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Halocarbons Associated with Arctic Sea Ice

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Abstract

Short-lived halocarbons were measured in Arctic sea-ice brine, seawater and air above the Greenland and Norwegian seas (~81°N, 2 to 5°E) in mid-summer, from a melting ice floe at the edge of the ice pack. In the ice floe, concentrations of C_2H_5I, 2-C_3H_7I and CH_2Br_2 showed significant enhancement in the sea ice brine, of average factors of 1.7, 1.4 and 2.5 times respectively, compared to the water underneath and after normalising to brine volume. Concentrations of mono-iodocarbons in air are the highest ever reported, and our calculations suggest increased fluxes of halocarbons to the atmosphere may result from their sea-ice enhancement. Some halocarbons were also measured in ice of the sub-Arctic in Hudson Bay (~55°N, 77°W) in early spring, ice that was thicker, colder and less porous than the Arctic ice in summer, and in which the halocarbons were concentrated to values over 10 times larger than in the Arctic ice when normalised to brine volume. Concentrations in the Arctic ice were similar to those in Antarctic sea ice that was similarly warm and porous. As climate warms and Arctic sea ice becomes more like that of the Antarctic, our results lead us to expect the production of iodocarbons and so of reactive iodine gases to increase.

1. Introduction

There has been much speculation about sources of reactive halogens in the polar troposphere. The presence of high concentrations of both iodine and bromine monoxide (IO and BrO) over Antarctica and its sea ice [*Saiz-Lopez et al.* 2007, *Schoenhardt et al.* 2008] suggests an iodine-selective mechanism, as the sum of iodide plus iodate is 1000 times less abundant than bromide in seawater. Although IO has been measured above sub-Arctic sea ice at amounts of up to 4 pptv [*Mahajan et al.* 2010], this is less than a quarter the Antarctic concentrations.

Iodine and bromine radicals in the atmosphere form oxides via ozone depletion mechanisms [*Chameides and Davis* 1980, *Davis et al.* 1996] and the oxidising capacity may be altered by reactions involving HO_x (OH + HO_2) and NO_x (NO +NO_2) [*Davis et al.* 1996]. Iodine compounds are also important because they form higher oxides which can form new particles [*O'Dowd et al.* 2002]; if they grow to the size of cloud condensation nuclei they may impact climate via increased scattering of sunlight [*Slingo*, 1990]. Hence understanding the processes which control the volatilisation and release of halogens in polar regions is important for regional chemistry and climate.

Diatoms are known to live in sea ice brine channels [*Garrison & Buck* 1989], and the production of halocarbons by diatoms is well established [*Sturges et al.* 1992, *Tokarczyk & Moore* 1994], via enzymes active in the metabolism of the cell [*Manley* 2002, *Moore et al.* 1996].

Previous halocarbon measurements in the Arctic are summarised in Supplementary Tables S1 and S2. Enhanced concentrations have been measured in sea ice brine and ice covered water. In Hudson Bay, halocarbons were observed in air in the absence of open leads [*Carpenter et al.* 2005]; for some iodocarbons they were the highest atmospheric concentrations ever recorded. The authors proposed an abiotic mechanism for their production via the reaction of HOI with humic material in the quasi-liquid layer on the surface of sea ice.

Halocarbon measurements have so far been unable to account for the iodine atom flux necessary to maintain the high concentrations of IO found in Antarctica [e.g. *Carpenter et al.* 2007], but inorganic iodine compounds are implicated [*Atkinson et al.* 2012]. Until recently, there was a large difference in the sea ice of the Arctic and Antarctic, the Arctic being thicker, colder, and more likely to be multi-year [*Arrigo and Thomas*, 2004]. As the planet warms and Arctic sea ice thins and retreats, the ice is becoming ever more like that of the Antarctic, which has implications for ice biota and the release of compounds produced.

Here, we present halocarbon measurements from air, sea ice brine and underlying seawater, from a ship moored against an ice floe while it drifted south and partly melted, and from the nearby open ocean – for the first time in the pack ice of the Arctic Ocean. We estimate the fluxes and loss processes, discuss production pathways and the effect of ice conditions. We also compare the results to those from very different sub-Arctic ice in early spring, and to earlier results in Antarctic sea ice with similar properties to those in the Arctic summer.