

Distribution of chloride and bromide across the snow-sea ice-seawater
interface in natural and mesocosm environments and its implication for
halogen activation in polar regions

by

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Abstract

Halogen chemistry in the polar boundary layer has received much scientific attention in recent years due to the observations of high concentrations of reactive halogens in springtime. Despite extensive studies in the past two decades, the source of reactive halogen species and the site for halogen activation remain a subject of debate, with snow being increasingly recognized as the most important substrate for halogen activation. In this thesis, chloride, bromide and sodium ions across the snow-sea ice-seawater interface were measured to study the cryospheric halide distribution and the role of different substrates in the Arctic springtime halogen activation. Comparative studies were carried out in both experimental and natural sea ice environments. The results show halides/ Na^+ molar ratios (Br^-/Na^+ and Cl^-/Na^+ ratios) in snow are commonly higher than that in seawater, suggesting snow scavenges halides from sources other than sea salt. The decrease in the halides/ Na^+ ratios in the surface snow layer indicates a loss of halides from the snow, supporting snow as an important substrate for halogen activation. There is no change in the halides/ Na^+ molar ratios throughout ice cores, suggesting sea ice is not involved in the halogen activation process. Furthermore, a mechanism for snow-assisted halogen activation is proposed based on the variation of the Br^-/Cl^- ratio in the snow.

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List of acronyms

AMDEs – Atmospheric Mercury Depletion Events

BEEs – Bromine Explosion Events

Br^- – Bromide

Br_2 – Bromine Molecule

BrCl – Bromochloride

BrO – Bromine Monoxide

CIMS – Chemical Ionization Mass Spectrometry

ClO – Chlorine Monoxide

Cl^- – Chloride

Cl_2 – Chlorine Molecule

GEM – Gaseous Elementary Mercury

HOBr – Hypobromous Acid

LP-DOAS – Long-Path Differential Optical Absorption Spectroscopy

MAX-DOAS – Multi Axis-Differential Optical Absorption Spectroscopy

O_3 – Ozone

OCIO – Chlorine Dioxide

ODEs – Ozone Depletion Events

QLL – Quasi-Liquid Layer

RGM – Reactive Gaseous Mercury

SERF – Sea-ice Environmental Research Facility

THg – Total Mercury

VOC – Volatile Organic Compounds

Chapter 1: Introduction

Abstract

Tropospheric ozone (O_3) depletion events (ODEs), which appear every year in springtime in polar regions, have motivated the study of halogen chemistry since the 1980s. During ODEs, the O_3 concentration in the polar boundary layer is rapidly depleted (from normal concentration of 30-40 to several nmol mol^{-1}) (Oltmans 1981). Not long after the first observation of ODEs, filterable bromine (f-Br) in the air is found to have negative correlation with the O_3 concentration, leading to the postulation that bromine related species are responsible for depleting O_3 in the boundary layer (Barrie et al. 1988). The role of reactive chlorine species in the polar boundary layer has been underestimated until recently when high concentrations of molecular chlorine (Cl_2) were detected in the polar boundary layer (Liao et al. 2014). The chlorine atoms produced by photolysis of molecular chlorine can oxidize volatile organic compounds (VOC) and also deplete O_3 in the air. Given the fact that reactive halogens directly influence the polar boundary layer, it is important to understand the sources of the halogens. It is speculated that those halogen species are photochemically activated and released from saline substrates, such as snow, ice surfaces, frost flowers and aerosols (Simpson et al. (2007c) and references therein). During ODEs, the reactive halogen species substitute the role of O_3 in the boundary layer and become the major oxidizers, resulting in changes of atmospheric oxidation pathways. These potential changes have driven many field measurements and laboratory experiments to study halogen activation in the polar boundary layer. In this introduction section, I summarize the current knowledge of halogen activation, with a focus on bromine and chlorine in the Arctic boundary layer; the role of

different types of substrate in halogen activation; and the effects of halogen activation on mercury chemistry.

1.1 Objectives

While a lot of progress has been made in the understanding of springtime halogen activation in the Arctic region, many unanswered questions still remain. The transport and transformation of Cl^- and Br^- throughout the snow-ice-seawater interface are complicated due to the complex microenvironments and weather condition in the Arctic. The current view is that snow deposited on sea ice is vital in controlling the activation and transport of reactive halogen species to the atmosphere. The distribution of halides in snow is affected by upward diffusion and migration from the underlying substrate, the deposition of aerosols and the air-snow exchanges caused by heterogeneous reactions. In order to understand the role of snow in halogen activation better, further investigation of the halide source and distribution in snow and behavior of halides during halogen activation is needed. Moreover, changes in the Br^-/Cl^- ratio in snowpack during halogen activation need to be studied further to understand the mechanism and effect of the activation.

Therefore, the objectives of this study are:

- a) to study sources and behaviors of halides across the snow-sea ice-ocean interface,
- b) to investigate the role of snow and sea ice in halogen activation, and,
- c) to improve current understanding of the halogen activation mechanism.

1.2 Halogen chemistry in Arctic boundary layer

1.2.1 Reactive bromine and chlorine related species

Bromine related species BrCl and Br_2 were first directly measured by using atmospheric pressure chemical ionization-mass spectrometry (CIMS) in the high Arctic. During ODEs, the mixing

ratio of BrCl (up to 35 pmol mol⁻¹) is found to be higher than Br₂ (up to 27 pmol mol⁻¹), but Br₂ showed a stronger negative correlation with O₃ than BrCl (Foster et al. 2001, Spicer et al. 2002). High concentrations of BrO (up to 41 pmol mol⁻¹) which is another reactive bromine species, are also detected during ODEs later on by the long-path differential optical absorption spectroscopy (LP-DOAS) technique (Pöhler et al. 2010). The maximum BrO appear in the morning and evening while the minimum BrO occur at noon. Simultaneous measurement of bromine species, including Br₂, HOBr and BrO is also made recently by using CIMS (Liao et al. 2012). Br₂ is found not to be strongly correlated with O₃ concentration during the night. While BrO and HOBr mixing ratios agree well at low wind speeds, BrO is enhanced when wind speeds are higher (> 6 m s⁻¹).

Our understanding of chlorine chemistry in the polar boundary layer lags behind that of bromine chemistry. Based on the depletion of hydrocarbon concentrations in the air, an early study estimated that the concentrations of chlorine atoms in the boundary layer during ODEs are 7.5×10^4 molecules cm⁻³ (Boudries and Bottenheim 2000). While molecular chlorine (Cl₂) was not detected directly in the polar boundary layer in earlier studies (Foster et al. 2001, Spicer et al. 2002, Pöhler et al. 2010), the depletion of BrO concentration indicates the presence of reactive chlorine (Pöhler et al. 2010). And the study suggests that the decrease in BrO mixing ratio at noontime is due to reactive chlorine in the air. Not until recently, high concentrations of Cl₂ (up to 400 pmol mol⁻¹) are reported in the Arctic boundary layer during spring with characteristic maxima during morning and late afternoon and minimum at night (Liao et al. 2014). Also, in this study, the high concentrations of Cl₂ appear in the daytime instead of at night, suggesting chlorine behaves differently from bromine. The correlation of Cl₂ with O₃ concentration implies that Cl₂ formation requires O₃ and sunlight. Another chlorine species – chlorine dioxide (OCIO,

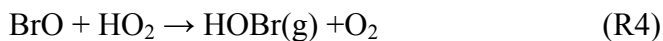
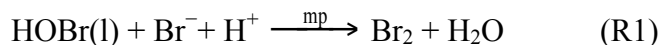
up to 25 pmol mol⁻¹) is only observed before polar sunrise in a previous study and it is suggested to be produced from inter-halogen reactions of BrO and ClO (Pöhler et al. 2010).

In summary, these measurements indicate that reactive halogen species in the polar boundary layer link with each other and have correlations with O₃ concentration. Meteorological condition plays an important role in these correlations. Further studies on simultaneous measurement of halogen species, O₃ concentration and meteorological data are needed to elucidate the mechanism behind these observations.

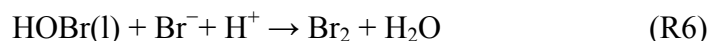
1.2.2 Mechanisms of halogen activation

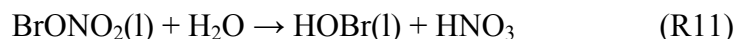
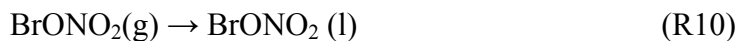
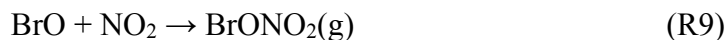
It has been suggested that reactive halogen species in the polar boundary layer are produced by a series of heterogeneous photochemical reactions in which halide ions on saline condensed phases (sea ice, snow, frost flowers and aerosols) are converted into reactive halogens and released to the air. In particular, the mechanism of high-level Br₂ production in springtime, known as bromine explosion events (BEEs), has been proposed by many studies (Simpson et al. 2007c, Abbatt et al. 2012, Nghiem et al. 2012, Pratt et al. 2013). The summarized chemical reaction cycles are:

Cycle 1:



Cycle 2:





Chloride ions (Cl^-) are also suggested to participate in bromine activation by producing bromine chloride (BrCl) (Vogt, Crutzen and Sander 1996, Fickert 1999):

Cycle 3:



Cycle 3 is a branch of Cycle 1 and Cycle 2. In Cycle 3, Br_2 produced in R15 continues on to react in R2 in Cycle 1 or R7 in Cycle 2 and then completes the cycles. Cl^- produced in R15 will continue to be involved in Cycle 3. According to these reactions, both Br^- and Cl^- react with HOBr , converting Br^- in condensed phases into reactive bromine in the air and this consequently results in BEEs. The Br^-/Cl^- ratio in the condensed phases is thus a potentially important tracer in studying halogen activation. The changes in this ratio will be discussed further in the later part of this chapter.

Studies have suggested that a small amount of halogens are required as precursors to initiate the reaction cycles (Simpson et al. 2007c, Abbatt et al. 2012). Specifically, BEEs need initial formation of bromine atoms at the beginning and then the whole bromine activation cycles can

occur spontaneously. Depending on whether the sunlight is needed or not, there are two mechanisms to produce reactive bromine precursor in the Arctic boundary layer.

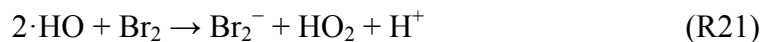
Bromine initiation in the absence of sunlight (during the dark period)

Before polar sunrise, Br^- in the saline condensed phases such as sea ice, snow grains or aerosols, can be oxidized by O_3 and the initial bromine atoms are released to the air. The bromine precursor eventually reacts with other oxidants (HOBr, nitrite and OH) after polar sunrise to produce more reactive bromine species (Abbatt et al. 2012). This assumption is built based on the experiments in which O_3 is absorbed efficiently onto NaBr frozen solutions and an abundance of Br_2 and BrCl is formed during this process (Oum, Lakin and Finlayson - Pitts 1998, Oldridge and Abbatt 2011, Wren et al. 2010, Wren, Donaldson and Abbatt 2013). The reactions are summarized by R16-R18:

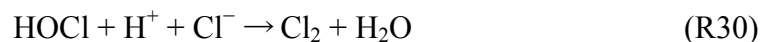
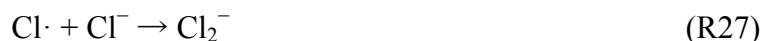


Bromine initiation in the presence of sunlight (after polar sunrise)

Another way to initiate bromine activation is proposed by Pratt et al. (2013). In their experiment, natural snow and first-year sea ice are used as substrates to simulate the formation of reactive bromine species. There is no bromine species detected under dark conditions even if O_3 concentration is increased to $140 \text{ nmol mol}^{-1}$. Thus they conclude that the initial bromine atom is produced from photochemical reactions where Br^- in condensed phases is oxidized by hydroxyl radicals ($\cdot\text{OH}$) (R19 - R23). The produced reactive bromine atoms then participate in other photochemical reactions to release more reactive bromine species.



The mechanism of chlorine formation in the polar boundary layer is also speculated by several studies. The proposed reactions are (Oum et al. 1998, Knipping et al. 2000):

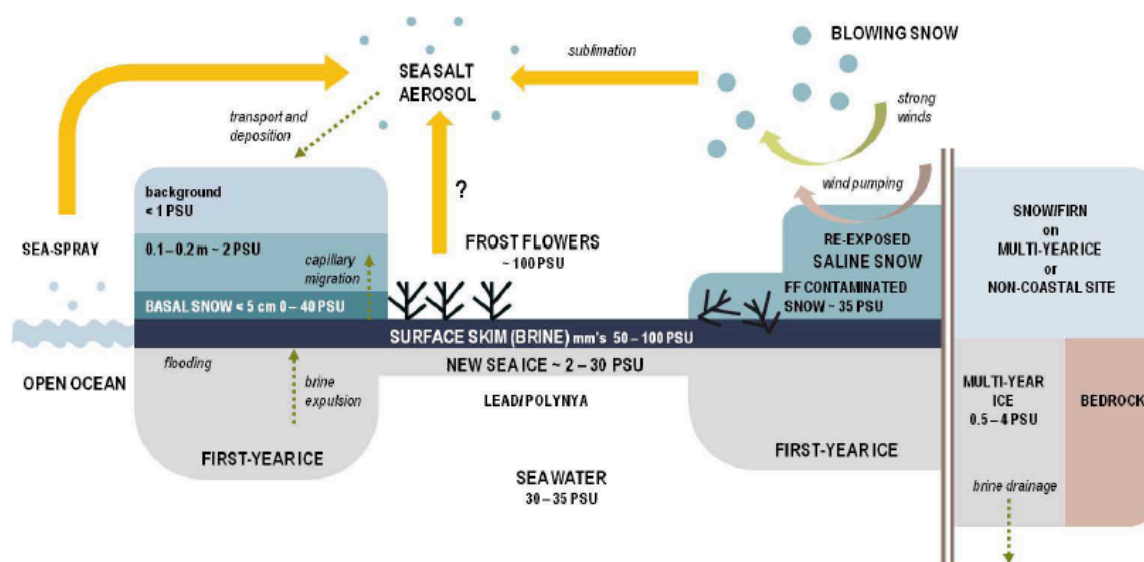


The direction of R24 is determined by the competition of H^+ in the following step (R25) (Oum et al. 1998). More HOCl^- is produced when there are more H^+ available (pH is less than 7). Since Cl_2 in this sequence of reactions can be produced by three reactions: R26, R28 and R30, this mechanism is likely to lead to the observed high concentrations of Cl_2 in the springtime Arctic boundary layer (Liao et al. 2014).

1.2.3 The role of different substrates in halogen activation

The dynamics of halogen activation are complicated because the activation involves a series of photochemical heterogeneous reactions as discussed above. Any saline condensed surface (Figure 1-1) that is exposed under solar radiation during springtime is a potential source of halides. In situ measurements (Avallone et al. 2003, Foster et al. 2001, Pöhler et al. 2010), back trajectory of air-mass calculations (Simpson et al. 2007a, Frieß et al. 2011) and satellite observations (Wagner et al. 2001, Nghiem et al. 2012) are used to determine whether halogen abundance match with areas of snow, sea ice, frost flowers or distributions of aerosols. Also, several simulative experiments have been conducted to investigate whether halogen related species are released from different condensed surfaces (Abbatt et al. 2012, Pratt et al. 2013, Adams 2002, Wren et al. 2013). In this section, snow, sea ice, frost flowers and aerosols as a site for halogen activation in the Arctic springtime are discussed, with primarily focusing on bromine chemistry.

Figure 1-1. Possible sources for halides in the polar boundary layer with their salinity (Abbatt et al. 2012) (Used under a permission obtained on February 12, 2015 from Jon Abbatt)



A. Sea ice

Different halogen measurements and calculations suggest that sea ice, especially first-year sea ice, is a possible place for halogen activation. A laboratory experiment shows that HOBr is absorbed effectively onto frozen sodium halide solutions (Huff and Abbatt 2002). The subsequent release of Br₂ and BrCl from the frozen solution supports the view that halogen activation can occur at the atmosphere/ice interface. Moreover, the observed BrO-enhanced area from satellite correlates with areas of first-year sea ice, indicating young saline sea ice is related to bromine explosion (Wagner et al. 2001, Nghiem et al. 2012). Multi Axis-Differential Optical Absorption Spectroscopy (MAX-DOAS), which is a ground-based measurement technique, also detected the enhanced BrO concentrations over the first-year sea ice areas in the Antarctic (Wagner et al. 2007). By using back trajectory calculations, the air mass containing high BrO concentrations is found to have previous contact with first-year sea ice areas (Frieß et al. 2004, Simpson et al. 2007a), which reinforces the suggestion that halogen species can be produced by saline sea ice.

However, more saline frost flowers on the first-year sea ice are very common in the Arctic and in the springtime, ice is often entirely covered by snow. Therefore, it is also possible that the enhanced reactive bromine species observed above the ice are released from the overlying frost flowers or snow.

B. Frost flowers

Frost flowers are primarily observed on young sea ice in polar regions, providing an efficient medium for exchange of matter and energy between sea ice and the atmosphere. Two mechanisms are proposed to relate frost flowers to bromine activation. Frost flowers either

directly release reactive halogens or produce halide-contained aerosols which then produce reactive halogens (Simpson et al. 2007c). In this section, frost flowers as a direct source of halogen species is summarized. Aerosols produced from frost flowers as a halogen source is discussed in Section D below.

Frost flowers could provide an effective environment to facilitate bromine activation. Measurements show that the Br^- concentration in frost flowers are 2 - 3 times higher than in seawater (Rankin, Wolff and Martin 2002), which implies that more halides are available in frost flowers than in any other condensed surfaces. The potential frost flowers (PFF) coverage on young sea ice is calculated by a model study, which reveals that the area of PFF on sea ice correlates well with the enhanced BrO area from satellite observations (Kaleschke et al. 2004). Even though there is no apparent bromine depletion observed in frost flowers, the bromine balance calculation between frost flowers and the atmosphere implies that a 0.5% change of Br^- concentration in frost flowers is sufficient to result in BrO concentration as large as 50 (pmol mol^{-1}) in the atmosphere (Alvarez-Aviles 2008).

Despite the fact that the pH of melted frost flowers is alkaline which is not consistent with bromine production mechanism (Kalnajs and Avallone 2006, Hare et al. 2013), frost flowers-released aerosols could easily be acidified due to the carbonate precipitation (Sander, Burrows and Kaleschke 2006). Therefore, the role of frost flowers in halogen activation is still open to debate.

C. Snowpack

The observation that reactive halogen species are abundant above the snowpack provides evidence that the snowpack could be a source of halogens (Spicer et al. 2002, Avallone et al.

2003). Lower O₃ concentration and higher reactive bromine species concentration in the interstitial air of the surface snow layer (Foster et al. 2001) further indicates that reactive bromine species is produced via snow photochemical reactions which then depletes O₃ in the snow.

Recently, productions of reactive halogens from both artificial snow and natural snow under different conditions (e.g., different O₃ concentrations, Br⁻/Cl⁻ ratios in the snow and pH of the snow) were studied in simulative halogen activation experiments (Wren et al. 2013, Pratt et al. 2013). The proposed mechanism of bromine activation in snow is: reactive bromine atoms are produced through photochemical reactions in the interstitial air of snowpack and are transported to the atmosphere via wind pumping. This mechanism is supported by BrO observation using a forward-looking DOAS system, which shows elevated BrO concentrations near snow surface (Pratt et al. 2013). In addition, a one-D model developed by Toyota, Dastoor and Ryzhkov (2014) simulates that heterogeneous reactions occur efficiently in the interstitial air of snowpack, which leads to an in-snow bromine explosion and O₃ loss.

In addition to the snowpack, blowing snow is also considered as a contributor to halogen activation. In conjunction with measurements of Br₂, BrCl and BrO, modeling calculations indicate that blowing snow is a source of Br⁻ that can sustain BEEs during a storm or after halides-contained aerosols deposit onto snowpack (Buys 2012). Subsequent modeling studies (Jones et al. 2009) suggest that blowing snow itself can trigger halogen activation. In addition to directly providing a place for bromine activation, blowing snow triggered by strong winds also produces sea-salt aerosol to sustain the reaction cycle (Yang, Pyle and Cox 2008). The aerosol produced by blowing snow as a source of bromine is discussed in Section D below.

D. Aerosols

Early studies on the mechanism of bromine production suggest that heterogeneous reactions between aerosols and air are efficient and the resulting reactive bromine species from aerosols are sufficient enough to explain the observed O₃ depletion in the polar boundary layer (McConnell et al. 1992, Fan and Jacob 1992, Vogt et al. 1996). Thus aerosols that can be produced from sea spray, frost flowers or blowing snow, are considered as one of the most important places for halogen activation. Later on, modeling calculations of aerosol production rate imply that aerosols can be produced efficiently from blowing snow, which potentially represents a considerable atmospheric bromine source (Yang et al. 2008). A subsequent model study (Yang et al. 2010) successfully simulated the occurrence of BEEs during blowing snow events in which sea salt aerosols were formed.

The satellite BrO observations and model calculations show that enhanced BrO plume coincided with high wind speeds which could eventually result in blowing snow (Begoïn et al. 2010, Choi 2012). As well, measurement of vertical aerosol extinction distribution demonstrates that the enhanced BrO from MAX-DOAS is strongly correlated with high aerosol extinctions at high wind speeds (Frieß et al. 2011). Thus a large quantity of aerosols produced during blowing snow events, could lead to the efficient production of reactive bromine species in the air mass.

1.2.4 Behaviors of bromide, chloride and sodium during sea ice formation

Cl⁻ and Na⁺ are the major ions in seawater. Their respective concentrations are 566 and 486 mmol kg⁻¹ in the standard seawater (with a salinity of 35) (Millero 2013). Br⁻ is a minor ion in seawater, with a concentration of 0.83 mmol kg⁻¹ (Millero 2013). When temperature decreases, pure water freezes into pure ice where brine pockets, which contain salt ions, are then formed in

the ice matrix between crystals. As temperature continues to decrease, salts in the saturated brine will precipitate in order to maintain phase equilibrium, establishing known relationships among ionic concentration, salt precipitation and temperature (Assur 1960). In particular, Na^+ is predicted to crystallize and be removed gradually from brine through the precipitation of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and hydrolite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) when temperature decreases to -8.2°C and -22°C , respectively. In addition, Cl^- in the brine also crystallizes as $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ at -18°C and KCl at -36°C . When Na^+ is used as a reference to trace behaviors of other ions in seawater, the removal of Na^+ from brine would have potential effect on the results. For example, an increase in Br^-/Na^+ ratio might be caused by $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ precipitation which leads to a decrease in Na^+ concentration (Wagenbach et al. 1998, Rankin et al. 2002). Thus the precipitation of salts in brine would affect ionic composition of the brine layer on the surface of sea ice and snow layer contaminated by the sea ice.

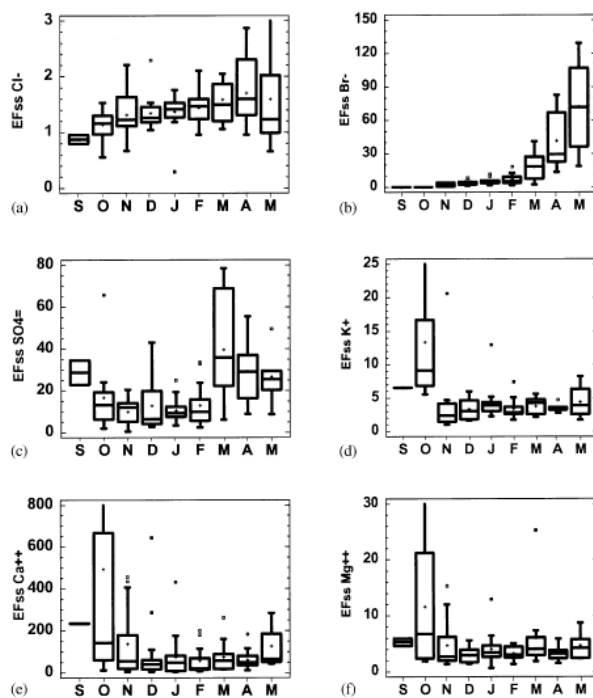
1.2.5 Characteristics of halide distributions in snow

As previously discussed, when Na^+ is used as a sea salt tracer, the halides/ Na^+ ratios (Br^-/Na^+ and Cl^-/Na^+ in sea ice or snow could be affected by the deposition of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. This explains that an enhancement of halides in snow compared to that in seawater could result from Na^+ depletion. However, when considering whether halides in snow are enhanced or depleted, the initial snow composition is of greater importance. The initial snow composition is affected by both sea salt source and non-sea salt sources in the air, the underlying sea ice or tundra and atmospheric reactions.

Fresh snow absorbs gas species and scavenges aerosols during its settling, which gives snow the initial ion composition. A four-year continuous measurement on fresh snowfall chemistry at Alert, Canada (Canadian Arctic Archipelago) provides background information on the chemical

composition of fresh snow in the high Arctic (Toom-Sauntry and Barrie 2002). As depicted in Figure 1-2, Br^- and Cl^- are enhanced with respect to Na^+ in the snowfall compared to sea salt demonstrates that snowfall absorbs halides in the atmosphere from non-sea salt sources. Also, as the season changes from winter to spring, Cl^- enhancement increases in snowfall and diminishes in aerosols, suggesting a mass transfer from the aerosols to the snowfall. In contrast, Br^- enhancement increases from winter to spring in both snowfall and aerosols, indicating gaseous bromine-related species are more reactive in the Arctic boundary layer. The observation also implies that Br^- and Cl^- in the polar boundary layer behave differently.

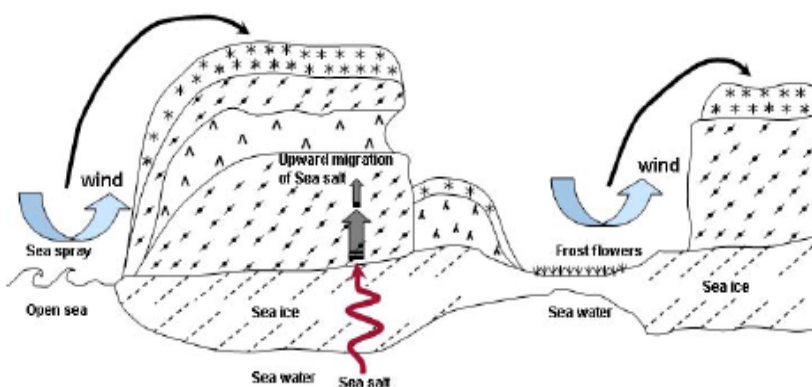
Figure 1-2. Br^- and Cl^- enrichment factors ($\text{EF}_{\text{ss}} = [\text{X}/\text{Na}]_{\text{SNOW}}/[\text{X}/\text{Na}]_{\text{SEA}}$) in weekly snowfall samples on a monthly basis at Alert for 1990-1994 (Toom-Sauntry and Barrie 2002) (Used under a permission obtained on Feb. 12, 2015 from Elsevier)



After deposition, the composition of the snow is affected by the tundra or the sea ice onto which the snow is accumulated (Figure 1-3). A previous study suggests that the upward transport and migration of ions from the underlying sea ice can affect the snow up to 17 cm above the snow-

ice interface (Domine et al. 2004). At the same time, the deposited snow also exchanges gas and aerosol with the atmosphere and is influenced by atmospheric chemistry. Weather conditions are also a factor impacting snow chemical composition. For example, wind can transport and deposit sea-salt aerosols onto the snow layer (Figure 1-3), which increases ion concentration in the surface a few cm of the snow. Therefore, snow chemical composition changes with time and space.

Figure 1-3. Potential pathways to supply sea-salt ions to snow in polar regions: transport from sea spray and frost flowers by wind, upward diffusion and migration from sea ice (Domine et al. 2004) (Used under a permission obtained on Feb. 13, 2015 from Florent Domine)



By using Na^+ as a reference, Cl^- enhancement in snow is found compared to seawater when Na^+ concentration is low (Simpson et al. 2005, Jacobi et al. 2012, Krnavek et al. 2012). As previously discussed, fresh snow absorbs chlorine species (e.g., HClO and HCl) from gas phase but also snow can be affected by relative high ion concentrations of sea ice after deposition on the ice. Therefore, Cl^- enhancement in the snow is only distinguishable in the snow where there is no influence observed from the underlying ice. Br^- concentration, on the other hand, is believed to be influenced largely by atmospheric reactions. Br^- in snowpack on tundra is found to be depleted in the upper 15 cm of the snowpack and enriched in the lower layers (Jacobi et al. 2012).

They conclude that Br^- depletion in the upper layer of the snowpack is due to the ongoing BEEs and Br^- enrichment in the lower layer is caused by dry deposition of soluble Br^- when these lower layers were exposed as the snow surface in the past. Simpson et al. (2005) agrees that Br^- concentration in snow is mainly affected by the atmospheric chemistry, but they also include other factors such as transport distance of various sea salt aerosols and reacting time. Their study shows that reactive bromine species can be transported much farther than Na^+ -rich aerosols. In this manner, if reactive bromine atoms are transformed to Br^- and deposit in an area where there are small amounts of Na^+ , the Br^- would be enhanced. If reactive bromine atoms are transported to a place where Na^+ concentration is high, then Br^- would be depleted. Also, the process by which Br^- is converted to reactive bromine and then released from snow requires time. Snow may not show Br^- depletion as soon as BEEs occur. Especially, snow with a high Br^- concentration would need a longer time to show the depletion.

1.2.6 Implication of the Br^-/Cl^- molar ratio on BEEs

In many previous studies on bromine activation in the Arctic environment, Cl^- was chosen as a reference to trace the behavior of Br^- (Avallone et al. 2003, Simpson et al. 2005, Domine et al. 2004, Jacobi et al. 2012) because their similarities as halide and because both of them are usually analyzed simultaneously by the technique. The values of bromide to chloride molar ratio (Br^-/Cl^- ratio) in the standard seawater is 1/650 (Millero 2013), which is usually taken as the “normal” value. If a substrate (e.g., frost flowers, snow or sea ice) has a Br^-/Cl^- ratio that is higher than 1/650, the substrate is considered to be bromine enhanced. On the contrary, a substrate is thought to be bromine depleted if it has a Br^-/Cl^- ratio that is lower than 650. The enhancement and depletion are records of the behavior of Br^- before, during and after bromine activation.

Changes in the value of the Br^-/Cl^- ratio in different substrates are results of salt precipitation in sea ice, sea salt and non-sea salt aerosols deposition and air-substrate exchanges caused by heterogeneous reactions. There are several studies on the changes in the value of the Br^-/Cl^- ratio in brine during salt precipitation process. Experiments show that both Br^- and Cl^- are enhanced by more than an order of magnitude during the freezing process which could accelerate heterogeneous bromine activation (Koop et al. 2000). Taking only temperature into account, Br^- concentration is calculated to increase by a factor of 38 when temperature decreases from 273 K to 240 K whereas Cl^- concentration increases only by a factor of 11 in their study. In other words, the Br^-/Cl^- ratio increases from the normal value of 1/650 at 273 K to 1/250 at 240 K. This is in agreement of FREZCHEM modeling which shows that Br^-/Cl^- ratio in brine increases from 1/650 to 1/175 when temperature decreases from 273 K to 238 K (Morin et al. 2008). The enhancement of Br^- in brine is expected to accelerate bromine activation in three ways (summarized in (Simpson et al. 2007c, Abbatt et al. 2012)): a) an extrusion of Br^- -enhanced brine to the surface of sea ice could directly increase the reaction rates in transformation of Br^- to reactive bromine if the activation occurs readily at the sea ice surface; b) The quasi-liquids layer (QLL) formed by Br^- -enhanced brine on the sea ice surface can be blown up by wind to become aerosol in the air. These Br^- enhanced aerosols could also increase bromine activation if the aerosol surface is an active site for bromine activation; and c) The QLL on the ice surface can also be transported to the overlying snowpack by upward migration, resulting in Br^- enhancement in the snow. Bromine activation in the interstitial air of the snowpack thus can be accelerated.

Laboratory experiments show that different values of the Br^-/Cl^- ratio in a frozen, salty solution affect BrCl and Br_2 yields. Adam et al. (2002) observed that both bromine gas (Br_2) and BrCl are

released from a simulating salty solution surface. When the Br^-/Cl^- ratio of the solution is around 1/660, which is comparable to that of the standard seawater, the main product is Br_2 . When the Br^-/Cl^- ratio is 10 times lower, the ratio of BrCl to Br_2 yielded is higher than that of the previous experiment. Huff and Abbatt (2002) also studied the reaction between a frozen Br^- and Cl^- solution and the gas-phase of HOBr . They concluded that the Br^-/Cl^- ratio of the initial frozen solution is one of the most important factors to determine the ratio of produced Br_2 to BrCl . In conclusion, when the Br^-/Cl^- ratio of a condensed phase is close to the ratio of the standard seawater, Br_2 is the favored product. On the other hand, more BrCl is produced when the Br^-/Cl^- ratio in a condensed phase is lower.

Recent outdoor chamber experiments suggest that the value of the Br^-/Cl^- ratio in snow is an important indicator that determines the occurrence of bromine activation (Pratt et al. 2013). In the experiment, the release of Br_2 , BrCl and Cl_2 from snow, sea ice and brine samples that have different values of Br^-/Cl^- ratio and pH were observed under simulative halogen activation conditions. Those snow samples that are found to produce Br_2 are characterized by a high Br^-/Cl^- ratio (1/148 to 1/38) and a low pH. Other condensed phases including sea ice, brine and lower layer of snowpack from where no Br_2 release is found have lower Br^-/Cl^- ratio (1/526-1/230). The authors speculate that the relatively high Cl^- concentration could increase the time for Br_2 production and/or reduce the production of HOBr , leading to the interruption of Br_2 production in the lower Br^-/Cl^- ratio conditions. In addition to the study of bromine activation, a simulative experiment also shows the role of Br^-/Cl^- ratio in snow in chlorine activation. The production of Cl_2 , BrCl and Br_2 from artificial saline snow are observed Wren (Wren et al. 2013). Less Cl_2 and BrCl were measured when Br^- concentration in the snow is decreased which leads

to lower Br^-/Cl^- ratio, implying that the ratio also affects the production of chlorine related species.

The values of Br^-/Cl^- ratio in condensed phases are not only considered to affect the final products of halogen activation, but also suggested to be records of the behavior of Br^- during halogen activation. Compared to the initial composition, a condensed phase would show Br^- depletion if Br^- is activated to reactive bromine and released to the air. On the contrary, a condensed phase would show Br^- enhancement after bromine activation when catalytic cycle is terminated by the transformation of gaseous reactive bromine species into Br^- and then Br^- deposits back onto the substrate (Simpson et al. 2005). It is thought that the removal rate of Br^- from snow is determined primarily by Br^- concentration in the snow and the addition rate of Br^- into the snow relates to snow physical properties (Krnavek et al. 2012). Domine et al. (2004) analyzed snow samples on the Arctic sea ice and in the coastal regions. Only in a few snow samples, Br^-/Cl^- ratio was found to be close to the ratio in seawater, which is a result of upward migration and transport from the underlying sea ice. Most other snow samples had higher Br^-/Cl^- ratios (1/25 -1/137). They suggest that the higher ratios are caused by Br^- produced in BEEs deposits back onto the snow and lead to Br^- enrichment compared to Cl^- . It is also thought that the same snow experiences both addition and removal of Br^- during halogen activation in springtime but Br^- in surface snow is more depleted than enhanced (Krnavek et al. 2012). Therefore, snow tends to be a source of Br^- .

In conclusion, the value of the Br^-/Cl^- ratio is an important factor to determine the occurrence and the final products of halogen activation. It is important to note that the ratio also indicates the behavior of Br^- and Cl^- in halogen activation. Many laboratory experiments have been conducted to simulate halogen activation and observe the final products using different Br^-/Cl^-

ratios in frozen solution, artificial snow and natural snow. However, so far, Br^-/Cl^- ratios in different substrates in the Arctic have not been measured extensively over time and space and the changes in this ratio before, during and after springtime halogen activation are not well known.

Bromine to chlorine molar ratio (Br/Cl ratio) in the air

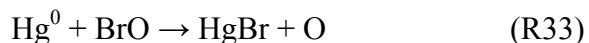
In terms of the Br/Cl molar ratio in the gas phase in the polar boundary layer, different measurements and estimation methods were used in previous studies. In most of the studies, Br/Cl ratio was measured during ODEs. Since halogen activation plays an important role in ODEs, the Br/Cl ratio in the air could also provide useful information for studying halogen activation. Based on a steady state analysis, Impey et al. (1997) estimated that the Br/Cl ratio ranges from 100 to 300 during ODEs at Alert, Nunavut. At the same location, an estimate of the Br/Cl ratio was also obtained by using the absolute decay rate for alkanes; the ratio was around 190 during ODEs (Boudries and Bottenheim 2000). By measuring VOC produced from bromine and chlorine atoms, Keil and Shepson (2006) reported that Br/Cl ratio ranges from 80 to 990 at Barrow, Alaska when O_3 concentration was above 15 nmol mol^{-1} . Overall, the Br/Cl ratio in the air is highly variable from 80 to 990 and the ratio is higher compared to the Br^-/Cl^- ratio in the condensed phases (1/85 to 1/650). Future studies are needed to clarify the connections between air and condensed phases in halogen activation and calculate the fluxes of halogens across the air/condensed surfaces interface.

1.2.7 Effects of halogen activation on mercury chemistry

At the same time when ODEs occur, another springtime events, known as atmospheric mercury depletion events (AMDEs), also take place in the polar boundary layer (Schroeder et al. 1998). During AMDEs, gaseous elementary mercury (GEM) is being converted to reactive gaseous

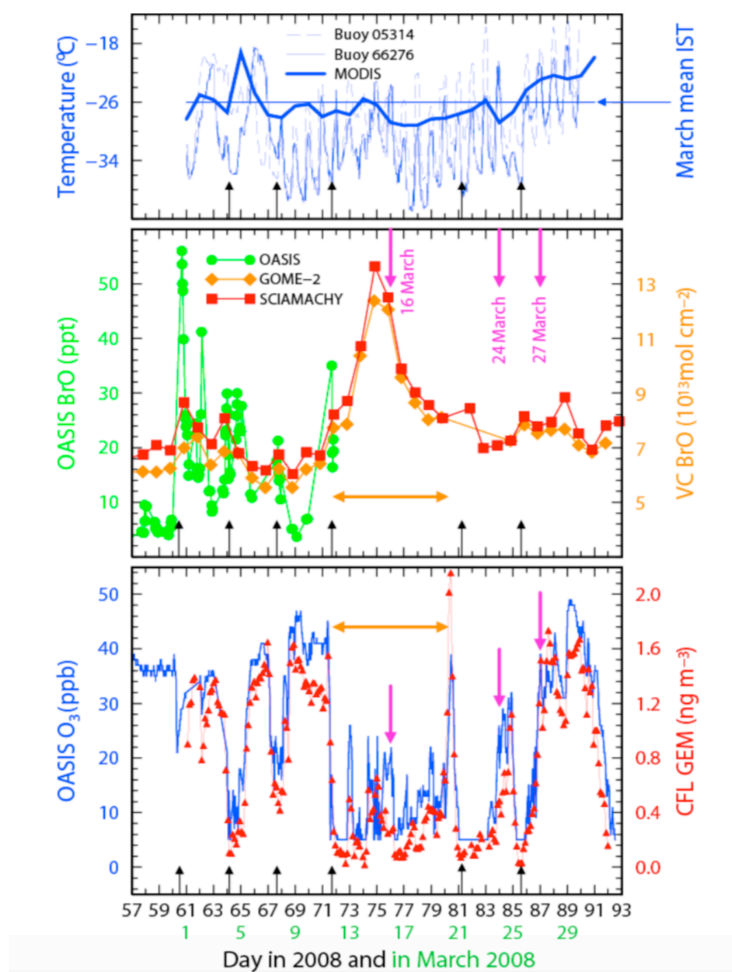
mercury (RGM: Hg(II)) (Lindberg et al. 2001, Lu and Schroeder 2004). The converted RGM is more reactive and hygroscopic than GEM and it readily deposits onto snow/ice surface or is absorbed onto aerosol in the air (Lindberg et al. 2001, Lin and Pehkonen 1999, Skov et al. 2006, Ariya, Khalizov and Gidas 2002). Through these pathways, RGM eventually enters into the Arctic ecosystem, which leads to potential threat to the health of wildlife and people who live in northern areas.

It is believed that halogen chemistry, which drives ODEs, also causes AMDEs. In addition to the satellite observations that found enhanced BrO concentration is well correlated with occurrences of AMDEs, model studies successfully simulate that high concentrations of Br and BrO lead to the occurrence of AMDEs and ODEs in the springtime polar boundary layer (see Steffen et al. (2008) and references therein). Also, simultaneous measurement of BrO, O₃ and GEM at the Amundsen Gulf reveals that BrO increase, O₃ depletion and mercury depletion are often recorded at the same period (Figure 1-4, (Nghiem et al. 2012)). Thus reactive halogen species are considered to oxidize GEM and thus result in AMDEs in the polar boundary layer (Ferrari et al. 2004, Brooks et al. 2006). Laboratory Experiments have studied reactions between halogens and Hg and the mechanism of AMDEs is summarized below in Reactions 31-34 (Hg⁰ is GEM and the oxidized Hg species are RGM) (see (Steffen et al. 2008, Simpson et al. 2007c) and references therein):



In addition to halogen species in the air that affect AMDEs, Cl^- in the snowpack also plays an important role in Hg photoreactions (Ferrari et al. 2004). Snow samples with lower Cl^- concentration are observed to produce more Hg^0 through photochemical reactions (Lalonde et al. 2003). Also, a simulative experiment in which Cl^- -containing salts are added to snow samples further explains that the additional Cl^- inhibits photoreduction of $\text{Hg}(\text{II})$ significantly. The mechanism could be that $\text{Hg}(\text{II})$ and Cl^- can form chlorocomplexes which are stable and probably not involved in any photoreactions (Ferrari et al. 2004, Louis et al. 2007, Qureshi et al. 2009).

Figure 1-4. In-situ measurements of temperatures, BrO , O_3 , and gaseous elemental mercury (GEM) at Amundsen Gulf in March 2008 (Nghiem et al. 2012) (Used under a permission obtained on Feb. 13, 2015 from John Wiley Sons)



RGM or aerosols that contain RGM can deposit directly onto snow or sea ice. Sea ice in polar regions are covered by snow most of the time in the spring (Kwok et al. 2011). Snow thus plays an important role in AMDEs. Total mercury (THg) concentration in snow at Barrow is found to be higher (up to 90 ng L^{-1}) than background regions (Lindberg et al. 2002), implying RGM deposits onto the snow. Moreover, A 20-fold increase in THg concentration in snow after polar sunrise compared to that in dark period supports the view that springtime AMDEs lead to the deposition of Hg into snow (Steffen et al. 2002).

However, it is also speculated that the converted GEM can be reduced and re-emitted back from the snow to the air. Ferrari et al. (2005) reported that there is no increase in THg concentration in snow at Svalbard even though seven AMDEs are recorded, which indicates that the deposited Hg is released back into the air. During AMDEs, the GEM concentrations near snow surface or in the interstitial air of snowpack were observed being continuously higher than that in the ambient air, while O_3 concentration measured at the same place decreased over the same period (Albert et al. 2002, Steffen et al. 2002). It is thus considered that snow is either a source of GEM or GEM oxidation is inhibited in the interstitial air of snow. The process where Hg is re-emitted back into the air is important because if more Hg is released into the air, then less Hg would enter into the marine ecosystem.

Snow has been proposed to be the most likely place to produce reactive halogen species in recent studies (Pratt et al. 2013, Wren et al. 2013). These halogen species produced in the snow interstitial air could be responsible for the oxidation of GEM. However, the mechanism of redox reactions between halogen species and Hg remains unknown. And the formation of Hg-halide complexes in the snow interstitial air or on snow grains is not fully understood. The relationship

between halogen activation and Hg redox reactions and the role of snow in these reactions need to be elucidated further.

1.3 Thesis organizations

This thesis is organized into 4 chapters. Chapter 1 reviews the relevant literature on halogen activation in the Arctic boundary layer and related topics. Chapter 2 reports the distribution of Cl^- , Br^- , Na^+ and halides/ Na^+ ratios across the snow-sea ice-ocean interface in springtime at Cambridge Bay in the Canadian Arctic Archipelago, which contributes to the understanding the role of snow and sea ice in halogen activation and the mechanism of halogen activation. In Chapter 3, the distribution of Cl^- , Br^- and halides/ Na^+ ratios in a mesocosm sea ice environment is studied. It provides concentrations and behaviors of halides in snow, sea ice and seawater in the absence of springtime photochemical reactions. Finally, Chapter 4 provides a general summary of this study with perspectives on future directions of research in this field.

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Chapter 2: Distribution of chloride and bromide across the snow-sea ice-ocean interface and its implication for halogen activation in the Arctic boundary layer

Abstract

High concentrations of reactive halogen species have been observed in the Arctic boundary layer during springtime. These halogens react with ozone (O_3) and elementary mercury (Hg^0) in the air, resulting in the occurrence of tropospheric ozone depletion events (ODEs) and atmospheric mercury depletion events (AMDEs), respectively. While extensive studies to determine the role of different substrates such as snow, sea ice, frost flowers and aerosol in halogen activation, the main site where halogen activation occurs still remains a subject for debate. Here we report the profiles of halides (Br^- and Cl^-), Na^+ , and mercury (Hg) across the snow-sea ice-seawater interface at a coastal site in the Canadian Arctic Archipelago in mid-March and June 2014. The occurrence of halogen activation and AMDEs from snowpack during the sampling period is confirmed by the high Hg concentrations measured in the snowpack. Results show that the halides/ Na^+ molar ratios (Br^-/Na^+ and Cl^-/Na^+ ratios) in the snowpack are typically higher than that in the seawater, indicating that the snow absorbs halides from non-sea salt sources. The loss of halides from the upper snow layer is estimated and the results show that the loss is more than sufficient to produce the observed reactive halogens in the air, suggesting snow is the most likely place for halogen activation. Based on the characteristics of Br^-/Cl^- molar ratio profiles in the snowpack, a mechanism for halogen activation is proposed, which shows the dominant halogen species produced during the activation changes as the Br^-/Cl^- ratio changes in the snow.

2.1 Introduction

In the springtime Arctic boundary layer, episodes of high concentrations of reactive bromine species were observed, which is known as bromine explosion events (BEEs). High concentrations of chlorine related species (Cl , Cl_2 and OClO) in the Arctic boundary layer were also detected in previous studies (Jobson et al. 1994, Impey et al. 1997, Impey et al. 1999, Boudries and Bottenheim 2000, Pöhler et al. 2010, Liao et al. 2014). These reactive halogen species are proposed to drive both ODEs (Barrie 1988) and AMDEs (Ferrari et al. 2004, Brooks et al. 2006) in the Arctic springtime. During ODEs, the reactive halogen species substitute the role of O_3 in the boundary layer and become the major oxidizers, resulting in changes of atmospheric oxidation pathways; reactive gaseous mercury (RGM) produced in AMDEs is more reactive and readily deposits onto snow surface to bring potential threat for northern people and animals. Therefore, the study of halogen activation in the Arctic is important.

Different types of substrate, such as snow, sea ice, frost flowers, and aerosols, have been proposed to be possible sites for the activation of inert Br^- and Cl^- into reactive bromine and chlorine species followed by their release to the air (see (Simpson et al. 2007c, Abbatt et al. 2012)) and the references therein). Sea ice could be a place for halogen activation because the elevated BrO area from satellite observation is found to correlate with areas of first-year sea ice (Wagner et al. 2001, Nghiem et al. 2012). Also, back-trajectory calculation reveals that the air mass containing high BrO concentrations have previously contacted with the first-year sea ice areas (Frieß et al. 2004, Simpson et al. 2007a). Frost flowers are very common on young sea ice and 2 - 3 times higher Br^- concentration in frost flowers than in seawater makes frost flowers are possible halide source in halogen activation (Rankin, Wolff and Martin 2002). But the pH in frost flowers is found to be too alkaline to provide an acidic environment for halogen activation

(Hare et al. 2013). In the Arctic springtime, sea ice is often entirely covered by snow; thus snow is considered as an important site for halogen activation. A model study simulates that heterogeneous reactions occur efficiently in the interstitial air of the snowpack (Toyota, Dastoor and Ryzhkov 2014). Also, productions of reactive halogens from both artificial snow and natural snow are observed in simulative halogen activation (Wren, Donaldson and Abbatt 2013, Pratt et al. 2013). In addition to the snowpack, blowing snow itself and/or sea salt aerosol produced from blowing snow are believed to relate to BEEs (Begoin et al. 2010, Choi 2012, Frieß et al. 2011, Yang et al. 2010), which reinforces the important role of snow in halogen activation.

Several studies have been done to investigate chemical composition of snow. Using Na^+ as a reference, both halide enrichment and depletion in the upper snow layer (Krnavek et al. 2012, Jacobi et al. 2012) compared to the standard seawater have been reported at different locations in the Arctic. Br^- and Cl^- depletion in snow is believed to be caused by halides in the snow that are converted to reactive bromine and chlorine species which subsequently are released into the atmosphere; Br^- and Cl^- enrichment in snow is thought to be due to the deposition of reactive halogens back to the snow (Jacobi et al. 2012, Simpson et al. 2005, Simpson et al. 2007c). However, sources of halides in snow and the initial halides/ Na^+ ratios (Br^-/Na^+ and Cl^-/Na^+ ratios) before the activation in snow are not clear; behaviors of halides during the activation and the effect of the activation on changes in the halides/ Na^+ ratios in snow remain unknown.

In this study we report vertical distribution of Br^- and Cl^- in snow, sea ice and seawater in the springtime and summer 2014 at a coastal Arctic site near Cambridge Bay, Nunavut, Canada. By analyzing Br^-/Na^+ and Cl^-/Na^+ ratios across the snow-ice-seawater interface, our measurements provide new insights into the sources and behaviors of halides in the Arctic snowpack and the first-year sea ice. The results are further used to estimate the loss of halides from snow to the air

and to determine the role of ice and snow in halogen activation. In addition, a mechanism suggesting different products formed in different stages of halogen activation is proposed in this study.

2.2 Materials and procedures

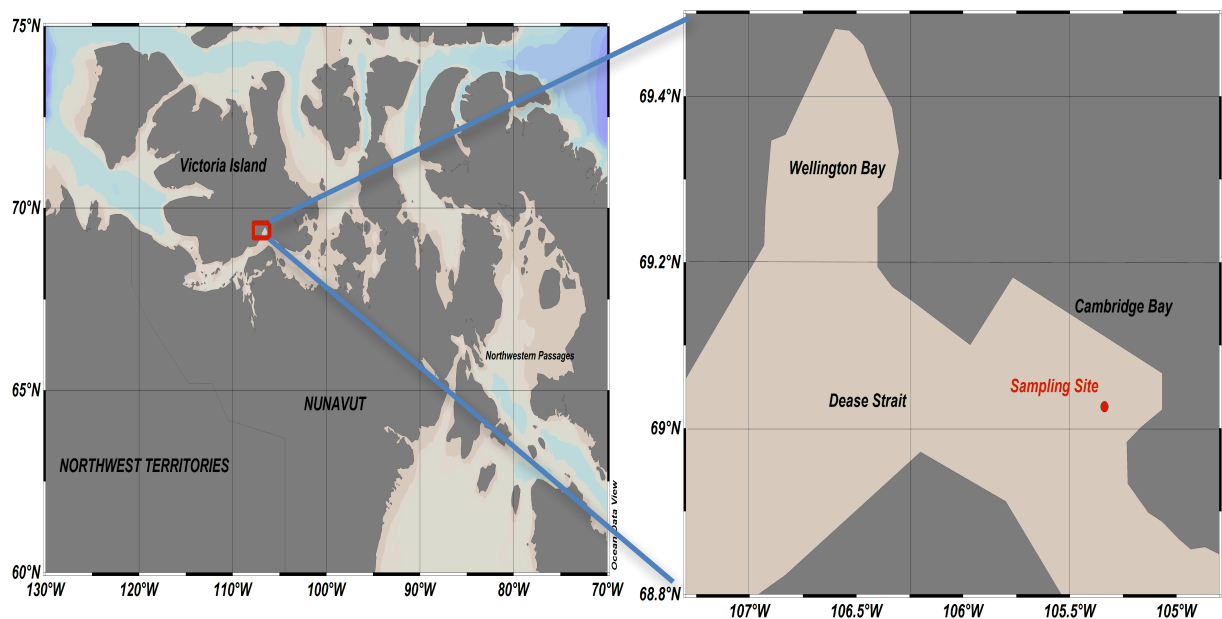
2.2.1 Study area

In March 2014, sea ice, the overlying snow and underlying seawater were sampled at a coastal site (69.026° N, 105.337° W) near Cambridge Bay in the Canadian Arctic Archipelago, about 7 km from the shoreline (Figure 2-1). At the time of sampling, the thickness of the snow on sea ice ranged from 20 cm to 40 cm due to the local morphology and blowing snow; no major fresh snowfall occurred during the March sampling period. The ice thickness was around 150 cm and the water depth beneath was about 60 m. Sampling period was from March 7 to March 18. Snow samples were collected every two days. Sea ice and seawater samples were collected every three days. Except from March 17 to March 18 were cloudy days and precipitation on March 16, the rest of the sampling days were sunny. Sampling normally was done in the morning and the air temperature ranged from -21.5 to -34.5 °C. In June 2014, snow samples from the same study area were also collected, though no sea ice cores were sampled.

In order to avoid cross contamination, all the snow samples for Cl^- and Br^- analysis were collected using 50 mL polypropylene Falcon tubes (BD) while wearing powder free polyethylene gloves. At each site, a snow pit was dug out to the ice surface by using a metal shovel. The surface 2-3 cm of the vertical section of the snow pit was then removed by a plastic shovel which had been rinsed by Milli-Q water. Triplicate snow samples were taken from the snow pit with a vertical resolution of 4 cm. After removing the overlying snow from the sea ice surface, duplicate ice core samples were taken using a Mark II Kovacs core barrel (i.d. = 9 cm). Ice cores

were cut into 5 cm sections and stored in polyethylene bags. Around 1 m below sea ice, triplicate seawater samples were collected using a Beta water sampler (PVC) and stored in new Falcon tubes (BD).

Figure 2-1. A map showing the sampling location near Cambridge Bay of the Canadian Arctic Archipelago



Snow samples for total mercury (THg) measurement were collected by following the “clean-hands –dirty-hands procedure” (Fitzgetald, 1999). Each snow pit (~ 30 cm) was divided into 5 vertical layers and snow samples were taken from each layer. Field and procedural mercury blanks were collected after each sampling.

All the snow samples were kept in a freezer after being taken from the field and then packed into coolers and shipped to the University of Manitoba for analysis. All the sea ice samples were melted in new Ziplock bags and then separated into two subsamples: one sample for conductivity measurement and the second sample for ions analysis. The measurement for conductivity was done immediately after the ice was melted. Seawater samples were treated the same way as the

melted sea ice samples. After shipping back, all the snow samples were melted one day before analysis.

2.2.2 Sample preparation and analysis

Major ion analysis was completed using ion chromatography (Dionex ICS 1000 Ion Chromatography system) in the Soil Science Laboratory at the University of Manitoba. Anions were analyzed after separation through an AG18 (4 x 50 mm) guard column and an AS18 (4 x 250 mm) analytical column with 30 mM NaOH as the eluent. Cations were analyzed using a CG12A-5 μm (3 x 30 mm) guard column and a CS12A-5 μm (3 x 150 mm) analytical column with 20 mM methanesulphonic acid (MSA) as the eluent. The flow rate was set to 0.5 ml min^{-1} for anions analysis and 1.0 ml min^{-1} for cations. The detectors for both anion and cation analysis were conductivity cells.

Standard calibration solutions were prepared from 1000 mg L^{-1} standard solutions of corresponding salts (Fisher Scientific). The standard calibration curves were separated into two concentration ranges since Cl^- and Br^- concentrations in seawater differ greatly. A low calibration curve (ranging from 0 to 5 ug mL^{-1}) was applied for the measurement of Br^- , whereas a high calibration curve (ranging from 5 to 50 ug mL^{-1}) was applied for Cl^- . Typically, the R^2 of a linear regression for calibration curves was greater than 0.95. The method detection limit (MDL) of the instrument was calculated by multiplying the standard deviation of eight near-zero replicates by a factor of three. The MDL for Cl^- and Br^- measurements were 0.4×10^{-3} and $1.2 \times 10^{-4} \text{ mmol kg}^{-1}$, respectively. Operating procedure references (1 ug mL^{-1} and 25 ug mL^{-1}), which were prepared from a 1000 mg L^{-1} standard solution of salts (HIGH-PURITY), normally were analyzed every 25 samples. The measurement deviation of the operating procedure references was always found to be less than 10% of the original concentrations. All seawater, melted ice

and snow samples were diluted with Milli-Q water to a desired concentration range before analysis in order to ensure the samples fell into the calibration range of the instrument.

The analysis for total mercury (THg) was done by cold vapor atomic fluorescence spectroscopy (Tekran 2600 Hg analyzer) in the Ultra-Clean Trace Elements Laboratory (UCTEL) at the University of Manitoba. The MDL for mercury concentration was 0.04 ng L^{-1} . The R^2 of a linear regression for the mercury calibration curve was greater than 0.999. Quality control was checked by analytical blanks, an Ongoing Precision and Recovery (OPR) standard ($\sim 5 \text{ ng L}^{-1}$), and a certified reference material BCR-579 (coastal seawater; $[\text{Hg}]_{\text{T}} = 1.85 \pm 0.5 \text{ ng L}^{-1}$). OPR was measured every 10 samples and the measurement deviation was $< 10\%$. The recovery of the BCR-579 was 98% of the certified value. THg concentration in the field blanks ranged from 0.25 to 0.72 ng L^{-1} .

In situ temperature was measured using a model 4000 thermometer (Traceable Control Company). Once a snow pit was dug, the snow temperature was measured by inserting the thermometer into the snow pit at a resolution of 4 cm. Sea ice temperature was measured immediately after core retrieval by inserting the thermometer tip into holes which were drilled into the ice core at a resolution of 5 cm. The conductivity of the seawater, melted snow and sea ice samples was measured using a sensION 156 conductivity meter (HACH Company). Bulk salinity of the ice and snow samples was calculated from the corresponding temperature and conductivity values.

2.3 Results

2.3.1 Major ion distribution across the snow-sea ice-seawater interface

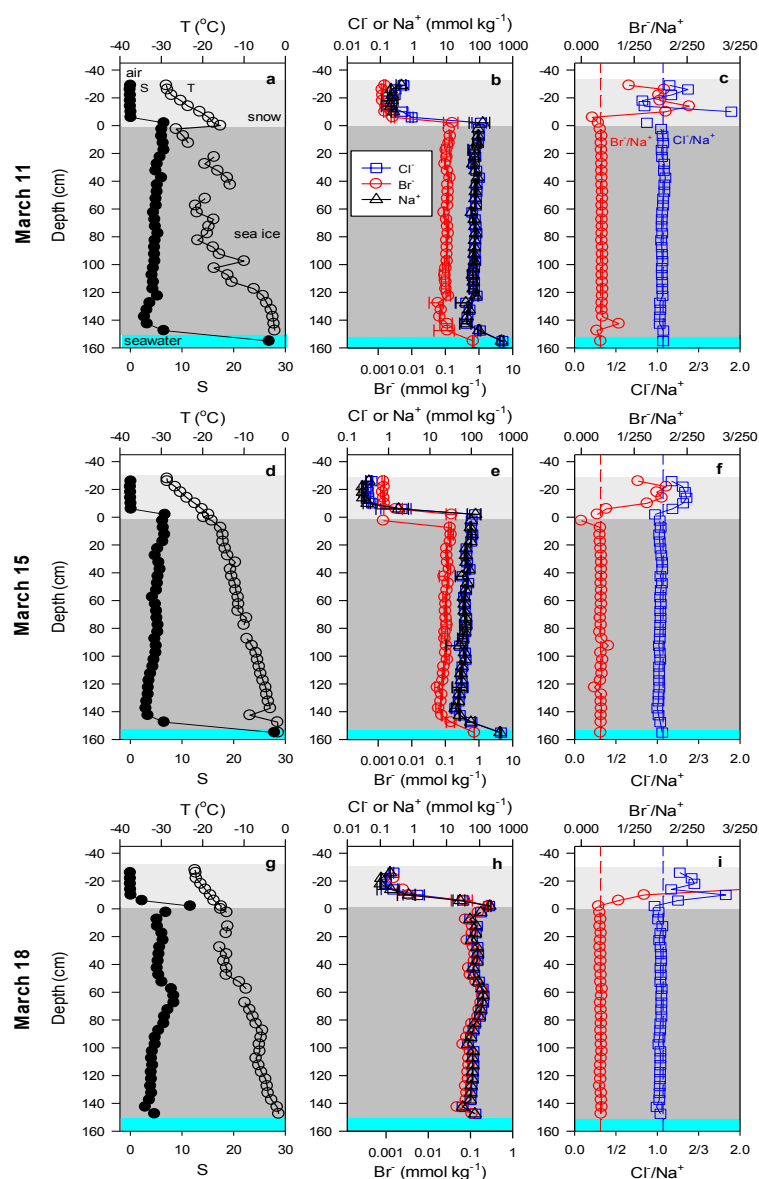
Complete profiles of temperature, salinity, and major ions (Br^- , Cl^- and Na^+) in sea ice and the overlying snowpack were obtained on three occasions in March (March 11, 15, and 18) as shown in Figure 2-2. On two of the occasions, the seawater immediately underneath the sea ice (approximately 10 cm below the ice) was also sampled and analyzed for salinity and major ion composition.

The temperature of surface snow ranged from -29 to -22 °C (Figure 2-2a,d and g) and it increased almost linearly to around -1.7 °C at the bottommost layer of sea ice. The March 11 ice core was cracked into several segments and the temperature was not measured immediately, thus the temperature profile obtained on that day might be erroneous. As expected, the salinity in the snowpack was very low (typically ≤ 0.1) throughout most of the depths except in the bottom 14 cm where salinity rapidly increased to as high as 15 due to salt input from the sea ice (Domine et al. 2004). Salinity of the bulk sea ice was less than 10 during the study period, with the highest values at the surface and bottommost layers, following a C-shaped distribution characteristic of the sea ice growth phase (Thomas and Dieckmann 2010). The underlying seawater salinity was 27, which was about 5 times higher than that of the bulk sea ice.

Br^- , Cl^- and Na^+ concentrations across the snow-sea ice-seawater interface showed a similar profile as salinity. They were high in the seawater (Br^- : 0.69, Cl^- : 504 and Na^+ : 471 mmol kg⁻¹) and low ($\text{Br}^- < 0.01$ mmol kg⁻¹ and Cl^- and $\text{Na}^+ < 1$ mmol kg⁻¹) in the snowpack. The average Br^- , Cl^- and Na^+ concentrations in the ice core were 0.11, 74 and 69 mmol kg⁻¹ which were nearly 100 times higher than that in the overlying snowpack. Although the concentrations of the three ions showed the typical C-shaped profile in the bulk ice core, the molar ratios of $\text{Br}^- / \text{Na}^+$

and Cl^-/Na^+ remained stable at 1/680 and 1, respectively, throughout the ice core, which were comparable to that in the underlying seawater. However, the Br^- , Cl^- and Na^+ concentrations and halides/ Na^+ ratios varied greatly in the overlying snowpack so a higher frequency sampling was carried out to examine the specific evolution pattern in the snowpack.

Figure 2-2. Profiles of temperature (T), salinity (S), major ion concentrations and their molar ratios across the snow-sea ice-seawater interface at Cambridge Bay in mid-March, 2014. The dashed lines in c, f, and i denote the molar ratios of Br^-/Na^+ (red) and Cl^-/Na^+ (blue) in the underlying seawater.

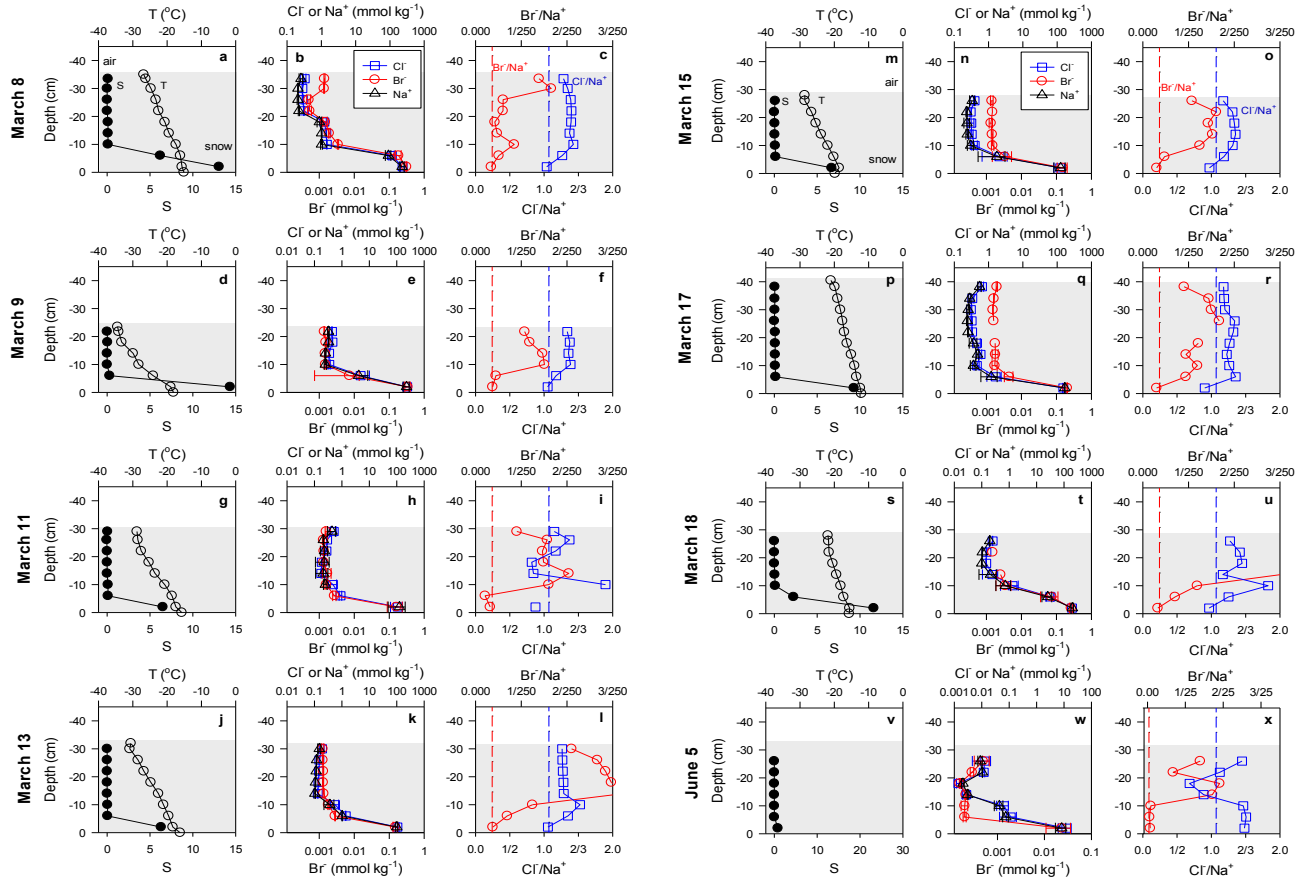


2.3.2 Temporal evolution of major ions and their ratios in snowpack

High frequency profiles of temperature, salinity, and major ions (Br^- , Cl^- and Na^+) in the snowpack overlying sea ice were obtained from March 8 to 18, as well as on June 5 (Figure 2-3). All the sampling locations were within an approximately 500 m of radius. As shown in Figure 2-3, there was always a steady increase in temperature from the snow surface (ranging from -20°C to -34°C) to the snow/ice interface (ranging from -12°C to -18°C). Salinity in the snow typically showed a consistent profile during the sampling period in March. Since the salinity in the snowpack was very low (typically ≤ 0.1) throughout most of the depths except in the bottom 14 cm where salinity increased rapidly to as high as 15, we define the bottom 14 cm of a snowpack as “the lower layer” of a snowpack and the layer above as “the upper layer”. The average snow salinity in June was lower compared to that in March; the salinity was near 0 throughout most of the depths in June except for the bottom 4 cm layer which had a salinity of 0.83 (Figure 2-3v).

In March, Br^- , Cl^- and Na^+ concentrations had very similar distribution profiles throughout the snowpack (Figure 2-3b, e, h, k, n, q and t), resembling that of the salinity profile. In the upper layer of the snowpack, Br^- , Cl^- and Na^+ concentrations were consistently low ($\text{Br}^- < 0.01 \text{ mmol kg}^{-1}$ and Cl^- and $\text{Na}^+ < 1 \text{ mmol kg}^{-1}$) except for the surface 5 cm layer where ion concentrations were slightly higher. Similar to salinity, Br^- , Cl^- and Na^+ concentrations increased in the lower layer of the snowpack where their concentrations reached as high as that of the underlying sea ice (0.11, 74 and 69 mmol kg^{-1} for Br^- , Cl^- , and Na^+ , respectively).

Figure 2-3. Profiles of temperature (T), salinity (S), major ion concentrations and halides/Na⁺ molar ratios in the snowpack overlying sea ice. The dashed lines in c, f, i, l, o, r, u and x denote the molar ratios of Br⁻/Na⁺ (red) and Cl⁻/Na⁺ (blue) in the underlying seawater.



As shown in Figure 2-3w, the concentrations of the three ions in the snowpack in June were at least 10 times lower than those in March, and exhibited different profiles. Na⁺ and Cl⁻ concentrations in June showed a similar profile, which was different from that of Br⁻ concentrations. From the top snow layer to a depth of 10 cm from the surface, the concentrations of all three ions decreased moderately. From the 10 cm depth downwards, Na⁺ and Cl⁻ concentrations increased sharply to the highest (8.2 and 12 mmol kg⁻¹) in the bottommost layer of the snowpack. Br⁻ concentration, on the other hand, remained low until 8 cm above the ice interface, and reached as high as 0.02 mmol kg⁻¹ at the interface.

In terms of the molar ratios, the Cl^-/Na^+ ratio and Br^-/Na^+ ratio changed differently in the snowpack in March. Cl^-/Na^+ ratio increased from around 1 in the bottommost snow layer to 1.5 at 14 cm above the ice interface. From the 14 cm depth upwards, the ratio remained nearly constant but decreased slightly in the surface 5 cm snow layer. March 13 was an exception when no clear decrease in the surface 5 cm was observed. Overall, the Cl^-/Na^+ ratio in the snowpack was just above the ratio in the underlying sea ice.

On the other hand, the Br^-/Na^+ ratio in the snowpack in March showed a reversed C-shaped profile with an exception of the profiles on March 8 and 18. From the bottommost snow layer up to the surface, the Br^-/Na^+ ratio increased at first and then decreased. The bottommost snow layer had the lowest Br^-/Na^+ ratio ($\sim 1/770$). The Br^-/Na^+ ratio (up to $1/77$) peaked at around 14 cm above the ice interface and from there upwards the ratio decreased to about $1/300$. The Br^-/Cl^- ratio in the snowpack followed the same vertical trend as the Br^-/Na^+ ratio and both ratios were higher in the snowpack than in the underlying sea ice.

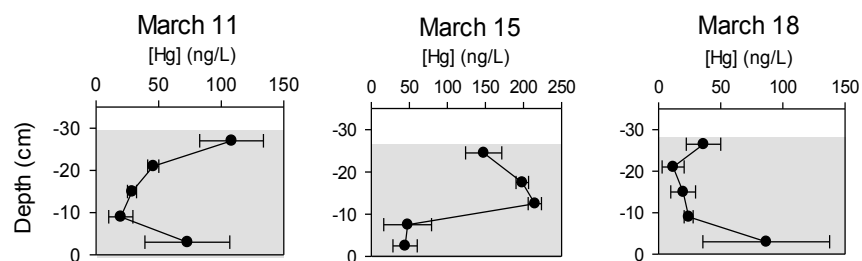
In June, the Cl^-/Na^+ and Br^-/Na^+ ratios remained nearly constant in the bottom 12 cm of the snowpack. The Br^-/Na^+ ratio in the snowpack was comparable to that in the underlying sea ice and the Cl^-/Na^+ ratio was slightly lower than that in the sea ice. From the 12 cm depth to the surface, both ratios showed a reversed C-shaped profile except for a slight increase in the Br^-/Na^+ ratio in the surface 5 cm snow layer.

2.3.3 Mercury concentrations in snowpack in springtime

The THg concentration in the snowpack ranged from 12 to 215 ng L^{-1} , and varied considerably with space and time within a short period of one week. While the THg concentration was the highest at the surface and bottommost layers on March 11 and 18, it peaked in the mid-layer on

March 15 (Figure 2-4). Overall the concentration range is consistent with those reported in the Arctic during AMDEs (see (Steffen et al. 2008) and the references therein). THg concentration on March 15 generally was higher than the other two days and it decreased from 215 at 10 cm depth to 150 ng L⁻¹ at surface. In contrast, THg concentration from the 10 cm depth to the surface increased on March 11 (from 20 to 108 ng L⁻¹) and March 18 (from 24 to 36 ng L⁻¹).

Figure 2-4. The distribution of mercury in the snowpack on March 11, 15 and 18



2.4 Discussion

2.4.1 Surface snow as a site of halogen activation

Br⁻, Cl⁻ and Na⁺ concentrations in the bottom 14 cm of the snowpack are higher than that in the snow above, implying the bottom 14 cm is affected by the underlying sea ice. This is consistent with measurements found near Alert (Canadian Arctic Archipelago) where upward migration and transport of sea ice brine could affect up to 17 cm of the snow (Domine et al. 2004). Ion concentrations are much lower from 14 cm depth of the snowpack to the surface. In particular, the ion concentrations in the surface 5 cm are slightly higher than those in the layers immediately below (except for the bottom 14 cm). This could be due to the deposition of blowing snow which was a common occurrence during the study period. Bare ice without any snow cover was observed during the sampling period within 7 km of the sampling site and the saline snow layer on the top of the ice could be the source of blowing snow in this area. Thus the deposition of the blowing snow on the top of the snowpack would increase the ion concentrations at the surface.

The snowpack at the study site has been accumulating since the beginning of the ice growth season. During settling, snow absorbs aerosols, ions and gases in the air. A four-year continuous measurement of fresh snowfall chemical composition during dark winter near Alert (Canadian high Arctic) indicates both Br^- and Cl^- in the fresh snow are enriched compared to the standard seawater (Toom-Sauntry and Barrie 2002). Chemical composition analysis of snowpack on tundra showed that a snow type that is characterized as depth hoar and locates mostly in the middle and bottom layer of snowpack where snow has accumulated at the beginning, is found to be Br^- enriched (Jacobi et al. 2012). In our study, Br^- and Cl^- in the snowpack in early spring were enriched compared to the seawater (Figure 2-2c, f, i, l, o, r and u), which is consistent with the previous observations. These halide enrichments in the snowpack demonstrate that additional Br^- and Cl^- from non-sea salt source in the atmosphere contribute to the initial composition of the snow.

The decreases in Br^-/Na^+ and Cl^-/Na^+ ratios from 14 cm depth of the snowpack to the surface in our study reveal the loss of Br^- and Cl^- with respect to Na^+ . The halide loss from the snowpack implies springtime halogen activation is occurring. Snow thus plays an important role in halogen activation, which is in agreement with recent studies in which reactive halogen productions from snow are observed (Pratt et al. 2013, Wren et al. 2013). In addition, the high concentrations of THg (up to 215 ng L^{-1}) measured in the snowpack confirm the presence of activated halogen species in our study area. It has been thought that GEM in the air can be oxidized by reactive halogen species (Br, Cl or BrO) and then become RGM which will readily deposit onto condensed surfaces during AMDEs (see Simpson et al. (2007c) and references therein). Therefore, high concentrations of Hg in the snowpack are most likely a result of springtime

AMDEs which are believed to be driven by halogen activation, leading to the deposition of Hg onto the snowpack (See (Steffen et al. 2008, Mann et al. 2014) and references therein).

The loss of halides from the snowpack increased from the 14 cm depth of the snowpack to the surface. The highest Br^-/Na^+ and Cl^-/Na^+ ratios, which are commonly at 14 cm depth, reflect the initial snow composition when the snow is not or less affected by photochemical reactions. We thus propose that before polar sunrise, the Br^-/Na^+ and Cl^-/Na^+ ratios keep steady throughout the upper layer of the snowpack. After polar sunrise, the halogen activation occurring within the snowpack leads to the loss of Br^- and Cl^- from the snow, resulting in a decrease in both Br^-/Na^+ and Cl^-/Na^+ ratios. As discussed previously, the initial halides/ Na^+ ratios in the snow are higher than that in the seawater, the loss of halides from snow driven by halogen activation could deplete the ratios to a level less than found in the seawater. This is consistent with previous studies reporting the halides/ Na^+ ratios can be both higher and lower than the ratios found in underlying seawater at the same location (Simpson et al. 2005, Domine et al. 2004, Jacobi et al. 2012, Krnavek et al. 2012). Our samples were collected at the beginning of the spring, a time when the loss of Br^- and Cl^- from the snowpack had just begun. This loss was not as significant to observe the halides/ Na^+ ratios in the snow decreasing below ratios in the seawater.

The different profiles of the Br^-/Na^+ and Cl^-/Na^+ ratios in the upper snow layer reveal different behaviors of Br^- and Cl^- in halogen activation. While the Br^-/Na^+ ratio typically decreases from the 14 cm depth of the snowpack, the Cl^-/Na^+ ratio only decreases in the surface 5 cm layer (other than on March 13 when there was no obvious decrease in Cl^-/Na^+ ratio). These observations suggest that chlorine activation may only occur in the top-most layer of the snowpack, whereas bromine activation could take place both at the surface and deeper layer in the snowpack. In June, the Br^-/Na^+ and Cl^-/Na^+ ratios show an increase in the surface 5 cm snow,

suggesting that after springtime halogen activation, reactive bromine and chlorine atoms are reduced back to Br^- and Cl^- ions and deposited on the top 5 cm of the snowpack, as suggested in an earlier study (Simpson et al. 2005).

2.4.2 Estimation of the loss of Br^- and Cl^- from snowpack

Based on the data, reactive halogen production from snowpack due to the loss of halides with respect to Na^+ can be calculated. The depth of the snowpack in our study averages 30 cm. The Br^-/Na^+ ratio decreases from the 14 cm depth of the snowpack to the surface. Our measurement shows that the change in the Br^-/Na^+ molar ratio ranges from 1/588 to 1/217 and Na^+ concentration at the 14 cm depth of the snowpack is about $0.358 \text{ mmol kg}^{-1}$. If all of the reactive bromine molecules in the air are produced from the upper 16 cm of the snow layer with snow density of $0.2 - 0.4 \text{ g cm}^{-3}$ (Domine et al. 2008), the loss of Br^- from the snowpack would be $(12 - 63) \times 10^{14} \text{ molecules cm}^{-2}$, which is an order of magnitude higher than the BrO mixing ratios observed in the Arctic boundary layer during springtime BEEs (Nghiem et al., 2012). This simple calculation suggests that a small change in the Br^-/Na^+ ratio in the snowpack is more than sufficient to produce the high concentrations of BrO in the air observed during BEEs. However, it should be noted that this simple calculation does not consider weather conditions. If wind keeps pumping air from snowpack and moving the local air mass away, the BrO produced from a certain area could be distributed to larger areas. Therefore, a defined region of snow tends to lose more Br^- to yield a wider area of BrO distribution in the air.

The same calculation is also used to estimate the reactive chlorine production from the snowpack. The decrease in Cl^-/Na^+ ratio shows in the surface 5 cm snow layer, so we consider Cl^- is only lost from the surface 5 cm of the snowpack. Based on the measurements, the change in Cl^-/Na^+ ratio is from 1/25 to 1/4 and Na^+ concentration in the 5 cm surface layer averages 0.255 mmol

kg⁻¹. The calculation shows that the loss of Cl⁻ from the snowpack is (6 - 77) x 10¹⁵ molecules cm⁻², which can cause 125 – 1564 pmol mol⁻¹ chlorine molecules up to 10 km high. High concentrations of chlorine molecules (up to 400 pmol mol⁻¹) measured in a recent study (Liao et al. 2014) are in the range of our estimation. Our calculation also shows the loss of Cl⁻ from the snowpack is higher than the loss of Br⁻, even though only 5 cm snow layer is considered to be responsible for the Cl⁻ loss whereas Br⁻ is released from 16 cm depth of the snowpack. Thus we conclude that reactive chlorine concentration could be higher than reactive bromine concentration in the polar boundary layer.

2.4.4 The implication of Br⁻/Cl⁻ on the mechanism of BEEs in snow

The Br⁻/Cl⁻ ratio in springtime in our study overall decreases from 14 cm depth of the snowpack to the surface and the highest ratio (up to 1/97) at 14 cm depth represents the initial ratio prior to polar sunrise as discussed before. The loss of halide from the snowpack driven by halogen activation after polar sunrise could lead to the Br⁻/Cl⁻ ratio to decrease as low as to 1/800 (Figure 2-5). Recent chamber experiments reveal that snow samples that were found to produce Br₂ were characterized by a high Br⁻/Cl⁻ ratio (1/38 -1/148) (Pratt et al. 2013). Previous laboratory experiments show that when the Br⁻/Cl⁻ ratio of a condensed phase is close to the ratio in the standard seawater (1/650), Br₂ is the favored product; more BrCl is produced when the Br⁻/Cl⁻ ratio is low (Adams 2002, Huff and Abbatt 2002). When the Br⁻/Cl⁻ ratio is much lower than the ratio in the seawater, both Cl₂ and BrCl are produced from artificial snow (Wren et al. 2013). Also, in their experiment, a decrease in Cl₂ production when Br⁻ concentration in the snow decreases implies that the formation of Cl₂ needs initial production of Br₂ and BrCl.

Combining previous studies and our results of initial Br⁻/Cl⁻ ratios in snowpack and the changes in this ratio during the process of halogen activation, we proposed the following mechanism

which explains the changes in dominant products from halogen activation as Br^-/Cl^- ratio in snow changes. With the initial high Br^-/Cl^- ratio (up to 1/97) in the snowpack in our study, we suggest that the formation of Br_2 occurs first in halogen activation, which would lead to the loss of Br^- over Cl^- at the beginning. Br_2 production has been observed in the dark period (Spicer et al. 2002, Wren et al. 2013) and it provides the “seeds” for the subsequent reaction cycles. The proposed reactions are R1-3 (Oum, Lakin and Finlayson - Pitts 1998, Oldridge and Abbatt 2011, Wren et al. 2010, Wren et al. 2013):

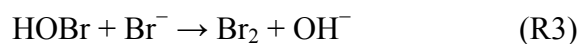
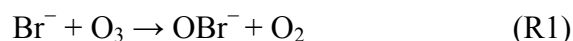
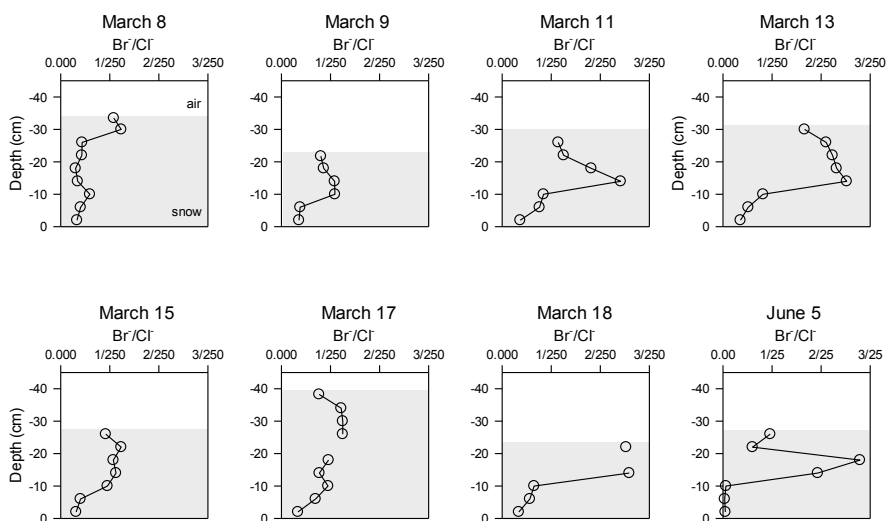


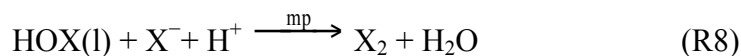
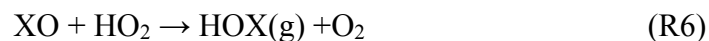
Figure 2-5. The vertical distribution of Br^-/Cl^- ratio in the snowpack at Cambridge Bay in March 2014



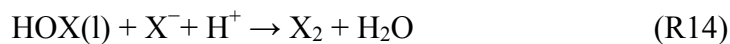
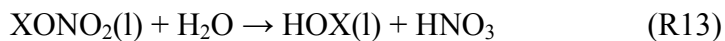
After polar sunrise, Br_2 keeps producing through Cycle 1-2 below (X mainly represents Br in this first stage of halogen activation). As the Br^-/Cl^- ratio in the snowpack keeps decreasing, BrCl would be produced by Cycle 3. Cycles 1-3 are the major reactions in the mechanism of halogen activation (Fan and Jacob 1992, McConnell et al. 1992, Vogt, Crutzen and Sander 1996,

Simpson et al. 2007c, Piot and von Glasow 2008, Nghiem et al. 2012, Pratt et al. 2013). When Br^-/Cl^- ratio in the snowpack decreases to even lower values due to the prevalent loss of Br^- over Cl^- at the first stage of the activation, Cl_2 would be produced. In the reactions in Cycle 1 and 2, Cl^- would be the dominant halogen species (X mainly represents Cl in this stage).

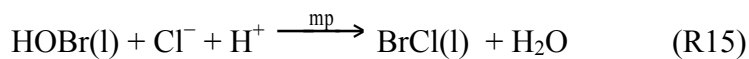
Cycle 1:



Cycle 2:



Cycle 3:



Cycle 3 is a branch of cycle 1 and cycle 2. In cycle 3, Br_2 produced by R18 continues on to react in R4 in cycle 1 or R9 in cycle 2 and then completes each cycle.

It should be noted that although we explain the mechanism of halogen activation by separating different halogen species produced from the activation into different reaction stages, it does not mean the cycles involving different halogen species cannot occur at the same time. Here our main purpose is to emphasize the dominant halogen species in different stages of halogen activation according to the changes in Br^-/Cl^- ratio in snowpack.

2.4.6 Halides in sea ice

The salinity in sea ice is mainly attributed to brine which comes from the underlying seawater (Thomas and Dieckmann 2010). Our results show both Cl^- and Br^- concentrations throughout the ice core have the similar profiles as the bulk ice salinity. Moreover, both Br^-/Na^+ and Cl^-/Na^+ ratios throughout the ice core remain stable which are comparable to that in the seawater (Fig. 2-1). These conservative behaviors of halides throughout the ice core suggest that sea ice or its surface is not the site where halogen activation takes place. This is most likely due to the high pH values in surface sea ice (Hare et al., 2013) which does not favor the multi-phase reactions (R8, R14, R15).

2.5 Conclusions

Halogen related species are reactive oxidants in the polar boundary layer. High concentrations of halogens can consume O_3 and oxidize GEM in the air. Those reactive halogen species are proposed to be activated from different substrates and then released to the air. Snow is ubiquitous in the Arctic springtime and may play an important role in heterogeneous reactions in halogen activation. Measurements of Br^- and Cl^- concentrations in first-year sea ice, the overlying snow

and underlying seawater in our study suggest that halides in snow could originate from seawater and atmospheric deposition. Higher halide concentrations in the bottom 14 cm snow are due to the upward diffusion and migration of halides from the underlying sea ice and ultimately from the seawater. The slightly higher concentration of halides in the surface 5 cm of the snowpack is due to the deposition of blowing snow. In the upper layer of the snowpack where snow is not affected by the underlying ice, halides/ Na^+ ratios are commonly found to be higher than that in the seawater, indicating that halides in the snow also come from non-sea salt source in the air.

The loss of halides with respect to Na^+ from the snowpack is observed in our study, which supports the current view that snow plays an important role in halogen activation and the heterogeneous reactions occur at snow/air interface. In particular, the loss of halides from the surface 5 cm snow layer is more obvious, implying the surface snow layer plays a more important role in halogen activation. The estimated loss of Br^- and Cl^- from the snowpack is found to be more than sufficient to produce the high concentrations of reactive halogen species observed in the boundary layer during Arctic springtime, further suggesting the role of snow as the site for halogen activation.

The Br^-/Cl^- ratio in snow is crucial to determine the final product of halogen activation. Combining our result with previous studies, a mechanism of halogen activation showing different dominant products in different phases of halogen activation is proposed. With the initial higher Br^-/Cl^- ratio (up to 1/97) in the snowpack, Br_2 is the dominant production of halogen activation. As the ratio decreases to around the ratio in standard seawater (1/650), which is due to the prevalent loss of Br^- over Cl^- , the snow tends to produce both Br_2 and BrCl . Eventually, Cl_2 would be a favored product in halogen activation when the Br^-/Cl^- ratio in the snow becomes much lower.

2.6 References

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Chapter 3: Distribution of bromide and chloride across the snow-ice-seawater interface in a mesocosm environment

Abstract

High concentrations of reactive halogen species, which are observed in the springtime polar boundary layer, lead to ozone depletion events (ODEs) and atmospheric mercury depletion events (ADMEs). Those reactive halogens are thought to be activated photochemically from a condensed phase (e.g., snow, sea ice, frost flowers, aerosols) and released to the atmosphere, though it remains unclear which condensed phase is the most important site for halogen activation. In this paper, vertical distribution profiles of bromide (Br^-), chloride (Cl^-), sodium (Na^+) and halides/ Na^+ molar ratios (Br^-/Na^+ and Cl^-/Na^+ ratios) across the snow-ice-seawater interface were studied in an experimental sea ice mesocosm to examine the role of snow in halogen activation. The results show that slush snow on the surface of sea ice has higher halide concentrations than the underlying sea ice, implying they are affected by the brine layer on the ice. Despite the very low halide concentrations in fresh snow, the halides/ Na^+ ratios are found to be higher than that in the seawater, suggesting the snow scavenges halides from non-sea salt sources during its settling. Furthermore, the Br^-/Cl^- ratio in the snow is found to be greater than or equal to the ratio in the underlying seawater (1/500). Since different values of Br^-/Cl^- ratio in the snow are known to lead to different products in halogen activation, we suggest that the snow tends to produce more Br_2 and BrCl than Cl_2 in halogen activation.

3.1 Introduction

Halogen chemistry in the polar boundary layer has received much scientific attention in recent years due to the observations of high-concentration reactive halogen species in the springtime (Saiz-Lopez and von Glasow 2012). The reactive halogens produced during halogen activation react with ozone (O_3) and gaseous elemental mercury (GEM; Hg^0), resulting in the occurrence of ozone depletion events (ODEs) and atmospheric mercury depletion events (ADMEs) (Simpson et al. 2007, Abbatt et al. 2012). The reactive halogen species substitute the role of O_3 in the boundary layer during ODEs and become the major oxidizers, resulting in changes of atmospheric oxidation pathways; reactive gaseous mercury (RGM) produced in AMDEs is more reactive and readily deposits onto the snow surface or open ice leads threatening the health of northern people and animals. Therefore, the understanding of halogen activation in the Arctic boundary layer is important.

While high concentrations of halogen species are proposed to be activated from different types of condensed phases (e.g., snow, sea ice, frost flowers and aerosols), snow is believed to be an important site for halogen activation. Satellite observation shows that reactive halogen species above snowpack are abundant (Foster et al. 2001, Spicer et al. 2002, Avallone et al. 2003). Also, higher reactive bromine concentrations and lower O_3 concentration measured in the interstitial air of the surface snow layer further indicates that the produced bromine species via photochemical reactions then depletes O_3 in the interstitial air of the snow (Foster et al. 2001). Recently, productions of reactive halogens from both artificial snow and natural snow are observed in simulative halogen activation experiments (Wren, Donaldson and Abbatt 2013, Pratt et al. 2013), which provide direct evidence that reactive halogens can be released from heterogeneous reactions in snow. In addition, our field measurement near Cambridge Bay

(Canadian high Arctic) also supports the idea that snow is the most likely place for halogen activation (Chapter 2).

To further study the role of snow in halogen activation, here we report a mesocosm study at the Sea-ice Environmental Research Facility (SERF) located in Winnipeg, Canada where photochemical processes are expected to occur very differently from the Arctic.

3.2 Method and materials

3.2.1 Study area

Figure 3-1. A photo showing SERF during its operation in winter 2013 (Feiyue Wang; used under a permission obtained on Mar. 13, 2015 from Feiyue Wang)



During the winter of 2014, the Sea-ice Environmental Research Facility (SERF) sea ice pond (Figure 3-1), located on the University of Manitoba campus, was used to simulate the Arctic environment. This outdoor pool has capacity to fit 380 m³ volume (155.5 m² surface area by 2.6 m deep) of operative seawater (Hare et al. 2013) and is exposed to natural environment (e.g., ambient temperature, solar radiation and weather conditions). The artificial seawater in the pool

is made following the natural average seawater chemical composition (Millero 2013) and the actual major ion concentration of the seawater in the pool is listed in Table 3-1.

Table 3-1 Chemical composition of seawater at SERF

| Component | Concentration (mmol kg ⁻¹) | Component | Concentration (mmol kg ⁻¹) |
|------------------|--|-------------------------------|--|
| Na ⁺ | 510.36 | Cl ⁻ | 568.32 |
| K ⁺ | 10.52 | Br ⁻ | 1.24 |
| Mg ²⁺ | 58.00 | SO ₄ ²⁻ | 20.76 |
| Ca ²⁺ | 11.73 | NO ₃ ⁻ | 0.04 |

Samples of ice, the underlying seawater and overlying snow were taken during the growth of sea ice at SERF. During the sampling period, the sea ice grew from 2 cm thick on January 25 to 36 cm thick on February 11. Sampling was typically done in the morning and the air temperature ranged from -15 ~ -20 °C. Fresh snowfall events yielding 2~3 cm of snow occurred on January 26 and February 11. On these days, fresh snow samples deposited on the top of the existing snow layer on the ice were sampled. On other days, slush snow on the sea ice was sampled.

In order to avoid cross contamination, all the snow samples for Cl⁻, Br⁻ and Na⁺ analysis were collected using 50 mL polypropylene Falcon tubes (BD) while wearing powder free polyethylene gloves. Triplicate snow samples were taken every time. Then, after removing the overlying snow from the sea ice surface, duplicate ice core samples were taken using a Mark II Kovacs core barrel (i.d. = 9 cm). Ice cores were cut into 5 cm sections and stored in polyethylene bags. Around 3 cm below sea ice, triplicate seawater samples were collected using a Beta water sampler (PVC) and stored in new Falcon tubes (BD). All the snow and ice samples were melted in Ziplock bags and then separated into two subsamples; one sample for conductivity measurement which was analyzed immediately after the snow and ice were melted, the second

sample for Cl^- , Br^- and Na^+ analysis. Seawater samples were treated the same way as the melted sea ice samples.

3.2.2 Sample preparation and analysis

Major ion analysis was completed using ion chromatography (Dionex ICS 1000 Ion Chromatography system) in the Soil Science Laboratory at the University of Manitoba. Anions were analyzed after separation through an AG18 (4 x 50 mm) guard column and an AS18 (4 x 250 mm) analytical column with 30 mM NaOH as the eluent. Cations were analyzed using a CG12A-5 μm (3 x 30 mm) guard column and a CS12A-5 μm (3 x 150 mm) analytical column with 20 mM methanesulphonic acid (MSA) as the eluent. The flow rate was set to 0.5 ml min^{-1} for anions analysis and 1.0 ml min^{-1} for cations. The detectors for both anion and cation analysis were conductivity cells.

Standard calibration solutions were prepared from 1000 mg L^{-1} standard solutions of corresponding salts (Fisher Scientific). The standard calibration curves were separated into two concentration ranges since Cl^- and Br^- concentrations in seawater differ greatly. A low calibration curve (ranging from 0 to 5 ug mL^{-1}) was applied for the measurement of Br^- , whereas a high calibration curve (ranging from 5 to 50 ug mL^{-1}) was applied for Cl^- . Typically, the R^2 of a linear regression for calibration curves was greater than 0.95. The method detection limit (MDL) of the instrument was calculated as multiplying the standard deviation of eight near-zero replicates by a factor of three. The MDL for Cl^- and Br^- measurement were 0.4×10^{-3} and $1.2 \times 10^{-4} \text{ mmol kg}^{-1}$, respectively. Operating procedure references (1 ug mL^{-1} and 25 ug mL^{-1}), which were prepared from a 1000 mg L^{-1} standard solution of salts (HIGH-PURITY), normally were analyzed every 25 samples. The measurement deviation of the operating procedure references was always found to be less than 10% of the original concentrations. All seawater, melted ice

and snow samples were diluted with Milli-Q water to a desired concentration range before analysis in order to ensure the samples fell into the calibration range of the instrument.

In situ temperature measurements were done by using a model 4000 thermometer (Traceable Control Company). The snow temperature was measured by inserting the thermometer into the snow. Sea ice temperature was measured immediately after core retrieval by inserting the thermometer tip into holes which were drilled on the ice core at a resolution of 5 cm. The conductivity of the seawater, melted snow and sea ice samples was measured using a sensION 156 conductivity meter (HACH Company). Bulk salinity of the ice and snow samples was calculated from the corresponding temperature and conductivity values.

3.3 Results

3.3.1 Temperature and salinity

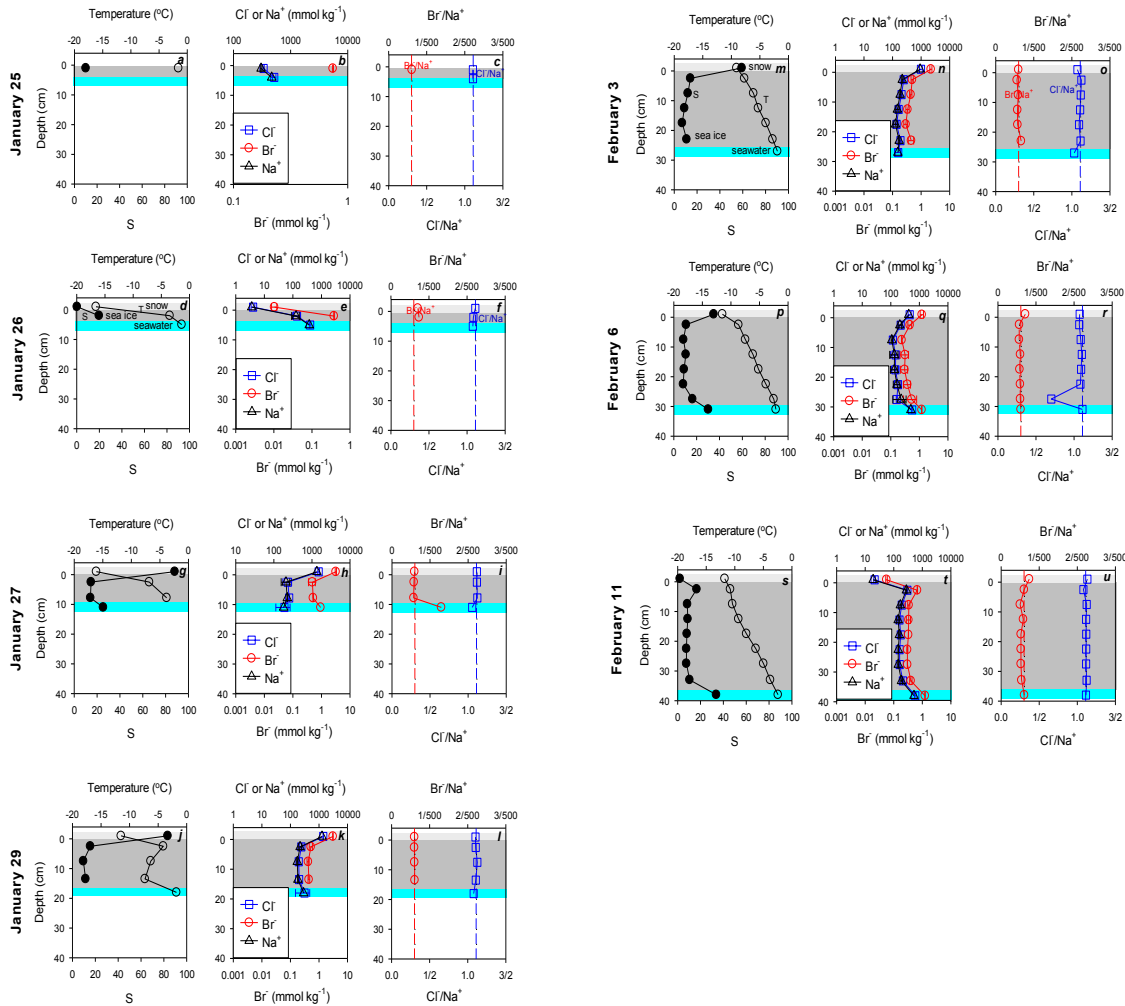
The vertical distribution profiles of temperature, salinity, the concentrations of Br^- , Cl^- and Na^+ , and the halides/ Na^+ ratios at SERF during the study period are shown in Figure 3-2. Temperature in the snow layer ranged from -9 to -17 °C, and it increased steadily throughout the sea ice to approximately -1.7 °C in the seawater. The salinity in the seawater was generally 32 and the bulk salinity in the sea ice decreased during the process of ice growth. When the ice grew to 30 cm thick on February 6, the salinity profile in the ice showed an obvious C-shaped profile. As expected, salinity was low (from 0.2 to 2) in the fresh snow and very high (up to 88) in the slush snow.

3.3.2 Ion distribution and halides/ Na^+ ratios across the snow-ice-seawater interface

Br^- , Cl^- and Na^+ concentrations exhibit a similar distribution profile, resembling that of the salinity, across the snow-ice-seawater interface (Figure 3-2 b, e, h, k, n, q and t). In the seawater,

the concentrations of Br^- , Cl^- and Na^+ were 1.23, 564 and 508 mmol kg^{-1} , respectively. While their concentrations in the sea ice were slightly lower than that in the seawater, the concentrations varied greatly in the snow. Typically, Br^- and Cl^- concentrations were very high (up to 3.19 and 1500 mmol kg^{-1} , respectively) in the slush snow, but were as low as 0.01 and 4.04 mmol kg^{-1} in the fresh snow, respectively.

Figure 3-2. Profiles of temperature (T), salinity (S), major ion concentrations and their molar ratios across the snow-sea ice-seawater interface at SERF in winter 2014. The dashed lines in c, f, i, l, o, r and u denote the molar ratios of Br^-/Na^+ (red) and Cl^-/Na^+ (blue) in the underlying seawater



Although the concentrations of the three ions show the typical C-shaped profile throughout the ice core (Thomas and Dieckmann 2010), the Br^-/Cl^- and Na^+/Cl^- ratios remain nearly constant at

1/420 and 1.10, respectively, throughout the ice core (Figure 3-2 c, f, r, l, o, r and u), which are comparable to that in the underlying seawater (except for January 27). On January 27, the Br^-/Na^+ ratio of the thin ice was slightly higher (1/340) than that in the seawater. While the Br^-/Na^+ and Cl^-/Na^+ ratios in the snow usually were close to that in the ice, the ratios on January 26 and February 11 when fresh snow fall occurred, were slightly elevated above that observed in the ice (Br^-/Na^+ ratio: 1/340 and Cl^-/Na^+ ratio: 1.13).

3.4 Discussion

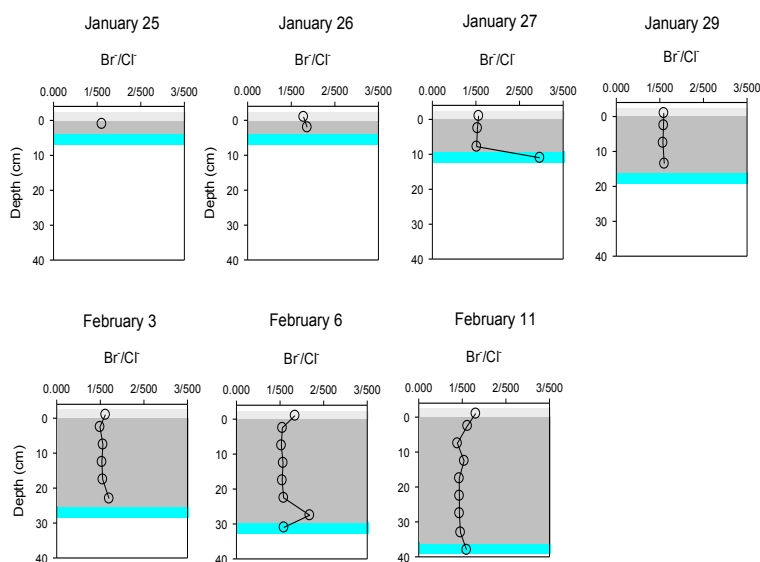
The conservative behavior of Br^- , Cl^- and Na^+ when compared with salinity across the snow-ice-seawater interface suggests that these ions in the ice and snow are mainly from the underlying seawater. Throughout the ice core, the C-shaped profiles of the bulk salinity and the ion concentrations result from advection during the ice growth (Thomas and Dieckmann 2010). Fresh snow absorbs gases and scavenge aerosols in the air during its settling process and are less influenced from the underlying ice, therefore Br^- , Cl^- and Na^+ concentrations in the fresh snow were low (Toom-Sauntry and Barrie 2002). The slush snow deposited on the ice is affected by the high concentration brine which is excluded from the ice surface, thus the slush snow samples had higher ion concentrations than the underlying sea ice.

We have no evidence to suggest the occurrence of photochemical halogen activation at SERF during the study period. Studies have suggested that halogen “seeds” for halogen activation are accumulated during long dark period before polar sunrise (See (Simpson et al. 2007, Abbatt et al. 2012) and reference therein). There is such no long dark period at SERF during which halogen seeds can accumulate. O_3 and THg measurements in the winter of 2012 and 2013 also did not show the occurrence of ODEs and AMDEs (Feiyue Wang, personal communication). Therefore

we assume the snow composition at SERF is not affected by halogen activation reactions as seen in the Arctic.

By using Na^+ as a reference, the behavior of Br^- and Cl^- in the snow can be studied. Our results show that the Br^-/Na^+ and Cl^-/Na^+ ratios in the slush snow are close to the ratios in the sea ice, suggesting that halides in the slush snow come from the ice where ions originate from the underlying seawater. However, the Br^-/Na^+ ratios in the fresh snow samples are slightly higher than the ratio in the seawater, implying fresh snow scavenges additional halides from non-sea salt source. A 4-year continuous study about fresh snow chemical composition in the Arctic reveals that Br^- and Cl^- concentrations with respect to Na^+ in fresh snow are higher than that in seawater (Toom-Sauntry and Barrie 2002). In the process of snowfall, snow absorbs gases and scavenges aerosols in the air, resulting in an additional input of halides from non-sea salt sources to the snow. Thus the initial snow composition has higher halides/ Na^+ ratios compared to sea salts.

Figure 3-3. The vertical profiles of Br^-/Cl^- ratio throughout snow, ice and seawater during sea ice growth at SERF in winter 2014



The Br^-/Cl^- ratio in snow is considered as an important factor to determine the occurrence and the final production of halogen activation. The Br^-/Cl^- ratio in the sea ice remains near constant around 1/500 in our study (except for January 27), which is the same as that in the seawater (Figure 3-3). The ratio in snow samples is higher (1/350) than that in the ice on January 26, February 6 and February 11 whereas it is comparable to that in the ice on other sampling days. Thus we conclude that snow in natural environment tends to have a Br^-/Cl^- ratio that is more than or close to the ratio in the underlying sea ice or seawater.

A laboratory study shows that when the Br^-/Cl^- ratio of the condensed phase is close to the ratio in the standard seawater (1/650), Br_2 is the favored product; on the other hand, more BrCl is produced when the Br^-/Cl^- ratio is lower (Adams 2002). Snow samples which were found to release Br_2 in a recent chamber experiment are characterized by a high Br^-/Cl^- ratio (1/38 -1/148) (Pratt et al. 2013). As well, the production of Cl_2 and BrCl are observed from artificial snow with a Br^-/Cl^- ratio that is much lower than the ratio in the standard seawater (Wren et al. 2013). According to our study, the Br^-/Cl^- ratio in the snow at SERF is generally greater than or equal to 1/650, which is consistent with the ratio in some of the snowpack from our field measurement (Chapter 2). Under these conditions, Br_2 and BrCl would be predominant products in halogen activation.

3.5 Conclusions

SERF is a simulated sea ice environment of the Arctic and the results in our study illustrate halide distributions in snow, sea ice and seawater in the absence of springtime photochemical reactions. Br^- and Cl^- concentrations show a typical C-shaped profile in the sea ice while their concentrations are variable in the snow. Slush snow has higher halide concentrations than the sea ice, implying the snow is contaminated by high-concentrated brine layer on the surface of the ice.

Despite the very low halide concentrations in fresh snow, halides/ Na^+ ratios are slightly higher than that in seawater. We believe that there are non-sea salt halides source in the atmosphere and they can be scavenged by snow during snow settling process. In addition, the Br^-/Cl^- ratio in the snow is generally greater than or equal to the ratio in the standard seawater, which suggests that snowpack on sea ice in natural environment tends to produce more Br_2 and BrCl than Cl_2 in halogen activation.

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Chapter 4: Conclusions and future directions

4.1 Research conclusions

Although various condensed substrates (e.g., snow, sea ice, frost flowers, aerosols) have been proposed to be the site where boundary layer halogen activation takes place during springtime in the Arctic, many previous studies support that snow is the most likely place for such halogen activation (Foster et al. 2001, Spicer et al. 2002, Avallone et al. 2003, Wren, Donaldson and Abbatt 2013, Pratt et al. 2013). Halides (Br^- and Cl^-) in snow are found to show both enrichment and depletion, with respect to Na^+ , compared to that in sea salt (Jacobi et al. 2012, Krnavek et al. 2012, Simpson et al. 2005). Thus the initial concentrations of halides in snow and their behaviors during halogen activation are important for understanding the chemical process in the snow associated with halogen activation.

As discussed in Chapter 1, the objectives of this study are to analyze Br^- and Cl^- distributions across the snow-sea ice-seawater interface and to investigate the halide behaviors in the absence or presence of halogen activation. The study also aims to shed new insight into the mechanism of halogen activation based on halogen species produced at different stages of the activation as the Br^-/Cl^- ratio changes in the snow.

Comparative studies were carried out in the experimental sea ice environment in a mesocosm facility (SERF) in Winnipeg during winter 2014 and in the natural sea ice environment near Cambridge Bay of the Canadian Arctic Archipelago during spring 2014. At both sites, sea ice, the underlying seawater and overlying snow were sampled and analyzed for Br^- , Cl^- and Na^+ , along with ancillary parameters such as temperature, salinity and total mercury concentration.

At the Cambridge Bay field site (Chapter 2), the Br^- and Cl^- concentrations in the upper snow layer (less than 0.002 and 0.7 mmol kg^{-1} , respectively) of the snowpack are generally lower than that in the bottom 14 cm (up to 0.35 and 240 mmol kg^{-1} , respectively). Moreover, the surface 5 cm snow layer is commonly found to have slightly higher Br^- and Cl^- concentrations than the layers below (except for the bottom 14 cm). We conclude that higher halide concentrations in the bottom 14 cm snow compared to other layers are a result of upward migration and diffusion from the underlying sea ice where the ions originate from the seawater. The slightly higher concentrations of halides in the surface 5 cm snow layer are due to the deposition of blowing snow that scavenges halides from non-sea salt sources.

The halides/ Na^+ ratios in the snowpack are typically higher than that in the underlying seawater and the ratios decrease from the 14 cm depth of the snowpack to the surface. Based on previous studies on snow chemical composition, we suggest that fresh snow scavenges non-sea salt halides during its settling, which results in halide enrichment in the initial snow compared to the seawater. The decrease in the halides/ Na^+ ratios in the upper snow layer is indicative of the loss of halides from the snowpack, which is consistent with the recent finding that snow is the most likely place for halogen activation. The occurrence of halogen activation in the study area is confirmed by the high THg concentrations in the snowpack. The production of halogens from the snow is estimated by calculating the loss of halides from the snowpack. The results show that halogens that are released from the snow can indeed explain the observed reactive halogen concentrations reported in the springtime polar boundary layer. Also, the calculation indicates that snow releases more reactive chlorine than reactive bromine.

Based on the profiles of the Br^-/Cl^- ratio in the snowpack, a mechanism of halogen activation is proposed. The continuous halogen activation would lead to the changes in the Br^-/Cl^- ratio in the

snow, which eventually affects the dominant products formed in the activation. The initial Br^-/Cl^- ratio is higher in our study (up to 1/97), which would result in the predominant production of Br_2 . As the Br^-/Cl^- ratio in the snow decreases to around 1/650 which is close to the ratio in the standard seawater, the snow tends to produce both Br_2 and BrCl . More BrCl would be formed if the Br^-/Cl^- ratio in the snow decreases further. Eventually, when the ratio is much lower than that in seawater, Cl_2 would be the favored product from snow.

In the SERF mesocosm study (Chapter 3), halides in the fresh snow are enriched, with respect to Na^+ , compared to in the seawater. This measurement reinforces the observation from Chapter 2 that snow scavenges non-sea salt halides from the atmosphere which leads to halide enrichment in the initial snow compared to the seawater. Moreover, the Br^-/Cl^- ratio in the snow is typically greater than or equal to the ratio in standard seawater (1/650), suggesting that snow tends to produce more Br_2 and BrCl than Cl_2 in the halogen activation.

Our study provides the initial halide concentrations in snow and supports the current view that snow, which scavenges halides from non-sea salt sources, plays a vital role in halogen activation. The proposed mechanism of halogen activation could improve our understanding about the effect that changes in the value of the Br^-/Cl^- ratio have on the products formed from halogen activation in snow, which could eventually help evaluate the potential influence of halogen activation on ODEs and AMDEs.

4.2 Future directions

Snow has been proposed as the most likely place for halogen activation and thus a better understanding of snow physical and chemical properties as related to halogens is needed. In this study, we analyzed concentrations of halides (Br^- and Cl^-) across the snow-sea ice-seawater

interface in the springtime Arctic and in a mesocosm sea ice environment, which provides new insight in investigating the role of snow in halogen activation. In future studies, we suggest to analyze halide concentrations and other snow properties (e.g., pH, NO_3^- concentration, density and morphology) at the same time to identify effects of different snow properties on halogen activation. In the meantime, in-situ reactive halogen species (e.g. BrO , BrCl or Cl_2), O_3 and GEM in the air above the snow surface and in the interstitial air of snowpack are recommended to be measured to help to interpret the data obtained from the condensed snow phase.

In order to better understand the loss of halides from snow and the effects of halogen activation on halide concentrations, changes in the halides/ Na^+ ratios in the snow before, during and after polar sunrise should be thoroughly investigated. In addition to field measurements, simulative experiments about halogen activation from snow can also be conducted in laboratories. Halogen activation can be simulated using artificial snow; measurements of changes in the Br^-/Cl^- ratio in the snow before, during and after halogen release would help to understand the mechanism of halogen activation.

In addition, since elevated concentrations of iodine oxide (IO , $\sim 3.4 \text{ pmol mol}^{-1}$) have been also detected within 100 m above the surface in the eastern coast of Hudson Bay (Canadian high Arctic), which can greatly increase the rate of bromine-catalyzed O_3 depletion (Mahajan et al. 2010). Thus the measurement of iodide and iodate in snow in the Arctic is also suggested. The relationship of iodine related species in the air to ODEs and AMDEs needs to be investigated further.

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