



CO₂ and N₂O dynamics in

the ocean-sea ice-atmosphere system

Thesis submitted by Marie KOTOVITCH

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Supervisors: Doctor Bruno DELILLE (Université de Liège)

and Professor Jean-Louis TISON (Université Libre de Bruxelles)



ABSTRACT

Greenhouse gases such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are well known to be indirectly responsible for many changes in the sea ice cover in the polar regions, as these regions are sensitive to global warming. The objective of this manuscript is to look at the two climatic gases addressed (CO₂ and N₂O) and their behaviour in the ocean – sea ice – atmosphere system in the actual warming climate, thus more specifically in the Arctic.

On the one hand, the dynamic of CO_2 has been studied through artificial sea ice during an experiment performed on two series of mesocosms: one was filled with seawater (SW) and the other one with seawater with added filtered humic-rich river water (SWR). The addition of river water almost doubled the dissolved organic carbon (DOC) concentration in SWR and consequently affected the partial pressure of carbon dioxide (pCO₂). This experiment supports previous observations showing that the pCO_2 in sea ice brines is generally higher in Arctic sea ice compared to that from the Southern Ocean, especially in winter and early spring. Indeed, DOC is larger in the Arctic seawater: higher concentrations of DOC would be reflected in a greater DOC incorporation in sea ice, enhancing bacterial respiration, which in turn would increase the pCO_2 in the ice. Within the same experiment, air-ice CO_2 fluxes were measured continuously using automated chambers from the initial freezing of a sea ice cover until its decay. Cooling seawater prior to sea ice formation acted as a sink for atmospheric CO₂, but as soon as the first ice crystals started to form, sea ice turned to a source of CO_2 , which lasted throughout the whole ice growth phase. Once ice decay was initiated, sea ice shifted back again to a sink of CO_2 . Combining measured air-ice CO_2 fluxes with the pCO₂ in the air and sea ice, we determined two strongly different gas transfer coefficients of CO_2 at the air-ice interface between the growth and the decay phases (2.5 mol m⁻² d⁻¹ atm⁻¹ and 0.4 mol m⁻² d⁻¹ atm⁻¹ respectively).

In the other hand, we present in this work the first winter to spring N_2O observations in the sea ice and the upper ocean of the western Nansen Basin (Arctic Ocean). In the seawater, a general N₂O undersaturation with respect to the atmosphere was identified at the surface, with a clear enrichment north of 82°N originating from the water masses passing through the Arctic polar circle. We show that the main source of N₂O enrichment originates from the East Siberian Arctic Shelf, a key place for benthic denitrification and sea ice formation rejecting brine - including N₂O - in the seawater. Sea ice shows N₂O oversaturation throughout winter and spring in both first-year (FYI) and second-year ice (SYI). Further, SYI, with expected lower salinity than FYI, is enriched in N₂O compared to the dilution curve for salinity. This non-conservative N₂O content of SYI with salinity is likely due to (i) SYI formation further east than FYI, (ii) in situ biological activity, (iii) flushing of N₂O-rich ice surface meltwater (i.e. brine skim) through decaying FYI and (iv) strongly reduced permeability in SYI. Finally, we suggest that the high N₂O concentrations observed in the snow cover results from a combination of brine rejection at the top of the ice (brine skim) and chemical N₂O production (under the process of chemodenitrification).

RÉSUMÉ

La glace de mer, principalement située dans les régions polaires, est un milieu sensible au réchauffement climatique, et de manière accentuée en Arctique où la réduction significative de l'étendue et de l'épaisseur de la glace de mer sont actuellement en cours. Ce réchauffement est causé par des gaz à effet de serre comme le dioxyde de carbone (CO₂), le méthane (CH₄) et l'oxyde nitreux (N₂O), dont les concentrations augmentent avec l'industrialisation. Ces mêmes gaz sont par ailleurs incorporés dans les saumures liquides et les poches gazeuses de la glace de mer, et par conséquent, leurs concentrations se trouvent affectées par les fluctuations biogéochimiques de la glace de mer. L'objectif de cette thèse est d'étudier la dynamique de deux de ces gaz biologiquement actifs – le CO₂ et le N₂O – au sein de la glace de mer et aux interfaces avec l'océan et l'atmosphère.

La dynamique du CO_2 a été étudiée lors d'une expérience sur de la glace de mer artificielle présentant deux types de mésocosmes : l'un rempli avec de l'eau de mer (SW), l'autre rempli avec un mélange d'eau de mer et de rivière (SWR). L'addition d'eau de rivière a presque doublé la concentration en carbone organique dissous (DOC) dans le SWR, affectant la pression partielle en CO_2 (p CO_2). Cette expérience confirme d'autres études montrant que la pCO₂ mesurée dans les saumures de la glace de mer est plus élevée en Arctique qu'en Antarctique. En effet, l'Océan Arctique a un contenu en DOC plus important ; une plus grande concentration en DOC dans l'eau de mer mène à une plus grande incorporation de DOC dans la glace de mer lors de sa formation, renforçant la respiration bactérienne qui, en retour, augmente la p CO_2 dans la glace. Lors de cette même expérience, des mesures en continu de flux de CO₂ air-glace ont été réalisées, de la formation à la fonte de la glace de mer. Le refroidissement de l'eau de mer a d'abord agi comme un puits de CO₂ pour l'atmosphère, une situation qui s'est inversée lors de la formation des premiers cristaux de glace, devenant alors une source de CO₂ pour l'atmosphère durant toute la période de croissance de la glace. Enfin, lors de la fonte de la glace, celle-ci s'est repositionnée en puits de CO₂ envers l'atmosphère. En combinant les flux air–glace de CO₂ avec la pCO₂ mesurée dans l'air et dans la glace de mer, deux coefficients de transfert de gaz distincts ont été déterminés ; $K = 2.5 \text{ mol } m^{-2} d^{-1}$ atm⁻¹ pour la phase de croissance et $K = 0.4 \text{ mol } m^{-2} d^{-1} \text{ atm}^{-1}$ pour la phase de fonte.

Quant à la dynamique du N₂O, celle-ci a été étudiée à travers un set de données innovant de mesures de N₂O réalisées sur une période de six mois dans la glace et l'eau de mer de l'Océan Arctique, à l'ouest du Basin de Nansen. Une soussaturation générale est observée à la surface de l'océan par rapport à l'atmosphère, majoritairement due à l'origine Atlantique de ces masses d'eaux. Cependant un enrichissement en N₂O est observé au nord de 82°N, également dû à l'origine de ces masses d'eaux, qui elles proviennent du plateau arctique de la Sibérie orientale, un lieu intense de dénitrification benthique et de formation de glace de mer, rejetant d'importantes quantités de sels et de gaz dans l'eau sous-jacente. Les mesures dans la glace de mer montrent une sursaturation tout au long de l'étude, dans les deux types de glace étudiées ; celle de première année (FYI) et celle de seconde année (SYI). Cette dernière présente des salinités plus faibles du au lessivage des saumures qui a lieu en fin du premier cycle de croissance, cependant les concentrations en N₂O sont similaires à celles de la FYI. Ce comportement non conservatif par rapport à la salinité peut être dû : (i) à la formation plus à l'est de la SYI, (ii) à de la potentielle activité biologique, (iii) au lessivage de la surface de la glace enrichie en N₂O (iv) à la faible perméabilité de la SYI. Enfin, il est suggéré que les fortes concentrations en N₂O rencontrées à la surface de la glace sont dues au rejet des saumures vers la surface, combiné à un processus chimique de production de N_2O .

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LIST OF ABBREVIATIONS

AIW: Atlantic Intermediate Water **AOU:** Apparent Oxygen Utilization AW: Atlantic Water **BEPSII:** Biogeochemical Exchange Processes at Sea Ice Interfaces BrV: Brine Volume S_{br}: brine Salinity Chl a: Chlorophyll a DIC: Dissolved Inorganic Carbon DOC: Dissolved Organic Carbon **GHG:** Greenhouse Gases **GWP:** Global Warming Potential FYI: First Year Ice MAW: Modified Atlantic Water NDW: Nordic seas Deep Water pCO₂: Partial pressure of Carbon dioxide pN₂O: Partial pressure of Nitrous Oxide POC: Particulate Organic Carbon **PSW:** Polar Surface Water **PW:** Pacific Water SW: Seawater SWR: Seawater with additional River water SYI: Second Year Ice TA: Total Alkalinity

CHAPTER I: Introduction

I.1. Motivation

Significant changes in sea ice extent¹, volume and seasonal dynamics are ongoing in the polar regions, as these regions are very sensitive to a warming climate (IPCC, 2013). This warming is due to the greenhouse gases (GHGs) such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) that absorb and emit thermal radiations within the infrared range (wavelengths up to 1050 nm) due to their molecular vibrations. Representative concentration pathways (RCP) in the fifth assessment report of the IPCC (2013) propose four projections on global warming depending on GHG emissions for the 10 to 100 years to come. Across all RCPs, a rise by 0.3 to 4.8 °C of the global mean temperature of the earth surface is projected by the late-21st century. But as these gases conduce to global warming, they are affected in return by sea ice extent changes among other feedbacks, resulting in still unclear evolution on the cycling of these climatic gases.

The global contribution of the ocean in the atmospheric CO_2 and N_2O is already attributed; ocean biogeochemistry is seen as a significant sink for CO_2 with both its solubility and biological pump, and a source of N_2O via biological processes. However the sea ice contribution to these gases is still being questioned.

In the North, Arctic sea ice is changing dramatically, retreating at a record rate (Cavalieri and Parkinson, 2012). Remote sensing observations in Serreze and Stroeve (2015) document a downwards decrease in Arctic sea ice extent of -13.3% decade⁻¹ over the period 1979–2014, taking the largest trend in September, i.e. the end of the melt season. Other studies that include the sea ice thickness of the Arctic in the winters of 1979–2011 reveals that the multi-year sea ice extent is declining at an even more rapid rate of -15.1% (Comiso, 2012). In parallel to the extent component, multi-year ice will progressively shift to a younger, thinner, more porous and seasonal (first-year) sea ice, which forms in winter and completely melts in the summer (IPCC, 2013; Maslanik et al., 2011; Meier et al., 2014; Stroeve

¹ The sea ice extent is defined as the area represented by an ice concentration of at least 15%.

et al., 2012). Changes in the sea ice cover are correlated with surface temperature which is increasing even faster in the Arctic compared to the rest of the world (Comiso, 2012; IPCC, 2013).

In the Southern Ocean, however, sea ice extent increases (Simmonds, 2015) except in the Antarctic Peninsula, where a significant decrease is observed due to its small size and northerly location, and because this region is one of the most rapidly warming places in the world (Stammerjohn et al., 2008; Vaughan et al., 2003). Still, climate projections predict that Antarctic sea ice will retreat in the next decades (IPCC, 2013).

As sea ice forms from the freezing of seawater, its structure is heterogeneous and composed of a matrix of pure ice and brine inclusions (Eicken, 1992), including pockets and channels. Brine channels can be connected with the underlying seawater or with the atmosphere. Till recently, sea ice was assumed to be impermeable to gas exchanges in large-scale climate models. But pioneer gas measurements and evidence on the role of sea ice on ocean-atmosphere exchange of climatically active biogases (Delille et al., 2007; Rysgaard et al., 2007; Semiletov et al., 2004; Zhou et al., 2014c) indicates that sea ice may, in fact, be permeable to gas exchanges. At the ocean-sea ice interface, i.e. the bottom of the ice, convective process resupply nutrients (Vancoppenolle et al., 2007) and gases (Zhou et al., 2013). While at the sea ice-atmosphere interface, i.e. the ice surface, gas concentration gradient between the air and the brine exposed to the air is responsible for gas exchanges. Today there is body of evidence that gases (such as CO_2) exchange between seawater underneath the sea ice and the air above (Anderson et al., 2004; Delille et al., 2007; Loose et al., 2009; Nomura et al., 2009; Rysgaard et al., 2009; Tison et al., 2017). Sea ice processes that drive these exchanges include; brine rejection during sea ice formation in winter, while sea ice melting seems to act as a sink for atmospheric CO_2 (Delille et al., 2014; Rysgaard et al., 2011), but the impact of these processes on sea ice freeze and melt on CO_2 exchange with the atmosphere are still mostly unknown (Parmentier et al., 2013).

A first motivation for the thesis was to better assess the role of sea ice in CO_2 cycling by looking at the factors that drive air-ice CO_2 fluxes. Measurements of

these fluxes have been intensified in both the Arctic (Geilfus et al., 2012a; Miller et al., 2011b, 2011a, Nomura et al., 2018, 2010a; Semiletov et al., 2007) and the Southern Ocean (Delille, 2006; Delille et al., 2014; Geilfus et al., 2014; Zemmelink et al., 2006).

While CO_2 dynamics in sea ice has received increased attention in the last decade, our understanding of sea ice N_2O dynamics is still in its infancy. To date, Randall et al. (2012) presented the only N_2O measurements in sea ice: the authors pointed out that sea ice formation and melt has the potential to generate sea-to-air or airto-sea fluxes of N_2O , respectively.

A second motivation is then to provide an innovative data set of N_2O measurements in sea ice and the underlying seawater, to propose emerging hypothesis on the processes driving N_2O concentrations during sea ice growth and decay.

With a global sea ice extent of 18×10^6 km² at its minimum to 27.30×10^6 km² at its maximum, the general motivation for these measurements is to better understand the role of sea ice in the biogeochemical cycling of CO₂ and N₂O.

I.2. Thesis outlines

In accordance with the motivations mentioned above, I investigated sea ice at both the macroscopic scale (gas exchanges at its two interfaces) and the microscopic scale (gas transports associated to sea ice structure and gas content).

This dissertation starts with an exhaustive state of the art to describe the processes covered in the body of the thesis, build around three papers.

The two first papers are issued from the INTERICE V experiment held in Hamburg on artificial sea ice. This experiment supports previous observations showing that the pCO_2 in sea ice brines is generally higher in Arctic sea ice compared to those from the Southern Ocean, especially in winter and early spring. Indeed, organic content (DOC and POC) of Arctic seawater is larger than in the Southern Ocean by several orders of magnitude: higher concentrations of organic matter in surface water in surface waters translate in a larger organic matter incorporation in sea ice, enhancing bacterial respiration, which in turn increase the pCO₂ in Arctic sea ice (chapter III). Within the same experiment, air-ice CO₂ fluxes were measured continuously using automated chambers from the initial freezing of a sea ice cover until its decay to investigate sea ice exchanges with the atmosphere in a controlled environment (chapter IV). A sea ice model was developed in two papers to which I also collaborated, i.e. Moreau et al. (2015a) and Moreau et al. (2015b). The Moreau et al. (2015b) paper deals with the drivers of inorganic carbon dynamics in sea ice, while Moreau et al. (2015a) was investigating the impact of bacterial respiration on the O₂ budget. The sea ice model was then implemented in the two published papers presented in this dissertation (chapters III and IV).

Chapter III: Zhou J., **Kotovitch M.**, Kaartokallio H., Moreau S., Tison J.-L., Kattner G., Dieckmann G., Thomas D. & Delille B. (2016) The impact of dissolved organic carbon and bacterial respiration on pCO_2 in experimental sea ice. Progress in Oceanography, 141, 153–167.

Chapter IV: **Kotovitch M.**, Moreau S., Zhou J., Vancoppenolle M., Dieckmann G. S., Evers K.-U., Van der Linden F., Thomas D. N., Tison J.-L. & Delille B. (2016). Air-ice carbon pathways inferred from a sea ice tank experiment. Elem. Sci. Anthr. 4, 000112. https://doi.org/10.12952/journal.elementa.000112.

The third paper deals with natural sea ice from the Arctic Ocean – North-West of Svalbard – and focuses on another potent greenhouse gas; the nitrous oxide (N₂O). Our results give the first six-month data set of N₂O measurements in seawater and sea ice. This manuscript constitutes the Chapter V:

Chapter V: Kotovitch M., Silyakova A., Nomura D., Fransson A., Chierici M., Granskog M., Dodd P., Duarte P., Van der Linden F., Moreau S., Deman F., Tison J.-L. & Delille B. (in progress). Winter to spring ocean-sea ice-atmosphere N₂O partitioning in the Arctic Ocean (north of Svalbard). *Progress in Oceanography.*

A conclusion closes this thesis by summarizing the research and findings achieved during this 5 years Ph.D. work.

CHAPTER II: State of the art

This section gives the tools to understand the following chapters. First, it highlights the climatic relevance of the two climatic gases addressed: CO_2 and N_2O . Then it describes sea ice as a composite of pure ice, liquid brine and gas bubbles. Finally, it gives an introduction and an overview of CO_2 and N_2O dynamics in seawater and sea ice.

II.1. The climatic relevance of CO_2 and N_2O in the polar marine environment

II.1.1. A quick look at the global warming main cause and feedback on sea ice melt

The anthropogenic warming of the Earth is due to greenhouse gases (GHGs) such as CO_2 , CH_4 and N_2O . While 97% of the radiations received on earth from the sun range between 280 to 2800 nm, GHGs absorb and re-emit earth thermal radiations within the infrared range, wavelengths beyond 2500 nm. This is due to the vibrations of the molecular structure of the GHGs, which slow the rate at which the radiations emitted by the earth escape to space. GHGs act like a blanket insulating the Earth making it suitable for life (at reasonable GHGs concentration in the atmosphere). The increasing GHGs concentration in the atmosphere is thus responsible for the increasing Earth warming called "global warming". Each GHG acts differently on the Earth's warming, depending on: (i) their *radiative efficiency*, i.e. the ability to absorb energy and (ii) their *lifetime*, i.e. how long they stay in the atmosphere (EPA, 2019).

II.1.2. A positive feedback on sea ice melt: the decreasing albedo

The albedo characterizes the "whiteness" of a surface; it is the ratio of radiation reflected from the surface to the incident radiation. The albedo is dimensionless and measured on a scale from zero (no reflection, black surface) to 1 (perfect reflection of a white surface). The seawater surface has then a lower albedo than the snow that is retained on the solid sea ice surface. This means that the incident radiation is absorbed at a higher ratio when it arrives on the seawater than on the snow with the consequence that the seawater gets warmer than the snow surface.

In the Arctic, as the global warming melts more ice, the global snow surface of the Earth and thus the Earth albedo both decrease, leading to a positive feedback where a bigger seawater surface absorbs the incident radiation and warms the Arctic Ocean (Figure II-1). This last figure is to be taken with care; the snow and ice albedo cannot be attributed to only one value as their albedo can easily differ according to their environment.



Figure II-1 : Albedo changes among marine environment (Arctic Monitoring and Assessment Programme, https://www.amap.no).

II.1.3. Atmospheric relevance of CO₂ and N₂O

Greenhouse gases such as carbon dioxide (CO_2) , methane (CH_4) and nitrous oxide (N_2O) are recognised to be indirectly responsible for significant changes in the sea ice cover in the polar regions, as these regions are sensitive to global warming. (IPCC, 2013). Representative concentration pathways (RCP) presented in the fifth assessment report of the IPCC (2013) propose four projections on global warming depending on GHG emissions for the 10 to 100 years to come. Across all RCPs, a

rise by 0.3 to 4.8 °C of the global mean temperature is projected by the late-21st century.

 CO_2 is a gas that is recognised to be the primary anthropogenic greenhouse gas responsible for global warming. It is produced naturally or by human activities through fossil fuel or biomass combustion. The atmospheric concentration of CO_2 increased from about 280 ppm before the industrial era to more than 400 ppm (Figure II-2). The radiative effect of CO_2 is also used as a reference for other greenhouse gases as its global warming potential is set at a value equal to 1.



Figure II-2 : Changes in atmospheric CO₂ abundance for the last 1019 years as determined from air trapped in ice cores, firn air, and whole air samples. Data are from https://www.co2levels.org/#sources

 N_2O is a trace gas showing an electric dipole due to its asymmetry, providing similar properties than CO_2 , i.e. their solubility and their diffusivity in water are comparable (King et al., 1995; Wilhelm et al., 1977). With a lifetime of 114 years in the atmosphere (Ehhalt et al., 2001) and a global warming potential (GWP) up to 298 times that of CO_2 (Forster et al., 2007), N_2O is recognized as a potent greenhouse gas naturally present in the atmosphere that exerts a significant influence on both climate and atmospheric chemistry. The atmospheric N_2O abundance determined from air trapped in ice cores, firn air and whole air samples shows a stable mixing ratio from 1000 to 1850 AD, between 265 to 275 ppb (or nmol mol⁻¹) while since 1850, N₂O mixing ratio increases until today, where the monthly mean value reached 332 ppb in January 2019 (Figure II-3).



Figure II-3: Changes in atmospheric N₂O abundance for the last 1019 years as determined from air trapped in ice cores, firn air, and whole air samples. Data are from http://www.n2olevels.org/#sources

The primary cause of this atmospheric increase in N_2O is assumed to be the agriculture and in particular, the use of synthetic fertilizers that enhance microbial activity and the animal waste management (Syakila and Kroeze, 2011). On the other hand, natural sources for N_2O are significant and include terrestrial soils by 61% and the ocean by 33% (Syakila and Kroeze, 2011). Due to its relatively long lifetime and thus its ability to reach the stratosphere, N_2O is subject to photochemical reactions in the stratosphere, a process that destroys the ozone so that N_2O is the dominant ozone-depleting substance emitted in the 21st century (Ravishankara et al., 2009).

II.1.4. The marine cycle of carbon and nitrogen

Nitrogen occupies a central position in the marine biogeochemistry, and has a significant influence on the carbon cycle (Figure II-4; Capone, 2008). The cycles start with carbon fixation during the photosynthesis in the upper ocean, a step that cannot take place without a supply of nitrogen-rich nutrients. This organic matter is respired or remineralized in the upper ocean, or exported and

remineralized in the ocean interior. From the deeper ocean, the matter that is returned to its inorganic form is transported back to the upper ocean by circulation and mixing (Capone, 2008). This biologically driven biogeochemical loop is fundamental for Earth's climate, as it is one of the processes that determines the concentration of CO_2 in the atmosphere. If this biogeochemical loop were eliminated today, atmospheric CO_2 would raise by more than 200 parts per million (ppm) (Gruber and Sarmiento, 2002).



Figure II-4: Marine nitrogen cycle coupled with carbon, oxygen and phosphorus cycles. Figure from Capone (2008).

II.2. From a free-ice to an ice-covered seawater

II.2.1. Sea ice formation conditions and its resulting structure

Sea ice forms from the freezing of seawater and its properties give indications on the seawater turbulence conditions during the formation of the first centimetres of sea ice. Sea ice crystallises in a specific system called Ih (Bragg, 1922; Weeks and Ackley, 1986), where H₂O molecules are found to be tetrahedrally arranged within themselves in a rotational symmetry of order 6 in the basal plane (c-axis in Figure II-5). The fasted growth occurs within the a-axis as it is an already build plane, while the orientation of the crystal is given by the c-axis, perpendicular to this basal plan (Figure II-5, Hobbs et al., 1974).



Figure II-5: Sea ice crystalline structure, where black points symbolise hydrogen atoms and white circles symbolise oxygen atoms (from Weeks and Ackley, 1986).

The addition of salt to the water lowers the temperature of maximum density (t_{pmax} , Figure II-5). Once the salinity exceeds 24.7 (most Arctic surface water is 30-35), the water starts to freeze (by reaching t_g) while getting denser. It may seem, then, that the whole water column in an ocean has to be cooled to the freezing point

before freezing can begin at the surface, but in fact the Arctic Ocean is composed of layers of water with different properties, and at the base of the surface layer there is a big jump in density (known as a pycnocline), so convection only involves the surface layer down to that level (about 100-150 metres). This convection develops until the whole mixed layer (i.e. the water mass lying in between the surface and the pycnocline) reaches the freezing point, leading to the first crystal formation.



Figure II-6: Evolution of the maximum density temperature ($t_{\rho max}$) and the freezing temperature (t_{g}) with salinity (adapted from Weeks and Ackley, 1986).

This specific crystalline structure confers characteristic properties to sea ice:

- a lower density than the one of liquid water, responsible for its buoyancy;
- the limited incorporation of ions into the sea ice crystal lattice. In fact, during sea ice growth, most of the ions originally present in seawater (Na⁺, K⁺, Ca⁺, Mg⁺, Cl⁻, SO₄²⁻, CO₃²⁻) are either rejected back into the water column, or trapped into liquid and gaseous inclusions into the sea ice matrix (Hobbs et al., 1974; Weeks and Ackley, 1986; Weeks and Gow, 1978);
- an advantageous growth rate within the basal plane, where molecules are preferentially added following a-axis (Hobbs et al., 1974).

II.2.2. Sea ice growth

Two processes limit crystal growth: the heat transfer and the transport of solutes through the liquid phase. During sea ice growth, it turns out that the heat transfer from the warm water mass to the cold interface is faster than the ions transport (rejected out the ice structure) in the opposite direction. A layer constitutionally supercooled then develops just below the growing ice (Weeks and Ackley, 1986) with a lower temperature than the freezing point. A minor disturbance of the supercooled ocean—sea ice interface triggers sea ice growth and results in thin vertical lamellar blades of ice crystals separated by films of brines (Weeks and Ackley, 1986). Heat and salts dissipations are local, non-linear inhomogeneous processes that favour growth where salts are concentrated (Nakawo and Sinha, 1981). The bottom end of the growing ice, called skeletal layer, is especially porous (around 30%) with a temperature just below the freezing point (Weeks and Ackley, 1986).

II.2.3. Sea ice texture

The analysis of the sea ice texture (i.e. its crystal morphology and fabric) gives indications on the way sea ice forms. The texture depends on the seawater conditions during sea ice formation (see *growth conditions* in Figure II-7) and the sea ice thickness (see *depth* and *stratigraphy* in Figure II-7). A typical succession of the different sea ice texture along with the first-year sea ice depth shows from top to bottom: granular ice, transition ice and columnar ice (Figure II-8).

• Granular ice

The first unconsolidated crystals that form in turbulent waters are frazil ice crystals. Due to turbulence, these first crystals are small (1 to 10 mm long and less than 1 mm thick), randomly shaped, and randomly oriented. This particular texture in fully formed sea ice is referred to as granular ice (Figure II-8a).



Figure II-7: Synthesis of the different type of sea ice including the texture, the growth conditions among the time scale, and typical winter profiles of temperature and salinity for first-year sea ice (Petrich and Eicken, 2010).

• Transition ice

A transition ice layer can be found between the granular and the columnar ice. The transition ice is composed of an intermediate texture with granular and columnar crystals (Figure II-8b).

• Columnar ice

Once a thin layer of frazil covers ice and insulates the sea surface, congelation ice (or columnar ice) starts to form at the base of this frazil layer (Weeks and Ackley, 1986). Crystals of columnar ice have a specific prismatic, vertical, and elongated shape (Figure II-8c). This crystal orientation is due to a geometrical selection of advantageous vertical growth (Weeks and Gow, 1978). Columnar ice may also start to grow at the sea surface provided relatively calm conditions.



Figure II-8: Pictures of three sea ice section from the Young Sound fjord (Greenland), on the 23/06/2014, observed with cross-polarized light. a) Top section (0 to 7 cm) of granular ice. b) Central section (33 to 40 cm) of transition ice. c) Bottom section (103 to 110 cm) of columnar ice.

• Landfast ice and pack ice

Depending on the distance to the coast, two types of sea ice are commonly observed: the *landfast ice* and the *pack ice*. The *landfast ice* is formed close to the coasts, generally within quiet conditions, and remains fastened to the coast.

• The presence of snow and seawater in the ice structure

Snow can contribute to the ice structure by the development of: (i) snow-ice, mostly at the beginning of the winter (e.g. Jeffries et al., 1997; Leppäranta, 1983) but also in spring and summer, or (ii) superimposed-ice that forms mostly at the beginning of the spring (e.g. Holt and Digby, 1985; Kawamura et al., 1997) at the ice surface.

Accumulation of snow on thin sea ice in winter depresses sea ice surface below the sea level. Seawater then floods snow and freezes due to the low temperature of the snow. Frozen flooding seawater in the snow is referred as snow-ice. Snow-ice formation is observed in the Arctic Ocean and the Baltic Sea (Granskog et al., 2003) and the Okhotsk Sea (Nomura et al., 2010b). But it is more common in Antarctica where snow load is significant (Maksym and Jeffries, 2000).

In spring, snow is exposed to warmer temperatures and lower albedos (due to early melt of thinner snow patches), creating a pool of meltwater. As this meltwater percolates downwards, it starts to refreeze when it reaches lower temperatures deep in the snow or at the snow-ice interface (Holt and Digby, 1985; Jeffries et al., 1994). This process is responsible for the formation of superimposed-ice, with a typical structure of hard fresh ice, creating an impermeable layer for gases. Superimposed-ice is also reported in Arctic regions like the Baltic and Beaufort seas (Eicken et al., 2004; Granskog et al., 2006) and over fast ice in Svalbard (Nicolaus et al., 2003).

• The presence of microorganisms in the sea ice structure

Cold-adapted sea ice communities are present in the ice structure (Bowman et al., 1997; Junge et al., 2002) including microalgae, bacteria, micrograzers and virus that use different energy sources and comprise multiple trophic levels. Microorganisms are incorporated in the ice at the beginning of the ice growth (Garrison et al., 1989) and further develop in the sea ice that serves as a substrate (Horner et al., 1992) and protection against larger grazers (Krembs and Deming, 2008). Microalgae consist of mainly diatoms (about 90% in most studies), flagellates like prymnesiophytes, dinoflagellates, prasinophytes, chlorophytes among others. Smith et al., (1990) even present the ice (especially in the bottom few centimetres of the ice, closer from the nutrients reservoir) as one of the most favourable habitat for diatoms and other microalgae in the world's oceans. However, the biomass of bacteria in a sea ice core can exceed algal biomass in winter (thanks to extracellular polymeric substances produced by bacteria and protecting them) and during algal bloom (Collins et al., 2008; Krembs et al., 2002, 2000).The organisms or bacteria groups that achieve the complete remineralization of organic compounds use different metabolic pathways and requiring diverse environmental conditions, such as aerobic and anaerobic microzones (Fripiat et al., 2014; Rysgaard and Glud, 2004).

II.3. <u>The significant role of salts in sea ice</u>

Sea ice salinity is a crucial tracer of physical processes and set several environmental conditions of importance for biogeochemistry. It is an indicator of sea ice biogeochemical properties since salts are concentrated in brine together with gases, nutrients and other impurities. Salinity and temperature play a critical role with respects to brine dynamics (described in section II.5.1), gas solubility and sea ice permeability (Hunke et al., 2011).

Salinity may be defined as absolute or practical salinity. Absolute salinity (S_A, g kg⁻¹) is defined as the mass fraction of dissolved material in seawater and based on the "density salinity" as presented in the TEOS-10 (IOC, 2010). Practical salinity (*S*_P, dimensionless) is defined by the relation between the electrical conductivity of a sample and the conductivity of a standard solution and is then converted in a practical salinity scale (IOC, 2010; UNESCO, 1978). These equations are valid for a range of salinity from 2 to 42 and for a temperature superior to -2° C.

II.3.1. What does salinity profiles state

Since around 80% of salts are rejected from sea ice during its formation, bulk sea ice salinity is lower than seawater salinity from which sea ice forms. After the initial salts rejection, salinity evolves across the seasons (Figure II-9, Malmgren, 1927; Nakawo and Sinha, 1981), and through years. Mean surface salinity of first-year ice is about 2 to 12, while that of multiyear ice approaches 0 (Weeks and Ackley, 1986).



Figure II-9: Evolution of sea ice salinity profiles with depth across the seasons (from Malmgren, 1927). The C-shape salinity profile from October to March corresponds to the young first-year ice. Note that the reduction in surface salinity in June is due to meltwater flushing with the onset of summer melt.

II.3.2. Brine volume fraction and brine salinity relationships

As stated before, only a small amount of the salts is entrapped in the sea ice structure, within brine inclusions. The salinity and volume of these inclusions can be quantified in order to estimate the amount of impurities in the ice and its permeability to liquid and gases exchanges (see sections II.3.4 and II.4.2 respectively for more information).

• Brine volume fraction

The brine volume fraction (BrV) is computed as a function of sea ice temperature and salinity according to the relationships proposed by Cox and Weeks (1983) and based on Assur (1958):

$$BrV = \frac{V_{br}}{V} = \left(1 - \frac{V_a}{V}\right) \frac{\rho_i S_i}{F_1(T) - \rho_i S_i F_2(T)} \qquad Equation II-1$$

where V, V_{br} and V_a are the sea ice volume, the brine volume and the air volume in m³ respectively. The density of pure ice, ρ_i in kg m⁻³, is given by Equation II-2, where T is in °C and the two functions F₁(T) and F₂(T) are given in Table II-1 following Equation II-3.

$$\rho_i = 917 - (1,403 \times 10^{-4} T)$$
 Equation II-2

$$F_i(T) = a_i + b_i T + c_i T^2 + d_i T^3 \qquad Equation II-3$$

т, °С	aı	bı	C 1	dı
0 ≥ T > - 2	- 0.041221	- 18.407	0.58402	0.21454
– 2 ≥ T ≥ – 22.9	- 4.732	- 22.45	- 0.6397	- 0.01074
– 22.9 > T ≥ – 30	9899	1309	55.27	0.7160
т, °С	a1	b1	C1	dı
0 ≥ T > - 2	0.090312	- 0.016111	1.2291 x 10 ⁻⁴	1.3603 x 10 ⁻⁴
– 2 ≥ T ≥ – 22.9	0.08903	- 0.01763	- 5.330 x 10 ⁻⁴	-8.801 x 10 ⁻⁶
– 22.9 > T ≥ – 30	8.547	1.089	0.04518	5.819 x 10 ⁻⁴

Table II-1: Coefficients for $F_1(T)$ and $F_2(T)$ for different temperature intervals by Cox and Weeks (1983) and Leppäranta and Manninen (1988).

In first-year ice, the air volume fraction V_a/V can be neglected, because it is much smaller than V_b/V . It is not the case in multiyear ice, warm ice and snow-ice where V_a/V should be taken into account in the Equation II-1 (Timco and Frederking, 1996). As a result, V_b/V can be considered as a good approximation of the sea ice porosity $(V_a+V_b)/V$.

• Brine salinity

The brine salinity (S_{br}) is a function of sea ice temperature only. A change in temperature will induce a change in the BrV by the freezing or melting of pure water in the brine inclusion (Hunke et al., 2011).

Several relationships between S_{br} and T have been proposed.

Cox and Weeks (1986) suggest a relation derived from Assur (1958) where the coefficients used can be found in

Table II-2:

$$S_{br} = \alpha_0 + \alpha_1 T + \alpha_2 T^2 + \alpha_3 T^3 \qquad Equation II-4$$

Notz (2005) suggests another relation based on (Assur, 1958), where T is the temperature in $^{\circ}C$:

$$S_{br} = -1.2 - 21.8 T - 0.919 T^2 - 0.0178 T^3$$
 Equation II-5

т, °С	α ₀	α_1	α ₂	α3
– 2 ≥ T > – 22.9	- 3.9921	- 22.700	- 1.0015	- 0.019956
– 22.9 ≥ T > – 44	206.24	- 1.8907	- 0.060868	- 0.0010247

Table II-2: Coefficients used for S_{br} in Equation II-4 (Cox and Weeks, 1986).

Finally, Vancoppenolle et al. (2019) provide a new estimate of the S_{br} based on an agreement between observations and the Gibbs-Pitzer theory implemented in the FREZCHEM code (Marion et al., 1999). This gives the following equation:

$$S_{br} = -18.7 T - 0.519 T^2 - 0.00535 T^3$$
 Equation II-6

II.3.3. Brine concentration and dilution

In sea ice, gas concentration in brines strongly depends on ice temperature: when temperature decreases (i.e. during sea ice growth), the brine channels inclusions shrink in size by freezing pure water on the wall of the channels, concentrating salts, gases and other impurities in the brines – the so-called brine concentration process (e.g. Delille et al., 2014; Zhou et al., 2013). In opposite, when temperature increases, the melting of ice with the increase in the size of the brine inclusions dilutes their content – the so-called brine dilution process (Hunke et al., 2011; Notz and Worster, 2009).

II.3.4. Permeability threshold for liquid brine

Brine volume (denoted as BrV) provides information on how brine channels are connected together, and with the air above and the seawater below. Golden et al. (1998) suggested that sea ice permeability increases sharply for a BrV of 5%, a threshold that is well accepted. Below 5%, sea ice is considered as impermeable to brine transport, while above 5%, sea ice is considered as permeable, and as sea ice becomes permeable, air-ice gas exchange increases (Delille et al., 2014). The BrV threshold of 5% corresponds to an ice temperature of 5°C and a bulk ice salinity of 5.

II.3.5. Desalinisation processes

The desalinisation of sea ice encompasses the mechanisms by which brines – with its content in dissolved gas, nutrients and other impurities – are evacuated from the ice (Tsurikov, 1979). Sea ice can be approximate by two models; the boundarylayer that suggests a salt fractionation at the sea ice-seawater interface during sea ice formation, and the mushy-layer theory that suggests a continuum of salinity at the sea ice-seawater interface, and only considers two phases (ice and brine, no gas).

The best way to illustrate desalinisation processes is to compare the winter firstyear sea ice salinity profiles with that of summer or multi-year sea ice (Figure II-9) to quantify the salt lost from sea ice growth to sea ice melt.

Several processes can explain the salinity variation within sea ice across the seasons, but only a few of them are relevant for this study (for more information, see Weeks, 2010, pp.156–170). Gravity drainage is the main process responsible for the rejection of dissolved gases to the ocean during ice growth (Moreau et al., 2014). Flushing by surface meltwater is commonly recognised to be the main desalinisation process during ice decay in the Arctic. Finally, brine rejection can develop upwards, at the sea ice-atmosphere interface; gas rejection potentially occurs in parallel with this salt rejection towards the ice surface, leading to significant air-sea ice gas fluxes during sea ice growth (Tison et al., 2017).

• Initial brine rejection and incorporation

During the growth phase (see section II.2.2) and according to the boundary-layer theory, the growing sea ice rejects most of the salts at a freezing front (Burton et al., 1953; Cox and Weeks, 1975). Those salts then concentrate in the seawater at the interface of the freezing front, increasing the seawater salinity. Part of this saline seawater incorporates in the growing sea ice and forms the brine. The layer where the ice volume fraction varies from 0 to 30% is referred to as the skeletal layer (this paragraph is taken from Petrich and Eicken, 2010). According to the mushy-layer theory, the salinity in the skeletal layer is equal to the salinity of seawater at the ice interface, revealing that no salt is directly expelled at the advancing ice-seawater interface (Hunke et al., 2011; Notz and Worster, 2009).
• Brine expulsion

This process occurs again during sea ice growth. Within the cooling sea ice, part of the liquid brine continues to freeze, forming pure ice. As pure ice is less dense than the brine, it will occupy a larger volume than the former brine and may create a fracture in the ice. This results in an upward or downward expulsion of brine (Bennington, 1963).

• Gravity drainage

In wintertime, brine salinity generally decreases with temperature from the ice surface to its bottom. This salinity gradient creates, at the same time, an unstable density gradient that leads to brine convection where the ice is permeable. The convection of brine and its replacement with underlying seawater is referred to as gravity drainage through the mushy-layer theory (Notz and Worster, 2009; Worster and Wettlaufer, 1997).

Rayleigh number (Ra) introduced by Notz and Worster (2009) is a proxy for brine convection and is calculated using temperature, bulk ice salinity, derived brine salinity and brine volume fraction of the ice. However, as Ra depends on the gradient of brine salinity, the salts loss by drainage during ice core extraction, or the sampling resolution may lead to a different range of Ra values. However, there is no consensus on the critical value of Ra, leading to brine convection; Notz and Worster (2008) suggest that convection occurs above a Ra = 7, Notz and Worster (2009) then identify a critical Ra = 10, while some authors suggest to use the Ra in a qualitative way only, by comparing profiles to each other (Vancoppenolle et al., 2013; Zhou et al., 2013).

• Flushing

During the melt season, the pressure of the snow meltwater creates a downward movement of brine (Eicken et al., 2002, 2004), reducing drastically the sea ice salinity.

• Causes of a saline sea ice surface

The sea ice surface shows unique properties that may play a role in chemical processes occurring in the lower polar troposphere. For example, under intense

surface cooling, liquid water in brine freezes, increasing the dilating pure ice volume. This increase in volume can fracture the ice and therefore drive the expulsion of the remaining brine along the cracks to the ice surface (Bennington, 1963). This upward expulsion of brine (brine wicking) results in a high saline layer of brine skim (Untersteiner, 1968). Snow and frost flowers – a vapour-deposited ice crystals under strong relative humidity and temperature gradient at the ice–air interface (Barber et al., 2014) – can also influence the sea ice surface salinity by draining brine by capillarity, from the brine channels to the surface. Upward brine drainage by capillarity significantly increasing sea ice surface salinity, and thus the concentration in major ions, significantly (Domine et al., 2004; Douglas et al., 2012). Finally, flooding (see section II.2.3) may also add salts and impurities over the ice surface. Flooding then has the potential to impact the vertical salinity distribution in sea ice (Vancoppenolle et al., 2005, 2007). All the above mentioned physical processes are sources of salts and ions for the ice surface and create a suitable place for potential chemical reactions.

II.4. <u>Gas bubbles within sea ice</u>

This section describes the processes controlling gas bubbles content in sea ice.

II.4.1. Gas bubbles formation

Gas bubbles can be incorporated as air inclusions during sea ice formation. As brines are rejected at the sea ice-seawater boundary layer, their accumulation can be responsible for gas concentration that exceeds the solubility. Some studies (Killawee et al., 1998; Loose et al., 2009; Tison et al., 2002; Tsurikov, 1979) show that nucleation can occur in the boundary layer due to gas oversaturation, leading to the formation of gas bubbles that can be incorporated in sea ice. Moreover, observations show that turbulent conditions enhance gas incorporation in sea ice (Tison et al., 2002).

However, bubbles may also form within the ice during sea ice growth. Increase in gas concentration in brine due to the shrinking of brine inclusions (i.e. brine concentration, see section II.3.3) triggers the nucleation of bubbles (Tsurikov, 1979; Killawee et al., 1998; Tison et al., 2002; Light et al., 2003). The partitioning of gases between dissolved and gaseous forms in sea ice brine is a function of gas solubility, following Henry's law:

$$C_{i,br} = K_0 \times p_i$$
 Equation II-7

where $C_{i,br}$ (mol L⁻¹) is the concentration of a gas dissolved in the solution, K_0 (mol L⁻¹ atm⁻¹) is the Henry's constant, and p_i (atm) is the partial pressure of the gas. K_0 is temperature and salinity dependant. During sea ice growth, the decrease in brine temperature increases the solubility of the gases, while oppositely, the increase in brine salinity decreases the gas solubility. The net process is a decrease in gas solubility due to stronger salinity effect (see Figure 1b and 2a in Crabeck et al., 2019), leading eventually to an oversaturation. Bubbles then potentially form when the sum of the partial pressures of all the dissolved gases exceed the local hydrostatic pressure in brine (Crabeck et al., 2019; Delille et al., 2014; Geilfus et al., 2012a). In Crabeck et al. (2014a), bubbles started to form when the concentration exceeds 2.7 times the saturation with respect to the atmosphere. Crabeck et al. (2019) observed that the inner pressure in liquid brine is higher than

the atmospheric pressure during sea ice freezing, increasing gas solubility in discrete brine inclusions.

Besides the physical processes exposed above, biological activity may also contribute to the presence of gas bubbles in sea ice (e.g. Delille et al., 2007; Tsurikov, 1979; Zhou et al., 2014a).

II.4.2. Total gas content

The air volume fraction (V_a) of sea ice can be determined from bulk temperature, salinity, and density measurements (Cox and Weeks, 1983). Other methods use imaging to describe and quantify air inclusions within sea ice. For instance, Light et al. (2003) used transmitted light with a relatively poor resolution. A new method developed in Crabeck et al. (2016) involves computed tomography with X-ray imaging and gives a much higher resolution. In this last study, total gas content was estimated for the full length of some ice cores with a high vertical resolution (see the red curve in Figure II-10 where V_a range between 0 and 20%) in parallel with the sea ice texture (thin sections in Figure II-10). Such approach confirmed that the permeability of granular ice is lower than the one of the columnar ice as previously suggested in other studies (Golden et al., 1998). Finally, Crabeck et al. (2016) suggested that sea ice structure and gas solubility control the air volume fraction contained in sea ice.

II.4.3. Permeability thresholds for gas bubbles

The presence of gas bubbles in a gas permeable sea ice promotes gas exchange with the atmosphere. Bubbles migrate upwards when the brine network is connected, which is assumed to happen above a given brine fraction threshold, reported as higher for gases (BrV = 7 to 10%, in Moreau et al., 2014; Zhou et al., 2013), compared to liquids (BrV = 5%, see section II.3.4). This higher threshold for gases was ascribed to ice tortuosity that hampers bubble movement in the brine network (Zhou et al., 2013).



Figure II-10: Sea ice thin sections and air volume fraction (red curve) for 14, 16 and 25 of January. The zero depth is fixed at the boundary between granular and columnar ice (Crabeck et al., 2016).

II.5. <u>Gas transport in sea ice</u>

Gases can be found in sea ice in either solid contribution (i.e. salt precipitates, like ikaite), dissolved (i.e. brines) or gaseous phases (i.e. bubbles in liquid brines or within the ice matrix, e.g. O_2 , Ar, CH₄ in Crabeck et al., 2014a; Moreau et al., 2014 and Zhou et al., 2013). The presence of gases in sea ice under one of these three phases will have a totally different impact on their further transport (Crabeck et al., 2019): solid phase is likely to be trapped in sea ice (Delille et al., 2014), dissolved gases in brine will follow the brine dynamics, while gas bubbles will be subject to buoyancy and upward migration (Crabeck et al., 2016), potentially driving air-ice gas exchanges.

II.5.1. Brine and bubbles dynamics from sea ice growth to sea ice decay

Zhou et al. (2013) suggested that bubbles and brine dynamics from sea ice growth to its decay can be divided into three stages (Figure II-11).

- During the cold stage, an initial entrapment of gas first occurs with sea ice formation, followed by bubble nucleation during sea ice growth. This stage is associated with low permeability in the ice, which limits gas transport to sea ice bottom layer convection and molecular diffusion.
- (ii) During the transition stage, freshwater from internal melting increases the brine volume and lowers its salinity. Three factors promote bubble nucleation: changes in temperature (T) and salinity (S), the presence of hydrophobic impurities, and full-depth convection. Bubbles can then migrate upwards in permeable layers due to their buoyancy, while the liquid phase (including dissolved gases) moves with brine convection. Gas diffusion (Crabeck et al., 2014a; Loose et al., 2011) and the formation of superimposed ice may also control gas content in permeable sea ice.
- (iii) The warm stage corresponds to brine stratification as a result of prior convection or ice melting that reduces brine density anomalies and cut convection (despite sea ice permeability). During this phase, bubbles are less abundant since the source of bubble formation dies out, as internal

melting decreases gas concentration in brine below the saturation threshold.



Figure II-11: A schematic view of the three stages of brine dynamics described in Zhou et al. (2013). More information in section II.5.1.

II.5.2. Gas diffusion

In the absence of brine convection, gases are transported in the ice by diffusion. In the literature, two paths for gas diffusion have been brought out:

- The diffusive path of dissolved gases in brines: these gases diffuse in brines following the concentration gradient (Crabeck et al., 2014a; Loose et al., 2011).
- The diffusive path for gaseous phase: Gosink et al. (1976) and Loose et al.
 (2011) suggest that gas bubbles can migrate along the grain boundaries within the ice matrix.

II.6. $\underline{CO_2}$ dynamics within the ice and at the interfaces

II.6.1. Overview of the carbonate chemistry system

In seawater and brines, the major species that compose the carbonate system are CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} . Carbonate species are in equilibrium according to the dissociation constants of the carbonate system (K₁ and K₂, the first and the second dissociation constants, see Figure II-12), while CO_2 concentration is in equilibrium with atmospheric CO_2 according to Henry's law, *Ko* being the solubility coefficient of CO_2 in seawater. These constants are temperature, salinity and pressure dependants (Zeebe and Wolf-Gladrow, 2001). To date, studies of CO_2 in sea ice has been carried out with constants developed for seawater at positive temperature and within the range of salinity commonly observed in the ocean. It was assumed that the constants are valid at sub-zero temperature and high salinities. It was suggested that the best set of constants is Goyet and Poisson (1989; Brown et al., 2014). A more obvious approach is computation of carbonate system using Pitzer type parametrisation (Marion, 2001).



Figure II-12: Simplified overview of the carbonate system in the ocean in contact with the atmosphere and in standard conditions (adapted from Zeebe and Wolf-Gladrow, 2001).

The sum of the dissolved C-species is named *DIC*, in µmol kg⁻¹, for dissolved inorganic carbon:

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$
 Equation II-8

Speciation of the carbonate system can be computed using a few measurable parameters. Among them, total alkalinity (*TA*) measures the equilibrium of weak acids (pK < 4.5 at 25°C and zero ionic strength) with their conjugate bases:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4]$$
Equation II-9

The partial pressure of CO_2 (*pCO*₂) correspond to the pressure of CO_2 if it occupied alone the volume of the original mixture at the same temperature. pCO₂ can be obtained using this expression:

$$pCO_2 = x_{CO_2} \times P$$
 Equation II-10

where x_{CO_2} is the molar fraction of CO₂ and *P* is the total pressure.

We can compute the concentration of CO_2 dissolved in the solution from pCO_2 using Henry's law in Equation II-7, where the dependency of K_0 on temperature and salinity for CO_2 is given in Weiss (1974).

In the standard conditions, in seawater, carbonate precipitation (CaCO₃) may occur according to:

$$2HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 + H_2O + CO_2$$
 Equation II-11

The reverse equation of Equation II-11 gives the $CaCO_3$ dissolution.

II.6.2. The carbonate system within sea ice

Salinity impacts on TA and DIC

DIC and TA can be normalized to a constant salinity in order to test the conservative behaviour of the observed variable (TA, DIC) to salinity. See Equation II-12 and Equation II-13 where SN is the salinity selected for normalisation (e.g. the mean salinity of the sea ice) and S is the local salinity measured in the ice:

$$DIC_{SN} = \frac{DIC \times SN}{S}$$

$$Equation II-12$$

$$TA_{SN} = \frac{TA \times SN}{S}$$

$$Equation II-13$$

• Factors controlling CO₂ in the ice

Measurements of pCO_2 in sea ice and brines have increased in the last decade in both the Arctic (Crabeck et al., 2014b; Geilfus et al., 2012a; Miller et al., 2011a, 2011b) and the Southern Ocean (Delille, 2006; Delille et al., 2007; Geilfus et al., 2014). The motivation for these measurements is to better understand the role of sea ice in the carbon cycle, including its role in air–sea exchange of CO_2 , and the potential feedback effects between the changing ice cover, CO_2 fluxes, and climate change. Several factors control the CO_2 dynamics in sea ice and therefore the p CO_2 within sea ice (Zhou et al., 2015): (i) the initial content of DIC (dissolved inorganic carbon), (ii) the changes in brine concentration/ dilution due to temperature changes, (iii) the precipitation and dissolution of the carbonate minerals (CaCO₃), (iv) the biotic processes such as primary production and respiration, (v) the gas transport through sea ice, and (vi) the gas exchange at both sea ice interfaces.

- (i) As sea ice is formed from seawater during the autumn freeze-up, it appears that the dissolved inorganic and organic compound concentrations in sea ice depend on those of the parent water (Petrich and Eicken, 2010; Weeks, 2010). Indeed, Geilfus et al. (2012a) reported larger sea ice pCO₂ in the Arctic Ocean compared to the Southern Ocean, especially in winter and early spring. It was suggested that this difference could be due to enhanced respiration in the Arctic sea ice, driven by massive particulate organic carbon (POC) and dissolved organic carbon (DOC) content (see Figure III-1, Geilfus et al., 2012a) as a result of Arctic rivers supply.
- (ii) Brine concentration and dilution (see section II.5.1 for more information) concentrate or dilute the impurities contained in the brines (Hunke et al., 2011; Notz and Worster, 2009) including CO₂.
- (iii) The precipitation and dissolution of calcium carbonate produce and consume CO₂, respectively (Dieckmann et al., 2010, 2008; Geilfus et al., 2013). These processes alter the CO₂ budget in the ice when sea ice is semi-permeable and if the calcium carbonate precipitates remain in the ice while the generated CO₂ is rejected in the under-ice water (Delille et al., 2014; Rysgaard et al., 2007) or to the atmosphere (Geilfus et al., 2013; Loose et al., 2011).
- (iv) The microorganisms that can find their habitat in sea ice may consume CO₂ through photosynthesis or produce CO₂ through respiration (Papadimitriou et al., 2007). The buffer factor describes the change in pCO₂ relative to the DIC change induced by an input (i.e. respiration) or output of dissolved CO₂ and is a function of several physicochemical

conditions (Delille et al., 2005; Frankignoulle, 1994). The homogeneous Revelle factor (6) was introduced by Sundquist et al. (1979):

$$\beta = \frac{\Delta p C O_2}{\Delta D I C} \times \frac{D I C}{p C O_2} \qquad Equation II-14$$

(v) The gas transport processes describe in section II.5.

II.6.3. CO₂ exchanges at the sea ice–seawater interface

Brine convection or gravity drainage (Notz and Worster, 2009; Hunke et al., 2011) is thought to be a significant process responsible for the rejection of dissolved gases to the ocean during ice growth (Moreau et al., 2014) and thus leading to sea ice-seawater exchanges. In the absence of convection, the diffusion of dissolved gases becomes the main pathway to transport dissolved gas across the ice (Gosink et al., 1976; Loose et al., 2011; Shaw et al., 2011) as bubble buoyancy do not account in downwards exchanges. This diffusive flux is driven by dissolved gas concentration gradients (Delille et al., 2007; Nomura et al., 2010c; Miller et al., 2011b).

The diffusive CO₂ fluxes at the sea ice–seawater interface can be assessed using the Fick's law given in the following equation:

$$F = k \times \Delta C$$
 Equation II-15

where F is the flux in mol m⁻² s⁻¹, k is the gas transfer velocity coefficient in m s⁻¹ and ΔC is the concentration gradient, in mol m⁻³, of the studied gas, here CO₂, at the sea ice–seawater interface. We assumed that this interface corresponds to the film model. In this model, exchange of gas across the interface is mainly limited by molecular diffusion through a stagnant layer or film water at the interface with a constant thickness which depends on given circumstances; i.e. the influence of wind is limited due to the sea ice cover (Whitman, 1923). In this model, k is proportional to D, the molecular diffusion coefficient in m² s⁻¹, and inversely proportional to the Schmidt number (i.e. the ratio of water viscosity to molecular diffusivity), and is dependent to sea ice permeability and tortuosity.

II.6.4. CO₂ fluxes at the atmosphere–sea ice interface

The magnitude and direction of CO_2 flux at the atmosphere-sea ice interface are mainly modulated by the permeability of the ice (see sections II.3.4 and II.4.3) and the air-ice pCO₂ gradient (Delille et al., 2014; Geilfus et al., 2012a). These parameters are likely to change rapidly during the growth of sea ice. Indeed, temperature and salinity influence permeability (Golden et al., 2007), while all the processes described above in section II.6.2 (see *Factors controlling CO₂ in the sea ice*) influence the sea ice content in CO₂ and thus the air-ice pCO₂ gradient (Delille et al., 2014; Geilfus et al., 2012a; Nomura et al., 2010a).

The Fick's law (Equation II-15) can be written using the pCO_2 instead of the concentration in CO_2 thanks to the Henry's law given in Equation II-7:

$$F = K \times \Delta pCO_2$$
 Equation II-16

where K is the gas transfer coefficient expressed in mol $m^{-2} d^{-1} atm^{-1}$, and ΔpCO_2 is the CO₂ partial pressure gradient, in atm, between the two interfaces studied, i.e. the air and the ice. K is proportional to k through the following relation (Wanninkhof, 1992):

$$K = k \times K_0$$
 Equation II-17

where K_0 is the Henry's constant, a function of temperature and salinity, expressed in mmol m⁻³ atm⁻¹ given by Weiss (1974):

 $ln K_0 = A_1 + A_2(100/T) + A_3 ln(T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2]$ Equation II-18 We assume that K is dependent to wind speed, a factor that is hard to parametrize on sea ice due to the strong variability of snow cover and sea ice surface structure.

When pCO_2 in the sea ice is higher than in the air, sea ice has the potential to release CO_2 to the atmosphere leading to a positive flux. The inverse process leads to a negative flux. Gas bubbles may also provide an alternative gas transport pathway (Zhou et al., 2013; Crabeck et al., 2014a). The efficiency of this pathway depends on whether bubbles can only diffuse molecularly (Loose et al., 2011) or rise due to their buoyancy (Moreau et al., 2014). Other parameters such as sea ice cover (e.g. snow, Nomura et al., 2010c or frost flowers, Barber et al., 2014) and algal communities present at the surface (Zemmelink et al., 2006) can change the direction and the amplitude of the CO_2 flux at the atmosphere–sea ice interface.

II.7. N_2O dynamics within the ice and the seawater

II.7.1. Processes controlling N₂O concentration

• N₂O solubility

Weiss and Price (1980) suggest to compute the solubility of N_2O (C_{N_2O} in mol L⁻¹) in a liquid in equilibrium with moist air according to the following equations:

$$C_{N_2O} = F \times x_{N_2O} \times P$$
 Equation II-19

$$\ln F = A_1 + A_2 \left(\frac{100}{T}\right) + A_3 \ln \left(\frac{T}{100}\right) + A_4 \left(\frac{T}{100}\right)^2 + S \left[B_1 + B_2 \left(\frac{T}{100}\right) + B_3 \left(\frac{T}{100}\right)^2\right] \qquad Equation$$

$$II-20$$

With the function F, in mol L⁻¹ atm⁻¹, x_{N_20} is the dry mole fraction of atmospheric N₂O, P is the pressure in atm, S is the salinity and T is the temperature in K. The constants of the polynomial are: A₁ = -165.881, A₂ = 222.8743, A₃ = 92.0792, A₄ = -1.48425, B₁ = -0.05624, B₂ = 0.031619 and B₃ = -0.004847. The polynomial Equation II-20 is valid for a temperature range of 0 to 40°C and a salinity range of 0 to 40.

• Biological processes producing N₂O in seawater

In the aquatic environment, N_2O is mainly produced by microbial processes, namely (i) nitrification and (ii) denitrification (see Figure II-13).

- (i) Nitrification is the oxidation of ammonium, NH₄⁺, in nitrite, NO₂⁻, and ultimately in nitrate, NO₃⁻ by nitrifying bacteria (Yoshinari, 1976 and Nevison et al., 2003). This reaction takes place in oxic environments and can be limited by light inhibition (Ward B., 2008). N₂O appears as a by-product of the autotrophic final step of this reaction, and its production by ammonia-oxidizing bacteria yield strongly increases of N₂O as O₂ levels decrease (Goreau et al., 1980; Nevison et al., 2003). N₂O can also be formed during heterotrophic nitrification, but the relevance of this process is not known yet (Stein and Yung, 2003; Wrage et al., 2001).
- (ii) Denitrification is the anaerobic reduction of NO₃⁻ to N₂ by bacteria (denitrifiers) that can use different electron donors, with N₂O as an intermediate product of the reaction (Suntharalingam and Sarmiento, 2000). The most commonly encountered is heterotrophic denitrification,

which simply uses organic matter. Denitrifiers are facultative anaerobic bacteria that reduce NO_3^- under suboxic conditions (i.e. $0 < O_2 < 2.5 \mu mol L^{-1}$), such as sediments and oxygen minimum zones (Capone et al., 2008; Codispoti et al., 2005). However, in the presence of O_2 at trace level concentrations, denitrification chain may not be complete and then stops at the N₂O stage. Thus, denitrification can act as a sink or a source of N₂O.

 N_2 fixation is another biological process involved in the nitrogen cycle and is the inverse reaction than that of denitrification, see Figure II-4, Gruber and Sarmiento, 1997) but is not known to consume or produce any N_2O . However, N_2O fixation has been suggested by Cornejo et al. (2015) as a contribution to the N_2O sinks for the atmosphere. But this process is still weakly documented to be included in the N_2O budget.



Figure II-13: Processes involved in the N₂O distribution in the ocean and the atmosphere. Adapted from Capone (2008).

Hence, it is not possible to distinguish the sources of N_2O solely based on bulk N_2O concentrations or environmental conditions. Other parameters are then used, as N^* and AOU.

The nitrate excess, N^* (in µmol kg⁻¹) is a parameter that provides insights on the impact of N₂ fixation and denitrification on the nutrient fields. N^* is defined as the following equation (Deutsch et al., 2001):

$$N^* = [NO_3^-] - 16 \times [PO_4^{3-}] + 2.9$$
 Equation II-21

Following the N:P Redfield ratio 16:1 (Redfield, 1933), a positive N^* indicates an excess in nitrate (NO₃-) in comparison to phosphate (PO₄³⁻) and implies that N₂ fixation occurs at higher rates than denitrification. A negative N^* thus indicates that denitrification outweighs the N₂ fixation (Capone et al., 2008). Note that N^* does not give any information on the rate of these two processes.

The apparent oxygen utilisation, AOU (in µmol L⁻¹), was calculated as the difference between the O₂ gas solubility (O_2^* , in µmol L⁻¹) and the measured O₂ concentrations (O_2 in µmol L⁻¹):

$$A0U = 0_2^* - 0_2 \qquad \qquad Equation II-22$$

The O_2^* values are calculated using the equation of Garcia and Gordon (1992) based on the O_2^* values of Benson and Krause (1984). AOU represents an estimate of the O_2 consumed or produced by auto- and heterotroph microbial processes (Redfield et al., 1963). A positive relation between N_2O_{sat} and AOU may be a sign of nitrification.

II.7.2. The N₂O dynamic in the Arctic Ocean

The status of the Arctic Ocean – as a source or sink of N₂O for the atmosphere – is unclear due to the paucity of data and the coexistence of both N₂O undersaturation and oversaturation in surface waters with respect to the atmosphere (Figure II-14). In spring and summer, from East to West (see Figure II-15), the Nansen Basin and the Amundsen Basin are mostly undersaturated in N₂O, with a patch oversaturated in the Amundsen Basin (Verdugo et al., 2016). The Greenland Sea also appears to be undersaturated in N₂O (Weiss et al., 1992; Zhan et al., 2016, 2015), showing an oversaturation southwards (Weiss et al., 1992). The Canada Basin and the Chukchi Sea – except near the Bering Strait – are undersaturated in N₂O (Fenwick et al., 2017; Hirota et al., 2009; Zhan et al., 2015) while the Canadian Archipelago and the Baffin Bay surface waters are mostly oversaturated in N₂O in summer (Fenwick et al., 2017; Gagné, 2015; Kitidis et al., 2010). To our best knowledge, only one study has reported autumn N₂O values (Fenwick et al., 2017) and no data are available since 1982 in winter and spring, preventing from providing a robust yearly budget of air–sea N₂O fluxes for the Arctic Ocean.



Figure II-14: Schematic view of Arctic Ocean saturation in N_2O with respect to the atmosphere in a) in spring and summer ,and b) winter, from available studies referenced as numbers 2 to 10 (see Table II-3 for the correspondence of each number).

Number	Reference	Cruise		
2	Fenwick et al., 2017	SWL 2015-07/ 1502/ LSSL 2015-06		
3	Verdugo et al., 2016	LOMROG III		
4	Zhan et al., 2015 & 2016	5th CHINARE		
5	Zhang et al., 2015	4th CHINARE		
6	Randall et al., 2012	IPY-CFL 2008		
7	Gagné 2015	CCGS Amundsen 2007-08 Leg 11a		
8	Hirota et al., 2009	R/V Mirai MR06-04		
9	Kitidis et al., 2010	Beringia 2005		
10	Weiss et al., 1992	TTO/NAS		

Table II-3: References and cruises related to the numbers on Figure II-14.

On the shelves, in shallow water columns, nitrification is limited by light inhibition (see section II.7.1), and denitrification is inhibited by aerobic conditions. Thus the observed oversaturation in N_2O is more likely due to the release of N_2O from the sediment (Zhang et al., 2015).

Off the shelves (e.g. Beaufort or Greenland Seas), the overall undersaturated N_2O vertical distribution does not seem to be significantly affected by biological processes (i.e. nitrification or denitrification).

It has also been hypothesized that sea ice cover affects the distribution of N_2O in surface waters. Sea ice formation and the subsequent release of brine may lead to surface waters N_2O oversaturation (Randall et al., 2012), similar to what was reported for other gases (e.g. CO_2 ; Delille et al., 2007; Loose et al., 2009; Tison et al., 2002). Later in the season, it has been repeatedly hypothesised that dilution of surface waters by sea ice meltwater promotes N_2O undersaturation (Kitidis et al., 2010; Randall et al., 2012; Verdugo et al., 2016; Zhang et al., 2015).

II.7.3. The N_2O dynamic in sea ice

A study on nitrification and anaerobic bacterial cultures showed that N_2O production could occur in sea ice (Priscu et al., 1990). Similarly to CO_2 , N_2O in sea ice might be subject to several biological, chemical and physical processes (Tison et al., 2017; Tsurikov, 1979; Zhou et al., 2014a): brine dilution and concentration (section II.3.3), bubbles nucleation (section II.4.1), gas transport and exchanges

across depths within the sea ice, between the atmosphere and the ice, and between the ice and the seawater (section II.5).

To date, only one study presents N₂O measurements in sea ice (Randall et al., 2012). Randall et al. (2012) pointed out that sea ice formation and melt has the potential to generate sea-air or air-sea fluxes of N₂O, respectively and ascribed low levels of N₂O measured at the bottom of sea ice to potential bacterial denitrification. The process of denitrification could be responsible for significant N₂O accumulation in ice. Denitrification in O₂-depleted sea ice has been suggested by Kaartokallio (2001), Nomura et al. (2009) and Rysgaard et al. (2008), although it would have to be associated with anoxic microenvironments, while oxygen is usually observed at or above saturation in sea ice (Zhou et al., 2014a).

II.8. <u>The Arctic Ocean</u>

II.8.1. Arctic Ocean topography

One of the key features of the Arctic Ocean is its central position in extensive shallow continental shelves: the Chukchi Shelf and the Beaufort Shelf along North America; the Lincoln Shelf along northern Greenland; the Barents Shelf, Kara Shelf, Laptev Shelf, and East Siberian Shelf along Eurasia (see Figure II-15). The shelves represent around 50% of the Arctic seafloor and are recognized as a productive place (Carmack and Wassmann, 2006).



Figure II-15: Bathymetric chart of the Arctic Ocean annotated with the names of seafloor features. Figure and legend edited by Hobart M. King on the following website: https://geology.com/articles/arctic-ocean-features/.

II.8.2. Arctic Ocean circulation

The Arctic Ocean is mainly circumpolar, not including Fram Strait that allows the major flow of water masses to pass in and out the Arctic Ocean (Figure II-16). Both Atlantic waters (AW) and Pacific waters (PW) enter the Arctic Ocean. However, the inflow of AW through Fram Strait and the Barents Sea is on average 5 times larger than the inflow of Pacific Water (PW) through Bering Strait (e.g. Schauer et al., 2002; Woodgate et al., 2005). In addition, the Bering Strait maximum depth is 49 m, and therefore, only shallow waters can enter in the Arctic Ocean through that strait. The Gulf Stream, carrying warm AW, enters in the Arctic Basin in the Norwegian Sea and moves northwards along the coast of Norway. It divides into two main branches and continues northwards with one branch on either side of Spitzbergen.

In the Arctic Ocean, the AW is either cooled – becoming denser and sinks – or forms the polar surface water (PSW) after mixing with riverine input and Pacific water inflow, and interaction with sea ice. River runoff and sea ice meltwater are the major contributors to the freshening of the Arctic Ocean surface water (Bauch et al., 1995; Rudels et al., 1996). After circulating in the North Polar Basin, the PSW leaves the Arctic Ocean, mainly through Fram Strait between Svalbard and Greenland. AW inflow has, therefore, a significant imprint on the PSW chemical properties.

In addition, PW circulates with the anticyclonic Beaufort Gyre of the Canadian Basin, and then exits into the North Atlantic through Fram Strait or the Canadian Archipelago (Jones et al., 2003; Kawai-Yamamoto and M., 2006). PW masses are distinct from AW masses by their lower salinities, higher nutrients and distinct biological communities (Carmack and Wassmann, 2006).



Figure II-16: Major surface currents in the North Atlantic Ocean (figure 3.29 from Arctic Monitoring and Assessment Programme, 1998). Red arrows correspond to warm currents, blue arrows correspond to cold currents, and square boxes indicate the denser inflowing waters that are submerging under the Polar Surface Water.

CHAPTER III: The impact of dissolved organic carbon and bacterial respiration on pCO₂ in experimental sea ice

Jiayun Zhou^{1,2,3}, Marie Kotovitch^{1,2}, Hermanni Kaartokallio⁴, Sébastien Moreau⁵, Jean-Louis Tison¹, Gerhard Kattner⁶, Gerhard Dieckmann⁶, David N. Thomas^{4, 7}, Bruno Delille²

¹ Laboratoire de glaciologie, DSTE, Université Libre de Bruxelles, Belgium

- ² Unité d'océanographie chimique, MARE, Université de Liège, Belgium
- ³ Division of Earth and Ocean Sciences, Duke University, Durham, NC, USA

⁴ Marine Research Centre, Finnish Environment Institute (SYKE), Helsinki, Finland

⁵ Georges Lemaître Centre for Earth and Climate Research, Earth and Life Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium

⁶ Alfred Wegener Institute Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany

⁷ School of Ocean Sciences, Bangor University, Menai Bridge, United Kingdom

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J. Zhou ^{a,b,c,*}, M. Kotovitch ^{a,b}, H. Kaartokallio ^d, S. Moreau ^e, J.-L. Tison ^a, G. Kattner ^f, G. Dieckmann ^f, D.N. Thomas ^{d,g}, B. Delille ^b

^aLaboratoire de glaciologie, DSTE, Université Libre de Bruxelles, Belgium

^bUnité d'océanographie chimique, MARE, Université de Liège, Belgium

^c Division of Earth and Ocean Sciences, Duke University, Durham, NC, USA

^d Marine Research Centre, Finnish Environment Institute (SYKE), Helsinki, Finland

e Georges Lemaître Centre for Earth and Climate Research, Earth and Life Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium

^fAlfred Wegener Institute, Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany

^gSchool of Ocean Sciences, Bangor University, Menai Bridge, United Kingdom

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ABSTRACT

Previous observations have shown that the partial pressure of carbon dioxide (pCO₂) in sea ice brines is generally higher in Arctic sea ice compared to those from the Antarctic sea ice, especially in winter and early spring. We hypothesized that these differences result from the higher dissolved organic carbon (DOC) content in Arctic seawater: Higher concentrations of DOC in seawater would be reflected in a greater DOC incorporation into sea ice, enhancing bacterial respiration, which in turn would increase the pCO2 in the ice. To verify this hypothesis, we performed an experiment using two series of mesocosms: one was filled with seawater (SW) and the other one with seawater with an addition of filtered humic-rich river water (SWR). The addition of river water increased the DOC concentration of the water from a median of 142 μmol L_{water}⁻¹ in SW to 249 μmol L_{water}⁻¹ in SWR. Sea ice was grown in these mesocosms under the same physical conditions over 19 days. Microalgae and protists were absent, and only bacterial activity has been detected. We measured the DOC concentration, bacterial respiration, total alkalinity and pCO2 in sea ice and the underlying seawater, and we calculated the changes in dissolved inorganic carbon (DIC) in both media. We found that bacterial respiration in ice was higher in SWR: median bacterial respiration was 25 nmol C Lice⁻¹ h⁻¹ compared to 10 nmol C Lice⁻¹ h⁻¹ in SW. pCO₂ in ice was also higher in SWR with a median of 430 ppm compared to 356 ppm in SW. However, the differences in pCO₂ were larger within the ice interiors than at the surfaces or the bottom layers of the ice, where exchanges at the air-ice and ice-water interfaces might have reduced the differences. In addition, we used a model to simulate the differences of pCO2 and DIC based on bacterial respiration. The model simulations support the experimental findings and further suggest that bacterial growth efficiency in the ice might approach 0.15 and 0.2. It is thus credible that the higher pCO₂ in Arctic sea ice brines compared with those from the Antarctic sea ice were due to an elevated bacterial respiration, sustained by higher riverine DOC loads. These conclusions should hold for locations and time frames when bacterial activity is relatively dominant compared to algal activity, considering our experimental conditions.

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1. Introduction

Sea ice is formed from the freezing of seawater and covers about 6% of the Earth's ocean surface. It has a heterogeneous structure composed of a matrix of pure ice and brine inclusions. Although sea ice is currently assumed to be impermeable to gas exchange in large-scale climate models, theoretical considerations

http://dx.doi.org/10.1016/j.pocean.2015.12.005 0079-6611/© 2015 Elsevier Ltd. All rights reserved. (Golden et al., 1998) and pioneer gas measurements (Gosink et al., 1976) indicate that sea ice may be permeable under specific conditions of ice temperature and salinity. Measurements of pCO_2 in sea ice and brines have been intensified in both the Arctic (Crabeck et al., 2014; Geilfus et al., 2012a; Miller et al., 2011a, 2011b) and the Southern Ocean (Delille, 2006; Delille et al., 2007; Geilfus et al., 2014). The motivation for these measurements is to better understand the role of sea ice in the carbon cycle, including its role in air–sea exchange of CO_2 , and the potential feedback effects between the changing ice cover, CO_2 fluxes, and climate change.

^{*} Corresponding author at: Division of Earth and Ocean Sciences, Duke University, Durham, NC, USA.

Current measurements indicate that sea ice may act as a source or a sink for atmospheric CO₂, depending on the interplay of four processes:

- (i) Brine concentration and dilution are associated with changes in ice temperature. When cooling a sea ice sample, some of the liquid water of the brine freezes, reducing the brine volume and inclusions and increasing the concentration of the impurities in the brine – this is the so-called brine concentration. In contrast, when warming a sea ice sample, some of the pure ice melts, increasing the volume of the brine inclusion and decreasing the concentration of the impurities in brine – this is the so-called brine dilution (Hunke et al., 2011; Notz and Worster, 2009).
- (ii) Biological activity, which includes the photosynthesis and respiration by organisms, respectively, consumes and produces CO₂ (e.g., Papadimitriou et al., 2007).
- (iii) The precipitation and dilution of calcium carbonate, which produces and consumes CO_2 , respectively (Dieckmann et al., 2010, 2008; Geilfus et al., 2013), effectively alters the CO_2 budget in the ice when sea ice is semi-permeable, and when the calcium carbonate precipitates remain in the ice while the generated CO_2 is rejected into the under-ice water (Delille et al., 2014; Rysgaard et al., 2007) or to the atmosphere (Geilfus et al., 2013; Loose et al., 2011).
- (iv) Gas transport through sea ice is not yet well constrained, but it is commonly assumed that sea ice is permeable for gas transport when its brine volume fraction is above 5% (Golden et al., 1998). Brine drainage – the intensity of which is estimated using Raleigh numbers – is thought to be a significant process for ice-water exchange (Notz and Worster, 2009), while gas bubble formation potentially plays an important role in air-ice exchange (Moreau et al., 2014; Zhou et al., 2013). The diffusion of CO₂ through sea ice also affects air-ice exchange, but seems to be much slower, i.e., less efficient than gas bubble transport (Loose et al., 2014).

Previous studies indicate that, for a given brine temperature, the pCO_2 in sea ice brine in the Arctic Ocean (Geilfus et al., 2014, 2012a) was generally higher than that in the Southern Ocean (Delille et al., 2014; Geilfus et al., 2014), especially when the average ice temperature was below $-4 \,^{\circ}C$ – which generally corresponds to the winter and early spring period (Fig. 1). In this study, we hypothesized that the higher pCO_2 was associated to the more intense bacterial respiration in the Arctic sea ice, due to



Fig. 1. pCO_2 measurements in sea ice and brine in the Arctic and Antarctica after Geilfus et al. (2014). The horizontal line indicates a pCO_2 of 400 ppm – a reference value considering current atmospheric pCO_2 .

the large input of riverine particulate organic carbon (POC) and dissolved organic carbon (DOC) in the Arctic Ocean (e.g., Dittmar and Kattner (2003), Hansell et al. (2009)). Ice temperature is unlikely to explain the Arctic-Antarctic discrepancies, because at a given temperature, the effect of brine concentration on pCO₂ is expected to be the same in both hemispheres. However, the impact of DOC availability on bacterial respiration and pCO₂ in sea ice has not yet been demonstrated by systematic DOC and POC measurements in parallel. Therefore, we performed an indoor experiment using two series of mesocosms: One was filled with seawater (SW) and another with seawater and an addition of filtered river water (SWR) to simulate riverine DOC input. The objective of the present paper is to verify whether or not higher DOC concentrations in seawater, due to an addition of riverine DOC, induce larger DOC concentrations in sea ice, which in turn enhance bacterial respiration and pCO₂ in the ice.

2. Material and methods

2.1. Experimental setting, and sampling routine and initial conditions

The experimental setting and sampling routine has been described in Zhou et al. (2014). Briefly, we ran a 19-day experiment in the Arctic Environmental Test Basin facility of the Hamburg Ship Model Basin (www.hsva.de) from May to June 2012. We used 21 polyethylene experimental mesocosms each with a volume of 1.2 m³. Eleven of the mesocosms were filled with 1000 L of seawater from the North Sea (referred here after as SW), and the remaining ten were filled with 900 L of seawater from the North Sea and 100 L of filtered river water collected at a peat-dominated catchment of the River Kiiminkijoki, in Finland (referred here after as SWR).

The addition of river water caused a significantly higher DOC concentration in the SWR mesocosms (paired *t*-test, p < 0.001): Median salinity-normalized DOC concentrations were 140 µmol L_{water}^{-1} in SW and 251 µmol L_{water}^{-1} in SWR (salinity 30.9), with a standard deviation of 3% in the SW mesocosms and 9% in SWR. However, salinity-normalized dissolved organic nitrogen (DON) was not significantly different between both mesocosm series (median of 16 μ mol L_{water}⁻¹ in SW and 19 μ mol L_{water}⁻¹ in SWR), because its concentration in river and North Sea water were almost the same, and the standard deviation was relatively high (17%) in both SW and SWR mesocosms. The carbonate chemistry was also not significantly different for both mesocosm series: median salinity-normalized total alkalinity was 2314 µmol kgwater⁻¹ in SW and 2336 µmol kgwater⁻¹ in SWR; median salinity-normalized dissolved inorganic carbon (DIC) were 2113 $\mu mol~kg_{water}{}^{-1}$ in SW and 2161 μ mol kg_{water}⁻¹ in SWR; and median pCO₂ were 212 ppm in SW and 231 ppm in SWR, respectively. The salinities of the SWR mesocosms were adjusted to the SW values by adding aquarium standard salt (Tropic Marin®). Nitrate (NO3⁻) and phosphate (PO_4^{3-}) concentrations were also adjusted to concentrations that would not limit bacterial growth in both series of mesocosms, and that were representative of areas in both Arctic and Southern Oceans (Zhou et al., 2014).

Ice was grown from day 0 to 14, during which the air temperature was maintained at -14 °C, and then the air temperature was increased to -1 °C to trigger a decay phase. We collected ice, brine and seawater at various occasions from day 0 to day 19 for the measurements of temperature, salinity, DOC, inorganic nutrients, bacterial abundance, and bacterial activity (Zhou et al., 2014), as well as pCO₂ and total alkalinity.

Because the physical constraints were similar for both the SW and SWR mesocosms, we expected bacterial activity to be the only process affecting the difference of pCO_2 in both water and ice.

Median bacterial abundance was 922 cells L_{water}^{-1} in SW at the beginning of the experiment and was not significantly different from the 972 cells L_{water}^{-1} in SWR. Protists and active photoautotrophs were absent in the experiment (checked daily by microscopy and epifluorescence microscopy, respectively). As a corollary, there was no autochthonous production of DOC and our experiment focuses on the impact of the additional allochtonous DOC (added by the river water) on bacterial respiration and pCO₂ in both water and ice. Although photoautotrophs were absent in our experiments, we believe that it would not drastically affect the verification of the hypothesis, because the largest observed difference of pCO₂ in brine corresponds to the lowest ice temperature (Fig. 1), which mostly correspond to the ice interior (over winter and early spring) where algal activity is relatively limited compared to the bacterial activity (Baer et al., 2015).

2.2. Brine volume fraction and Raleigh number

The brine volume fraction is used here as a proxy of sea ice permeability and is calculated from the ice temperature and salinity following the relationship of Cox and Weeks (1983). We assume that the sea ice was permeable for a brine volume fraction exceeding 5% (Golden et al., 1998). We also calculated the Rayleigh number (Ra), which is a proxy for brine convection as described by Notz and Worster (2008). Theoretically, convection is possible in an ice layer (of a thickness h) when Ra exceeds 1 and decreases from the top to the bottom of that layer (Notz, personal communication). We thus simply assume the critical Ra being 1 following those theoretical considerations.

2.3. DOC and DON

Samples for the determination of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were stored frozen $(-20 \,^{\circ}\text{C})$ in glass vials (Wheaton; pre-combusted at 500 $\,^{\circ}\text{C}$ for 5 h) and determined by high temperature catalytic oxidation and subsequent non-dispersive infrared spectroscopy and chemiluminescence detection, respectively (TOC-VCPN, Shimadzu). After each batch of five samples, one reference standard (DOC-DSR, Hansell Research Lab, University of Miami, US), one ultrapure-water blank and one potassium hydrogen phthalate standard for DOC and potassium nitrate for TDN were measured. DON concentrations were calculated as difference of TDN and inorganic nitrogen. The accuracy of the measurements was $\pm 5\%$.

2.4. Bacterial respiration

Bacterial respiration has been calculated as the difference between the bacterial carbon demand and bacterial production. We measured bacterial production (see below) and assumed that it represented 34.8% (bacterial growth efficiency, BGE) of the bacterial carbon demand to deduce the bacterial respiration. BGE was derived as mean estimate from available sources for sea-ice bacteria or bacteria in very cold temperatures (Kuparinen et al., 2011; Nguyen and Maranger, 2011; Rivkin and Legendre, 2001).

For the bacterial production measurements, samples containing a known amount of crushed ice and sterile-filtered seawater (Kaartokallio, 2004) were prepared in a cold room as follows: each intact 5–10 cm ice core section was crushed using a spike and electrical ice cube crusher. Approximately 10 mL of crushed ice was weighed in a scintillation vial. To better simulate the brine pocket salinity and ensure an even distribution of labelled substrate, 3 ± 1 mL of sterile filtered (through a 0.2 µm filter) seawater from the sample bags were added to the scintillation vials. Bacterial production was measured immediately after sample collection using the [³H]-thymidine incorporation method (Fuhrman and Azam,

1982, 1980). Two aliquots and a formaldehyde-fixed absorption blank were amended with [3H]-thymidine (PerkinElmer, USA, specific activity 20 $\rm Ci\,mmol^{-1}$). The added concentration was 30 nmol L⁻¹ for all sample types. The samples were incubated in the dark at -0.6 °C on crushed ice in an insulated container according to the projected level of activity: ice samples were incubated between 19 h and 22 h, water and brine samples between 4 h and 6 h. The incubations were stopped by addition of formaldehyde and samples were processed using the standard cold-TCA extraction and filtration procedure. Samples were extracted for 15 min in ice-cold 5% TCA and labelled macromolecules collected on 0.2 µm mixed cellulose ester membrane filters (Osmonics). Filters were rinsed five times with ice-cold 5% TCA and placed in clean scintillation vials. A Wallac WinSpectral 1414 counter and InstaGel (Perkin-Elmer) cocktail were used in scintillation counting. Bacterial production was calculated using a cell conversion factor of 2.09×10^{18} cells mol⁻¹ (Smith and Clement, 1990), a cell volume of 0.3 µm³ (Kaartokallio, 2004; Smith and Clement, 1990) and a carbon conversion factor of 0.12 pgC μm^{-3} (Nagata and Watanabe, 1990; Pelegrí et al., 1999).

2.5. pCO₂

The pCO₂ of the seawater was measured in-situ using a custommade equilibration system, which is described in Delille et al. (2014). Briefly, the system consists of a membrane contractor equilibrator (Membrana®, Liqui-cell) that is connected to a nondispersive infrared gas analyser (IRGA, Li-Cor® 6262) via a closed air loop. Seawater and air flow rates through the equilibrator and IRGA were approximately 2 L min⁻¹ and 3 L min⁻¹, respectively. Temperature was simultaneously measured in situ and at the outlet of the equilibrator using Li-Cor[®] temperature sensors. Temperature correction of pCO₂ was applied assuming that the relation of Copin-Montegut (1988) is valid at low temperature and high salinity. Data were stored on a Li-Cor® Li-1400 data logger. All devices, except the peristaltic pump, were enclosed in an insulated box that contained a 12 V power source providing enough warming to keep the inside temperature above 0 °C. Uncertainty is less than 5 µatm.

The method for the pCO2 measurements in ice is the same as in Geilfus et al. (2012b), but with longer equilibrium times following Crabeck et al. (2014). The ice samples were cut with a band saw, in a cold room at -25 °C and adjusted to the container's inner volume $(4 \text{ cm} \times 4 \text{ cm} \times 4.4 \text{ cm})$. The sample was sanded down using finegrained sandpaper so that it fitted tightly into the container to minimize the headspace volume. Then, the container was placed into a Dewar vessel filled with ethanol, which was cooled to -30 °C with liquid nitrogen. The container was then connected to the extraction line (tap closed). The line was first evacuated down to a pressure of 10^{-3} Torr, after which the container was evacuated for 5 min. The low temperature of the vessel insures sea ice impermeability, i.e., the CO2 of the ice was not vacuumed during this process. The standard gas was then injected into the container at 1013 mbar. The container was subsequently removed from the extraction line (tap closed), placed in a thin plastic bag and submerged in a thermostatic bath (set to the in situ temperature, i.e., that was measured on the ice samples directly after the extraction). After 20 h of equilibrium, the container was placed in a Dewar filled with ethanol cooled at the in situ temperature and reconnected to the evacuated (10^{-3} Torr) extraction line. At the same time, a water trap consisting of a Dewar filled with an ethanol bath at -65 °C was placed on the line just before the GC. The gas was finally injected into the GC. Immediately after the injection, the ice sample temperature was measured using a calibrated thermometer (Testo 720[®]). Reproducibility of the measurement is 2.9%

2.6. TA and DIC

Total alkalinity (TA) was measured on melted bulk ice and seawater samples. Ice cores were cut at a 2 cm-depth resolution (about 50 g of ice for each section) and melted. Melted bulk ice and seawater samples were poisoned with a solution of supersaturated HgCl₂ and then stored in the dark, until analysis (one year after the sampling). TA was measured by open-cell titration with 0.11 M HCl and the endpoints were determined according to Gran (1952). Routine analyses of Certified Reference Materials (provided by A.G. Dickson, Scripps Institution of Oceanography) ensured that the uncertainty of the TA measurements was less than 4 µmol kg⁻¹.

Dissolved inorganic carbon (DIC) was calculated from TA and pCO₂ using CO2SYS (Lewis and Wallace, 1998), the CO₂ acidity constants of Mehrbach et al. (1973) refitted according to Dickson and Millero (1987) and other constants advocated by DOE (1994). We assumed that the CO₂ dissociation constants were applicable at sub-zero temperatures as suggested by Marion (2001) and Delille et al. (2007). To compare DIC in seawater and in melted bulk ice, we normalized the DIC values to a salinity of 7 (DIC₇), for consistency with previous studies. The salinity of 7 is also the mean salinity of the ice in this study. Uncertainty of DIC₇ deduced from the reproducibility of TA and pCO₂ has been evaluated to be $0.8 \,\mu\text{mol} \,\text{kg}^{-1}$ using Monte Carlo procedure (Anderson, 1976).

2.7. Differences between the SW and SWR series and statistical tests

The ice thickness was different between the SW and SWR mesocosms (up to 3 cm (15%) of difference) at day 14 and day 15. This was due to an unavoidable temperature gradient in the experimental basin (Zhou et al., 2014). In spite of the gradient of temperature in the experimental basin, we do not think that it has affected the results. The SW and SWR mesocosms sampled the same day were adjacent mesocosms located on the same row (minimizing the differences in physical conditions). For day-to-day sampling, the SW/ SWR pairs of mesocosms were randomly selected in space. In spite of that random selection, we still could see a trend in the physical parameters (Zhou et al., 2014), which means that the temperature gradient in the experimental basin did not significantly bias our results. However, to be rigorous, when the ice thicknesses were different for SW and SWR, we calculated the difference of the parameters (e.g., pCO₂) on normalized ice depth, and then multiplied the normalized ice depth by the ice thickness of the SW series. In addition, two parameters were assumed to be similar (i.e., no significant difference between the SW and SWR series), when a minimum similarity score of 0.95 was achieved.

3. Results

3.1. Physical sea ice conditions

As described in Zhou et al. (2014), the differences in the physical properties of the ice between the SW and SWR mesocosms were insignificant. The brine volume fraction was above 5% during the whole experiment, which suggests that the ice was always permeable (Golden et al., 1998). The maxima in the brine volume fraction were all found at the bottom of the ice, while the minima were found in the ice interior, and decreased from 13.3% on day 1 to 5.7% on day 14, but increased from day 15 onwards, due to the increase of the air temperature from -14 °C to -1 °C. The Rayleigh numbers were higher than 1, indicating favourable conditions for brine convection at all ice depths on day 2, and thereafter only at the bottom of the ice until day 14. From day 15 onwards, the Rayleigh numbers were always below 1, indicating that brine convection was unlikely (Fig. 2). A large difference of Ra has been observed at the bottom of the ice between SW and SWR mesocosms, from day 6 to 14, and was likely due to an underestimation of salinity in SWR, and the propagation of that bias in the calculation of Ra (Zhou et al., 2014), but is not significant for the purpose of the present study.

3.2. DOC and DON

DOC concentrations in sea ice and water and their difference between the SW and the SWR mesocosms have been presented and discussed in Zhou et al. (2014) and Jørgensen et al. (2015). Most importantly, the salinity-normalized DOC concentrations in the



Fig. 2. Brine volume fraction (BrV, in %) and Rayleigh number (*Ra*) in the SW and SWR mesocosms during the experiment. The black dots are the data points from the sampling, while the colour in between results is from interpolation (natural neighbours in Surfer 8 © software) (Zhou et al., 2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

underlying water were higher in the SWR mesocosms than in the SW mesocosm during the experiment (paired *t*-test, p < 0.001); the medians were 142 µmol L_{water}^{-1} in SW and 246 µmol L_{water}^{-1} in SWR (salinity of 30.9), which were similar to the initial conditions. Median DOC concentrations in ice were 71 µmol L_{ice}^{-1} in SW and 109 µmol L_{ice}^{-1} in SWR. These are equivalent to 287 µmol L_{ice}^{-1} and 409 µmol L_{ice}^{-1} respectively, once normalized to a salinity of 30.9 as for the underlying water (paired *t*-test, p < 0.001); they are higher than the values in water, which indicate a preferential retention of DOC in sea ice.

DON concentrations have not been systematically measured as for DOC (n = 18 in water and 15 in ice for DON compared to n = 20and 110, respectively, for DOC (SW + SWR)). The limited number of data we have show that the salinity-normalized DON concentrations were not significantly different in SW and SWR mesocosms, not before the experiment (median of 21 µmol L_{water}⁻¹), or during the experiment, in both the water and ice (medians of 17 µmol L_{water}⁻¹ and 21 µmol L_{ice}⁻¹, respectively) (data not shown). No significant trend in DON has been detected in the water and the ice over the experiment.

3.3. Bacterial activity

Median bacterial abundance in the underlying water increased over the experiment, reaching 1470 cells L_{water}^{-1} in SW and 1505 cells L_{water}^{-1} in SWR. This difference was not significant, despite the significantly higher bacterial production (BP) in the SWR mesocosms (paired *t*-test, *p* = 0.007), with a median of 69 nmol C L_{water}^{-1} h⁻¹ in SWR compared to 51 nmol C L_{water}^{-1} h⁻¹ in SW. Bacterial respiration (BR) in water was also higher in the SWR mesocosms (paired *t*-test, *p* = 0.027), with a median of 98 nmol C L_{water}^{-1} h⁻¹ in SW and 129 nmol C L_{water}^{-1} h⁻¹ in SWR, respectively (Fig. 3a, left).

Median bacteria abundance in ice was 299 cells L_{ice}^{-1} in SW and 352 cells L_{ice}^{-1} in SWR, with a net loss of 24 cells L_{ice}^{-1} d⁻¹ in SW and 16 cells L_{ice}^{-1} d⁻¹ in SWR over the experiment. Median BP was 5 nmol C L_{ice}^{-1} d⁻¹ in SW and 13 nmol C L_{ice}^{-1} h⁻¹ in SWR, and median BR, 10 nmol C L_{ice}^{-1} h⁻¹ in SW and 25 nmol C L_{ice}^{-1} h⁻¹ in SWR (Fig. 3a, right). To compare bacterial activity in ice with that in seawater, we assumed that all these parameters were conservative against salinity. Once normalized to a salinity of 30.9, median



Fig. 3. (a) Bacterial respiration (BR_TdR), (b) DIC₇ and (c) pCO₂ in water and sea ice. Note that for sea ice, we plotted the median value of each ice core. The vertical dashed line shows the transition from ice growth to ice decay.

bacterial abundance reached 1220 cells L_{ice}^{-1} in SW and 1440 cells L_{ice}^{-1} in SWR; median BP of 23 nmol C L_{ice}^{-1} h⁻¹ in SW and 53 nmol C L_{ice}^{-1} h⁻¹ in SWR; and median BR of 42 nmol C L_{ice}^{-1} h⁻¹ in SW and 100 nmol C L_{ice}^{-1} h⁻¹ in SWR. Note that all these values were higher in SWR than in SW (paired *t*-test, *p* < 0.001), but lower than in seawater (paired *t*-test, *p* < 0.001 for BP and BR in SWR; *p* = 0.001 in SW; *p* = 0.004 for bacterial abundance in SWR). The vertical distribution of BR in ice was similar in the SW and SWR mesocosms (Fig. 4): It increased from the top to the bottom of the ice, where the largest differences were observed.

3.4. DIC7

For data comparison with literature, we normalized DIC to a salinity of 7. Differences of DIC7 between SW and SWR were not significant for both the under-ice water and the ice. DIC7 in seawater varied around a median value of 455 µmol kg_{water}⁻¹, when excluding the outlier of SWR on day 5. Median DIC7 in ice for the same mesocosms was slightly higher than in seawater, reaching 486 μ mol kg_{ice}⁻¹ (Fig. 3). DIC₇ in both media increased from day 2 to day 16 and then remained constant. DIC7 in the ice increased from the top to the bottom of the ice in SW and SWR mesocosms (Fig. 5). At the bottom of the ice, it increased throughout the experiment and was always higher than the DIC7 of the under-ice water by an average of 40 µmol kg_{ice}⁻¹. The difference of DIC₇ between SWR and SW was higher in the ice interior at 8-12 cm depth. For comparison with bacterial respiration in ice, median DIC in ice that is not salinitynormalized was 434 µmol kg_{ice}⁻¹, which is equivalent to 400 μ mol L_{ice}⁻¹.

3.5. pCO₂

 pCO_2 in water was not significantly different between both mesocosm series, with a median pCO_2 of 270 ppm. pCO_2 in ice was also not significantly different between both mesocosm series probably as a result of the large variability. Median pCO_2 in ice was

360 ppm with a large range spanning from 223 ppm to 651 ppm (Fig. 3). Median pCO_2 was higher in the ice than in seawater during ice growth (day 2 to day 14), despite similar concentrations of DIC_7 in the seawater and in the ice and lower bacterial respiration in ice than in seawater (Fig. 3c, Sections 3.3 and 3.4).

The pCO₂ in ice had a similar temporal evolution in the SW and SWR mesocosms (Figs. 3c and 6). Considering that the average atmospheric pCO₂ was 460 ppm during the experiment, pCO₂ in ice was at first under-saturated on day 2, and then became increasingly supersaturated until day 14, and then under-saturated again from day 15 onwards. Despite the similar temporal evolution of pCO₂ in ice, pCO₂ was generally higher in the SWR mesocosms, with a median value of 430 ppm compared to the 356 ppm in the SW mesocosms. The differences in pCO2 were generally higher from the top to the ice interior to about 8 cm depth, except on day 2, when the ice was relatively thin (6 cm); on days 5 and 19, the difference of pCO2 at the bottom of the ice was likely biased due to the large difference of CO₂ in the under-ice water (Fig. 3c, left). Indeed, for days 5 and 19, the differences in pCO₂ in the under-ice water between SW and SWR were 100 ppm and 86 ppm, respectively, while they generally approached 0-20 ppm in the other mesocosms on all other sampling days (Fig. 3c, left).

4. Discussion

The addition of river water led to an enrichment of the overall DOC concentrations in the SWR water, compared to SW, by a factor of 1.8 (251 μ mol L_{water}⁻¹/140 μ mol L_{water}⁻¹). The preferential retention of DOC in sea ice during ice formation (Giannelli et al., 2001; Müller et al., 2013; Zhou et al., 2014) led to a salinity-normalized DOC concentration in ice that was higher than the under-ice water (409 μ mol L_{ice}⁻¹/287 μ mol L_{ice}⁻¹), but the difference of DOC enrichment between SWR and SW dropped to 1.4. The mechanisms underlying the preferential retention of DOC in sea ice is not fully understood, but other measurements during our experiment suggested that sea ice formation increases the lability of DOM in ice (Jørgensen et al., 2015). We therefore speculate that the more labile forms of DOC were better retained in sea ice than the more refractory ones. Because SWR contained a larger



Fig. 4. Bacterial respiration (BR_TdR, in nmol C $L^{-1} h^{-1}$) in ice in the SW and SWR mesocosms during the experiment, and the difference between both mesocosms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. DIC₇ (µmol kg⁻¹) in ice of the SW and SWR mesocosms during the experiment, and the difference between both mesocosms. Insignificant differences of DIC₇ are set in white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. pCO₂ (µatm) in ice in the SW and SWR mesocosms during the experiment, and the difference between both mesocosms. Insignificant differences of pCO₂ are set in white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fraction of less labile terrestrial humic acids due to the addition of river water (Jørgensen et al., 2015), the DOC enrichment in ice in SWR was lower than in SW. We show below that the segregation of DOC between water and ice, in addition to the difference in temperature and salinity, likely contributed to the difference of bacterial activity in water and ice.

4.1. Impact of riverine DOC addition on bacterial activity

Available under-ice or partially ice covered water respiration estimates for Western Arctic vary from 19 to 39 nmol C $L_{water}^{-1} h^{-1}$

(Kirchman et al., 2009; Nguyen and Maranger, 2011; Nguyen et al., 2012), which is an order of magnitude lower than our respiration estimate for water (median of 98 nmol C $L_{water}^{-1} h^{-1}$ in SW and 129 nmol C $L_{water}^{-1} h^{-1}$). However, our experimental system was based on North Sea water with a high DOC content and added inorganic nutrients, which are both likely to support higher bacterial production than the more oligotrophic Arctic waters.

Assuming that bacterial activity took place 24 h a day, a consumption of 23.3 μ mol C L_{water}⁻¹ in SW and 31.5 μ mol C L_{water}⁻¹ in SWR is necessary to support the observed BP over the 19-day experiment. These represent 16% and 13% of the DOC pool,

respectively. However, no significant changes have been detected in the DOC and DON concentrations in the under-ice water, or in the concentrations of inorganic nutrients (Zhou et al., 2014). A possible explanation is that bacteria used particulate organic matter (POM) as a carbon source for growth, despite the large pool of DOC. We did not measure POM concentrations in our experiment, but considering the absence of protists and active algae in seawater (in spite of the use of unfiltered seawater), we assumed that they died in the mesocosms, providing an additional source of carbon for bacterial growth. If this assumption is correct, BP would represent a smaller fraction of the DOC pool. The fraction was likely smaller than 3% in SW and 9% in SWR (the standard deviation of DOC concentrations among the mesocosms in the initial waters), because we would have detected significant changes otherwise.

Although BP only represented a small fraction of the DOC pool, the addition of riverine DOC was the most plausible factor causing the significantly higher BP in the SW water, since all the other parameters (bacterial abundance, DON, inorganic nutrients, temperature) were not significantly different between the SW and SWR mesocosms.

Published sea-ice respiration values originate from batch culture incubations using sea ice bacteria and are either derived from total Arctic sea ice community respiration measurements made in water phase incubations (Nguyen and Maranger, 2011) or from experimental systems with Baltic sea ice bacteria (Kuparinen et al., 2011). The estimated mean bacterial respiration in western Arctic ice was 50 nmol C $L_{ice}^{-1} h^{-1}$ (Nguyen and Maranger, 2011) and in the Baltic Sea experiments approximately 80 nmol C $L_{ice}^{-1} h^{-1}$ (Kuparinen et al., 2011). Our respiration estimate for ice was lower but of the same order of magnitude, despite major differences in methodology and experimental setup.

Bacterial activity in ice was different from that in the under-ice water. Bacterial abundance in sea ice was lower than in seawater, even when normalized to the same salinity. This has been observed before in similar experiments (Eronen-Rasimus et al., 2014) and likely resulted from the low ice temperature and high brine salinity.

Although the overall BP and bacterial abundance were lower in the ice than in the under-ice water, the ratio between both the SW and SWR mesocosms were more pronounced in the ice. Bacterial production in SWR ice was 2.6 times higher than in SW, i.e., twice as high as the ratio (SWR/SW) observed in the water. Bacterial abundance was 20% higher than the SW ice, while no significant difference was found in the under-ice water. The only plausible factor driving these SWR/SW differences in ice was the higher DOC concentration in the SWR ice. Ice microalgae and protists were indeed absent (verified by microscopy) and no significant difference has been found in the DON concentrations and the physical properties of the ice.

It is curious as to why the differences of BP between both series of mesocosms were larger in ice (SWR/SW ratio of 2.6) than in the water (ratio of 1.3), considering that the differences of DOC concentrations between both mesocosms series decreased (ratio of 1.4 in ice compared to 1.8 in water). This might be associated with the changes of the organic matter quality towards more labile (bioavailable) forms in the ice during sea ice formation (Jørgensen et al., 2015). In seawater, the addition of riverine DOC promoted higher BP in the SWR mesocosms. In sea ice, the absolute DOC concentrations in SWR are not only higher than in SW, their lability might also have increased compared to the SWR underice water; both might explain the larger difference of BP in ice between the SW and SWR mesocosms compared to the under-ice water. DOC can directly contribute to bacterial growth as a carbon source; it may also support the formation of exopolymeric substances (EPS) in growing sea ice (Aslam et al., 2012) - a substance that is known to support microorganisms survival under the extreme conditions in sea ice (Krembs et al., 2011). Further, it might also have favoured the development of a bacterial community that is different from that in SW, as it has been observed by Eronen-Rasimus et al. (2014).

4.2. Similarities of DIC and pCO₂ in ice in the SW and SWR mesocosms

DIC₇, which ranged from 423 μ mol kg_{ice}⁻¹ to 512 μ mol kg_{ice}⁻¹ (in SW and SWR), was consistent with previous measurements on natural sea ice (Geilfus et al., 2014, 2012a; Rysgaard et al., 2007). pCO₂ measurements for natural sea ice are scarce (Crabeck et al., 2014; Geilfus et al., 2014) and have been mainly obtained from the spring-summer period. Therefore, they were generally under-saturated relative to the atmosphere (i.e., below 400 ppm) (Crabeck et al., 2014; Geilfus et al., 2014). The pCO2 below 400 ppm in ice during the decay period of our experiment was thus consistent with data from natural sea ice in spring and summer. Because of the lack of pCO2 measurements in natural ice during ice growth (and especially in autumn), we extended the comparison to the pCO₂ in brine. Considering that the median ice temperature approached -4.5 °C during ice growth in this experiment (Zhou et al., 2014), and that temperature would correspond to a pCO₂ of about 800 ppm in Arctic sea ice brine (Fig. 1), our in situ measurements of up to 724 ppm are realistic.

Brine concentration and dilution and gas transport are likely to be the two main physical processes determining the similarities in the temporal and vertical pattern of pCO_2 between the SW and SWR mesocosms (Fig. 7). When plotting pCO_2 in ice (SW and SWR) against the brine volume fraction, 10 mesocosms over 14 (represented by the circles in Fig. 7) followed a decreasing trend ($r^2 = 0.836$, p < 0.03). These events include the very beginning of ice growth (day 2) and the ice growth and ice decay, except day 5, day 15 and two other outliers.

When cooling an ice sample, part of the water present in the brine inclusion will freeze, forming a thicker surrounding pure ice matrix, which results in a higher concentration of the dissolved constituents into smaller brine inclusions. Therefore, pCO_2 in sea ice became increasingly supersaturated, as the brine volume fraction decreased (from day 0 to day 14). In contrast, when warming an ice sample, the surrounding pure ice matrix is expected to melt, increasing the size of the brine inclusion and diluting the concentration of the dissolved constituents in the brines. pCO_2 in sea ice thus became under-saturated as a result of the warming air temperature (from day 15 onwards) (Figs. 6 and 7).

A rapid and one-time decrease of pCO₂ in ice was observed on day 15. This was a particular event, occurring the day after the rapid increase of the air temperature, when the sea ice surface temperature sharply increased from -10 °C to -2 °C within 20 h (Kotovitch, personal communication). Different processes may explain this drastic decrease of pCO2, e.g., rapid release of gas bubbles (Zhou et al., 2013) and/or melt of CO2-poor surface ice layers and seepage of the meltwater (Geilfus et al., 2014), while the equilibrium of air-ice pCO2 occurs at a much slower rate. However, considering that day 15 was a particular event, it is unlikely that these pCO₂ changes would be representative of those observed in natural conditions, so we will not further discuss the different plausible processes. Another outlier corresponded to the surface ice layer, where ice melt might have induced the low pCO2 (153 ppm). We currently have no explanation for the other outlier on day 5. Nevertheless, excluding these data, pCO₂ was significantly correlated with the brine volume fraction, which indicates the major role of brine concentration and dilution in regulating pCO₂ in ice.

To further demonstrate the importance of brine concentration and dilution for pCO_2 dynamics, we compared our values with the theoretical pCO_2 considering only the changes in temperature



Fig. 7. Relationship between pCO_2 in ice and brine volume fraction. The circles are the data used to draw the fit (black curve), the other discrete symbols are not considered (see explanation in the text). The blue curves are the 95% confidence bands of the fit and the red dashed curve is the relationship predicted by CO2SYS (Lewis and Wallace, 1998). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and brine salinity. The theoretical pCO₂ was calculated using the CO2SYS program (Lewis and Wallace, 1998), the constants of Goyet and Poisson (1989), and the median temperature, salinity, total alkalinity and DIC in the parent water as initial conditions. We then used the median ice salinity (6.3) to calculate the brine volume fraction associated with each prescribed temperature. The theoretical pCO₂ (red curve in Fig. 7) reproduced the observations well between 10% and 20% of brine volume fraction (i.e., for about half of the data set), but overestimated the pCO2 in ice (up to 320 ppm, i.e., 44%) for brine volume fractions below 10%. We attribute this overestimation to a significant escape of CO₂ from the ice to the atmosphere during ice growth, which is not taken into account by the CO2SYS. Another explanation could be that the constants used in CO2SYS might be incorrect for sea ice, since they were developed for temperature and salinity ranges of seawater, which are less extreme than those of sea ice. However, the error in the estimate of pCO₂ should approach 10% according to Brown et al. (2014), when using TA and DIC as input parameters and the constants of Goyet and Poisson (1989). Hence, the error on the seawater-derived constant is not great enough to explain the difference in pCO₂ between the CO2SYS estimate and the observations, and therefore the escape of CO₂ from the ice to the atmosphere remains the most plausible explanation.

The DIC₇ profiles confirm that gas transport through sea ice affected pCO₂ in ice (Fig. 5), in addition to brine concentration and dilution. If sea ice would be a closed system, and the air-ice and ice-water exchange absent, DIC would be conservative against salinity. Hence, the value of DIC7 would be the same at all ice depths and in seawater. In our study, the ice was always permeable, with the brine volume fraction always above 5% (Golden et al., 1998). Gas exchange through the ice was thus possible and resulted in the deviation of the DIC₇ in ice from the conservative behaviour. Values of DIC7 in ice that decreased from the bottom to the top of the ice indicate an escape of CO₂ from the surface of the ice to the atmosphere (Fig. 5) (Geilfus et al., 2013), and the observed decrease was also consistent with the air-ice fluxes we have measured during the growth phase of this experiment (Kotovitch, personal communication). At the bottom of the ice, DIC7, which approached the values in the under-ice water, indicate that ice-water exchange took place, which was possible through brine convection (high Rayleigh number, Fig. 2). The DIC₇ at the bottom of the ice increased throughout the entire period of ice growth, following the increase in DIC₇ in the under-ice water as a result of the expulsion of DIC from the ice and bacterial respiration in the water during ice growth (Fig. 3) (Moreau et al., 2015a).

4.3. Differences of DIC and pCO_2 in ice between the SW and SWR mesocosms

DIC₇ and pCO₂ in ice were higher in SWR than in SW. However, these differences between SW and SWR were not significant, despite the significantly higher BR in SWR, which should result in a larger accumulation of DIC and CO2 in SWR. Because the dynamics of DIC₇ and pCO₂ not only depend on bacterial activity, but also on physical processes (which were the same in both SW and SWR), the absence of significant differences might indicate that the physical processes have offset the bacterial impact on DIC₇ and pCO₂. For instance, if the differences of DIC₇ and pCO₂ were only due to bacterial activity, it is curious as to why the largest differences of DIC7 and pCO2 were observed in the ice interior (Figs. 5 and 6), instead of at the bottom of the ice, where the difference in bacterial respiration was the largest. We interpret this as the result of gas exchange at the air-ice and ice-water interfaces, in addition to bacterial respiration. Since the difference of pCO2 was smaller between the bottom of the ice and the water than between the surface of the ice and the atmosphere, we conclude that ice-water exchange might have been more efficient than air-ice exchange in decreasing the difference of pCO₂ between SWR and SW due to bacterial respiration. This is in agreement with the higher Rayleigh numbers observed at all times at the bottom of the growing sea ice, that indicate enhanced convection and therefore exchanges with the under-ice water.

Bacterial respiration in bulk ice (10 nmol C $L_{ice}^{-1} h^{-1}$ in SW and 25 nmol C L_{ice}^{-1} h⁻¹) over 19 days only represent 1–3% of the stock of DIC (400 μ mol C L_{ice}⁻¹). It is therefore curious as to how such a low bacterial respiration may have caused a significant difference of pCO₂ in the ice interior. An explanation could be the increase of the buffering effect of the carbonate system with the decrease of temperature and the increase of salinity in brine (brine concentration). The chemical buffer factor ($\beta = \Delta p CO_2 / \Delta DIC$) describes the change in pCO2 relative to the DIC change induced by an input (i.e., respiration) or output of dissolved CO₂. It results from the interplay of equilibrium dissociation reactions of the carbonate system and is a function of several physico-chemical conditions (Delille et al., 2005; Frankignoulle, 1994). In a closed system, β of brines increases significantly with decreasing temperature and the associated increase of brine salinity (Fig. 8). Providing that bacterial respiration could explain the accumulation of DIC, an increase of DIC (even small) can result in a larger increase in pCO₂ in cold saline brine compared to warmer underlying seawater (Fig. 8). Considering that the difference of DIC7 in the ice interior approached 15 μ mol kg_{ice}⁻¹ (Fig. 5) and that at β approached 4 at -4.5 °C



Fig. 8. Buffer factor of the carbonate system for decreasing temperature and related increase of salinity due to brine concentration/dilution in a closed system. Initial conditions was S = 35.17, T = -1.8 °C, TA = 2578 µmol kg⁻¹, DIC = 2450.4 µmol kg⁻¹, pCO₂ = 400 µatm. β is provided for an increase of DIC of 20 µmol kg⁻¹.

(median temperature of the ice), an expected difference of pCO_2 due to buffer factor changes should approach 60 ppm, which is relatively close to our observation (Fig. 6).

An alternate explanation is the underestimation of the bacterial respiration in bulk ice. We calculated bacterial respiration based on thymidine incorporation and different conversion factors. Our choice of BGE might have led to an underestimation of the estimate of bacterial respiration, as discussed in the next section.

4.4. Modelling the impact of bacterial respiration on pCO₂ in ice

In a closed system, bacterial respiration would induce an accumulation of DIC. In our semi-enclosed system, DIC also changed due to physical processes (ice-air and ice-water exchanges). The interplay of these various processes makes it difficult to use a simple calculation to prove (i) whether the difference in bacterial respiration caused the observed difference of DIC and pCO₂ in the ice interior, and (ii) whether ice-air and ice-water exchanges have offset the difference of DIC and pCO₂ caused by respiration at the surface and the bottom of the ice, respectively.

To tackle these issues, we used the one-dimensional thermodynamic sea ice model of Moreau et al. (2015b) which includes iceair gas exchanges and sea ice carbon dynamics. The model features ice growth and melt, ice-air and ice-water exchanges, as well as representations of full inorganic carbon and basic organic carbon dynamics within the ice. For the model simulations, all the parameters used are those described in Moreau et al. (2015b), except for biological activity where primary production was shut down in the model runs. Bacterial respiration is prescribed with the median values of the bacterial respiration for SW and SWR, i.e., 10 nmol C L_{ice}^{-1} h⁻¹ in SW and 25 nmol C L_{ice}^{-1} h⁻¹ in SWR, which corresponded to the use of a bacterial growth efficiency (BGE) of 0.348. Based on the initial conditions of the experiment, we prescribed the initial seawater TA and DIC concentrations (2244 μ mol kg_{water}⁻¹ and 2039 μ mol kg_{water}⁻¹, respectively) and the initial sea ice TA and DIC concentrations (847 μ mol kg_{ice}⁻¹ and 748 $\mu mol \ kg_{ice}{}^{-1}$). The model was run over 19 days (duration of the experiment), with a 1-h time step.

Because the model has different temporal and spatial resolutions than the observations, we decided to only compare the temporal evolution of the median values in the ice (modelled versus measured variables). Overall, the model reproduced the ice thicknesses, median ice temperatures and salinities, as well as the standing stock of DIC and the median pCO_2 in ice in the same magnitude as those observed (Fig. 9). We first ran the model with the median values of the observed bacterial respiration for SW and SWR by using a BGE of 0.348 (Kuparinen et al., 2011). Given these bacterial respiration rates, the model reproduces the spatial pattern of the observed DIC₇ standing stock and the median pCO_2 (Fig. 9) but not the magnitude of their difference between SW and SWR (Table 1). Therefore, we re-calculated bacterial respiration rates for SW and SWR using different BGE. Reducing BGE to 0.2 or 0.15 is plausible considering that BGE ranges from 0.05 to 0.6 (i.e., from 5% to 60%), depending on the environmental conditions (e.g., the quality of the dissolved organic matter) (Del Giorgio and Cole, 1998; Nguyen et al., 2012; Rivkin and Legendre, 2001).

Firstly, changing the BGE to 0.2 or 0.15, and hence increasing the BR, did not change the total stock of DIC and the median pCO₂ significantly (Fig. 9, coloured curves), which supports our previous suggestions about the importance of the physical processes, such as brine concentration and dilution and gas transport, in regulating the dynamics of DIC and pCO2 in sea ice. However, changing the BGE to 0.2 or 0.15 enhanced the differences in DIC7 and pCO₂ in ice between SW and SWR (Table 1). The modelled median difference of DIC₇ fits the observations better when using a BGE of 0.2 and 0.15 (Table 1), and considering the reproducibility of $\pm 0.8 \ \mu\text{mol} \ \text{kg}^{-1}$ for DIC. The median difference of pCO_2 is then higher than the observed differences in pCO₂ between SW and SWR, but considering that the model slightly overestimates the pCO₂ near the ice surface (Kotovitch, personal communication), differences in DIC₇, rather than pCO₂, would be a better indicator of the difference in bacterial impact. The model simulations therefore suggest that the bacterial respiration in ice might be up to 3 times higher than our previous estimate (Table 1).

The estimate of BGE for the entire period of the experiment (0.15–0.2), as suggested by the model simulations, was lower than assumed. Our BGE estimate of 0.348 was based on empirical values obtained in liquid batch cultures in above-zero temperature (Kuparinen et al., 2011; Nguyen and Maranger, 2011) combined with calculated temperature-dependent estimate (Rivkin and Legendre, 2001). Measuring bacterial process rates, especially respiration in sea-ice systems is complicated and direct respiration measurements were not available. The lower actual BGE suggested by the model in our experimental system compared to the previous published values is plausible because of the extremely low temperatures and high salinities in brine. Extreme conditions are in general forcing bacteria to invest more energy for survival than for growth. Along these lines, the actual BGE may vary throughout the ice growth, being lower during ice growth (where the conditions were more extreme), and higher during ice melt (where the conditions were milder). Further investigations are encouraged to verify this hypothesis. Furthermore, BGE in water column and ice may be different with higher BGE in water where conditions are less extreme. Higher BGE from 0.4 to 0.5 were suggested by Moreau et al. (2015a) for the under-ice water, in the same experimental system. Higher BGE for under-ice water would also lower the respiration estimate towards values measured in other studies (Kirchman et al., 2009; Nguyen and Maranger, 2011; Nguyen et al., 2012) albeit in the high Arctic under different nutrient and dissolved organic carbon regimes.

The comparison of Fig. 5 with Fig. 10, and Fig. 6 with Fig. 11 shows that the model reproduced the temporal and spatial pattern of DIC_7 and pCO_2 well. DIC_7 decreased from the bottom to the top of the ice due to air-ice gas exchange, except in the bottom most layer where DIC_7 is underestimated due to an improper parameterization of heat and salt transfer in this layer (Moreau et al., 2014; Vancoppenolle et al., 2010). pCO_2 was supersaturated in the ice during the entire ice growth period, except in the bottom layer where brine convection pulled the pCO_2 towards the under-saturated pCO_2 value of the under-ice water, pCO_2 in ice



Fig. 9. (Clockwise) Temporal changes of the ice thickness, median ice temperature, median ice salinity, the standing stock of DIC and the median pCO₂ in the ice. The dots refer to the measurements (white for SW and black for SWR), while the curves refer to the simulated results. The vertical dashed line shows the transition from ice growth to ice decay. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Calculated median bacterial respiration (BR) in ice in SW and SWR using different bacterial growth efficiencies (BGE), the measured median difference of pCO2 and DIC (SWR
minus SW) during the experiment (Diff pCO ₂ and Diff DIC ₇), and the modelled difference of pCO ₂ and DIC for each set of BGE-dependent BR.

	Observations					Model	
	BR_ice_SW (nmol C $L^{-1} h^{-1}$)	$BR_ice_SWR \ (nmol \ C \ L^{-1} \ h^{-1})$	Diff pCO ₂ (µatm)	Diff DIC7 (µmol kg ⁻¹)	Diff pCO ₂ (µatm)	Diff DIC7 (µmol kg ⁻¹)	
BGE = 0.348	10	24.7	13	2.8	8.3	0.9	
BGE = 0.2	21.5	52.6			19.3	1.9	
BGE = 0,15	30.4	74.6			31.9	2.7	

then also became under-saturated, as it was observed, as a result of the increase of air temperature (and the related brine dilution). In addition, due to the higher bacterial respiration in SWR compared to SW, DIC_7 and pCO_2 were higher in SWR than in SW. The differences of pCO_2 are alleviated at the bottom of the ice because of brine convection, and slightly at the top of the ice due to air-ice gas exchange, but they are greater in the ice interior, which has to be associated with the difference in bacterial respiration – the sole difference between the two runs: SW and SWR.

There are two main differences between the model simulations and the observations: The absolute values of DIC_7 and pCO_2 are higher in the model than in the observations, and the differences of DIC_7 and pCO_2 between SWR and SW present a smoother pattern in the model than in the observations (Figs. 5, 6, 9 and 10). Ice–air gas fluxes are currently not yet well constrained in the model, resulting in a slight underestimation of the ice–air gas fluxes, and thus an overestimation of the modelled DIC and pCO_2 content in the ice (Kotovitch, personal communication). The smoother pattern in the modelled differences of DIC_7 and pCO_2 may result from the higher spatial and temporal resolution in the model than in the observations: Hourly time step and calculation on the 10 ice layers in the model compared to the almost daily sampling with 1–4 measured ice layers on each ice core.

In brief, differences exist between the model simulations and the observations, probably due to the parameterization of air-ice gas exchange and the difference of spatial and temporal resolution, but the model was able to reproduce the temporal and spatial patterns of DIC₇ and pCO₂, confirming therefore the importance of brine concentration and dilution, and gas transport in controlling their dynamics. Most importantly, the model reproduced the observed median difference of DIC₇ in the ice by introducing the measured bacterial respiration (for a lower BGE of 0.15 or 0.2), confirming that higher bacterial respiration could indeed cause a larger accumulation of DIC and a larger pCO₂ in the ice.

A corollary to the higher bacterial respiration, DIC and pCO₂ in SWR in the model is an enhanced ice–air CO₂ flux during ice growth by 17% (1.68 mmol m⁻² d⁻¹ and 1.97 mmol m⁻² d⁻¹ in SW and SWR, respectively), and a reduced CO₂ flux during ice decay by 38% ($-1.52 \text{ mmol m}^{-2} d^{-1}$ and $-0.93 \text{ mmol m}^{-2} d^{-1}$ in



Fig. 10. Modelled DIC_7 (µmol kg⁻¹) in ice, in SW and SWR mesocosms, and the difference SWR minus SW, using a median bacterial respiration in ice associated with a BGE of 0.15 (Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 11. Modelled pCO_2 (µatm) in ice, in SW and SWR mesocosms, and the difference SWR minus SW, using a median bacterial respiration in ice associated with a BGE of 0.15 (Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

SW and SWR, respectively) if we assume a BGE of 0.15 (simulated fluxes not shown). The enhanced CO_2 fluxes during ice growth are obviously due to the higher pCO_2 in the ice resulting from the higher bacterial respiration. The negative CO_2 fluxes (i.e., from the air to the ice) are due to brine dilution (e.g., Nomura et al., 2010), and the flux is less negative in SWR because the larger

bacterial respiration in SWR better compensates the effect of brine dilution. The integrated CO_2 flux over the 19 days of the simulation was 0.16 mmol m⁻² d⁻¹ and 1.04 mmol m⁻² d⁻¹ in SW and SWR, respectively. Hence, the addition of DOC might have induced an air-ice CO_2 flux that was more than 6 times higher than without the addition of DOC.

5. Conclusion and large scale implications

The aim of the study was to verify the hypothesis as to whether a larger input of riverine DOC in the Arctic water could induce a higher DOC concentration in sea ice, which would promote bacterial respiration, leading to a higher pCO_2 in brine. Although the overall trend of pCO_2 in both mesocosm series strongly depends on the ice temperature (Fig. 1) as a result of the effect of brine concentration and brine dilution, the differences (SWR–SW) in observations and model simulations support our hypothesis.

The difference of pCO_2 between SW and SWR was much lower than the difference of pCO_2 in brine between the Arctic Ocean and the Southern Ocean. However, if we have added more labile DOC instead of humic-rich riverine water to our mesocosms and if we extended the duration of the experiment with lower air temperature, we may have observed larger differences of DIC and pCO_2 , closer to those observed in natural conditions. The availability of more labile autochthonous DOC may promote higher bacterial respiration and higher accumulation of CO_2 in ice. Further, extending the duration of the experiment to several months, with further decrease of the ice temperature, would increase the respiration burden, reduce the ice permeability, and therefore reduce gases and DIC losses through the ice.

Because the addition of riverine DOC to seawater causes larger pCO_2 in ice, the Arctic Ocean, which receives a large input of terrestrial DOC through rivers, might induce more positive (or less negative) ice–air CO_2 fluxes than the Southern Ocean, for the same environmental conditions. Similarly, Arctic coastal waters might also be associated with a more positive (or negative) ice–air CO_2 fluxes than the central Arctic. This is at least true for the ice growth period when algal growth is limited, as considered by the absence of autochthonous DOC in our experiment. Algal growth would consume CO_2 but will also produce labile autochtonous DOC that enhances bacterial production. Further experiments are therefore needed to refine the net impact of algal and bacterial growth on pCO_2 in ice and on the inter-hemispheric differences.

The inter-hemispheric difference of pCO₂ in ice and brine likely results from the impact of ice temperature on the ice permeability and the buffering effect of the carbonate system, in addition to the DOC input. Lower ice temperatures are associated with larger buffering effects, i.e., the increase of pCO2 in the ice interior in response to a given increase of DIC (due to bacterial respiration) would be enhanced. If the ice temperature is low enough so that the ice becomes impermeable to gas exchange, the accumulation of pCO₂ would have been more obvious, resulting in the larger observed inter-hemispheric difference of pCO₂ in ice and brine. On the contrary, higher ice temperatures are associated with lower buffering effects and larger ice permeability. Exchange may occur through the ice, and offset the bacterial accumulation of CO₂. In our study, the impact of bacterial respiration on pCO2 was most obvious in the ice interior, because ice-air gas exchange and brine convection have offset the increase of pCO2 associated with bacterial respiration at the ice interfaces.

Considering the drastic decline in Arctic sea ice, we may also wonder how air-sea and air-ice CO_2 fluxes may change in the future. If the ice cover is replaced more and more by open water, the most common scenario is that air-sea CO_2 fluxes increase, because gas exchange is more efficient via an open sea surface than a semi-permeable ice cover. Our work highlighted the fact that the dynamics regulating the p CO_2 gradient will be different too. Due to the buffering effect of the carbonate system, brine concentration makes the p CO_2 more sensitive to DIC increase in ice than in seawater, and a small accumulation of DIC, due to low bacterial respiration may result in a large increase of p CO_2 in the ice. At some specific locations, where bacterial activity is more intense in the ice than in the underlying water, the consequence of bacterial respiration on pCO_2 in ice may be even more significant, especially when algal activity is limited. The interplay between gas transfer velocity and the pCO_2 gradient needs to be taken into consideration while assessing the future evolution of the air-sea and airice CO_2 fluxes in the polar regions.

Contributions

JLT, BD, GD, HK, GK planned and designed the experiment under the lead of DT; JZ, MK, JLT, BD, GD and DT provided the data on sea ice physics and carbonate chemistry, HK, the bacterial data, GK, the DOC data, and SM, the model simulations. JZ, BD, HK, SM wrote the paper with the valuable comments and inputs from all the other co-authors.

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CHAPTER IV: Air-ice carbon pathways inferred from a sea ice tank experiment

Marie Kotovitch^{1, 2, *}, Sébastien Moreau³, Jiayun Zhou^{1, 2, 4}, Martin Vancoppenolle⁵, Gerhard S. Dieckmann⁶, Karl-Ulrich Evers⁷, Fanny Van der Linden¹, David N. Thomas^{8, 9}, Jean-Louis Tison² and Bruno Delille¹

¹ Unité d'Océanographie Chimique, MARE, Université de Liège, Liège, Belgium

² Laboratoire de Glaciologie, DSTE, Université Libre de Bruxelles, Brussels, Belgium

³ Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Tas, Australia

⁴ Division of Earth and Ocean Sciences, Nicholas School Of the Environment, Duke University, Durham, NC, USA

⁵ Sorbonne Universités, UPMC Paris 6, LOCEAN-IPSL, CNRS/IRD/MNHN, France.

⁶ Alfred Wegener Institute Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany

⁷Arctic Technology Department, HSVA, Hamburg, Germany

⁸ Marine Research Centre, Finnish Environment Institute (SYKE), Helsinki, Finland

⁹ School of Ocean Sciences, Bangor University, Menai Bridge, United Kingdom

* Corresponding author



Air-ice carbon pathways inferred from a sea ice tank experiment

Marie Kotovitch^{1,2*} • Sébastien Moreau³ • Jiayun Zhou^{1,2,4} • Martin Vancoppenolle⁵ • Gerhard S. Dieckmann⁶ • Karl-Ulrich Evers⁷ • Fanny Van der Linden^{1,2} • David N. Thomas^{8,9} • Jean-Louis Tison² • Bruno Delille¹

¹Unité d'Océanographie Chimique, MARE, Université de Liège, Liège, Belgium

²Laboratoire de Glaciologie, DSTE, Université Libre de Bruxelles, Brussels, Belgium

³Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Tas, Australia

⁴Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North Carolina, United States

⁵Sorbonne Universités, UPMC Paris 6, LOCEAN-IPSL, CNRS/IRD/MNHN, France

⁶Alfred Wegener Institute, Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany

⁷Arctic Technology Department, HSVA, Hamburg, Germany

⁸Marine Research Centre, Finnish Environment Institute (SYKE), Helsinki, Finland

⁹School of Ocean Sciences, Bangor University, Menai Bridge, United Kingdom

*Marie.Kotovitch@ulg.ac.be

Abstract

Given rapid sea ice changes in the Arctic Ocean in the context of climate warming, better constraints on the role of sea ice in CO₂ cycling are needed to assess the capacity of polar oceans to buffer the rise of atmospheric CO₂ concentration. Air-ice CO₂ fluxes were measured continuously using automated chambers from the initial freezing of a sea ice cover until its decay during the INTERICE V experiment at the Hamburg Ship Model Basin. Cooling seawater prior to sea ice formation acted as a sink for atmospheric CO₂, but as soon as the first ice crystals started to form, sea ice turned to a source of CO2, which lasted throughout the whole ice growth phase. Once ice decay was initiated by warming the atmosphere, the sea ice shifted back again to a sink of CO2. Direct measurements of outward ice-atmosphere CO2 fluxes were consistent with the depletion of dissolved inorganic carbon in the upper half of sea ice. Combining measured air-ice CO2 fluxes with the partial pressure of CO_2 in sea ice, we determined strongly different gas transfer coefficients of CO_2 at the air-ice interface between the growth and the decay phases (from 2.5 to 0.4 mol m⁻² d⁻¹ atm⁻¹). A 1D sea ice carbon cycle model including gas physics and carbon biogeochemistry was used in various configurations in order to interpret the observations. All model simulations correctly predicted the sign of the air-ice flux. By contrast, the amplitude of the flux was much more variable between the different simulations. In none of the simulations was the dissolved gas pathway strong enough to explain the large fluxes during ice growth. This pathway weakness is due to an intrinsic limitation of ice-air fluxes of dissolved CO2 by the slow transport of dissolved inorganic carbon in the ice. The best means we found to explain the high air-ice carbon fluxes during ice growth is an intense yet uncertain gas bubble efflux, requiring sufficient bubble nucleation and upwards rise. We therefore call for further investigation of gas bubble nucleation and transport in sea ice.

1. Introduction

Among the natural systems, the role of sea ice in CO_2 cycling is not well constrained. Several studies report air-ice CO_2 fluxes that show that sea ice is a permeable medium under certain conditions of temperature and salinity (Semiletov et al., 2004; Nomura et al., 2006, 2010b; Miller et al., 2011b; Delille et al., 2014), thereby refuting the assumption that sea ice impedes the air-ocean gas exchange. However, observational difficulties, in particular the lack of continuous observations covering the entire ice growth and decay cycle, hinder the understanding of carbon exchange processes in ice-covered seas. Some studies suggest that active sea ice processes are significant (Rysgaard et al., 2011; Delille et al., 2014), while others assume them to be Domain Editor-in-Chief Jody W. Deming, University of Washington

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Received: May 29, 2015 Accepted: May 19, 2016 Published: June 28, 2016 negligible (Cross et al., 2014). Given the rapid sea ice changes in the Arctic Ocean in the context of global warming (IPCC, 2013), better constraints on the role of sea ice in CO_2 cycling are needed to assess the future capacity of polar oceans to buffer the rise of atmospheric CO_2 concentration.

Sea ice is a composite of pure ice, brine and gas inclusions. Various biological, chemical and physical parameters may affect the concentration of gases in sea ice (e.g., Tsurikov, 1979; Zhou et al., 2014a). Temperature appears to be one of the main controls of CO_2 concentration in sea ice (Geilfus et al., 2012a; Delille et al., 2014). When temperature decreases, brine inclusions shrink, concentrating salts, gases and other impurities in the brine. In contrast, when temperature increases, the melting of ice with the increase in size of brine inclusions dilutes their content (e.g., Vancoppenolle et al., 2013; Delille et al., 2014). The increasing concentration of gases in brine due to the shrinking of brine inclusions triggers the nucleation of bubbles (Tsurikov, 1979; Killawee et al., 1998; Tison et al., 2002; Light et al., 2003). Gases are therefore found in sea ice in both dissolved (i.e., brines) and gaseous forms (i.e., bubbles). Bubbles are indeed observed at the onset of sea ice growth, when air inclusions are trapped within the ice structure. Crabeck et al. (2014b) and Zhou et al. (2014a) suggested that bubbles further develop during ice growth when the gases concentraties within the brine. Conversely, during ice decay, brine dilution and the related decrease of gas concentration is hypothesized to promote the dissolution of gases in the brines.

Sea ice is considered as permeable when the brine fraction is above 5% (Golden et al., 1998). As sea ice becomes permeable, air-ice gas exchange increases (Delille et al., 2014). Brine convection or gravity drainage (Notz and Worster, 2009; Hunke et al., 2011) is the main process responsible for the rejection of dissolved gases to the ocean during ice growth (Moreau et al., 2014). In the absence of convection, the diffusion of dissolved gases becomes the main pathway to transport dissolved gas across the ice (Gosink et al., 1976; Loose et al., 2011; Shaw et al., 2011). This diffusive flux is driven by dissolved gas gradients (Delille et al., 2007; Nomura et al., 2010b; Miller et al., 2011b). Gas bubbles may provide an alternative gas transport pathway (Zhou et al., 2013; Crabeck et al., 2014a). The efficiency of this pathway depends on whether bubbles can only diffuse molecularly (Loose et al., 2011) or rise due to their buoyancy (Moreau et al., 2014).

Considering the need to better understand carbon cycling in ice-covered seas, the absence of measurements over the whole ice growth and decay cycle and the difficulty of performing these measurements on natural sea ice, we carried out a controlled ice growth and decay experiment during which the air-ice CO_2 fluxes were monitored using the chamber method. The CO_2 transfer coefficient during both ice growth and ice decay was computed and compared to a sea ice model integrating carbon dynamics.

2. Methods

2.1 Experimental setting

The experiment was carried out at the Arctic Environmental Test Basin facility of the Hamburg Ship Model Basin (http://www.hsva.de) in the framework of the INTERICE V project. Eleven polyethylene bags of 1.2 m³ were filled with about 1000 L of filtered seawater from the North Sea. The experiment reproducing ice growth and ice decay took place over a period of 19 days. The day "0" of the experiment was 30 May 2012. The air temperature above the mesocosms was set to -14 °C the first 14 days (hereafter denoted as the "growth phase"), then to -1 °C until the end of the experiment (the "melting phase"). More information about the experimental settings are provided by Zhou et al. (2014b).

We carried out continuous *in situ* measurements of ice temperature and air-ice CO_2 fluxes: A chain of 10 thermistors was placed at 2 cm intervals through the whole ice thickness. Ice cores were also collected regularly (every 1 to 3 days). On a given day, all samples (ice, under-ice water) came from the same mesocosm. Once the ice in a mesocosm was sampled, it was compromised and not used again in the experiment. So each sampling day corresponded to a different mesocosm, except on day 19, when we sampled two mesocosms. Ice cores were wrapped in polyethylene bags for storage below -25 °C in the dark and for subsequent measurements of bulk ice salinity, total alkalinity (TA) and partial pressure of CO_2 (p CO_2).

2.2 Ice pCO_2 at high vertical resolution

We applied the method developed by Geilfus et al. (2012b) and reviewed by Crabeck et al. (2014b) and Geilfus et al. (2015) for the measurement of the bulk pCO_2 (denoted as $pCO_{2\,ball}$) within permeable sea ice. The goal is to equilibrate the sea ice samples with a N₂/CO₂ gas mixture of known concentration at a temperature as close as possible to the *in situ* temperature (the temperature of the ice upon sampling). Samples were cut to fit tightly into a square container, 4×4 cm, that was 4.4 cm high to minimize the headspace. The container containing the sample was sealed and connected to a vacuum pump for 15 min. A standard gas of known concentration (500 ppm of CO₂) was then injected at a pressure of 1013 mbar. Standard gas and ice sample were equilibrated for 20 hours in a constant temperature bath at the *in situ* temperature. Gas was then recovered and injected in a Varian 3300 gas chromatograph to measure the CO₂ concentration. Shortly afterward, the

sample temperature was measured to check for experimental drift. Measured $pCO_{2 balk}$ was corrected for the temperature difference between the sample and the *in situ* temperature according to the corrections proposed by Copin-Montegut (1988).

2.3 Total alkalinity

We measured total alkalinity (TA) on melted sea ice (TA_{bulk}) using 50 g of sea ice melt collected at a 2 cm vertical resolution. TA was measured on all mesocosms except SW 9. We derived TA for all SW 9 ice sections using the strong linear regression between salinity and TA observed for all of the other samples. We also collected seawater for TA measurement. Melted bulk ice and seawater samples were poisoned with a solution of super-saturated HgCl₂ and then stored in the dark, until analysis (one year after the sampling). TA was measured by open-cell titration with 0.11 M HCl and the endpoints were determined according to Gran (1952). Routine analyses of Certified Reference Materials (provided by A. G. Dickson, Scripps Institution of Oceanography) ensured that the uncertainty of the TA measurements was less than 4 μ mol kg⁻¹.

2.4 Dissolved inorganic carbon

We computed the dissolved inorganic carbon of bulk ice from TA_{bulk} and $pCO_{2\,bulk}$ using a 2 step computation. We estimated the salinity of brines according to the ice temperature using the relationship of Cox and Weeks (1983) derived from data compiled by Assur (1960). We then computed TA_{brines} at the salinity of brines from the linear relationship between TA and salinity. We computed the total dissolved inorganic carbon (DIC) of brines (denoted as DIC_{brines}) from TA_{brines} and $pCO_{2\,bulk}$ using the CO2SYS program for the carbonate system (Lewis and Wallace, 1998). We used the CO₂ dissociation constants of Mehrbach (1973) refitted by Dickson and Millero (1987) and the other constants advocated by Dickson and Goyet (1994). We then converted DIC_{brines} to DIC_{bulk} assuming a linear relationship between DIC and salinity. Nonetheless, there are some limitations with this approach that should be noted: the dissociation constants have been established for the ranges of temperatures and salinities of open ocean waters (i.e., temperatures above 1 °C and salinities of 35). We assumed that the CO₂ dissociation constants were applicable at sub-zero temperatures, as suggested by Marion (2001) and Delille et al. (2007). We refer the reader to Brown et al. (2014) for a discussion on the validity of the constants.

2.5 Seawater pCO₂

To measure the underlying seawater pCO_2 a hole was drilled through the sea ice cover. Seawater was pumped from the hole using a peristaltic pump (Masterflex[®] - Environmental Sampler) and supplied to a sea ice equilibrator system (SIES; Delille et al., 2007) for measurements of the pCO_2 and recycled back to the seawater through the same hole. The SIES is based on a membrane contractor equilibrator (Membrana[®] Liqui-cell) coupled to an infrared gas analyzer (IRGA, Li-Cor[®] 6262). Seawater flowed into the equilibrator at a maximum rate of 1 L min⁻¹ and a closed air loop ensured circulation through the equilibrator and the IRGA at a rate of 3 L min⁻¹. The IRGA was calibrated before and after the experiment with N_2 and CO_2 : N_2 mixtures with mixing ratios of 388 and 813 ppm supplied by Air Liquide Belgium. During the experiment, the drift of the IRGA was corrected with N_2 . Uncertainty during this experiment was less than 6 μ atm.

2.6 Air–ice CO₂ fluxes

2.6.1 Measurements at the automated chamber

In this paper, positive CO_2 flux refers to CO_2 flux from the ice to the atmosphere, while negative CO_2 flux refers to a flux from the atmosphere to the ice. We measured air-ice CO₂ fluxes using an automated chamber placed above the water surface or on top of the ice. The chamber consisted of a mobile cap and a plastic cylinder, or so-called collar, with a diameter of 20 cm and a height of 9.7 cm. A rubber seal surrounded the cylinder and ensured an airtight connection between the ice and the chamber. Each hour, the cap closed the chamber and the pCO_2 was measured over 15 min. At the beginning of the experiment one chamber was set above the surface of the water with the collar lowered a few millimetres below the water surface of a dedicated mesocosm apart from the 21 mesocosms used for ice collection. However, ice freezing and consolidation pushed the collar upward so that the collar was not properly sealed. After the fifth day of the experiment, the chamber was therefore moved to mesocosm 11 and was properly sealed. A pump within the LI-COR Multiplexer (LI-8150) circulated the air in the chamber at a flow rate of 2.1 L min⁻¹. When the pCO_2 of ice is higher than atmospheric pCO₂, CO₂ is transferred from the ice to the atmosphere and the automated chamber records a positive flux. A negative flux is observed in the opposite case. Water-corrected CO2 flux was computed automatically with LI-8100 File Viewer 3.1.0 package provided by LI-COR Biosciences. The flux was either calculated with a linear or an empirical exponential regression depending on which method provided the best fit (assessed from the normalized sums of the squares of the residuals).

2.6.2 Computation of a gas transfer coefficient for CO₂

As described above, gases are transported through sea ice to the atmosphere by convection, diffusion and/or the ascent of bubbles to the ice surface. In the present study, we calculated an effective gas transfer coefficient for CO_2 (*K*, in mmol m⁻² d⁻¹ atm⁻¹), using the equation developed by Liss and Slater (1974) and Sarmiento and Gruber (2004):

$$F = K(\rho CO_{2 \ bulk} - \rho CO_{2 \ air}) \tag{1}$$

where F is the air-ice CO₂ flux in mmol m⁻² d⁻¹, $pCO_{2 \text{ balk}}$ is the pCO₂ in the ice and $pCO_{2 \text{ air}}$ is the pCO₂ in the air, both expressed in atm. In this equation we assume that F and K reflect both diffusive flux and bubble buoyancy (i.e., the rise of bubbles to the ice surface).

2.7 Assessment of the precision of derived variables

A Bootstrap resampling statistical analysis procedure, using random values of the measured parameters (temperature, salinity, pCO₂, DIC and TA) between the mean \pm precision over 1000 iterations, was used to estimate the propagation of errors to the computed parameters (ΔDIC and K). This method was used as a way to show the effects of the imprecision of the data set on the calculated parameter.

2.8 Modelling air-ice CO₂ fluxes

In order to understand the factors that drive air-ice CO_2 fluxes during the experiment, we ran a one-dimensional thermodynamic sea ice model representing sea ice halo-thermodynamics and carbon dynamics, including air-ice CO_2 fluxes (Vancoppenolle et al., 2010; Moreau et al., 2015). Vertical carbon transport and air-ice carbon fluxes are explicitly separated between dissolved and gaseous form contributions.

The dissolved gas pathway combines the vertical transport of dissolved inorganic carbon in brine and the diffusive air-ice CO_2 flux, F^{CO_2} (mmol m⁻² d⁻¹), which is assumed proportional to the CO_2 partial pressure (pCO₂) difference between the surface brine (in the top 5 cm of the ice) and the atmosphere, and is a function of the near-surface brine fraction:

$$F^{CO_2} = k^{CO_2} \cdot e^{2/3} \cdot (\zeta^{CO_2} - K_0 f^{CO_2})$$
⁽²⁾

where k^{CO_2} (m s⁻¹) is the piston velocity, *e* is the brine fraction near the ice surface, e^{2G} represents the fractional surface open to brine-air diffusive CO₂ fluxes, ζ^{CO_2} is the brine CO₂ concentration (mmol m⁻³), f^{CO_2} is the atmospheric CO₂ fugacity (atm), and K₀ is the Henry's constant (mmol m⁻³ atm⁻¹). We consider that $f^{CO_2} = p_{atm} * r^{CO_2}$, atm, where p_{atm} is the atmospheric pressure (atm) and $rCO_{2,atm}$ is the atmospheric CO₂ mixing ratio measured within the chamber. The piston velocity is calculated from the molecular diffusion coefficient of dissolved CO₂ (D_{diff} in m² s⁻¹) and the thickness of the diffusive boundary layer (z_{BL} in µm):

$$k^{CO_2} = D_{diff} / \mathbb{Z}_{pr}$$
(3)

This piston velocity neglects the effects of snow and wind, absent in these tank experiments, and only includes the contribution of dissolved CO₂. In contrast, equation 1 includes both gas bubble and dissolved contributions as F and $pCO_{2 bulk}$ are direct measurements without distinction between dissolved and gaseous forms. The z_{BL} is highly uncertain and therefore has been used as a tuning parameter to adjust the magnitude of air-ice CO₂ fluxes, whereas D_{diff} is better constrained by observations. For our control simulation (CTRL), we used $D_{diff} = 0.97 \ 10^{-9} \ m^2 \ s^{-1}$ (the diffusion coefficient of CO₂ in water from Broecker and Peng, 1974) and $z_{BL} =$ 0.5 µm (Moreau et al., 2015; Table 1).

The gas bubble pathway was developed in the model to simulate Argon dynamics (Moreau et al., 2014) and implies explicit gas bubble reservoirs in every layer. The gas concentration in the bubble reservoir changes due to bubble nucleation/dissolution, upward migration of buoyant gas bubbles, and bubble escape to the atmosphere. Nucleation of gas bubbles transfers dissolved CO_2 from brine to the bubble compartment as a function of the CO_2 super-saturation. At each time step, a fraction R^{bub} of the CO_2 super-saturation is transferred to bubbles. The bubbles migrate upward when the brine network is connected, which is assumed to happen above a given brine fraction threshold (e.g., $e_T^{gas} = 0.07$, Zhou et al., 2013; Moreau et al., 2014). If the fraction of sea ice with $e > e_T^{gas}$ includes the ice surface, all gas bubbles escape to the atmosphere and contribute to the air-ice CO_2 flux. For our CTRL simulation, we used $R^{bub} = 10\% h^{-1}$ and $e_T^{gas} = 0.07$ (Table 1).

In order to understand the potential reasons to explain the underestimation of the observed air-ice CO₂ fluxes by the model, we performed three series of sensitivity experiments (Table 1). First, we tested the impact of a more intense dissolved CO₂ pathway, by changing D_{diff} and z_{BL} (runs 2–4). The D_{diff} value of Broecker and Peng (1974) is derived from seawater and only includes diffusive effects. We tested the slightly higher D_{diff} value of Loose et al. (2011), derived from sea ice experiments, which can potentially include both diffuse and bubble contributions. A lower z_{BL} (0.05 µm) value was also tested. In a second series of experiments

Run	Name	R^{bab}	e_T^{gas}	D_{diff}	z_{BL}	Ikaite precipitation	Number of ice layers	Misfit
1	CTRL	10	0.07	0.97	0.5	Yes	10	0.1
2	Loose-D _{diff} ^b	0	0.07	24	0.5	Yes	10	0.08
3	No-bub	0	0.07	0.97	0.5	Yes	10	0.08
4	Low-z _{BL}	0	0.07	0.97	0.05	Yes	10	0.08
5	No-ikaite	0	0.07	0.97	0.5	No	10	0.10
6	20-layers	0	0.07	0.97	0.5	Yes	20	0.06
7	Low-bub	1	0.07	0.97	0.5	Yes	10	0.07
8	High-bub	20	0.07	0.97	0.5	Yes	10	-0.05
9	Moreau-bub ^c	0.1	0.07	0.97	0.5	Yes	10	0.08

Table 1. Description of the sensitivity runs used to test the sensitivity of air-ice CO₂ fluxes to model parameterization^a

^aDifferent parameterizations include the bubble formation rate ($R^{i_{bb}}, \%$ h⁻¹), the molecular diffusion rate ($D_{i_{b}}, 10^{\circ} \text{ m}^{-2} \text{ s}^{-1}$), the boundary layer thickness (z_{22} , um), ikaite precipitation and the number of vertical ice layers. Model-data misfit (mmol m⁻² d⁻¹) are also presented for each run.

^bLoose et al. (2011)

'Moreau et al. (2015)

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(runs 5–6), the impacts of higher resolution (20 layers instead of 10) and ikaite precipitation/dissolution were investigated. Third, we tested the impact of a more intense gas bubble pathway by changing $R^{\delta u \delta}$, the bubble nucleation rate (runs 7–9), which is highly uncertain.

To evaluate which scenario is closest to the observed fluxes, we computed a model-data misfit for each of the model runs. The misfit were computed from the difference between the flux observed and the flux modelled. We report averages for each of the model runs in Table 1.

All other parameters are from Moreau et al. (2015). The simulation spans 31 May – 18 June 2012. The time step is 1 h. Based on the present observations, initial seawater TA and DIC concentrations were set to 2300 mmol m^{-3} and 2090 mmol m^{-3} , and sea ice TA and DIC concentrations were set to 850 mmol m^{-3} and 750 mmol m^{-3} .

3. Results and discussion

Detailed information about sea ice physical properties can be found in Zhou et al. (2014b). Briefly, the first phase of the experiment – the growth phase – lasted from day 1 to day 15. Air temperature above the tank was set to -15 °C and sea ice grew continuously, reaching a maximum thickness of 24 cm. A strong temperature gradient was observed between the top and the bottom of the ice. Salinity exhibited a typical C-shape profile with a lower salinity at the ice interior compared to the top and the bottom of the ice. Then from day 16 to 19, the air temperature was set to -1 °C, sea ice thickness slightly decreased, temperature exhibited a more homogeneous profile through the whole thickness, and salinity decreased in the top and bottom parts. The brine volume fraction remained above 5% during the whole experiment. On the whole, the sea ice remained thin, warm and permeable during both the growth and the melting phase.



Figure 1 Linear regression between TA

and salinity within bulk sea ice. The ice growth and melting phases are colored in blue and red

phases are colored in blue and red, respectively. doi: 10.12952/journal.elementa.000112.f001

3.1 Total alkalinity

TA concentrations in bulk sea ice (i.e., melted sea ice) are consistent with the values reported in the literature (Gleitz et al., 1995; Delille et al., 2007; Nomura et al., 2010b; Fransson et al., 2011; Miller et al., 2011a; Geilfus et al., 2012a; Rysgaard et al., 2013) and were highly correlated with salinity ($r^2 = 0.95$; Figure 1).

The repeated inspection of freshly melted ice using a binocular microscope (Leitz Laborlux[®] with 125 to 500 x magnification) did not reveal the presence of ikaite, a hydrated calcium carbonate polymorph (CaCO₃·6H₂O). Taking into account the thermodynamic constraints (Papadimitriou et al., 2013) and the kinetics to simulate the ikaite precipitation (Papadimitriou et al., 2014), the maximum value of ikaite simulated by the model in the ice surface layer was 13 µmol kg⁻¹, whereas the error on TA measurement was 4 µmol kg⁻¹.(parameters from the CTRL simulation of Moreau et al., 2015). This concentration falls at the lower end of the range of ikaite concentrations reported in sea ice (7–93 µmol kg⁻¹ in Dieckmann et al., 2008; 15–19 µmol kg⁻¹ in Geilfus et al., 2013; 100–900 µmol kg⁻¹ in Rysgaard et al., 2013). This evidence indicates that if ikaite precipitated during the experiment, it was not significant.

3.2 CO₂ exchange at the air-ice interface

3.2.1 Continuous measurements of air-ice CO2 fluxes

During seawater cooling, and before the formation of the ice crystals, CO_2 fluxes measured with the automated chamber showed negative values, down to -6 mmol m⁻²d⁻¹ (Figure 2). Within hours after the formation of the first ice crystals, CO_2 fluxes became mostly positive (ranging between -0.4 mmol m⁻²d⁻¹ and 0.75 mmol m⁻²d⁻¹ with an average of 0.2 mmol m⁻²d⁻¹ for the growth phase), consistent with the observed super-saturation of CO_2 in bulk ice (i.e., $pCO_{2 bulk}$ above 400 ppm). During the melting phase, CO_2 fluxes turned to negative (ranging between -2.1 mmol m⁻²d⁻¹ and 0 mmol m⁻²d⁻¹ with an average of -0.24 mmol m⁻²d⁻¹) in parallel with the decrease of $pCO_{2 bulk}$ that passed below saturation. The pCO₂ of the underlying seawater remained under-saturated during the whole experiment, while the surface (first 5 cm) $pCO_{2 bulk}$ showed values above or below the atmospheric pCO₂ during the growth and the melting phase, respectively.

Although the chamber was not properly sealed between day 0 and day 5, air-ice CO_2 fluxes from the whole measurement period were consistent with previous measurements carried out with chambers over artificial sea ice (between 0 and 0.27 mmol m⁻² d⁻¹; Nomura et al., 2006) and slightly lower than measurements over natural sea ice. Delille et al. (2014) measured CO_2 fluxes ranging from -5.2 mmol m⁻² d⁻¹ to 1.9 mmol m⁻² d⁻¹ on Antarctic pack ice in spring, and ascribed these fluxes to seasonal pCO₂ gradients between the brine and the atmosphere. Geilfus et al. (2012a) measured CO_2 fluxes at the sea ice interface ranging from -2.63 mmol m⁻² d⁻¹ up to 0.84 mmol m⁻² d⁻¹ in the Arctic coastal zone, while Nomura et al. (2010a) measured CO_2 fluxes ranging from -1 mmol m⁻² d⁻¹ to 0.7 mmol m⁻² d⁻¹ over land fast ice in Barrow at the end of spring.



Figure 2

Air-ice CO_2 fluxes, sea ice surface temperature and pCO_2 over time.

a) Evolution of the air-ice CO₂ flux (black corresponds to a period with the chamber not properly sealed, blue to a period with a correct sealing of the chamber) and temperature 2 cm above the air-ice interface (in red). The green horizontal step line corresponds to the flux calculated from the DIC anomaly. The shaded areas refer to working hours and the related increase of atmospheric pCO2. b) Atmospheric (black line), ice surface (green triangles down) and seawater (blue triangles up) pCO₂. The ice surface pCO₂ corresponds to the first 5 cm of the bulk sea ice measured with the method of high vertical resolution

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Air-ice carbon pathways



Figure 3

Bulk sea ice DIC and surface DIC depletion during ice growth.

a) Bulk DIC profiles and b) DIC profiles normalized to a salinity of 7 (DIC₇), where the grey area refers to the DIC depletion zone. doi: 10.12952/journal.elementa.000112.003

The temperature and the pCO_2 air measured within the automated chamber exhibited daily variations, rising during "working hours" due to the presence of the researchers in the experimental room and decreasing outside "working hours". The pattern of air-ice CO₂ fluxes is clearly opposite and strongly affected by the rise of atmospheric pCO₂ during working hours. These imperfections are inherent to the environmental constraints of this experimental study and could hardly be avoided. Nevertheless, the results can still be interpreted in terms of the main factors driving the CO₂ fluxes, and the overall pattern of observed air-ice CO₂ fluxes is consistent with *in situ* observation of a seasonal cycle, with upward CO₂ fluxes during ice melt (Delille et al., 2010a; Geilfus et al., 2012a; Delille et al., 2014) and downward CO₂ fluxes during ice melt (Delille et al., 2014; Geilfus et al., 2015).

3.2.2 Integrated estimates of air-ice CO2 fluxes

In parallel with direct measurements of air-ice CO_2 fluxes, we derived air-ice CO_2 fluxes from DIC depletion in the top layers of the ice (Geilfus et al., 2013). DIC was normalized to a salinity of 7 (7 corresponds to the mean bulk ice salinity during the whole experiment, noted as DIC₇) to remove the salinity-related changes (brine rejection, concentration and dilution; Figure 3). If no biogeochemical processes occurred (biological activity, CaCO₃ precipitation, CO₂ transfer to the gas phase and CO₂ exchange with the atmosphere), DIC₇ profiles should be homogeneous over the ice column. During the growth phase, a clear decrease in the top 12.5 cm of the young ice was measured compared to the bottom ice horizons. Because no significant primary production was possible due to absence of primary producers (Zhou et al., 2014b) and ikaite precipitation was insignificant (section 3.1), we assumed that DIC₇ depletion in the top 12.5 cm of the growing ice was due to CO₂ release from the super-saturated ice to the atmosphere above. Whereas, during the melting phase we observed a DIC₇ increase in the top 12.5 cm. This increase can be linked to the downward air-ice CO₂ flux measured during the melting phase.

Besides the measurements of air-ice CO₂ fluxes, the amount of CO₂ released to the atmosphere during the sea ice growth was assessed using a method proposed by Geilfus et al. (2013). First, a "theoretical DIC" (DIC_{tb}) was calculated from the raw DIC concentration at 12.5 cm ($DIC_{12.5 \text{ cm}}$), assuming that, if biogeochemical processes are null, DIC and salinity (*S*) should follow a linear relationship:

$$DIC_{tb, i} = DIC_{12.5 \, cm} \cdot (S_i / S_{12.5 \, cm})$$
 (4)

where $DIC_{tb,i}$ and $DIC_{12.5 \text{ on}}$ are computed for each sampling event and expressed in µmol kg⁻¹. The index, *i*, refers to the upper two sampling depths, 2.5 cm and 7.5 cm. From the theoretical DIC, we derive the "DIC anomaly" for each sampling day (ΔDIC_t in mmol m⁻²):

$$\Delta DIC_t = \Sigma (i = 2.5 \text{ to } 12.5 \text{ cm}) (DIC_{th,i} - DIC_i)$$
(5)

As the DIC anomaly was mainly due to the release of CO_2 from the ice to the atmosphere during the present experiment (see above), integrating DIC anomalies over time gives the theoretical air-ice CO_2 flux between two sampling events:

$$F = \left(\left(\Delta DIC_{t+At} - \Delta DIC_t \right) / \Delta t \right) \cdot dx \cdot \rho \tag{6}$$

Table 2. Gas transfer coefficient calculated for each day of the experiment*

Day of the experiment	Т	Bulk S	K	
2	-3.0	11.5	2.43 (±0.9)	
5	-5.1	8.8	2.59 (±0.9)	
8	-5.0	9.5	2.66 (±0.9)	
14	-5.8	8.0	2.22 (±0.9)	
15 ^b	-3.3	3.0	2.1	
16 ^b	-2.5	6.1	2.9	
19	-1.8	6.9	0.5 (± 0.08)	
19	-1.8	6.9	0.3 (±0.08)	

^aMean ice surface temperature (T, °C), bulk salinity (*Bulk S*) and gas transfer coefficient for CO₂ at the air-ice interface (K, mol m⁻² d⁻¹ atm⁻¹) for each day of the experiment

^bRefers to the transition period

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where Δt is the time frame between two sampling events in days, dx is the distance in meters between two sampling depths, and ρ is the sea ice density for each layer defined from temperature and salinity and using relationships given by Cox and Weeks (1982), in kg m⁻³. Based on the precision of the measured variables (salinity, temperature, TA, pCO₂; see Methods section), the precision on F is assessed at \pm 0.03 mmol m⁻² d⁻¹ (which represents an error of 15% for the averaged CO₂ flux of 0.2 mmol m⁻² d⁻¹).

From these DIC anomalies, the calculated air-ice CO_2 fluxes (black triangles in Figure 2a) are in good agreement with the observed air-ice CO_2 fluxes, except on day 16 where the difference represents more than 1 mmol m⁻² d⁻¹; integrated measurements cannot accurately capture the rapid transition from the freezing to the melting decay phase. With the exception of this transition phase, the consistency between the continuous and integrated fluxes suggest that in an indoor experiment, the automated chamber provides accurate measurements of air-ice CO_2 fluxes when snow cover is absent, despite the large variation of the atmospheric pCO_2 .

3.3 Determination of a gas transfer coefficient for CO_2 in artificial sea ice

Using equation 1 for gas exchange, we calculated a gas transfer coefficient for CO_2 at the air-ice interface for each sampling day of the experiment (see K; Table 2), where F corresponds to the air-ice CO_2 fluxes measured with the automated chamber, $pCO_{2 \, sir}$ to the pCO_2 at the air interface and $pCO_{2 \, balk}$ to the pCO_2 at the ice interface (0 cm to 5 cm). The numbers in light grey in Table 2 refer to the transition phase which was not taken into account in the final value computed for K. The values for K and ancillary data detailed in Table 2 are close during the whole growth period. The mean K for the sea ice growth period, from day 2 to day 14 inclusive, is $K = 2.5 \text{ mol m}^{-2} d^{-1} \text{ atm}^{-1}$. A Bootstrap resampling statistical analysis of the propagation of the uncertainties of the measured variables (salinity, temperature, measured CO_2 fluxes, $pCO_{2 \, balk}$ and $pCO_{2 \, air}$) gives an uncertainty for K of 0.9 mol m⁻² d⁻¹ atm⁻¹ where standard error deviation is only 0.25 mol m⁻² d⁻¹ atm⁻¹. For the melting phase (which corresponds to two measurements on day 19) the mean K value was 0.4 mol m⁻² d⁻¹ atm⁻¹ (the uncertainty derived from a Bootstrap resampling statistical analysis was 0.08 mol m⁻² d⁻¹ atm⁻¹). K was therefore 6 times higher during the growth phase than during the melting phase. In order to get a measure of gas exchange that does not depend on the gas solubility, Wanninkhof (1992) proposed to use k, the gas transfer velocity, defined from:

$$K = k$$
. Sol (7)

where Sol (mmol m⁻³ atm⁻¹) is the solubility of CO_2 in salt water (here brine), a function of temperature (*T*) and salinity (*S*), following Weiss (1974):

$$\ln \text{Sol} = A_1 + A_2 (100/T) + A_3 \ln (T/100) + S [B_1 + B_2 (T/100) + B_3 (T/100)^2]$$
(8)

We used the T and S of sea ice brine. The resulting value, $k = 0.164 (\pm 10\%) \text{ cm h}^{-1}$, falls within the range of values given by Liss and Merlivat (1986) for a smooth surface regime and the values given by Crusius and Wanninkhof (2003) for gas exchange over a lake at low wind speed. However, solubility as described by eq. 8 is most likely not adequate for the range of temperature and salinity encountered within sea ice, as suggested by Zhou et al. (2014a). K, the gas transfer coefficient, is solely deduced from measurements and does not depend on an uncertain solubility value.

Thin sections of the ice cores were processed following Tison et al. (2002). Bubbles were observed during the growth phase, particularly near the ice surface (Figure 4). We suggest that these bubbles (trapped at the very beginning of ice growth or newly formed) were likely moving upward due to their own buoyancy. Once



Figure 4

Thin sections of surface ice cores.

Thin sections of ice cores for day 2, 5, 14 and 15 of the experiment. The contrasted circles and tubes are bubbles while the gray-shaded features are brine inclusions.

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bubbles reached the ice surface, they collapsed and CO_2 was released to the atmosphere, corresponding to an ebullition flux. K-values calculated during the growth and melting phases indicate that gas transport was about 6 times faster during ice growth than during ice decay. We hypothesize that air-ice CO_2 fluxes during the melting phase are driven mainly by molecular diffusion, while during the growth phase, ebullition fluxes add to molecular diffusion. This hypothesis suggests that the ebullition fluxes are a dominant pathway for gas transport and exchange during the growth phase.

3.4 Model sensitivity experiments on the CO_2 transport pathways through sea ice

Here we use the model to frame the CO_2 flux into further theoretical considerations. The various model simulations described in Table 1 are compared to the observations, in order to understand which parameters are most influential in shaping the model response (Figure 5).

First, the sign of the CO_2 flux is consistent between observations and all model simulations. All model runs show an efflux of CO_2 during the growth period and an influx during the melt period. The direction of the flux depends mostly on the dissolved gas pathway, itself driven by the air-brine pCO_2 difference, ultimately set by the near-surface ice temperature evolution, which is quite well understood. In addition, some of the short-term variations of the observed CO_2 fluxes are reproduced. The model gives a good estimation of downward CO_2 fluxes during ice melting although the time of the onset of downward CO_2 fluxes occurs earlier than observed in the model.

By contrast, the magnitude of the air-ice CO_2 flux is highly variable among the different model runs, in particular during the growth phase. The most influential but uncertain factors clearly lie within the gas bubble pathway (Figure 5c). By contrast, the dissolved pathway is found rather insensitive to parameterization choices (e.g., gas diffusivity D_{diff} , boundary layer thickness z_{BL} , vertical resolution, ikaite, etc.). In turn, the total (dissolved + bubble) air-ice CO_2 flux is essentially determined by the gas bubble nucleation rate R^{bub} , which acts as a bottleneck parameter for the efflux of CO_2 to the atmosphere via the gas bubble pathway. This bottleneck effect explains why R^{bub} was used as a tuning parameter, set to 10% h⁻¹ in the CTRL run, the value that gave the best agreement with observations.

Why is the dissolved pathway rather insensitive between the different runs? As in Moreau et al. (2015), we investigated whether the dissolved gas pathway could have been more intense than simulated. To answer this question, we tested to what extent modifying the uncertain parameters z_{BL} and D_{diff} could increase the upward CO_2 fluxes during ice growth. None of our trials was successful. For example, increasing D_{diff} up to 2.4 x 10⁻⁸ m² s⁻¹ (run 2: Loose- D_{diff}) barely affects the upward CO₂ fluxes during ice growth. Decreasing z_{BL} down to 0.05 µm did not significantly increase the simulated air-ice CO₂ fluxes either. This model behavior arises because the ultimate limitation for the air-ice CO_2 diffusive flux is the near surface stock of DIC: supply to the near-surface DIC is not rapid enough to sustain CO_2 fluxes to the observed magnitude. This result was already obtained by Moreau et al. (2015; see their Figure 9b where the simulated outward CO_2 fluxes during winter at Barrow reach asymptotically 1.3 mmol m⁻² d⁻¹ when z_{BL} is decreased down to 10⁻³ µm). By contrast, the gas bubble pathway is much more variable between the different runs and characterized by much larger uncertainties, because gas bubble flux can originate further down in the ice and is not limited by near-surface DIC stocks. The model-data misfit presented in Table 1 shows that the best model-observation agreement was achieved for a strong gas bubble pathway, which corresponds to high values of R^{bub} (10-20%) h^{-1}). Yet, the bubble nucleation rate R^{bub} is far from being well constrained from observations. In Moreau et al. (2014), this value was tuned to 0.1% h⁻¹, corresponding to a characteristic time scale of 40 days, in order to match observed gas bubble concentrations over simulations spanning several months. In the present context (curve Moreau-bub in Figure 5c), such value gives a weak gas bubble pathway and an underestimation of CO_2 fluxes by the model. Forty days is rather long for bubble nucleation, much larger than expected, typically less than one hour (see, e.g., Brennen, 1995). The most obvious reason why such an unrealistically large 40 day



Figure 5

Observed and simulated air-ice CO₂ fluxes.

a) Simulated air-ice CO₂ fluxes (mmol m⁻² d⁻¹) for runs Loose-D_{aig} (grey, where $D_{aig} = 24 \ 10^{-9} \ m^2 \ s^{-1}$), No-bub (green, where $R^{bab} = 0\% \ h^{-1} \ and \ D_{aig} = 0.97 \ 10^{-9} \ m^2 \ s^{-1}$) and Low- z_{BL} (dark blue in dash, where $z_{BL} = 0.05 \ \mu m$). The three curves for runs Loose- D_{aig} No-bub and Low- z_{BL} are confounded on the plot. Observed CO₂ fluxes are given in blue.

b) Simulated air-ice CO_3 fluxes (mmol m⁻² d⁻¹) for runs No-ikaite (dark red, where there is no ikaite precipitation) and 20-layers (dark blue, where the number layers of ice was set to 20 instead of 10). Observed CO_2 fluxes are given in blue.

c) Simulated air-ice CO₂ fluxes (mmol m⁻² d⁻¹) for runs CTRL (in black), Low-bub (grey, where $R^{tw\delta} = 1\%$ h⁻¹), High-bub (cyan, where $R^{bw\delta} = 20\%$ h⁻¹) and Moreau-bub (dark grey, $R^{bw\delta} =$ 0.1% h⁻¹). Observed CO₂ fluxes (mmol m⁻² d⁻¹) are given in blue. doi: 10.12952/journal.elementa.000112.005

value had to be used by Moreau et al. (2014) is that pressure effects are missing in the model, which should quickly inhibit gas bubble nucleation once a large enough stock of gas bubbles is built up, which would typically occur for impervious sea ice over a few days. Larger $R^{\delta u\delta}$ values of 10–20% h⁻¹ strongly intensify the gas bubble pathway. They also correspond to more realistic time scales for gas bubble nucleation (4–8 hours).

The influence of several other processes, known to occur in natural conditions and contribute to the iceair CO_2 fluxes, was also considered. As far as frost flowers are concerned, they were not observed in the tank experiment, and hence are not relevant to the present discussion of air-ice CO_2 fluxes. The precipitation of ikaite could have influenced ice-atmosphere CO_2 fluxes (e.g., Geilfus et al., 2013; Rysgaard et al., 2014); however, as discussed above, ikaite precipitation was not observed under the microscope and the model CTRL simulation predicts a rather low ikaite concentration of 13 µmol kg⁻¹. The lack of ikaite influence is further corroborated by the model run with no ikaite precipitation (and no bubbles; Run 6, Table 1) which barely differs from the no-BUB run in terms of air-ice CO_2 flux (Figure 5b).

We also tested the role of vertical resolution of the simulated CO_2 fluxes by running the model with 20 vertical ice layers instead of 10, and with no bubbles (Figure 5b). More layers better resolve and increase the near-surface pCO_2 , which slightly intensifies the dissolved gas pathway during the growth phase.

3.5 Synthesis

As detailed in Zhou et al. (2014b), the artificial sea ice was likely permeable to gas exchange during the whole experiment. Convection was likely only present during the growth period and limited to near the ice-water interface (see Rayleigh numbers in Figure 3 of Zhou et al., 2014b) and was nearly negligible during

the whole period of decay. We therefore consider that only diffusion and/or buoyancy processes occurred in the upper parts of the ice. Both the computation of the gas transfer coefficient and the model sensitivity analysis support this assumption. As described previously, bubbles were observed during the growth phase, particularly near the ice surface (Figure 4).

The values of K were about 6 times lower during the melting phase as compared with the growth phase (Table 2). At this stage, based on model simulations, we cannot explain this difference without assuming a significant contribution of the gas bubble pathway during the growth of sea ice. However, this explanation is not based on direct observation of gas bubble processes but rather on inference from model simulations characterized by large uncertainties, in particular in terms of the gas bubble nucleation rate. The latter is the key tuning bottleneck parameter sourcing gas bubbles to the model gas bubble ice-atmosphere pathway. All the other surface processes that we could envision were, to the best of our present investigation capability, not able to supply enough carbon to the atmosphere. During ice melt, the model is in agreement with the much lower K values, suggesting that air-ice CO_2 fluxes are dominated by the dissolved pathway, apart from the short under-sampled transition period when other processes such as episodic convection events might have taken place.

Using our best model run (CTRL), we compared the contribution of all processes based on the computation of the model DIC budget, following Moreau et al. (2015; see Figure 6). Sea ice is gaining DIC throughout its growth (Figure 6a). Large quantities of DIC are incorporated into sea ice by growth, although 80% of this DIC is rejected through brine drainage (Figure 6b). Ikaite precipitation does not significantly contribute to the budget of DIC. Ice-atmosphere CO_2 fluxes (Figure 6c) are dominated by the escape of gas bubbles during ice growth. However, only the dissolved pathway affects CO_2 fluxes during ice melt. As suggested by Moreau et al. (2015) the budget of DIC in sea ice is driven mainly by physics while biogeochemical processes (only chemical here), although significant, are secondary.

Based on these considerations, we expand to ice-atmosphere exchanges of CO_2 the suggestion that gas bubbles provide important contributions to the stocks of gaseous compounds in sea ice (Mock, 2002; Tison et al., 2002; Rysgaard and Glud, 2004; Zhou et al., 2013; Moreau et al., 2014). The conceptual view that we propose is based on three key arguments. 1. Gas bubbles easily form in sea ice because brine shrinking with temperature induces drastic increases in gas concentrations, and because there is a net decrease in gas solubility with decreasing temperature in brine inclusions. 2. Gas bubbles in the liquid brine rise upward if the connectivity of the brine network is sufficient. 3. The dilution of brines during warming brings CO_2 concentration in brine below saturation, which brings trapped gas bubbles back into dissolved form. Because there is no analytical method to assess the partitioning of gases between dissolved and gaseous forms in sea ice brine, it is difficult for the time being to confirm this conceptual view directly. In natural sea ice, other surface processes likely affect air-ice CO_2 fluxes as well (e.g., the formation of frost flowers, brine skim; Geilfus et al., 2013; Barber et al., 2014). In the present experiments, however, they were not observed.



Figure 6 CO₂ budget.

a) Daily budget of vertically integrated DIC (TDIC, mmol m⁻²) dissolved into CO₂ (black), CO₃²⁻ (light grey), and HCO³ (grey) for the CTRL run. b) Corresponding daily mean changes (mmol m-2 day-1) in TDIC due to total sea ice growth and melt (dark blue), brine drainage (light blue), and ikaite precipitation/dissolution (red). c) Corresponding daily mean changes (mmol m-2 day-1) in TDIC due to diffusive CO2 fluxes (light blue) and gas bubble fluxes (dark blue).

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Finally let us stress that there are only a few processes able to sustain enhanced CO_2 fluxes during a long period. The presence of frost flowers would be transient and have only short-term effects on CO_2 fluxes. Other processes (e.g., melting/freezing cycle of the ice surface) modulate air-ice CO_2 fluxes, but few of them can actually sustain CO_2 fluxes for extended periods of time as we observed during the experiment. Processes that sustain CO_2 for extended periods of time must involve either the production of CO_2 , like bacterial respiration, or the transfer of CO_2 from a large reservoir (like the ice interior or the ocean) to the surface.

4. Conclusions

The first aim of this study was to determine experimentally the air-ice CO_2 transfer coefficient from continuous CO_2 flux measurements during an ice growth and decay cycle in an ice-tank experiment. Discrete measurements of air-ice pCO_2 gradients and DIC anomalies reflected well the amplitude and the patterns of the air-ice CO_2 fluxes, supporting the reliability of our methods and results, including the calculation of a bulk gas transfer coefficient. The second aim was to discriminate the different drivers of air-ice CO_2 fluxes using a 1D sea ice carbon cycle model (Vancoppenolle et al., 2010; Moreau et al., 2015), including explicit empirical representations of dissolved gas and gas bubble ice-atmosphere pathways and testing for several gases (Ar, O_2 , CO_2) at a few locations.

There are three key findings in the paper. 1. The observation-based gas transfer coefficient, retrieved by dividing the observed CO_2 flux by the air-brine pCO_2 difference, was ~6 times higher during growth $(K = 2.5 \text{ mol m}^{-2} \text{ d}^{-1} \text{ atm}^{-1})$ than during melt $(K = 0.4 \text{ mol m}^{-2} \text{ d}^{-1} \text{ atm}^{-1})$. 2. The time evolution of the sign of the air-ice CO_2 flux, characterized by an efflux from the ice during growth and an influx during melting, was consistent between observations and the nine model simulations, as well as with previous literature (Nomura et al., 2010a; Geilfus et al., 2012a; Delille et al., 2014; Geilfus et al., 2015). Such evolution must therefore be seen as typical and robust. 3. The magnitude of the observed CO_2 flux is consistent with previous literature but not between the different model simulations. The simulated dissolved CO_2 flux clearly underestimates the observed value because of an intrinsic limitation by DIC stocks in the model already identified by Moreau et al. (2015). The observed magnitude of the ice-air CO_2 flux can only be reached in the model by invoking an intense escape of gas bubbles through an ice-atmosphere pathway. Such an intense pathway was achieved by tuning the gas bubble nucleation time scale down to a few hours, which contrasts with the value of a few weeks used in a previous 6-month simulation of Argon dynamics in natural sea ice (Moreau et al., 2014).

Based on these concordant findings, we infer that the gas bubble ice-atmosphere pathway is likely a significant contributor to air-ice flux in young growing sea ice, next to diffusion. This intense gas bubble pathway in growing sea ice proposed here is plausible at this stage but subject to caution, because it does not rely on direct process observations, but rather on inference from air-ice CO_2 flux and a single sea ice model, characterized by a number of assumptions. Further evaluation of the proposed scenario and reduction of uncertainties rely on improvements of both observation and modelling techniques. Observations of gas bubbles from X-ray tomography (Crabeck et al., 2016) provide new insights on gas bubble size and number distribution, and might be used to document the upward migration of gas bubbles. Future models should include at least pressure effects on gas bubble nucleation and perhaps tortuosity effects on gas bubble rise, as well as improved representations of brine dynamics (e.g., Griewank and Notz, 2013; Turner et al., 2013; Rees Jones and Worster, 2014).

The multiphase nature of CO_2 in sea ice is well established, with contributions of dissolved species, gas bubbles (Tison et al., 2002; Zhou et al., 2013; Crabeck et al., 2014a; Moreau et al., 2014, 2015) and ikaite crystals (Papadimitriou et al., 2004; Dieckmann et al., 2008), a solid inorganic compound that contains inorganic carbon. This multiphase nature of CO_2 is, to our best knowledge, a unique feature in marine environments. Clarifying the partitioning of CO_2 between the gaseous and dissolved phases and the gas transport pathways, as well as the contribution of surface ice processes, is a critical challenge for future research related to gas dynamics and the carbon cycle in ice-covered seas.

CHAPTER V: Winter to spring ocean-sea ice-atmosphere N₂O

partitioning in the Arctic Ocean (north of Svalbard)

Marie Kotovitch^{1,2}, Anna Silyakova³, Daiki Nomura^{4,5,6}, Agneta Fransson⁷, Mats A. Granskog⁷, Paul Dodd⁷, Pedro Duarte⁷, Fanny Van der Linden^{1,2}, Sébastien Moreau^{7,8,9}, Florian Deman¹⁰, Jean-Louis Tison² & Bruno Delille¹

¹ Unité d'océanographie chimique, MARE, Université de Liège, Belgium

² Laboratoire de Glaciologie, DGES, Université Libre de Bruxelles, Belgium

³ CAGE, Centre for Arctic Gas Hydrate, Environment and Climate, Tromsø, Norway

⁴ Faculty of Fisheries Sciences, Hokkaido University, 3–1–1, Minato–cho, Hakodate, Hokkaido 041–8611, Japan

⁵ Arctic Research Center, Hokkaido University, Kita–21, Nishi–11, Kita–ku, Sapporo, Hokkaido 001–0021, Japan.

⁶ Global Station for Arctic Research, Global Institution for Collaborative Research and Education, Hokkaido University, Kita–8, Nishi–5, Kita–ku, Sapporo, Hokkaido 060–0808, Japan

⁷Norwegian Polar Institute, Fram Centre, 9296 Tromsø, Norway

⁸ Georges Lemaître Centre for Earth and Climate Research, Earth and Life Institute, Université Catholique de Louvain, Louvain-La-Neuve, Belgium

⁹ Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Tasmania

¹⁰ Analytical, Environmental, and Geochemistry, Earth Sciences Research Group, Vrije Universiteit Brussel, Brussels, Belgium

Abstract

We present the first winter to spring nitrous oxide (N_2O) observations in snow, sea ice, and upper ocean from the N-ICE2015 expedition in the western Nansen Basin (Arctic Ocean) north of Svalbard between 80°N and 83°N. In seawater, a general N_2O undersaturation with respect to the atmosphere was identified at the surface, with a clear N₂O enrichment north of 82°N. We assign the N₂O undersaturation to the inflow of undersaturated Atlantic Water in the Arctic Ocean associated to a sea ice melt contribution of around 20%, and suggest that the main source of N_2O enrichment is from benthic denitrification on the East Siberian Shelf. Sea ice shows N₂O oversaturation throughout winter and spring in both first-year ice (FYI) and second-year ice (SYI). Further, SYI, with lower salinity than FYI, is enriched in N₂O compared to the dilution curve for salinity. We suggest that N₂O is (i) produced *in situ* by microbial communities, (ii) brought with the flushing of N_2O -rich ice surface meltwater and/or (iii) stored in the less permeable SYI, limiting gas exchange. Finally, we suggest that observed high N₂O concentrations in the snow cover result from a combination of brine rejection at the top of the ice (brine skim), brine wicking, bacterial activity and potentially chemical N_2O production (by chemodenitrification). On the whole surface waters act as sink for atmospheric N₂O from winter to spring, while sea ice acts as a source.

V.1. Introduction

Significant changes in sea ice extent, volume and seasonal dynamics are ongoing in the polar regions, as these regions are very sensitive to a warming climate (IPCC, 2013). With a residence time of 114 years in the atmosphere and a global warming potential 298 times that of carbon dioxide (CO₂) for 100 years (Forster et al., 2007), nitrous oxide (N₂O) is one of the most important greenhouse gases (GHG) present in the atmosphere along with CO₂ and methane (CH₄). N₂O is subject to photochemical reactions in the stratosphere, a process that has the potential to destroy ozone to such extent that N₂O is the dominant ozone-depleting substance emitted in the 21st century (Ravishankara et al., 2009). In addition to anthropogenic sources of N₂O to the atmosphere, known natural sources include soils, ocean sediments and seawater. In the aquatic environment, N₂O is mainly produced by microbial processes, namely nitrification (i.e. the oxidation of ammonium, Yoshinari, 1976 and Nevison et al., 2003) and denitrification (i.e. the reduction of nitrate, Suntharalingam and Sarmiento, 2000). However, the natural sources and sinks of N_2O are still poorly quantified.

The status of the Arctic Ocean as a source or sink of N_2O for the atmosphere is unclear due to the paucity of data and the coexistence of both N_2O undersaturation and oversaturation in its surface waters with respect to the atmospheric N_2O . In summer, the Nansen Basin and the Amundsen Basin are mostly undersaturated in N_2O , with a patch oversaturated in the Amundsen Basin (Verdugo et al., 2016). The Greenland Sea also appears to be undersaturated in N_2O (Weiss et al., 1992; Zhan et al., 2015, 2016), showing an oversaturation southwards (Weiss et al., 1992). The Canada Basin and the Chukchi Sea – except near the Bering Strait – are undersaturated in N_2O (Fenwick et al., 2017; Hirota et al., 2009; Zhan et al., 2015) while the Canadian Archipelago and the Baffin Bay surface waters are mostly oversaturated in N_2O in summer (Fenwick et al., 2017; Gagné, 2015; Kitidis et al., 2010). To our best knowledge, only one study has reported autumn N_2O values (Fenwick et al., 2017) and no data are available in winter and spring, precluding a robust annual budget of air–sea N_2O fluxes for the Arctic Ocean.

Away from the continental shelves (e.g. in Beaufort and Greenland Seas), the globally undersaturated N₂O vertical distribution does not seem to be significantly affected by biological processes (i.e. nitrification or denitrification) but reflects either a preindustrial relic or vertical mixing in an area dominated by deep water formation (Zhan et al., 2015, 2016). On the shelves, the observed oversaturation in N₂O has been ascribed to the release of N₂O from sediments (Zhang et al., 2015), a signature which can be observed away from the shelves for CH_4 (Damm et al., 2018; Fenwick et al., 2017).

It has also been hypothesized that sea ice cover affects the distribution of N_2O in surface waters. Sea ice formation and the consequent release of brine may lead to N_2O oversaturation in the surface waters (Randall et al., 2012), similar to what has been observed for CO_2 (e.g. Delille et al., 2007; Fransson et al., 2013; Loose et al., 2009; Tison et al., 2002). Later in the summer, it has been repeatedly hypothesized that sea ice meltwater dilutes the surface water, leading to N_2O undersaturation (Kitidis et al., 2010; Randall et al., 2012; Verdugo et al., 2016; Zhang et al., 2015). To date, Randall et al. (2012) presented the only N_2O measurements in sea ice pointing out that sea ice formation and melt have the potential to generate sea-to-air or air-to-sea fluxes of N_2O , respectively.

A study on ammonium oxidation and anaerobic bacterial cultures showed that N_2O production may occur in sea ice (Priscu et al., 1990). Like other gases, N₂O might be subject to various physical, chemical and biological processes (Tison et al., 2017; Tsurikov, 1979; Zhou et al., 2014a). For instance, in sea ice, gas concentration in brines strongly depends on ice temperature: when temperature decreases, the brine channels shrink in size, concentrating salts, gases and other impurities in the brine; in contrast, when temperature increases, the brine channels broaden and their content is diluted (Hunke et al., 2011; Notz and Worster, 2009). It has also been suggested that the concentration of gases in brine may trigger the nucleation of bubbles (Crabeck et al., 2014a, 2019; Killawee et al., 1998; Light et al., 2003; Tison et al., 2002; Tsurikov, 1979; Zhou et al., 2013). Hence, gases in sea ice may either exist in gaseous (i.e., bubbles) or dissolved phase. Sea ice is commonly assumed to be permeable when its brine volume fraction is above 5% (Golden et al., 1998). When sea ice is permeable, the exchange (or transport) of dissolved gases can occur vertically within the sea ice, between the atmosphere and the ice, and between the ice and the seawater. However, the permeability threshold might actually be higher for the gaseous phase (i.e., 7 to 10%, Moreau et al., 2014; Zhou et al., 2013).

Denitrification may occur in hypoxic conditions, i.e., with dissolved oxygen (DO) at trace level concentrations < 6 μ mol kg⁻¹ (Seitzinger et al., 2006), while brines are at solubility around 300 μ mol kg⁻¹. If it occurs under such conditions, the denitrification chain may not be complete and stop at the N₂O stage. This process could be responsible for significant N₂O accumulation in sea ice. Denitrification in DO-depleted sea ice has been suggested by Kaartokallio (2001), Nomura et al. (2010) and Rysgaard et al. (2008), although it would have to be associated with microenvironments, given that oxygen is usually observed at or above saturation in sea ice (Zhou et al., 2014a).

The sea ice surface shows unique properties that may play a role in chemical processes occurring in the lower polar troposphere. For example, under strong surface cooling conditions, liquid water in brine freezes and may lead to the fracture of the ice and the expulsion of brine along cracks onto the ice surface (Bennington, 1963). This upward expulsion of brine (brine wicking) results in a high saline layer of brine skim (Untersteiner, 1968). Snow and frost flowers – vapor-deposited ice crystals under strong relative humidity and temperature gradient at the ice-air interface (Barber et al., 2014) – can also influence the sea ice surface salinity by draining brine by capillarity, from the ice channels to the surface, significantly increasing sea ice surface salinity, and thus the concentration of major ions (Domine et al., 2004; Douglas et al., 2012). Brine skim and frost flowers have been shown to mediate the transfer of gases such as halocarbons and CO₂ between sea ice and air (e.g. Fransson et al., 2015; Geilfus et al., 2015). Flooding – which occurs when a heavy snow cover depresses the sea ice below the water surface – may also add salts and impurities to the ice surface. These physical processes are all sources of salts, ions and wetness for the ice surface, creating a suitable place for chemical reactions.

In this paper, we present a unique time series of N_2O dynamics in snow, sea ice and the underlying seawater in the Arctic Ocean, from winter to spring 2015. We aim to discuss (i) N_2O distribution in the water column in winter and spring, (ii) N_2O concentration in sea ice and (iii) the interactions of N_2O dynamics in sea ice with the underlying water and the atmosphere.

V.2. <u>Sampling area</u>

The Norwegian young sea ICE expedition (N-ICE2015) took place north of Svalbard, in the western Nansen Basin, from January to June 2015, when R/V *Lance* drifted with the pack ice, providing a unique seasonal data set for the region (for details, see Granskog et al., 2016, 2018). The campaign consisted of four separate drifts (Floes 1 to 4) with R/V Lance anchored to an ice floe from January 15th to June 22th, 2015 (Figure V-1). Research camps were established on these floes. Three camps were initially set up near 83°N, drifted and broke up either by ice dynamics or due to the vicinity of the ice edge, which forced relocations and the

start of new ice camps (Granskog et al., 2018). The last floe (Floe 4) drifted from June 7th to 22nd 2015 (Figure V-1b, see Granskog et al., 2018).

Water masses during the entire expedition are described in Meyer et al. (2017), using the classification of Rudels et al. (2000, see Table V-1). In winter, the mixed layer was cold and located between 50 to 100 m deep, while at the end of the spring, the mixed layer was warmer and shallower (Meyer et al., 2017). For more information on the water masses vertical distribution, see Figure 6 in Meyer et al. (2017). Pressure (dbar) and depth (m) are interchangeable in this study.

Patches	Density σ_0	Conservative temperature Θ
Atlantic Intermediate Water (AIW)	$27.97 < \sigma_0, \sigma_{0.5} < 30.444$	$\Theta < 0^{\circ} C$
Atlantic Water (AW)	$27.70 < \sigma_0 < 27.97$	$\Theta > 2^{\circ}C$
Nordic seas Deep Water (NDW)	$\sigma_{0.5} > 30.444$	/
Modified Atlantic Water (MAW)	$27.70 < \sigma_0 < 27.97$	$\Theta < 2^{\circ}C$
Polar Surface Water (PSW)	$\sigma_0 < 27.70$	$\Theta < 0^{\circ} C$
Warm PSW	$\sigma_0 < 27.70$	$\Theta > 0^{\circ}C$

Table V-1: Water mass properties used in this study

The thickness of the pack ice samples for this study ranged from 10 to 182 cm (including refrozen leads, first and second year ice), and was generally covered with a relatively thick snow cover (a mean of 0.3 m excluding refrozen leads), affecting the sea-ice mass balance with the presence of snow-ice formation (Granskog et al., 2017). Relatively thin ice and thick snow appear typical for the region (Rösel et al., 2018). The oldest ice in the study area was likely from fall 2013, originating from the Laptev Sea (Itkin et al., 2017).



Figure V-1: a) Paths of the Atlantic water in the Arctic Ocean. Red arrows correspond to incoming relatively warm currents and blue arrows correspond to cold outcoming currents. More description is given in the text. © A. Igesund/Norwegian Polar Institute. b) Composite of ice conditions on 25th May 2015 and the drift tracks of N-ICE2015 Floes 1 to 4 in winter and spring 2015 in the region north of Svalbard. Credit: RADARSAT-2 images provided by NSC/KSAT under the Norwegian-Canadian RADARSAT agreement. RADARSAT-2 Data and Products © Maxar Technologies Ltd. (2015). All Rights Reserved. RADARSAT is an official mark of the Canadian Space Agency. Map created by the Norwegian Polar Institute / Max König.

V.3. <u>Material and methods</u>

V.3.1. Seawater sampling (on-ice and ship rosette)

Seawater samples for dissolved oxygen (DO), N₂O, stable oxygen isotope ratio ($\delta^{I8}O$) from H₂O, nutrients (NO₃⁻ and PO₄³⁻), chlorophyll a (Chl *a*) and salinity were collected from Niskin bottles deployed as part of two Conductivity-Temperature-Density (CTD) packages: (i) a ship-based rosette equipped with a Sea-Bird Electronics SBE911 CTD and (ii) an on-ice rosette (Hydro-Bios SlimLine 6 with integrated CT-set) that was deployed 300–400 m away from the ship. The ship-based rosette was composed of 11 x 8 L Niskin bottles, with a weekly sampling down to bottom. The on-ice rosette was composed of 6 x 3.5 L Niskin bottles with 1000 m wire.

From the ship-based rosette, hydrography, chemistry and biology were sampled weekly. For the one-ice rosette, DO and Chl *a* were sampled weekly while $\delta^{18}O$, nutrients and N₂O were sampled bi-weekly. More information can be found in

already published papers: Meyer et al. (2017) for DO, Assmy et al. (2017b) for nutrients.

A detailed description of the CTD data from the N-ICE2015 expedition is given in Meyer et al. (2017). Salinity samples were taken from all Niskins and measured on board with a Guildline 8410A salinometer. Conservative temperature (Θ) and absolute salinity (S_A) were computed using the Thermodynamic Equation Of Seawater 2010 (TEOS-10).

DO samples were collected directly after the rosette was lifted on deck through a connected tube at the outlet into 115 mL bottles and filled from the bottom with water overflow, preferably before other sampling. N₂O samples were collected as for DO from the Niskin bottle into 60 mL or 160 mL glass serum bottles. $\delta^{18}O$ samples were collected in 40 mL glass vials filled almost completely, closed and sealed with parafilm. Inorganic nutrients were collected in 20 mL scintillation vials, then fixed with 0.2 mL chloroform and kept in the refrigerator until later analysis on board. A variable volume (from 100 to 5000 mL) was collected for Chl *a* and phaeopigments.

V.3.2. Sea ice sampling

Sea ice sampling took place weekly at representative sites. Ice cores were collected using Kovacs ice corers with internal diameter of 9 cm or 14 cm (Mark II or Mark V, Kovacs Ent., Roseburg, USA). Immediately after the ice core recovery, temperature was measured *in situ* with a calibrated probe (Testo 110 NTC, Brandt Instruments, Inc., USA) with a resolution of 10 cm. Ice cores were cut in 10 cm sections, then placed in airtight plastic bags (5 L, Smart bags, GL Science, Japan) emptied with a vacuum pump and melted at +4°C in the dark. Melt water was sampled following the same procedure as for seawater described above and analyses were conducted for the same parameters, i.e. salinity, $\delta^{I8}O$, nutrients, Chl *a* and N₂O. Half of the samples for N₂O measurements were melted on board (we will refer to as "*in situ* samples") while the other half were stored on board and transported to the laboratory at -20°C, and melted at +4°C at the Norwegian Polar Institute in Tromsø, Norway, in October 2016 (these we refer to as "stored samples"). All samples for N₂O measurements were transferred to 60 or 160 ml serum bottles and poisoned with 50 μ L of saturated mercuric chloride. Bottles were immediately sealed with pre-treated butyl stoppers (15 min in boiling deionised water, 3 times) and aluminium caps and stored in the dark at +4°C until measurements.

Sea ice salinity was measured either with a conductivity sensor (Cond 315i, WTW GmbH, Germany) or Guildline 8410A salinometer. Only the conductivity meter Cond 315i (WTW GmbH, Germany) was used to measure salinity on snow, slush and frost flower (see section V.3.3 below).

V.3.3. Snow sampling

Snow was sampled with a plastic shovel, placed into plastic bags tightly sealed, and slowly melted in the dark at +4°C. Sample of snow bottom including brine skim (scratched ice surface after removing snow) was collected on Floe 2. The temperature of the snow and of frost flowers was measured during CO_2 flux measurements (as described in Nomura et al., 2018) using a needle-type temperature sensor (Testo 110 NTC, Brandt Instruments, Inc., USA). The sampling of N₂O from melted snow follows the same procedure as that of melted sea ice described above (section 3.2), using 60 mL glass bottles. However, the values derived from this method have to be taken with care as the snow is much more porous than the ice and contain significant amount of air. On one hand, the vacuum pump removed most of the air (and thus N₂O) contained in the snow, but on the other hand, the measurements are likely to be biased by any remaining air contaminated by atmospheric N₂O.

V.3.4. Nutrients and dissolved oxygen analysis

Concentrations of nitrate (NO₃⁻) and phosphate (PO₄³⁻) were measured spectrophotometrically at 540, 810 nm, respectively, on a modified Skalar auto analyser (Assmy et al., 2017b), following Bendschneider and Robinson (1952) and RFA Methodology, for NO₃⁻, and Grasshoff (1965), for PO₄³⁻. The measurement uncertainty is 10% or less for nitrate and phosphate. Oxygen data concentration was determined with the Winkler method, following standard procedures described in Carpenter (1965).

V.3.5. Oxygen isotope analysis

 $\delta^{18}O$ analysis is based on a standard equilibration with carbon dioxide (Epstein and Mayeda, 1953). The samples from Floe 1 (15 Jan to 21 Feb) were analysed at the G. G. Hatch laboratory at the University of Ottowa, Canada using a Thermo Delta Plus XP mass spectrometer and automated preparation line with a precision of 0.05‰. All the other samples were analysed at the British Geological Survey, Keyworth, UK, using an Isoprime 100 mass spectrometer and automated preparation line with a reproducibility better than 0.05.

Meteoric water and sea ice meltwater fractions were calculated using a 3endmember balance following the approach of Östlund and Hut (1984). Salinity endmember values were: 34.9, 0 and 3 for Atlantic water, meteoric water and sea ice meltwater respectively. $\delta^{18}O$ endmember were 0.3‰, -18.4‰ and 0.4‰ (relative to Vienna Standard Mean Ocean Water) for Atlantic water, meteoric water and sea ice meltwater respectively. Meteoric water includes river runoff and precipitation. Sea ice melt can be positive (excess sea ice meltwater) or negative (excess brine from sea ice growth).

V.3.6. N_2O concentration analysis

N₂O concentration was determined using the headspace technique as in Farías et al. (2009), Upstill-Goddard et al. (1996) and Walter et al. (2005). Here, the ratio was 25 mL headspace in 60 mL bottles, and 30 mL headspace in 160 mL. The samples were randomly measured in a gas chromatograph (SRI® 8610) equipped with an Electron Capture Detector. A three-point calibration curve was performed with certified CH₄:CO₂:N₂O:N₂ mixtures (Air Liquide® Belgium) of 0.2, 2 and 5.8 ppm N₂O. Concentration of N₂O was computed using the solubility coefficients of Weiss and Price (1980) and taking into account the weight before and after the preparation of the headspace in order to determine the exact volume of both gas and liquid phases. The precision of N₂O measurements is \pm 3.2%. However, as suggested by Wilson et al (2018) accuracy may not be better than 2.6 \pm 1.9%.

The N₂O solubility in seawater and brine (C^* in mol L⁻¹) in equilibrium with moist air (P = 1 atm) can be computed with the relationship and constants proposed by Weiss and Price (1980; equations 8, equation 13 and table II) assuming that they are valid at temperature below 0°C and salinity higher than 36. We assumed atmospheric N₂O value based on the average mixing ratios for the Arctic. The mean from January to June 2015 was 328.65 ppb (provided by the NOAA ESRL Global Monitoring Division, Colorado, USA; http://esrl.noaa.gov/gmd/).

 N_2O saturation in seawater, N_2O_{sat} (%), was computed following equation (V-1):

$$N_2 O_{sat} = \frac{C_{sw}}{C_{sw}^*} \times 100 \tag{V-1}$$

where C_{sw} (nmol L⁻¹) is the N₂O concentration measured in seawater and C_{sw}^* (nmol L⁻¹) is the N₂O concentration in seawater in equilibrium with the atmosphere. Using the same equation with $C_{sw}^* \otimes -1.7$ computed for a temperature set at -1.7 °C instead of the *in situ* temperature, we obtain $N_2O_{sat} \otimes -1.7$.

Solubility in bulk sea ice, C_{bi}^* (nmol L⁻¹), was derived from the solubility in brine, C_{br}^* (nmol L⁻¹) and the brine volume fraction, BrV, of the ice according to:

$$C_{bi}^* = C_{br}^* \times BrV \tag{V-2}$$

Concentration of N₂O in brine, C_{br} (nmol L⁻¹), was derived from the concentration of N₂O measured in bulk sea ice, C_{bi} , according to equation (V-3):

$$C_{br} = \frac{C_{bi}}{BrV} \tag{V-3}$$

With C_{br} and C^*_{br} , we also calculated the partial pressure of N₂O within the brine $(pN_2O_{br}, \text{ in atm})$ according to:

$$pN_2O_{br} = \frac{c_{br}}{c_{br}^*} \times pN_2O^* \tag{V-4}$$

where pN_2O^* correspond to the partial pressure of N₂O in brine in equilibrium with the atmosphere (328.65 µatm at atmospheric pressure of 1 atm).

V.3.7. Chl a analysis

Chl *a* and phaeopigments samples were filtered on 25-mm GF/F filters (Whatman), extracted in 100% methanol overnight on board the ship and measured fluorometrically with an AU10 Turner Fluorometer (Turner Design, Inc.). Precision of Chl *a* measurement was 5.5%. Further details are provided by Assmy et al. (2017b).

V.3.8. Calculation for N* and AOU

The nitrate excess, N^* (in µmol L⁻¹) is a parameter that gives an indication on the impact of N₂ fixation (positive N^*) and denitrification (negative N^*) on the nutrient field. N^* is defined as the following equation (Deutsch et al., 2001):

$$N^* = [NO_3^-] - 16 \times [PO_4^{3-}] + 2.9 \tag{V-5}$$

The apparent oxygen utilization, AOU (in µmol kg⁻¹), was calculated as the difference between the DO gas solubility (DO^* , in µmol kg⁻¹) and the measured DO concentrations (DO in µmol kg⁻¹):

$$A0U = 0_2^* - 0_2 (V-6)$$

The DO^* values were calculated using the equation of Garcia and Gordon (1992) based on the DO^* values of Benson and Krause (1984). AOU represents an estimate of the DO utilized or produced due to biochemical processes (Redfield et al., 1963): a positive AOU reflects processes of respiration or degradation, while a negative AOU is related to primary production.

V.3.9. Calculation for brine volume and brine salinity

Brine salinity and brine volume fraction were derived from relationships proposed by Cox and Weeks (1983, 1986).

V.3.10. Cross-variable statistics

To evaluate the relationships between variables, non-parametric Spearman's rank correlations were used.

V.4. <u>Results</u>

As the expedition lasted for nearly 6 months and the sampling sites were spatially scattered over a large area due to the *RVLance* drifts (Floes 1 to 4, see Figure V-1), the results of this study reflect a large temporal and spatial variability in the Arctic Ocean water column and sea ice conditions.

*V.4.1. N*₂*O* distribution within the water masses

Average N₂O concentrations in the water column ranged from 10.4 nmol L⁻¹ to 17.2 nmol L⁻¹ (Figure V-2a and Figure V-3a). Atlantic Water (AW, Table V-1), mostly found between 100 to 500 m from May to June, had a mean N₂O concentration over the 6 months survey of 12.5 ± 1.1 nmol L⁻¹ (89.35% of saturation in average). The Modified Atlantic Water (MAW, Table V-1) had a mean N₂O concentration of 13.6 \pm 1.2 nmol L⁻¹ (91.6% of saturation in average). The maximum N₂O concentrations were observed in Polar Surface Water (PSW, Table V-1), with a mean of 14.8 \pm 1.4 nmol L⁻¹ (87.5% of saturation in average). This represents a difference of 15% in N₂O concentration between the AW and the PSW while the saturation is a little higher in AW.



Figure V-2: Conservative Temperature (°C) versus Absolute Salinity (g kg⁻¹) versus a) N_2O concentrations (nmol L⁻¹) and b) N_2O saturation (%). Potential density relative to the surface is contoured in grey, and the presence of various water masses (cf. Table 1) are indicated, where AIW refers to Atlantic Intermediate Water, AW refers to Atlantic Water and MAW refers to Modified Atlantic Water.

V.4.2. Temporal and spatial variation of N_2O in the water column

 N_2O saturation in the water column ranged between 68 and 107% (Figure V-2b and Figure V-3b). Maximum were observed at the end of April in the northern most part of the surveyed area, around 83°N. This maximum corresponds to the start of Floe 3 drift. Overall, we noted that surface seawater contained more N_2O in winter and at the beginning of spring (15.6 nmol L⁻¹ and 92.6% of saturation in average) compared to the end of spring (13.6 nmol L⁻¹ and 82.9% of saturation in average). Towards spring time, the vessel was closer to the open ocean and sea ice started to melt.



Figure V-3: Time series of a) N_2O concentration (nmol L^{-1}) and b) N_2O saturation (%) in the water column (<1000 m depth) all legs includes. Vertical grey bars indicate the different floes sampled during this study, where each flow drifts from North to South.

The N₂O saturation (N_2O_{sat}) in the upper ten meters of the water column ranged from 70 to 101% (Figure V-4a), and showed a southward-decreasing gradient from the northern part of the surveyed area (north of 82°N) that was enriched in N₂O, to the southern part of the surveyed area (south of 82°N), where N_2O_{sat} was lower.

V.4.3. Biological properties of the water column

We compared the biological parameters including AOU and N^* to the N_2O_{sat} for each water mass. There were no clear trends or significant correlations between N_2O_{sat} and either AOU or N^* (see Table V-2) which would otherwise indicate a biological production of N₂O in the water masses studied. A positive relation between N_2O_{sat} and AOU may be a sign of nitrification. A positive or negative relation between N_2O_{sat} and N^* indicates potential N₂ fixation or denitrification respectively. However, the relations may be garbled as the magnitude for oxygen concentrations is 3 to 5 orders higher than the nitrous oxide concentrations.

Table V-2: Mean AOU, *mean* N*, *correlation coefficient*, r, *and p*-value for the relations N₂O_{sat}:AOU and N₂O_{sat}:N* for each water mass.

Water masses	Mean <i>AOU</i> (µmol kg ⁻¹)	Mean <i>N</i> * (µmol kg ^{_1})	r between <i>N2Osat</i> and <i>AOU</i>	p-value	r between N2Osat and N*	p-value
AIW	/	0.4	/		-0.16	0.45
AW/MAW	/	0.4	/		-0.005	0.98
AW	37.5	0.8	-0.029	>0.9999	-0.23	0.18
NDW	/	-0.3	/		-0.11	0.75
MAW	16.0	0.6	0.12	0.59	-0.086	0.46
PSW	3.59	0.1	0.20	0.20	0.003	0.97

V.4.4. Relationships to freshwater fractions, sea ice meltwater fraction and brine rejection

The N₂O concentration in the top 10 meters of the water column was reasonably well and positively correlated to the fraction of meteoric water (Figure V-4b and Figure V-4d, r = 0.62, p-value = 0.0002). On the other hand, the sea ice meltwater fraction in the upper 10 meters of the water column (Figure V-4c) is reasonably well correlated to the N₂O concentration (Figure V-4e). Higher sea ice meltwater fractions were observed south of 82°N. This fraction was lesser north of 82°N, with negative sea ice meltwater fractions north of 82.5°N, actually corresponding to brine rejection from the ice to the seawater.



Figure V-4: a) Spatial distribution of N_2O_{sat} (nmol L^{-1}) in the upper 10 meters of the water column. b) Meteoric Water Fraction (MWF in %) and c) Sea Ice Meltwater Fraction (SIMF in %) in the upper 10 meters of the water column. d) N_2O concentration (in nmol L^{-1}) versus MWF in the surface water (<10 m) and e) N_2O versus SIMF in the surface water (<10 m). Regressions and prediction intervals at 95% are presented in figures d) and e).

The correlation factor between N₂O concentration in the top 10 meters of the water column and the sea ice meltwater fraction was also significant but negative (Figure V-4e, r =-0.66, p-value < 0.0001). Note that N₂O saturation also present a positive correlation with the meteoric water (r = 0.58, p-value = 0.0002) and a negative correlation with the sea ice meltwater fraction (r = -0.57, p-value < 0.0001).

V.4.5. Sea ice biogeochemistry

In the bulk sea ice, N₂O concentrations ranged between 2 nmol L⁻¹ and 16 nmol L⁻¹ with an average of 5.2 nmol L⁻¹. In contrast, N₂O brine concentrations, estimated from bulk ice concentrations corrected for brine volume fraction, ranged between 12 nmol L⁻¹ and 1500 nmol L⁻¹. The N₂O concentration and solubility in the ice cores that had more than 3 discrete vertically distributed measurements are presented in Figure V-5. The distinction between first-year ice (FYI) and second-year ice (SYI) is described in Granskog et al. (2017). The positive deviations of the N₂O concentration to the N₂O solubility are on average higher from January to mid-May, than from mid-May to June, and higher at the top of the ice cores than at the bottom.

However, N_2O concentrations show no clear increase in the upper layers of the sea ice cover, as seen in previous studies for other gases (see overview in Tison et al., 2018), apart from the very first station (22 Jan) and two singular values on the third station (05 Mar). Bulk ice N_2O profiles get closer to the N_2O solubility values in the ice for the stations in the end of spring. Finally, no clear distinction can be made between FYI and SYI profiles.

The relationship between N_2O concentration and salinity in sea ice and snow is shown in Figure V-6a for 5 different types of samples: FYI, SYI, top 15 cm of sea ice, brine skim, and snow. In addition, the brine volume fraction for the same types of samples is shown in Figure V-6b.



Figure V-5: N_2O concentration and solubility in bulk sea ice in ice cores of both first-year ice (FYI) and second-year ice (SYI). The stored samples are noted as "stored", while the in situ samples are free from note.

Figure V-6a represents the conservative behaviour of N₂O against the dilution curve (i.e. the dilution of brines and thus salts and gases like N₂O associated with the melting of ice crystals as temperature increases, Cox and Weeks, 1983). The dilution curve is forced at graph origin and the end-member corresponds to the mean value of N₂O (14.42 ± 1.43 nmol L⁻¹) and salinity (34.09 ± 0.44) in the top 10 meters of the water column.

Takin into account all the samples, both salinity and brine volume fraction decreased from FYI to SYI (Figure V-6a and Figure V-6b respectively) due to the flushing of meltwater (Untersteiner, 1968), but the average N₂O concentration was similarly around 5 nmol L⁻¹ in both FYI and SYI, if considering sea ice samples below 15 cm. In SYI, most of the ice below 15 cm was under the permeability threshold for liquids and gases (dotted line at 5% and solid line at 7% respectively, Zhou et al., 2013, Figure V-6b).



Figure V-6: a) N_2O concentration against salinity for first year ice (FYI), second year ice (SYI), top 15 cm of FYI and SYI, brine skim and snow. The grey solid and dashed lines correspond to the conservative dilution curve and its standard deviation respectively (more details in section 4.5). b) Brine volume with middle depth of the whole ice (FYI, SYI and top 15 cm of ice). The black dotted line and the solid line are permeability threshold for liquids (5%) and bubbles (7%) in sea ice, respectively.

The highest N₂O concentrations were observed at the snow-ice interface during the survey of Floe 2 (February 24th to March 19th 2015, the only floe where snow/slush was sampled for gases). N₂O was measured at concentrations as high as 25.81 nmol L⁻¹ and 24.65 nmol L⁻¹ on sea ice surface (brine skim) of March 5th and 19.09 nmol L⁻¹ and 16.64 nmol L⁻¹ on March 12th. These values correspond to high salinities and are presented under the "brine skim" group in Figure V-6a, as they may correspond to the rejection of brines from the inner ice core to the ice surface (as described in the introduction section). These N₂O concentrations are higher than those found in the underlying seawater at these dates (16 nmol L⁻¹ maximum).

V.5. <u>Discussion</u>

V.5.1. Origin of N₂O undersaturation in surface waters

During N-ICE2015, the surface waters were mainly N₂O undersaturated compared to the atmosphere. This has also been reported in other Artic regions. In summer, the Canada Basin, the Chukchi Sea – away from the Bering Strait –, the Greenland Sea – except in 1991 –, many parts of the Nansen Basin, patches in the Canadian Archipelago and Baffin Bay are undersaturated in N₂O (e.g. Fenwick et al., 2017; Gagné, 2015; Kitidis et al., 2010; Verdugo et al., 2016; Zhan et al., 2016, 2015; Zhang et al., 2015). Thus, summer surface waters N₂O undersaturation is a common feature in the Arctic Ocean. Most of the studies above hypothesized that this undersaturation was due to sea ice meltwater (also observed in Randall et al., 2012). Our data set in Figure V-4e shows a consistent decrease of N_2O concentration with the increase of the sea ice meltwater fraction which might lend support to this assumption. Note also that a local N₂O surface oversaturation in mid-April (Figure V-3b) could also be related to this specific period of the year where permeability is re-established, allowing bursts of gravity drainage, temporarily delivering highly oversaturated N_2O brines to the underlying sea water, before dilution through sea ice melt takes over later in the season.

We estimated the significance of the sea ice melt using a simple box model (Table V-3). We considered the average value of salinity and N₂O concentration in the ice

and in the underlying mixed layer at the maximum of sea ice growth (i.e. Floe 3). We also used the average ice thicknesses and the mixed layer depths provided by Meyer et al. (2017). Three scenarios (1, 2 and 3, see Table V-3) were considered and the results compared with the observations at the end of spring when the ice started to melt (Floe 3 and Floe 4): 1) the sea ice cover is completely melted within the mixed layer with the properties (i.e. salinity, N_2O concentration) and depth of the water column underneath Floe 3; 2) the sea ice cover is completely melted within a mixed layer with the properties (salinity, N₂O concentration) of the water column underneath Floe 3 but with a shallower depth equal to the mixed layer depth underneath Floe 4, more representative of end of spring conditions; 3) the sea ice cover is partially melted within a mixed layer with the properties (i.e. salinity, N₂O concentration, salinity) of the water column underneath Floe 3 with a depth equal to the mixed layer depth underneath Floe 4. In the latter scenario, we considered a melting sea ice of 9.4% in order to mimic the salinity observed underneath Floe 4. This scenario appears to be more realistic than scenario 2 where the salinity drops down to 28.63, which is unrealistic compared to the salinity of 33.54 observed underneath Floe 4.

Scenarios 1 and 3 exhibit similar realistic salinity and consistent N_2O concentration of 14.20 nmol L⁻¹ on average. This corresponds to a decrease of 2.1% compared to the concentration observed underneath Floe 3. The N₂O concentration in the surface waters derived from scenarios 1 and 3 is significantly higher than the value observed underneath Floe 4 (13.3 nmol L⁻¹ on average), hence sea ice melting explains only a small part (around 20%) of the observed undersaturation. This simple box model is prone to several biases, in particular to spatial variability and gradual change in mixed layer depth that are neglected. However, if the sea ice melting appears to decrease the N₂O concentration of the surface water, this effect is relatively limited, so that other processes must be involved in the observed N₂O undersaturation of the surface water.

Date (Floe)	Mixed layer salinity	Mixed layer N ₂ O concentration (nmol L ⁻¹)	Mixed layer depth (m) (Meyer et al. 2017)	Ice thick- ness (m)	Sea ice salinity	Sea ice N2O concentration (nmol L ⁻¹)	Melting fraction (%)
22/04 to 14/05/2015 (Floe 3)	34.22	14.52	47.8	1.44	4.2	4.03	
07/06 to 22/06/2015 (Floe 4)	33.54	13.3	4.2	0.97	5	4.8	
Scenario 1: ice of Floe 3 totally melted in the 47.8 m mixed layer of Floe 3	33.58	14.21	47.8				100
Scenario 2: ice of Floe 3 totally melted in the 4.2 m mixed layer of Floe 4	28.63	11.85	4.2				100
Scenario 3: ice of Floe 3 partially melted in the 4.2 m mixed layer of Floe 4	33.54	14.19	4.2				9.4

Table V-3: Box model simulations to explain N_2O undersaturation observed at the seawater surface during N-ICE2015.

An alternate process has been proposed to explain surface water undersaturation in N₂O in eastern south Pacific (Cornejo et al., 2015; Farías et al., 2013), and the Arctic Ocean (Verdugo et al., 2016). ¹⁵N-N₂O tracer experiments reported high N₂O consumption rates in both surface waters and sea ice brines in Amundsen and Nansen basin in summer (Verdugo et al., 2016). Verdugo et al. (2016) suggested that this consumption was related to N₂ fixation by autotrophic and heterotrophic bacteria. Since, gene analysis and microscopic observation of cyanobacteria suggested that the Arctic Ocean has a potential for N₂ fixation (Díez et al., 2012), the related N_2O consumption may contribute to the observed decrease of N_2O saturation. Recent studies reveal the presence of diazotrophs gene in the Arctic Ocean that may contribute to nitrogen fixation (Blais et al., 2012; de Sousa et al., 2019; Díez et al., 2012; Fernández-Méndez et al., 2016). However, the low temperature and high dissolved oxygen in Arctic waters should limit oceanic N_2 fixation (Brauer et al., 2013). Our experimental setup does not allow to assess the significance of this process. This assessment requires further studies (Fernández-Méndez et al., 2016).
However, undersaturation of N_2O in the Arctic Ocean should also be discussed in the light of the saturation level of the AW that is the main water mass entering in the ocean basin and imprint some of the chemical characteristics to the Arctic Ocean waters. Warm AW enters through the Norwegian Sea (Figure V-1a), and moves northwards along the coast of Norway. It divides into two main branches and continues north on either side of Svalbard. In the Arctic Ocean, the AW is either cooled – becoming heavier and sinking – or forms polar surface water (PSW) after mixing with riverine input and Pacific water inflow, and interaction with sea ice. After circulating in the North Polar Basin, the PSW leaves the Arctic Ocean, mainly through Fram Strait between Svalbard and Greenland. AW inflow has therefore a significant imprint on the PSW chemical properties.



Figure V-7: N_2O sat and $N_2O_{sat@-1.7}$ for N-ICE2015. Each colour corresponds to a specific water mass (see legend).

The baseline level of N₂O of the Nansen Basin, if not of the entire Arctic Ocean, should therefore be set by the inflow of Atlantic water. We computed N₂O_{sat @ -1.7} corresponding to the hypothetical N₂O saturation of deep waters if they would reach the surface and loose heat without other processes involved. The mean N₂O_{sat} @ -1.7</sub> calculated for AW is 75%, so that AW appears to be strongly undersaturated in N₂O, as has been documented before (Zhan et al., 2016). Strong undersaturation

of the AW is likely to be the main driver of the overall undersaturation in N₂O observed off the shelves. As a result, N₂O_{sat@-1.7} for all water masses between 5000 m and 50 m has a mean of 81.2%, only slightly higher than the mean N₂O_{sat@-1.7} of the AW. PSW, however, exhibits a mean N₂O_{sat@-1.7} of 87% (red dots in Figure V-7) suggesting an enrichment in N₂O during the circulation and transformation of AW within the Arctic Basin, as discussed in the next section.

V.5.2. Origin of the N₂O enrichment in PSW

 N_2O enrichment of the PSW is the most obvious north of 82°N (Figure V-2 and Figure V-4a) where surface water exhibits N_2O saturation close to 100% or slightly above. Below, we describe three processes that may explain such N_2O concentration gradient between north and south of 82°N.

The first physical process is linked to the effect of sea ice formation on the underlying seawater. Sea ice formation leads to brine rejection (including salts and gases) to the seawater or the ice surface (e.g. Anderson et al., 2004; Fransson et al., 2013; Rysgaard et al., 2007) and has the potential to increase N_2O concentration during sea ice formation, as shown by the correlation in Figure V-4e. The increase of N₂O concentration due to brine rejection in the water column has been estimated using a simple box model. We considered the average value of salinity and N₂O concentration in the brine and in the underlying mixed layer at the beginning of the survey (i.e. Floe 1). One scenario (see Table V-4) was considered and the results compared with the observations underneath Floe 2, when the maximum of N₂O concentration were observed in the underlying water and ice was growing (i.e. rejecting brine in the underlying water). According to Figure V-4c, 1% of the underlying water corresponds to a sea ice brine input. In this scenario, the estimated salinity increase ($\Delta S = 0.15$) is consistent with the observations. The estimated increase in N₂O concentration due to brine rejection is 0.27 nmol L⁻¹, corresponding to 16% of the observed increase in N_2O concentration. Sea ice formation therefore, explains only a moderate part of the observed N₂O enrichment.

Date (Floe)	Mixed layer salinity	Mixed layer N ₂ O concentration (nmol L ⁻¹)	Sea ice brine salinity	Sea ice brine N ₂ O concentration (nmol L ⁻¹)	Brine fraction in water column (%)
15/01 to 21/02/2015					
(Floe 1)	34.25	15.30	49	42.47	
24/02 to 19/03/2015 (Floe 2)	34.40	17.05			
Scenario : 1% brine					
fraction of Floe 1 in the					
mixed layer of Floe 2	34.40	15.57			1%

Table V-4: Box model simulations to explain N_2O enrichment observed at the seawater surface during N-ICE2015.

A second process is biological activity. However, no significant relationship was found between the biological parameters and the N₂O concentration (see Table V-2). Neither nitrification seemed to have taken place offshore as we observed no correlation between N_2O_{sat} and AOU. Potential offshore denitrification appears to be limited based on the lack of consistency in N^* data set, that should be mostly negative if significant denitrification had taken place.

A third process that may explain the N₂O enrichment of the PSW is the active nitrogen cycling taking place on eastern Siberian shelves. We observed a positive correlation between the N₂O saturation and the meteoric water fraction (Figure V-4d). The Arctic Ocean is surrounded by shelves with various sources of N₂O such as riverine inputs or benthic denitrification (Fripiat et al., 2018). We expect East Siberian Arctic shelf waters to contain a relatively high meteoric water fraction due to the large inflow of riverine waters (Semiletov et al., 2016). The N₂O maximum we observed in PSW was previously attributed to microbial activity under low sedimentary oxygen conditions in the Bering and Chukchi Seas by Fenwick et al. (2017). We hypothesise that a similar phenomenon occurred on the eastern Siberian shelves and produced the higher N₂O concentration we observed under sea ice in the Nansen Basin. In addition, benthic denitrification in the East Siberian Arctic shelf has been reported (Chang and Devol, 2009; Devol et al., 1997; Fripiat et al., 2018; Mctigue et al., 2016) as well as an enhanced gas transfer if polynyas developed (Preußer et al., 2016).

We estimated the N_2O concentration that should characterize the meteoric water end-term from the mixing line (best fit line) between observed N_2O concentration and the percent of meteoric water fraction in the upper 10 meters along the drift tracks (Figure V-4d). The best fit equation is $[N_2O]$ in nmol $L^{-1} = 1.02 \text{ x}$ (% of meteoric water) + 13.12 nmol L^{-1} . Taking the % meteoric water line as 100% gives an end-term concentration ranging between 65 nmol L^{-1} and 162 nmol L^{-1} . Such a high concentration and related large oversaturation cannot be confirmed due to a lack of *in situ* observation close to the Siberian shelves. Also, this estimation should be considered carefully as the ocean-atmosphere exchanges are omitted and as the correlation factor between the two parameters considered is only equal to 0.62. Nevertheless, other studies using the water oxygen isotopes composition, $\delta^{18}O$, have similarly shown that the eastern Siberian shelves are a source of gases and/or nutrients to the rest of the Arctic Ocean (Damm et al., 2018; Fripiat et al., 2018).

Although the main cause of the N_2O enrichment in PSW north of 82°N cannot be established with certainty and the impact of pelagic nitrification cannot be discarded, we therefore attribute the sources of N_2O in our study area to both sea ice formation and the active nitrogen cycling taking place on eastern Siberian shelves.

V.5.3. N_2O concentration in first and second-year sea ice

Like other dissolved compounds, gas distribution in sea ice is initially controlled by brine dynamics. Gases in newly formed sea ice are initially conservative against bulk salinity and overall increase with increasing bulk ice salinity and vice-versa for gas dilution, following a dilution curve (Delille et al., 2014). Deviations from the N₂O solubility curve (Figure V-5) and from the dilution curve (Figure V-6a) are however frequent, and can be attributed to other specific processes such as bubble nucleation and transport in the gaseous phase, exchanges with the atmosphere and underlying sea water (diffusive and/or convective) or biotic processes within the ice (Tison et al., 2018). Low salinities in the SYI are due to brine flushing processes, while the low salinities observed in some ice samples in the top 15 cm have been related to the presence of snow (Granskog et al., 2017).

Typical abiotic gas profiles observed until now show the following common main characteristics (Tison et al., 2018): a) bottom gas concentrations are at ice solubility, unless the water column itself shows oversaturation (e.g. for CH_4 in the Arctic, Zhou et al., 2014b); b) gas concentrations increase in the top half of the sea

ice cover during the growth phase, a process ascribed to bubbles nucleation and upward gas migration in the permeable ice (Zhou et al., 2013); c) observed profiles level-off at the ice solubility during the warm decaying phase, due to bubble escape to the atmosphere and d) temporary accumulation of gases can occur near the surface, in the case of superimposed ice growth (Nomura et al., 2018).

In that context, our N-ICE2015 sea ice profiles show several peculiar characteristics: a) and c) bottom ice concentration are much higher than sea ice solubility, while there is a generalized surface water undersaturation, as discussed above. Only at the very last stations (June) is the observed profile hovering around ice solubility. This is, however, due to the fact that the ice solubility curves shift towards higher values, due to decreasing salinity within the brine system of decaying sea ice, rather than to significant loss of gas from the ice (as is usually observed for other gases). Note that flushing and replacement with (fresher) snow melt waters would have enhanced this increase in ice solubility; b) and d) even if superimposed ice was observed during the survey (see in Nomura et al., 2018), enrichment of gases in the upper half of the sea ice cover is not clearly observed during the growth period, apart maybe from the very first station (22 Jan) and two singular values in early March (05 Mar). This could be the result from a much higher solubility for N_2O (one order of magnitude) than for other gases (e.g. Ar, O_2 , CH₄), maybe requiring higher oversaturations for degassing. Although not demonstrated in this study, this property might explain why N₂O did not contribute to the gas phase in the nucleating bubbles, therefore with no significant enrichment of the upper layers through bubbles buoyancy.

To explain that SYI profiles are very similar to those of FYI, with equivalent N_2O concentration values in the 3–5 nmol L⁻¹ range, which is well above ice solubility – notwithstanding their divergent salinity (Figure V-6a) – we hypothesise four processes. (i) The oldest ice in the study area was likely originating from the Laptev Sea (Itkin et al., 2017), which means further east than FYI, from a possibly more saturated seawater than that of the study. (ii) Heterotrophic N₂O production within the brine as suggested by Kaartokallio (2001) and Priscu et al. (1990) may have been offset by either sea ice–atmosphere gas exchanges, or with sea ice–surface water gas exchange. Bacterial activity and diversity has not been

measured within the ice, but the bacterial communities in the underlying water surface show a potential for nitrifying activity (de Sousa et al., 2019). (iii) SYI concentration in N₂O have been inherited from brine skim (Figure 6a, yellow dots) flushed in late-summer (as shown by the June profiles of FYI, Figure V-5). Indeed, the flushing of rich-N₂O brine skims (20 to 25 nmol L⁻¹ N₂O, Figure V-6a) through FYI with 20% brine volume, leads to a N₂O bulk ice concentration of 5 nmol L^{-1} , as state the mean N₂O concentration in SYI. These concentrations could have persisted due to the very low porosity observed in the upper layer of the SYI (Figure V-6b). (iv) N₂O accumulated during sea ice growth may be stored in bubbles in a gaseous phase considering that SYI is less permeable to air-ice N₂O exchanges due to brine (Tison et al., 2008). The lower permeability for gas is supported by SYI brine volumes values mainly under the permeability threshold for gas transport (Figure V-6b). Nomura et al. (2018) established the same conclusion on the basis of CO₂ fluxes, showing that snow covered multi-year ice found during the same survey was acting as a barrier for gas exchange. The formation of bubbles has already been observed when temperature decreases and each brine inclusions shrinks in size, the concentration of gases can increase to a point where oversaturation results in the nucleation of bubbles (Crabeck et al., 2014b; Killawee et al., 1998; Light et al., 2003; Tison et al., 2002; Tsurikov, 1979; Zhou et al., 2014a). The third and four hypothesis together may explain the high deviation observed between the N_2O concentration and solubility (Figure V-5), as bacterial activity was not measured within the ice.

V.5.4. N_2O exchanges at the air-ice interfaces

As it is assumed that impurities, like salts and gases, are concentrated in the brine during sea ice formation, we were thus more inclined to look at the partial pressure of N₂O in the brine (pN_2O_{br} as calculated with equation (3) and (4)) to look at the air-ice pN_2O difference that can potentially lead to gas exchange at the air-ice interface. In fact, the partial pressure gradient is the main driver of gas exchanges alongside bubbles buoyancy. When pN_2O_{br} is higher than in the air (328.65 atm as described in section 3.6, and assuming ideal gas equation), ice is a potential source to the atmosphere, while in the opposite situation ice is a potential sink. Figure V-8 shows that sea ice was a potential source for the atmosphere, except the 15^{th} and the 17^{th} of June.



Figure V-8: The partial pressure of N_2O (pN₂O, in atm) in the brine in the upper 10 cm of the ice (blue diamonds) and in the air above the ice (green dotted line).

V.5.5. Biological and chemical production of N_2O taking place at the snow-ice interface

A specific highlight of our dataset (Figure V-6a) is the high N_2O concentration in the brine skim, at the snow-ice interface that was found over FYI and under a thick snow cover during the sampling of Floe 2. Below we review the processes leading to N_2O production in these conditions to seek for a potential source of this interesting feature.

Snow-ice interface properties

The high concentration in N₂O observed at the snow-ice interface in March could be associated to three processes that may take place on the top of the sea ice: (i) the wicking of brine by capillarity into surface snow layers, actually not observed during our sampling period, but likely to occur, (ii) high concentration brine skim observed on 5th of March as it is associated to low salinity (< 1.2), low brine volume (< 2%) and high N₂O concentration observed in the middle of the ice core compared to the top, the same day, and (iii) flooding (salty slush sampled on the 12th of March). However, flooding has to be followed with an evaporation event since N₂O concentrations were higher at the snow-ice interface than in the under-ice water.

■ Biological production of N₂O

Bacterial activity was not measured during N-ICE2015, however, nitrate and phosphate concentrations can be used as a guide. Ammonium was not measured in these samples. In the snow/slush, nutrients were measured on 5th and 12th March and reached concentrations up to 17 μ M nitrate and 1 μ M phosphate (Assmy et al., 2017a; Fernández-Méndez et al., 2018). The snow/slush N* calculated from these values are high and positive (a mean of 6 μ mol L⁻¹ on 8 samples), that can provide an indication of N₂O net production from denitrification.

Chemodenitrification

As microbial activity was no measured and cannot certainly be associated with the high concentrations in N₂O observed at the ice surface, we suggest a contribution of the chemical process of chemodenitrification, i.e. an abiotic reduction of NO_x^- by positively charged metal (valence II) as a potential source. This is known to occur in soils at pH < 5.47 or in the presence of Fe²⁺ or Cu²⁺ or Mn²⁺ (Zhu et al., 2013). This abiotic reaction has already been shown to produce NO and N₂O gases as byproducts, and is well documented (Buchwald et al., 2016; Buresh and Moraghan, 1976; Cleemput, 1998; Grabb et al., 2017; Kampschreur et al., 2011), even at high salinities (e.g. Samarkin et al., 2010).

In the presence of microbial activity, N_2O produced by chemodenitrification is assumed to be a marginal process (0.1 to 1.3% in Zhu et al., 2013), but in contrast, other studies (Cleemput, 1998; Grabb et al., 2017; Kampschreur et al., 2011) suggest that conditions whereby the denitrification process becomes marginal, or in the presence of high concentrations of Fe (II) and oxidized forms of nitrogen, chemodenitrification could be a non-negligible cause of N_2O production. Such chemodenitrification would act as a source of N_2O for the atmosphere.

Overall, sea ice during the N-ICE2015 expedition appears to act as a source of N_2O to the atmosphere. However, the assessment of the magnitude of ice-air N_2O flux requires further investigations, with either direct air-ice N_2O fluxes measurements or modelling in sea ice covered areas.

V.6. <u>Conclusion</u>

This study is, to our best knowledge, the first original data set of N_2O distribution in the Arctic winter and spring. It examines a data set of N_2O distribution in snow, sea ice and water column in winter and spring from the western Nansen Basin (Arctic Ocean). We observed that the water column in winter and spring was globally undersaturated in N_2O , highlighting the north of Svalbard as a permanent sink for N_2O as it has already been shown in other studies for the summer period (Fenwick et al., 2017; Zhan et al., 2016). We assign that this undersaturation is mainly due to the inflow of undersaturated AW in the region that set the baseline level of N_2O concentration in the surface waters of the Nansen Basin, while sea ice melting contribute for about 20% to this undersaturation.

Nevertheless, comparing water mass properties, we observed an enrichment in PSW and in the surface waters north of 82°N. While the impact of pelagic nitrification cannot be discarded to explain off shelves enrichment in N_2O , we suggest that one of the major contributors was the spreading of shelf water from the eastern Siberian shelves.

In opposite to the water column, the sea ice cover is a potential source of N_2O for the atmosphere. Vertical profiles of N_2O concentration in the ice differ from profiles observed for other gases. We ascribed these differences to the higher solubility of N_2O and related differences in the partitioning of gas and liquid phase. Non conservative N_2O content of SYI with salinity is likely due to: (i) SYI formation further east than FYI, (ii) *in situ* biological activity, (iii) flushing of N_2O -rich ice surface meltwater (i.e. brine skim) through decaying FYI and (iv) strongly reduced permeability in SYI.

High concentrations of N₂O found in few FYI brine skim samples taken during Floe 2 drift may actually take place all along the ice growth period. In the plausible scenario where FYI will tend to replace multiyear ice in the Arctic Ocean (Maslanik et al., 2011), sea ice will be more subject to brine skim and frost flower formation at its surface. These processes are more favourable to the transport of gases like N₂O to the ice surface and therefore to increase the potent of the ice to be a source of N₂O for the atmosphere.

Overall, assessing the role of our study area as a source or sink of N_2O for the atmosphere requires to budget both the air-sea exchanges and the air-ice exchanges, while for the time being, robust parametrisation of air-sea exchanges in ice-covered area and air-ice exchanges is still in its early days. This also calls for a better documentation of the impact of east Siberian shelves on N_2O saturation in the water column of the central Arctic, to the direct measurements of air-ice N_2O exchanges, and future emphasis in studies on air-sea gas exchanges parametrisation in ice-covered surface waters.

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CHAPTER VI: Conclusions

The objectives of this work were to better constrain the role of sea ice in the CO_2 and N_2O cycling within the ocean-sea ice-atmosphere system. We provided two main data set related to either CO_2 (Chapters III and IV) or N_2O (Chapters V).

VI.1. Synthesis of the INTERICE V findings on the CO₂ dynamics

The 19-day tank experiment on artificial ice carried out at the Hamburg Ship Model Basin – INTERICE V – resulted in several observations and conclusions related to the regulation of dissolved components (DOC, DIC and nutrients) in the air-sea ice-seawater system. We performed this indoor experiment using two series of mesocosms: ten were filled with filtered seawater (SW) and ten with a mixture of filtered seawater and filtered river water (SWR) to simulate riverine DOC input. pCO_2 in the ice and air-ice CO_2 fluxes were also measured continuously in both mesocosms. In this section, the main conclusions that have emerged from the three INTERICE V manuscripts on which I contributed (i.e. Kotovitch et al., 2016; Zhou et al., 2015, 2014b) are presented.

First of all, physical parameters indicate that there were two main stages in the brine dynamics: bottom convection during ice growth and brine stratification during ice decay. In addition, observation of vertical CO_2 profiles led us to distinguish three layers that presented specific temporal patterns: the top, the interior and the bottom.

During the ice growth, the incorporation of dissolved compounds (including nutrients, DIC, DOC and DOM²) into the sea ice was not conservative and was affected by bacterial activity (i.e. remineralization) and brine convection that themselves depend on the length of the freeze-melt cycle. The differences between the two mesocosms (SWR–SW) in observations and model simulations support the hypothesis that higher DOC content enhances bacterial respiration and pCO_2 in the ice. Different forms of DOC have different properties and hence incorporation

 $^{^2}$ Note that the initial addition of DOM, containing humic acids, increased the total alkalinity in the initial setting of SWR treatments.

efficiencies; terrestrial DOC (i.e. from the river water) was less efficiently incorporated into sea ice than marine DOC. However, in natural systems, algal growth would produce more labile DOC that promotes higher bacterial respiration. The presence of algae then contributes both to direct CO_2 consumption through photosynthesis and indirect CO_2 production through labile DOC production that enhances bacterial respiration. Further experiments are therefore needed to define the net balance of algal and bacterial growth on pCO_2 in sea ice on both poles.

The artificial sea ice was likely permeable to gas exchange during the whole experiment. The impact of bacterial respiration on pCO_2 was most obvious in the ice interior because air-ice gas exchange in the top section and brine convection in the bottom section have offset the increase of pCO_2 related to bacterial respiration.

In terms of air-ice CO_2 exchanges, while cooling of seawater acts as a sink for atmospheric CO_2 as repeatedly observed, the seawater surface shifted to a source as soon as the first ice crystals are forming. Then sea ice is a net CO_2 source during ice consolidation and subsequent thickening, and shifts to a net CO_2 sink during the melt (Figure VI-1).



Figure VI-1: Temperature and air-ice CO_2 flux measured in continuous with a chamber over the ice. Sea ice shifts from (i) a sink during the first crystals formation, (ii) to a source during ice growth and, finally (iii) return to a sink during ice melt.

Gas diffusion and/or buoyancy-driven upwards transport of bubbles developed in the upper parts of the ice. Both the computation of the gas transfer coefficient and the model sensitivity analysis support this assumption. Gas bubbles in the liquid brine rise upward if the connectivity of the brine network is sufficient. As described in Kotovitch et al. (2016), bubbles were observed during the growth phase, particularly near the ice surface (see Figure 4 of the latest mentioned paper). Buoyancy-driven upwards transport of bubbles enhances significantly air-ice gas exchanges.

Finally, the Arctic Ocean, especially coastal waters, might induce more positive air-ice CO_2 fluxes than the Southern Ocean, for the same biogeochemical conditions.

VI.2. <u>Determination of an air-ice gas transfer coefficient for CO₂</u>

Combining measured air-ice CO₂ fluxes with the partial pressure of CO₂ in sea ice, we determined significantly different gas transfer coefficients of CO₂ at the air-ice interface between the growth $(2.5 \pm 0.9 \text{ mol m}^{-2} \text{ d}^{-1} \text{ atm}^{-1})$ and the decay phases $(0.4 \pm 0.08 \text{ mol m}^{-2} \text{ d}^{-1} \text{ atm}^{-1})$. We suggested that the difference in gas transfer coefficients are due to bubbles upwards transport – observed in thin sections – that occurs mainly during ice growth, while only molecular diffusion occurs during ice melt. In fact, gas bubbles are forming in growing sea ice since brine shrinking with temperature induces drastic increases in gas concentrations. If the connectivity of the brine network is sufficient, gas bubbles then rise upward. The dilution of brines during warming decreases CO₂ concentration in brine below saturation with respect to the atmosphere. This drives the dissolution of bubbles.

The computation of a gas transfer coefficient was chosen instead of a diffusion coefficient since the measured air-ice CO_2 fluxes and pCO_2 ice integrate both the molecular diffusion and the buoyancy of the bubbles containing CO_2 .

Wanninkhof (1992) suggests to compute k, the gas transfer velocity coefficient according to the equation II-17 given in section II.6.4. The resulting k_{ice} for the growing ice is equal to 0.04 (± 10%) m d⁻¹ as a mean of the coefficient computed for each mesocosm during the growth. However, Zhou et al. (2014a) question the reliability of the equation for solubility in the range of temperature and salinity encountered within sea ice. It seems then more accurate to use K, derived from direct measurements.

The k_{ice} computed during INTERICE V is not comparable with other studies estimating a k_{ice} of 10^{-5} m d⁻¹ (Loose et al., 2014) or 5×10^{-4} m d⁻¹ (Lovely et al., 2015), because (i) the methods of these studies include the whole sea ice section, while our method only accounted for the upper layer, and (ii) bubble buoyancy does not appear in both studies cited above, while our study include this component.

VI.3. N₂O distribution in the Arctic Ocean

The status of the Arctic Ocean as a source or sink of N₂O for the atmosphere is unclear due to the paucity of data and the coexistence of both N₂O undersaturation and oversaturation in its surface waters with respect to the atmospheric N₂O. Figure VI-2 reports surface waters saturation in N₂O with respect to the atmosphere found in the current literature from 1981 to 2015, including the N-ICE2015 data set (see Table VI-1 for the references and cruises, and Annexe B for the complete data sets). Figure VI-2a refers to spring and summer, while Figure VI-2b refers to the winter. This distinction has been made to highlight the lack of data in the winter time. In addition, and to our best knowledge, no robust budget of air-sea N₂O has been established for the Arctic Ocean.

During N-ICE2015, we observed that the water column in winter and spring was globally undersaturated in N₂O, highlighting the north of Svalbard as a permanent sink for N₂O as it has already been shown in other studies for the summer period (Fenwick et al., 2017; Zhan et al., 2016). We suggest that this undersaturation is mainly due to the inflow of undersaturated AW in the region that set the baseline level of N₂O concentration in the surface waters of the Nansen Basin, while sea ice melting contributes for about 20% to this undersaturation. Comparing water mass properties, we observed an enrichment in PSW and the surface waters north of 82°N. While the impact of pelagic nitrification cannot be discarded to explain off shelves enrichment in N₂O, we suggest that one of the major contributors was the spreading of shelf water from the eastern Siberian shelves.

In opposite to the water column, the sea ice cover is a potential source of N_2O for the atmosphere. Vertical profiles of N_2O concentration in the ice differ from profiles observed for other gases. We ascribed these differences to the higher solubility of N_2O and related differences in the partitioning of gas and liquid phase. The nonconservative N_2O content of SYI with salinity is likely due to (i) SYI formation further east than FYI, (ii) *in situ* biological activity, (iii) flushing of N_2O -rich ice surface meltwater (i.e. brine skim) through decaying FYI and (iv) strongly reduced permeability in SYI.



Figure VI-2: Schematic view of Arctic Ocean saturation in N_2O with respect to the atmosphere in a) in spring and summer ,and b) winter, from available studies referenced as numbers 1 to 10 (see Table VI-1 for the correspondence of each number).

Number	Reference	Cruise		
1	Kotovitch et al., in progress	N-ICE2015		
2	Fenwick et al., 2017	SWL 2015-07/ 1502/ LSSL 2015-06		
3	Verdugo et al., 2016	LOMROG III		
4	Zhan et al., 2015 & 2016	5th CHINARE		
5	Zhang et al., 2015	4th CHINARE		
6	Randall et al., 2012	IPY-CFL 2008		
7	Gagné 2015	CCGS Amundsen 2007-08 Leg 11a		
8	Hirota et al., 2009	R/V Mirai MR06-04		
9	Kitidis et al., 2010	Beringia 2005		
10	Weiss et al., 1992	TTO/NAS		

Table VI-1: References and cruises related to the numbers on Figure VI-2.

Documentation of N₂O isotopes in aquatic systems with potent new sensitive laboratory measurement needs to be done. The stable isotope analysis can be achieved by the examination of the natural isotopic abundances of N_2O (Naqvi et al., 1998) or of N₂O produced in incubations with addition of labelled ¹⁵N-NH⁴⁺ and/or ¹⁵N-NO³⁻ (Punshon and Moore, 2004). Generally speaking, for enzymatic reactions, compounds containing the lighter isotope react faster, and therefore the products of the reaction tend to have less of the heavy isotopes compared to the reactants. For example, during denitrification, the $\delta^{15}N$ value of the N₂O that is formed is more negative than the original NO³⁻. Also, N₂O produced through nitrification tends to be very depleted in δ^{15} N. However, the N₂O SP is determined mainly by the enzymatic mechanism, rather than by the substrate $\delta^{15}N$ value (Wuchter et al., 2007). The SP of N_2O produced during nitrification is +30% to +38%, while N₂O produced from denitrification presents SP values of -10% to +5%(Sutka et al., 2006). Use of SP rather than $\delta^{15}N^{\text{bulk}}$ of N₂O allows then to discriminate the underlying processes without prior knowledge of $\delta^{15}N$ of substrates.

VI.4. <u>Perspectives: Arctic sea ice CO₂ and N₂O dynamics in a changing environment</u>

Assessing the role of the Arctic Ocean as a source or sink of CO_2 and N_2O for the atmosphere requires to budget both the air-sea exchanges and the air-ice exchanges, while for the time being, robust parametrisations of air-sea exchanges in ice-covered area and air-ice exchanges are still in their early days. This also calls for more direct measurements of air-ice CO_2 and N_2O exchanges, and future emphasis in studies on air-sea gas exchanges parametrisation in ice-covered surface waters. Despite the uncertainty in current budget of air-sea ice and air-sea fluxes of CO_2 and N_2O , nonetheless, we could provide some insights about the potential impacts of Arctic sea ice changes on these budgets.

As detailed in the motivation section (I-1), Arctic sea ice is currently subject to drastic changes in its structure and extent. These changes will impact both the amplitude and the direction of air-sea and air-ice CO_2 and N_2O fluxes in the future. We propose two scenarios that are used by the Biogeochemical Exchange Processes at Sea Ice Interfaces (BEPSII) to envisage future changes in Arctic sea ice biogeochemistry. First scenario gathers predicted changes in ice structure and relates to thinner, warmer, younger, more permeable, more mobile and more deformed sea ice in association with increasing rain and less snow accumulation. The second scenario relates to changes in ice coverage. This includes the decrease of sea ice volume and area, and changes in sea ice seasonality.

• Changes in sea ice structure

Sea ice structure changes will lead to new dynamics in the CO_2 and N_2O content within the ice, and thus impact the air-ice pCO_2 and pN_2O gradient. There are only a few processes able to sustain enhanced air-ice gas fluxes during an extended period. For example, the transient presence of frost flowers has only short-term effects on CO_2 fluxes. Other processes (e.g. melting/freezing cycle of the ice surface) modulate air-ice CO_2 fluxes, but few of them can actually sustain CO_2 fluxes for extended periods of time as we observed during the INTERICE V experiment. Processes that sustain CO_2 for extended periods of time must involve either the production of CO_2 , like bacterial respiration or the transfer of CO_2 from a large reservoir (like the ice interior or the ocean) to the surface.

Brine concentration makes the pCO_2 more sensitive to DIC increase in ice than in seawater due to the lower buffering capacity of brines at the high pCO_2 encountered in Arctic sea ice in winter. Higher DIC production, due to enhanced bacterial respiration would, therefore, result in a larger increase of pCO_2 in the ice compared to underlying seawater. At some specific locations, where the bacterial activity is more intense in the ice than in the underlying water, the consequence of higher bacterial respiration on pCO_2 in warmer ice can be even more significant, especially when algal activity is limited. The interplay between gas transfer velocity and the pCO_2 gradient needs to be taken into consideration while assessing the future evolution of the air–sea and air–ice CO_2 fluxes in the polar regions.

Regarding N₂O, more deformed ice can potentially increase the occurrence of anaerobic environment. In fact, as light is more available in deformed ice, algal blooms can take place earlier and stimulate heterotrophic bacteria activity such as oxygen is fully consumed, leaving anoxic inclusions in sea ice (Rysgaard et al., 2008; Rysgaard and Glud, 2004; Thomas, 2017). This might promote denitrification and then N₂O production in sea ice. Alternatively, nitrification has been reported in sea ice (Fripiat et al. 2018), a process coupled to primary production, that produces N₂O. In addition, higher permeability of saltier and warmer sea ice can potentially increase production of N₂O in Arctic sea ice and thereafter release N₂O to the atmosphere.

In the additional scenario where FYI will tend to replace multiyear ice in the Arctic Ocean (Maslanik et al., 2011), sea ice will be more subject to brine skim and frost flower formation at its surface. These processes are more favourable to the transport of gases like CO_2 and N_2O to the ice surface and therefore to increase the potential of the ice to be a source of CO_2 and N_2O for the atmosphere.

• Changes in sea ice coverage

As gas exchanges are more efficient in the open water than through a semipermeable sea ice cover, a commonly proposed scenario suggests that air-sea CO_2 and N_2O fluxes will increase in magnitude with the reduction of the Arctic sea ice extent. Taking into account that sea ice appears to release CO_2 and N_2O to the atmosphere, sea ice loss is likely to reduce the release of both gases by sea ice, and then promote CO_2 and N_2O uptake by the Arctic Ocean.

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APPENDIX A: List of publications

In addition to the three manuscripts presented in this thesis, I have also participated to the writing of three peer reviewed publications listed below.

• Publications as a first or second author, presented in this thesis :

Zhou J., Kotovitch M., Kaartokallio H., Moreau S., Tison J.-L., Kattner G., Dieckmann G., Thomas D. & Delille B. (2016) The impact of dissolved organic carbon and bacterial respiration on pCO_2 in experimental sea ice. *Progress in Oceanography*, 141, 153-167.

Kotovitch M., Moreau S., Zhou J., Vancoppenolle M., Dieckmann G. S., Evers K.-U., Van der Linden F., Thomas D. N., Tison J.-L. & Delille B. (2016). Air-ice carbon pathways inferred from a sea ice tank experiment. *Elementa: Science of the Anthropocene*, 4, 000112. https://doi.org/10.12952/journal.elementa.000112

Kotovitch M., Silyakova A., Nomura D., Fransson A., Chierici M., Granskog M., Dodd P., Duarte P., Van der Linden F., Moreau S., Deman F., Tison J.-L. & Delille B. (in progress). Winter to spring ocean-sea ice-atmosphere N₂O partitioning in the Arctic Ocean (north of Svalbard). *Progress in Oceanography*.

• Publications from my co-authorship :

Zhou J., Delille B., Kaartokallio H., Kattner G., Kuosa H., Tison J.-L., Autio R., Dieckmann G., Evers K., Jørgenesen L., Kenenedy H., **Kotovitch M.**, Luhtanen A.-M., Stedmon C.A. & Thomas D. (2014). Physical and bacterial controls on the distribution of inorganic nutrients and DOC in sea ice during an experimental ice growth and decay cycle. *Marine chemistry*, *166*, 59-69.

Moreau S., Vancoppenolle M., Delille B., Tison J. L., Zhou J., **Kotovitch M.**, ... & Goosse H. (2015). Drivers of inorganic carbon dynamics in first-year sea ice: A model study. *Journal of Geophysical Research: Oceans*, *120*(1), 471-495.

Moreau S., Kaartokallio H., Vancoppenolle M., Zhou J., **Kotovitch M.**, Dieckmann G., Thomas D. N., Tison J.-L. & Delille B. (2015). Assessing the O₂ budget under sea ice: An experimental and modelling approach. *Elementa: Science of the Anthropocene*, 3(1), 000080.

Reference	Cruise	Latitude	Longitude	Station	Year	Month	N2O conc (nmol/L)	N₂O sat (%)
Kotovitch et al., in progress	N-ICE2015	83.0	19.0	2	2015	1	16.3	96.2
	N-ICE2015	83.0	20.4	5	2015	1	15.8	92.8
	N-ICE2015	83.1	18.0	7	2015	1	16.1	94.9
	N-ICE2015	83.0	17.2	10	2015	1	16.2	95.6
	N-ICE2015	81.7	19.7	13	2015	3	13.8	82.3
	N-ICE2015	81.6	19.3	16	2015	3	14.8	88.0
	N-ICE2015	83.2	23.7	29	2015	3	15.5	91.5
	N-ICE2015	83.1	21.6	32	2015	3	15.1	89.4
	N-ICE2015	82.8	21.1	36	2015	3	15.6	91.9
	N-ICE2015	83.0	15.2	22	2015	4	16.7	98.3
	N-ICE2015	83.0	15.2	22	2015	4	16.7	98.3
	N-ICE2015	82.4	15.2	26	2015	4	16.8	99.2
	N-ICE2015	82.8	16.3	43	2015	4	16.9	99.8
	N-ICE2015	82.2	13.9	47	2015	4	16.1	95.0
	N-ICE2015	82.4	15.2	26	2015	4	16.8	99.2
	N-ICE2015	82.8	16.3	43	2015	4	16.9	99.8
	N-ICE2015	82.2	13.9	47	2015	4	16.1	95.0
	N-ICE2015	81.8	13.1	29	2015	5	12.9	76.4
	N-ICE2015	81.3	9.7	36	2015	5	15.2	89.5
	N-ICE2015	80.9	8.6	39	2015	5	14.6	86.0
	N-ICE2015	82.0	12.9	48	2015	5	15.1	89.2
	N-ICE2015	81.9	13.0	52	2015	5	12.5	73.9
	N-ICE2015	81.7	12.8	53	2015	5	14.6	86.0
	N-ICE2015	81.6	11.5	55	2015	5	14.1	83.4
	N-ICE2015	81.4	9.6	57	2015	5	14.2	84.0
	N-ICE2015	81.4	9.3	62	2015	5	14.6	86.4

APPENDIX B: N₂O saturation in the Arctic Ocean surface waters

Reference	Cruise	Latitude	Longitude	Station	Year	Month	N₂O conc (nmol/L)	N2O sat (%)
Kotovitch et al., in progress	N-ICE2015	81.3	9.8	65	2015	5	16.1	94.9
	N-ICE2015	80.9	8.5	68	2015	5	13.5	80.0
	N-ICE2015	80.8	8.3	72	2015	5	12.5	73.9
	N-ICE2015	80.7	6.8	75	2015	5	12.3	72.6
	N-ICE2015	80.7	6.2	42	2015	6	12.7	74.6
	N-ICE2015	80.8	12.4	46	2015	6	13.8	83.6
	N-ICE2015	80.5	9.6	47	2015	6	12.2	76.4
	N-ICE2015	80.2	7.2	48	2015	6	13.0	82.6
	N-ICE2015	80.6	5.7	78	2015	6	13.9	81.9
	N-ICE2015	81.1	14.9	83	2015	6	13.5	80.1
Fenwick et al., 2017	SWL 2015-07/ 1502/ LSSL 2015-06	63	-175	1	2015	7	/	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	65	-170	1	2015	7	1	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	67.5	-170	1	2015	8	1	± 101
	SWL 2015-07/ 1502/ LSSL 2015-06	68	-168	/	2015	8	1	± 101
	SWL 2015-07/ 1502/ LSSL 2015-06	71	-162	/	2015	8	1	± 90
	SWL 2015-07/ 1502/ LSSL 2015-06	71	-159	/	2015	8	/	± 90
	SWL 2015-07/ 1502/ LSSL 2015-06	75	-150	/	2015	8	1	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	71.5	-152	1	2015	8	/	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	70.5	-140	1	2015	9	/	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	72	-136	1	2015	9	1	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	71	-123	1	2015	9	/	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	69.5	-101	/	2015	9	/	± 110
	SWL 2015-07/ 1502/ LSSL 2015-06	74	-97	1	2015	9	/	± 105

Reference	Cruise	Latitude	Longitude	Station	Year	Month	N2O (nmol/L)	N2O sat. (%)
Fenwick et al., 2017	SWL 2015-07/ 1502/ LSSL 2015-06	74	-91	/	2015	9	/	± 105
	SWL 2015-07/ 1502/ LSSL 2015-06	74	-81	1	2015	10	/	± 95
	SWL 2015-07/ 1502/ LSSL 2015-06	73	-67	/	2015	10	/	± 90
Verdugo et al., 2016	LOMROG III	83	15	1	2012	8	± 13	± 85
	LOMROG III	86.8	2	2	2012	8	± 18	± 105
	LOMROG III	87.7	-40	3	2012	8	± 18	± 105
	LOMROG III	88.3	-59.4	4	2012	8	± 16	± 95
	LOMROG III	89.2	-57	5	2012	8	± 16	± 90
	LOMROG III	85.75	7.5	8	2012	9	± 16	± 95
	LOMROG III	84.75	5	9	2012	9	± 12	± 75
	LOMROG III	83.4	16	10	2012	9	± 13	± 80
	LOMROG III	82.7	15	11	2012	9	± 15	± 90
	LOMROG III	82.25	9.25	12	2012	9	± 12	± 75
Zhan et al., 2015 & 2016	5th CHINARE	74.7	1	BB09	2012	8	± 13	± 80
	5th CHINARE	74.4	2	BB08	2012	8	± 13	± 80
	5th CHINARE	74	3	BB07	2012	8	± 13	± 80
	5th CHINARE	73.5	4	BB06	2012	8	± 13	± 80
	5th CHINARE	73.2	5	BB05	2012	8	± 13	± 80
	5th CHINARE	72.5	8	BB04	2012	8	± 12	± 75
	5th CHINARE	72	8.5	BB03	2012	8	± 11.5	± 70
	5th CHINARE	71.5	9	BB02	2012	8	± 11.5	± 70
	5th CHINARE	71.5	8	BB01	2012	8	±11	± 65
	5th CHINARE	69.5	2.5	AT05	2012	8	±11	± 65
	5th CHINARE	69	2	AT06	2012	8	±11	± 65
	5th CHINARE	68.5	1.5	AT07	2012	8	±11	± 65
	5th CHINARE	68	1	AT08	2012	8	± 10	± 60
	5th CHINARE	67.2	-2	AT09	2012	8	± 10	± 60

Reference	Cruise	Latitude	Longitude	Station	Year	Month	N₂O conc (nmol/L)	N2O sat (%)
Zhan et al., 2015 & 2016	5th CHINARE	66.5	-3	AT10	2012	8	± 10	± 60
Zhang et al., 2015	4th CHINARE	67	-169	SR01	2010	8	16	117
	4th CHINARE	67.5	-169	SR02	2010	8	13.7	106
	4th CHINARE	68	-169	SR03	2010	8	15.2	111
	4th CHINARE	68.5	-169	SR04	2010	8	16.3	118
	4th CHINARE	69	-169	SR05	2010	8	12.2	99
	4th CHINARE	69.5	-169	SR06	2010	8	11.4	96
	4th CHINARE	70	-169	SR07	2010	8	13.4	96
	4th CHINARE	71	-169	SR08	2010	8	12.7	95
	4th CHINARE	72	-169	SR09	2010	8	12.9	97
	4th CHINARE	73	-169	SR10	2010	8	15.4	99
	4th CHINARE	74	-169	SR11	2010	8	16.2	100
	4th CHINARE	74.5	-169	SR12	2010	8	16.4	99
	4th CHINARE	75	-172	M07	2010	8	16.3	92
	4th CHINARE	75.3	-172	M06	2010	8	16.6	92
	4th CHINARE	75.6	-172	M05	2010	8	16.7	93
	4th CHINARE	76	-172	M04	2010	8	16.7	93
	4th CHINARE	76.5	-172	M03	2010	8	16.9	94
Randall et al., 2012	IPY-CFL 2008	71.1	-124	97	2008	4	± 11	± 65
	IPY-CFL 2008	71.2	-124.5	102	2008	4	± 12	± 70
	IPY-CFL 2008	70.75	-122.5	107	2008	4	± 10	± 60
	IPY-CFL 2008	70.7	-123.7	120	2008	4	± 15	± 85
	IPY-CFL 2008	70.8	-124.7	123	2008	4	± 18	±111
Gagné 2015	CCGS Amundsen 2007-08 Leg 11a	74.2	-90	303	2008	9	19	120
	CCGS Amundsen 2007-08 Leg 11a	74.1	-83	301	2008	9	12.5	82
	CCGS Amundsen 2007-08 Leg 11a	73.9	-74	141	2008	9	17.5	115

Reference	Cruise	Latitude	Longitude	Station	Year	Month	N2O conc (nmol/L)	N2O sat (%)
Gagné 2015	CCGS Amundsen 2007-08 Leg 11a	74.5	-78	134	2008	9	12.5	85
	CCGS Amundsen 2007-08 Leg 11a	74.7	-73.5	136	2008	9	17.2	125
	CCGS Amundsen 2007-08 Leg 11a	74.8	-69	138	2008	9	12	83
	CCGS Amundsen 2007-08 Leg 11a	74.9	-64	140	2008	9	15	110
	CCGS Amundsen 2007-08 Leg 11a	76.32	-71.2	115	2008	9	12.7	95
	CCGS Amundsen 2007-08 Leg 11a	76.28	-73.2	111	2008	9	13.1	98
	CCGS Amundsen 2007-08 Leg 11a	77.35	-73.4	126	2008	9	19.1	140
	CCGS Amundsen 2007-08 Leg 11a	76.75	-71.8	233	2008	9	12.2	86
	CCGS Amundsen 2007-08 Leg 11a	76.26	-74.5	108	2008	9	16.7	108
	CCGS Amundsen 2007-08 Leg 11a	76.8	-76.75	202	2008	9	16	99
	CCGS Amundsen 2007-08 Leg 11a	76.35	-77.5	101	2008	9	12.8	78
	CCGS Amundsen 2007-08 Leg 11a	77.22	-78.75	205	2008	9	15.8	95
	CCGS Amundsen 2007-08 Leg 11a	76.3	-75.5	105	2008	9	15.75	98
Hirota et al., 2009	R/V Mirai MR06-04	73	-165	12	2006	8	18.8	126
	R/V Mirai MR06-04	72.5	-166	Extra 12	2006	8	20	129
	R/V Mirai MR06-04	68.5	-168	16	2006	8	13.5	112
	R/V Mirai MR06-04	67	-167	17	2006	8	12.1	108
	R/V Mirai MR06-04	64	-168.5	18	2006	8	11.6	102
	R/V Mirai MR06-04	62	-169	20	2006	9	12.7	114
	R/V Mirai MR06-04	60	-192.5	27	2006	9	13.2	113
	R/V Mirai MR06-04	58	-166	29	2006	9	13.7	112

Reference	Cruise	Latitude	Longitude	Station	Year	Month	N2O conc (nmol/L)	N₂O sat (%)
Kitidis et al., 2010	Beringia 2005	72.5	-70	/	2005	7	/	± 105
	Beringia 2005	74	-80	/	2005	7	/	± 105
	Beringia 2005	74	-90	/	2005	7	/	± 105
	Beringia 2005	72.5	-95	/	2005	7	/	± 105
	Beringia 2005	69	-100	/	2005	7	/	± 95
	Beringia 2005	68	-110	/	2005	7	/	± 105
	Beringia 2005	70	-120	/	2005	7	/	± 105
	Beringia 2005	70.5	-130	/	2005	7	/	± 105
	Beringia 2005	71	-140	/	2005	7	/	± 105
Weiss et al., 1992	TTO/NAS	60	20	/	1981	7	1	± 115
	TTO/NAS	70	0	/	1981	7	/	± 115
	TTO/NAS	78	5	/	1981	7	/	± 90
	Hudson 82-001	75	10	/	1982	2	11	75
	Hudson 82-001	70	10	/	1982	3	11	75
	Hudson 82-001	80	10	/	1982	3	11	75