.

Snowpit measurements (Fig. 10, Table 5) were performed adjacent to IMBs during the cold to warming cycle between Brussels core sampling events 4 and 5. Snowpit 3B on 17 October was measured with 0.19 m snow thickness and was located in proximity to the radiometer IMB. The cold ice interface temperature is reflected in the profile with steep negative thermal gradient (-36.4 °C/m) in the snow pack, resulting in primarily faceted snow grains. Snowpit 3E on 20 October (after the warming event) consisted of 0.15 m snow thickness and was located in proximity to the Seabird 2 buoy. The temperature profile for snowpit 3E shows a reversal in gradient ($+2.3$ °C/m) and near isothermal conditions. A 0.02 m saline slushy layer was present in snowpit 3E at the snow/ice interface with salinity of 18. Additional snowpit measurements performed at Brussels indicate the snow cover is relatively consistent in grain shape and size, with a crusted surface layer generally present.

4.3. Liège site

The sea ice at Liège was generally thicker than Brussels (between 0.90 and 1.20 m), and had significantly different textural characteristics. The profile at Liège was predominantly granular

Table 4
Summary of snow and ice measurements for sites at Ice Station Belgica.

Parameter	n	Minimum	Maximum	Mean	Std. dev.
Brussels (3 October 2007)					
Elevation (m ASL)	402	0.07	0.27	0.13	0.03
Snow thickness (m)	402	0.01	0.19	0.08	0.03
Calculated freeboard (m)	402	-0.07	0.20	0.05	0.03
Measured freeboard (m)	28	0.01	0.11	0.03	0.03
Ice thickness (m)	28	0.47	0.69	0.57	0.06
Brussels (7 October 2007)					
Snow thickness (m)	201	0.01	0.22	0.11	0.04
Brussels (21 October 2007)					
Snow thickness (m)	27	0.03	0.13	0.09	0.03
Brussels (22 October 2007)					
Snow thickness (m)	201	0.03	0.43	0.14	0.08
Brussels (Radiometer IMB)					
Snow thickness (m)	260	0.02	0.11	0.07	0.01
Ice thickness (m)	257	0.51	0.66	0.61	0.04
Brussels (Seabird 2 IMB)					
Snow thickness (m)	132	0.06	0.16	0.08	0.02
Ice thickness (m)	129	0.52	0.57	0.55	0.01
Liège (snowpit and core)					
Snow thickness (m)	10	0.25	0.70	0.43	0.14
Liège (IMB)					
Snow thickness (m)	215	0.49	0.73	0.53	0.03
Fabru (1 and 2 October 2007)					
Elevation (m ASL)	599	0.07	1.67	0.67	0.30
Snow thickness (m)	598	0.00	1.70	0.70	0.32
Calculated freeboard (m)	598	-0.63	1.26	-0.03	0.28
Fabru (7 October 2007)					
Elevation (m ASL)	901	0.08	1.54	0.68	0.29
Snow thickness (m)	900	0.07	1.90	0.68	0.31
Calculated freeboard (m)	900	-0.59	1.34	0.00	0.25
Fabru (10 and 11 October 2007)					
Snow thickness (m)	60	0.10	1.48	0.65	0.36
Measured freeboard (m)	57	-0.45	0.27	-0.03	0.14
Ice thickness (m)	60	0.60	5.00+	2.34	1.25
Fabru (21 October 2007)					
Elevation (m ASL)	602	0.05	1.53	0.66	0.29
Snow thickness (m)	602	0.07	1.58	0.70	0.32
Calculated freeboard (m)	602	-0.65	1.35	-0.04	0.20
Patria (8 October 2007)					
Elevation (m ASL)	21	0.23	0.51	0.36	0.07
Snow thickness (m)	101	0.17	0.55	0.36	0.09
Calculated freeboard (m)	21	-0.07	0.06	0.00	0.04
Measured freeboard (m)	19	-0.07	0.04	-0.01	0.03
Measured ice thickness (m)	19	0.49	1.00	0.79	0.14
Patria (22 October 2007)					
Elevation (m ASL)	101	0.22	0.50	0.32	0.06
Snow thickness (m)	101	0.11	0.50	0.31	0.08
Calculated freeboard (m)	101	-0.08	0.16	0.01	0.03

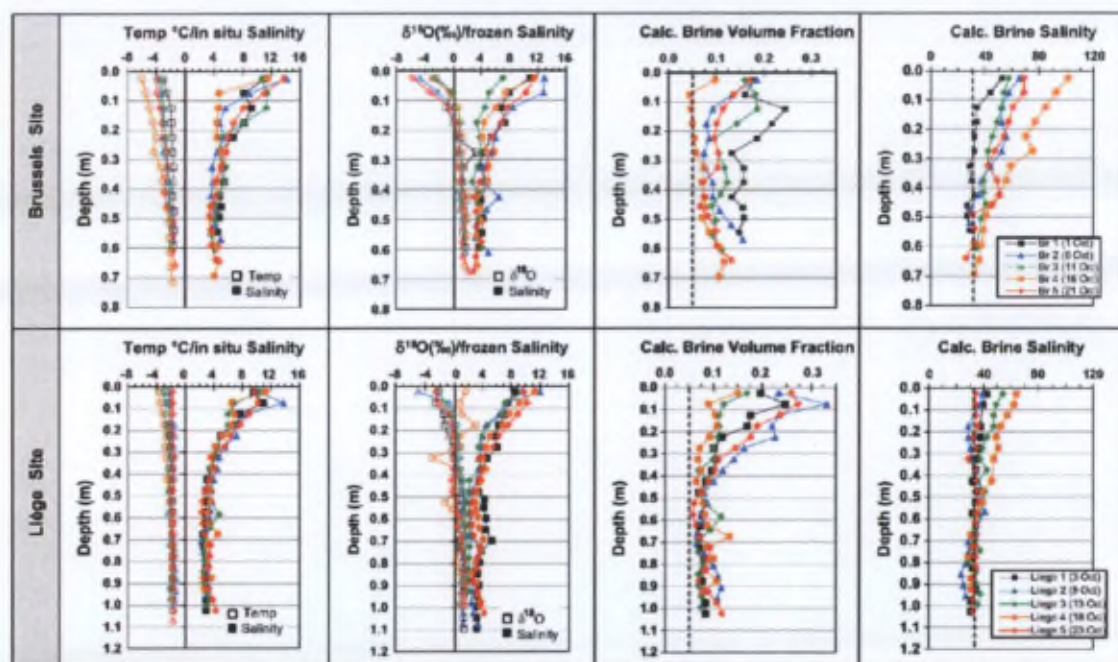


Fig. 7. Brussels (top) and Liège (bottom) plots of “in situ” temperature and salinity (left) measured in the field T/S core for each sampling cycle (1–5); “frozen” salinity and $\delta^{18}\text{O}$ values (left center) from the Sbio core processed on the NBP for the 5 sampling cycles; calculated brine volume fraction (right center); and calculated brine salinity (right) are included for the 5 sampling cycles.

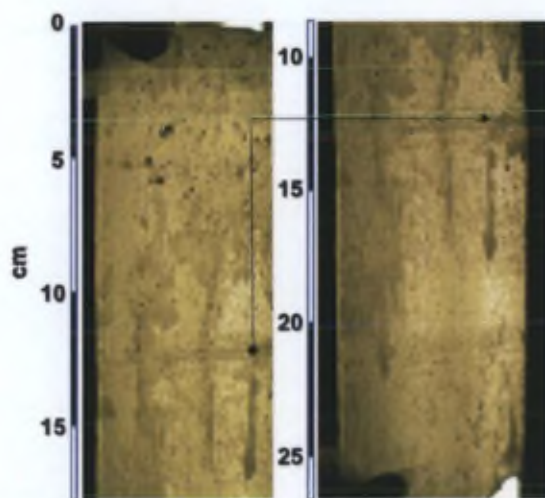


Fig. 8. Photographs of transmitted light through a 1-cm-thick section of sea ice cut from the Brussels 4 core. The arrow indicates the match point for the photographs. Note the descending linear tube features containing refrozen brine.

(~57%), with high grain size variability and numerous facies disturbances shown by inter-layering of columnar ice (~17%) and snow-ice (~26%) present at different levels of the profile. The presence of inclined layers, inclusions, mixture of ice types, and

recurrent positive $\delta^{18}\text{O}$ with depth suggests a dynamic origin and subsequent rafting events (Fig. 6). Liège had thicker snow cover than Brussels with mean snow thickness of 0.43 ± 0.14 m and a measured range 0.2–0.70 m, including slush. Time-series snow thickness measurements from the single IMB at Liège give a range of snow thickness from 0.49 to 0.73 m with a mean of 0.53 ± 0.03 m. The freeboard, although initially positive, shows a clear trend towards flooding of the ice interface from cycle 3 (13 October) onwards. Brine inclusions are also frequently observed, but with a different geometry than observed in Brussels cores, consisting of large coalescent cavities rather than elongated tubes. As shown in Fig. 6, one very large cavity was present at Liège 5 (23 October) initiating at an approximate depth of 0.40 m and extending down to 0.70 m below the ice interface, apparently following a strong textural boundary.

The salinity, temperature, and oxygen isotope data for all Liège cores and calculated brine volume and brine salinity are given in Fig. 7. The in situ temperature and salinity measurements in Liège cores show little variation between the different sampling events, however the frozen salinity measurements are contrasting. Ice with a granular texture is present in the upper portion of each core and negative $\delta^{18}\text{O}$ values indicate snow-ice in the upper 0.20–0.30 m. While there is significant variation in brine volume for the entire length of the Brussels cores, the brine volume at Liège changes primarily in the upper 0.40 m of the core with brine volumes below this depth remaining between approximately 5% and 10%. The calculated brine salinity for all Liège cores below a depth of 0.5 m is similar to sea water salinity (mean of all cores 32.6). Between Liège 1 and 2 core sampling events (3 and 8 October, respectively) temperature in the upper profile increased with corresponding increase in brine volume and decrease in brine salinity. By Liège 4, ice temperature in the upper profile decreased to the minimum

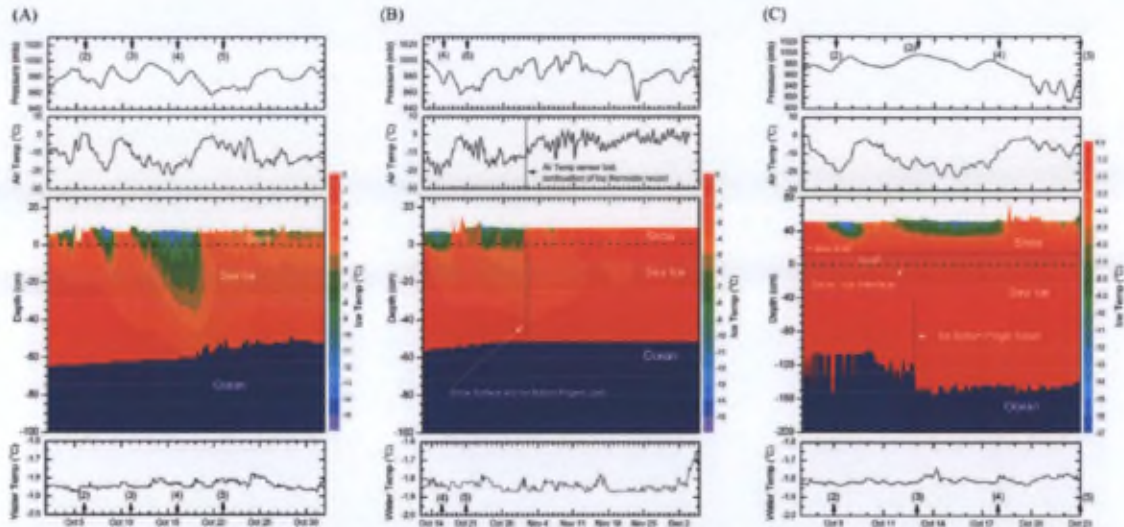


Fig. 9. Ice mass-balance buoy records for the (A) Brussels Radiometer, (B) Brussels Seabird 2, and (C) Liège Seabird 1. The IMB plots show time series of barometric pressure, air temperature, snow top surface, ice bottom surface, snow and ice temperature fields (color contours), and ocean water temperature. Dashed lines show the initial position of ice interface and slush levels. Arrows along the top and bottom time axis (differing time scales) give the dates of the core extractions at each site. The first sampling event at Brussels and Liège occurred prior to the IMB installations. The ice bottom pinger at Liège was reset on 12 October after removing the CTD from its mast for repairs.

measured with corresponding transition to low brine volume/high brine salinity. The warmer ice temperatures between Liège 4 and 5 (18 and 23 October, respectively) returned brine volume and brine salinity to near the Liège 1 values.

The time series of measurements obtained from the IMB at Liège are shown in Fig. 9C. Upon installation of the IMB, the initially dry snow/ice interface flooded with sea water to the ~ 0.10 m level due to negative freeboard and sea water rising through the borehole. In the early part of the IMB record, the ice bottom pinger provided highly variable readings. The bottom pinger was reset in the afternoon of 12 October, after removal of the malfunctioning CTD on the same mast, and the variation in pinger readings was subsequently reduced. The under-ice conditions at Liège were highly variable with rafted floes, cavernous voids, and large ice blocks present. The initial variation in ice bottom readings is believed to be the result of shifting ice blocks that were out of range when the pinger was reset (Fig. 11).

The initial snowpit measurements at Liège (snowpit 4A, Fig. 12A) occurred at the onset of the first cooling cycle of ISB in which snow/ice temperature in the upper snow pack showed a steep thermal gradient, but the lower portion of the snow pack (below 0.30 m) was isothermal. Moisture transport through the lower part of the snow pack was apparent by the presence of depth hoar and the prevalence of rounded and clustered grains with ice bonds above. Salinity of 0.3 was measured in the surface of the snow pack, which may be attributed to windblown deposition. Density in the depth hoar and the layers immediately above were low, increasing in the middle of the snow pack and then decreasing again near the surface. No slush layer was present in snowpit 4A on 6 October, after the installation of the IMB. In snowpit 4B, about 11 days later, a stronger thermal gradient was present with the start of the warming trend, apparent in the upper 0.1 m. The overall density of the profile increased with consolidation. Slush (0.09 m) was present in the lower portion of the snowpit, of which 0.02 m had frozen at the hydrostatic level in the snow (Fig. 12B). The presence of a 0.02 m wet snow layer was noted above the frozen slush.

4.4. Fabra site

Fabra was characterized as highly deformed multi-year ice with mean thickness of 2.33 ± 1.25 m based on 60 auger holes along a 300 m transect (Table 4). The ice thickness measurements at Fabra ranged from 0.6 m to greater than 5 m in ridged locations. Auger holes were terminated at 5 m depth due to equipment constraints; however, five holes consisted of ice that was thicker. The mean surface elevation was about 0.67 m above sea level and the mean snow depth generally exceeded that, yielding a mean negative freeboard in each survey. To corroborate elevation survey measurements and the finding of significant portions of negative freeboard across Fabra, 10 snowpits were excavated on 6 October along the two transect lines (1B through 1F, 2B through 2F; Table 5). Results showed the presence of slush in 9 of 10 locations with slush thickness varying from 0.08 to 0.45 m, thus verifying the prevalence of negative freeboard and extensive snow/ice interface flooding across Fabra. Based on elevation survey data, it is estimated that the Fabra transects varied from approximately 55–80% negative freeboard during the three weeks.

Although transient storms through the duration of ISB were observed to significantly redistribute the snow cover, the mean snow surface elevation did not change appreciably between surveys (Fig. 13). Analysis of variance performed on the elevation data indicated no statistically significant difference in the mean elevation between any combination of the three surveys performed along the Lines 1 and 2 (see Weissling et al., 2011). In general, the primary ridge features remained in the same location along the transect lines, but intermediate snow cover between these features was redistributed, losing elevation in some places and gaining in others (i.e. migration of snow drifts). The mean ice freeboard similarly was negative in all surveys and only varied within a few centimeters. Although the wind-driven storm events around 7 and 21 October included significant snow precipitation (Leonard and Cullather, 2008), the wind proved to be the dominant factor in snow accumulation, suggesting that losses of windblown snow to

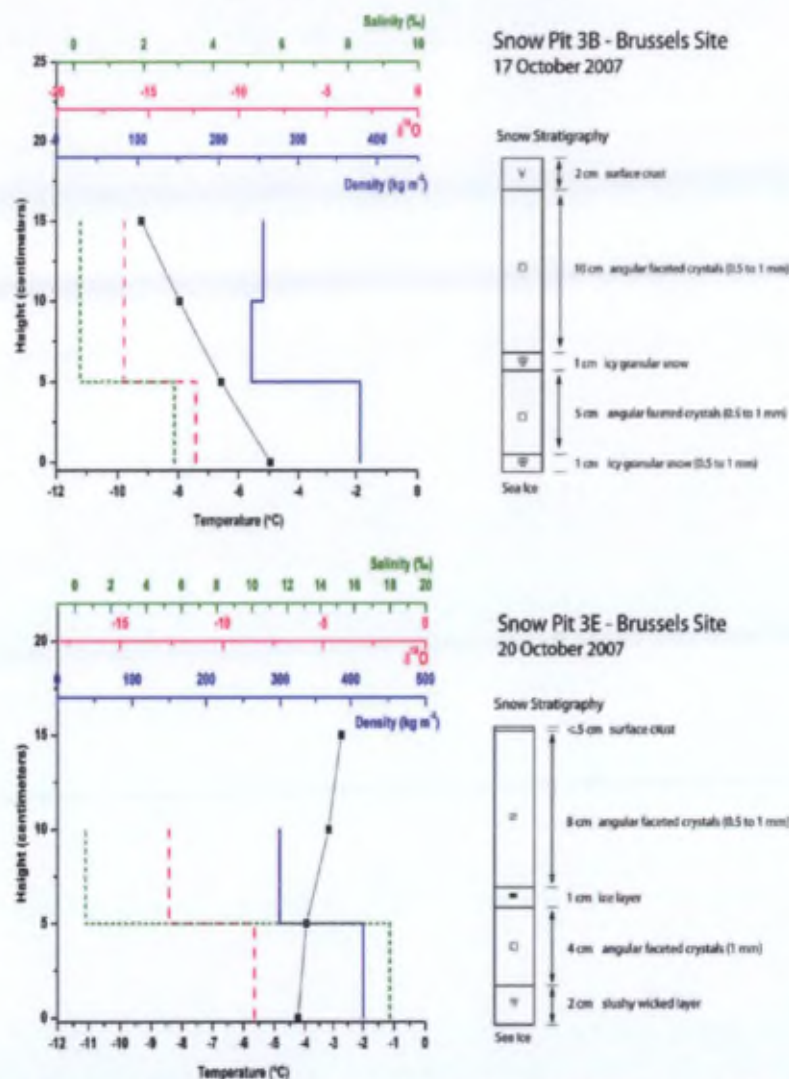


Fig. 10. Snowpit profiles and snow characteristics adjacent to IMB locations. Snowpit 3B (top) was adjacent to the Brussels Radiometer buoy and Snowpit 3E (bottom) was adjacent to the Brussels Seabird buoy.

open leads between ice floes may be sufficient to offset any significant elevation gains by deposition of precipitation. The mean snow density shown in Table 5 at Fabra between snowpits 1A and 2A (2 October) and snowpits 1G and 2G (16 October) sampled along the transect lines 1 and 2 in the same approximate location two weeks apart, indicates that snow densification cannot explain the apparent lack of elevation change during precipitation events.

One particular example of the effects of changing snow cover distribution at Fabra is seen in snowpit 2G, approximately 200 m along the transect Line 2. The slush layer of 0.3 m thickness was measured on 16 October (Fig. 14). In the upper fine-grain portion of the snow pack, the thermal gradient was lower and the snow grains were rounded. The thermal gradient increased toward the slush

layer and grains transformed to mixed/faceted morphology. Low density depth hoar formed in the bottom 0.05 m above the slush layer, where the temperature gradient was greatest. Upward moisture transport and recrystallization of the snow was indicated and the salinity of the snow increased slightly above the depth hoar. As seen from the air temperature record in Fig. 14, a strong warming (storm) event with high winds initiated on 17 October and continued to a peak air temperature on 19 October, during which temperatures in the snow pack increased. As seen in Fig. 13, surface elevation at snowpit 2G did not change, however, the snow in the immediate vicinity of the snowpit changed dramatically as the adjacent snow drift (at 195 m along the transect line) moved down line to about 210 m and increased in volume. The original and

Table 5
Summary of snowpit measurements.

Snowpit	Date (2007)	Snow thickness (m)	Slush thickness (m)	Surface temp (°C)	Snow/ice interface temp (°C)	Avg. snow temp gradient (°C/m)	Mean density (kg/m ³)
Fabra							
1A	2 October	0.25	0.17	−4.4	−1.9	−9.9	319
1B	6 October	0.30	0.21	ND	ND	ND	ND
1C	6 October	0.45	0.24	ND	ND	ND	ND
1D	6 October	1.05	0.16	ND	ND	ND	ND
1E	6 October	0.55	0.28	ND	ND	ND	ND
1F	6 October	0.74	0.20	ND	ND	ND	ND
1G	16 October	0.45	0.00	−13.1	−1.7	−25.3	318
1H	16 October	0.71	0.30	−12.4	−2.0	−14.6	370
2A	2 October	0.72	0.45	−7.3	−2.0	−7.4	362
2B	6 October	0.48	0.08	ND	ND	ND	ND
2C	6 October	0.45	0.21	ND	ND	ND	ND
2D	6 October	0.62	0.48	ND	ND	ND	ND
2E	6 October	0.72	0.00	ND	ND	ND	ND
2F	6 October	0.58	0.16	ND	ND	ND	ND
2G	16 October	0.51	0.30	−12.8	−2.2	−20.8	362
Brussels							
3A	3 October	0.13	0.00	−8.8	−3.0	−45.0	232
3B	17 October	0.19	0.00	−11.9	−5.0	−36.4	292
3C	17 October	0.07	0.00	−11.9	−8.1	−54.4	273
3D	20 October	0.12	0.02	−2.4	−4.0	13.3	393
3E	20 October	0.15	0.02	−3.6	−4.0	2.3	358
3F	20 October	0.11	0.00	ND	ND	ND	ND
3G	20 October	0.43	0.00	ND	ND	ND	ND
Liège							
4A	6 October	0.55	0.00	−7.5	−3.3	−7.7	282
4B	17 October	0.61	0.09	−12.0	−2.5	−15.5	363
4C	20 October	0.44	0.13	−4.3	−2.0	−5.1	353
4D	20 October	0.46	0.00	−3.8	−3.1	−1.5	303
4E	20 October	0.25	0.00	−2.5	−2.3	−0.9	370
Patria							
5A	9 October	0.80	0.02	−2.0	−2.0	−0.1	323
5B	22 October	0.18	0.00	−4.3	−2.4	−10.8	ND

ND = no data.

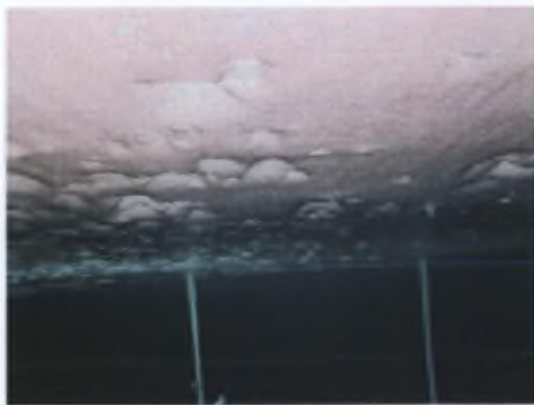


Fig. 11. Under ice photograph from the Brussels site on 2 October 2007 showing brine drainage beneath the level ice. The brine partially obscures the clarity of ocean water in proximity to the submerged IMB mast. (Photo courtesy Chris Fritsen).

post-storm snow surface levels were also confirmed by marks placed on the data logger stake. The snowpit was again excavated on 22 October and an additional 0.25 m increase in the thickness of the slush layer was observed. Based on the snow temperature record, it is estimated that the additional flooding of the snow layer

occurred in conjunction with the peak of the storm event. As snow redistributed and temperatures in the snow pack rose above the sea water freezing point, the slush level raised and temperature in the snow pack remained above the freezing point of sea water.

4.5. Patria site

Patria was located directly across ISB about 1500 m from the ship (Fig. 2A). The site was investigated on two occasions; however, no ice cores were drilled at this location. Patria had surface deformation features and ice thickness similar to Liège, and deeper snow than was recorded at Brussels. The mean snow thickness on 9 October was 0.36 ± 0.09 m with calculated and measured mean freeboard that was -0.01 m. Snowpit 5A measurements, obtained in a drift near the thickness transect line, indicated the presence of thick (0.80 m) snow cover with a slight (0.02 m) slush layer at the base, consistent with the slightly negative freeboard. The thermal gradient, although averaged through the profile was slight, showing a reversal from a positive gradient (8.2 °C/m) in the upper 0.42 m of the profile to a negative gradient (-8.9 °C/m) in the lower 0.40 m of the profile, thus reflecting the strong warming trend between the second and third core sampling cycles. Patria was revisited on 22 October, near the end of ISB following the strong warming event of 19 October. The mean snow thickness decreased about 0.05 m to 0.31 ± 0.08 m due to snow redistribution and the mean freeboard increased to a slightly positive value (< 0.01 m). Snowpit 5B in an area adjacent to the previous drift showed a snow thickness of only 0.18 m with no slush present.

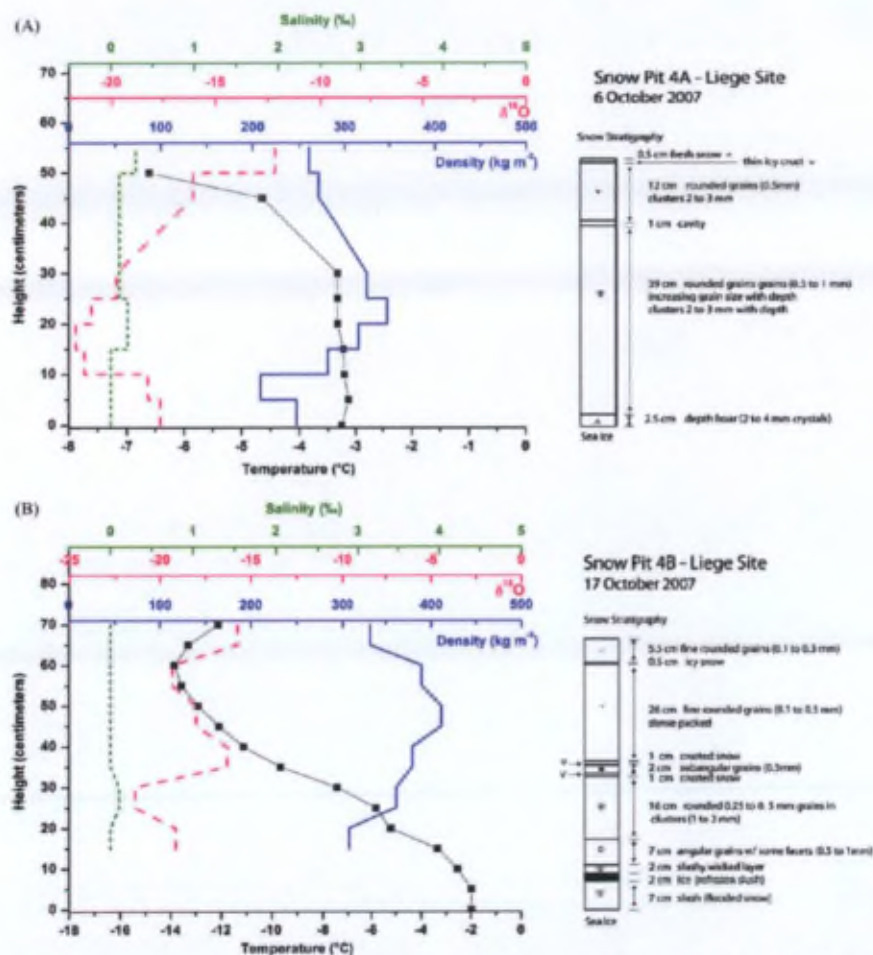


Fig. 12. Snowpit profiles and snow properties adjacent to the Liège IMB location: (A) snowpit 4A occurred after IMB installation and before ice interface flooding was recorded in cycle 3 and (B) snowpit 4B occurred at the start of the warming trend in cycle 4.

5. Discussion

During the 2007 winter-spring transition in the Bellingshausen Sea, there were several meteorological cycles of varying duration and intensity that consisted of warm atmospheric fronts from the north, generally accompanied by high velocity winds and precipitation, followed by colder air temperatures and little precipitation (Vancoppenolle et al., 2011). These cycles, generally varying from four to eight days, are apparent in the records of the IMBs and core samples from the SIMBA sites, resulting in not only temporal changes in the snow cover distribution, but also in the sea ice properties and observed morphology at ISB. A similar pattern of meteorological conditions has been noted in the Bellingshausen Sea by others (Jeffries et al., 1994; Sturm et al., 1998) and in other areas of the Antarctic (Massom et al., 1997; Worby et al., 1998) indicating that this meteorological pattern is common in late winter-early spring in the Antarctic sea ice zone (Massom et al., 2001). Although, common in this seasonal period, north-south cycling of atmospheric fronts have also been noted in the spring-summer transition in the Weddell Sea (Willmes et al., 2006) in which lower atmospheric pressure resulted in

wind change and influx of moisture from the north, sustained warm air temperatures, and increased melt of the snow cover.

5.1. Importance of snow cover

During SIMBA, we found a wide range of snow conditions and ice types, both at short-term ice stations and at ISB. Temperature gradients in the sea ice are driven by atmospheric fronts. Over the three weeks of ice core sampling at Brussels (Fig. 7), the greatest fluctuations in ice temperature occurred in the upper portions of the cores reflecting not only the limited thermal insulation provided by thin snow cover, but also the short duration and amplitude of weather events. However, at Liège, the amplitude of temperature changes was muted due to the greater accumulation of snow cover. Due to the effective thermal conductivity of snow being approximately one-eighth that of sea ice (Sturm et al., 1998; Massom et al., 2001), the cold fronts do not appreciably penetrate the snow covers to reach the sea ice interface. In the lower Liège profiles, below about 0.50 m depth, the ice temperature only ranged from -1.3 to -2.3 °C on all dates.

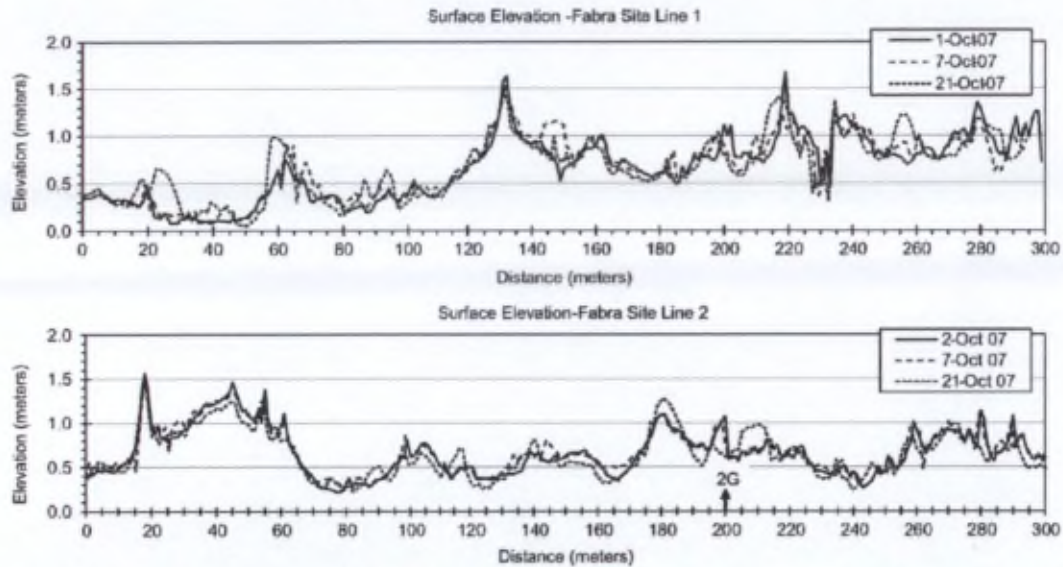


Fig. 13. Comparison of surface elevation surveys at the Fabra site along the transect Line 1 and Line 2 over three separate survey events. The approximate location of Snow Pit 2G is indicated on the profile of Fabra Site Line 2.

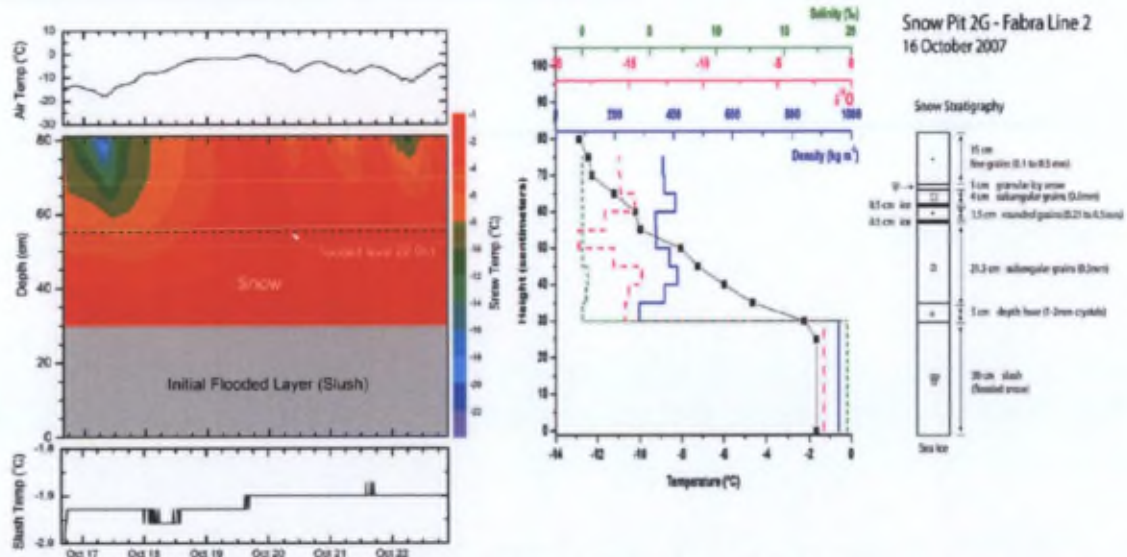


Fig. 14. (left) Time series of temperature recorded in Snow Pit 2G. The lower plot shows the temperature of the flooded (slush) layer, center plot shows temperature contours of the unflooded snow pack, and above is the air temperature record taken from the Brussels Radiometer IMB. (right) Snow pit properties and texture obtained on initial installation of the temperature dataloggers.

The thermal forcing, or lack of forcing, directly affects temporal changes in the ice salinity and brine salinity/volume. In the snowpit 2G thermal profile of Fabra (Fig. 14), it is apparent that even strongly negative air temperatures were mitigated by the low thermal conductivity of snow cover.

Snow thickness has been reported to be greater in the Bellingshausen, Amundsen, and Ross seas than other regions of the Antarctic

based on observations from field campaigns (Jeffries et al., 2001; Massom et al., 2001) and remote sensing studies (Markus and Cavalieri, 1998). Snow thickness in the Bellingshausen Sea was reported by Sturm et al. (1998) from two cruises in late winter with mean values of 0.285 and 0.224 m, including sites ranging from 62°S to 70°S. These values are less than the mean values of all SIMBA sites, except for level ice at Brussels and station 3, and considerably less

than the mean thickness of Fabra. Information derived from SIMBA indicates that the thickness of snow cover played a significant role in regulating temperature flux and the physical regime in which sea ice developed and experienced morphological changes. The air and ice temperature records from IMBs (Fig. 9) indicate that the longest cold event reached a minimum between 15 and 16 October, just before the Brussels 4 core samples were extracted. As shown in the IMB records (Fig. 9A, B), the asymmetric profile of temperature contours in the ice are a direct result of the snow cover. There is an apparent time lag between the decline in air and ice temperatures as the cold front penetrates into the ice. The lag is a result of the insulating effect (low conductivity) of the snow cover. However, as air temperature rises, the ice temperature also rises but at a much faster rate due to the ocean heat flux, thus warming the ice from both top and bottom. In this regard, the snow cover tends to buffer effects of atmospheric temperature cycling on sea ice and thus affects morphological changes within it (Massom et al., 2001). This is particularly important in the seasonal transition, where periods of persistent cold winter temperatures yield to shorter cycles of warm weather fronts, resulting in a rapid warming of the sea ice profile.

The presence of thick snow cover not only insulates underlying sea ice from cold air temperatures, but also provides overburden that results in negative freeboard. Where sea ice is permeable, or cracks and fissures are present, the snow/ice interface is often flooded with sea water forming saline slush (Eicken et al., 1994; Massom et al., 1997, 2001). The temperature contours from the Liège IMB (Fig. 9C) indicate that the ice is relatively isothermal at temperatures near the freezing point for sea water for the duration of the record, where times of persistent cold do not completely penetrate the snow pack to reach the sea ice interface. This may be attributed in part to the increased heat capacity of sea ice at temperatures near the freezing point (Yen et al., 1991; Nicolaus et al., 2009). The level of flooding at the Liège IMB (inferred from thermistor temperatures) is believed to persist at about the 0.20 m level, above the snow/ice interface. This contrasts from the cores at Liège which had slightly thinner snow cover and (initially) a positive freeboard. Although the sea water flooding at the IMB (in this case) was induced by the IMB installation itself, the system is expected to reach a thermodynamic equilibrium over time and provide a representative temperature profile expected for a continuously flooded snow/ice interface. Snow-ice formation was observed at Liège in snowpit 4B (17 October) due to the freezing of saline slush. This phenomenon has previously been described as the "flood-freeze" cycle (Fritsen et al., 1994, 1998), although other mechanisms for snow-ice formation were also observed.

The time series of snow thickness measurements at Fabra are particularly interesting because they illustrate the effect of flood-freeze cycles on thermodynamic growth and buoyancy of the ice floe. As presented in Weissling et al. (2011), the mean snow surface elevation and snow thickness at Fabra did not change appreciably between 2 and 7 October; however, the ice freeboard increased, despite the trend of ice loss from the bottom. The change in buoyancy has been attributed to the conversion of slush to snow-ice (Weissling et al., 2011). Subsequent redistribution of snow at the surface on 21 October (Fig. 13) resulted in an overall decrease in freeboard as additional flooding of the snow/ice interface occurred. Since ice thickness holes drilled at Fabra before 10 and 11 October were limited to 2 or 3 benchmarks at least 100 m apart and 20 m separate (away) from the ice thickness transects and snowpits, they would not affect flooding in earlier snowpit or survey line measurements. The ice thickness holes drilled on 10 and 11 October were placed in 5 m increments only along the Line 1 at Fabra, which was located at least 100 m separate from Line 2. The decrease in freeboard observed on 21 October occurred after the cold front of 16 October in which re-freezing of the holes would be expected for snow thickness less than 0.40 m (see Fig. 14).

Given the similar changes in freeboard observed along the transect Line 2 where no extensive drilling was performed and the warm ice conditions, the ice thickness holes did not appreciably affect the freeboard assessment. In the case of snowpit 2G, the thermal pulse from cold air temperatures was of insufficient duration to penetrate deeper than 0.40 m into the snow profile, thus slush was not converted to snow-ice. An increase in the thickness of flooded slush layer occurred from adjacent increases in snow thickness and adjustments to isostatic balance (Fig. 13).

Nicolaus et al. (2009) identified two snow thickness regimes during Ice Station Polarstern (ISPOL) in the Weddell Sea of Antarctica which persisted throughout a 35-day drift station in the spring–summer transition. Thinner snow cover present on first-year sea ice (FYI) was noted to have more extensive flooding than thicker snow cover on second-year ice (SYI). This finding contrasts with the observations of this study in which thicker deformed ice (Fabra) was extensively flooded. In addition, Nicolaus et al. (2009) found that snow temperatures were lower on SYI because it was thicker and colder, acting as a cooling reservoir and insulating it from warmer air temperatures above. Again in contrast, the thinner snow cover at Brussels resulted in lower snow temperatures and thicker snow at Fabra retarded cold air temperature fronts from penetrating the snow pack. These observations highlight the differences in region and season.

5.2. Sea ice processes

The differences in snow and ice characteristics between the Brussels and Liège are most apparent when examining the mean profile for each site, shown in Fig. 15. Mean profiles and distribution of ice types were developed by procedures similar to Jeffries et al. (1998) where ice types were distinguished by either columnar, granular marine (frazil) with $\delta^{18}\text{O} > 0\text{‰}$, or snow-ice $\delta^{18}\text{O} \leq 0\text{‰}$. Columnar ice dominates the Brussels mean profile with minor inclusions of frazil lower in the profile, indicating a relatively calm growth environment with little spatial variability between core locations. The temporal variability within each interval is greatest in the upper portions of the profile, where temperature changes are also large. Snow-ice in the upper portion of the profile composes 100% of the top interval and declines by $\sim 2/3$ with each subsequent interval. The mean textural profile for Brussels consists of 75.2% columnar ice, 9.6% frazil, and 15.2% snow-ice. The mean profile at Liège shows contrasting structure and composition with mean textural profile of 17.4% columnar, 57.0% frazil, and 25.6% snow-ice. The large proportion of frazil ice indicates an overall more dynamic growth environment. Both the presence of a high percentage of columnar ice as inclined layers and blocks in the intermediate intervals, and the presence of large percentages of snow ice deeper in the Liège profile suggest that rafting processes were an important growth mechanism. Although spatial variability in the Liège profile appears larger than that in Brussels, the overall trend in salinity and $\delta^{18}\text{O}$ profiles are similar and suggest that temporal variability (related to atmospheric temperature cycling) may be the dominant factor in differences between cores.

Based on model studies of sea ice properties by Ono (1968), thermal conductivity of sea ice generally increases with both decreasing salinity and temperature, most significantly in the range 0 to -2°C . Focusing on the major cooling/warming event at Brussels between 12 and 19 October (Fig. 9A), it is apparent that the temperature increased in the upper half of the ice cover during warming (Br 4 to Br 5 in Fig. 7, top left). Therefore, we should expect to see the thermal conductivity of the ice decrease. However, we note from the IMB records (Fig. 9A) that the ice warmed considerably faster than it cooled. In addition, we see the rate of basal melt appeared to increase significantly after 18 October.

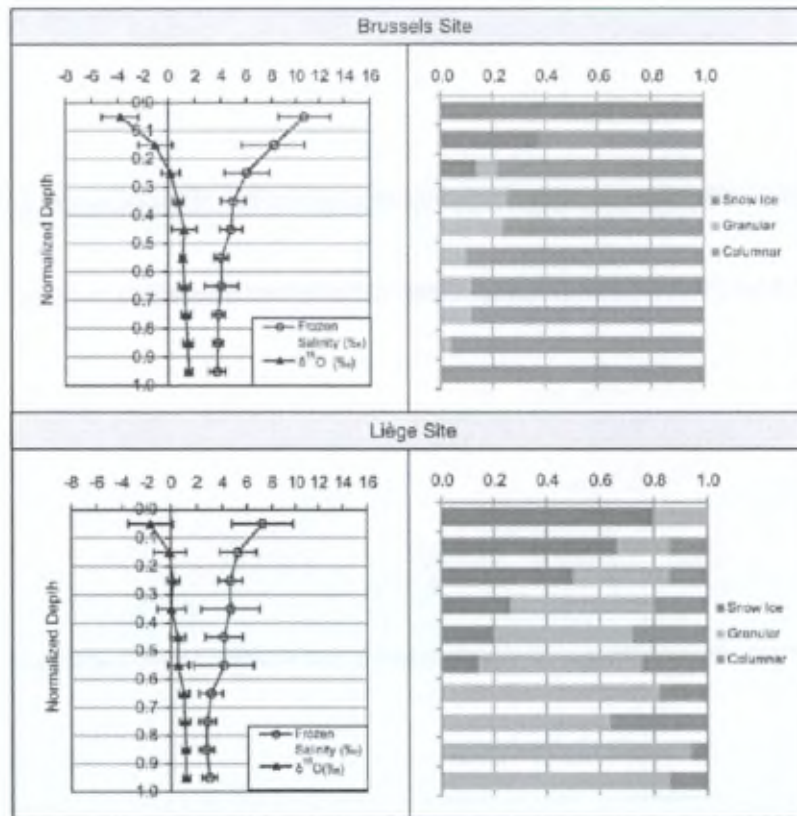


Fig. 15. Brussels site (top) and Liège site (bottom) mean profiles of Salinity and $\delta^{18}\text{O}$ (left side) and fraction of different ice types (right side) for the five sampling cycles in October 2007. Ice thickness is normalized for the varying core lengths. Error bars are 1σ.

With the albedo of snow of 0.83, only 17% of the incident solar radiation is transmitted and is further attenuated to a few percent in the overlying snow cover. Since the incident short wave radiation during this time period also shows a decrease of approximately 50 W/m^2 (Vancoppenolle et al., 2011), the warming did not result from solar penetration. The differences between cooling and warming rate, however suggest a mechanism of thermal flux not strictly limited to conduction. If the ice is permeable, a convective cycle driven by thermal forcing (Niedrauer and Martin, 1979; Lytle and Ackley, 1996) could bring seawater upward into the ice column, reducing brine salinity and potentially increasing brine volume as the temperature warms. The presence of a network of brine tubes at the granular/columnar interface (Figs. 6 and 8), the relatively stable textural profile at Brussels, and the changes in observed brine/seawater wicking in snowpits between cores Brussels 4 and 5 (16 and 21 October, respectively) provide further support for this concept.

Brine wicking (Massom et al., 1997, 1998) also explains snow-ice formation that is limited to the upper part of the sea ice at Brussels (Fig. 15), considering the overall positive freeboard (absence of flooding) and relatively thin snow cover (low overburden) that persisted for the duration of ISB. The icy granular layer of frozen snow that is present at the ice surface of Brussels has greater salinity and density than surface snow layers and is likely nascent snow-ice. Similar layers of frozen snow were noted at the surface of Brussels ice cores. Snowpit 3E (0.15 m depth) was located

in proximity to the Seabird 2 buoy during the warming trend between Brussels 4 and 5. The temperature profile shows a reversal in gradient ($+2.3^\circ\text{C/m}$) and near isothermal conditions. Not only does this change the morphology of the snow pack, but also the snow/ice interface was warmed and brine volume within the ice increased, thereby reducing brine salinity. The 0.02 m slushy layer present at the snow/ice interface resulted from brine wicked up into the snow by capillary forces. This phenomenon has been noted in a number of studies in different regions of Antarctica (Massom et al., 1997, 1998; Sturm et al., 1998). The slush has significantly higher salinity of 18, indicating a mixture of brine with the basal snow layer, despite the positive freeboard maintained across the site.

The calculated brine salinity at Liège (Fig. 7), initially near that of sea water, increased in the upper half of the ice cover with cold front penetration from Liège 3 to Liège 4 (13 and 18 October, respectively), and then decreased to sea water values. Brine volume never fell below 5% suggesting the ice profile remained permeable, provided that the granular ice in the profile behaved similarly to columnar ice. As discussed above, downward transfer of brines in a permeable sea ice cover may result in opposing upward transfer of sea water in a convection process. However, there are only indirect indications of this process at Liège during our measurement period, including (a) funnel-like cavities connected to brine tubes at the bottom of cores, (b) excursions in the temperature profiles, (c) variability of temperature between sampling events at a given

level, and (d) some snow–ice interface flooding produced by snow loading. Visual observations of core sections from Brussels (Fig. 8) show the presence of brine tubes indicating their potential role in the transfer of brine downwards, as the brine dissolves the warmer less saline ice below. These observations, different from brine channel initiation and dynamics during the growth phase (Wettlaufer et al., 1997), suggest that brine transfer actively increases permeability as it moves downward. Whether this process initiates brine convection or not depends on the severity of the downward cooling front (with associated increase in brine salinity) and the thickness of the ice profile, since thermodynamic readjustment will progressively compensate the contrast in density and salinity. It is therefore worth noting that brine inclusions at Liège often consisted of large coalescent cavities rather than elongated tubes (Fig. 6), which suggests a control of the texture and efficiency of downward brine transfer. These observations suggest that under these conditions, if the ice was permeable throughout, a convection regime in the ice profile may potentially exist, but would require a sufficient density gradient of the brine to initiate overturning.

In both Brussels and Liège cores, the *in situ* salinity profiles show greater regularity with fewer extreme values than the frozen salinity profile. This likely occurs due to brine drainage that inevitably results in the field from processing the *in situ* core at warmer temperatures. The stronger discrepancies between *in situ* and frozen salinity occur in the upper half of the Liège 4 core. This is attributed to the enhanced spatial variability imposed by multiple rafting dynamics and is clearly illustrated by the anti-correlated $\delta^{18}\text{O}$ salinity signature. This signature is present in thin snow–ice layers brought to depth below columnar ice during the rafting process. A similar signature is not apparent in the *in situ* salinity profile. These salinity profiles also demonstrate how measurements can differ under the combined effect of spatial variability and different sampling procedure. The salinity data given for stations 1–3 in Fig. 5 show that frozen salinity profiles provide different mean salinities and enhanced contrasts between measurements from different cores in close proximity to each other. However, additional study will be required to resolve differences in core length, sampling interval, and sampling process.

5.3. Regional characteristics

Although the ice and snow cover characteristics from ISB represent the range of conditions present on a single ice floe, the various sites display significant similarities to the ice floes observed on the inbound short-term ice stations. Station 1 has a predominantly granular profile with thin columnar layers, and the top 42% consisting mainly of snow–ice (indicated by negative $\delta^{18}\text{O}$ values). The dominance of granular ice texture is indicative of formation in a dynamic environment affected by wind and ocean wave interaction, and flooding. Although there were no clear signs of rafting, the overall ice thickness (1.1 m), snow thickness (0.4 m) and relative composition of the ice profile resembles that of Liège. The core from station 2 shows thicker (2.5 m) ice with structure, salinity and $\delta^{18}\text{O}$ profiles indicative of rafting/deformation processes. The ice thickness and composition of this core resembles the greater complexity of ice types present at Fabra. Mean snow thickness at station 2 is greater than station 1 and more closely aligned with the mean snow thickness present at Fabra. Station 3 has thinner (0.6 m) ice predominantly of columnar texture. This profile is indicative of ice growth in a relatively calm environment with vertical brine drainage tubes and a thin layer of granular snow–ice at the top. Mean snow thickness (0.17 m) is relatively thin compared to other stations. This profile has a striking resemblance to the ice and snow characteristics observed at Brussels. Although not conclusive, the

random nature in which the short-term stations were occupied and the similarities between these stations and the sites at ISB may have implications relating to the regional scale processes involved in genesis and development of ice floes in the Bellingshausen Sea. The three principal sites at ISB (Brussels, Liège, and Fabra) consist of differing distribution of ice types, snow and ice thickness, and ice growth processes that appear to recur in stations 1–3.

The average ice textural profiles from two cruises (NBP 93–5 and 95–5) in the Bellingshausen Sea were reported by Jeffries et al. (2001) for the late winter (August–September). Mean values of the various ice types were reported for: columnar ice (25.5% and 34.6%, respectively), frazil (44.3% and 40.8%, respectively), and snow–ice (23.8% and 21.6%, respectively) with the balance classified as “other”. The percentage of snow–ice reported for the Bellingshausen Sea was generally greater than reported for other regions of Antarctica (Jeffries et al., 2001). The overall mean ISB textural profiles, obtained by combining cores from both Brussels and Liège, indicate that ice generally consisted of 46.3% columnar, 33.3% frazil, and 20.4% snow–ice. As compared to the results of Jeffries et al. (2001), the ISB textural profile indicates the percentage of columnar and frazil were roughly reversed and snow–ice was consistent. However, this comparison only represents the average consistency of two “type” sites for ISB, not including the (thick ice) Fabra site. In addition, the Jeffries et al. (2001) profiles were developed from floes along the ship transects in the Bellingshausen Sea that rarely exceeded latitude 70°S. Consequently, it is difficult to make a direct comparison considering the limited spatial extent of the samples at ISB and apparent bias. Given that the bias excludes thicker ice areas of ISB, it is expected that the mean textural profile should more closely resemble previously reported results.

As noted by Sturm et al. (1998), regional scale variability in snow cover is predictable due to the sequence of warm–cold atmospheric cycles and the larger scale of processes involved. On smaller scales, the heterogeneity of any particular floe may be significant (e.g. differences between sites); however, the characteristics of ice and snow cover are driven by atmospheric and oceanic processes that work on a more regional basis, trending toward larger scale homogeneity (i.e. same “type” sites recurring over larger distances). Current patterns of atmospheric circulation have been attributed to a trend of declining sea ice extent and a reduction in the number of ice season days within the Bellingshausen Sea (Stammerjohn et al., 2008). However, the changes in sea ice extent detected from PM remote sensing do not address the mass balance of sea ice and snow cover for the region. We note from our measurements that due to the insulating properties of the snow cover, cold air temperatures, if short in duration (i.e. two to three days) and limited in amplitude, may not effectively penetrate the snow to result in snow–ice formation. At Fabra, where snow cover was thick and flooding was prevalent, the sea ice profile is likely to be isothermal near the freezing point of sea water. Perovich et al. (2004) observed similar behavior, deep snow cover, flooding, and isothermal sea ice profiles further north (~68° to 66°S) in the Bellingshausen Sea in Marguerite Bay.

6. Summary and conclusion

During SIMBA, sea ice and snow characteristics were observed for a 27-day drift interval on a single ice floe in the Bellingshausen Sea. The ISB floe contained distinct sites with varying ice and snow thickness, morphology, and freeboard. These sites were each measured multiple times to observe changes in response to atmospheric forcing. A weather pattern similar to that reported by previous investigations of this region during the same season, consisting of warm fronts with high winds and precipitation, followed by cold and relatively calm periods was experienced

through four cycles of varying duration and intensity. Snow cover at ISB and the short-term stations was generally thicker than mean values reported in previous cruises for this region in a similar seasonal time frame. Strong winds resulted in significant redistribution of snow across ISB, with accumulation occurring in areas of deformed ice. The thickness of snow cover was of primary significance in regulating the temperature flux and the physical regime in which sea ice developed and underwent morphological changes. Level ice areas showed little snow accumulation and experienced greater thermal fluctuations than areas with thicker snow accumulation. Sea ice cores showed corresponding changes in brine volume and salinity in response to thermal cycling. Areas of thicker snow cover experienced a muted response (limited to a few tens of centimeters of the profile) from thermal forcing as a result of the insulating properties of the snow.

The cycling of atmospheric fronts also affected the temporal evolution of brine volume and salinity within the sea ice profiles as the limited duration of these events restricted cooling of the ice. The different heat transfer rates noted in the temperature profiles from IMB records between cooling and warming indicate potential convective sea water exchange and permeable sea ice conditions. Snow cover not only mitigated the transfer of cold fronts in sea ice, but also provided sufficient overburden to induce flooding of the snow/ice interface. Flooding was prevalent in areas with deformed ice features and thick snow cover. Snow–ice formation was noted in differing relative proportions in both positive and negative freeboard situations resulting from different mechanisms of formation. In negative freeboard conditions, snow–ice is formed through flood–freeze cycles. However, the presence of thick snow cover and short duration of cold fronts may sufficiently retard cooling at the snow/slush interface to prevent snow–ice formation. In positive freeboard condition, snow–ice is formed through wicking of brine/sea water in permeable ice conditions.

Mean ice profiles for Brussels and Liège showed both similarities and also significant contrasts. Although mean salinity and $\delta^{18}\text{O}$ have similar vertical trend, their ice composition and growth history are drastically different. The overall mean texture of both sites combined is slightly different than reported by Jeffries et al. (2001) for this region because of the bias in SIMBA profiles toward thinner ice. The thicker ice areas (i.e. Fabra) are not included in the mean profiles resulting in an over-representation of columnar ice and an under-representation of frazil ice. The percentage of snow–ice is consistent with prior studies, but slightly lower (mean 20.4%) compared with Jeffries et al. (2001) mean values of 23.8% and 21.6% from 2 cruises.

Although the characteristics and composition of sea ice and snow are notably different between sites at ISB, the comparison of these “type” sites to inbound stations and to results from other studies in the region indicate that the processes (atmospheric and oceanic) that control the sea ice and snow cover work on larger scales and therefore trend toward homogeneity at this level. This study supports conclusions derived by Sturm et al. (1998) regarding the heterogeneous nature of snow conditions at local scales trending toward regional homogeneity. In addition, we noted the same behavior, heterogeneous locally and homogeneous regionally, was apparent for the sea ice cover. We see during this seasonal transition that thin ice sites (0.6 m) have reached their limit of thermodynamic growth and have shown melt instead, due to the shorter duration of cold fronts that cannot sufficiently penetrate the sea ice and overcome the strong ocean heat flux that drives basal melt. Yet, we note that the mean ice thickness of the ISB floe was considerably greater due to other thickening processes (rafting and ridging) in the sea ice.

Under climate change, with trends toward wind-driven compaction of sea ice and greater precipitation from atmospheric anomalies, the Bellingshausen Sea ice and snow cover may have already shown

significant changes (Stammerjohn et al., 2008). The effects of these changes have decreased sea ice extent, but may have increased sea ice thickness by enhanced mechanical thickening processes (Massom et al., 2008). While rafting and ridging are the processes that result in higher ice thicknesses reported here, it is indeterminate from either our data or other studies of whether this has increased recently. Increased surface roughness in deformed ice indicates thicker snow cover; however, in this study we have observed the limiting effect of snow cover insulation on creation of snow–ice, balanced by basal melt from ocean heat flux and thus limited, if any, thermodynamic thickening in the early spring period, either from snow–ice formation or basal freezing. Warmer ice conditions, created by thicker snow, did result in greater ice permeability and increases in flooding of the snow/ice interface. These conditions are also consistent with regional remote sensing observations of earlier ice breakup and a shorter sea ice season, seen more recently in the Bellingshausen Sea.

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CHAPTER IV: Temporal evolution of DMS, DMPS and DMSO in Antarctica sea ice: between seasonal and spatial contrasts

Paper 4 :

High-resolution dimethyl sulfide and dimethylsulfoniopropionate time series profiles in decaying summer first-year sea ice at Ice Station Polarstern, western Weddell Sea, Antarctica, 2010. *J. Geophys. Res.*, 115, G04044, 16 pp. by Tison J.-L., F. Brabant, I. Dumont and J. Stefels.

Contribution of F. Brabant: Analysis of the data. Drawing of the figures. Co-writing of the paper.

High-resolution dimethyl sulfide and dimethylsulfoniopropionate time series profiles in decaying summer first-year sea ice at Ice Station Polarstern, western Weddell Sea, Antarctica

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[1] High-resolution profiles of ice dimethyl sulfide (DMS) and dimethylsulfoniopropionate (DMSP) concentrations were measured together with a suite of ancillary physical and biological properties during a time series of decaying summer-level first-year sea ice throughout December 2004 during the Ice Station Polarstern drift experiment (western Weddell Sea, Antarctica). Ice DMSP and DMS concentrations were always maximum at the bottom of the ice sheet (636–2627 and 292–1430 nM, respectively) where the highest chlorophyll *a* levels were also found (15–30 $\mu\text{g L}^{-1}$). Throughout the observation period, the autotrophic surface community (32–205 $\mu\text{g C L}^{-1}$) was dominated by *Phaeocystis* sp. while the bottom community (1622–3830 $\mu\text{g C L}^{-1}$) mainly consisted of pennate diatoms. This illustrates that, although being known for lower DMSP-to-chlorophyll *a* ratios than *Phaeocystis* sp., diatoms dominated the overall DMSP production because of their much larger biomass. Decreasing DMSP concentrations and increasing DMS-to-DMSP ratios in the bottom layers with time suggested active DMSP-to-DMS conversion in a slowly degrading environment. Drastic temporal brine volume and brine salinity changes associated with the decaying sea ice cover are shown to directly impact (1) the migration of DMSP and DMS through the brine network, (2) the DMSP-to-DMS conversion processes within the ice interior, and (3) the physiological response of the ice algae. First-order flux estimates show that decaying summer-level first-year sea ice alone can significantly contribute to the regional sulfur budget of the Weddell Sea with an estimated average loss rate of 5.7 $\mu\text{mol DMS(P) m}^{-2} \text{ d}^{-1}$ toward the atmosphere and the ocean.

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1. Introduction

[2] Dimethyl sulfide (DMS) is a biogenic semivolatile organic compound mainly produced by the enzymatic conversion of dimethylsulfoniopropionate (DMSP). DMSP is synthesized by a limited number of phytoplankton taxa in oceanic environments [Keller et al., 1989]. A complex ecosystem network that involves most of the microbial food web affects the concentrations of DMS and DMSP in the environment, resulting in strong seasonal and latitudinal variations in concentration in surface ocean waters (reviewed by Stefels et al. [2007]). DMS accounts for 50%

to 60% of Earth's total natural sulfur emissions to the atmosphere, and 90% of this DMS flux originates in marine environments. DMS has been brought forward to the scene of climate change as a potential mitigation agent of global warming from increasing concentrations of greenhouse gases. Indeed, once released in the atmosphere, DMS is oxidized to, among other compounds, sulfate that can either directly (as aerosols) or indirectly (as cloud condensation nuclei) increase the reflectivity of the atmosphere and of the clouds, thereby cooling the Earth. Charlson et al. [1987] suggested that the temperature increase resulting from global warming would raise biogenic production of DMS that would in turn increase the rate of formation of sulfate aerosols, thereby impeding the temperature increase, at least partially. This assumption is challenged by the observation that not all microalgae are able to synthesize DMSP and that the effect of climate change on the growth of DMSP producers is not known because of a lack of understanding of the factors controlling DMSP variability in phytoplankton cells as well as those factors acting on DMSP-to-DMS

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Table 1. Summary of Available Sea Ice DMS and DMSP Data in the Literature

Location	Ice Type	Season ^a	DMSP ^b (nM)	DMS ^b (nM)	DMS+DMSP ^b (nM)	Source
Weddell Sea	Pack ice	Sp	322 (4–1664)	NA	NA	Kirst et al. [1991]
Resolute Passage	Pack ice	Sp	325 ^c (0–6014) ^f	NA	950 ^b (nd–15051) ^d	Levasseur et al. [1994]
Bellinghousen Sea	Pack ice	Sp-Su	200 (17–546)	NA	NA	Turner et al. [1995]
Prydz Bay	Pack ice	Sp	144 (8–725)	NA	NA	Curran et al. [2003]
Dumont D'Urville Sea	Pack ice	Wi	40 (nd–193)	NA	NA	Curran et al. [2003]
Ross Sea	Pack ice	Sp-Su	212 (5–980)	NA	NA	DiTullio et al. [1998]
Ross Sea	Fast ice	Sp	150 (81–219)	NA	NA	DiTullio et al. [1998]
Offshore Prydz Bay	Pack ice	Sp	107 (6–767)	NA	NA	Trevena et al. [2003]
Baffin Bay	Pack ice	Sp-Su	126 ^e (8.66–987) ^f	NA	NA	Lee et al. [2001]
Prydz Bay	Fast ice	Sp-Su	112 (9–1478)	NA	NA	Trevena et al. [2003]
Gerlache Inlet	Fast ice	Su	NA (4.4–450)	NA	NA	Gambara et al. [2004]
Indian sector of SO	Pack/fast ice	Sp	185 ^{cd} (45–796) ^f	12 (<0.3–75)	NA	Trevena and Jones [2006]
Dumont D'Urville Sea	Fast ice	Sp	NA	NA (4–74)	NA	Dehille et al. [2007]
Western Weddell Sea	Pack ice	Summer	171 (5–2627)	58 (0.5–1430)	229 (6–3340)	This study

^aSp, spring; Su, summer; Wi, winter; NA, not available; SO, Southern Ocean.^bMean is given in bold, followed by the range in parentheses.^cDMSP_p only.^dDMSP_p + DMS.^eCalculated for ice categories with ice thickness <1.20 m.^fNumber of cores weighted average.

transformation. Among the unknowns, processes in sea ice form the biggest gap in our knowledge, even though sea ice is known to be a habitat for strong DMSP-producing algal species [Kirst et al., 1991; Levasseur et al., 1994]. Another potential by-product of the marine DMS released to the atmosphere, which is also of climatic significance, is methylsulfonic acid, which is found in continental ice cores and often used as a paleoclimatic indicator of regional sea ice extent, at least in coastal areas [Mulvaney et al., 1992; Welch et al., 1993; Pasteur et al., 1995; Meyerson et al., 2002; Curran et al., 2003; Wolff et al., 2006; Abram et al., 2007; Rhodes et al., 2009].

[3] Suggested biological functions for DMSP are an osmotic pressure regulator, a cryoprotectant, an oxygen radical scavenger, an overflow compound for excess energy dissipation, and a grazing deterrent. Although DMSP seems to be a multifunctional compound, the regulation of its production and conversion is still unresolved. Several environmental factors such as salinity, light intensity and history, temperature, and nutrient supply may affect the DMSP synthesis by algal cells (reviewed by Stefels [2000] and Stefels et al. [2007]). Unlike the relatively stable pelagic environment, sea ice forms a habitat where extremely high salinities and low temperatures favor the enhanced production of DMSP in algal cells. Subsequent melting of ice results in very low salinities and higher temperatures, which mediates the release of DMSP from cells and increases the conversion to DMS. During spring-time, light conditions at the ice surface may become inhibiting. Under such conditions, an increased DMSP production is expected, although the mechanisms are still enigmatic. Moreover, in field samples, the multitude of processes are difficult to follow separately and the overarching effect of high light conditions may be the inhibited conversion of DMS and DMSP by bacteria and an increased photochemical conversion of DMS to dimethylsulfoxide (DMSO) [Slezak et al., 2001]. Release of DMSP from algal cells is mediated by active exudation, cell lysis due to senescence or viral attack, or grazing. The conversion of DMSP into DMS and acrylic acid is mainly mediated through bacterial or algal enzymes; however, in sea ice,

chemical conversion should be considered as well. Hydroxide decomposition of DMSP does not take place at the pH of seawater, but the potentially alkaline conditions of sea ice brine inclusions, with pH values sometimes rising as high as 10 [Gleitz et al., 1995], do favor abiotic conversion. Whether these alkaline conditions also favor the enzymatic conversion of DMSP is unknown. Although it was observed that the pH optimum of DMSP lyase in a temperate *Phaeocystis* species was indeed alkaline [Stefels and Dijkhuizen, 1996], various strains of *Emiliania huxleyi*, another Haptophyte species, indicated the existence of various isoforms of DMSP lyase that have different pH optima [Steinke et al., 1998]. There is nothing known about DMSP lyase activity and its characteristics in ice algae. To date, sea ice DMSP and DMS studies were mainly focused on DMSP (Table 1), and only two of these studies report individual DMS concentrations. Even though they are scarce, published values confirm the assumption of sea ice as an environment favorable to DMSP and DMS production, with concentration levels up to three orders of magnitude higher than background (subnanomolar) values in seawater [e.g., Kirst et al., 1991; Turner et al., 1995; DiTullio et al., 1998]. This paper presents the first high-resolution DMS and DMSP time series profiles in the level spring/summer first-year sea ice of 2004 at the ISPOL “cleann site” [Tison et al., 2008] in the western Weddell Sea and discusses how these profiles are related to the decay processes of the ice. More specifically, we focus on deciphering the relative contribution and potential interactions between physical and biological processes in controlling the DMS(P) cycle within the sea ice and we provide first estimates of the sulfur fluxes to the ocean and the atmosphere from summer sea ice in the western Weddell Sea.

2. Site Description

[4] DMS and DMSP measurements were obtained from samples collected at the ISPOL clean site, which was described extensively by Tison et al. [2008]. Briefly, ice cores, brines, and under ice water samples were collected at regular 5 day intervals from 29 November to 30 December

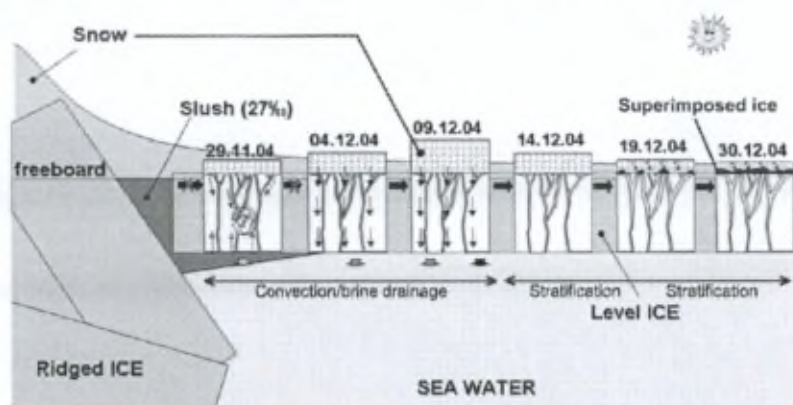


Figure 1. Schematic evolution of the decaying first-year sea ice cover at the ISPOL clean site [after Tison et al., 2008]. Vertical arrows indicate brine drainage in the first half of the observation period. Horizontal arrows indicate lateral brine movement. Station 25 December is similar to 30 December (30.12.04) and is not shown. Note that the position of stations relative to the ridges is not respected [see Tison et al., 2008].

2004, in close (few meters) proximity to each other. The ice cover was homogeneous, unflooded (positive freeboard) first-year sea ice about 90 cm thick, with a thin snow cover (6–25 cm). The potential scenario of the sea ice cover decay (Figure 1) was discussed extensively elsewhere [Tison et al., 2008]. In short, at the beginning of the observation period, the brine network was unstable in terms of density, as shown by computed brine salinity profiles (Figure 2b). Calculated relative brine volumes ranged from 9% to 33% (Figure 2a) and, therefore, were well above the 5% threshold for increased permeability and connectivity in columnar ice [Buckley and Trodhal, 1987; Golden et al., 1998, 2007; Golden, 2003]. This suggests that brine inclusions (be it in liquid, gaseous, or particulate form) were largely interconnected throughout the whole sampling period. Large increases of relative brine volumes with time characterized the upper part of the sea ice cover, although important variability may have been related to spatial heterogeneity and potential sampling biases (e.g., partial loss of brine in pockets, channels, or tubes) as sea ice decays [Tison et al., 2008]. Interconnectivity and above-seawater salinities of brines resulted in downward brine migration, especially during stations 29 November to 9 December. Values of $\delta^{18}\text{O}$ for bulk sea ice were used to detect changes in the composition of the brines (considering that the signature of the pure ice crystals remained constant with time). On 9 December, decreasing $\delta^{18}\text{O}$ values indicated that, as surface brine traveled downward, it was mainly replaced by slush from flooded ridges nearby (lower $\delta^{18}\text{O}$ values from snow contribution), whereas internal melting was the main process later on (higher $\delta^{18}\text{O}$ values from melting crystals). Increased brine volumes in the upper 50 cm after 9 December also reflected internal melting. Following internal melt, brine salinity dropped below the seawater value in the second half of the observation period (station 14 December onward), which resulted in stratification of the brine network. Under such circumstances, solute exchange is mainly

controlled by molecular diffusion processes driven by concentration gradients. Textural observations indicated that superimposed ice formation started in the second half of the period, as melting surface snow infiltrated and refroze at the top of the saltier granular frazil ice. The initial mean ice thickness was 90 ± 0.5 cm. Statistical estimates of the evolution of the ice cover during the observation period corroborate model predictions of a moderate bottom melting (5–10 cm) from ocean heat flux [Tison et al., 2008; McPhee, 2008].

3. Materials and Methods

[5] Ice cores were immediately wrapped into PE bags on retrieval and stored on the sampling site in an insulated box filled with individual cooling bags, precooled at -30°C , to limit brine drainage from samples as much as possible. Cores were transported back to the ship as soon as possible and stored at -35°C until further analysis. Holes were drilled into the ice cover at 20 and 60 cm depth (80 cm also on 29 November) to allow gravity-driven brine collection known as the sackhole brine sampling technique [Thomas and Papadimitriou, 2003]. Brine and under ice seawater (interface, 1 m, and 30 m deep) were then pumped up using a portable peristaltic pump (Cole-Palmer, Masterflex E/P) and tubing. The preparation and analysis of DMS and DMSP samples from ice is extensively described elsewhere (J. Stefels, The analysis of dimethylsulfide and dimethylsulphoniopropionate in sea ice: dry-crushing and melting using stable isotope additions, submitted to *Marine Chemistry*, 2010). In short, $5 \times 3 \times 1$ cm ice samples were introduced, together with two stainless steel balls, into a stainless steel vessel fitted with two in/out valves. The vessel was kept at -25°C at all times by means of cooling bags, apart from the brief period during which crushing occurred. The vessel was tightly bolted to a custom-made shaker and subjected to fast up-and-down movements. As a result, the ice sample was

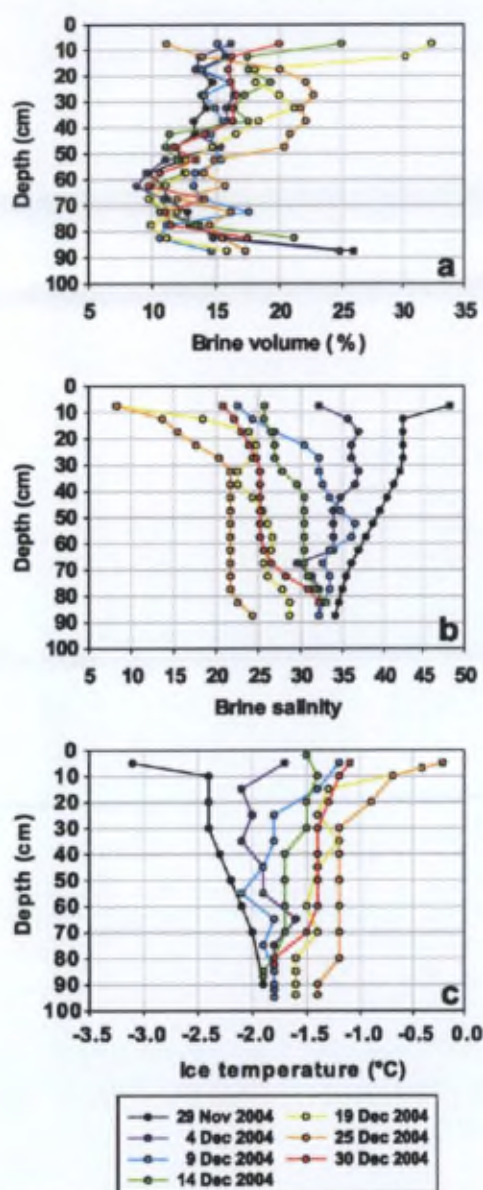


Figure 2. Profiles of computed brine volume and brine salinity in the ice [after Tison *et al.*, 2008].

reduced to a very fine powder. The crushing vessel was then hooked to the inlet line of a proton-transfer-reaction mass spectrometer (PTRMS, Ionicon Analytik, Innsbruck), and the DMS was flushed from the sample with high-purity synthetic air. The principles of proton-transfer-reaction mass spectrometry were described extensively elsewhere [Lindinger *et*

al., 1998; de Gouw *et al.*, 2003; de Gouw and Warneke, 2007]. Instrument settings for DMS analysis in discrete samples is given in the work of Stefels *et al.* [2009]. After analysis, the ice powder was weighed and a subsample melted in the presence of excess NaOH, to convert total DMSP into DMS after 24 h. The resulting DMS was bubbled from the solution and directly analyzed by PTRMS. Brine and water samples were treated in the liquid state, following the same procedure: first DMS was analyzed and then base was added to convert DMSP into DMS. In those samples in which the solid fraction was analyzed as well, a subsample was filtered gravimetrically over a Whatman GF/F filter and the filtrate was analyzed in two steps as explained earlier in this section. Direct analysis of DMS by PTRMS resulted in an exponentially decaying peak. Total amounts were calculated by integration of peak areas. Calibration curves were prepared from DMS standards (Sigma-Aldrich) in seawater and proved to be linear over more than three orders of magnitude, with typical correlation coefficients larger than 0.999, and a detection limit of 10 pmol DMS [Stefels *et al.*, 2009]. DMS and DMSP concentrations in ice (expressed in nM) should be read as nanomoles per kilogram of ice. Discrete chlorophyll *a* measurements were performed at six different depths on a dedicated ice core: two at the top, two in the interior ice, and two at the bottom. Five cm ice core slices (14 cm diam) were collected and melted in a known volume of filtered seawater (1:4 volume ratio) at 4°C, in the dark. The melted samples were then gently filtered onto Whatman GF/F filters using Gelman filtration devices. The filters were stored in cryovials at -80°C for chlorophyll *a* measurements back in the home laboratory. They were extracted in acetone (90% vol/vol) in the dark at 4°C for 24 h, and quantified with a Kontron SFM 25 fluorometer (Kontron Instruments, Neufahrn, Germany) at excitation and emission wavelengths of 430 and 672 nm, respectively, according to the work of Yentsch and Menzel [1963]. Ice core sections sampled for the determination of abundance and biomass of microorganisms were melted in the same manner as for the chlorophyll *a* analysis described earlier and analyzed as fully described in the work of Dumont *et al.* [2009]. To compare DMS (P) concentrations in sackholes with those in ice, potential sackhole concentrations were calculated from bulk-ice DMS(P) concentrations, assuming that sackhole brines are a homogeneous mixture of brine material seeping out from the entire ice column above. First, at each depth, DMS(P) concentrations in ice were converted to brine concentrations by multiplying by the density value of 0.91 for first-year sea ice [Timco and Frederking, 1996] and dividing by the corresponding relative brine volume as calculated from observed bulk ice salinity and temperature [Cox and Weeks, 1983; Leppäranta and Manninen, 1988; Eicken, 2003]. Subsequently, potential DMS(P) concentrations in sackholes were calculated by averaging reconstructed brine concentrations above the sackhole depth.

4. Results

[6] The highest chlorophyll *a* values (up to 30 $\mu\text{g L}^{-1}$) were observed in the lowest 10 cm of the ice cover (Figure 3a). Although bottom melting occurred, no systematic change in chlorophyll *a* was found in these layers. A secondary maximum (1–2 $\mu\text{g L}^{-1}$) occurred in the surface layer on 9

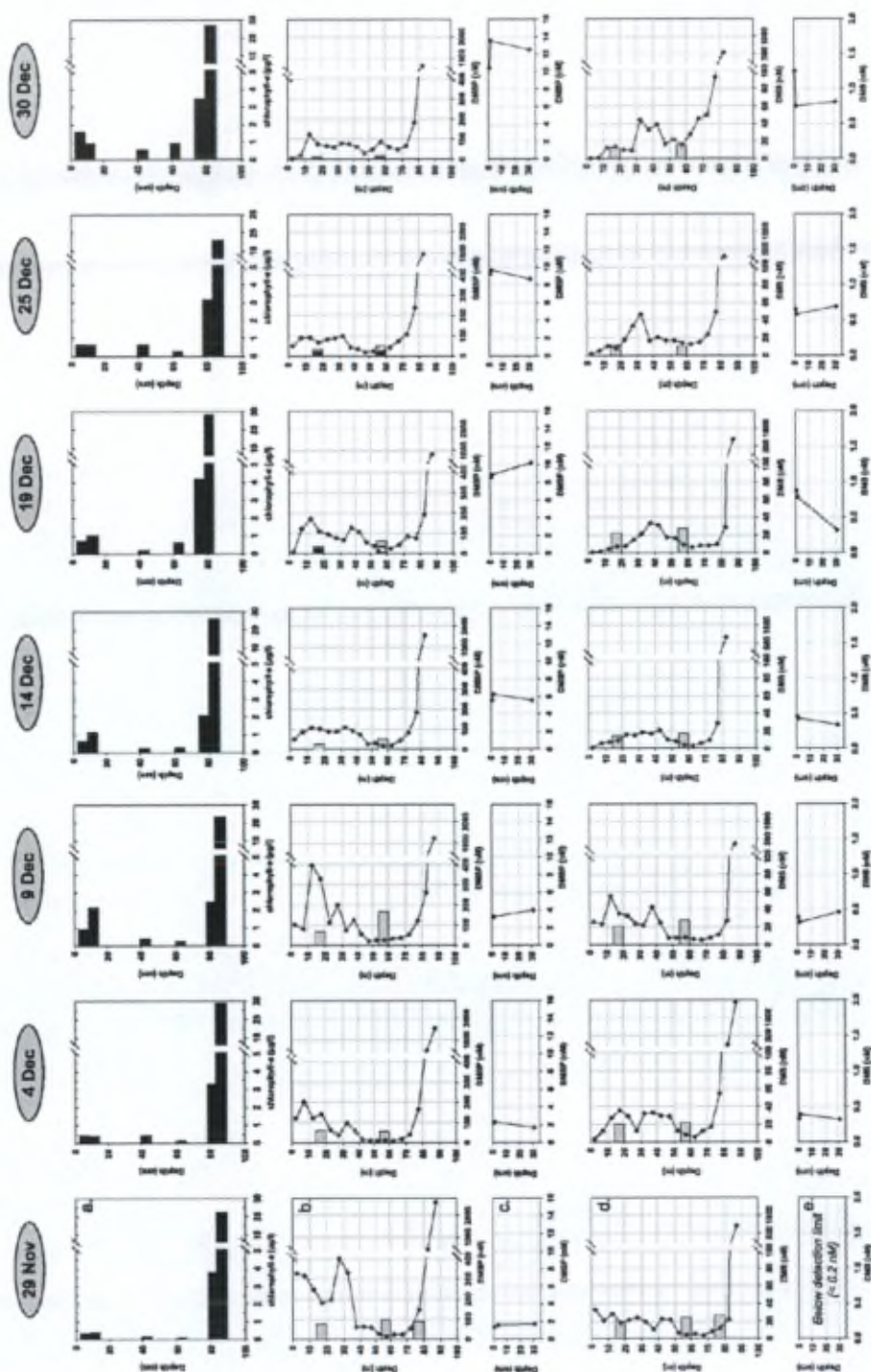


Figure 3

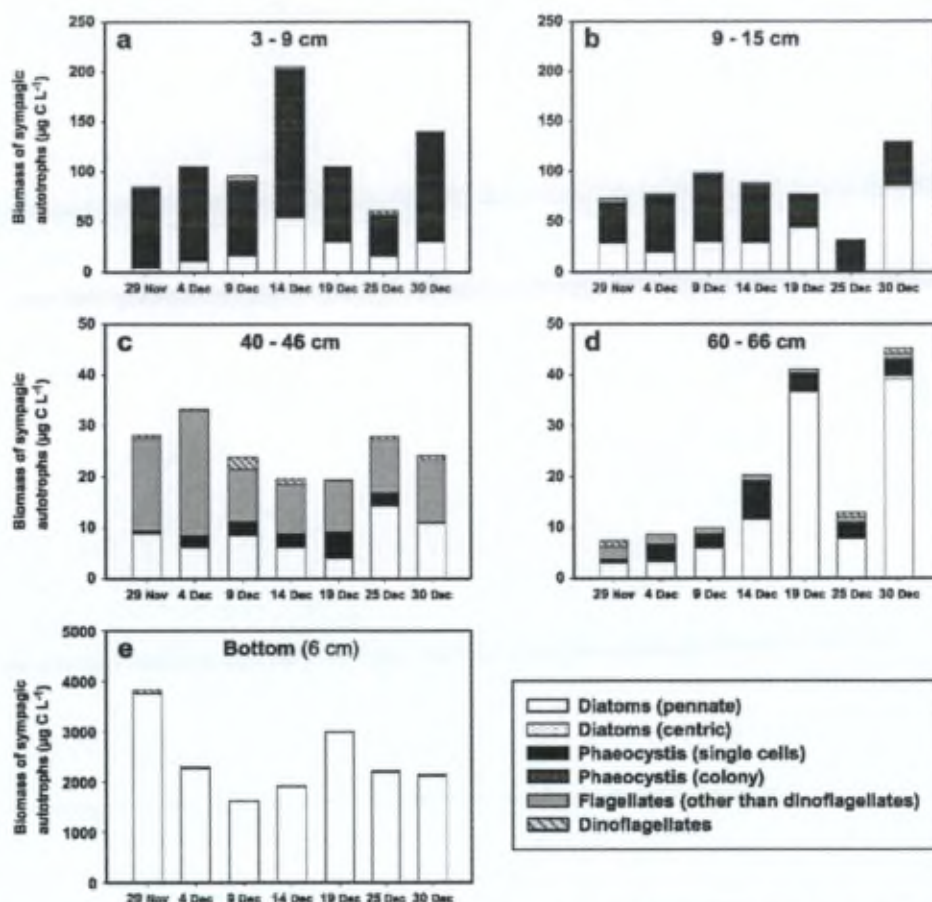


Figure 4. Autotrophic biomass composition observed at five different depths in the ice. Note the difference in vertical scale for the top layers (3–9 and 9–15 cm), the interior layers (40–46 and 60–66 cm), and the bottom (partly from Dumont [2009]).

December. Otherwise, chlorophyll *a* remained mostly below $1 \mu\text{g L}^{-1}$ throughout the upper 70 cm of the sea ice cover for the whole period, though we might have missed some features due to discontinuous sampling. Biomass of sea ice algae was determined at five different depths in the ice corresponding to those where chlorophyll *a* was determined (Figure 4). Autotrophic biomass ranged from 32 to $205 \mu\text{g C L}^{-1}$ in the top 15 cm (Figures 4a and 4b). Throughout the whole observation period, assemblages in this layer were mainly dominated by *Phaeocystis* sp., which accounted for 34%–95% of the total autotrophic biomass. Pennate diatoms also contributed significantly to the upper ice assemblages

with a biomass ranging from 0% to 66% of the total autotrophic biomass. The contribution of the other identified taxa (centric diatoms, dinoflagellates, and other flagellates) to the autotrophic biomass amounted to generally less than 2%. The highest autotrophic biomass levels (from 1622 to $3830 \mu\text{g C L}^{-1}$) were observed in the bottom 6 cm of the ice, where pennate diatoms systematically dominated the assemblage, accounting for 98%–100% of the autotrophic biomass (Figure 4e). The lowest levels of autotrophic biomass (from 7 to $45 \mu\text{g C L}^{-1}$) were observed in interior ice (Figures 4c and 4d). The upper interior layer (Figure 4c) was most of the time dominated by flagellates (other than dinoflagellates), which

Figure 3. Evolution of (a) ice chlorophyll *a*, (b) ice DMSP (black dots) and brine DMSP (horizontal shaded bars show DMSP_p concentration at the sackholes depth, and DMSP_p proportion is shown as black area on the horizontal bars for the last three stations), (c) underlying seawater DMSP, (d) ice DMS (black dots) and brine DMS (horizontal shaded bars), and (e) underlying seawater DMS at the ISPOL clean site. DMS and DMSP concentrations in ice expressed in nM should be read in nanomoles per kilogram of ice.

represented 38%–73% of the total autotrophic biomass at that depth in the ice. The lower interior ice level (Figure 4d) was characterized by a relatively well mixed assemblage at the beginning of the observation period (pennate diatoms, 39%; flagellates, 33%; dinoflagellates, 17%; and *Phaeocystis* sp., 11%) and became largely dominated by pennate diatoms (from 59% to 89% of the total autotrophic biomass) from 9 December onward. A more detailed analysis can be found in the work of Dumont et al. [2009]. The evolution in time of total DMSP and DMS in ice profiles is given in Figures 3b and 3d, respectively. DMSP values in the ice spanned the whole range between a few nM and about 2600 nM, with maximum values localized within the levels of maximum chlorophyll *a*. Two secondary DMSP maxima (300–400 nM) were initially present in the upper half of the sea ice cover (one subsurface and one at about 30 cm depth). The subsurface one was associated with relatively low chlorophyll *a* levels. These maxima rapidly diminished (station 4 December) and stabilized at a mean value around 100 nM for the rest of the period, with the noticeable exception of station 9 December, which displayed a broad maximum (up to 400 nM) between 10 and 40 cm depth, with a corresponding increase of chlorophyll *a* visible in the top 15 cm. The bimodal structure of the upper DMSP maxima, however, remained present throughout the observation period. The interior ice (45–75 cm) showed typical DMSP values of a few tens of nM, with no obvious trend with time. In contrast to chlorophyll *a* levels, DMSP concentrations in the lowest 15 cm on average reduced in time. DMS values in the ice (Figure 3d), ranged from negligible (upper layers at the end of the period) to values as high as 1500 nM in the bottom layers where both DMSP and chlorophyll *a* levels were highest. As for DMSP, the main changes of DMS concentrations occurred in the upper half of the profile. Two events can be distinguished: Initially at about 20 nM, DMS increased up to 60 nM, somewhat mimicking the double maximum in DMSP at stations 4 and 9 December. From station 14 December onward, DMS concentrations dropped to negligible values near the surface and a linear gradient established toward a maximum of 45 nM DMS at about 40 cm depth. The interior ice and bottom layers showed less variability in DMS with time, apart from the last two stations, where concentration levels tended to increase within the interior ice. DMSP values in brine from sackholes ranged between 20 and 167 nM (horizontal bars in Figure 3b). Brine DMSP concentrations decreased with time, with most of the changes occurring in the first half of the observation period, in parallel to that observed in the ice from the upper part of the sea ice cover. From 9 December onward, concentrations in samples from 60 cm depth were consistently higher than those from 20 cm depth. Particulate DMSP concentrations in brine are only available for the second half of the observation period. They were always higher than that for dissolved DMSP. DMS concentrations in brines from sackholes (horizontal bars on graphs of Figure 3d) fluctuated between 10 and 30 nM and showed less of a reduction in time than DMSP concentrations. At all stations, brine DMS values from the two sampled depths were similar.

[7] DMSP and DMS concentrations in the underlying water (Figures 3c and 3e, respectively) increased steadily with time at all three measured depths. Both increased about one order of magnitude: DMSP increased from about 1.5 to

14 nM, and DMS (from <0.2 to 1 nM) remained in the subnanomolar range, with the exception of one sample at the ice-water interface during the final station. Profiles of DMS to DMSP ratios in ice (Figure 5a) systematically showed minimum values in the top 20 cm (mean 0.11, range 0.01–0.29), whereas the bottom 5 cm always displayed higher values (mean 0.56, range 0.27–0.93). The interior ice layer above 60 cm depth was the most dynamic, with a maximum at all stations between 40 and 55 cm. Starting from a maximum value of 0.37 on 29 November, the DMS-to-DMSP ratio reached its maximum value at 50 cm depth on station 4 December (2.75). The ratio rapidly diminished on 9 December with a maximum value of 0.44 and then increased again toward the end of the observation period (0.89 on 25 December). At the last station, a remarkable increase of the ratio in the bottom 20 cm was observed. DMS-to-DMSP ratios in the underlying water column (Figure 5b) reduced in time from approximately 0.17 to 0.06 (mean of the 1 and 30 m depth samples). Profiles of DMSP-to-chlorophyll *a* ratios (Figure 5c) showed relatively high and variable values (mean, 169 nmol μg^{-1} ; range, 13–946 nmol μg^{-1} ; and standard deviation, 187 nmol μg^{-1}). Owing to the discrete nature of the chlorophyll *a* data and the fact that these data were obtained from a different core than DMSP data, results should be treated with care. Again two phases could be distinguished: During the first two stations, peak values were observed in the subsurface samples, whereas this feature disappeared completely from 9 December onward. The maxima observed in interior ice on 14 and 19 December resulted from relatively low chlorophyll *a* levels, not from high DMSP concentrations, and it is difficult to judge whether this is a firm feature. The relationship between DMSP and chlorophyll *a* concentrations shows a positive linear trend ($R^2 = 0.706$; $P < 0.001$; Figure 6a). There is also a fairly good relationship between DMS and chlorophyll *a* concentrations ($R^2 = 0.818$; $P < 0.001$) (Figure 6b). However, these positive correlations are mainly shaped by the extremely high values of all parameters in the bottom ice layers. When these relationships at chlorophyll *a* levels lower than 5 $\mu\text{g L}^{-1}$ (top and internal layers) were investigated, no significant trend could be observed.

5. Discussion

5.1. DMSP and DMS Ranges

[8] The observed range (5–2627 nM) and mean value (171 nM) of DMSP at the ISPOL clean site are similar to what was previously reported in the literature for spring-summer pack ice (Table 1). DMSP maximum values reported in this study are, however, the highest ever observed in Antarctic sea ice, except for the extremely high values measured in a particular case of thick rafted sea ice (concentration up to 13,525 nM of DMSP measured in an interior slush ice layer) [Trevena and Jones, 2006]. DMS mean and maximum values were significantly higher than the values previously reported by Dehille et al. [2007] and Trevena and Jones [2006]. Values of under-ice water DMS (range, <0.2–1.2 nM; mean, 0.5 nM) and DMSP (range, 2–14 nM; average, 6 nM) were consistent with values previously observed in under-ice seawater [Gibson et al., 1990; Kirst et al., 1991; Trevena and Jones, 2006].

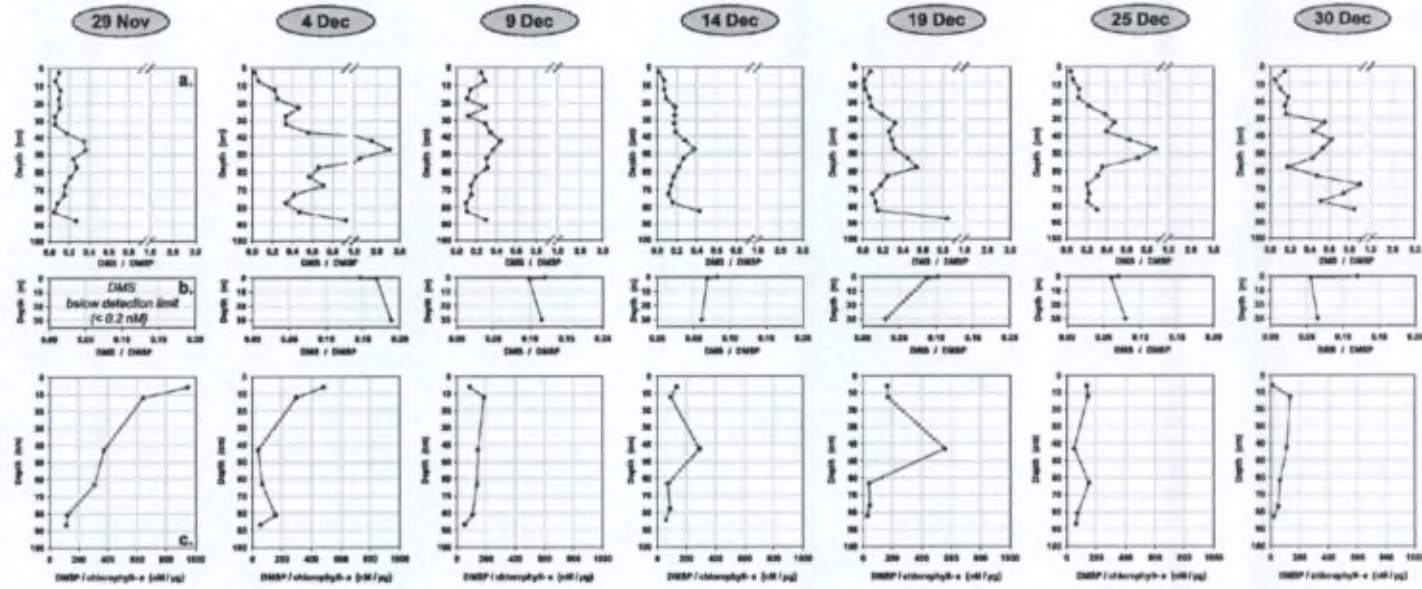


Figure 5. Evolution of (a) DM5-to-DMSP ratio in the ice, (b) DMS-to-DMSP ratio in the underlying seawater, and (c) DMSP-to-chlorophyll *a* in the ice at the ISPOL clean site.

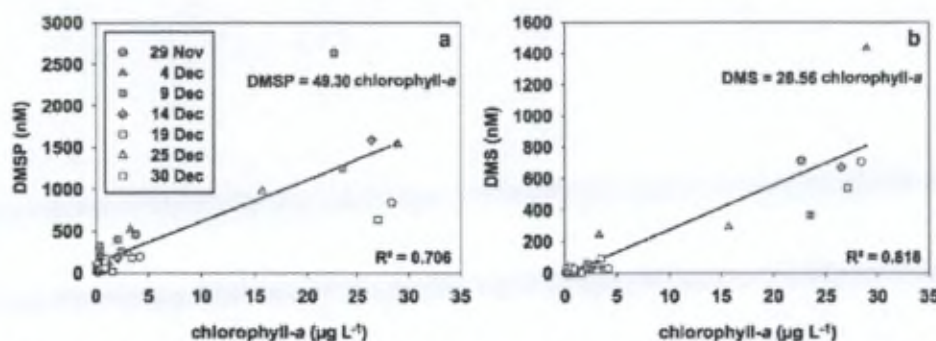


Figure 6. Relationships between chlorophyll *a* and (a) DMSP and (b) DMS at six different depths in the ice.

5.2. DMSP and DMS Dynamics in the Ice

[9] In this section, we discuss both the initial status and the temporal evolution of the DMSP and DMS concentrations within the sea ice cover. Because of the strong contrasts in microbial communities and temporal variability of the thermohaline regime (higher sensitivity in the surface layers as compared to the bottom part), we treat bottom communities and surface and interior communities separately.

5.2.1. Initial Concentration and Temporal Evolution of the DMSP and DMS Profiles in the Bottom Layer

[10] Available chlorophyll *a* (Figure 3a) and autotrophic biomass data (Figure 4) indicate that active primary producers were mainly located in the bottom community. The fairly good linear positive relationship between chlorophyll *a* concentration and DMSP levels (Figure 6a) suggests close links between algal biomass and DMSP concentrations. As previously emphasized by *Levasseur et al.* [1994], it is interesting to note that, although they are known as less efficient DMSP producers compared to *Phaeocystis* sp. or dinoflagellates [*Stefels et al.*, 2007], diatoms are in this case the key drivers of the overall DMSP stock within our sea ice cover at the ISPOL clean site. Note, however, that a different conclusion might have been reached in other areas of the ISPOL floe where flooding of the surface resulted in the development of high biomasses in surface communities of *Phaeocystis* sp. (not shown). There is also a good linear relationship between chlorophyll *a* and DMS. This increase of the DMS content with chlorophyll *a*, especially in the bottom 5 cm where chlorophyll *a* content is above $15 \mu\text{g L}^{-1}$ (Figure 6b), suggests that, as DMSP production is increased, the various processes leading to the cleavage of DMSP into DMS are also increased (see the work of *Stefels et al.* [2007] for a thorough review of all potential processes). As DMS concentration increases in the bottom layer, so does the DMS-to-DMSP ratio (ranging from 27% to 93%, Figure 5a). Such an increase of the DMS-to-DMSP ratio cannot be attributed to a community shift of autotrophic species because the bottom assemblage remained at all times largely dominated by pennate diatoms (Figure 4). However, protozoa biomass showed a drastic change on 30 December, compared to the previous stations. The biomass of heterotrophic dinoflagellates suddenly peaked at over $550 \mu\text{g C L}^{-1}$ in the bottom ice of station 30 December, whereas their

biomass was below $15 \mu\text{g C L}^{-1}$ for station 29 November to 25 December [*Dumont*, 2009]. This heterotrophic dinoflagellate population may have exerted an increased grazing pressure on autotrophic DMSP producers of the bottom ice. Grazing by heterotrophic dinoflagellates already proved to be a determining process in the generation of the dissolved pool of DMS and dissolved DMSP (DMSP_d) [*Archer et al.*, 2001].

5.2.2. Initial Conditions in the Upper Layers

5.2.2.1. Subsurface DMSP Maximum

[11] The existence of an initial secondary maximum (300–400 nM DMSP) at about 30 cm depth could be attributed to the ice formation process. Such a process would have resulted in the accumulation of suspended particulate matter at the ice–water interface, and with it particulate DMSP, due to physicochemical processes and its subsequent entrapment in the ice during freezing. Alternatively, the observed DMSP concentration may have originated from a past active autumnal subsurface community. Control measurements of a DMSP profile performed several months later on a twin core (taken at a maximum distance of a few tens of centimeters) in the home laboratory also revealed the presence of a subsurface DMSP maximum at 30 cm on 29 November (not shown), showing this was a general initial feature of the first-year sea ice at the ISPOL clean site. Measurement of continuous gas composition (O_2 , N_2) at a 5 cm resolution on the same core revealed oxygen supersaturation and increased O_2/N_2 ratio between 20 and 40 cm depth, witnessing past production of photosynthetic O_2 by an interior algal community (not shown). Even though chlorophyll *a* data are not available at the depth where DMSP peaked, the very low chlorophyll *a* levels ($<0.5 \mu\text{g L}^{-1}$) available 15 cm above and 10 cm below the occurrence of the 30 cm DMSP maximum (Figure 3b) suggest that the community was not active anymore at the time of sampling. Progressive disappearance of the 30 cm depth oxygen supersaturation (*F. Brabant*, unpublished data, 2008) at the next stations, as increased permeability and brine instability drainage developed (see previous sections), is also in favor of an algal community that was either previously active or still living in the ice but in a bad physiological state. The observed 30 cm depth DMSP maximum would therefore be, at least partially, the result of past primary production, although passive scavenging or attachment to the ice platelets of the

skeletal layer during ice growth probably contributed to the initial algal entrapment in autumn. Another indication that we are looking at "old" DMSP is the fact that its concentration quickly decreased between 29 November and 4 December as observed for the oxygen supersaturation. Trevena *et al.* [2003] also attributed the occurrence of a high DMSP peak in interior ice to remains of an algal community. The high DMSP-to-chlorophyll *a* ratio these authors observed was explained by assuming that the degradation of chlorophyll *a* had been faster than that of DMSP.

5.2.2.2. Elevated Surface DMSP-to-Chlorophyll *a* Ratios

[12] The ratios of DMSP to chlorophyll *a* observed in this study (mean, 169 nmol μg^{-1} ; range, 13–946 nmol μg^{-1} ; and SD, 187 nmol μg^{-1}) compare well with the values previously observed in thick Antarctic fast ice (mean, 243 nmol μg^{-1} ; range, 1–3200 nmol μg^{-1} ; and SD, 440 nmol μg^{-1}) by Trevena *et al.* [2003]. This is particularly high compared to the mean ratio of 52 ± 37 observed in open waters with Haptophytes [Stefels *et al.*, 2007] among them *Phaeocystis antarctica*, well known for its high DMSP content and its ability to form communities in sea ice. Both environmentally dependent physiological processes within algal cells and community species composition affect the DMSP-to-chlorophyll *a* ratio. It was shown that increasing light intensity [Stefels *et al.*, 2007, and references therein] and increasing salinity [Stefels, 2000] of the medium both induce higher DMSP-to-C ratios (and indirectly DMSP-to-chlorophyll *a* ratios) in *Phaeocystis* cells. The initial profile of 29 November showing a steady increase of the DMSP-to-chlorophyll *a* ratio toward the surface may illustrate the adaptation of autotrophic organisms in the ice in response to a gradient in light intensity and/or brine salinity both increasing toward the surface. Alternatively, this profile could reflect the strong contrast in the autotrophic community between the bottom layer dominated by pennate diatoms (Figure 4e) and the surface layers dominated by *Phaeocystis* sp., with diatoms being known for lower DMSP-to-chlorophyll *a* ratios [Stefels *et al.*, 2007]. We find further arguments to dissociate these factors in section 5.2.3.2, which discusses the time evolution of the profiles.

5.2.3. Temporal Evolution of the Upper Layers

5.2.3.1. Changes in DMSP and DMS Profiles

[13] As stated above, most of the DMSP concentration changes occurred in the upper part of the ice cover during the first half of the period under a regime of active brine drainage. The specific situation of station 9 December, where concentrations increased drastically in the upper 30 cm, was probably linked with localized surface infiltration of nutrient- and microorganism-rich slush that likely temporarily boosted the primary production within the brine network [Tison *et al.*, 2008]. Increased DMSP levels (about 400 nM) were indeed paralleled by increases in algal standing stock ($2 \mu\text{g L}^{-1}$ chlorophyll *a*). DMSP concentration profiles were less subject to changes during the second half of the period, when the brine network became stratified and transport became limited to settling of particles due to gravity and diffusion along concentration gradients for dissolved elements [Tison *et al.*, 2008]. Differences in DMS profiles between the first and second half of the observation period in the upper part of the sea ice cover also coincided with the change in brine regime. A linear DMS gradient, established

between negligible concentration at the surface and a stable 40 nM maximum at about 40 cm depth, replaced the initial bimodal structure of the profile as the brine system switched from downward drainage to stratification (14 December onward). Several mechanisms can explain this sudden decrease of DMS in the upper 40 cm. As indicated by Tison *et al.* [2008], the large increase in relative brine volume between 14 and 30 December may have caused partial loss of brines and gaseous inclusions upon ice core retrieval, even though caution was taken to cool down the cores just after extraction. However, the fact that a gradient was still clearly observed at all stations after 14 December (as opposed to no trend or total loss) does not support a dominant impact of such a sampling bias. Another potential mechanism for the observed DMS gradient is photo-oxidative conversion to DMSO within the surface layers. However, we do not have indications for such a mechanism. Ongoing DMSO measurements show very stable profiles in the upper half of the sea ice cover from 14 December onward, with even a subsequent decrease in the top 30 cm for the last two stations (F. Brabant, unpublished data, 2008). Alternatively, increasing permeability could favor DMS transfer to the atmosphere and therefore establish the observed gradient, provided a source existed in the intermediate layers (see section 5.2.3.3). As discussed by Tison *et al.* [2008], discontinuous superimposed ice was only observed to form during the last two stations and therefore would only have hampered DMS fluxes to the atmosphere at the end of the observation period. Direct CO_2 flux measurements at the ice surface showed that the influx of CO_2 was indeed hampered during the last two sampling dates and could be reestablished by removing the superimposed ice layer (B. Delille, personal communication, 2008). The moderate increase in DMS observed for the last two stations in the lower interior ice (below 60 cm) was probably linked to diffusion processes from the steady bottom maximum upward within the stratified brine medium as the decaying season proceeded and as the DMS production in the bottom community increased.

5.2.3.2. Decrease of the DMSP-to-Chlorophyll *a* Ratio in the Surface Layers

[14] Figure 5c clearly shows a strong decrease of the DMSP-to-chlorophyll *a* ratio in the surface layers during the first half of the observation period. As shown in Figure 7, there is a fairly good relationship between computed brine salinity and DMSP-to-chlorophyll *a* ratio in the upper 12.5 cm for all stations. This simultaneous decrease of DMSP-to-chlorophyll *a* ratio and brine salinity as a consequence of the progressive dilution of the sea ice brine with meltwater during sea ice decay might be interpreted as a physiological adaptation but might also reveal a general community shift with time. In the latter case, species characterized by a lower DMSP-to-chlorophyll *a* ratio (e.g., diatoms at the expense of *Phaeocystis* sp.) would have progressively become dominant in the community. The evolution of the autotrophic biomass with time in the upper layer (Figures 4a and 4b), however, supports the hypothesis that the change of DMSP-to-chlorophyll *a* ratio was rather driven by the brine salinity drop. No drastic change in the contribution of the different species to the autotrophic biomass (almost systematically dominated by *Phaeocystis* sp.) was observed from 29 November to 9 December when most of the change occurred in the ratio of DMSP to chlorophyll *a*.

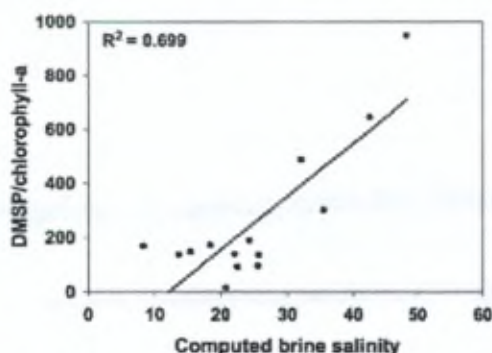


Figure 7. Values of DMSP-to-chlorophyll *a* ratio against computed brine salinity in the upper 12.5 cm of the sea ice cover.

5.2.3.3. DMSP-to-DMS Conversion

[15] To investigate the conversion dynamics of DMSP into DMS in the ice, we consider hereafter the evolution of the DMS-to-DMSP ratio (Figure 5a). A few common features characterize all stations, independent of time. First, the DMSP originally linked to algal cells fixed to the walls of brine channels and brine pockets was released into the brine medium (see section 5.3) throughout the observation period as a result of the progressive rise in temperature and consequential internal ice melting. Second, all stations showed a layer of minimum brine volume located between 55 and 70 cm depth (Figure 2a) potentially acting as a local constriction of the sea ice brine network, slowing down the downward movement of solutes and particulate matter. Indeed, even after the interconnectivity of the brine network has been reestablished above the 5% brine volume threshold, permeability still increases with increasing brine volume [e.g., Golden *et al.*, 2007]. Finally, the DMS-to-DMSP ratio (Figure 5a) indicated that conversion of DMSP to DMS occurred above the area of brine network constriction. The active brine drainage that characterized the first phase of the observation period (stations 29 November and 4 December) induced an effective downward transfer to the level of minimum brine volume of both DMS and DMSP available in the brine network, favoring accumulation of material in the layers above the brine network constriction. The local maximum of the DMSP-to-chlorophyll *a* ratio that developed at about 40 cm depth at stations 14 and 19 December (Figure 5c) may indicate that the local accumulation of degrading algal cells indeed occurred, because such an increase cannot be explained by either an increase in light intensity or an increase in brine salinity. Also, there have been no significant changes in the contribution of different species to the autotrophic assemblage (Figure 4c). The slush infiltration event that occurred at station 9 December [Tison *et al.*, 2008] is likely responsible for the more homogenous DMS/DMSP profile observed. The increased transfer of solutes (along with DMS and DMSP in the brine) through the brine network down to the seawater would have made the DMS/DMSP profile more uniform than the profile of the previous station. Note, however, that this could also be the result of spatial variability since station 9 December was

located closer to border ridges and therefore more prone to slush infiltration. The second phase of the observation period (from station 14 December onward), however, is characterized by a drastic slowdown in fluid movement and solute transport through the ice cover because of the stratification of the sea ice brine network. This stratification implies that DMSP released from the brine channels or brine pocket walls overhead was transferred more slowly downward by sedimentation through the brine network. DMSP therefore accumulated at a lower rate above the depth of minimum porosity than under the influence of brine drainage. The lower rate of DMSP accumulation would have slowed down the production of DMS and delayed the new buildup of the DMS/DMSP maximum. In addition, the intensity of the DMS/DMSP maximum must have been affected by the rate of DMS loss either through brine drainage (first phase) or diffusion (second phase), especially toward the atmosphere as suggested by DMS profiles. Several factors may explain the conversion of DMSP to DMS in this particular zone. Exudation of DMSP by some algal species in the surrounding environment may have occurred in response to the brine dilution caused by the steady internal ice melting. Such a process has already proven to occur with some algal species (*Phaeocystis* sp.) in response to a salinity decrease in the environment [Stefels and Dijkhuizen, 1996]. In situ conversion of DMSP_d to DMS may have occurred under the influence of algal or bacterial DMSP lyase, a salinity decrease being additionally favorable to the enzyme activity [Stefels and Dijkhuizen, 1996]. Heterotrophic dinoflagellates and ciliates were also observed to increase in this layer, although at lower concentrations than in the bottom layer [Dumont, 2009]. They also may have played a role in the production of DMS by grazing on autotrophic DMSP producers like *Phaeocystis* sp. and dinoflagellates [Archer *et al.*, 2001]. Along the same lines, the general increase of the DMS-to-DMSP ratio below 60 cm is very likely attributed to the sudden increase of heterotrophic dinoflagellates, which would be responsible for an increased DMS production by grazing as stated earlier.

5.3. DMSP and DMS Dynamics in the Brine

[16] DMS(P) concentrations from 20 cm depth sackhole brines appeared to be lower than the concentrations measured in bulk ice samples. This finding was unexpected, considering that pure ice crystals are devoid of the two compounds, and brines formed between 9% and 33% of the bulk sea ice volume (Figure 2a). Also DMS(P) concentrations from 60 cm depth sackhole brines, although both relatively and absolutely higher than brines from 20 cm depth, were still lower than expected. One way to visualize that concept is to reconstruct DMSP and DMS concentrations in the brine from observed bulk ice values and relative brine volumes. Results of this exercise are shown in Figures 8a (DMSP) and 8b (DMS). Clearly, both calculated DMSP and DMS concentrations are higher than measured values by a factor of up to 20. As far as DMSP is concerned, this can be explained with a well-known feature that algal cells are mainly fixed to the walls of brine channels and pockets rather than floating freely into the brine medium [Krembs *et al.*, 2002]. Algae biomass percentage attached to brine channel walls evolved from 97% to 57% during the ISPOL experiment (S. Becquevort, personal communication, 2008).

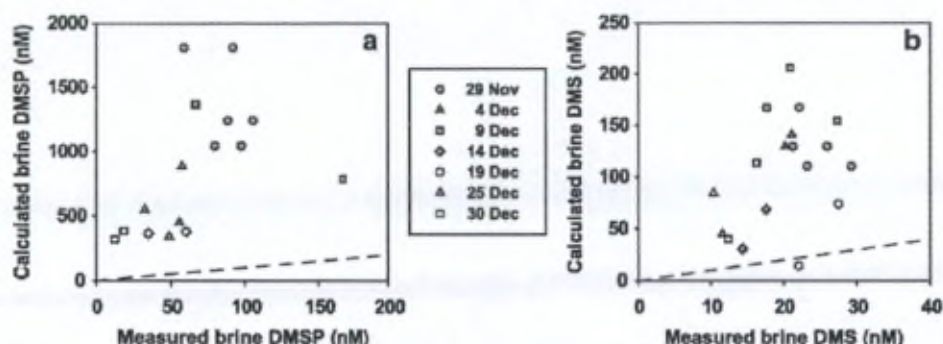


Figure 8. (a) Relationship between measured brine DMSP and calculated brine DMSP and (b) relationship between measured brine DMS and calculated brine DMS. The dashed line represents a one-to-one relationship. Note the difference in vertical and horizontal scales between Figures 8a and 8b.

This can be explained by the increasing release into the brine medium of material fixed to the walls of brine inclusions (including intracellular or particulate DMSP_p) by melting. Such a process is confirmed by our observation that the discrepancy between measured and reconstructed brine DMSP values became globally smaller as the sea ice cover decayed. The fact that DMSP concentrations from 20 cm depth sackholes are generally lower than those at 60 cm and further below the bulk ice values, especially at the first two stations, may be attributed to a lower ice temperature toward the surface. Reduced melting at lower temperatures indeed releases a smaller amount of particulate material into the sackhole, because that material still adheres to the brine inclusions walls.

[17] Differences between observed and reconstructed brine DMS values were less expected, because that compound should essentially exist as a solute in the brine medium. The only plausible explanation, which is in accordance with the observed DMS profiles in the ice of the upper layers during the second half of the observation period, is that the in situ production of DMS was so important that it maintained high levels of concentration at all times well above saturation. These were then potentially responsible for substantial losses during sackhole brine collection, either through bubbles degassing or through enhanced diffusion. DMS concentration in brines in equilibrium with the atmospheric DMS concentration values (from 0.2 to 5 nmol m⁻³), measured by Zemmelenk *et al.* [2008] during the same experiment, were calculated. According to Dacey *et al.* [1984], DMS in seawater at -0.8°C (average temperature of the brine within the top 20 cm of the ice from stations 19 to 30 December) has a Henry's constant of 0.676. Considering an average air temperature of -4.8°C during the study period and the atmospheric DMS concentration values measured by Zemmelenk *et al.* [2008], DMS partial pressure ranged from 4.4×10^{-12} atm to 1.1×10^{-10} atm. The DMS concentration in seawater in equilibrium with the latter partial pressure range from 6.5×10^{-3} nM to 1.6×10^{-1} nM, which is two to four orders of magnitude less than the concentration measured in the brines collected at 20 cm depth (from 11 to 22 nM). As a result, high concentration gradients were established with

the atmosphere leading to substantial losses of DMS, especially for the brine accumulating in the sackholes as compared to those sampled together with the bulk ice. Furthermore, if supersaturation had led to DMS-rich bubble formation in the ice, these would have been detected by the dry extraction technique, while clearly escaping from the collected sackhole brines, strengthening the discrepancy. Again, the latter was likely to be reduced as the warming of the sea ice progressed and as the brine volume increased drastically in the upper layers of the sea ice cover, potentially enhancing exchange of the bulk ice DMS with the atmosphere or with the snow pack above (Figure 8b). A complementary process that would sustain these enhanced exchanges is presented in section 5.4.

5.4. DMSP and DMS Dynamics in the Water

[18] Both DMSP and DMS concentration increased with time in the water underneath the sea ice cover. Concentration levels, however, remained quite low (1%–5%) as compared to the values observed within the bottom ice layers (Figures 3c and 3e). Figure 5b also shows that initially, with the exception of station 29 November, the relative proportion of DMS was higher, possibly reflecting the contribution from brine drainage during the first half of the observation period. Later on, the relative proportion of DMSP in the water increased, probably as a result of the progressive release into the brine medium of DMSP fixed to the brine channel walls. In situ production of DMSP in the water column is indeed less of an option given the very low and constant chlorophyll *a* levels observed during the first half of the observation period (0.03–0.06 $\mu\text{g Chl } a \text{ L}^{-1}$). Contemporaneous observations of DMS and DMSP concentrations in the leads nearby [Zemmelenk *et al.*, 2005] are worth comparing to our data set. Their measurements, performed between 0 and 4 m depth with a decimeter resolution in the upper 30 cm, showed values similar to our water concentrations, below 30 cm depth. However, surface values reached much higher levels of about 45 and 100 nM for DMS and DMSP, respectively. These are intermediate between those that were found in sea ice (40 and 100 nM) and brine (10–30 and 30–167 nM) at the ISPOL clean site. It therefore suggests that a lateral connection was present

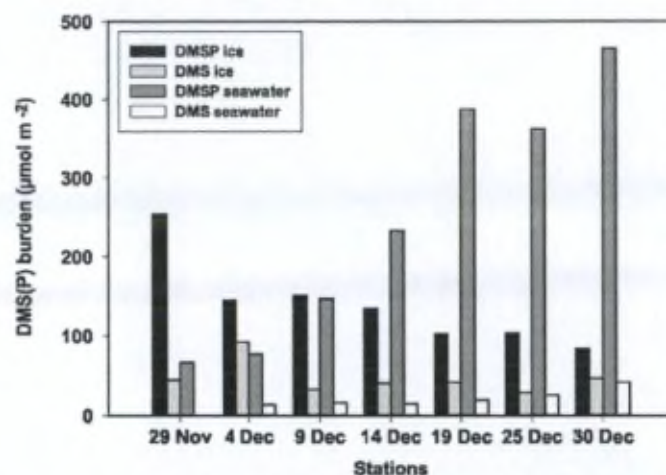


Figure 9. DMSP and DMS burden evolution in the ice and underlying 40 m water column.

between the brine existing within the upper 40 cm honeycomb-like ice layer and the surface waters of the leads. The relatively low salinity of those surface brines (down to 21) favored buoyancy and contribution to the signature of the surface layer of the leads nearby. Together with the patchy biologically enriched flooded surface layers existing in other areas of the ISPOL floe (D. N. Thomas, personal communication, 2006), the honeycomb-like layer that characterizes decaying summer sea ice [Haas *et al.*, 2001; Ackley *et al.*, 2008] was therefore a potentially major contributor to DMS release.

5.5. Impact of Sea Ice on the Regional DMSP and DMS Budget

[19] DMSP and DMS burdens were calculated in the ice and in the water (Figure 9). Clearly, these should only be considered rough estimates. Although the measurements were made on a limited area of the same ice floe, the floe had been drifting for more than 100 km northward during the course of the experiment, thereby partially decoupling the ice cover from underlying sea water at the small scale. However, as far as sea ice is concerned, DMSP burdens decreased regularly throughout the observation period from 254 to 84 $\mu\text{mol m}^{-2}$. After a peak at 92 $\mu\text{mol m}^{-2}$ on 4 December, DMS burdens stabilized around a mean value of 39 $\mu\text{mol m}^{-2}$ for the rest of the observation period. In the under-ice water column, DMSP and DMS burdens were calculated based on the interface, 1 m, and 30 m measurements and integrated over the mixed layer depth of 40 m [Absy *et al.*, 2008]. DMSP burdens increased steadily from 67 $\mu\text{mol m}^{-2}$ to culminate at 465 $\mu\text{mol m}^{-2}$ on 30 December while DMS burdens slowly increased from 0.4 to 42 $\mu\text{mol m}^{-2}$. The progressive fall of DMSP burdens in the ice might be seen as a result of DMSP loss to the seawater through brine drainage and in situ conversion to DMS and biological consumption. The occurrence of an ice DMS burden peak on 4 December corresponded with the sharpest decrease of DMSP burden observed between the first two stations,

which suggests that a part of the DMSP had likely been converted to DMS in the ice. Stabilization of the ice DMS burden from 9 December onward reflects the fact that a balance was reached between the production of DMS and its removal from the ice through degassing and diffusion to the atmosphere, diffusion to the ice-water interface, photochemical oxidation, and bacterial consumption. The increase of water DMSP burden concurrent with the decrease of ice DMSP burden suggests that sea ice was an important source of DMSP for the water column at that moment of the year. The moderate increase of DMS observed in the underlying seawater is likely to be the result of the balance between the release of DMS and DMSP from sea ice, the conversion of DMSP to DMS in the water column, and the biological or photochemical removal of DMS from the water column [Slezak *et al.*, 2001, 2007].

[20] To assess the impact of sea ice on the regional sulfur budget, total DMSP + DMS fluxes in ice and water were calculated as the difference between the DMS + DMSP burdens of two consecutive sampling days, within ice and water, respectively (Table 2). The constantly negative DMS (P) flux from the ice reflects a continuous loss of DMSP and DMS through different processes of degassing and diffusion of DMS to the atmosphere and downward migration of DMSP and DMS with the draining brines at the beginning of the observation period. The evolution of burdens (Figure 9) clearly shows that most of the flux from the ice was due to DMSP loss. The contrast between the strong fluxes observed for the first two stations, where most of the DMSP and DMS loss rapidly occurred (69% of the total observed loss from the ice occurred between stations 29 November and 9 December), and the rest of the observation period corresponded with the change in brine regime. Rapid loss of DMSP and DMS coincided with the sharpest decrease of salinity observed between the first three stations, reflecting mass transport of solutes through the brine inclusions network under the influence of brine drainage

Table 2. Calculated Total Ice and Water (DMS + DMSP) Flux

	Time Step						Average Flux
	29 Nov to 4 Dec	4–9 Dec	9–14 Dec	14–19 Dec	19–25 Dec	25–30 Dec	
Ice DMS(P) flux ^a ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	-12.2	-10.6	-1.7	-6.2	-2.0	-0.4	-5.4
Water DMS(P) flux ^a ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	4.8	14.5	16.9	31.9	-3.3	23.8	14.2

^aA negative value means an outgoing flux.

events [Tison et al., 2008]. This emphasizes the importance of brine drainage in the control of the sea ice DMSP and DMS dynamics during sea ice decay. Integrated fluxes over the whole observation period (average fluxes in Table 2) were of the same order of magnitude as previous regional estimates of $9.4 \mu\text{mol DMS m}^{-2} \text{d}^{-1}$ in the Australian sector of the Southern Ocean [Curran and Jones, 2000] and measurement of $11 \mu\text{mol DMS m}^{-2} \text{d}^{-1}$ over the multiyear ice of the ISPOL floe [Zemmelink et al., 2008]. Our estimates, which include the contribution of both DMS and DMSP as well as the loss to the water column, seem low, however, in comparison to the value reported by Zemmelink et al. [2008], who solely measured ice-air DMS flux. Given the location of the flux tower on the multiyear ice zone of the ISPOL floe characterized by the presence of algal surface communities known to be highly productive [Kattner et al., 2004], it is reasonable to think that the average flux measured by Zemmelink et al. [2008] largely reflected DMS coming from such surface communities. These measured fluxes were also likely widely influenced by DMS emissions from surrounding leads where high DMS levels were observed in the surface microlayer [Zemmelink et al., 2005]. Such contributions of surface communities (not observed at the sampled clean site) and leads were not captured in our estimates. The difference between the calculated average fluxes (DMS + DMSP) from the ice ($5.4 \mu\text{mol DMS(P) m}^{-2} \text{d}^{-1}$) and to the water ($14.2 \mu\text{mol DMS(P) m}^{-2} \text{d}^{-1}$) by a factor of about 3 can have several causes: (1) uncertainty in the reconstruction of water burdens from only three concentration measurements for a 40 m water column; (2) potential decoupling of ice cover from underlying seawater because of ice drift; (3) potential underestimation of DMS and DMSP losses from the ice due to sampling biases, especially in the interface bottom layer; (4) temporal resolution of the flux calculation, implying a potential lack of information on DMS and DMSP production and losses from the ice occurring at rates higher than the 5 day time interval; and (5) the potential in situ algal DMSP production in the water column, which would contribute to the calculated positive flux.

6. Conclusions and Perspectives

[21] For the first time ever, we give a full description and discuss DMS and DMSP high-resolution profiles in sea ice, in a time series perspective. It is shown that the sea ice thermohaline regime plays a major role in controlling the DMS and DMSP dynamics within the sea ice cover, especially in the surface layers and interior of the sea ice cover, owing to the large changes in surface energy balance during spring and summer. This is either directly through the release of DMSP from the brine channel walls and the control of the DMSP and DMS migration within the brine

inclusion network or, indirectly, through promoting a physiological response of ice DMSP producers. In this case of the ISPOL clean site, where no flooding of the surface layers with seawater occurred (positive freeboard throughout), DMSP production was dominated by pennate diatoms within the bottom layers, because their much higher biomass overcompensated their known lesser DMSP synthesis efficiency per unit cell.

[22] We produce first estimates of the impact of decaying sea ice on the regional sulfur budget in the Weddell Sea and show that these are of the same order of magnitude as those previously reported in other studies for DMS in Antarctic open waters. Our fluxes are most probably underestimated, given the potentially huge contribution of surface communities that were not present at our study site. However, these estimates already demonstrate that sea ice acts at that moment of the year as an important and continuous source of DMSP and DMS with respect to the ocean and the atmosphere. This study also stresses the lack of available information on physiological adaptation of the ice community toward changing abiotic conditions during sea ice decay and the role DMS(P) metabolism plays in that adaptation. This is a fundamental prerequisite to adequate modeling of sea ice controls on the flux of climatically significant sulfur compounds to the atmosphere. Future work should therefore be dedicated to metabolic studies performed under real conditions where physiological and physicochemical processes can interact. DMSO concentration measurements would also provide essential information to complete the sulfur budget and shed more light on the sulfur cycle dynamics in sea ice. Finally, ongoing studies on algal and microbial determination and relationships to organic matter will certainly provide further clarification of the control processes of DMS, DMSP, and DMSO production and transformation within the sea ice medium.

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Paper 5 :

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Thermally-forced DMS, DMSP, DMSO and biogeochemical cycling in spring sea ice: a contrasting study

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ABSTRACT

Temporal evolution of dimethylsulphide (DMS), dimethylsulphoniopropionate (DMSP) and dimethylsulphoxide (DMSO) profiles and ancillary physical and biogeochemical variables was assessed in the sea ice cover of two contrasting study sites (Brussels and Liège) throughout Oct.-Nov. 2007 during the Sea Ice Mass Balance in Antarctica (SIMBA) cruise (Bellingshausen Sea, Antarctica). Several atmospheric cycles of cooling and warming succeeded during the observation period and strongly influenced the physical properties of the ice cover. Those conditions both induced an enhanced DMS/P/O production by sympagic organisms, subject to cyclic thermal and osmotic stress as well as the transfer of elevated concentrations of DMS/P towards the ocean. Most of the DMS/P/O production occurred in the surface layers of the ice cover at both sites. At both sites, the maximum value of DMS/P/O burden coincided with the most severe cold spell witnessed during the observation period, suggesting thereby an overall control of the environmental constraints on the ice DMS/P/O production. Along the 20 days study period, lower estimates of DMS flux from both sites to the atmosphere amounted to 3 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for the sole ice DMS burden contribution and to 17 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for the combined contribution of ice and seawater DMS burden contribution. Although releasing substantial amounts of DMS/P to the ocean via brine drainage, the spring sea ice cover of SIMBA was characterized by an overall net production of 140 $\mu\text{mol DMSP m}^{-2}$ and 14 $\mu\text{mol DMS m}^{-2}$ at Brussels and of 104 $\mu\text{mol DMSP m}^{-2}$ and 3 $\mu\text{mol DMS m}^{-2}$ at Liège site. At all times, a minority contributor to the total ice DMS/P/O pool, the overall net production of DMSO was 5 $\mu\text{mol m}^{-2}$ at Brussels and close to 0 $\mu\text{mol m}^{-2}$ at Liège. Sea ice was at that time of the year the only source of reduced sulphur species for the ocean and the atmosphere.

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1. INTRODUCTION

With an areal extent ranging between $3.6 \times 10^6 \text{ km}^2$ in winter and $18.8 \times 10^6 \text{ km}^2$ in summer [Comiso, 2010], Antarctic sea ice is the main contributor to the oceanic component of the cryosphere and might maintain this status in the future in the view of the trend towards a global increase of the sea ice extent in the Southern Ocean [Zhang et al., 2007] compared with the observed accelerating decline of sea ice in the Arctic [Stroeve et al., 2007]. Besides its largely acknowledged abiotic role in climate regulation of the polar regions, through its influence on the surface heat budget of the ocean and control on the global thermohaline circulation [Lubin and Massom, 2006 and references therein], the contribution of sea ice to the Southern Ocean biological pump in regulating notably the atmospheric CO_2 regional budget, recently emerged [Rysgaard et al., 2011]. This unrecognized role to date led part of the scientific community to consider sea ice as an impermeable barrier to gas exchanges between the ocean and the atmosphere [Treguer and Pondaven, 2002]. The composite nature of the sea ice material developing and maintaining a liquid brine microstructure which evolves dynamically along with temperature variations makes from sea ice an interface prone to exchange material with the atmosphere and the ocean through gas or brine fluxes [Loose et al., 2011]. The persistence of a liquid brine microstructure even at low temperatures allows autotrophic organisms like microalgae to survive in the ice where they can develop substantial standing stocks [reviewed by Arrigo et al., 2010]. While living in the ice provides advantages to microalgae like access to sufficient light levels by the maintain at the sea surface [Arrigo et al., 2010] and protection against large grazers due to the geometry of the brine microstructure, it also necessitates that ice algae have developed the capability of responding to salinity, light, temperature, pH, nutrients and gas fluxes stress encountered within the sea ice medium [Mock and Thomas, 2005]. In the view of the important concentrations of dimethylsulphoniopropionate (DMSP) measured in sea ice (typical average concentrations of a few hundreds of nM) compared with the concomitant low levels typically observed in the water column (tenths of nM) [Kirst et al., 1991; Turner et al., 1995; Tison et al., 2010], DMSP could represent a physiological adaptation of sympagic algae to grow in the sea ice environment characterised by high levels of environmental stress (temperature and salinity, notably). DMSP is indeed

acknowledged to fulfil a series of physiological roles and potentially act as cryoprotectant, osmotic regulator, antioxidant or overflow mechanisms for excess energy dissipation, sulphur release and nitrogen maintenance, notably [reviewed by Stefels et al., 2007]. Salinity fluctuations within the sea ice brine and melting of the sea ice [Trevena and Jones, 2006] provide favourable conditions for the release of DMSP in the ambient medium where it can be enzymatically cleaved into dimethylsulphide (DMS) and acrylate by algal or bacterial DMSP-lyases. DMS is a volatile organic sulphur compound which can, once emitted to the atmosphere, affect the radiative budget of the atmosphere directly by backscattering part of the incoming solar radiation and indirectly by acting as condensation nuclei favouring the formation of clouds (cloud condensation nuclei or CCN). Only a minor part (~10%) of the DMS produced in the marine environment will eventually be vented to the atmosphere [Archer et al., 2002] where it can exert influence on the regional climate altering the optical properties of cloud and modifying the precipitation patterns [Krüger and Graßl, 2011]. Major part of the marine DMS pool is subtracted from climatic influence and is consumed by bacteria. A substantial proportion of the marine DMS pool can be bacterially or photochemically oxidised leading to the formation of dimethylsulfoxide (DMSO) [reviewed by Hatton et al., 2005]. Cellular roles as cryo-osmoregulator, free radical scavenger and intracellular electrolyte modifier proposed by Lee and de Mora [1999] for DMSO are similar to those played by DMSP.

As observed for DMSP, sea ice concentrations of DMSO are several orders of magnitude higher than those observed in the water column [Lee et al., 2001]. Although all studies conducted over Antarctic sea ice to date agree in terms of range of DMS/P levels observed [Trevena et al., 2003; Tison et al., 2010], they hardly contribute to give a clear picture of existing seasonal or regional patterns. Particularly winter and time series studies are lacking. To date, the only ice time series study reports the evolution of DMS/P levels in a typical first-year summer sea ice cover in the Weddell Sea, brine and underlying waters controlled by the thermal regime of the ice cover [Tison et al., 2010]. At that period of the year, the sea ice environment provides favourable conditions to the production of DMS from DMSP and generates significant combined flux of DMS and DMSP to the ocean [Tison et al., 2010]. Other time series studies have been dedicated to gas flux measurement. Zemmink et al. [2008] and Nomura

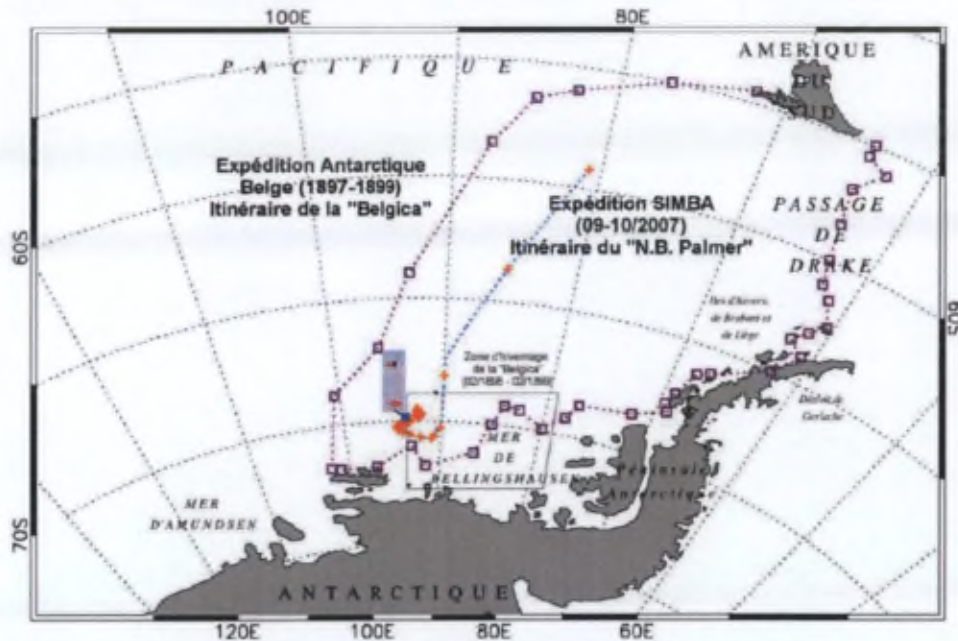


Figure 1 Navigation and drift plot of the RV/IB N.B. Palmer during the SIMBA cruise 2007 (orange crosses) and the expedition of the Belgica in 1897-1899 (purple squares)

et al. [2012] demonstrated that Antarctic sea ice could generate significant fluxes of DMS to the atmosphere, further asserting the biogeochemical importance of sea ice in climate regulation. In this study, the temporal evolution of DMS, DMSP, DMSO and a series of ancillary biogeochemical variables in the sea ice cover at the winter – spring transition in the Bellingshausen Sea is addressed and discussed in the perspective of its connection with the thermal evolution of the sea ice cover. Sensitivity of the ice cover to the atmospheric thermal forcing in relation to its snow and ice thickness is discussed and contribution of the sea ice cover to the regional sulphur budget is estimated with the computation of DMS/P/O fluxes inferred from the DMS/P/O burden change rate.

2. SITE DESCRIPTION

The present study is part of the SIMBA (Sea Ice Mass Balance in Antarctica) experiment which took place onboard the RV/IB N.B. Palmer in the Bellingshausen Sea during September – October 2007 [see Worby et al., 2011 and Lewis et al., 2011 for an overview of the whole experiment and location of the different sampling sites]. On arrival on the drifting

floe named “Ice Station Belgica” (ISB) in tribute to the first overwintering of Adrien de Gerlache and his crew on the ship “Belgica” in the Bellingshausen Sea (austral winter 1898-1899) (see Figure 1), two sites named “Brussels” and “Liège” were chosen to assess the temporal evolution of a suite of physical chemical and biogeochemical properties of the sea ice cover. The two sites were chosen according to three criteria. The chosen sites had to: 1) be internally homogeneous with respect to their surface properties (i.e. level ice, uniform snow thickness) to increase the chances to address a simple case study; 2) display contrasting features between each other in terms of mean snow and ice thickness, ice type (granular vs. columnar ice), freeboard (flooding vs. absence of flooding); 3) be large enough (minimum area of 100 m x 100 m) to allow the delimitation of at least five “clean” independent but adjacent smaller zones (10 m x 10 m) to be sampled at a regular time interval. The two sites were located at a reasonable distance of about 1 km to 2 km away from the ship.

3. MATERIAL AND METHODS

Sampling and samples processing

For every visit to either site, sampling and activities were conducted following a common sampling protocol to coordinate the sampling of snow, sea ice, brines and seawater in trace metal clean conditions and other scientific activities (geophysics, biology, meteorology, radiation balance,...) on the same homogeneous area similarly to what was done for the ISPOL drift experiment [Tison et al., 2008] and ARISE cruise [Lannuzel et al., 2006]. On each site of an area of about 100 m x 60 m, a clean zone was delimited with flags to prevent accidental contamination with respect to trace metals. Brussels and Liège sites were visited alternately every five days. Each time a site was visited a smaller sampling square zone (10 m x 10 m) was delimited. These small zones were kept fairly close to each other to minimise the impact of spatial variability [see Lewis et al., 2011]. Within the clean areas, access was only permitted to people wearing clean suits and plastic bags around the shoes. Ice cores were taken using a 14 cm diameter electropolished stainless-steel corer. Ice cores were immediately wrapped in PE bags and stored horizontally in an insulated box with cold packs frozen at -30°C beforehand. Under-ice seawater was sampled at interface, 1 m and 30 m depth using a Masterflex E/S portable sampler (Cole-Parmer) and transferred into 20 ml glass vials and immediately crimp sealed with a cap with a butyl/PTFE septum after ensuring there was no headspace. Sea ice brines were sampled after accumulation by gravity drainage into sackholes [Thomas et al., 2010] as described for seawater. Vials were stored in the dark at 4°C and rapidly analysed for DMS and DMSP once back on the ship. Sea ice cores were processed in a cold room at -30°C on the ship within the few days after sampling to ensure reliability of the DMS measurements. It has been demonstrated that the long term storage of meteoric ice cores could impact the reliability of the analysis with some compounds like methanesulphonic acid which can diffuse out of stored ice cores [Abram et al., 2008]. Significant DMS losses have been noticed on sea ice samples analysed after several months of storage in comparison with samples analysed on field a few hours after sampling [Stefels et al., 2012]. Sea ice samples dedicated to DMS, DMSP and DMSO measurement were cut from the inside of the ice core with a vertical resolution of 5 cm using a band-saw

Thermohaline properties of the sea ice cover

Ice temperature and bulk salinity profiles were measured on the same dedicated ice core. Ice

temperature was measured immediately after ice core withdrawal using a calibrated digital thermometer (Testo 110) equipped with a fast response temperature probe (precision $\pm 0.2^\circ\text{C}$) inserted in holes drilled at the diameter of the probe perpendicularly to the ice core wall. The ice core was then cut with a vertical resolution of 5 cm and the sections were stored in sealed plastic containers. Bulk ice salinity was determined onboard on melted ice core sections using a calibrated Orion (Thermo Finnigan) conductivity meter (precision ± 0.1 psu). Ice texture was revealed onboard on 2 mm thick sections of ice cores placed on a light table between crossed polarisers. The thick sections were performed on the ice core dedicated to the determination of DMS, DMSP and DMSO.

DMS, DMSP and DMSO analysis

DMS extraction – DMS was extracted from sea ice samples using a new method of dry crushing [Stefels et al., 2012] inspired by a gas extraction method developed for polar ice cores [Raynaud et al., 1982]. In brief, a sea ice sample of about 20 g was placed with two stainless-steel marbles into a stainless-steel vessel specifically designed for the analysis of DMS in sea ice samples. The hermetically closed vessel was then fixed onto a crushing device to be mechanically shaken (several hundred cycles min^{-1}) during 4 cycles of 45 seconds each in order to reduce the sample into fine ice powder and ensure that all gas bubbles and brine inclusions have been released from the ice matrix. After crushing, the vessel was connected to the extraction line and maintained at about -30°C during the purge of the vessel for 15 min by a UHP grade (99.999%) helium stream at a flow rate of 50 ml/min. During this step, DMS is carried out of the vessel by helium to a cryofocusing trap consisting of a PTFE loop immersed in liquid N_2 (-196°C). DMS was then thermally desorbed by plunging the PTFE loop in boiling water and injected into the GC for quantitation. The procedure was repeated twice for each sample to ensure the recovery of all the DMS contained in the sample. The total DMS content of the sample was calculated as the sum of the two successive injections.

This dry crushing extraction method was developed as melting of the sample was anticipated to alter the initial proportion of DMS and DMSP. In testing this dry-extraction technique to assess its validity against DMS and DMSP determination compared with melting, it was observed that the proportion of DMS

relative to DMSP was higher in melted samples than in samples treated following the dry crushing procedure. Although the shape of the DMS+DMSP profiles was similar, the mean DMS:DMSP ratio of the melted samples increased six fold in comparison with the dry crushed samples with a DMS concentration exceeding the DMSP by a factor nine on occasion [Stefels *et al.*, 2012]. As discussed in Brabant *et al.* [2011], DMSP of the melted sample would be released into the medium by sympagic algae by exudation or cell lysis in response to the hypo-osmotic shock undergone when released from hypersaline brine inclusions into the hypotonic sample melt. DMS production would then follow by unintentional enzymatic cleavage of released DMSP by algal or bacterial DMSP-lyase present in the sample. The overall result is an overestimate of the initial DMS content of the sample and a consequent underestimate of the DMSP content of the sample. The effect of crushing on the integrity of algal cells is not known. The dry crushing method is however assumed to be more conservative than the melting procedure regarding the proportion of DMS and DMSP initially present in the sample. Trevena *et al.* [2003] reported that the melting of a sea ice sample, acidified at pH 1 beforehand to preserve DMSP, resulted in the transfer of nearly all DMSP (total DMSP) in the dissolved fraction very likely as a result of cell damage during melting from salinity and pH stress. In addition, Kiene *et al.* [2007] recently reported that the acidification technique was unsuccessful in preserving DMSP in seawater samples in the presence of *Phaeocystis* *sp.* even if a cautious sampling procedure is followed [Kiene and Slezak, 2006]. DMSP-lyases in *Phaeocystis* *sp.* would indeed remain active for minutes after acid addition resulting in loss of cellular DMSP and production of DMS. As *Phaeocystis* *sp.* is an algal species commonly found in Antarctic sea ice algal assemblages, it is not unreasonable to think that such a process happens during the melting of a sea ice sample. Should algal cell break up and cytosol release within the sample happen with the dry crushing method, the unintentional enzymatic cleavage of DMSP within the sample is expected to be limited as the sample is maintained in solid state at low temperature all along the DMS extraction procedure.

For the analysis of DMS in under-ice water samples, between 1 and 10 ml of liquid was subsampled from the 20 ml sampling vial and transferred through the septum into a clean pre-sealed 20 ml vial. The vial was then connected to a simple purge-and-trap

system as described by Stefels [2009]. The sample was then purged for 30 min with UHP grade helium (>99.999%) at a flow rate of 25 ml/min and the DMS was trapped in the PTFE loop immersed into liquid N₂. After 30 minutes, the DMS was thermally desorbed by plunging the PTFE loop in boiling water and injected into the GC for quantitation.

Sample treatment for DMSP and DMSO analysis –

For the determination of DMSP in the under-ice water samples, NaOH was added to the same aliquot after DMS analysis to bring the OH⁻ concentration above 2N in order to induce the hydroxide decomposition of DMSP in DMS and acrylic acid [Dacey and Blough, 1987]. This procedure proved to be 100% efficient [Turner *et al.*, 1990]. Vials were immediately crimp sealed with a butyl/PTFE septum cap and stored at +4°C in the dark for at least 24h until analysis of the DMSP as DMS following the procedure described above. For DMSP and DMSO analysis in sea ice samples, the fine ice powder resulting from the crushing after the DMS quantitation was recovered and divided into 20 ml glass vials that were hermetically crimp sealed with a butyl/PTFE septum cap and stored at -30°C in the dark for further analysis. For DMSP, NaOH was added to vials containing the ice powder. The vials were immediately sealed with a butyl/PTFE septum cap and stored to melt at +4°C in the dark until analysis. Total DMSO (i.e. dissolved and particulate phase) in sea ice samples was measured in Belgium a few months after collection using the enzyme-linked method [Hatton *et al.*, 1994] adapted for the determination of DMSO in sea ice as fully described by Brabant *et al.* [2011]. The overall precision of the method is <5%.

Sulphur quantitation – Dissolved DMS and DMS stemming from the hydroxide decomposition of DMSP were measured on board using an Agilent 6890 gas chromatograph (GC) equipped with a six-port switching valve, a 1 m x 0.75 mm (i.d.) Restek Rt-XLSulfur packed column and a flame photometric detector (FPD) run either with a wavelength (394 nm) sulphur filter or with a wavelength (526 nm) phosphorus filter depending of the amount of DMS expected in the samples. In the sulphur mode, the flame was supplied by a flow rate of 60 ml/min of H₂, 72 ml/min of dry air and 20 ml/min of He (carrier). In the phosphorus mode, the flame was supplied by a flow rate of 150 ml/min of H₂, 110 ml/min of dry air and 25 ml/min of He as (carrier). In either mode, GC oven was operated using a

temperature program (60–180°C) and the detector temperature was set at 230°C. DMS eluted at around 2.2 min and at around 2.3 min in the sulphur and phosphorus mode, respectively. GC was calibrated against dilutions of pure (>99%) DMS (Merck) in ultra pure water. As the FPD response is proportional to the n power of sulphur amount and may vary depending on the analytical set-up (n is generally in the range $1.5 < n < 2.5$ [Farwell and Barinaga, 1986]), a linear regression of $\log(\text{area})$ vs. $\log(\text{number of mole})$ was applied, as recommended by Simó [1998], in the sulphur mode. Since the FPD response is prone to change at high sulphur masses due to an autoquenching phenomenon in the detector flame [Sola et al., 1997], a quadratic regression was applied to capture the data at best in the phosphorus mode. The analytical precision of the method is <10% for the quantitation of DMS and DMSP.

Biological proxies

Chlorophyll *a* – Discrete chlorophyll-*a* measurements were performed on a dedicated ice core taken in the close vicinity of the temperature-salinity and DMS-DMSP-DMSO cores (within a radius of a few tens of centimetres). The first half of the ice core (diameter 0.14 m) was cut onboard the ship with a 0.05 m vertical resolution to correspond with the DMSP-DMS-DMSO sampling depth intervals. The samples were melted as is at 4°C in the dark and then gently filtered onto Whatman glass fiber GF/F filters (0.7 µm). The second half of the ice core was processed with a 0.1 m vertical resolution to correspond with the sampling depth intervals of other biological variables for the purpose of further studies. The samples were melted in a known volume of seawater (1:4 V/V) prefiltered through 0.2 µm polycarbonate filters and then successively filtrated on 10 µm and then on 0.8 µm Nucleopore filters. All filters were stored in cryovials at -80°C until analysis. They were extracted in acetone (90% V/V) in the dark at 4°C for 24 h, and chlorophyll *a* was quantified fluorometrically according to Yentsch and Menzel [1963]. The total chlorophyll *a* content of the samples treated with the sequential filtration method was calculated as the sum of concentrations measured on 10 µm and 0.8 µm filters. Seawater samples taken below the sea ice were successively filtrated on 10 µm and then on 0.8 µm Nucleopore filters before chlorophyll *a* measurement as described above. Samples for microscopic determination of algae were preserved in glutaraldehyde-Lugol solution (1% final concentration).

Algae taxonomic composition – Algae taxonomic composition was studied back in Belgium by inverted light microscopy (100 × magnification and 320× magnification) according to the method described by Utermöhl [1958].

Nutrients – Ice sections were melted in the dark at 4°C and then filtered through 0.4 µm polycarbonate filters. Inorganic nutrients (nitrate, nitrite, ammonium, phosphate and silicate) were determined on filtrates according to the procedure described by Papadimitriou et al. [2007]. To avoid matrix effects, standards used for calibration were prepared in artificial seawater solutions with salinities similar to those of the analysed samples. Results are shown as the difference in concentration with the concentration predicted by the theoretical dilution line (TDL) with the assumption that the composition of seawater sampled to compute the TDL is representative of the composition of seawater during the ice formation.

Radiation data

Photosynthetically available radiation (PAR) and ultraviolet A (UVA) and B (UVB) data were acquired by a GUV-2511 multi-channel radiometer (Biospherical Instruments Inc., San Diego, CAL, USA) during most of the observation period.

PAR – The daily dose of PAR (400–700 nm) was computed as the time integral of instantaneous PAR readings.

UVA and UVB reconstruction – Spectral irradiance at selected wavelengths was used to reconstruct the spectral integral of UVA and UVB. Relationships to convert selected UV wavelengths to UVA and UVB irradiances were derived from measurements from Version 2 data from the GUV series multi-channel radiometer set at Palmer Station in the framework of the NSF UV Monitoring Network operated by Biospherical Instruments Inc. (<http://www.biospherical.com/nsf/Version2/Version2.asp>) during the period April 2006 – July 2007. For the UVA (315–400 nm), a linear regression of the spectral irradiance at 380 nm was used ($R^2=0.997$; $p<0.001$, $n=20667$) while for the UVB (290–315 nm), a multiple linear regression of spectral irradiance at 305 and 313 nm was used ($R^2=1$; $p<0.001$, $n=20612$) [Dr. Germar Bernhard, Biospherical Instruments Inc., personal communication, 2010]. After conversion of instantaneous spectral irradiance readings into UVA and UVB irradiances, time integrals were then

computed to estimate the daily doses of UVA and UVB.

Statistical analysis

Ice thickness evolution – The mean ice thickness evolution along the observation period at the ice core locations was derived from the ice core length dataset. The dataset was analysed using a statistical approach combining one-way analysis of variance (ANOVA) and the orthogonal contrast method. ANOVA (level of significance $\alpha = 0.05$) was first performed on the dataset collected at each site to reveal a possible difference amongst the mean sea ice core lengths at the different sampling events. Should a difference be detected, the method of orthogonal contrasts [Dagnelie, 1998] was then used to assess the temporal response of the mean ice core length.

Relationship between variables – Spearman's rank-order correlation was computed to investigate potential relationship between sulphur compounds and other physical and biogeochemical variables using R [R development core team, 2010].

4. RESULTS

Atmospheric forcing

General atmospheric conditions – The weather at Ice Station Belgica was typical of spring. Several recurring meteorological cycles of variable intensity and length (four to eight days) have been witnessed during Ice Station Belgica. Cold and dry periods with generally clear sky conditions associated with continental air masses from the South alternated with warm and wetter periods associated with oceanic air from the North [Vancoppenolle et al., 2011].

Air temperature – The important air temperature fluctuations observed along the study period are shown on Figure 2 along with the mean ice core temperature for each station. At least three successive cycles of cooling and warming were recorded at the ice mass balance buoy (IMBB) deployed at Brussels site [Lewis et al., 2011] with longest and most intense cooling cycle.

Radiations – The PAR dose increased at a mean rate of $62 \mu\text{E cm}^{-2} \text{d}^{-1}$ ($r^2 = 0.734$, $p < 0.001$, $n = 24$) as the spring season proceeded. The UVA dose increased following a similar trend as PAR and increased at a mean rate of $20 \text{ kJ m}^{-2} \text{d}^{-1}$ ($r^2 = 0.804$, $p < 0.001$, $n =$

24). The evolution of the UVB dose showed more variability along the study period and no significant trend could be detected.

Ice conditions

Snow and ice thickness and freeboard – Brussels and Liège sites displayed contrasting snow, ice thickness and ice texture conditions as summarised in Table 1. The grand mean of the ice thickness at the ice core locations derived from the ice core lengths dataset available was $60.9 \pm 7.8 \text{ cm}$ ($n = 50$) at Brussels and $104.3 \pm 9.4 \text{ cm}$ ($n = 46$) at Liège. ANOVA performed on this dataset revealed a difference amongst the mean sea ice thickness ($p < 0.001$) at both sites. Results of the ANOVA showed that the mean sea ice thickness decreased linearly with time ($p < 0.05$) at Liège whereas no trend was detected at Brussels (Figure 3). The ice freeboard, measured at the ice core locations on each sampling event, was positive at all times at Brussels but turned negative at Liège from station 4 onwards (Table 1).

Ice texture – The ice stratigraphy at Brussels showed little variations between the stations (Figure 4). The average profile consisted of snow-ice (15.2%) located exclusively in the top layers of the ice cover underlain by columnar ice (75.2%) with interlayering of frazil ice (9.6%) [Lewis et al., 2011]. During the ice core processing, large tubes of refrozen brine could be observed originating at the granular/columnar transition and progressing downwards through the columnar ice at some stations (e.g. Brussels 2 on Figure 6). The thicker texture profile at Liège dominated by granular ice was complex and often showed oblique inclusions of columnar or granular ice (Figure 5). The average texture profile consisted of snow ice (26%) mainly located in the top layers but also found in lower layers, frazil ice (57%) and intrusions of columnar ice (17%) [Lewis et al., 2011]. The large brine inclusions observed in Liège ice cores consisted of large merging vacuoles rather than the elongated tubes observed in Brussels ice cores. At both sites, the ice appeared peculiarly degraded in its upper half.

Thermohaline properties of the sea ice cover – At Brussels site, the initial temperature profile revealed a very warm (mean -1.9°C) and almost isothermal (st.dev 0.4°C) ice cover (Figure 7). An overall temperature decrease of the ice cover was observed at Brussels 2 (mean -2.6°C) and a similar temperature profile persisted at Brussels 3. The most dramatic

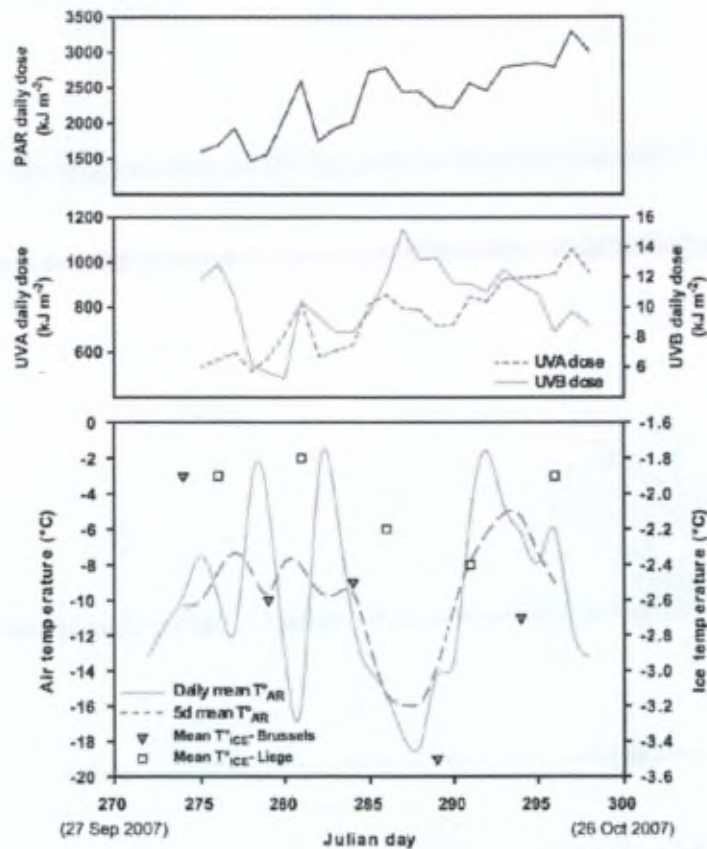


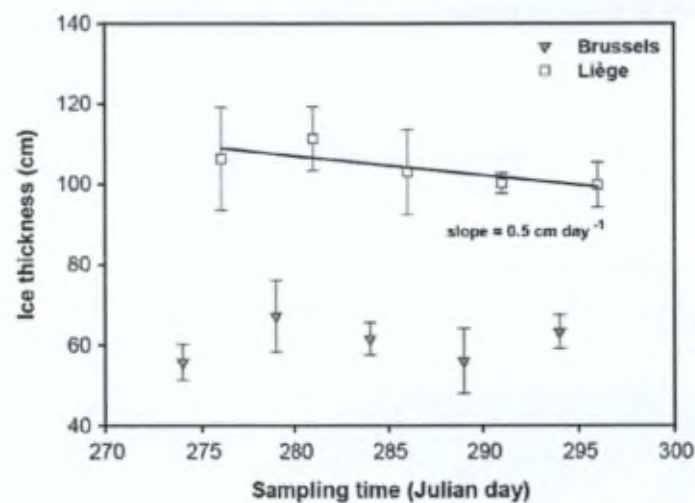
Figure 2 Evolution of the PAR daily dose, UVA and UVB daily doses, air temperature (one- and five-day moving average) recorded on the ship and the mean ice temperature for the five stations visited at Brussels and Liège sites.

shift in temperature was observed at Brussels 4 where the coldest temperature profile of the time series was recorded (mean -3.5°C). An overall warming of the ice cover was finally observed at Brussels 5. The evolution of the mean temperature of the ice cover is shown on Figure 2. As an inverse relationship of the ice temperature, the evolution of the brine salinity logically mirrored the evolution of the ice temperature with the main changes to be observed in the top 40 cm of the ice cover (Figure 9). The brine salinity profile underwent an apparent destabilisation from Brussels 1, where the brine salinity was close to seawater value overall, to Brussels 4 where the highest values of the time series (101 psu) were observed. The brine salinity profile partially stabilised again at Brussels 5 and showed a profile similar to Brussels 2. The bulk salinity profiles looked like incomplete C-shaped profiles missing the salinity increase at the bottom. As observed for the

temperature, the main changes occurred in the top layers. Brussels 4 showed a zone of particularly low salinity in the top 25 cm. To assess the evolution of the permeability of the ice cover, the profiles of relative brine volume were computed assuming thermodynamic equilibrium of the brine with surrounding ice [Cox and Weeks, 1983; Lepparanta and Manninen 1988; Petrich et al., 2010] and an air volume fraction of 1% (Figure 10). The relative brine volume initially showed high values throughout the profile at Brussels 1 but decreased overall at Brussels 2 and 3 but remained above 5%, the critical brine volume fraction above which the interconnection between brine inclusions become sufficient so that columnar sea ice exhibits a sharp transition in its fluid transport properties [Golden et al., 1998; 2007]. The lowest values were observed at Brussels 4 especially in the upper half of the profile displaying values below 5%. Finally, Brussels 5 returned to relative

Table 1 Summary of the main properties of the sea ice cover at the ice core locations of Brussels and Liège sites.

	Brussels	Liège
Station	1 ; 2 ; 3 ; 4 ; 5	1 ; 2 ; 3 ; 4 ; 5
Date (Julian day)	274 ; 279 ; 284 ; 289 ; 294	276 ; 281 ; 286 ; 291 ; 296
Mean snow thickness (cm)	10 ; 11 ; 25 ; 8 ; 15	28 ; 35 ; 37 ; 37 ; 38
Mean freeboard (cm)	+3 ; +1 ; +0.7 ; +1.5 ; +1.5	+2.5 ; +1 ; 0 ; -1 ; -0.1
Mean ice thickness (cm)	55.7±4.5 ; 67.2±8.9 ; 61.5±4.0 ; 56±8.1 ; 63.2±4.2	106.3±12.9 ; 111.3±8.0 ; 102.9±10.6 ; 100.2±2.5 ; 99.8±5.6
Ice texture	Typical first-year sea ice mainly columnar with ~15cm of granular ice on top. Thin inclusions of granular ice in the profile. Level ice.	Mainly granular with a very disturbed profile and large variation in grain size. Rafted ice.

**Figure 3** Evolution of the mean ice thickness ($\pm 1\sigma$) for the Brussels and Liège time series. The black line shows the temporal trend observed at Liège site (see text for details).

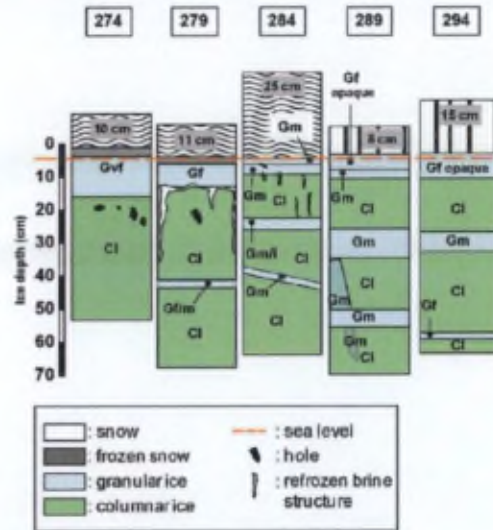


Figure 4 Drawing of the texture profile of the time-series at Brussels site revealed by 2mm thin sections under polarised light. The mean snow thickness is also shown. G: granular ice; C: columnar ice; vf: very fine; f: fine; m: medium; c: coarse; l: large; s: small.

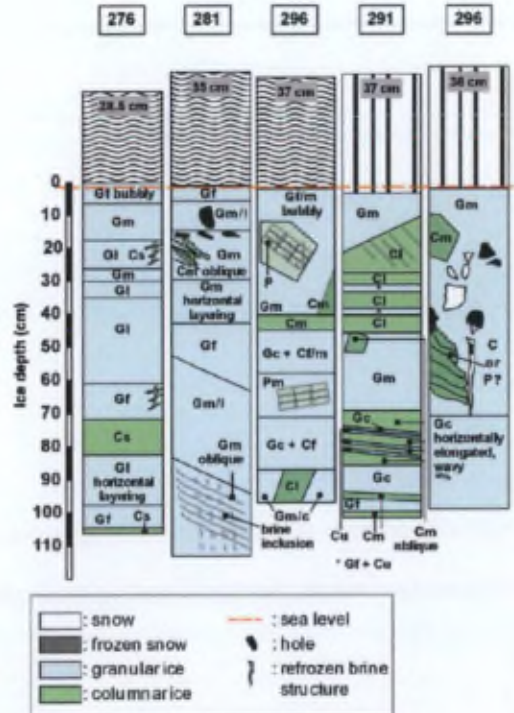


Figure 5 Drawing of the texture profile of the time-series at Liège site revealed by 2mm thin sections under polarised light. The mean snow thickness is also shown. G: granular ice; C: columnar ice; P: platy crystals, vf: very fine; f: fine; m: medium; c: coarse; l: large; s: small, u: undetermined.

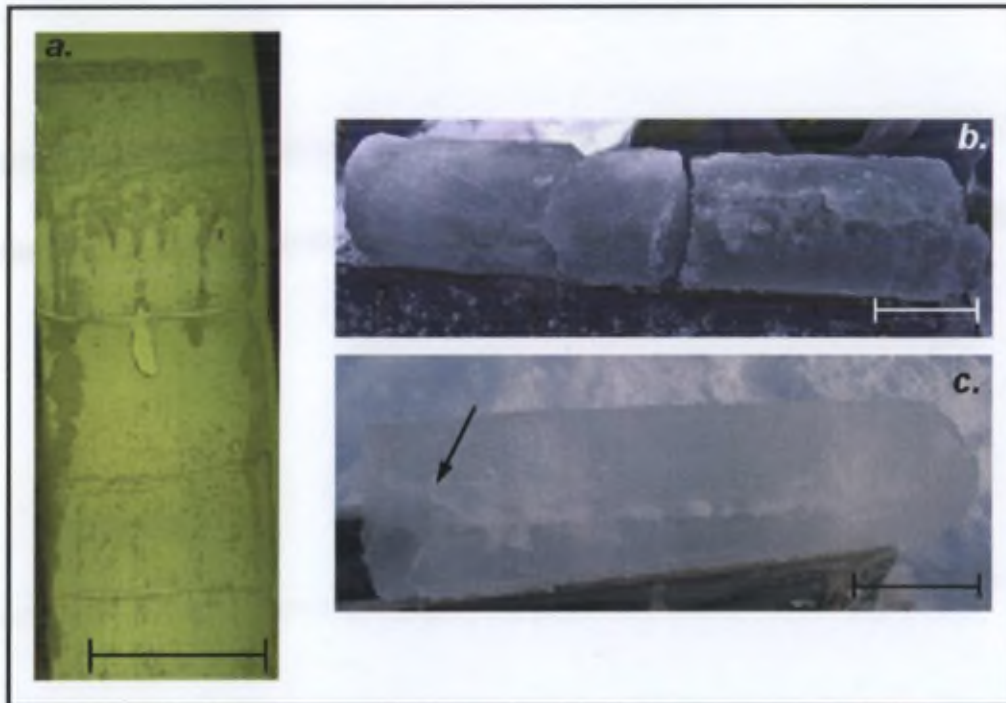


Figure 6 a) Large refrozen brine tubes visible as opaque structures in transmitted light in thin sections made in the top 40 cm of an ice core at Brussels station 2. b) Degradation state of the ice on a freshly taken ice core section at Liège station 4. c) A large brine tube connected to an inverted funnel-shaped cavity at the bottom of a freshly taken ice core at Brussels station 3. The arrow indicates the inverted funnel-shaped cavity. On all pictures, scale represents a length of 10 cm.

brine volume close to the values observed at Brussels 2 and 3. At Liège, the variations in the ice temperature (Figure 7) and brine salinity (Figure 9) observed between the different sampling events were smaller than those observed at Brussels site under similar changes of the atmospheric conditions. Temperature fluctuations of the ice at Liège site are clearly muted with respect to Brussels as attested by the mean ice cover temperatures plotted on Figure 2. The ice cover showed similar warm and isothermal temperature profile for Liège 1 (mean -1.9°C ; st.dev. 0.2°C) and Liège 2 with brine salinities close to seawater values. An apparent cooling of the profile initiated at Liège 3 and carried on to Liège 4 sampling event where the coldest temperature and highest brine salinity values of the time series were observed as for Brussels site. The evolution of the mean temperature of the ice cover is also shown superimposed to the air temperature graph on Figure 2. The initial ice temperature and brine salinity profiles observed at Liège 1 were recovered at Liège

5. Substantial changes were strictly limited to the top 40 cm of the ice cover. The bulk ice salinity profiles at Liège kept their incomplete C-shaped profile throughout the study period and showed little variations between the different sampling events. The mean bulk ice salinity was systematically lower at Liège than at Brussels site. The relative brine volume at Liège was at all times above 5%. The main drop was observed between Liège 2 and Liège 3. The minimum values were computed at Liège 4 as for Brussels. Finally, Liège 5 exhibited relative brine volume values similar to Liège 1.

Rayleigh number – In this context of important temporal variations of the temperature and salinity of the sea ice cover, susceptibility to gravity drainage was investigated by computation of a mush Rayleigh number (Ra) [Worster, 1992, 2000; Wettlaufer et al., 1997]. Profiles of local Ra were computed as described in the work of Notz and Worster [2008] for each station using the ice bulk salinity and ice temperature data interpolated at the mean depth of the

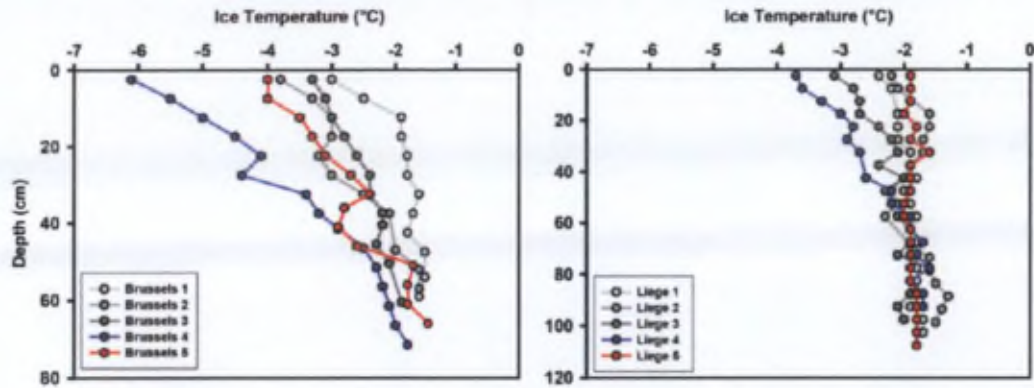


Figure 7 Ice temperature profiles measured at Brussels (left) and Liège (right) sites. Note the difference in vertical scale.

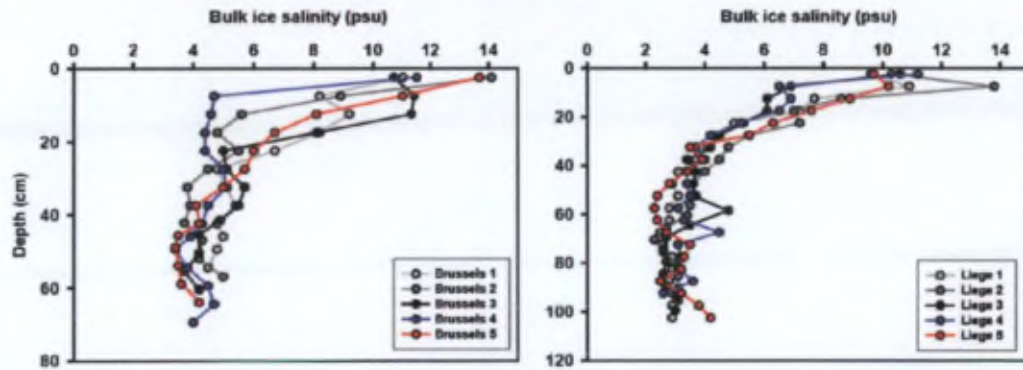


Figure 8 Bulk ice salinity profiles measured at Brussels (left) and Liège (right) sites. Note the difference in vertical scale.

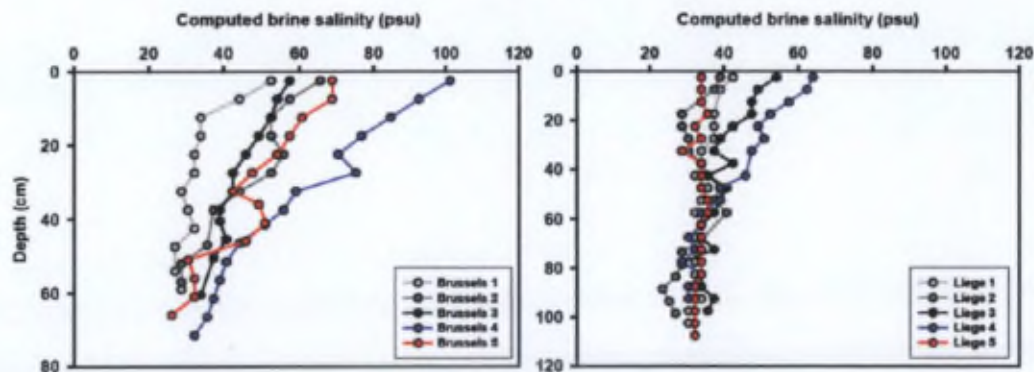


Figure 9 Profiles of brine salinity computed at Brussels (left) and Liège sites. Note the difference in vertical scale.

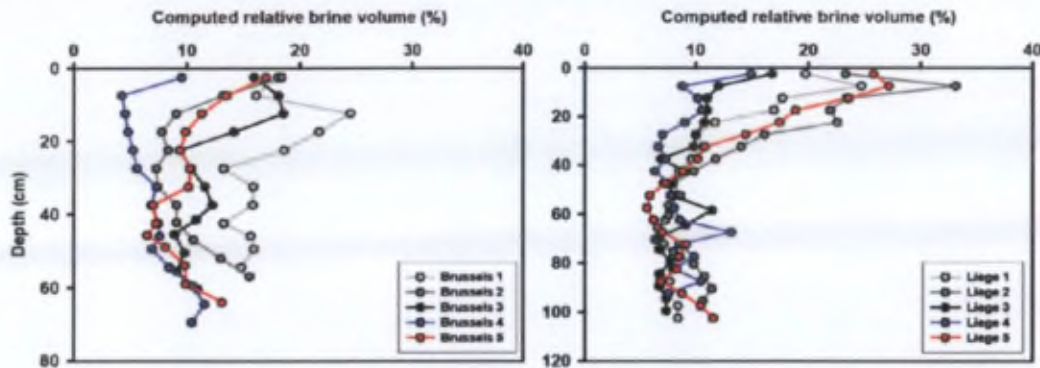


Figure 10 Profiles of relative brine volume computed at Brussels (left) and Liège (right) sites. Note the difference in vertical scale.

salinity samples (Figure 11). Highest values were to be found in the uppermost 20 cm at both sites. At Brussels site, R_a was high close to the surface at Brussels 1 (up to 24) and Brussels 3 (above 6) and was low for the last two stations. The lowest values in the top 20 cm were observed at Brussels 4. At Liège site, R_a displayed low values (0–4) at all times. Even in the layers close to the surface, R_a remained low and did not vary much with time (from 1 to 4).

Algal biomass and composition – Chlorophyll *a* data obtained with the direct melting/ single filtration procedure at a vertical resolution of 0.05 m and the buffered melting/ sequential filtration procedure at a vertical resolution of 0.1 m are shown together on Figure 12. At Brussels, the vertical distribution of chlorophyll *a* revealed by the direct melting/ single filtration procedure (range 0.51–21.5 $\mu\text{g L}^{-1}$, mean 4.02 $\mu\text{g L}^{-1}$, stdev 4.25 $\mu\text{g L}^{-1}$, $n=66$) was comparable to that revealed by the buffered melting/ sequential filtration procedure (range 1.35–16.0 $\mu\text{g L}^{-1}$, mean 5.94 $\mu\text{g L}^{-1}$, stdev 4.10 $\mu\text{g L}^{-1}$, $n=32$). Chlorophyll *a* was distributed vertically following a C-shaped profile that could be observed at all stations with highest values generally to be found at the bottom of the ice cover. The greatest local difference was to be found at the bottom of Brussels 4. At Liège, the vertical profiles of chlorophyll *a* produced by direct melting/ single filtration procedure (range 0.64–15.9 $\mu\text{g L}^{-1}$, mean 4.37 $\mu\text{g L}^{-1}$, stdev 3.45 $\mu\text{g L}^{-1}$, $n=104$) and the buffered melting/ sequential filtration procedure (range 1.11–25.7 $\mu\text{g L}^{-1}$, mean 6.59 $\mu\text{g L}^{-1}$, stdev 4.91 $\mu\text{g L}^{-1}$, $n=53$) were also in good agreement with each other. Both profiles showed an initial vertical distribution of chlorophyll *a* characterised by three chlorophyll *a* peaks located at the surface and around 0.3 m and 0.6 m depth. The

layers below 0.6 m exhibited generally the lowest chlorophyll *a* content of the profile with no prevalence of a bottom community as observed at Brussels site. The three peaks structure was still observed at Liège 2 and Liège 3 although the peak values were less important than for Liège 1. Liège 5 exhibited a general increase of chlorophyll *a* in the top 0.8 m of the ice cover.

To facilitate the comparison of the data obtained by either procedure, chlorophyll *a* concentrations measured with an initial vertical resolution of 0.05 were recomputed and shown with a resolution of 0.1 m along with the chlorophyll *a* concentrations measured with an initial vertical resolution of 0.1 m on Figure 13. A salient feature of the comparison is that the buffered melting/ sequential filtration method produced higher chlorophyll *a* values on up to 81% of the samples (mean difference: $2.63 \pm 2.77 \mu\text{g L}^{-1}$) taking into account a precision of 15% generally associated to the method [Yentsch and Menzel, 1963]. Analysis of the data according to the Bland-Altman plot procedure [Bland and Altman, 1986; 1999], following the recommendations of Dewitte et al. [2002] to construct the *y* axis with respect to the concentration range, did not reveal any trend between the observed difference and the average concentration of chlorophyll *a*. Chlorophyll *a* concentrations measured in the water column at three levels under the sea ice cover (interface, 1m, 30m) were low throughout the observation period as well at Brussels site (range 0.01–0.19 $\mu\text{g l}^{-1}$, mean 0.07 $\mu\text{g l}^{-1}$) as at Liège site (range 0.02–0.16 $\mu\text{g l}^{-1}$, mean 0.08 $\mu\text{g l}^{-1}$). The composition of the autotrophic biomass is available at a few depths, mainly in the top 20 cm of the ice cover where the main changes in physical and biogeochemical variables were observed.

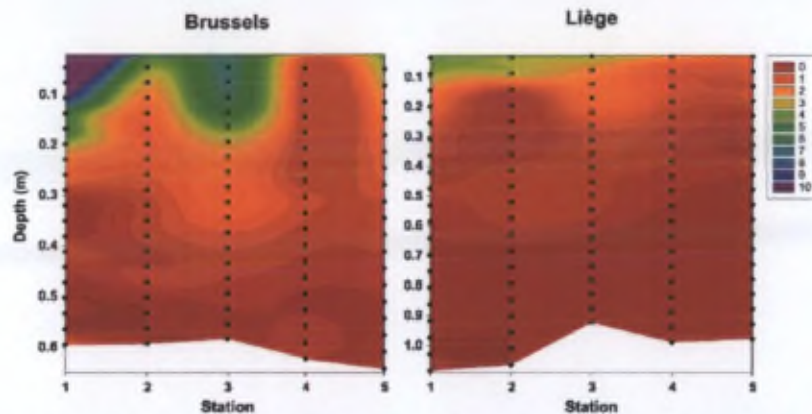


Figure 11 Comparative vertical profiles of the mush Rayleigh number (Ra) computed at the five stations of Brussels and Liège sites.

At Brussels site, all the investigated depths were generally clearly dominated by dinoflagellates and naked flagellates (Figure 14). At the surface of Brussels 2 and Brussels 5, the autotrophic biomass was dominated by flagellates, with dinoflagellates and naked flagellates accounting for more than 75% of the total autotrophic biomass. The remainder comprised small and large diatoms species. Surface sample of Brussels 4 was however dominated by diatoms (with *Nitzschia longissima* and *Plagiotropus* sp. identified amongst the small and the large diatoms, respectively). The autotrophic biomass of the 10–20 cm depth layer at Brussels 3, 4 and 5 was lower than in the top 10 cm and was largely dominated by dinoflagellates and naked flagellates. The autotrophic biomass in the bottommost 10 cm of the ice cover at Brussels 3 exhibited an important biomass ($687 \mu\text{g C l}^{-1}$) and was also largely dominated by dinoflagellates (81.5%) and flagellates, diatoms accounting for less than 2% of the total autotrophic biomass. A significant amount of empty frustules of dead diatom was also observed in that sample.

At Liège site, the autotrophic community of the layer 10–20 cm depth of Liège 1, 3, 4 and 5 was largely dominated by flagellates with an equal contribution of dinoflagellates and naked flagellates accounting for more than 44% at Liège 3, 4 and 5 (Figure 15). A significant amount of *Phaeocystis* sp. was observed amongst the naked flagellates. The proportion of dinoflagellates was higher at Liège 1 (70% of the total autotrophic biomass). As observed for the top layers, the autotrophic community located at about 50–60 cm depth at Liège 1, 3 and 5 was to a great

extent dominated by flagellates with dinoflagellates up to 77% of the total autotrophic biomass at Liège 1. A sample taken in the bottommost 10 cm of the ice cover Liège revealed a composition similar to the layer sampled above but with a lower total autotrophic biomass ($290 \mu\text{g C l}^{-1}$). Similarly to Brussels, a significant amount of empty frustules of dead diatom was observed in the bottom sample as well as in the samples taken at about 50–60 cm depth at Liège 1, 3 and 5.

Nutrient status of the ice cover – The concentration of phosphate, silicate, ammonium, nitrite and nitrate measured for each station at Brussels and Liège sites are summarised in Table 2 and Table 3, respectively. In order to visualise the nutrient status of the ice cover, data are plotted as vertical profiles of the difference between the measured concentration of a nutrient and its concentration predicted by the TDL.

At station 1 of Brussels site, all the nutrients with the exception of nitrate showed a clear enrichment in a zone centred around 20 cm depth (Figure 16 and Figure 17). From station 2 to 4, phosphate showed a C-shaped profile with a bottom value systematically enriched with respect to the TDL. At station 5, the depletion was maximal at the surface and then steadily decreased toward the bottom of the ice cover. Silicate showed the largest variations of all nutrients in the ice with a maximum mean enrichment of $28 \mu\text{mol L}^{-1}$ at station 1 and a maximum mean depletion of $9.4 \mu\text{mol L}^{-1}$ at station 2. Silicate is also the nutrient which showed the most variable concentration in the seawater samples taken under the ice cover of Brussels site as attested by the wide shaded area on Figure 16.

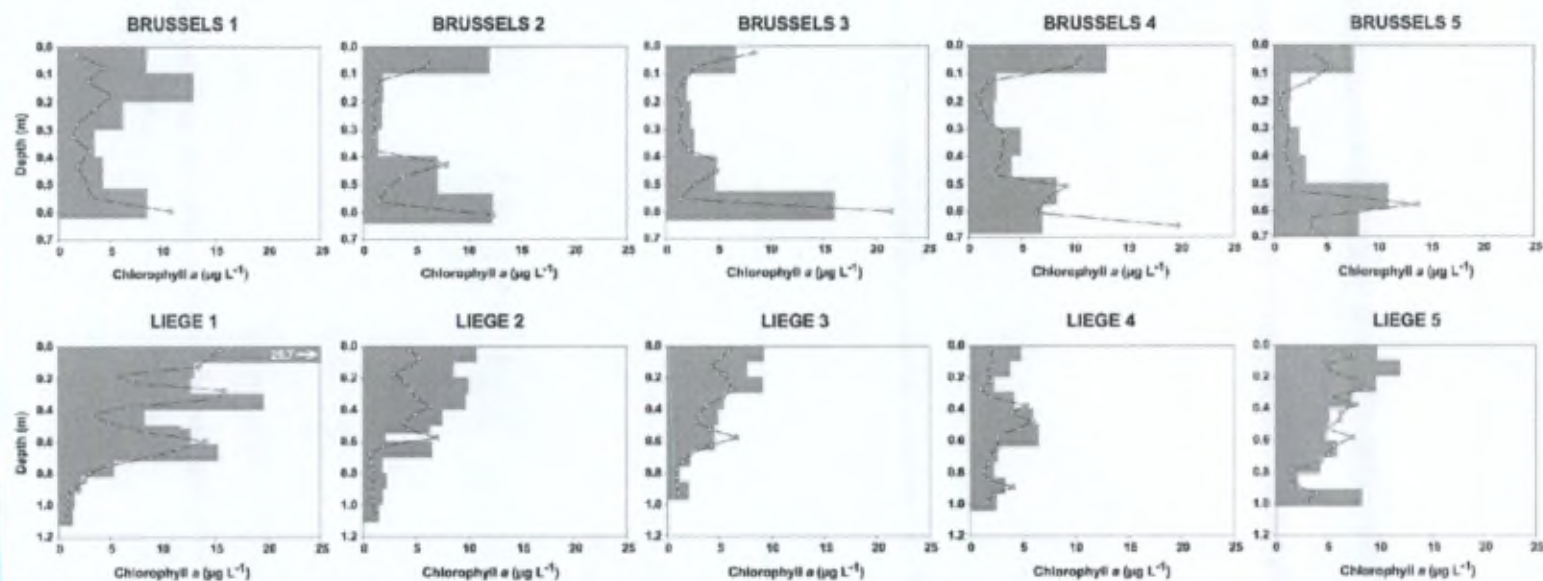


Figure 12 Comparative vertical profiles of chlorophyll a at Brussels and Liège sites. The horizontal bar charts show the chlorophyll a concentrations measured after buffered melting and sequential filtration (initial vertical resolution 0.1m). The white circles show the chlorophyll a concentrations measured after direct melting and single filtration (initial vertical resolution 0.05m). See text for details. Note the difference in vertical scale between the upper and lower graphs.

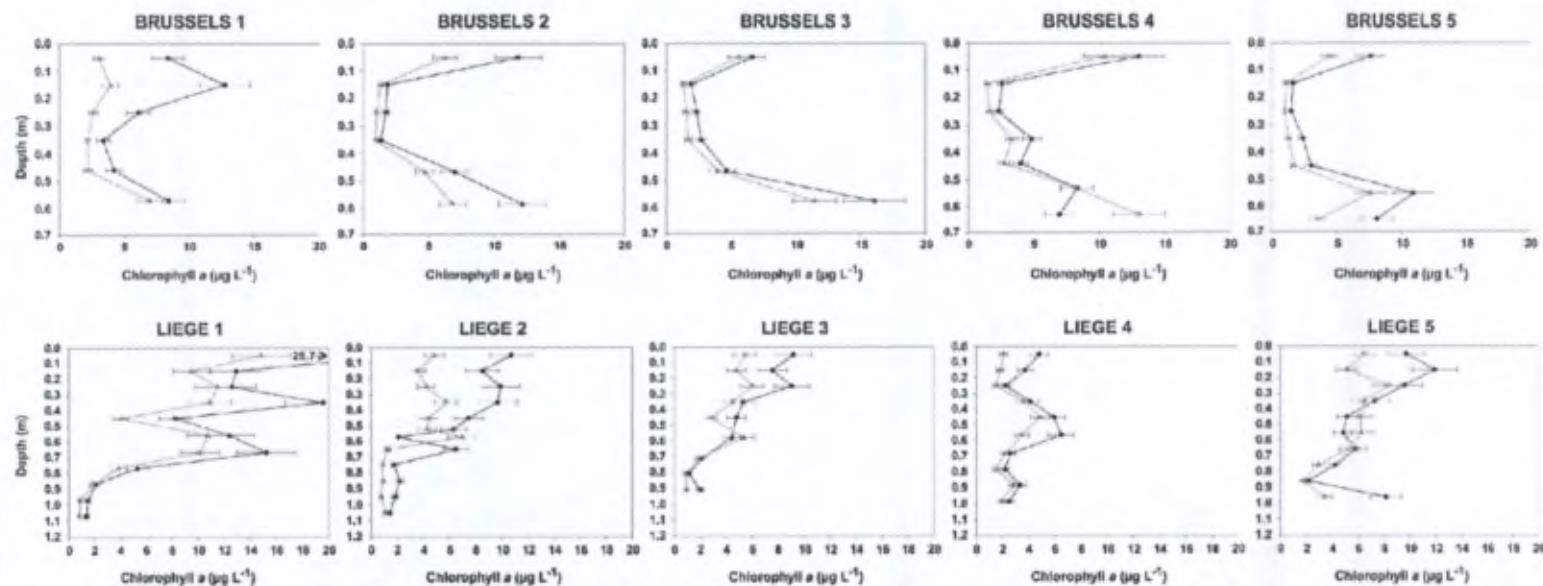


Figure 13 Comparative vertical profiles of chlorophyll *a* measured after direct melting and single filtration (gray triangles) or buffered melting and sequential filtration (black circles) shown along with the error of 15% on the method (horizontal error bars). Data from the direct melting method have been scaled down to a resolution of 0.01 m for comparison purpose. Note the difference in vertical scale between the upper and lower graphs.

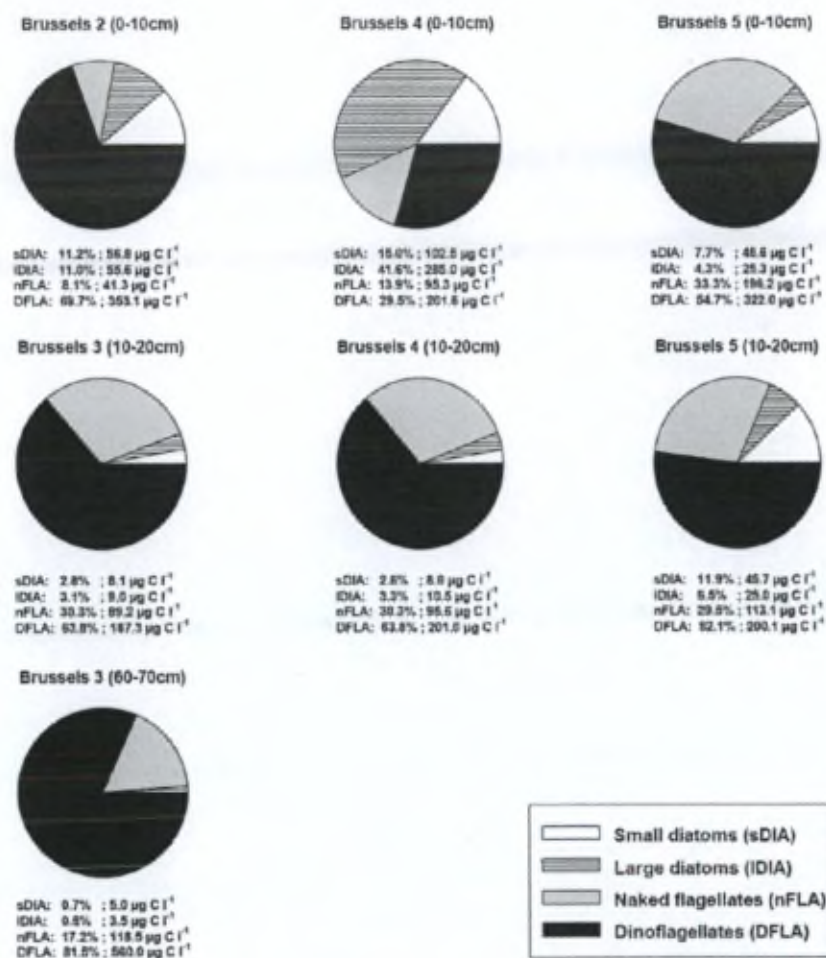


Figure 14 Autotrophic biomass composition in the ice cover of Brussels site at selected depths.

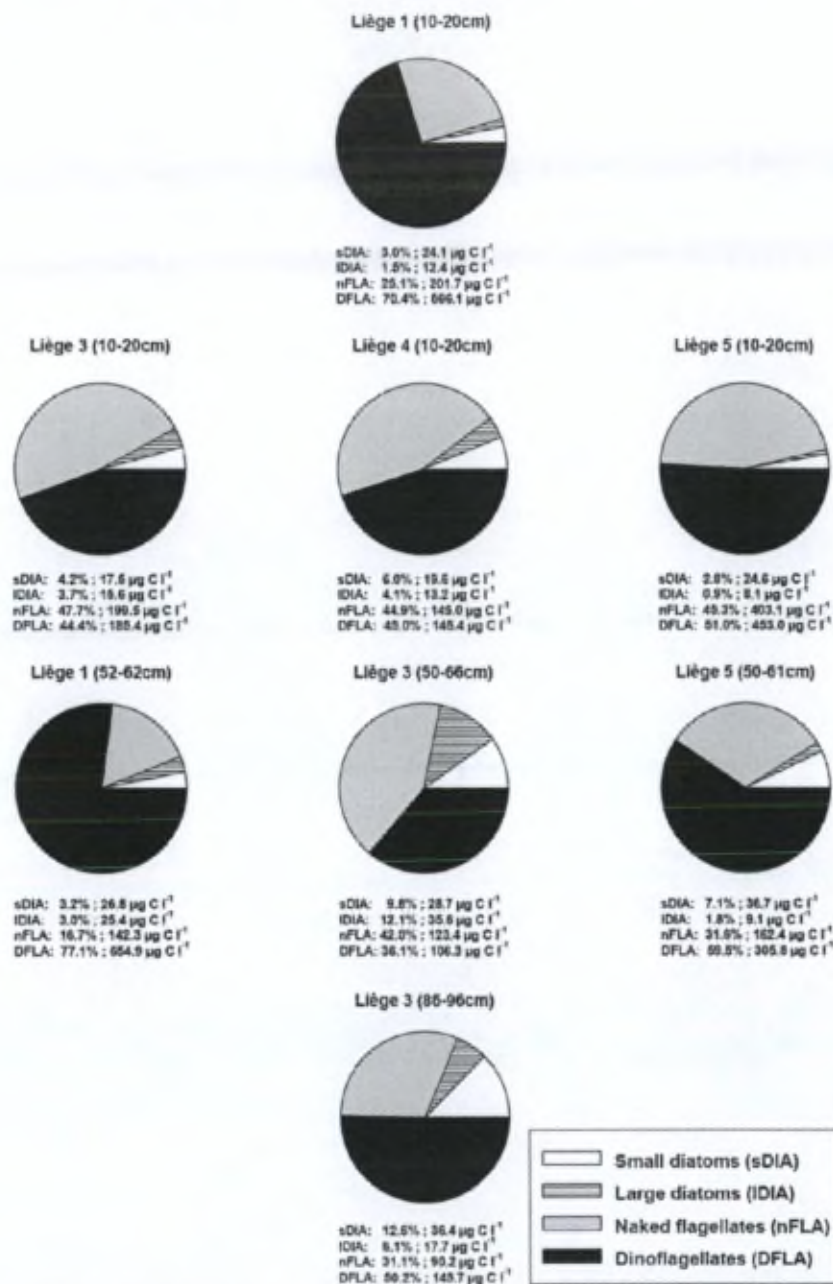


Figure 15 Autotrophic biomass composition in the ice cover of Liège site at selected depths.

Silicate showed the same behaviour from station 2 to 5. Silicate concentrations were close to the TDL in the top 30 cm and then decreased steadily with depth to reach a maximum of depletion between 40 and 60 cm and remained depleted to the bottom. From station 2 to 5, ammonium was enriched overall and showed the maximum values at the top or around 40-50 cm depth. Nitrite was systematically enriched with

respect to the TDL and showed a flat profile from station 2 to 5. Nitrate was at all times depleted with respect to the TDL. The most important variations occurred in the top 20 cm which also showed the maximum of depletion. Below 20 cm depth, the depletion remained fairly constant and stabilised around $-3 \mu\text{mol L}^{-1}$. At Liège site, stations 1 and 5 generally exhibited a distinct profile with respect to

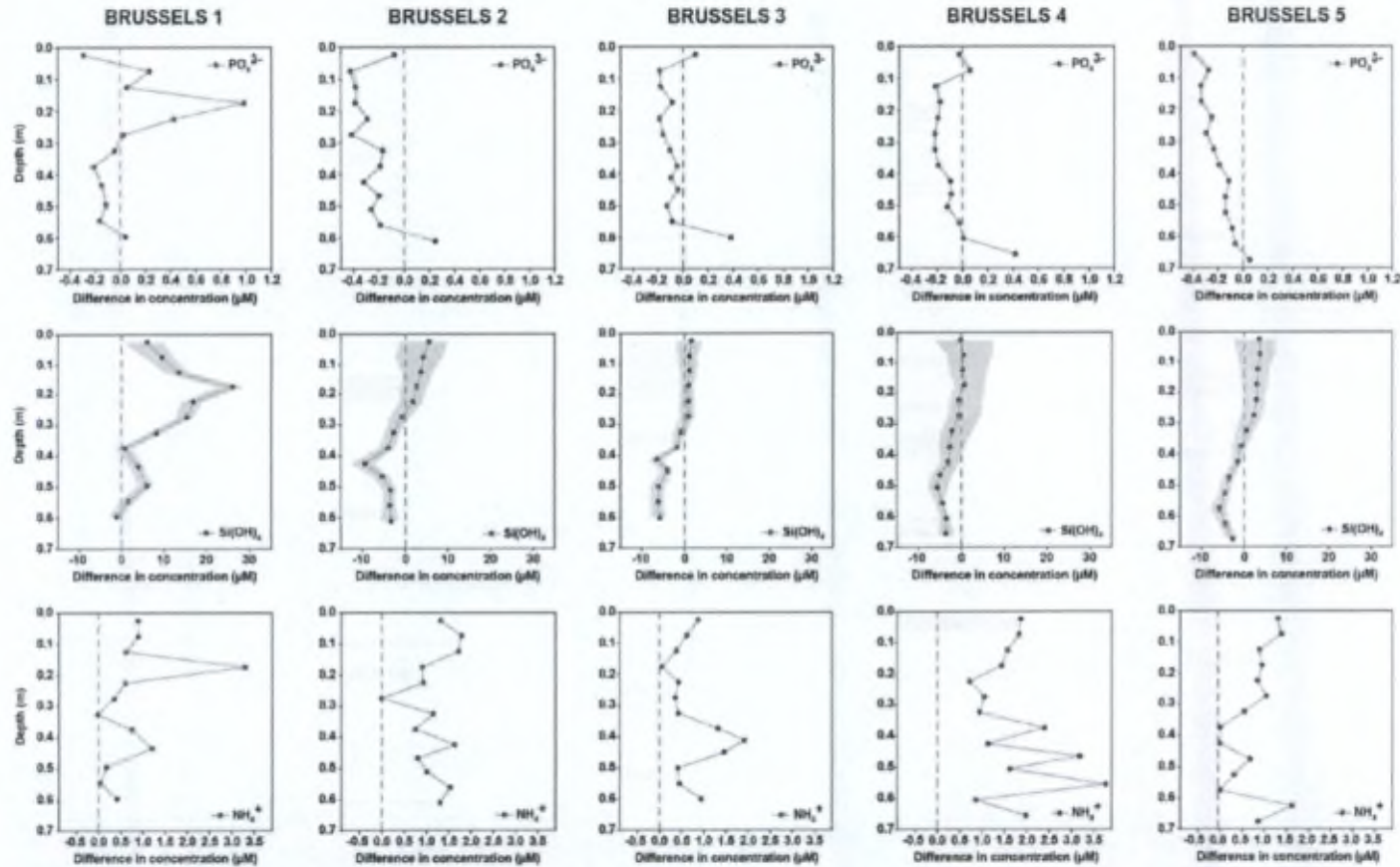


Figure 16 Vertical profiles of difference in concentration from the theoretical dilution line of PO_4^{3-} , Si(OH)_4 and NH_4^+ at Brussels site. The solid line with symbols shows the difference in concentration between the measured concentration and the concentration predicted by the mean TDL. The shaded area represents the variation range of the difference considering the minimum and maximum slopes for the computation of the TDL. Note the difference in horizontal scale.

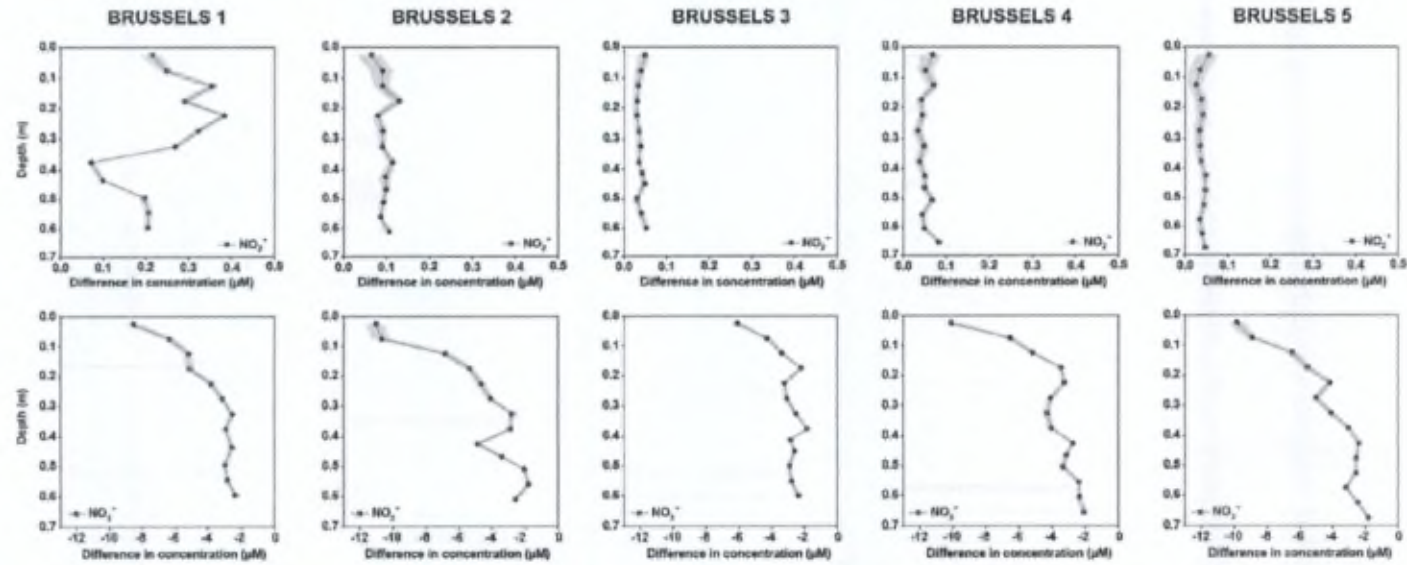


Figure 17 Vertical profiles of difference in concentration from the theoretical dilution line of NO_2^- and NO_3^- at Brussels site. The solid line with symbols shows the difference in concentration between the measured concentration and the concentration predicted by the mean TDL. The shaded area represents the variation range of the difference considering the minimum and maximum slopes for the computation of the TDL. Note the difference in horizontal scale.

Table 2 Bulk ice concentrations of nutrients in the ice cover at Brussels site. Mean $\pm$ standard deviation (range).

Station	Phosphate ($\mu\text{mol L}^{-1}$)	Ammonium ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Nitrate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
Brussels 1	0.4 $\pm$ 0.4 (0.1 - 1.4)	0.8 $\pm$ 0.9 (0.0 - 3.3)	0.2 $\pm$ 0.1 (0.1 - 0.4)	1.0 $\pm$ 0.2 (0.8 - 1.5)	18.8 $\pm$ 10.0 (5.2 - 39.1)
Brussels 2	0.2 $\pm$ 0.2 (0.0 - 0.7)	1.2 $\pm$ 0.4 (0.8 - 1.8)	0.1 $\pm$ 0.0 (0.1 - 0.1)	0.9 $\pm$ 0.3 (0.5 - 1.9)	10.3 $\pm$ 9.3 (2.0 - 28.4)
Brussels 3	0.2 $\pm$ 0.2 (0.0 - 0.6)	0.7 $\pm$ 0.5 (0.1 - 1.9)	0.0 $\pm$ 0.0 (0.0 - 0.1)	0.5 $\pm$ 0.3 (0.2 - 1.3)	5.8 $\pm$ 4.4 (0.1 - 14.2)
Brussels 4	0.2 $\pm$ 0.2 (0.1 - 0.7)	1.7 $\pm$ 0.9 (0.7 - 3.8)	0.1 $\pm$ 0.0 (0.0 - 0.1)	0.4 $\pm$ 0.2 (0.2 - 1.0)	6.7 $\pm$ 5.4 (1.5 - 20.1)
Brussels 5	0.1 $\pm$ 0.1 (0.0 - 0.4)	1.0 $\pm$ 0.4 (0.3 - 1.6)	0.1 $\pm$ 0.0 (0.0 - 0.1)	0.4 $\pm$ 0.2 (0.3 - 0.8)	9.5 $\pm$ 8.0 (1.4 - 23.9)

Table 3 Bulk ice concentrations of nutrients in the ice cover at Liège site. Mean $\pm$ standard deviation (range).

Station	Phosphate ($\mu\text{mol L}^{-1}$)	Ammonium ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Nitrate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
Liège 1	0.3 $\pm$ 0.1 (0.1-0.7)	1.6 $\pm$ 0.5 (0.8-2.5)	0.1 $\pm$ 0.0 (0.1-0.2)	1.6 $\pm$ 0.7 (0.7-2.5)	6.8 $\pm$ 2.6 (3.1-11.0)
Liège 2	0.1 $\pm$ 0.1 (0.1-0.3)	0.6 $\pm$ 0.3 (0.0-1.2)	0.1 $\pm$ 0.0 (0.0-0.1)	1.3 $\pm$ 0.8 (0.4-2.5)	5.1 $\pm$ 3.6 (2.2-18.8)
Liège 3	0.2 $\pm$ 0.1 (0.1-0.7)	0.7 $\pm$ 0.2 (0.4-1.2)	0.1 $\pm$ 0.0 (0.0-0.1)	0.8 $\pm$ 0.7 (0.2-2)	3.8 $\pm$ 3.6 (0.8-14.2)
Liège 4	0.1 $\pm$ 0.1 (0.1-0.2)	1.1 $\pm$ 0.6 (0.7-3.7)	0.1 $\pm$ 0.0 (0.0-0.1)	0.9 $\pm$ 0.8 (0.2-2.4)	5.3 $\pm$ 3.2 (1.5-14.1)
Liège 5	0.2 $\pm$ 0.3 (0.0-1.1)	0.9 $\pm$ 0.4 (0.4-1.7)	0.1 $\pm$ 0.0 (0.0-0.1)	1.5 $\pm$ 0.9 (0.5-3.6)	6.9 $\pm$ 2.8 (2.9-13.2)

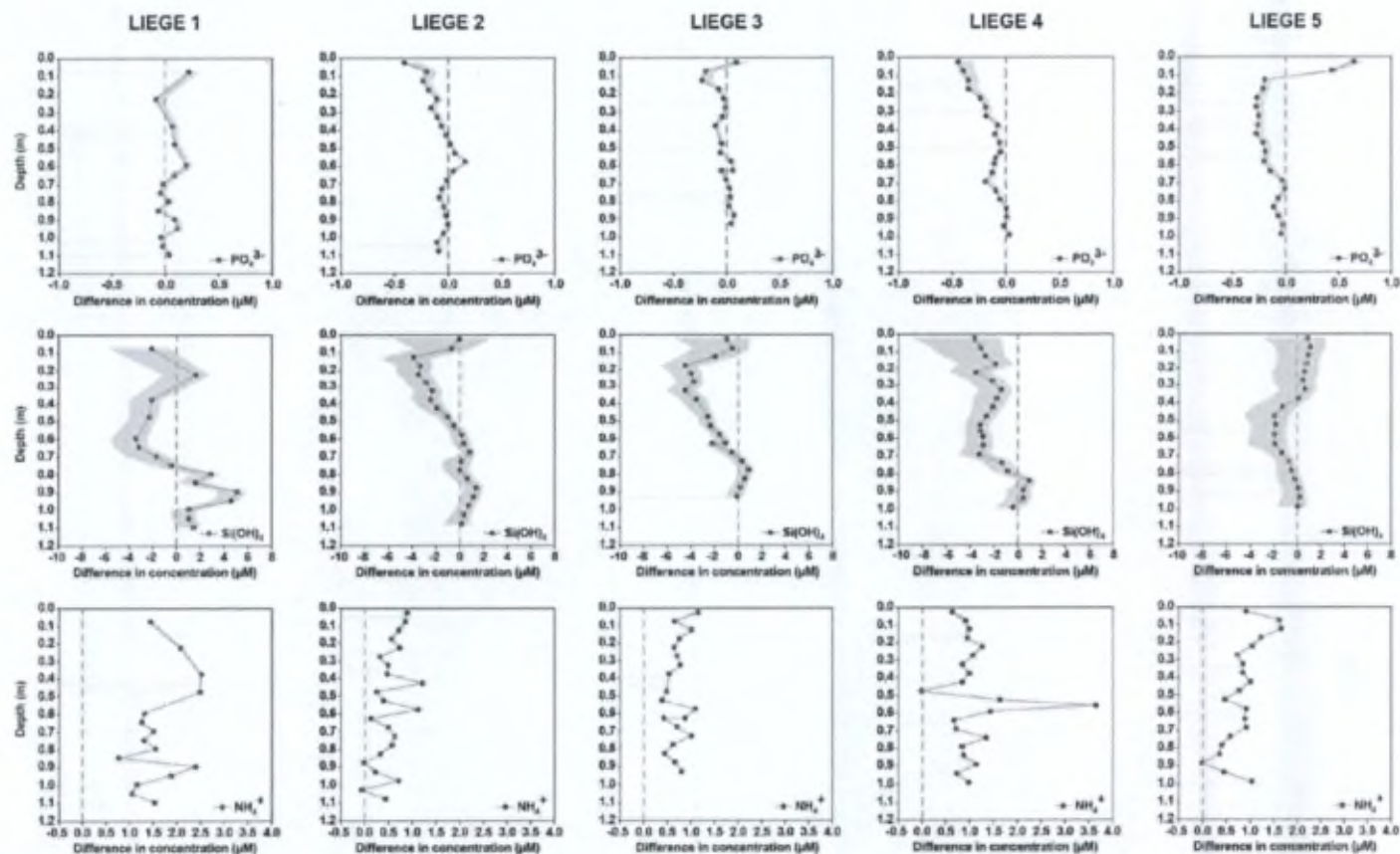


Figure 18 Vertical profiles of departure of concentration from the theoretical dilution line of PO_4^{3-} , Si(OH)_4 and NH_4^+ at Liège site. The solid line with symbols shows the difference of concentration between the measured concentration and the concentration predicted by the mean TDL. The shaded area represents the variation range of the difference considering the minimum and maximum slopes for the computation of the TDL. Note the difference in horizontal scale.

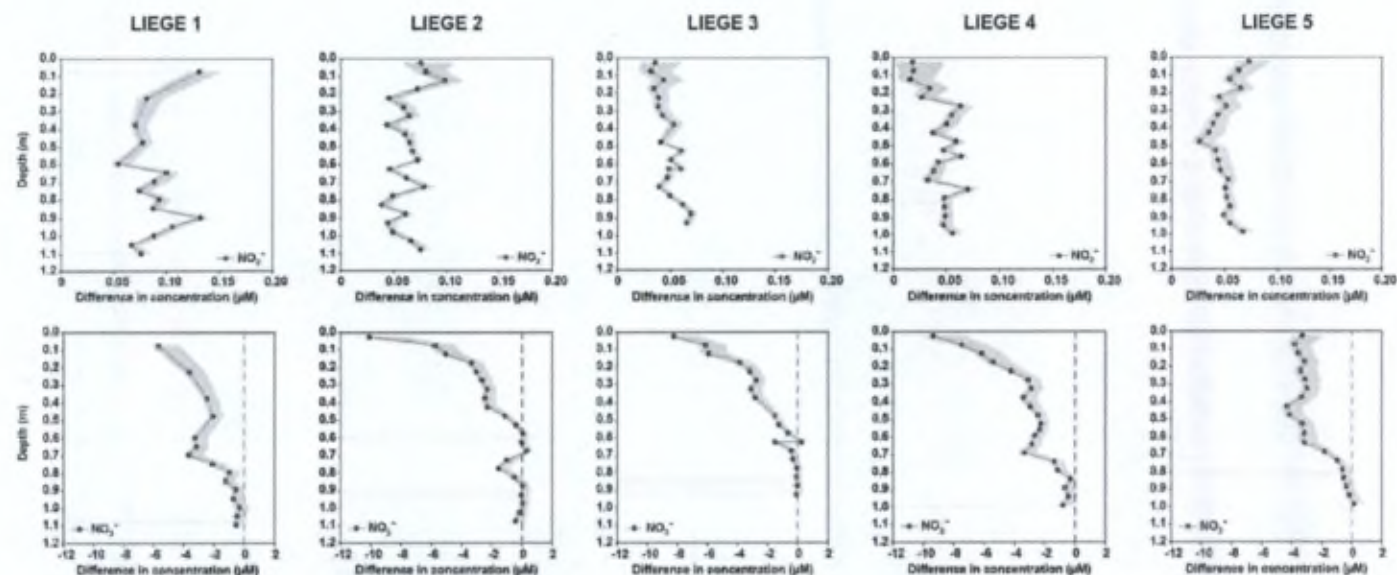


Figure 19 Vertical profiles of departure of concentration from the theoretical dilution line of PO_4^{3-} , Si(OH)_4 and NH_4^+ at Liège site. The solid line with symbols shows the difference of concentration between the measured concentration and the concentration predicted by the mean TDL. The shaded area represents the variation range of the difference considering the minimum and maximum slopes for the computation of the TDL. Note the difference in horizontal scale.

stations 2, 3 and 4. Phosphate showed concentration close to the TDL throughout the profile for all stations (Figure 18 and Figure 19). The greater depletion was to be observed at the surface of stations 2 and 4 while the most important enrichment was observed in the top 10 cm of station 5. To a lesser extent than at Brussels site, silicate is the nutrient which showed the largest variations in the ice with a maximum mean enrichment of $5.1 \mu\text{mol L}^{-1}$ at station 1 and a maximum mean depletion of $4.5 \mu\text{mol L}^{-1}$ at station 3. Silicate showed also the most variable concentration of all nutrients in the seawater samples taken under the ice cover as attested by the wide shaded area on Figure 18. Station 1 showed a inverted double S-shaped profile with a clear depletion zone centred around 55 cm depth and a marked enrichment zone below centred around 95 cm depth. Station 2, 3 and 4 exhibited a similar S-shaped profile with however a clear depletion appearing at the surface of station 4. Station 5 was characterised by a mean enrichment of silicate in the top 30 cm. Ammonium was generally enriched with respect to the TDL. Ammonium showed on average the most important enrichment at station 1 with a marked enrichment zone around 0.4 m depth. Profiles of stations 2 to 5 exhibited fewer variations at generally lower enrichment values with the exception of Liège 4 where ammonium clearly departed from the TDL around 55 cm depth ($+3.6 \mu\text{mol L}^{-1}$). Nitrite was at all times very slightly enriched overall with respect to the TDL. Nitrate exhibited a generally depleted inverted C-shaped profile from station 1 to 4 with the strongest depletion observed at the surface (down to $-10.1 \mu\text{mol L}^{-1}$ at station 2). Station 5 was characterized by a clear decrease of the depletion with respect to the TDL in the top 25 cm.

DMS, DMSP and DMSO – At Brussels site, ice DMSP concentrations ranged from 75 to 5349 nmol L^{-1} (mean 899 nmol L^{-1} ; st.dev. 1042 nmol L^{-1}) along the observation period (Figure 20). The highest values were to be found in the top 0.2 m of the ice cover. At station 1, relatively high DMSP concentrations could be observed in the upper half of the ice cover with values of 937 nmol L^{-1} at the surface increasing downwards to peak at 2175 nmol L^{-1} at 0.175 m depth, then dropping rapidly downwards and increase again to 664 nmol L^{-1} at the bottom. At station 2, DMSP concentrations peaked at 1158 nmol L^{-1} at 0.075 m depth and then rapidly dropped to relatively low values fluctuating around a mean value of about 160 nmol L^{-1} to the bottom. At station 3, a drastic increase of DMSP concentrations

was observed in the top 0.25 m of the ice cover with values peaking at 2075 nmol L^{-1} close to the surface. Station 4 was characterised by high values along the whole profile with the highest value of 5349 nmol L^{-1} to be found at 0.025 m depth. A second peak was also observed around 0.25 m depth. Lower values ranging from 841 nmol L^{-1} to 1641 nmol L^{-1} characterised the lower half of the profile. High values of DMSP (up to 3980 nmol L^{-1}) could still be observed in the top 0.1 m of station 5 but values rapidly dropped from 0.125 m depth downwards to the bottom. Ice DMS concentrations ranged from 6 to 2829 nmol L^{-1} (mean 300 nmol L^{-1} ; st.dev. 476 nmol L^{-1}). The distribution and the evolution of the DMS in the ice cover along the observation period was similar to what was observed for DMSP with most of the change to be observed in the upper half of the ice cover from station 3 onwards (Figure 20). As for DMSP, the highest DMS concentration value (2829 nmol L^{-1}) was measured close to the surface at 0.025 m depth at station 4 and a second peak (1553 nmol L^{-1}) was also present around 0.20 m depth. At station 5, the whole profile showed low values ($26 - 68 \text{ nmol L}^{-1}$) in the same range as station 1 and 2 with the exception of the elevated bottom value (732 nmol L^{-1}). Contrary to DMSP, no surface peak was observed close to the surface. DMSO was the compound whose concentration was the lowest in the ice amongst DMS, DMSP and DMSO (Figure 20). Ice DMSO concentrations ranged from 5 to 775 nmol L^{-1} (mean 47 nmol L^{-1} ; st.dev. 104 nmol L^{-1}). The distribution and evolution of DMSO in the ice cover was globally similar to those observed for DMSP and DMS. Major changes in the profile were observed in the top 0.3 m of the ice cover between stations 3 and 5. As for DMSP and DMS, the two peaks structure was also observed at station 4 with the highest value of 775 nmol L^{-1} of DMSO observed close to the surface at 0.025 m depth. On the contrary to DMSP and DMS, no increase of concentration could be observed in the top 0.25 m.

At Liège site, most of the changes in DMSP, DMS and DMSO were also observed in the top 0.2 m of the ice cover similarly to Brussels site (Figure 20). As the levels of DMSP, DMS and DMSO observed were generally lower in the ice cover of Liège site, a close-up of the distribution of the three compounds at that site is shown on Figure 21 to better render the variations in the top 20 cm of the ice cover. Almost no changes were observed below 0.6 m depth for neither of the compounds. All compounds varied in a narrower range than in the ice cover of Brussels site,

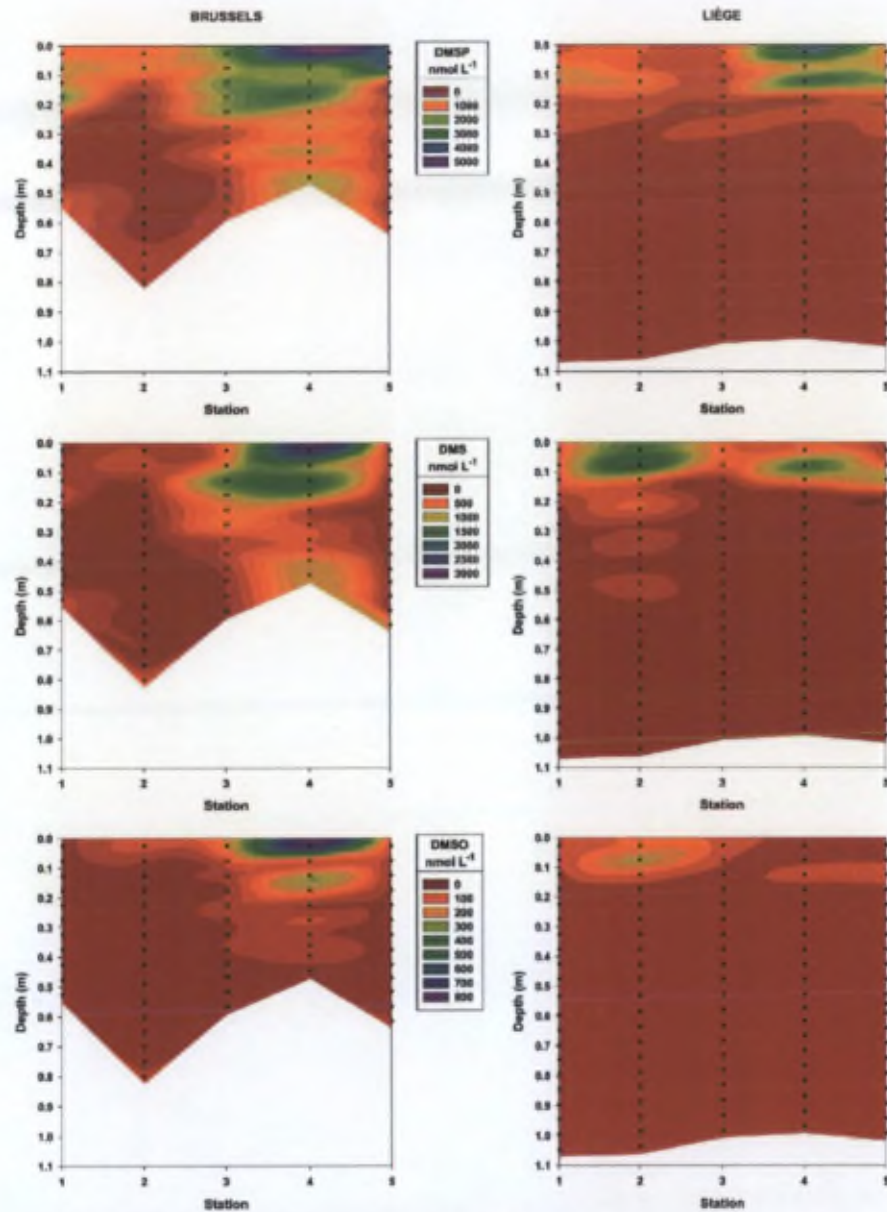


Figure 20 Comparative vertical profiles of DMSP (upper panel), DMS (middle panel) and DMSO concentrations (lower panel) at Brussels and Liège sites. The black dots show the mean sampling depths. Note the difference in colour scale for the different compounds.

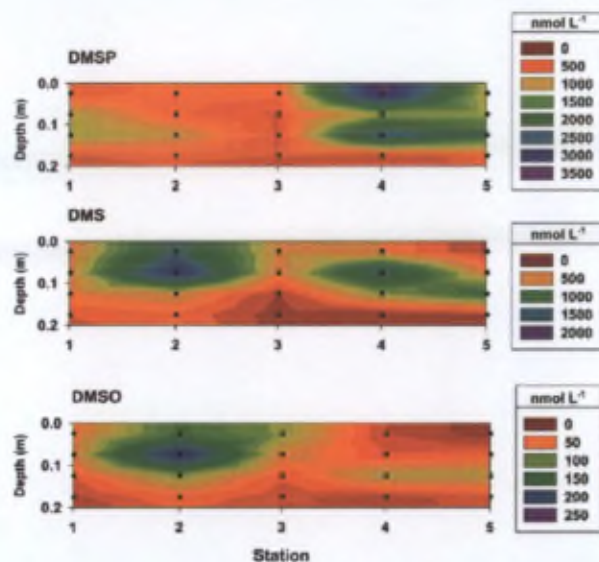


Figure 21 Close-up of the distribution of DMSP (upper panel), DMS (middle panel) and DMSO concentrations (lower panel) in the top 20 cm of the ice cover at Liège site. The black dots show the mean sampling depths. Note the difference in colour scale for the different compounds.

i.e. between 1.5 nmol L^{-1} and 3352 nmol L^{-1} for DMSP (mean 253 nmol L^{-1} ; range 496 nmol L^{-1}), between 0.6 nmol L^{-1} and 1788 nmol L^{-1} for DMS (mean 121 nmol L^{-1} ; st.dev. 291 nmol L^{-1}) and between 1.4 nmol L^{-1} and 219 nmol L^{-1} for DMSO (mean 16 nmol L^{-1} ; st.dev. 29 nmol L^{-1}). A subsurface peak of the three compounds could be observed at station 1 with concentration amounting to 1193 nmol L^{-1} for DMSP, 478 nmol L^{-1} for DMS and 58 nmol L^{-1} for DMSO. The concentration rapidly dropped downwards and stabilised below 0.6 m around a mean value of 21 nmol L^{-1} of DMSP, 4 nmol L^{-1} of DMS and 4 nmol L^{-1} of DMSO. The concentration of the three compounds increased in the top 0.6 m of the ice cover at station 2 with the most drastic increase to be observed close to the surface with values peaking at 953 nmol L^{-1} of DMSP, 1788 nmol L^{-1} of DMS and 219 nmol L^{-1} of DMSO. A global drop of DMSP, DMS and DMSO concentrations along the whole profile could be observed at station 3 with the highest values still to be seen in the top 0.1 m of the ice cover. As observed at Brussels site, an increase in concentration of DMSP, DMS and DMSO was to be observed in the top 0.2 m of the ice cover at station 4. At Liège site, although, only DMSP showed its maximum values of the observation period at station 4 with values as high as 3352 nmol L^{-1} in the top 0.05 m and 2497 nmol L^{-1} between 0.1 and 0.15 m depth. DMS and DMSO concentrations at the most amounted to 1334 nmol L^{-1} and 74 nmol L^{-1} ,

respectively in the top 0.15 m . Finally, as observed at Brussels site, station 5 was characterised by a widespread decrease of DMSP, DMS and DMSO along the profile with values remaining however at a substantial level in the top 0.15 m of the ice cover.

Under-ice seawater DMS and DMSP concentrations measured at the interface, 1 m and 30 m depth under the ice of Brussels and Liège sites are shown on Figure 22. Owing to problems with the sampling device, data are missing for station 1 (all depths) and for station 3 (30 m) at Brussels site. Significant concentrations of DMSP were observed in the seawater under the sea ice cover of Brussels site (mean 14 nmol L^{-1} ; st.dev. 8 nmol L^{-1} ; range $2 - 28 \text{ nmol L}^{-1}$) with the highest levels located in the uppermost meter of the water column. DMSP levels were found in the same order of magnitude at Liège site (mean 18 nmol L^{-1} ; st.dev. 19 nmol L^{-1} ; range $3 - 79 \text{ nmol L}^{-1}$) but showed more variability close to surface. At both sites 30 m DMSP concentrations were generally lower and never exceeded 30 nmol L^{-1} . Concentrations of DMS varied over a larger range of values in the under-ice water of Brussels site (mean 40 nmol L^{-1} ; st.dev. 33 nmol L^{-1} ; range $1 - 126 \text{ nmol L}^{-1}$) and exhibited the maximum value of the observation period at station 2. DMS concentrations at Liège site were in the range of those of DMSP (mean 23 nmol L^{-1} ; st.dev. 15 nmol L^{-1} ; range $4 - 60 \text{ nmol L}^{-1}$) and exhibited the highest value at station 3.

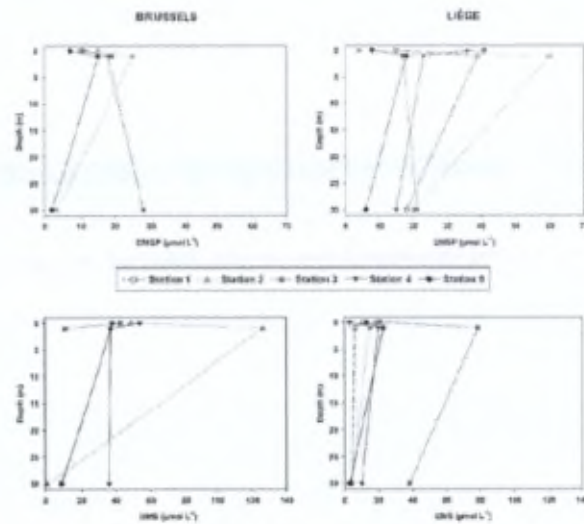


Figure 22 Concentrations of DMSP (upper panel) and DMS (lower panel) measured at the ice/water interface, 1 m and 30 m depth in the under-ice water of Brussels (left) and Liège (right) sites. Note the difference in horizontal scale for DMSP and DMS.

5. DISCUSSION

Spatial variability

During laboratory experiments, measurements can be performed on prepared sea ice whose growing conditions are controlled to minimise spatial variability and facilitate the interpretation of a series of jointly observed variables [e.g. Killawee et al., 1998; Tison et al., 2002]. Sea ice in the natural environment generally exhibits higher spatial variability at different scales [e.g. Eicken et al., 1991] due to the variety of environmental constraints prevailing during its growth. The sampling strategy adopted in the present study aimed mainly to emphasise differences in ice processes between two sites, chosen for their contrasting features while confining spatial variability within each of the sites at the same time. Texture profiles revealed little spatial variability between ice core locations at Brussels site (see Figure 4) but a higher level of inhomogeneity at Liège site (see Figure 5) [see also Lewis et al., 2011 for more details]. The similarity between the overall trend in salinity and $\delta^{18}\text{O}$ profiles and between the comparative bulk salinity profiles suggests however that spatial variability can be neglected with respect to temporal variability in the interpretation of the differences between stations [Lewis et al., 2011].

Comparison of chlorophyll *a* determination procedures

Both profiles logically exhibit the same shape as the samples originated from the same ice core. The local discrepancies between both profiles are likely to be attributed to the patchiness of the sea ice biota that can be important even at small scales [e.g. Gosselin et al., 1986; Garrison, 1991]. This factor can nevertheless not explain the elevated percentage of higher chlorophyll *a* values produced by the buffered melting/ sequential filtration method. Although the identification of the reasons of this difference lies beyond the scope of this work, it seems worthy to investigate a few leads to choose the most reliable chlorophyll *a* dataset for comparison with other variables and encourage the use of good practices for future studies.

To date, no study has focused on the best procedure to adopt to measure chlorophyll *a* on melted sea ice samples. The results obtained in the present study will thus be discussed in the light of studies that have been devoted to examine the best melting procedure for taxonomic analysis of ice algae [Garrison and Buck, 1986; Mikkelsen and Witowski, 2010] or bacteria [Junge et al., 2004]. Garrison and Buck [1986] recommended melting the sea ice sample in filtered seawater as the osmotic changes caused by direct melting of the sample proved to be deleterious to non silicified groups of ice algae. In a more recent study, Mikkelsen and Witowski [2010] suggested that the rate of change of the salinity of the sample melt would be more critical than its salinity alone. These

authors demonstrated that direct melting at 4°C, buffered melting at 4°C in seawater with salinities of 10 and 30 produced the same results with a negligible impact on all taxonomic groups of algae with the exception of chrysophytes. These authors recommended that direct melting at 20°C is avoided and that the melting time is comprised between one day and one week.

Degradation of chlorophyll a – Chlorophyll *a* is known to break down into a series of degradation products (phaeophytins and chlorophyllides which, in turn, decompose into phaeophorbides) when exposed to excess light, oxygen (air), elevated temperatures and acidic or basic conditions [Hosikian et al., 2010]. As all the samples underwent the same conditions during melting (at 4°C in the dark), light and temperature are expected to have similarly impacted the degradation of chlorophyll *a* in both procedures. Exposure to oxygen/air was also anticipated to have been comparable between the two procedures. Slightly longer exposure to air during melting of the directly melted samples might have occurred as direct melting is expected to proceed slower than melting into saline solution. Longer exposure to air might also have occurred during the filtration process of the samples submitted to single filtration on glass fiber filters which might have seen their porosity decreased as progressive clogging of the GF/F filter proceeded. Melting and filtration time have unfortunately not been recorded and the influence of this supposed longer exposure to air is therefore impossible to assess. Should the longer exposure to air be the cause of an accelerated degradation of chlorophyll *a* in the samples submitted to the direct melting/ single filtration procedure, then levels of degradation products (phaeopigments) are expected. Analysis of the phaeopigments concentrations and percentages revealed however that the vertical profiles were in close agreement for both procedures and that the observed difference in phaeopigments did not compensate the observed difference in chlorophyll *a* (data not shown).

Production of chlorophyll a – Production of chlorophyll *a* during melting would have been favoured in the samples melted in buffered seawater by the relative higher abundance of autotrophic sympagic organisms than in the samples melted directly. This assumption might hold as dinoflagellates and other flagellates, which are acknowledged to be amongst the most sensitive sympagic taxa to osmotic stress [Garrisson and Buck,

1986; Mikkelsen and Witowski, 2010], seem to be the dominant taxa everywhere in the ice cover of Brussels and Liège. It appears however less plausible considering that all the samples were maintained in strict darkness until filtration.

Extraction efficiency – A better efficiency of extraction of chlorophyll *a* retained on polycarbonate filters in relation to glass fibre filters is another assumption. Previous studies have compared the influence of the filter nature on the chlorophyll *a* determination and formulate recommendations about the best filter to use according to object of the study (chlorophyll *a*, taxonomic study, nutrients,...) [e.g. Burford and Pollard, 1994; Chavez et al., 1995; Kniefkamp et al., 2007]. None of those studies reported however comparison of the filters used in the present study.

Contamination by filtered seawater – Another option is that the filtered seawater used to buffer the melting of the ice samples initially contained extra amounts of chlorophyll *a* that would have been measured along with sea ice chlorophyll *a*. As the amount of buffering seawater added was similar between the samples, and hence the amount of seawater chlorophyll *a*, a constant bias would have been expected between the procedures. It nevertheless did not appear in the comparative profiles of chlorophyll *a* (Figure 13) which partially invalidates this argument.

As the likelihood to have lost chlorophyll *a* during the melting, filtration and extraction process seems higher than the contamination by filtered seawater or production of chlorophyll *a* during melting, data obtained by the buffered melting/ sequential filtration procedure will be considered as more reliable and used henceforth for comparison with other variables. As chlorophyll *a* is a widely-used proxy of algal standing stock [Arrigo et al., 2010], it appears crucial that further study is undertaken, including repeated measurements and close monitoring of factors of influence in order to select the best procedure to measure chlorophyll *a* in sea ice. Development of in situ imaging techniques like pulse amplitude modulated (PAM) fluorometry might provide an alternative to the classical melting approach [Ryan et al., 2011].

Thermohaline evolution of the sea ice cover under atmospheric thermal forcing

The mean snow thickness observed at the ice core locations for the different sampling events at Brussels and Liège sites are within the range of other snow thickness measurements performed elsewhere on the two sites [Lewis et al., 2011]. The mean ice thickness derived from the limited ice core length dataset at Brussels site is consistent with the value of 0.591 ± 0.043 m (including a substantially higher number of observation from manual gauging and two IMBB's time series measurements) reported by Lewis et al. [2011]. The trend towards melting (0.005 m d^{-1}) revealed at Liège site (see Figure 3) is consistent with the value of -0.0043 m d^{-1} computed at Brussels site from IMBB time series and with a computed mean value of ocean heat flux of 6 to 8 W m^{-2} [E.A. Murphy and S.F. Ackley, unpublished data, 2010]. The missing increase of the ice salinity at the bottom of the ice cover at both sites (Figure 8) supports the general occurrence of basal melting.

Although the short-lived cold air episodes were not sufficient to counteract the effect of ocean heat flux, significant changes were induced in the physical regime and morphological properties of the sea ice cover. Cooling from above during those cold air episodes were sufficient for unstable brine salinity gradients (hence density gradients) to develop within the ice cover of both sites, especially at station 4 (see Figure 9). Development of unstable brine salinity gradients can initiate overturning of brine and the mixing with underlying seawater moving upwards, provided the permeability of the sea ice is sufficient [Notz and Worster, 2009].

To date no technique proved to be sufficiently reliable to allow autonomous measurement of sea ice salinity and real time monitoring of brine overturning events in the field although a series of promising techniques based on the electrical properties of sea ice recently emerged (e.g. Pringle et al. [2009]). The occurrence of brine drainage episodes is usually revealed by indirect observations like excursions in the ice temperature profile [Hudier et al., 1995; Mc Guinness et al., 1998; Trodahl et al. 2000, 2011; Pringle et al., 2007] or modification of the diameter of brine channels [Martin, 1974; Eide and Martin, 1975]. Lewis et al. [2011] reported excursions in the ice temperature profiles from IMBB records at ISB as well as a marked difference between cooling and warming rate of the sea ice cover (e.g. clear faster warming of the entire ice cover at the end of the coldest air episode between Brussels 4 and 5) as expected in case of brine overturning which enhances

the heat transfer from the ocean to the ice. Presence of dissolution features observed on freshly extracted ice cores (Figure 6) and on thick sections (Figure 4 and Figure 5) were signs of the occurrence of brine gravity drainage over the floe during the study period. As discussed below, the analysis of additional variables further supports this hypothesis.

The geometrical features of brine inclusions illustrated in Figure 6 further support thermally-driven brine overturning within the sea ice cover. These features differ from the typical tree-like structure of brine channel and developed as large vertical brine tube, initiating at the upper granular/columnar ice interface. They sometimes ran throughout the whole ice thickness and connected to the ice/water interface as inverted funnels, suggesting turbulent microflow developing as outgoing brines encounter warmer inflowing seawater. The vertical migration of these brine tubes would have started after an atmospheric cooling event (Figure 2, bottom), as concentrated brines dissolved the warmer ice below, thereby increasing the ice permeability and eventually triggering a brine overturning event. This would be especially if the ice temperature rises again under a new warm spell.

Computation of vertical profiles of Ra (Figure 11) might reveal the potential for brine gravity drainage especially at Brussels. Ra assesses whether the available potential energy (originating from the unstable brine density gradient) is sufficient to overcome the combined effects of thermal dissipation and viscosity [Notz and Worster, 2008; 2009]. In their experiment, Notz and Worster [2008] demonstrated that convective overturning of brine systematically occurs when Ra exceeded the critical value of 10. According to this criterion, brine drainage could have only occurred at Brussels between stations 1 and 2. However, while brine overturning is certain to occur when the value of Ra exceeds 10, it could possibly start at lower values around 6–7 [D. Notz, personal communication, 2009]. This extends the likelihood of brine drainage at Brussels site between stations 3 and 4 (Figure 11). Despite systematically high brine volume fraction values (Figure 10), only low values of Ra were observed at Liège where moderate brine salinity (hence density) gradients developed mainly because of the thermal insulation provided by the thicker snow cover. Should brine drainage occur, an increase in concentration of nutrients in sea ice is anticipated, as saline nutrient-depleted brine is expected to mix

with nutrient-rich seawater. Given the temporal sampling resolution adopted in this study, a rapid uptake rate of nutrients by sympagic organisms after replenishment might however have concealed the expected increase in nutrient levels between two consecutive sampling events as a result of convective sea water exchange. The observation of the nutrients profiles suggest at least, two particular events of nutrient transport: 1) brine drainage between Brussels 1 and Brussels 2 as revealed by the disappearance of the local peak of phosphate, silicate, ammonium, nitrite (Figure 16 and Figure 17), DMSP and DMS (Figure 20) and 2) surface flooding and nutrient replenishment from above between Liège 4 and Liège 5 as attested by the general increase in the levels of all nutrients observed at Liège 5 (Figure 18 and Figure 19). Surface flooding seemed to have directly affected the autotrophic biomass as attested by the general increase of chlorophyll *a* in the top 0.7 m (Figure 12) mainly driven by the increase of the flagellates' biomass at 0.1–0.2 m (Figure 15). The variability of the under-ice water salinity was also investigated in an attempt to detect brine drainage events but it did not provide further information on the timing of brine drainage episodes. Statistical comparison of the mean salinity values of the 30 m under-ice water column (ANOVA, $\alpha=0.05$) did not reveal any significant difference ($p=0.079$) between stations. Brine drainage is a local and potentially sudden process. Martin [1970] described brine drainage as an oscillatory process with a periodicity of roughly one hour consisting of 8–15 minute seawater inflow followed by a 45 minute outflow of brine. Recent numerical experiments suggests it could last from 1 hour to 5 days depending on the parameterisation used for the effective salt diffusivity as estimated by numerical simulations [M. Vancoppenolle, unpublished data]. Given the transient nature of brine drainage, it is very likely that brine drainage events were missed given the temporal and spatial sampling resolution achieved in this study. Nevertheless, the findings presented above tally to support that brine gravity drainage was a general feature of the ice floe particularly at Brussels site during the study period.

Sea ice DMS, DMSP and DMSO ranges

The levels of DMSP and DMS observed in this study are in the range of those observed in previous sea ice DMSP studies (see Tison et al., [2010] and references therein; Brabant et al., [2011] for ice values and Asher et al. [2011] and Nomura et al. [2011] for values in sea ice brines) although the levels recorded at Brussels site are the highest ever observed in level pack ice. Sea ice DMSO concentration values are scarce in the literature. The DMSO concentration observed in the ice cover of Brussels and Liège stations exceed those observed by Lee et al. [2001] in the bottom 2 cm of spring Arctic first-year pack ice who only measured particulate DMSO nevertheless. In a recent study, Asher et al. [2011] characterised DMSO in the brines of summer first- and multiyear pack ice and landfast sea ice in the Ross Sea. These authors report values of DMSO which are generally below or comparable to the levels observed in the present study although the latter are bulk values. To compare data from both studies, bulk values should be converted into brine values by dividing observed values by the brine volume fraction (assuming that all of the DMSO occurs exclusively within the liquid phase). The DMSO (and DMSP and DMS) levels observed in the ice cover of Brussels and Liège sites would then exceed those measured by Asher et al. [2011] by a factor of about ten (average brine volume fraction of the sea ice cover of Brussels and Liège is 0.11). This discrepancy could originate from an underestimate of the actual DMSO/P concentrations as a result of the failure of the 'sackhole' brine collection method to recover the particulate matter as previously suggested by Brierley and Thomas [2002]. This assumption has ever since proved to hold for dissolved organic carbon (DOC) [Becquevort et al., 2009] and DMSP [Tison et al., 2010]. The discrepancy might also come from the fact that the ice covers studied in either studies exhibited contrasting ice history or algal and microbial community structure or that the observed concentrations values were driven by a different dynamics in either cases (spring vs. summer regime). The physical properties of the sea ice cover as well as a thorough characterisation of the sympagic biota were regrettably not reported in the work of Asher et al. [2011] making rash any further comparison.

Table 4 Spearman's rank-order correlation table for sulphur compounds and other physical and biogeochemical variables in vertical profiles of ice at Brussels and Liège ($n=149$). When applicable, the level significance of the coefficient is denoted by * ($p<0.05$), ** ($p<0.01$) or *** ($p<0.001$).

	DMS	DMSO	DMSP
Ice salinity	0.72 ***	0.74 ***	0.79 ***
Temperature	-0.43 ***	-0.51 ***	-0.54 ***
Chlorophyll <i>a</i>	0.24 **	0.22 **	0.27 ***
Phosphate	-0.17 *	-0.25 **	-0.26 **
Ammonium	0.14	0.19 *	0.21 **
Nitrite	-0.04	-0.07	-0.15
Nitrate	-0.57 ***	-0.64 ***	-0.72 ***
Silicate	-0.04	0.01	
DMSP	0.86 ***	0.85 ***	
DMSO	0.89 ***		

Relationships between DMS, DMSP, DMSO and physical and biogeochemical variables

The lack of homoscedasticity shown by the dataset being liable to introduce a strong bias in the results, non-parametric Spearman's rank-order correlation (ρ) was computed instead of the usual Pearson's product-moment correlation coefficient which moreover requires normally-distributed variables and existence of a linear relationship between variables. Results are shown in Table 4. Unlike the Pearson's product-moment correlation coefficient which assess the strength of linear dependence between two variables, the Spearman's rank-order correlation only assess the strength of monotonic dependence between those two variables. Relationship between variables is discussed below insofar as variables exhibit at least a moderate relationship ($\rho > 0.5$).

Physical controls on sea ice DMS, DMSP and DMSO

Texture – Sea ice texture can be expected to influence the initial vertical distribution of biogeochemical tracers like DMS, DMSP and DMSO during ice growth. Later in the season, sea ice texture can affect the transport of tracers across the ice cover by hampering or facilitating their diffusion within the sea ice matrix or their travel through the ice along with the draining brine. The stratigraphy of a 'typical' ice cover is generally not homogeneous and comprises layers of different ice types and generally consists of a sequence of granular ice, transitional layer and columnar ice [Petrich and Eicken 2010]. Frazil ice proved to incorporate higher concentrations

of biological matter from the water column than columnar ice during sea ice formation [Ackley and Sullivan, 1994]. Scavenging by frazil ice crystals [Ackley, 1982; Garrison et al., 1983] and wave pumping through the new frazil ice layer [Weissenberger and Grossmann, 1998] result in a random and non-selective entrapment of microorganisms in sea ice. Columnar ice formation leads on the contrary to a selective incorporation process favouring large sea ice protists [Rozanska et al., 2008]. Provided the composition of surface waters is not significantly modified, a contrast in species composition could then be expected to be observed between the granular and columnar ice layers as a result of those distinct entrapment processes during the growing season. It is acknowledged that the ability to produce DMSP (and potentially DMSO and DMS) is dependent on the algal species [Stefels et al., 2007]. A contrast in DMSP levels between granular and columnar ice layers could hence also be anticipated with potentially higher DMSP levels in granular ice. No strong evidence of such a control of the texture appears in our dataset as no systematic change in DMS, DMSP or DMSO was observed to correspond to ice texture changes nor were higher levels of those compounds found in granular ice. This is especially striking at Liège site below 20 cm where numerous stratigraphic changes were observed (Figure 5) while no significant deviation appeared in the DMS, DMSP or DMSO profile (Figure 20). During spring and summer, the transport of tracers (gas, solutes or particulate) towards the interfaces (ice/air and ice/water) can be hampered or facilitated depending on the ice texture. Recent experiments suggest indeed that columnar and frazil ice exhibit

different fluid transport properties with the latter requiring higher brine volume fractions (namely about 10% for fine grained ice [Dr. Kenneth Golden, University of Utah, personal communication]) to become permeable to fluid flow than the threshold of 5% reported for columnar sea ice [e.g. Golden et al., 1998, 2007]. As observed for summer pack ice [Tison et al., 2010], generally lower DMS levels were observed at the surface than in the underlying 0.05 to 0.15 m suggesting that DMS diffused towards the ice surface and was vented to the overlying snowpack and eventually to the atmosphere (Figure 20 and Figure 21). The notable exception observed at the surface at Brussels 4 could be explained by a production rate exceeding the diffusion/venting rate of DMS and a concomitant decrease in the brine volume fraction in response to the important atmospheric cooling witnessed at that station. The influence of texture on the mass transport of DMS, DMSP and DMSO with the draining ice brines is expected to have been the greatest at Liège. Prevalence of granular ice in the ice cover at that site (Figure 5) would have indeed reduced the chance for brine drainage to occur because of the higher percolation threshold reported to apply for granular ice. Other parameters like the thermal insulation provided by the snowpack and the ice thickness at Liège were also crucial in controlling the conditions for brine drainage by hampering the development of steep temperature and brine salinity gradients in the ice cover.

Ice temperature, ice salinity and brine salinity – Already two decades ago, Kirst et al. [1991] proposed that temperature and salinity conditions encountered in the sea ice environment could induce a response at the cellular level, with DMSP being produced as cryoprotectant and osmolyte by sympagic algae in the view of the high levels of DMSP they observed in various sea ice environments. It is generally assumed that following thermodynamic equilibrium, salinity of sea ice brine inclusions is solely determined by the ice temperature, with decreasing temperatures inducing increasing brine salinities [Petrich and Eicken, 2010]. Survival of sympagic organisms in brine inclusions requires therefore simultaneous protection against freezing and increased osmotic pressure of the medium. While only few studies report intracellular DMSP concentration adjustment in response to various temperatures (reviewed by Stefels et al. [2007]), no comparable experiment have been attempted so far for temperature and salinity conditions encountered in sea ice brine. In their

recent experiment, Lyon et al. [2011] submitted cultures of the sea ice diatom *Fragilariopsis cylindrus* to a progressive salinity shift in the lower range of sea ice brine salinities (from 35 to 70) and observed that intracellular DMSP had increased by 85%, confirming thereby that DMSP accumulation could be one amongst many physiological acclimation mechanisms used by some ice algae to mitigate salinity stress. The moderate negative correlation between ice temperature and DMSP (that would have been positive if brine salinity had been considered given the inverse relationship between the two variables) (Table 4) suggest that a similar mechanism might have been adopted by the algal community at ISB. The strong correlation between ice salinity and either DMS, DMSP or DMSO is thought to have been the result of the control of ice salinity on the relative brine volume. As the ambient (brine) salinity witnessed by sympagic organisms is solely determined by the ice temperature, one interpretation may be that high ice salinity values induced high relative brine volume values allowing to stock higher quantities of DMS, DMSP and DMSO. Ice temperature and salinity are key parameters determining the potential of a given sea ice profile to brine drainage. As discussed above, the witnessed meteorological conditions are thought to have periodically provided favourable conditions for brine drainage to take place in the ice cover, thereby influencing the vertical distribution of DMS/P/O especially at Brussels site.

PAR and UV radiations – Sea ice, especially in its upper layers, is prone to favour photochemical reactions as it proved to contain high amount of coloured dissolved organic matter encountered in sea ice, which acts as photosensitiser with a strong absorption of UV radiations [Belzile et al., 2002], and by maintaining compounds and organisms exposed to solar radiation. Absolute effects of PAR or UV radiations on the levels of DMS, DMSP and DMSO are hard to assess as numerous photochemical and microbial pathways, which at times can compensate each other, are possible. Although not all authors agree, increased levels of PAR proved to influence total or intracellular algal DMSP concentration, either positively [Hefu and Kirst, 1997; Stefels et al., 2007] or negatively [Harada et al., 2009], cause either an increase of DMS [Sunda et al., 2002] or a decrease by photolysis that can lead to the production of DMSO [Kieber et al., 1996]. Exposure of cultures of microalgae to increased levels of UV radiations also produced contrasting results even in the course of the

same experiment according to the time scale considered [Harada et al., 2009]. The contrast in location of the DMSO maximum at either site suggests that its production resulted from distinct pathways. The systematic occurrence of the maximum DMSO concentration at the top of the ice cover at Brussels site (Figure 20) suggests that DMSO resulted from DMS photo-oxidation while the thicker snowpack at Liège site would have hampered such a process by limiting the amount of incident solar radiation reaching the ice surface. Occurrence of the DMSO peak observed 0.05 to 0.15 m below the ice surface at Liège 1, 2, 4 and 5 (Figure 21) suggests that DMSO production followed another pathway. The cryoprotectant hypothesis for the production of DMSO by sea ice algae is therefore challenged as DMSO maximum values were anticipated at the ice surface where the magnitude of thermal and salinity changes was the widest.

Biogeochemical controls

Chlorophyll *a* – Correlation of the concentration of chlorophyll *a* with DMS, DMSP or DMSO was weak (Table 4). This lack of relationship is particularly striking when comparing the chlorophyll *a* (Figure 12) and DMS/P/O profiles (Figure 20) at Liège site. Those results are in agreement with previous sea ice DMSP studies which generally revealed a weak relationship between DMSP and chlorophyll *a* [e.g. Trevena et al., 2003] with the exception of particular cases following data selection prior to statistical investigation [Curran et al., 1998; Trevena and Jones, 2012]. No straightforward relationship between algal biomass parameters such as chlorophyll *a* and algal DMSP production has to be anticipated as the ability to produce DMSP is species-specific and physiological conditions of the algal cells affect DMSP production [Stefels et al., 2007].

Taxonomic composition of algal community – The apparent predominance of flagellates over all other autotrophic taxa revealed by the partial dataset (Figure 14 and Figure 15) at both sites is challenged by the observations made by Fritsen et al. [2011] who confirmed the predominance of dinoflagellates at Brussels site but found a diatom-dominated community at Liège site. These authors attribute this difference in algal community composition between sites to the acknowledged ability of dinoflagellates to synthesise elevated concentrations of mycosporine-like amino acids in response to increased UV radiations. The reduced snow depths hence higher

UV dose encountered at Brussels site would have favoured the development of dinoflagellates at the expense of diatoms unlike at Liège site where they would have remained dominating under the cover of a thicker snowpack. The discrete nature of the taxonomic observations performed at various depths amongst several stations in the present study and the depth integrated values of abundance reported for one station at each site by Fritsen et al. [2011] make it nevertheless difficult to compare both datasets. The Fritsen et al.'s scenario [2011], however, is contradictory to the transient predominance of diatoms observed in the upper layers at Brussels 4 (Figure 14) which coincided with the lowest snow thickness record at the ice core location (Table 4) and following a period of high UVB dose (Figure 2). It suggests that other processes were at stake to control that apparent fast change in surface community composition. Nutrients dynamics controlled by brine drainage is a plausible candidate. Nitrate refuelling of the surface layer by upwards seawater movement ensuing a brine drainage episode between Brussels 3 and Brussels 4, as suggested by the value of R_a at Brussels 3 (Figure 11), is expected to have temporarily restored favourable conditions for the growth of diatoms at the expense of flagellates. This explanation is debatable as not supported by the nutrient profiles. Processes occurring at rates higher than the sampling interval like intense uptake by the growing ice algal community might however have concealed the expected increase in nutrients. Thomas et al. [2010] suggested that differences in nitrogen assimilation patterns within sea ice assemblages would play a role in determining the species composition of the ice algal community. In temperate seas, Tungaraza et al. [2003] demonstrated that diatom growth was favoured by higher uptake rates of nitrate with respect to *Phaeocystis* when nitrate constituted the major dissolved form of nitrogen and ammonium levels were low. Diatom was, on the contrary, disfavoured with respect to *Phaeocystis* when ambient concentrations of reduced nitrogen (like ammonium) increased. Provided the same applies to sea ice algae, this might have explained the relative higher biomass of diatoms in the surface algal community at Brussels 4. Completion of the taxonomic observation dataset might allow to further support those assumptions. As discussed below, the widespread occurrence of dinoflagellates and other flagellates at both sites would have favoured the elevated concentrations of DMSP and DMS observed.

Nutrients – Significant deviation from the TDL indicates involvement of control processes distinct from conservative concentration/dilution during freezing/melting of sea ice, and rather associated with biological activity [Gleitz et al., 1995]. Excess concentrations of phosphate and ammonium with respect to the TDL have been proposed to result from osmotic cell lysis and ensuing phosphorus remineralisation [Thomas et al., 2010] and grazing activity coupled to heterotrophic nitrogen remineralisation, respectively [Schnack-Schiel et al., 2004]. In the view of the nutrients profiles (see Figure 16, Figure 17, Figure 18 and Figure 19), nitrogen remineralisation was a general feature of the ice cover at Brussels and Liège while phosphorus remineralisation is limited to the bottom of the sea ice cover at Brussels and in the top 0.1 m of Liège 5. The latter is likely to be attributed to the surface flooding event witnessed at that time that would have conveyed heterotrophic organisms from surrounding seawater. Depletion of nitrate and silicate with respect to the TDL reveal uptake and utilization by sympagic organisms [Gleitz et al., 1995]. Figure 17 and Figure 19 show that nitrate uptake was a general feature of the ice cover at both sites and was maximal in the surface layer indicating the predominance of the surface community. While nitrate concentration tended towards TDL values at the bottom of the ice in Liège, they remained clearly depleted at Brussels what might reveal a lower algal activity due to light limitation at the bottom of the ice cover at Liège. Silicate depletion in the lower half of the ice cover at Brussels and in the interior ice at Liège indicated uptake by diatoms as silicate is essential for the formation of their frustules [Thomas et al., 2010]. Taxonomic observations performed at depths corresponding to those depletion zones (Figure 14 and Figure 15) revealed that numerous empty frustules of diatoms were always present indicating thereby diatom mortality as remains of a potentially past important community. Even though there is no evidence of the dissolution of diatom frustules in the sea ice environment [Thomas et al., 2010], the elevated silicate concentrations observed in the top 0.3 m of the ice cover at Brussels 1 might result from such a process. As stated above, coincidence of this local maximum of silicate with those of phosphate, ammonium and nitrite might indicate that the ice cover had not witnessed brine drainage for some time allowing the local accumulation of those compounds as a result of heterotrophic activity. In the perspective of a nutrient control on algal DMSP and DMS production, a few studies have focused on nitrogen.

Sunda et al. [2007] demonstrated that some diatom species could respond to N-limitation by increasing their DMSP content. These authors suggest that DMSP would be produced to counteract the induced cellular oxidative stress on the one hand, and as an alternative to N-containing cellular osmolytes, saving N for other metabolic uses, on the other hand. Intracellular cleavage of DMSP into DMS and acrylate is very likely to ensue as those compounds proved to be far more effective at scavenging hydroxyl radicals than DMSP [Sunda et al., 2002]. As stated above in the view of the nutrients profiles, the ice cover at both sites seemed nitrate-limited. This observation is supported by the correlation analysis indicating that nitrate showed a moderate correlation with DMS and DMSO and a strong correlation with DMSP (Table 4). Further support or rejection of the hypothesis of the global nitrate-limitation within the sea ice cover of ISB might have been provided with the comparison of brine normalised concentrations of nitrate or total inorganic nitrogen with the half saturation constant for nitrate uptake as previously carried out by Becquevort et al. [2009] and Meiners et al. [2011]. To assess nitrate limitation in their sea ice brine samples, these authors used the half saturation constant for nitrate uptake by diatoms published by Sarthou et al. [2005]. Such a comparison to assess nitrate limitation at ISB would be invalid as the sympagic community of Brussels and Liège sites was apparently dominated by flagellates. Moreover, half saturation constants for nutrient uptake determined in the open ocean environment seem to be hardly applicable to the sea ice matrix and not appear in bulk ice or brine samples as nutrient limitation can occur at small scales (i.e. brine pocket) as demonstrated by Fripiat et al. [2007]. Whether and to what extent the apparent and systematic nitrate-limitation observed in the ice cover of Brussels and Liège site influenced the production of DMSP and DMS by the sympagic community in place at the time of the observation is not known. It is plausible that nitrogen limitation acted as co-stressor along with other factors like UV radiations to induce a physiological response from sympagic organisms involving DMSP and DMS as suggested by Sunda et al. [2007] and Harada [2009]. Besides this co-stressor role, global nitrate limitation of the ice cover might have been the trigger for the shift in community succession from an algal community dominated by diatoms to an algal community dominated by flagellates before arrival on site. As dinoflagellates and other flagellates like *Phaeocystis antarctica* are acknowledged to exhibit larger DMSP content and

DMSP lyase activity than diatoms [Stefels et al., 2007], this shift in algal community would have been critical in determining the ability of the ice cover to produce the observed amounts of DMS/P/O.

As already mentioned in previous sea ice studies, the overall lack of relationship between physical and biologically-mediated variables is not astonishing to result from field data. This lack of correlation between variables can be seen as the result of temporally decoupled physical and biological processes. The record of physical variables is to be considered as a snapshot and the measurement of dissolved constituents providing time-integrated information resulting from a suite of physical and biogeochemical processes [Meiners et al., 2009]. This decoupling between variables is expected to further widen when an active brine drainage regime has settled within the ice cover as in the course of this study.

Variations of sea ice DMS-DMSP-DMSO burdens and inferred fluxes

In attempting to take into account the atmospheric thermal and radiative forcing history to explain the evolution of biological and biologically-mediated variables, time integrated physical variables were computed and compared to burdens of chlorophyll *a*, DMS, DMSP, DMSO. Cumulative freezing degree days between stations were computed according to Weeks [2010] to estimate the "amount of cold" that was witnessed by sympagic organisms. Cumulative doses of PAR, UVA and UVB between stations were computed to estimate the amount of radiation received. Those variables were computed as quantities received by sympagic organisms as if they were located at the surface of the ice and do not encompass the insulation effect of the snow cover on temperature nor the attenuation effect of snow and ice on radiations. Focusing on the top centimetres of the ice cover where most of the changes were observed, this comparison may not be unreasonable. The steady increase of the cumulative dose of UVA logically paralleled that of PAR (Figure 23) as there is virtually no gaseous absorbers in the wavelength range of UVA in the atmosphere. As the amount of UVB reaching the surface is influenced by the presence of clouds, notably, it was anticipated to observe higher cumulative dose of UVB to coincide with the strongest cold episode witnessed at ISB (station 4 at Brussels and Liège) characterised by clear sky conditions.

DMS/P/O burdens – With the exception of Liège 2, Brussels site exhibited higher burden values as well in the top 0.2 m (Figure 23) as for the total thickness (Figure S1). DMS and DMSP burdens computed in this study were on the average 3–5 times and 2–4 times higher, respectively than those computed in summer first year sea ice in the Weddell Sea by Tison et al. [2010], stressing the favourable conditions brought by the spring transition for the production of DMS/P/O in the ice cover at ISB. Those authors report on the average, DMSO burdens values comparable (Brussels) to 2 times higher (Liège) than the DMSO burdens measured in this study (unpublished data). DMSO was a minor contributor to the total DMS/P/O pool with proportion ranging from 2 to 7%. This could be a widespread feature in sea ice as first year summer sea ice of the Weddell Sea also exhibited relatively low proportions ranging from 10 to 17% of the total DMS/P/O pool (unpublished data). Such observations are supported by Asher et al [2011] who recently identified DMSO reduction as a major pathway for DMS production in sea ice. As already observed by Tison et al. [2010], it is assumed that the vast majority of DMS and DMSP found in the water column (Figure 24) originated directly from the ice in the view of the very low levels of chlorophyll *a* observed at all times in the water column. It invalidates thereby the hypothesis of production within the water column. The parallel evolution of seawater DMS and DMSP burdens (Figure 23) with burdens in the ice, with the exception of DMS at Brussels 2 (Figure 24), further supports that DMS/P found in the water column originated from the ice. The systematically higher values of seawater DMS and DMSP burdens observed at Brussels site supported the greater occurrence of brine drainage at that site in relation to Liège site. Sea ice could be considered at that period of the year to be the main source of reduced sulphur compounds for the environment. The accumulation of freezing temperatures at stations 1, 2 and 3 at both sites was rather constant and hardly explained the variations of DMS/P/O burdens observed. At stations 4 and 5, both sites exhibited however the same behaviour. Drastic increase of the DMS/P/O burdens at station 4 coincided with the highest value of cumulative FDD. As the cumulative radiations doses increased steadily and did not show any strong deviation from the trend compared with the FDD, it

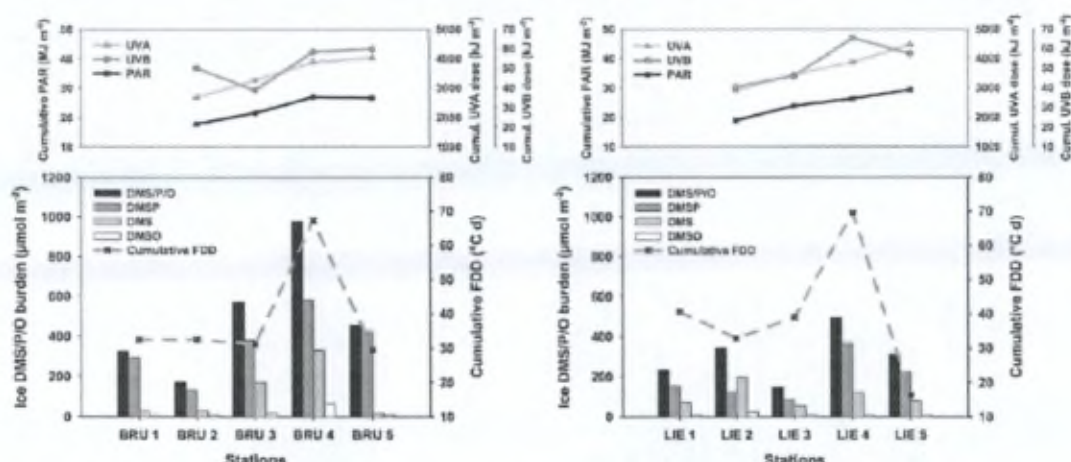


Figure 23 Evolution of cumulative dose of UVA, UVB and PAR computed between consecutive stations at Brussels (upper left panel) and Liège (upper right panel) sites. Top 0.2m ice DMS, DMSP and DMSO burdens shown with the cumulative freezing degree day (FDD) between consecutive stations at Brussels (lower left panel) and Liège (lower right panel) sites.

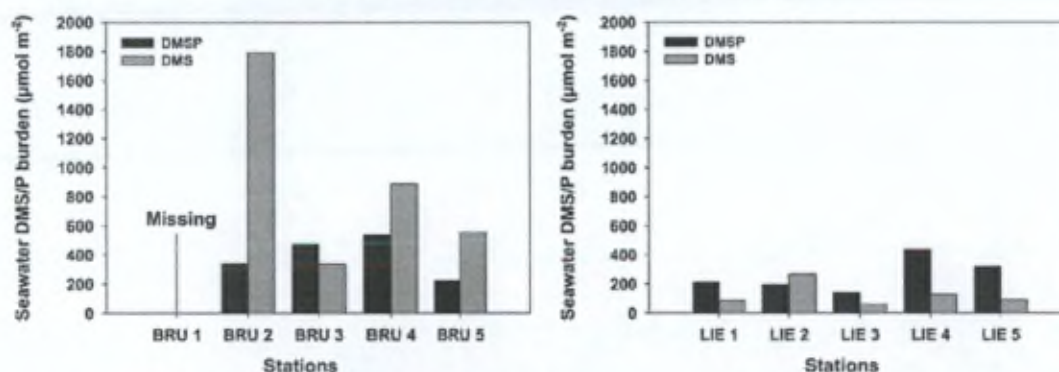


Figure 24 Evolution of seawater DMS and DMSP burdens at Brussels (left) and Liège (right) sites.

suggests that it was the accumulation of freezing temperatures, once a threshold value was exceeded, that triggered the response of the ice biota at ISB with an increase of DMS/P/O burdens. As already stressed in previous studies, the cycle of DMS/P/O is complex and determined simultaneously by numerous factors [Stefels et al., 2007] suggesting that synergistic effects of co-stressors (low temperature, high salinity, high amount of radiations) were very likely to occur in the ice cover at ISB. The individual contribution of those factors was nevertheless impossible to assess from field data of this study. The overall lower values of DMS/P/O burdens observed at Liège were likely the result of the insulation effect of the snowpack, mitigating thermal (hence osmotic) and radiative

stress to a higher extent, inducing therefore a weaker response of the ice algal community at that site than at Brussels. Occurrence of brine drainage is the best candidate to explain the drop of burdens observed between station 4 and 5 at both sites as suggested by the noticeable drop of DMS burden, only occurring in a dissolved state in the ice, compared with those of DMSP and DMSO, which also can occur in the particulate phase and may therefore exhibit a higher resistance to drainage from the ice with the brine as shown by Tison et al. [2010].

Increase in DMS/P/O burdens observed at Brussels 4 may have been partly related to the increase of the autotrophic biomass in the view of the parallel

Table 5 Ice DMS, DMSP, DMSO and total DMS/P/O fluxes computed between the sampling events at Brussels and Liège sites. A negative value means an outgoing flux. Values are in $\mu\text{mol m}^{-2} \text{d}^{-1}$.

Interval	DMSP	DMS	DMSO	DMS/P/O
Bru 1 - Bru 2	-38	2.9	1.5	-33
Bru 2 - Bru 3	78	39	2.2	119
Bru 3 - Bru 4	54	37	10	101
Bru 4 - Bru 5	-66	-76	-12	-155
Lie 1 - Lie 2	-4	36	3.9	36
Lie 2 - Lie 3	-11	-41	-3	-56
Lie 3 - Lie 4	59	14	-0.3	73
Lie 4 - Lie 5	-24	-8	-0.3	-32

increase in chlorophyll *a* (Figure S2). However, data showed an opposite trend at Liège 4, exhibiting a strong decrease of chlorophyll *a* with respect to Liège 3, but an increase in DMS, DMSP and DMSO burdens. This observation further supports a general control of the environmental constraints on the ice DMS/P/O dynamics.

DMS/P/O fluxes – The same approach as Tison et al. [2010] was used to compute fluxes of DMSP, DMS and DMSO from the sea ice with its associated drawbacks, notably the fact that the fate of the DMSP, DMS or DMSO (atmosphere and/or ocean) cannot be distinguished. A decrease of the sea ice DMS/P/O burdens between two successive stations can be seen as a global flux of matter from sea ice to both or either the atmosphere (as far as DMS is concerned) or the ocean. Negative fluxes of DMS/P/O were computed between Brussels 1 and 2, Brussels 4 and 5, Liège 2 and 3 and Liège 4 and 5 (Table 5). All those events are presumed to have contributed to increase seawater DMS and DMSP burdens as a result of brine drainage. Even though the potential for brine drainage would have only been sufficient between Brussels 1 and 2 according to the Ra criterion (Figure 11), the constantly low levels of chlorophyll *a* observed in the under-ice water column suggest a sustained input of DMS, DMSP (and presumably DMSO) from the sea ice cover rather than an algal production in the water column. In the view of the sustained strong wind episode and high air temperatures that were observed from day 289 to day 294 at ISB [Vancoppenolle et al., 2011], venting of DMS to the snowpack and then to the atmosphere is also very likely to have contributed to the negative fluxes of DMS computed between Brussels 4 and 5

and Liège 4 and 5. The average contribution of the ice cover of Brussels and Liège to the regional sulphur budget over the study period amounted to $31 \mu\text{mol m}^{-2} \text{d}^{-1}$ DMS, $36 \mu\text{mol m}^{-2} \text{d}^{-1}$ DMSP and $4 \mu\text{mol m}^{-2} \text{d}^{-1}$ DMSO. As observed for burdens, DMS/P/O flux values at Liège site were generally lower than those observed at Brussels site. It is assumed that the thicker snowpack at Liège site would have limited venting of DMS to the atmosphere. The potential for brine drainage would have been lowered at Liège due to the thicker snowpack and ice cover that would have acted together to hamper the development of sharp temperature and brine salinity gradients and the granular texture profile that would have raised the brine percolation threshold.

The average flux value of DMS+DMSP is up to 13 times higher than that computed for decaying summer sea ice by Tison et al. [2010]. Other studies reporting direct measurement of flux values for sulphur compounds from the sea ice are scarce and focused exclusively on DMS [Zemmelink et al., 2008; Nomura et al., 2012]. To compare the data of the present work to those studies, a worst-case scenario was considered assuming that 100% of the DMS flux from the ice was directed towards the underlying ocean. As it is generally admitted by several authors [e.g. Pedrós-Alió and Simó, 1999; Archer et al., 2002] that only about 10% of the seawater DMS would eventually be vented to the atmosphere, the contribution of sea ice to atmospheric DMS would have then amounted to about $3 \mu\text{mol m}^{-2} \text{d}^{-1}$. Moreover, as it has been assumed above that most of the DMS observed in the under-ice water column at that period originated from sea ice, the observed

variation of under-ice DMS burden would have generated an additional sea-air flux of $14 \mu\text{mol m}^{-2} \text{d}^{-1}$, presuming that the entirety of the 30 m water column had contributed to that flux. This value decreased to $0.8 \mu\text{mol m}^{-2} \text{d}^{-1}$ when the very top meter of the water column was considered. This contribution of sea ice to the atmospheric DMS is likely to be underestimated as meteorological conditions which prevailed during the study certainly favoured venting of DMS to the atmosphere. A non negligible part of DMSP which drained along with sea ice brines might also have been cleaved into DMS and eventually reached the atmosphere. The release of sympagic DMSP producers into the ocean with draining brines might have exposed organisms to a rapid salinity drop that would have favoured the release of DMSP in the seawater by exudation or cell lysis and then eventually led to an enhanced DMS production and would explain the high DMS:DMSP values (average ratio 3.0) observed in the under-ice water column. Due to the temporal resolution achieved in this study, missed brine drainage events, might have led to further underestimate the sea ice contribution to the regional sulphur budget. While those estimates fall within the range of ice-air DMS fluxes measured by Zemmelen et al. [2008] and Nomura et al. [2012], they seem low in comparison to the estimates of DMS flux made by Trevena and Jones [2012] over a variety of sea ice environment across the Antarctic sea ice zone. In the absence of any other existing parametrisation to compute ice-air gas exchanges, these authors used the flux calculation procedure of Liss and Merlivat [1986] and applied it to sea ice as if it was a free surface. While the assumption could hold for a surface slush layer, it is likely to overestimate gas exchanges if snow covers the ice surface or even in the case of bare sea ice which exposes a fairly lower cross-section of brine inclusions to the atmosphere. The role of the snowpack in controlling the gas emission from sea ice to the atmosphere had yet already been stressed for CO_2 by Nomura et al. [2010] and for DMS by Zemmelen et al. [2008]. In a more detailed study on the topic, Nomura et al. [2012] recently reasserted the primary importance of the snow cover as well as that of the superimposed ice in controlling the ice-air DMS flux. In view of those recent findings and as a variable snow cover was always present at the ice core locations, ice-air DMS fluxes were not computed using the approach of Trevena and Jones [2012]. Despite this active transfer of sulphur compounds from sea ice to the atmosphere and the ocean, DMS/P/O dynamics resulted along the 20 day

observation period in an overall net production of $140 \mu\text{mol DMSP m}^{-2}$ and $14 \mu\text{mol DMS m}^{-2}$ at Brussels and of $104 \mu\text{mol DMSP m}^{-2}$ and $3 \mu\text{mol DMS m}^{-2}$ at Liège site. The overall net production of DMSO was $5 \mu\text{mol m}^{-2}$ at Brussels and close to $0 \mu\text{mol m}^{-2}$ at Liège. The DMS/P production capacity of the spring sea ice cover at ISB contrasts with that of a typical summer sea ice cover as observed in the Weddell Sea by Tison et al. [2010]. These authors observed indeed a continuous outgoing flux of DMS/P along the 31 day observation period resulting in a net loss of $174 \mu\text{mol DMSP m}^{-2}$ and a slight gain of about $2 \mu\text{mol DMS m}^{-2}$ mainly as a result of the progressive leaching of the ice cover by the snow meltwater and bottom melting of the sea ice cover. The variation in the DMS flux values observed in the present study supports the view of Gabric et al. [2005] and Zemmelen et al. [2008] that this compound would be emitted from sea ice by pulses.

6. CONCLUSIONS

The cycling of atmospheric fronts witnessed at ISB induced a thermal forcing which influenced differently the two contrasting study sites. The overall nitrate depletion of the sea ice cover at both sites likely induced a shift in the sea ice algae community composition towards taxa renowned for their ability to synthesise high concentrations of DMSP and DMS (i.e. dinoflagellates and *Phaeocystis antarctica*). The observed levels of DMS, DMSP and DMSO were likely the result of complex interactions of environmental stressors and of the sulphur compounds with each other. The most important production event of DMS, DMSP and DMSO in the ice was apparently triggered by the accumulation of freezing temperatures and potential ensuing thermal and osmotic stress. Biota thriving in a relatively thin ice cover with little snow (likewise at Brussels site) is anticipated to provide a stronger response to thermal, osmotic and radiative stress than biota developing within a thicker ice cover overlaid by a thicker snowpack. Relatively thin ice covers comparable to that observed at Brussels site are also likely more prone to exchange of biogeochemical tracers (like DMS, DMSP and DMSO) with the environment through brine drainage. Sea ice cover at ISB behaved like a reactor during the spring transition in the Bellingshausen Sea, maintaining sympagic organisms exposed to environmental stress (thermal, osmotic and radiative) and actively producing and exchanging DMS, DMSP and DMSO with the environment as attested by the significant inferred DMS and DMSP

flux values, one order of magnitude higher than DMS and DMSP flux values reported for Antarctic summer sea ice [Tison et al., 2010]. Although the concentrations of DMS, DMSP and DMSO are not the highest ever reported in the sea ice environment, periodic forcing of the system by atmospheric thermal cycling could ensure a sustained production of DMS, DMSP and DMSO and their release in the environment. Shelf-life of the biological component of the system (production of DMS, DMSP and DMSO) is likely to be determined by nutrient availability while the physical component (release of DMS, DMSP and DMSO in the environment) is likely to be constrained by the amount of salt remaining in the ice cover. With the increasing occurrence of atmospheric anomalies in the Bellingshausen Sea, grows the chance to witness wind-driven compaction of sea ice and greater precipitations [Stammerjohn et al., 2008] affecting the distribution of snow at the ice surface. This may provide favourable conditions for periodic flooding of the ice surface and resupply of the ice cover with nutrients and salts, reactivating thereby the system pending the next event of atmospheric forcing. Trends towards overall less multiyear ice and preponderance of young sea ice in the Bellingshausen Sea could in the future positively impact the production and release of DMS, DMSP and DMSO by sea ice and extent it to the overall Bellingshausen Sea area. As already mentioned in previous studies [Tison et al., 2010], further controlled experiments in laboratory, potentially simplified with respect to the number of factors studied, with exposure of sympagic organisms to ranges of temperatures and salinity encountered in sea ice brines, are required to disentangle the complexity of the DMS/P/O dynamics in sea ice as it proved to be hardly feasible from field data.

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SUPPLEMENTARY MATERIAL

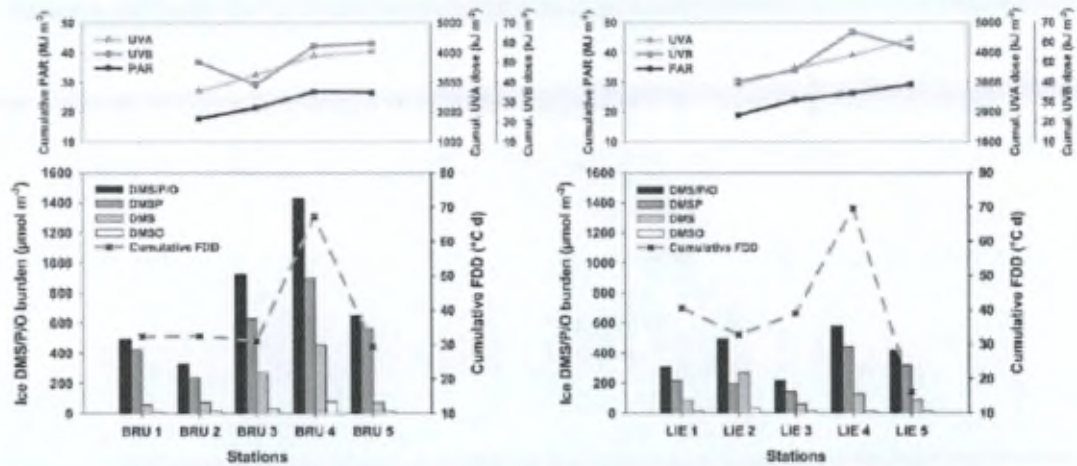


Figure S1 Evolution of cumulative dose of UVA, UVB and PAR computed between consecutive stations at Brussels (upper left panel) and Liège (upper right panel) sites. Total DMS, DMSP and DMSO burdens shown with the cumulative freezing degree day (FDD) between consecutive stations at Brussels (lower left panel) and Liège (lower right panel) sites.

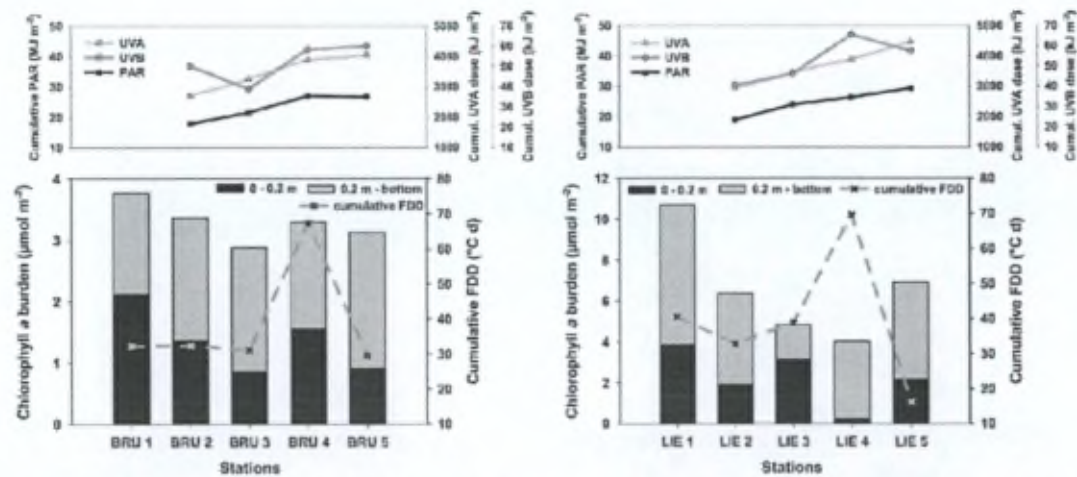


Figure S2 Evolution of cumulative dose of UVA, UVB and PAR computed between consecutive stations at Brussels (upper left panel) and Liège (upper right panel) sites. Sea ice surface (0.2 m) and total and chlorophyll a burdens at Brussels (BRU) and Liège (LIE) sites shown along with the cumulative freezing degree days (FDD) computed between successive stations.



CHAPTER V: Temporal evolution of gas properties in growing sea ice: revealing the impact of physicochemical processes

Paper 6 :

Physico-chemical controls on gas properties during natural and experimental sea ice growth.

In review. by Brabant F., V. Verbeke and J.-L. Tison, 2008.

Contribution of F. Brabant: Analysis of the data. Writing of the paper.

1 **Physico-chemical controls on gas properties during**
2 **natural and experimental sea ice growth**

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Abstract. This paper describes and discusses the evolution of gas properties (total gas content, gas composition in O_2 and N_2) in artificial (INTERICE III experiment) and natural sea ice (Mc Murdo Sound, Antarctica) during its growth. Using the O_2/N_2 ratio as a benchmark, we identify three physico-chemical processes that are able to significantly alter the gas properties of growing sea ice. *Initial dissolved gas entrapment* decreases O_2/N_2 slightly below the seawater value, *post-entrapment diffusion* induces a further drop of the ratio down to the *equilibrium* value of 0.48 and *bubble nucleation* (if present) is finally able to depress O_2/N_2 towards the value of the ratio in the atmosphere (0.27). The impact of the two first processes on the sea ice gas composition was estimated successfully using a boundary layer approach. This study finally underlines the importance of diffusion in controlling exchange processes between growing sea ice and the underlying sea water.

1. Introduction

Despite its gilt-edged importance for the mechanical, thermal and electromagnetic properties of sea ice, studies dedicated to gas inclusion in sea ice (both concerning total gas content and gas composition) are, as it were, almost nonexistent. More thorough study of the sea ice gas properties could also provide us with valuable information allowing to decipher the gas dynamics issue in sea ice. The latter is expected to be of primary importance for biogeochemical studies since sea ice has proven to be a permeable medium to gas exchange once particular conditions are fulfilled (the 'law of fives': brine volume fraction of 5% reached for a temperature $\simeq -5^{\circ}\text{C}$ assuming a bulk sea ice salinity of 5 [Golden *et al.*, 1998]).

Sea ice has been reported to have gas properties different from those of glacier or iceberg [Matsuo and Miyake, 1966]. Numerous processes can influence the gas content of sea ice during either its growth or its decay. In his work, Tsurikov [1979] identified up to nine processes able to modify the gas content of sea ice among which three purely physico-chemical ones are thought to be predominant: (1) the release of gases from solution during the initial freezing of sea water, (2) the substitution of gas for a part of the brine through the interconnected vertical brine channels in the course of melting and (3) the release of gas from entrapped brine as the result of its further freezing. The importance of process (1), both for total gas content and gas composition of sea ice will be discussed further in this paper. The total gas content in sea ice is smaller than in meteoric glacier ice (about 85–130 ml $\text{kg}_{\text{ice}}^{-1}$ [Raynaud and Lebel, 1979]) and generally less than the total gas content of instantly frozen seawater resulting in 23.75 ml STP $\text{kg}_{\text{ice}}^{-1}$ [Tison *et al.*, 2002]. The

most extreme values of total gas content in sea ice were observed by Matsuo and Miyake [1966]. These values are ranging between 2.2 and 21.2 ml STP $\text{kg}_{\text{ice}}^{-1}$. More recently, Tison *et al.* [2002] observed similar values for the total gas content in the artificially grown sea ice from the INTERICE II experiment (from 3.5 up to 18 ml $\text{kg}_{\text{ice}}^{-1}$). Rysgaard and Glud [2004] measured comparable total gas volume (0–20 $\text{cm}^3 \text{l}^{-1}$ sea ice) in the lower 50–60 cm of sea ice cores from Young Sound (Greenland) but astonishingly high values in the upper sea ice layers (70–130 $\text{cm}^3 \text{l}_{\text{ice}}^{-1}$). Given that there are no indication provided by the authors about the ice texture in this part of the ice cover, it is difficult to interpret this discrepancy.

The gas composition of sea ice (using here the O_2/N_2 ratio) also differs from glacier ice and from the atmosphere ($\text{O}_2/\text{N}_2 \simeq 0.27$). Tsurikov [1979] showed that sea ice can be either relatively depleted ($\text{O}_2/\text{N}_2 = 0.19$) or relatively enriched in O_2 ($\text{O}_2/\text{N}_2 = 0.46$). In case of negligible impact of biological activity on the gas composition within the ice, sea ice is usually depleted in O_2 as compared to sea water (0 °C, salinity: 35) saturated with air ($\text{O}_2/\text{N}_2 = 0.59$). Recent studies [Killawee *et al.*, 1998; Tison *et al.*, 2002] explain this relative lack of O_2 by chemical fractionation of gases diffusing through a boundary layer formed at the ice-water interface during the ice growth. The boundary layer approach postulates the presence of a thin layer of fluid ahead of the downward freezing front in which solute transport occurs by diffusion only and whose thickness (millimeter scale) is controlled by convection at its base. This concept has been used in previous studies to describe solutes exchanges in front of the ice-water interface during freezing of water [e.g. Weeks and Ackley, 1986; Souchez *et al.*, 1988; Tison and Haren, 1989; Eicken, 1998]. The boundary layer model was already shown to be relevant for studying the fractionation

of isotopic species at the interface during ice growth [Souchez *et al.*, 1987] and for the simulation of isotopic and salinity profiles in sea ice cores from the Weddell Sea [Eicken, 1998]. The boundary layer approach formulated as the Fick's first law of diffusion has also been used in predicting the dynamics of gases at the ice-water interface [Killawee *et al.*, 1998; Tison *et al.*, 2002]:

$$\Phi = D_x \frac{C_{iw} - C_{bw}}{z_{bl}} - C_{bw} \nu_i = 0 \quad (1)$$

where Φ is the flux of a given solute species x , D_x is the molecular diffusivity of the solute x (1.17 and $0.95 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at 0°C for O_2 and N_2 , respectively [Broecker and Peng, 1974]), C_{iw} is the solute concentration at the ice-water interface, C_{bw} is the solute concentration in the bulk water, z_{bl} is the boundary layer thickness and ν_i is the linear rate of advance of the freezing front. This formulation of the Fick's first law of diffusion applies when a steady state is reached (outgoing solutes flux from the boundary layer equal to the incoming solutes flux from the freezing process). This approach is theoretically restrained to the case of congelation ice with a smooth freezing interface (fresh water) but has been shown to be also valid for the growth of sea ice [Weeks and Ackley, 1986, and references therein]. By rearranging of equation 1, the *enrichment factor* or enrichment coefficient of a solute species at the interface (C_{iw}/C_{bw}) can also be defined as:

$$\frac{C_{iw}}{C_{bw}} = \frac{\nu_i z_{bl}}{D_x} + 1 \quad (2)$$

In his early work, *Carte* [1961] suggested that, on bubble nucleation, the composition of the gas phase is controlled by diffusion processes between the water close to the interface and the air bubble. In a more recent experimental sea ice study *Tison et al.* [2002] discussed the evolution of the gas composition at the ice-water interface in the absence of any biological activity. In their interpretation, bubbles originally have a gas composition close to that of the water from which they have nucleated ($O_2/N_2 = 0.59$ in sea water). As long as the bubbles are not isolated in the ice, diffusion of gas through the boundary layer occurs, decreasing the O_2/N_2 ratio according to the respective diffusion rates of the different gases ($D_{O_2} > D_{N_2}$). The O_2/N_2 ratio of the bubbles will therefore progressively tend to the atmospheric value of 0.27. In this paper we will further test and refine these interpretations by observing the evolution of the total gas content and the gas composition (here addressed by means of the O_2/N_2 ratio) of young sea ice during its growth in a new set of experiments under controlled conditions (INTERICE III experiment, see description below). At the conclusion of the study, three key processes, able to significantly alter the gas composition of sea ice (both dissolved and as bubbles) were identified on the basis of observations made on a short time series : 1) the *initial dissolved gas entrapment*, 2) the *post-entrapment diffusion* through the boundary layer and 3) the *bubble nucleation*. The relevance of the boundary layer approach to address the question of the gas diffusion at the ice-water interface will also be tested. To that purpose we chose to confront the results of the calculations with the measurements of the total gas content and composition performed in a previous study [*Verbeke et al.*, 2002] on cold mid-winter first-year sea ice cores from Mc Murdo Sound, Antarctica. The work focused on the gas properties of a

115 cm columnar ice portion of the ice cover located at a depth included between 22 cm
 and 137 cm. The rationale behind for re-analyzing the data of *Verbeke et al.* [2002] was
 guided on the one hand by the 'textbook case' nature of the ice (congelation ice, relative
 brine volume at any time <5%) and, on the other hand, because the influence of biological
 activity (if present) on gas properties of sea ice has proven to be negligible [*Verbeke et al.*,
 2002]. This last point ensures that any change observed in the gas properties is only of
 physical or chemical origin.

2. Sites description

2.1. INTERICE III experiment

The INTERICE III experiment has been held in the environmental basin at HSVA
 (Hamburgische Schiffbau- und VersuchAnstalt) in Hamburg, Germany from 30 April to 18
 May 2001. The aim of the overall project was the assessment of the relationships between
 the biological processes, the ice growth processes and the sea ice properties at the onset of
 freezing. Ten polyethylene tanks were placed into the main basin and filled with distilled
 water whose salinity were determined by addition of *Ocean Sea Salt* (Aquarium Systems,
 France). The layout of the tanks in the basin is depicted on figure 1. Tanks A, B and
 C were inoculated with the Antarctic algae *Fragilariopsis cylindrus* (initial chlorophyll *a*
 concentration of $11 \mu\text{g l}^{-1}$). Nutrients were also added to the tanks A to D. Finally, these
 four tanks were enlightened by fluorescent tubes (Osram, ultra-white) and exposed to an
 irradiance gradient ($34 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ for tanks A and B, $17 \mu\text{mol photons m}^{-2}$
 s^{-1} for tank C and no light provided to tank D). Ice from tanks D, E, F, G, H, I and J
 were not considered in the framework of this study. Ice growth was initiated seven days
 after algae inoculation by reducing the room temperature to $-10 \pm 2^\circ\text{C}$ and ice crystal

formation was initiated by spraying of distilled water over the water surface [Haas *et al.*, 1999; Giannelli *et al.*, 2001; Krembs *et al.*, 2001; Mock *et al.*, 2002]. In this paper, we focus on the gas properties of two time series sampled in tanks A (*High Light 1*) and C (*Low Light*). The sampling took place at days #3, #10 and #18 after growth initiation, following a procedure developed to minimize brine drainage from the sample and surface flooding [Cottier, 1999; Cottier *et al.*, 1999; Tison *et al.*, 2002]. Further details on the experimental setting can be found in the work of Mock *et al.* [2002] and Papadimitriou *et al.* [2003].

2.2. Natural sea ice samples (Arrival Heights, McMurdo Sound, Antarctica)

The cores of natural sea ice studied in this paper were taken in the course of October 1999 at Arrival Heights, a fast ice station close to Mc Murdo Station, Mc Murdo Sound, Antarctica (see map in figure 2, Verbeke *et al.* [2002]). The collected samples were then shipped back to Brussels at the constant temperature of -28°C for further laboratory analyses. The ice thickness at that location was more than 220 cm. The texture profile, revealed by ice thin sections, was comparable to what was previously observed by Jeffries *et al.* [1993] in the same sector and displayed the following sequence (from the top to the bottom): granular ice (0–22 cm), columnar ice (22–137 cm), mixed columnar/granular ice (137–198 cm) and platelet ice (198–222 cm). The columnar ice section of the ice cover showed banded features whose chemical and gas properties were thoroughly analysed by Verbeke *et al.* [2002] in order to elucidate the processes through which the banding originated. Further details about the ice characteristics at that location and season can be also be found in the work of Trodahl *et al.* [2000].

3. Methods

3.1. Measurements

Ice and water temperatures were measured with a resolution of 2 cm, starting from 2 cm above the water surface, using an array of Siemens K17 thermistors (see *Mock et al.* [2002] for further details). Ice bulk salinities were also measured with a resolution of 2 cm. The salinity of the melted ice samples, maintained at 25 ± 0.01 °C in a thermostatically controlled bath, were then measured using a Tacussel CD 810 conductimeter equipped with a XE100-type probe (Radiometer Analytical). The overall precision of the method is ± 0.05 [*Tison et al.*, 2002]. The total gas content was measured with a resolution of 2 cm using a melting-refreezing procedure coupled with a Toepler pump extraction [*Blunier et al.*, 1993; *Raynaud et al.*, 1988]. The relative standard error associated to the method is ± 2 –5% [*Martinerie et al.*, 1994]. Gas composition (O_2 , N_2) was measured each 2 cm using a dry-extraction technique by crushing [*Raynaud et al.*, 1982; *Barnola et al.*, 1983] prior to analysis with a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a molecular sieve column (precision: $\pm 0.8\%$). Because it occurs in a vessel initially evacuated at 10^{-3} Torr, the used dry-extraction procedure ensures the release of the gas contained in the ice both in a dissolved state in the brines and in the form of bubbles [*Tison et al.*, 2002; *Verbeke et al.*, 2002].

3.2. Theoretical estimates of the dissolved gas content at saturation in the sea ice brines

To support a thorough discussion of the gas profiles, it seemed useful to provide best estimates of the theoretical total gas content dissolved in sea ice brine inclusions at saturation. When thermodynamic equilibrium at atmospheric pressure is reached in sea ice,

the relative volume fraction of brine V_b/V and its salinity S_b can be deduced from phase relations [Assur, 1958]. Equations provided by Eicken [2003], compiled and rearranged according to Cox and Weeks [1983] and Lepparanta and Manninen [1988], allow to estimate the relative brine volume and brine salinity from measured ice temperature and bulk salinity. As a first step we calculate the brine salinity at a given depth, which is a function of the ice temperature assuming that thermodynamic equilibrium is reached, using:

$$S_b = \left(1 - \frac{54.11}{T}\right)^{-1} \times 1000 \quad (3)$$

where S_b is the brine salinity and T (°C) the measured ice temperature.

Knowing the bulk ice salinity, the relative brine volume V_b/V can be derived from:

$$\frac{V_b}{V} = \left(1 - \frac{V_a}{V}\right) \frac{\rho_i S_{si}}{F_1(T) - \rho_i S_{si} F_2(T)} \quad (4)$$

where V_a/V is the pore volume fraction, ρ_i is the density of pure ice, S_{si} is the bulk ice salinity and $F_1(T)$ and $F_2(T)$ are empirical polynomial functions derived from phase relations (coefficients to be found in Eicken [2003]). With the aid of the previously measured bulk salinity and ice temperature values, the relative brine volume can be calculated presuming that V_a is negligible, a reasonable assumption in cold ice [Eicken, 2003]. Empirical equations provided in the literature allow us to determine the solubility of a gas in a so-

lution on the basis of its temperature and salinity. *Garcia and Gordon* [1992] established such a relationship for O_2 :

$$\begin{aligned} \ln C_0^* = & A_0 + A_1 T_s + A_2 T_s^2 + A_3 T_s^3 \\ & + A_4 T_s^4 + A_5 T_s^5 \\ & + S(B_0 + B_1 T_s + B_2 T_s^2 + B_3 T_s^3) + C_0 S^2 \end{aligned} \quad (5)$$

with C_0^* the solubility of O_2 in μmol per volume of seawater, A_i , B_i , C_0 constant coefficients, S the salinity and T_s the scaled temperature. T_s is defined as follows:

$$T_s = \ln \left(\frac{298.15 - t}{273.15 + t} \right) \quad (6)$$

with t the temperature ($^{\circ}\text{C}$). *Hamme and Emerson* [2004] have empirically determined the different coefficients allowing to calculate the solubility of N_2 , Ar and Ne, using a similar relationship:

$$\begin{aligned} \ln C = & A_0 + A_1 T_s + A_2 T_s^2 + A_3 T_s^3 \\ & + S(B_0 + B_1 T_s + B_2 T_s^2) \end{aligned} \quad (7)$$

with C the gas concentration of N_2 , Ar or Ne at equilibrium with a moist atmosphere at 1 atm pressure ($\mu\text{mol kg}^{-1}$), A_i and B_i constant coefficients, T_s the scaled temperature as previously defined and S the salinity. At a given depth, the measured ice temperature and the calculated brine salinity are used both in the equation of *Garcia and Gordon* [1992]

to estimate O_2 solubility and in the equation of *Hamme and Emerson* [2004] to calculate N_2 and Ar solubilities. The theoretical total gas content (expressed in $ml_{air} STP kg^{-1}$) at saturation in brines at a given depth is finally calculated as the sum of the O_2 , N_2 and Ar solubilities (reasonably assuming that these three gases represent 100% of air) weighted by the value of the relative brine volume calculated at the same depth. This value can eventually be multiplied by a coefficient indicating the supersaturation level that has to be reached before bubbles nucleates. The value of the supersaturation coefficient depends upon the conditions reigning during sea ice formation. In calm conditions, a supersaturation level up to 2.2–2.5 must be fulfilled [Killawee *et al.*, 1998] while values of about 1.4 seem to be sufficient in the presence of a current that thins the boundary layer down [Tison *et al.*, 2002]. At a given depth, the difference between the computed solubility (multiplied by the supersaturation coefficient) and the measured total gas content should represent the fraction of the total gas content existing in the ice in the form of bubbles.

3.3. Caveats and limitations

Values obtained from this approach must be considered with precaution. Indeed, temperatures and salinities generally encountered in sea ice brines (especially in cold winter sea ice) are often beyond the salinity and temperature validity range of relationships allowing to compute the solubility of a given gas in a solution on the basis of its temperature and salinity. For the time being, no such relationship exists in the literature that could be directly applicable to the calculation of gases dissolved in sea ice brines [Thomas and Papadimitriou, 2003].

4. Results

4.1. Mc Murdo 99

In the cold natural ice from Mc Murdo Sound, the observed values of the total gas content are low (between 2 and 5.6 ml STP kg_{ice}^{-1}) although the observed total gas content is at any time higher than the computed air solubility in the brines (figure 2). Note however that the range of total gas content measured in the upper meter fits well with the calculated solubility range at the bottom of the sea ice cover.

On figure 3 it can be seen that the O_2/N_2 ratio varies scarcely along the studied ice core section. All measurement are located above the atmospheric value of the O_2/N_2 ratio (0.27) but below the *equilibrium* value of 0.48 (the physico-chemical meaning of which will be discussed later in this paper): O_2/N_2 ranges between 0.36 and 0.45 with a mean value of 0.43. Two couples of measurements located between 29.75 cm and 34.40 cm and between 56.90 cm and 58.65 cm show a relatively low O_2/N_2 ratio of 0.36 and 0.41 respectively. They are located close to natural fractures in the ice core.

4.2. INTERICE III

The total gas content profiles are similar in appearance for both the *Low Light* and the *High Light 1* experimental tanks at day #3 and day #10 (figure 4). The values of the total gas content range between 5.93 and 10.62 ml STP kg_{ice}^{-1} and are higher than the computed air solubility values already from the beginning of the experiment. On day #10, the profile of the measurements draws aside the profile of the computed air solubilities excepted for the two lowest values which meet the upper boundary of the 'solubility zone' (*Low Light*) or are included into it (lowest value in *High Light 1*). Here too, the relatively constant values of the upper layers (5-10 ml STP kg_{ice}^{-1}) fall into the range of expected

values from calculated solubilities in the bottom (permeable) layers. On day #18, the deviation of the profile with respect to the calculated air solubility profile remains in the first 10 cm of the ice cover while the total gas content increases dramatically up to 24.37 ml STP $\text{kg}_{\text{ice}}^{-1}$ (*Low Light*) beneath this depth (figure 4). By contrast with the total gas content, noticeably different values of O_2/N_2 can be observed between the profiles on day #3 as exhibited on figure 5. The measured O_2/N_2 values in the ice from the *Low Light* tank are close to the typical value of the ratio in the seawater (0.59) while those from the ice of the *High Light 1* tank are contained between the characteristic value of O_2/N_2 in the atmosphere (0.27) and the *equilibrium value* of 0.48. The contrast between the two tanks, although reduced in amplitude, is still present at day #10. Similarly in both tanks, the values of O_2/N_2 have decreased in the first centimeter in relation to the values observed at day #3. The shape of the profiles is also alike in both tanks starting from higher values at the bottom in the newly formed ice to lower values at the top in the older ice. The discrepancy between the two profiles persists on day #18 in the first 10 cm of the ice cover and disappear below this depth where the values of O_2/N_2 show a decrease towards the typical atmospheric value of O_2/N_2 and stabilize around 0.37.

5. Discussion

5.1. Mc Murdo 99

Since the extraction method ensures the collection of the totality of the gas content (both dissolved in the brines and in the form of bubbles), the fact that the measured values of the total gas content are at all times higher than the computed value of air solubility in the brines (see figure 2) implies that a part of the total gas content of the bulk ice should be in the form of bubbles. However, the values of the total gas content

measured in the columnar ice of Mc Murdo Sound are comparable to these performed in the ice from the INTERICE II experiment, that has grown in the absence of current, where no bubble nucleation was detected [Tison *et al.*, 2002]. Since the bubble content should be very low and its influence presumed limited on the gas composition, this implies that the observed gas composition at Mc Murdo Sound predominantly reflects the gas composition of the brines entrapped in the ice provided that, as discussed above [Verbeke *et al.*, 2002], biological activity was negligible in the studied layers. The gas composition is relatively constant in the 40 cm long studied section, especially if we except the two couples of ‘outliers’. The presence of a natural ice core break around 32 cm depth is thought to be the reason for the low O_2/N_2 ratio observed on both sides of the break. The fracture would have induced a partial balancing between the gas included in the ice and the atmosphere resulting in a decrease of the observed O_2/N_2 towards the atmospheric value. A similar atmospheric contamination process would have been responsible for the relatively lower value of 0.41 observed around 60 cm depth.

5.2. Initial entrapment

Fick’s first law of diffusion formulated as the enrichment coefficient of the water at the interface (see equation 2) can be used to estimate the influence of the initial gas entrapment on the gas composition. It can be seen from equation 2 that for a given solute species (with a fixed value of D_x), the enrichment at the interface depends only upon the thickness of the boundary layer and the freezing rate. Standard values of these two parameters have been chosen to simulate the initial entrapment process: a mean boundary layer thickness of 0.29 cm [Eicken, 1998] and an estimated value of the maximum freezing rate of $2.84 \cdot 10^{-5} \text{ cm s}^{-1}$ that occurred between 0.25 and 0.35m depth for the Mc Murdo Sound [Verbeke, 2005].

The O_2/N_2 ratio encountered at the interface under these conditions can be determined as the ratio of the O_2 to N_2 enrichment factors times the value of the O_2/N_2 ratio in sea water. The calculation yields the value of 0.54 (shaded value in table 1), which is lower than the value of O_2/N_2 in sea water (0.59). This means that diffusion occurs from the interface through the boundary layer from the beginning of the freezing, altering the gas composition. Nevertheless, this process cannot solely explain the much lower value of O_2/N_2 observed in the Mc Murdo 99 ice core.

5.3. Post-entrapment diffusion

Since the *close-off* (understand the reduction of the ice porosity below the threshold of 5% according to *Golden et al.* [1998]) is not instantaneous, it can be surmised that exchanges are likely to happen between the brine inclusions, entrapped in the ice during the advance of the freezing front, and the underlying sea water. If these exchanges occur only by diffusion, the effect of this further *post-entrapment diffusion* process on the gas composition can be estimated via the calculation of the enrichment factors and the resulting O_2/N_2 at the interface. Table 1 displays the evolution of O_2/N_2 at the interface for different values of the freezing rate and of the boundary layer thickness. It can be noticed from this table that O_2/N_2 tends towards lower values of the ratio for faster freezing rates and/or thicker boundary layers. For near zero-growth freezing rate and boundary layer thickness, the gas composition is, as expected, close to the value of O_2/N_2 in seawater (0.59). When the ice thickens further and as the bottom sea ice layer remains permeable (until the relative brine volume goes below 5%), this can be regarded as favourable to diffusion processes in a geometrical configuration equivalent to an increase of the z_M value by up to 5–10 cm. In the absence of bubbles, this post-entrapment diffusion process

should lead to an equilibrium post-entrapment O_2/N_2 value of 0.48, which is close to the observed values of the ratio in the columnar ice at Mc Murdo Sound.

5.4. INTERICE III

The values of the total gas content observed in both tanks for the whole experiment duration tally with the values of previous measurements [Matsuo and Miyake, 1966; Tison *et al.*, 2002] although several values on day #18 exceed the maximum value of 21.2 ml STP kg_{ice}^{-1} observed by Matsuo and Miyake [1966]. The evolution of the total gas content in the ice during the first ten days of growth is similar to what was observed in the ice of the INTERICE II experiment which has grown under comparable conditions [Tison *et al.*, 2002]. It reveals that the total gas content present in the upper colder layers of the sea ice cover is primarily inherited from solubility and supersaturation processes occurring within the lower permeable layer. Further cooling (below the temperature corresponding to the 5% brine volume threshold) mainly redistributes the same amount of gas between the dissolved and gaseous phases, in closed system. The dramatic increase of the total gas content visible under 10 cm on day #18 both in the *Low Light* and in the *High Light 1* tank is likely to have an artificial origin. The overflow pipes allowing water of the tank to stay in equilibrium with the atmosphere were not efficiently maintained working between day #10 and day #18. Consequently, gases expelled at the ice-water interface by the ice growth process would have been accumulated stepwise over the days in the tank, since there was no possibility anymore for it to escape into the atmosphere. This event would have been translated into a supersaturation of gases into the bulk water reservoir, in turn resulting in an increase of the total gas content of the newly formed ice.

325 The fact that O_2/N_2 values, observed at day #3 in both tanks, are lower than the typi-
 326 cal value in seawater (0.59) can be easily explained in the light of the processes mentioned
 327 above (*initial entrapment* and *post-entrapment diffusion*). The impact of the initial en-
 328 trapment process leads to $O_2/N_2 = 0.54$. This value was obtained considering a mean
 329 freezing rate of $2.68 \cdot 10^{-5} \text{ cm s}^{-1}$ measured for the first three days of the ice growth and a
 330 mean boundary layer thickness of 0.29 cm [Eicken, 1998]. Assuming an equivalent freez-
 331 ing rate but presuming a 10 cm scale boundary layer thickness (formed by the bottom
 332 portion of the ice cover where porosity >5% and acting as an upward extension of the
 333 boundary layer), O_2/N_2 stabilizes around 0.48 as a consequence of the post-entrapment
 334 diffusion process. The difference of O_2/N_2 between *High Light 1* and *Low Light* cannot,
 335 however, be attributed to these two processes. These are indeed thought to have similarly
 336 influenced the gas composition in the two tanks since the controlled experimental condi-
 337 tions which drive both the freezing rate and the boundary layer thickness (both, in turn,
 338 regulating the efficiency of the diffusion at the interface) are the same.

339 The difference is suspected to be biologically-driven. As a proxy of the biological ac-
 340 tivity, chlorophyll *a* concentrations were measured in centrifugated brines at day #3, day
 341 #10 and day #16 both in the *High Light 1* and in the *Low Light* tank. Data from table
 342 2 (S. Papadimitriou and D.N. Thomas, School of Ocean Sciences, University of Wales,
 343 Bangor, UK - unpublished data) show a contrast between the two tanks (respectively
 344 2.65 vs $11.77 \mu\text{g l}_{\text{brine}}^{-1}$) although the initial inoculum chlorophyll *a* concentration was
 345 identical. The decrease of the chlorophyll *a* concentration in the *High Light 1* tank as the
 346 result of a probable algae mortality remains unknown. Photoinhibition can be precluded
 347 as a cause of the observed decrease of the chlorophyll *a* concentration. The imposed irra-

diance amounts are indeed too low, even in the *High Light 1* tank ($34 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$), to induce photo-inhibition for autotroph microorganisms. *Fragilariopsis cylindrus* has proven not to manifest any evidential sign of photoinhibition at irradiance levels up to $385 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ [Mock and Hoch, 2005]. Photosynthetic O_2 production by a still relatively healthy algal community in the *Low Light* tank is thought to have compensated the effects of the initial entrapment and post-entrapment diffusion processes on O_2/N_2 . This would have therefore maintained the O_2/N_2 observed in this tank close to the typical value of the ratio in seawater. In the *High Light 1* tank, such photosynthetic O_2 production, if still present, was not sufficient to keep O_2/N_2 close to 0.59. This photosynthetically-driven contrast between the two tanks has persisted along the entire profile during most of the experiment. It has sluggishly vanished with time but was still marked at day #18 in the uppermost 10 cm of the ice cover. Given that O_2/N_2 stabilizes around 0.37 and not 0.48 at the end of the experiment in both tanks beneath 10 cm depth, an additional control process has to be considered.

5.5. Bubble nucleation

The impact on the gas composition of the progressive increase of the total gas content in both tanks, resulting from the gas supersaturation of the tank water, has not been considered yet. Once supersaturation has reached a critical level, whose value depends upon the local experimental conditions (presence or not of a current), bubbles start nucleating [e.g. Carte, 1961; Killawee *et al.*, 1998; Tison *et al.*, 2002]. As bubble nucleate, Tison *et al.* [2002] attributed the decrease of the O_2 concentration and of O_2/N_2 (concomitant with a reduction of the freezing rate) to an increase of the duration needed for the gas and the liquid phase (namely the brines) to become equilibrated. According to these

370 authors, the first bubble to form will be characterized by a gas composition close to that
371 of the water from which they have originally formed (the freezing rate is fast). As the ice
372 cover thickens the ice growth rate diminishes. This provides more time for gases to diffuse
373 between the gas and the liquid phase and for O_2/N_2 to decrease as a result of the faster
374 diffusion rate of O_2 relative to N_2 . This explanation must, however, be invalidated in the
375 light of the work of *Kanwisher* [1963]. This author has indeed demonstrated that gaseous
376 equilibration needs only a few hundredths of seconds to complete in the case of O_2 and
377 N_2 , duration which is largely exceeded before a brine inclusion becomes isolated from the
378 underlying reservoir. As an alternative explanation and since the gas composition analysis
379 technique used in this work collects gases both from dissolved and gaseous phases, the
380 progressive decrease of O_2/N_2 is hypothesized to be attributed to a progressive increase of
381 the gas fraction contained in the gas phase in relation to the fraction of the gas dissolved
382 in the brine, assuming an open system. Using the equation of *Coll* [1984] based on the
383 works of *Weiss* [1970, 1974], O_2/N_2 of a bubble in equilibrium with brine displaying a
384 O_2/N_2 ratio of 0.48 at -5°C (implying a salinity of about 84.59 according to equation 3)
385 can be estimated on the basis of the temperature and the salinity of the solution. This
386 calculation yields a value of 0.22. This estimate needs however to be considered with
387 caution since, as developed before, the salinity and the temperature encountered in such
388 a brine are beyond the limit of validity of the formula (temperature: -1 to 40°C , salinity:
389 0 to 40). Nevertheless, this value allows us to link, at least semi-quantitatively, higher
390 bubble contents, initiated by higher total gas contents, to a decrease of the O_2/N_2 ratio.

5.6. A simple conceptual model

Figure 6 summarizes the three main physico-chemical control processes potentially acting on the gas composition in the ice during its growth:

1. the *initial dissolved gas entrapment* where the gas composition is determined by the freezing rate and by the boundary layer thickness (mean thickness: 0.29 cm [Eicken, 1998]) (process 1° on figure 6).

2. the *post-entrapment diffusion*, acting as an *ageing* process on the sea ice brines, strengthens the contrast between the different gases according to their respective molecular diffusivity. The main drive of the process is the extension of the boundary layer (z_{bl} reaches easily up to 10 cm) through the bottommost part of the ice cover which is still permeable (relative brine volume >5%). In these conditions, O_2/N_2 usually stabilizes at the *equilibrium value* of 0.48 (see table 1 and process 2° on figure 6).

3. the *bubble nucleation* does not occur necessarily unlike the two previous processes. If supersaturation levels at the ice-water interface are sufficient for bubbles to form, the gas composition will evolve, inducing a decrease of O_2/N_2 proportional to the fraction of gas contained in the gas phase relative to the dissolved fraction, provided that the system is still open to gas exchanges with the water reservoir below. For example, if bubble nucleation happens after the *post-entrapment diffusion* process has equilibrated the O_2/N_2 value at 0.48, the final O_2/N_2 value of the sea ice gas content will be included between this last value and 0.22 (O_2/N_2 value for a bubble in equilibrium with brine characterized by $O_2/N_2 = 0.48$).

6. Conclusions and Implications

In this work we identified three main physico-chemical processes able to significantly alter the gas properties of sea ice during its growth. The use of a boundary layer concept has proven to be relevant to describe the evolution of the sea ice gas composition (seen as O_2/N_2) when the influence of biological processes is negligible. The succesful use of such an approach, to predict the gas composition of the ice samples studied in this work, emphasizes the importance of diffusion among the exchange processes occurring at the ice-water interface during the ice growth. The demonstration of the validity of a boundary-layer approach appears to be of prime importance for further modelling purpose of gas transport in sea ice, a fundamental topic for future estimates of its impact on exchanges of climatically significant gases (CO_2 , DMS, CH_4 ,...) between the ocean and the atmosphere. This work also stresses that considerable gas supersaturations can occur in the ice that are strictly driven by physico-chemical processes at work during ice growth. This is likely to have significant impacts on the use of oxygen concentrations in ice as an indicator of *in situ* primary production from sympagic (ice algae) organisms.

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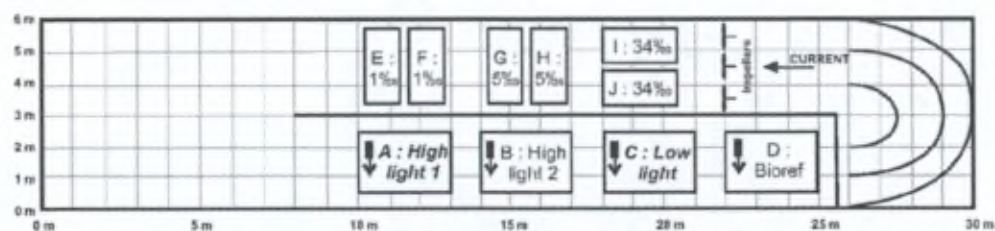


Figure 1. Layout of the HSVA basin during the first phase of INTERICE III experiment.

The ten polyethylene tanks, among which the tanks A to D equipped with mixing pumps (black rectangle with arrow), are shown. The location of the impellers in the hosting basin and the direction of the resulting current has also been shown.

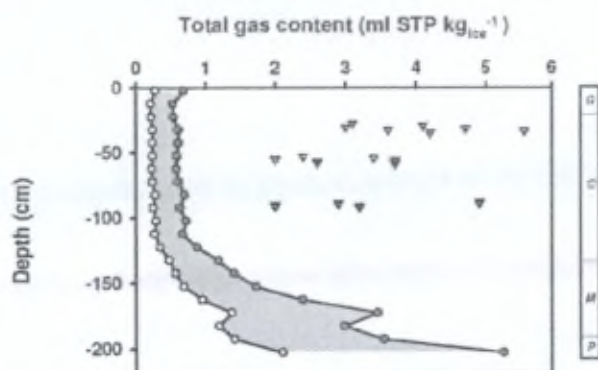


Figure 2. Total gas content measured in the columnar ice of Mc Murdo Sound (white triangles). The shaded zone depicts the range of theoretical total gas contents where supersaturation occurs without bubble nucleation for interface enrichment factors from 1 (white circles) to 2.5 (gray circles). The texture profile is also shown on the right of the graph (*G* for granular ice, *C* for columnar ice, *M* for mixed granular/columnar and *P* for platelet ice).

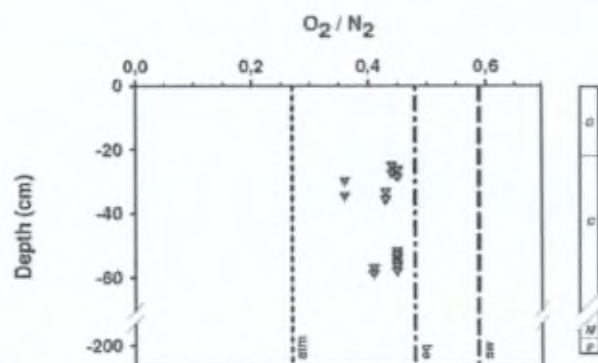


Figure 3. O_2/N_2 measurements in the ice of Mc Murdo Sound (gray triangles). O_2/N_2 typical values of 0.27 in the atmosphere (*atm* - dotted line), 0.48 at *equilibrium* (*eq* - dash-dotted line) and 0.59 in seawater (*sw* - dashed line) are also represented (see text for details). The texture profile is also shown on the right of the graph (*G* for granular ice, *C* for columnar ice, *M* for mixed granular/columnar and *P* for platelet ice).

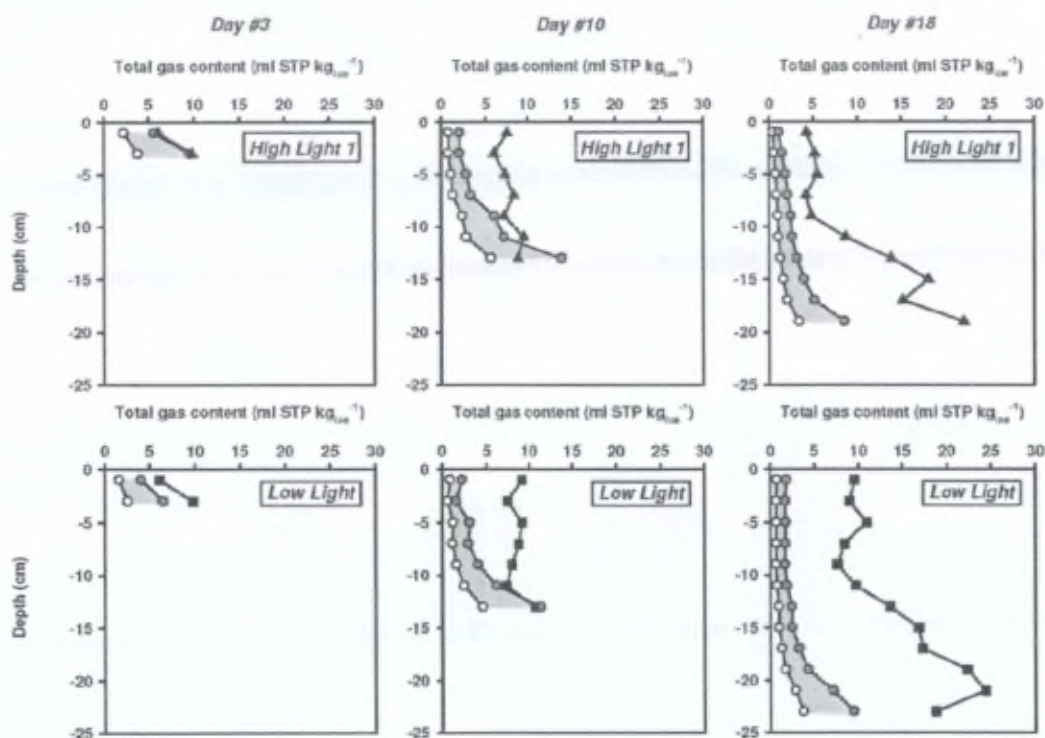


Figure 4. Total gas content profiles measured in the ice of INTERICE III at day #3, day #10 and day #18 from the *High Light 1* (black triangles - upper panel) and the *Low Light* (black squares - lower panel) tanks. The shaded zone depicts the range of theoretical total gas contents in zones where supersaturation occurs without bubble nucleation for interface enrichment factors from 1 (white circles) to 2.5 (gray circles).

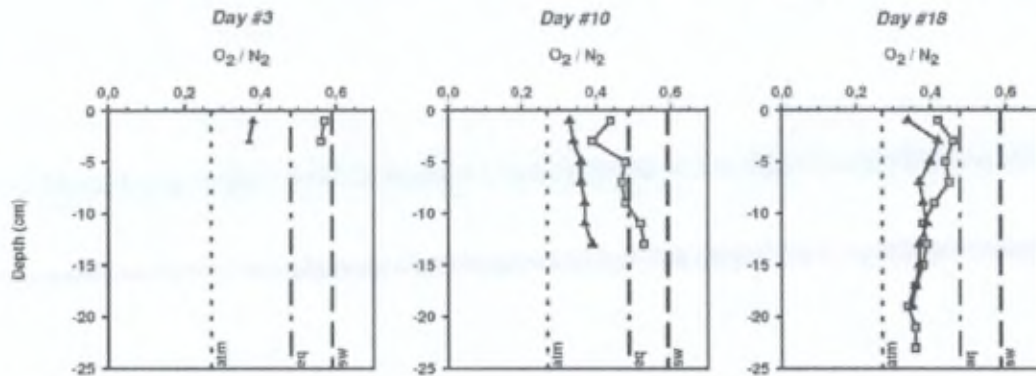


Figure 5. O_2/N_2 profiles measured in the ice of INTERICE III from the *High Light 1* (black triangles) and *Low Light* tanks (gray squares). O_2/N_2 typical values of 0.27 in the atmosphere (*atm* - dotted line), 0.48 at *equilibrium* (*eq* - dash-dotted line) and 0.59 in seawater (*sw* - dashed line) are also represented.

z_M (cm)	ν_i (cm s ⁻¹)						
	$2.78 \cdot 10^{-6}$	$1.39 \cdot 10^{-5}$	$2.68 \cdot 10^{-5}$	$2.78 \cdot 10^{-5}$	$2.84 \cdot 10^{-5}$	$1.39 \cdot 10^{-4}$	$2.78 \cdot 10^{-4}$
0.09	0.59	0.58	0.57	0.57	0.57	0.53	0.51
0.29	0.58	0.56	0.54	0.54	0.54	0.50	0.49
1	0.56	0.52	0.51	0.51	0.51	0.49	0.48
3	0.54	0.50	0.49	0.49	0.49	0.48	0.48
10	0.51	0.49	0.48	0.48	0.48	0.48	0.48
30	0.49	0.48	0.48	0.48	0.48	0.48	0.48

Table 1. Evolution of O_2/N_2 at the interface in parallel with an increase of the boundary layer thickness z_M and of the freezing rate ν_i . See text for further details.

Day	Sample location	<i>High Light 1</i>	<i>Low Light</i>
#3	overall	2.65	11.77
#10	top	10.94	21.57
	bottom	8.78	12.44
#16	top	0.74	6.32
	center	0.91	11.55
	bottom	0.32	2.51

Table 2. Chlorophyll *a* concentrations ($\mu\text{g l}^{-1}$) measured in centrifugated brines sampled at different locations in the ice cover of *High Light 1* and *Low Light* tanks. Sampling took place at three time steps (day #3, #10 and #16) (S. Papadimitriou and D.N. Thomas, School of Ocean Sciences, University of Wales, Bangor, UK - unpublished data).

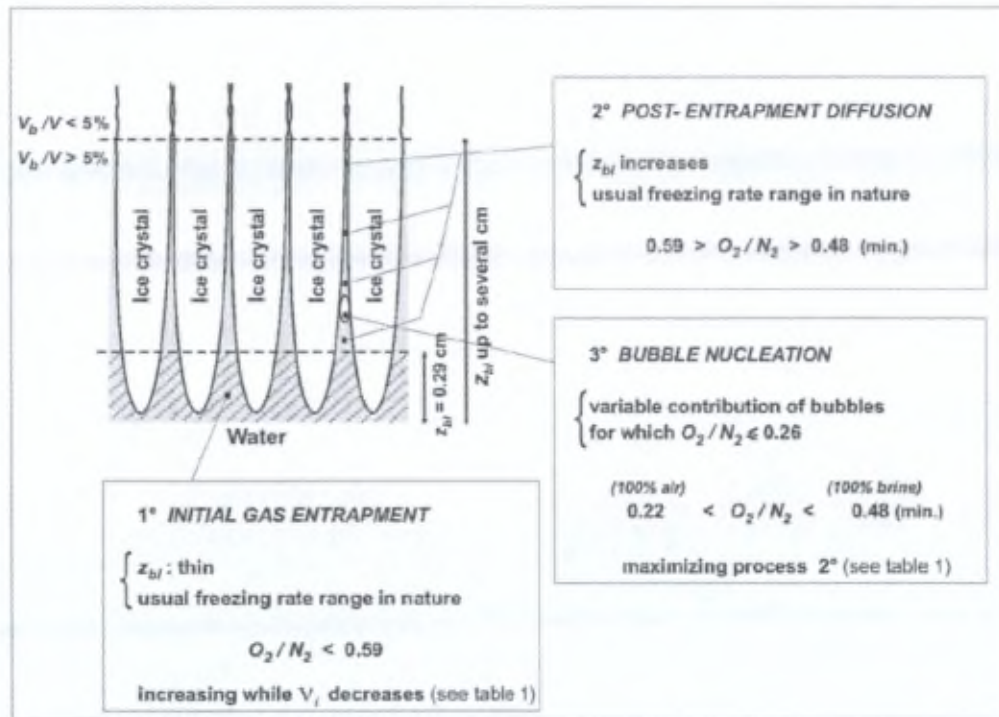


Figure 6. Summarizing scheme of the physico-chemical processes controlling the gas properties of sea ice during its growth. z_{bl} is the boundary layer thickness, v_i is the freezing rate and V_b/V is the relative brine volume. See text for further details.

CHAPTER VI: GENERAL CONCLUSIONS

The general objective of the present research work was to achieve a better understanding of the dynamics of DMS/P/O in Antarctic sea ice in relation to the physical and biogeochemical properties of the ice cover. This study distinguishes from previous sea ice DMS/P studies by an approach in a temporal perspective. To fulfil this general objective, it was necessary to answer four scientific questions:

- **What is the impact of melting of the sample on the determination of DMSO in sea ice and is it possible to get around this issue?**

In chapter II, it was shown that as previously demonstrated for taxonomic and other biogeochemical studies, processing sea ice samples appears to be equally challenging for the determination of DMSO as the necessary melting step induces a strong physiological response of the sympagic organisms involving DMSP and DMS. This physiological response is prone to significantly bias the measurement of DMS, DMSP or DMSO. This analytical finding is of prime importance and implies that previously published (but hopefully scarce) sea ice DMS data in bulk sea ice, obtained through the traditional melting method, have to be regarded with caution, as potentially overestimated in relation to DMSP. DMS extraction method by dry crushing has been used at large scale on an important amount of samples to produce all the bulk ice DMS data reported in the present work. Still under development when Antarctic sea ice DMS/P/O concentration measurements were being performed in the framework of this thesis, the extraction method by dry crushing has ever since confirmed to produce reliable results. The procedure recommended for the sequential determination of DMS, DMSP and DMSO includes extraction of DMS by dry crushing and determination of DMSO by a precise enzymatic method to produce unbiased results. A novel conception of the sea ice environment recently emerged where sympagic organisms are now considered to live within biofilms attached to brine inclusions walls or embedded in viscous gel-filled voids rather than being freely suspended in the liquid phase of brines. In order to produce reliable results, representative of bulk sea ice, it appears mandatory to perform biogeochemical analyses from a solid ice sample. The use of the procedure described in chapter II seems therefore suitable in

this perspective for the determination of DMS/P/O in sea ice and its use for future sea ice DMS/P/O studies should be encouraged.

- **How do the physical and thermohaline properties of sea ice temporally evolve under atmospheric thermal forcing?**

In chapter III, the temporal evolution of the physical and thermohaline properties of first-year Antarctic sea ice was addressed during spring and summer with an emphasis on the evolution of fluid transport properties of sea ice in the perspective of using it for the interpretation of ancillary variables in the framework of parallel biogeochemical studies. Time series experiments on pack ice are not legion, probably because of the logistic challenge they represent. In the framework of this thesis, the systematic choice of internally homogeneous sampling sites combined with a sufficiently long observation period allowed the spatial variability to be sidestepped and to reveal original and contrasting results between spring and summer. It is, to our knowledge, the first time that a cyclic pattern of intense brine drainage, as the one observed in the spring Antarctic sea ice in the Bellingshausen Sea, is observed in the field and corroborated by a series of variables of different nature. The comparative study of two sites of first-year sea ice with contrasting features showed that the ice at each site responded differently to the same atmospheric thermal forcing. This study confirmed by means of field data the importance of the ice texture, snow and ice thickness on the control of brine movement. The first-year sea ice cover investigated in December 2004 in the Weddell Sea revealed a dynamic environment in terms of exchange processes with the ocean and atmosphere although not comparable to those observed in thermally-forced spring sea ice in terms of magnitude of the processes. Opportunity was given to witness the transition from gravity drainage (that can occur under modest brine salinity gradients due to the high porosity of the ice cover at that time of the year) to diffusion controlled transport processes across sea ice. The observation of the development of features like the honeycomb-like structure in the upper layers of the ice cover and superimposed ice in the snowpack were also anticipated to have significant influence on the export of biogeochemical tracers towards the atmosphere and the ocean. Without a characterisation of the temporal evolution of the physicochemical (mainly texture, structure, temperature and salinity) properties of the sea ice cover prior to

biogeochemical investigations, a valid interpretation of biogeochemical dataset would have been compromised. For example, it would have been difficult to explain the periodic drops in DMS/P/O burdens observed in the spring ice cover during SIMBA without a prior identification of the existence of a cyclic brine drainage regime.

- **What is the distribution of DMS/P/O in spring and summer sea ice and how does it temporally evolve in conjunction with the evolution of the physical and thermohaline properties of the sea ice cover?**

The most exciting finding of this thesis lies in the observation of the reactor-like behaviour of the sea ice cover with respect to its ability to produce important amounts of DMS/P/O and then exchange them with either the atmosphere or the underlying ocean at the winter-spring transition in the Bellingshausen Sea. Despite the important loads of DMS/P/O released periodically by the sea ice cover, notably towards the ocean as a result of sustained brine drainage, the system was characterised by a net production of DMSP and DMS. The observation of a dynamics of DMS/P/O probably determined by the simultaneous effect of a series of factors but apparently triggered by thermal atmospheric forcing (with the regions with a thinner ice and snow cover exhibiting a higher sensitivity) might have major implications for the regional climate in a near future, provided DMS still exerts a significant climatic role. As opposed to the Arctic, the trend for Antarctic sea ice is not towards an overall decrease in sea ice extent. The ability of sea ice to produce and exchange DMS/P/O with the atmosphere or the Southern Ocean does not seem to be compromised on the short term by a decrease of the sea ice cover extent. The predicted or already observed changes in regional climatic patterns could even, at least temporarily, favour sea ice formation and ice conditions prone to lead to an increased production of DMS/P/O over an extensive zone of the ice-covered Bellingshausen Sea, potentially turning the area into a gigantic DMS/P/O plant. To validate this hypothesis, further studies are however required to assess whether the observations performed in the course of the spring 2007 are a widespread feature in the Bellingshausen Sea. Another original aspect of this thesis is the observation that DMSO within Antarctic sea ice, unlike in Arctic sea ice or in other marine environment, seems to

only marginally contribute to the total DMS/P/O pool, possibly because it is readily reduced into DMS in the sea ice environment as suggested by a recent study.

In the summer in the Weddell Sea, the overall system proved to be less active in terms of production of DMS/P and exchanges with the ocean and the atmosphere. Progressive decay of the dominating algal bottom community or the lack of environmental stress resulted in a net loss of DMSP over the study period. In terms of exchanges, the combined outgoing flux of DMS and DMSP was one order of magnitude lower than that observed at the spring transition. In summer sea ice, the release of DMS and DMSP from the decaying sea ice cover occurred indeed steadily and tended to slow down as progressive transition in brine regime towards stratification proceeded. Once sea ice brine network stratified, exchanges in DMS/P within the ice cover at that time became limited and were controlled by molecular diffusion exclusively while the release of DMS/P into the ocean was controlled by bottom melting. In the view of the very low values of chlorophyll *a* observed in the under-ice water column, similarly to what was observed during spring in the Bellingshausen Sea, sea ice constitutes the only source of DMS/P/O for the atmosphere and the Southern Ocean. Those findings demonstrate that the contribution of the sea ice cover to the regional DMS/P/O budget is not limited to the sole melting period as it is generally admitted in the literature. Future estimates or modeling efforts should therefore take this observation into account.

The studies of sea ice properties and sea ice DMS/P/O conducted in the form of time series allows to draft a potential scenario of the temporal dynamics of the DMS/P/O pool in sea ice, underlying water column and snow cover as well as the exchanges of DMS/P/O between those different reservoirs. It seems however necessary to keep in mind that this potential scenario is draft on the basis of studies covering limited spatial and temporal windows. Although the summer sea ice state observed during ISPOL in the Weddell Sea in 2004 could constitute a plausible evolution of the spring sea ice cover observed during SIMBA in the Bellingshausen Sea in 2007, the existence of specific regional meteorological and ice conditions as well as the lack of observations between end October and end November may compromise the proposed scenario. This first attempt to temporally integrate the DMS/P/O dynamics in sea ice could however inspire sea ice ecosystem modellers and suggest them the variables that should be taken into account or processes that should be further investigated.

Winter-spring transition and beginning of the atmospheric thermal cycle

The distribution of the biota in the sea ice cover is at the end of the winter partly inherited from the autumnal distribution of sympagic organisms that may develop again as permitted by the increasing ice temperature and light availability. Further development of the ice algal community may induce nutrient depletion that could in turn lead to the replacement of the dominant algal taxa by other species more adapted to the novel nutrient status of the ice cover. As the production of DMSP, notably, is acknowledged to be strongly species-dependent, the selection of the taxa that will dominate the ice algal community at that time of the year is crucial in determining the ability of the sea ice cover to produce DMSP (and thereby DMS/O). After the brine drainage event that may occur during the ice warming up when a critical temperature is reached that allows the ice porosity to be sufficient, transport of solutes become limited to molecular diffusion along concentration gradients. The "snow reservoir" is supplied with DMS while the "seawater reservoir" is supplied with DMS/P/O (panel 1 on Figure C 1).

As the season proceeds, cyclic atmospheric patterns characterized by an alternation of cold spells (driven by cold and dry air masses from the continent – clear sky) and warm spells (driven by warm and wet air masses from offshore – cloudy sky) may develop and interrupt the progressive warming up of the sea ice cover. Drop of atmospheric temperatures will cool down the ice and increase brine salinity (step 1, panel 2 on Figure C 1). Provided the duration of the cold spell is sufficient (especially if a thick snow cover is present at the ice surface, isolating it from important temperature variations), sympagic organisms may react to increasing thermal and osmotic stress by producing DMSP. Increased levels of radiations (PAR and UV) can superimpose to aforementioned stresses and further enhance DMS/P/O production. The intense cellular stress caused by the rapidly developing low temperatures and high salinity can induce cellular death, lysis and release of DMSP in the brine where it can be cleaved into DMS and acrylic acid by extracellular algal or bacterial DMSP-lyase. DMS can be bacterially or photochemically oxidised into DMSO which in turn can be reduced again into DMS via algal or bacterial pathways.

The local increase in DMS/P/O level will first enhance diffusion away from the place where DMS/P/O is produced. Concentration of salts by cooling can potentially lead to the up- and

downward expulsion of DMS/P/O with brine (step 2, panel 2 on Figure C 1). Provided the cold episode is long enough so that cold wave will propagate in the ice, an instable brine salinity (hence density) gradient will develop in the ice. If the latter is sufficient to counteract the energy dissipation imposed by the ice porosity (assessed by a mush Rayleigh number exceeding the critical value of 6-7), overturning of the brine will develop across the whole ice cover, leading to enhanced transfer of DMS/P/O to the underlying seawater, increasing the DMS/P/O pool of that reservoir and partly emptying the sea ice reservoir. One of the consequences of this process is that the global salt content of the sea ice will decrease. Nutrient resupply of the sea ice is expected to accompany upward seawater movement in the ice but is still speculative (step 3, panel 2 on Figure C 1). The DMS pool of the snow cover continues to increase, supplied by DMS diffusing from the ice. As there is at that time of the year no production of DMS/P/O in the water column, the increase of the DMS/P/O pool will be followed by a decrease driven by a series of processes like sinking of particulate matter to the ocean deep layers, bacterial consumption, venting of DMS through opening in the ice pack,... The amplitude of the effect of the cold event on the ice DMS/P/O pool will be even more important if an algal community is located close to the surface (thereby submitted to increased temperature and salinity gradients), contains taxa able to produce DMS/P/O and if the snow layer is thin. Beginning of a warm atmospheric temperature cycle will restore lower brine salinity values. This period is characterised by a lower level of environmental constraints on the sympagic organisms compared with the previous cold episode (panel 3 on Figure C 1). However, if the warming up of the ice occurs rapidly, it could lead to a salinity downshock for the ice algal cells that will enhance the release of DMSP into the ambient medium by active exudation or cell lysis and the ensuing production of DMS from dissolved DMSP through the already mentioned bacterial and algal pathways. At that time step, transport of DMS/P/O away from the locations where it is produced occurs across the ice cover and towards the seawater and snow reservoirs through molecular diffusion. During the following warm event, the DMS may be removed from the snow reservoir and released to the atmosphere by wind-pumping as warm events are generally characterised by strong wind episodes.

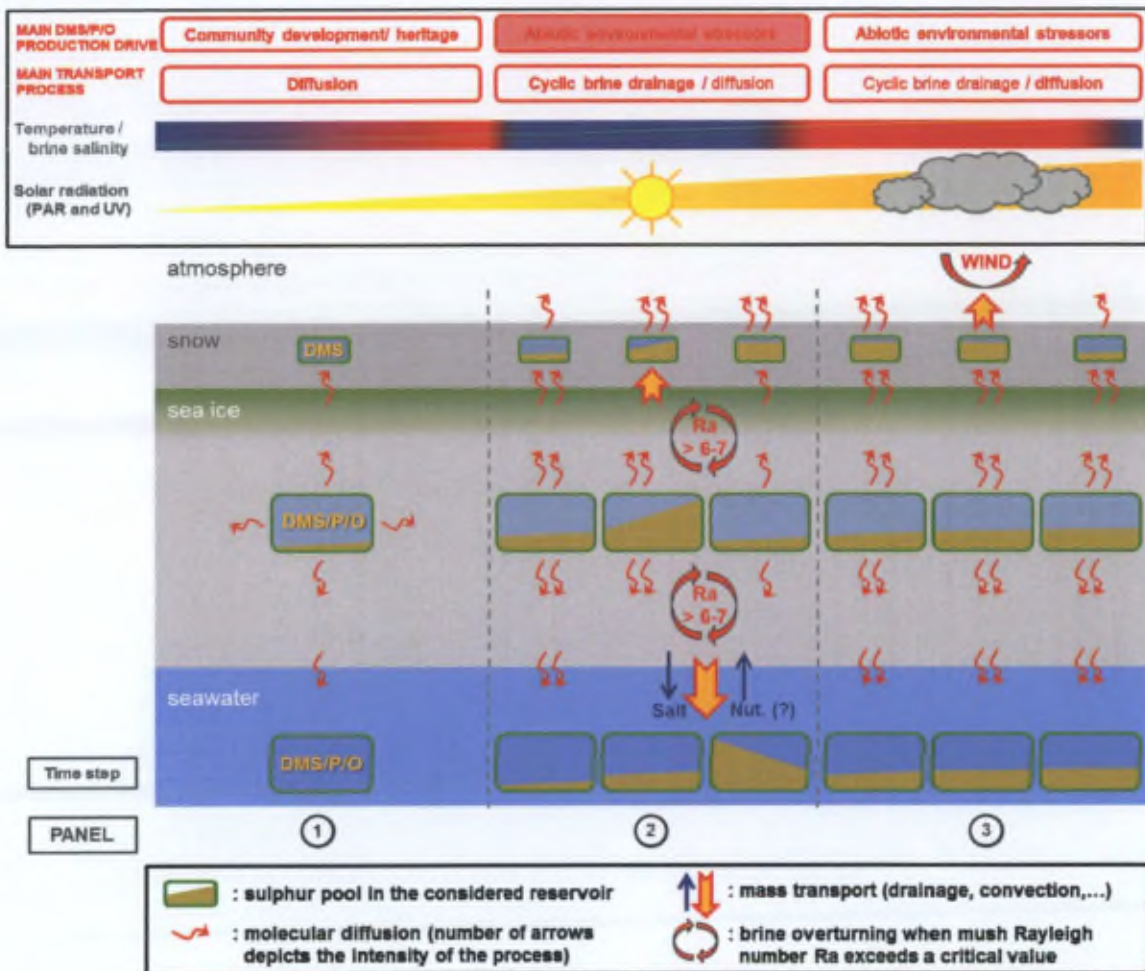


Figure C 1 Drawing of the DMS/P/O pool temporal evolution in sea ice and exchanges of DMS/P/O between sea ice, underlying water and the atmosphere at the winter-spring transition.

Spring conditions – the reactor concept and the case of unflooded sea ice

The reactor concept - The cyclic DMS/P/O production in sea ice and its transport towards the ice/water and ice/atmosphere interface may repeat as cold and warm spells are succeeded by one another driven by atmospheric forcing (Figure C 2). At that time of the year, the sea ice cover could compare with a reactor consisting of two components. Both components are thought to be mainly driven by atmospheric temperature changes which in turns induce ice temperature changes and brine salinity changes. The first “physical” component consists of the ice physical properties which will influence the fluid transport properties of the sea ice material (mainly ice texture and ice salinity) which will determine the magnitude of the transport of DMS/P/O with brine across sea ice towards the ocean under a given temperature gradient. The second “biological” component consists of the community of sympagic organisms capable of producing DMSP, DMS and DMSO and will primarily be influenced by the taxonomic composition of the algal community. Besides the thermal and osmotic stresses which are thought to be the main factors driving the DMSP production by ice algae, other environmental stress (UV and PAR, nutrients availability, grazing pressure,...) can be further added to the thermal and osmotic stresses to further enhance the algal DMSP production and mediate its conversion to DMS, DMSO or other compounds which cannot reintegrate the DMS cycle (mercaptopyruvate, methanethiol,...). Forced by the atmospheric thermal cycling, the system will periodically produce elevated quantities of DMS/P/O and release a major part of them in the underlying ocean. Two different scenarii are anticipated for the mid-term evolution of the system depending on whether the sea ice surface is flooded by seawater.

Unflooded sea ice - As the season proceeds the potential radiative stress, especially during the cold spells, increases with the level of solar radiation. Transformations within the DMS/P/O pool can be mediated by elevated radiation levels (i.e. photo-oxidation of DMS into DMSO) especially during the clear sky periods (corresponding to cold spells) as sea ice is acknowledged to contain significant amounts of photosensitiser (e.g. coloured dissolved organic matter). As substantial amounts of salts are expelled from the ice with each brine drainage event, the ice salinity (stock of salt) will decrease so that it becomes a limiting factor for brine drainage. If brine drainage stops, DMS/P/O transport to the underlying seawater will drastically slow down as restricted to molecular diffusion (panel 6, Figure C 2). In the absence of external salt resupply, brine drainage will not occur anymore until sea ice has sufficiently

warmed up for the ice porosity to be high enough to allow brine drainage under weaker instable brine salinity gradients (see summer conditions on Figure C 3). Upwards expulsion at the snow/ice interface during a cold event may still be possible as enough salt remains, depending on the severity of the low temperatures. As the season proceeds and algal community pursues its development, nutrient availability may become a limiting factor. Nutrient limitation can alter the ability of the ice algal community to produce DMS/P/O by inducing a shift in its composition or even by causing its decline. Unlike the ice salt stock that has to be replenished by external supply, resupply of the ice nutrient pool can occur from within through the bacterial remineralisation of organic matter, providing thereby reprieve for the working of the “biological” component of the system.

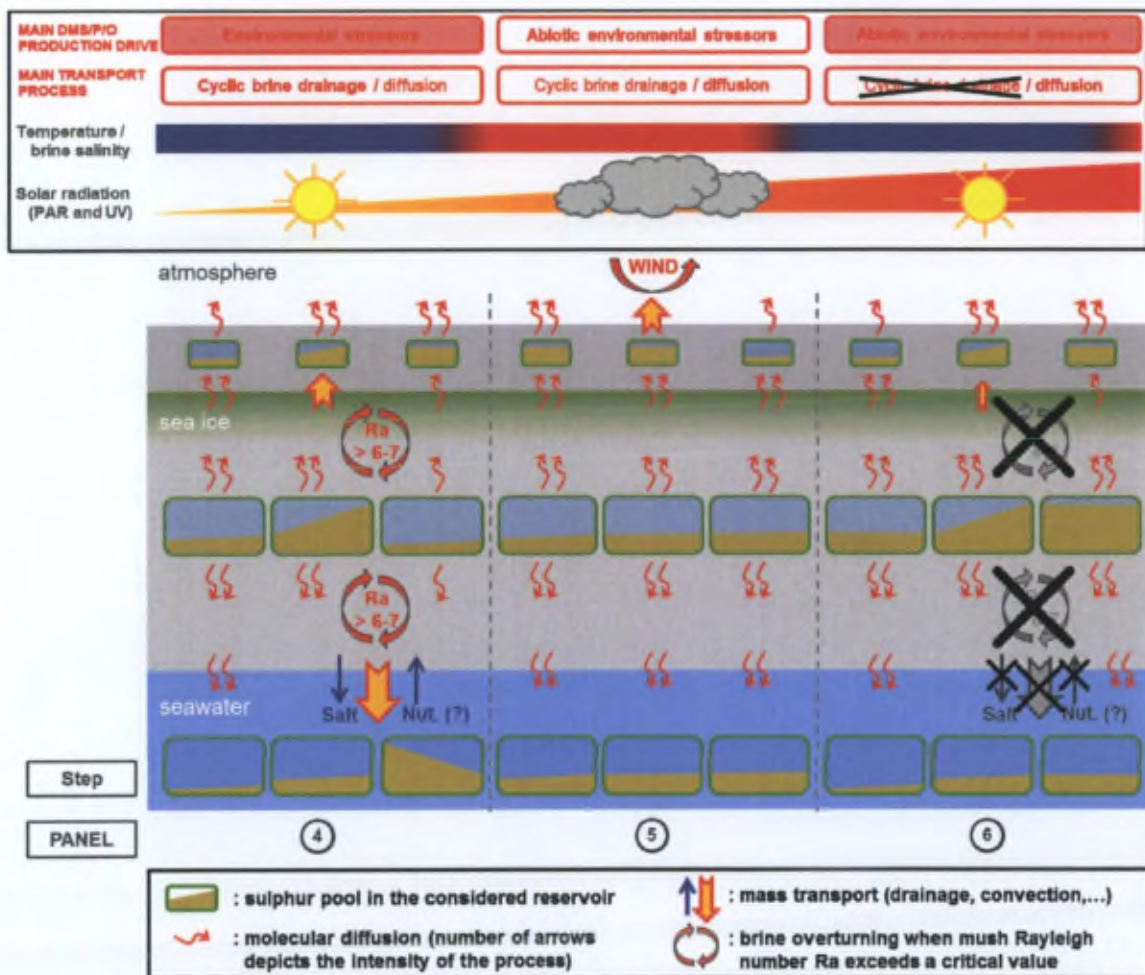


Figure C 2 Drawing of the DMS/P/O pool temporal evolution in sea ice and exchanges of DMS/P/O between sea ice, underlying water and the atmosphere during spring atmospheric thermal cycling – evolution of the system in unflooded areas of the pack ice.

Spring conditions – the case of flooded sea ice

As mentioned above, the maintain of the reactor-like behaviour of sea ice with respect to DMS/P/O production and transport is submitted to external resupply of salt (for transport) and in a lesser extent to that of nutrients (for production). Thanks to snowfall during warm events of snow redistribution at the sea ice surface by wind, local accumulation of snow may become sufficient to depress the sea ice surface below the sea level and allow the invasion of the snowpack by seawater conveying nutrients and salt that can percolate through sea ice, permeability conditions permitting (panel 8, Figure C 3). Depending on the amplitude of the flooding and provided the sea ice cover is permeable enough, surface flooding can induce a vertical redistribution of DMS/P/O in sea ice. Thanks to the salt and nutrients resupply, the transport and production components of the system may be able to perform longer than in the case of unflooded sea ice. As a thicker snow cover provides insulation from atmospheric temperature changes and partially blocks solar radiations, less abrupt temperature and salinity gradients will tend to develop in the ice resulting in a overall lower production of DMS/P/O and weaker brine drainage events.

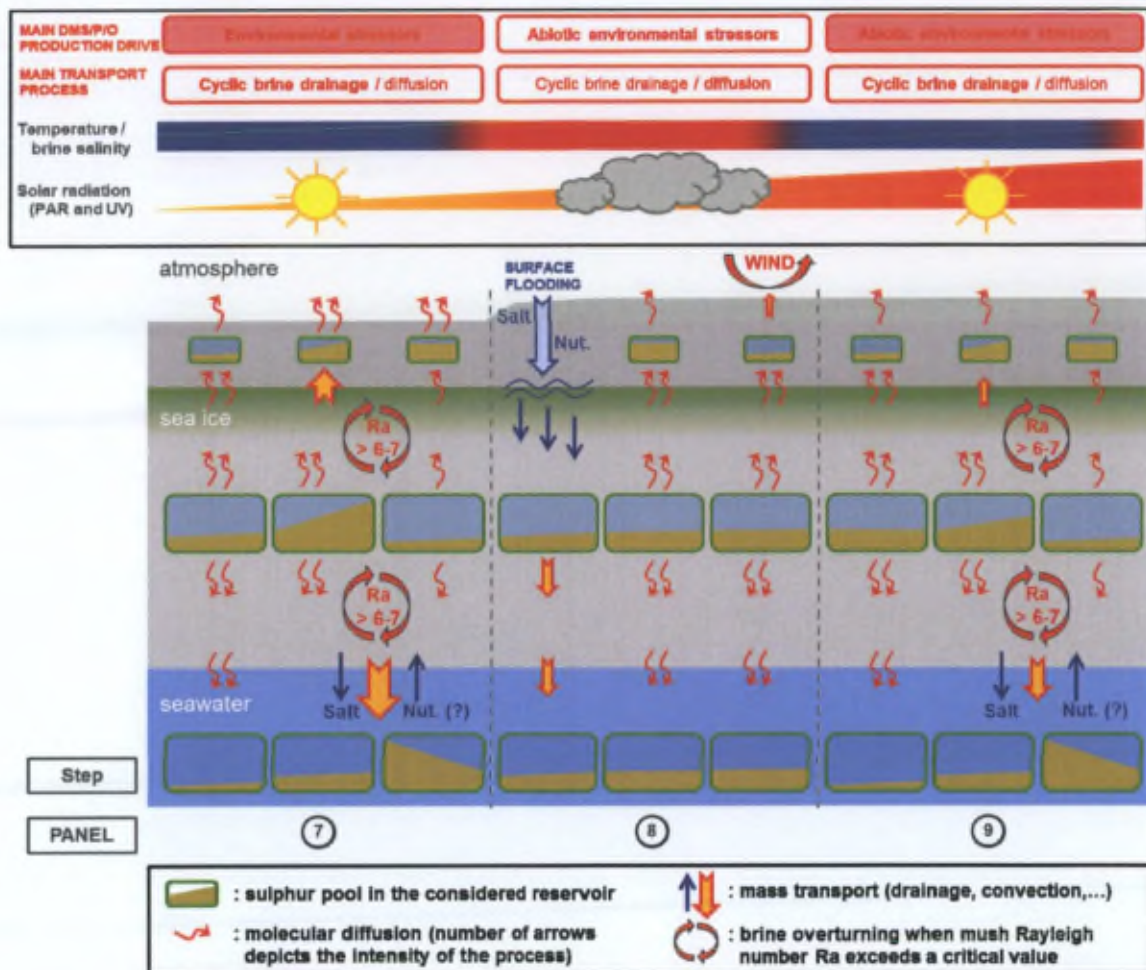


Figure C 3 Drawing of the DMS/P/O pool temporal evolution in sea ice and exchanges of DMS/P/O between sea ice, underlying water and the atmosphere during spring atmospheric thermal cycling – evolution of the system in surface flooded areas of the pack ice.

Summer conditions – the progressive decay of sea ice

At the beginning of summer, air and ice temperature (hence ice porosity) and solar radiation levels still increase as the season proceeds. In the presence of ocean heat flux, bottom melting initiates. In the absence of surface flooding, most of the autotrophic sympagic organisms are likely to be found at the bottom of the ice, a location warranting a better access to nutrients. Providing sea ice salinity remains sufficient, a last brine drainage event can occur thanks to the high porosity of the ice allowing brine to drain under weaker salinity gradient (panel 10, Figure C 4). Most of the summer flux of DMS/P/O (mainly dissolved DMSP and DMSO) to

the ocean will be due to that process. As porosity of the surface layers increases, so does the diffusion of DMS to the snow cover (panel 11, Figure C 4). The development of features like honeycomb-like structure may also favour lateral transfer of tracers, notably towards the surrounding leads where exchanges of DMS with the atmosphere is facilitated. Internal melting of the brine channel walls progressively dilutes brines and release particulate matter (amongst which DMSP) in the brine medium. Lower salinity may favour the release of DMSP by ice algae in the dissolved phase. Stratification of the sea ice brine column, dilution of the brine, and colonisation and/or development of heterotrophic organisms (grazers) in the ice may favour the conversion of DMSP to DMS. As the brine column is stratified, exchanges with seawater occur only through diffusion or melting with an increasing fraction of particulate material. The seawater DMS/P/O pool increases. As observed in spring, strong wind episodes can efficiently empty the snow DMS pool. With the decay of the snow pack, becoming coarsely granulated, venting of DMS to the atmosphere is highly facilitated. The development of superimposed ice as snow begins to melt may however severely impede the transfer of DMS to the atmosphere. Unless sea ice surface is flooded, and a (highly productive) surface community develops, potentially leading to the temporary production of elevated DMS/P/O levels, the productivity of the system and transfer of DMS to the atmosphere and DMS/P/O to the ocean will progressively drop until complete melting of sea ice.

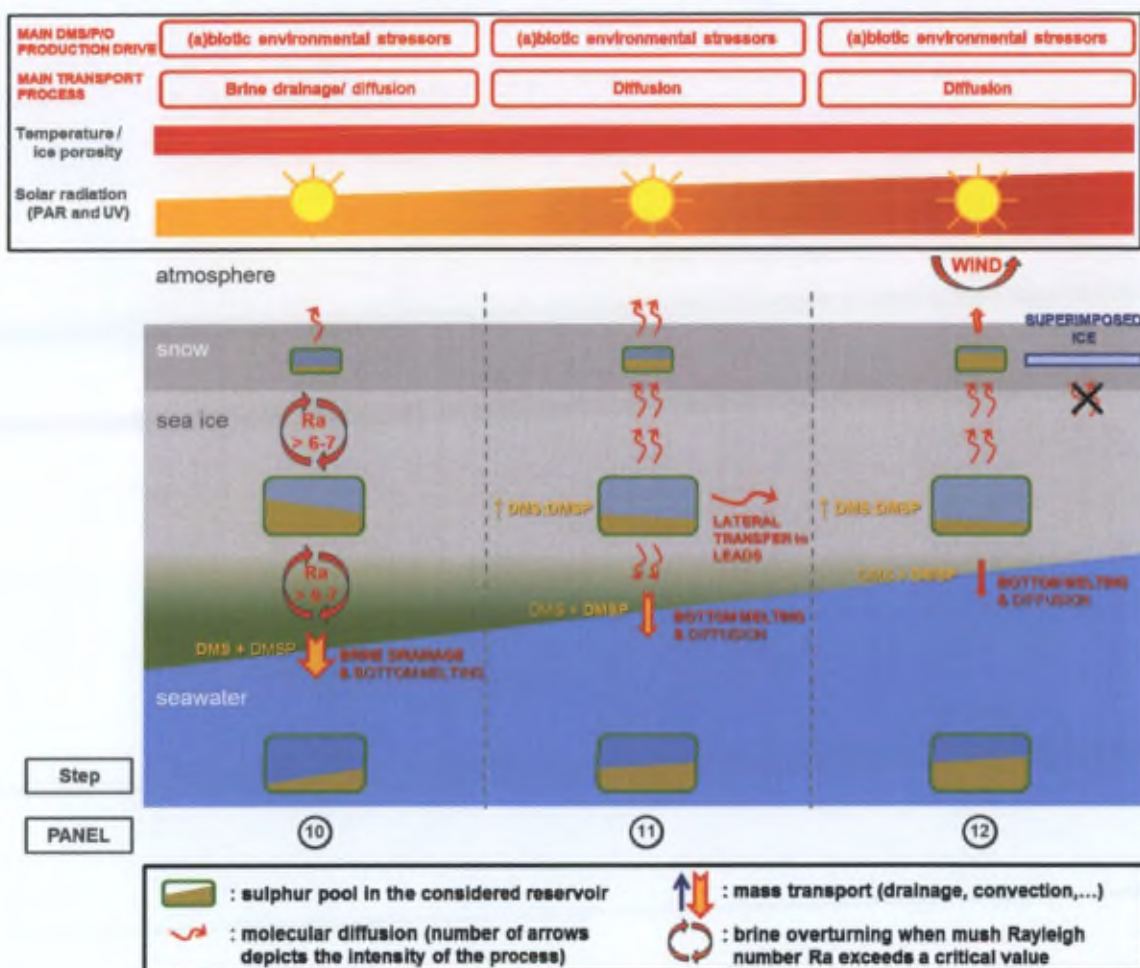


Figure C 4 Drawing of the DMS/P/O pool temporal evolution in sea ice and exchanges of DMS/P/O between sea ice, underlying water and the atmosphere during summer.

Although mentioned nowhere in the papers of the present thesis, field experience demonstrated that science is sometimes (only) a question of opportunity. In this respect, fire on board the N.B Palmer in the first days of the SIMBA cruise in 2007, was likely determining. This event delayed indeed the arrival of the scientists on the study site and the significantly shortened duration of the mission forced the chief scientist and principal investigators to upset their initial plans. In opting for a 20 day drift station in the Bellingshausen Sea, the opportunity was given to witness successive cycles of atmospheric cooling and warming and assess their major influence on the ice properties and on the dynamics of sympagic organisms and biogeochemical tracers.

- **How does the evolution of the physical and thermohaline properties of growing sea ice influence its gas properties?**

In chapter V, the results of the experiment performed on laboratory prepared growing sea ice demonstrated the relevance to use a boundary layer model to describe the initial entrapment of dissolved gas (amongst which DMS) and their evolution within the ice cover under the sole influence of physicochemical processes, amongst which molecular diffusion, bubble nucleation and brine transport combine. Such findings could represent a first step for modellers to parameterise gas dynamics in sea ice. Similar basin experiments could be reproduced in the future for more advanced stages of sea ice evolution.

Recommendations for future work

Faithfully simulating the dynamics of biologically mediated gases like DMS would require more intensive work we think is unlikely to emerge from field data only, owing to the specificities of the sea ice material (including the complexity in sympagic community composition) and the challenges posed by its sampling. To disentangle the intricate DMS cycle, controlled laboratory experiments addressing, at first, textbook case studies (e.g. physiological response involving DMSP of a given algal taxa in response to temperature and salinity changes – and change rates – in the range of values encountered in brine inclusions within sea ice) appear as a mandatory complement. Use of the stable isotopic tool to trace the numerous pathways leading to the production of DMS and related compounds may be promising. Once such simple case studies addressed, modelling could help elucidating more complex processes which seem hard to assess experimentally, like nutrient dynamics and availability within a composite material whose fluid transport properties change with temperature. In the view of the logistic challenges posed by field experiments in polar regions and sometimes the lack of spatial representativeness of the studies performed in those regions, recourse to numerical simulation seems unavoidable in order to produce large scale estimates of gas flux and finally assess the contribution of the oceanic cryosphere to the regulation of the earth's climate through its control on the dynamics of climatically significant

gases in Polar Regions. Field work, with focus on time series experiments, remains necessary to validate the output of numerical simulations and refine our understanding of the seasonal dynamics of DMS/P/O formulated in the present research work, especially in undersampled spatial and temporal windows. Emphasis should be put on the study of pack ice which represents more than 80% of the Antarctic sea ice cover. Due to the heavy logistics and expensive equipment they require, studies of ice-snow-air exchanges of climatically significant trace gases on drifting ice remain scarce. Hopefully as technological progress are achieved, less expensive and more portable equipment might be produced and allow to better constrain air/snow/ice fluxes of trace gases. It appears essential to validate large scale output of numerical models. This intimate use of field, experimental and numerical approach has been the backbone of the still undergoing SIBClim/BA²SICS international and multidisciplinary effort, initiated in Belgium and under the auspices of which this thesis has been completed.

Résumé

Il a récemment été démontré que la glace de mer antarctique pouvait jouer un rôle significatif dans la dynamique des gaz à effet climatique (dont le diméthylsulfure ou DMS) dans les régions polaires. Ce travail s'est d'abord attaché à la mise au point d'une méthode de mesure fiable du diméthylsulfoxyde (DMSO) dans la glace de mer, supprimant les interférences générées par la production de DMS au sein de l'échantillon en réponse au choc osmotique subi lors de la fonte de l'échantillon de glace. Une procédure de détermination séquentielle du DMS, par broyage à sec, puis du diméthylsulfoniopropionate (DMSP) et du DMSO sur le même échantillon de glace a été développée et utilisée à large échelle dans ce travail. Les données du présent travail ont été acquises dans le cadre de deux programmes d'observation intégrés menés sur la glace de mer antarctique à des saisons différentes mais avec une méthodologie commune : 1) choix de sites d'étude homogènes afin de minimiser l'impact de la variabilité spatiale sur l'interprétation des résultats dans une optique d'évolution temporelle et 2) priorité à la caractérisation du cadre physico-chimique (texture, température, salinité, couvert de neige, susceptibilité au drainage des saumures,...) avant toute autre analyse. L'étude menée dans le cadre du programme ISPOL (nov.-dec. 2004) a permis d'observer que la stratification des saumures a un impact positif sur la conversion du DMSP en DMS au sein de la glace mais ralentit les flux de DMS et DMSP vers l'océan. Le couvert de glace est caractérisé à cette période de l'année par une perte nette de DMSP et génère des flux combiné de DMS et DMSP du même ordre de grandeur que les flux de DMS atmosphériques mesurés dans le cadre d'autres études. L'étude menée dans le cadre du programme SIMBA (sept.-oct. 2007) a permis de mettre en évidence l'importance du forçage atmosphérique sur le régime thermique et la dynamique du DMS/P/O dans la glace. Les communautés d'algues de surface produisent de fortes concentrations de DMS/P/O en réponse au stress thermique, osmotique et potentiellement radiatif durant les périodes de refroidissement et la mise en place d'un régime soutenu de drainage des saumures contribue à évacuer périodiquement les hautes concentrations de DMS/P/O produites dans la glace vers l'océan sous-jacent. Le couvert de glace affichant une production nette de DMS/P/O à cette période de l'année génère des flux combinés de DMS et DMSP plus de dix fois supérieurs à ceux observés pour la glace estivale. L'étude menée sur de la glace artificielle a permis de mettre en évidence l'impact des processus physico-chimiques sur la signature en gaz de la glace en croissance constituant un premier pas vers la modélisation des transports de gaz dans la glace de mer et leurs échanges au travers des interfaces glace-océan et glace-atmosphère.

Abstract

It has recently been demonstrated that Antarctic sea ice recently demonstrated plays a potentially significant role in the dynamics of climatically significant gases (amongst which dimethylsulphide or DMS) in Polar Regions. This research work has initially focused on the development of a reliable method for the determination of dimethylsulphoxide (DMSO) within sea ice, avoiding interferences generated by DMS production within the sample in response to the osmotic shock caused by melting. A sequential determination procedure of DMS, dimethylsulphonioacetate (DMSP) and DMSO on the same ice sample has been developed and used on a large amount of samples in the present work. Data presented in this research project have been collected in the framework of two integrated sea ice observation programs focused on Antarctic sea ice at different seasons but following a common approach: 1) choice of homogeneous study sites to minimize the impact of spatial variability on the interpretation of the results in a time series perspective and 2) priority given to the characterization of the physicochemical framework (texture, temperature, salinity, snow cover, susceptibility to brine drainage,...) prior to any other study. The study conducted in the framework of the ISPOL experiment (Nov.–Dec. 2004) demonstrated that stratification of the brine inclusions network positively influenced the conversion of DMSP into DMS but decreased fluxes of DMS and DMSP towards the ocean. The ice cover at that time of the year is characterised by a net DMSP loss and generates combined DMS and DMSP fluxes whose values fall in the range of atmospheric DMS flux from sea ice measured in the frame of other studies. The study conducted in the framework of the SIMBA experiment (sept.–oct. 2007) emphasized the importance of atmospheric thermal forcing on the sea ice thermal regime and DMS/P/O dynamics. The surface community of algae produced elevated levels of DMS/P/O in response to thermal, osmotic and potentially radiative stress during periods of atmospheric cooling while the development of an intense brine drainage regime contributed to periodically release the elevated levels of DMS/P/O produced in the sea ice towards the underlying ocean. The ice cover exhibited at that time of the year a net production of DMS/P/O and produced combined DMS and DMSP fluxes more than ten times higher than those observed for summer sea ice. The study conducted on laboratory prepared growing sea ice emphasised the impact of physicochemical processes on the gas signature of growing sea ice and represents a first step towards modelling gas exchanges within sea ice and across its interfaces with the ocean and the atmosphere.
