The polar iodine paradox

The uneven presence of iodine in the polar regions presents a scientific challenge, which connects marine algae, ice and atmosphere.

Ozone has long been a research focal point in climate science as it protects life from extreme UV radiation in the upper part of Earth's atmosphere (stratosphere) and acts as a greenhouse gas, oxidant, and air pollutant in Earth's lower atmosphere (troposphere). Therefore, any gas or process that perturbs ozone concentrations could affect one (or more) of its vital functions.

Similar to other halogens (bromine, chlorine, fluorine), iodine (from the Greek word ioeides — meaning violet or purple due to the color of elemental iodine vapor) exists as a diatomic molecule $\text{I}_2(g)$. Iodine is commonly known as a vital human nutrient but is also used in a suite of other applications, such as disinfectants, solar cells, colposcopy, counterfeit banknote detection pens, and the production of select polymers.

Iodine appears to also be a dominant player in destroying ozone ($\text{O}_3(g)$) over coastal Antarctic sea-ice while bromine's role is comparatively less (Saiz-Lopez et al., 2007). Conversely, bromine governs ozone destruction over Arctic sea-ice while iodine has not been shown to participate (Simpson et al., 2007). Iodine also contributes to aerosol formation, which can lead to cooling Earth's atmosphere (O'Dowd et al., 2002).

In Antarctica, ground- (Saiz-Lopez et al., 2007a; Atkinson et al., 2012; Friess et al., 2001) and satellite-based instrumentation (Saiz-Lopez et al., 2007b; Schönhardt et al., 2008) have measured some of the highest levels of active atmospheric iodine species, iodine oxide ($\text{IO}_x(g)$), seen anywhere on Earth in air that had freshly advected over sea ice, but also recorded significant levels of IO in air which had spent several days over the interior of the continent. Satellite observations have also shown substantial and widespread levels of iodine close to the South Pole (Schönhardt et al., 2008). In contrast, only an order of magnitude smaller amounts of active iodine were detected sporadically and localized in the sub-Arctic troposphere, Kuujjuarapik, Hudson Bay, Canada (Mahajan et al., 2010), but not directly over Arctic sea-ice. This is in contrast to bromine and chlorine that are evenly present in the Arctic and Antarctic. What then, governs this Northern/Southern polar iodine dichotomy (Fig. 1)?

Antarctica contains the largest algal population of any

Fig. 1. Ice and iodine. Active iodine species produced by ice algae and surface inorganic processes are released to the Antarctic atmosphere, where they destroy ozone and form condensation nuclei. This active presence of iodine in the southern polar atmosphere is not present in the Arctic.
environment in the world, primarily as micro-algae (diatoms) (Thomas and Dieckmann, 2003). Moreover, both macro- and micro-algae species have been shown to be strong accumulators of iodine with enhanced iodine concentrations of up to \(-10^3\) to \(-10^6\) greater than in seawater (Leblanc et al., 2006). Scientists believe that algae accumulate iodine as an inorganic antioxidant, and upon oxidative stress the iodine is effluxed by these living organisms (Küpper et al., 2008). This mechanism could trigger the biological emission of iodine from ice algae contained within and underneath Antarctic sea ice, and escape to the atmosphere through sea ice brine channels or cracks (Saiz-Lopez, 2015).

Another major difference between the two polar regions is that coastal Antarctic sea-ice thickness is on average approximately 6 times less (\(-50\) cm) than Arctic sea-ice (\(-3\) m) (Thomas and Dieckmann, 2003). Therefore, it would take longer for iodine, released by algae at deeper depths in Arctic sea-ice to be transported to the surface of ice and to be liberated to the atmosphere. This difference in sea-ice thickness would also allow for greater propagation of sunlight, which induces algal oxidative stress and hence iodine production, to reach algae contained throughout the Antarctic sea-ice and underneath. Light transmitted through Antarctic sea-ice has an e-folding depth of \(-50\) cm and has significant transmission down to \(-1\) m (King et al., 2005). This potentially could lead to greater iodine excretion rates from Antarctic sea-ice algal populations (Küpper et al., 2008).

To bring clarity to some of these unresolved questions, iodine chemistry has been a focus of a suite of laboratory, field and modeling experiments. For instance, at low pH greater amounts of I\(_2\)(g) and IO\(_x\)(g) were released upon reacting iodine and ozone at aqueous surfaces (Sakamoto et al., 2009). Laboratory studies also showed that the type of organics present at such aqueous surfaces can promote (acetic, malonic, hexanoic, and octanoic acid, (Hayase et al., 2011)) or suppress (anionic phenolates, (Hayase et al., 2010)) IO\(_x\)(g) production. Additional work showed a decrease in the uptake of ozone onto deliquesced KI particles, coated with linear saturated fatty acids (Rouviere and Ammann, 2010). The pH of the Arctic and Antarctic sea-ice ranges from \(-4\) to 5 and \(-4.5\) to \(-6.5\), respectively (de Curitat et al., 2005; Ali et al., 2010). Combined field, laboratory, and modeling analyses showed that the abiotic production of iodine, on the surface of ice, plays a minor role in the overall production of iodine, which suggests a predominance of biological processes as a source of reactive iodine in the Antarctic region (Kim et al., 2016; Gálvez et al., 2015). Despite these studies, described therein, no measurement technique has measured any atmospheric active iodine over Arctic sea-ice. Is it then possible that Arctic sea-ice contains the right ingredients: 1) types of organic molecules, 2) overall pH, and 3) sea-ice thickness, to enhance the production and release of gaseous reactive iodine?

Iodine plays an important role in marine and atmospheric processes through the formation of condensation nuclei and the destruction of ozone while iodine ozone depletion efficiency is higher than that of bromine and chlorine. Interestingly, if the emission of iodine is found to be sensitive to sea ice thickness, the currently observed asymmetry in the iodine presence between both polar regions may change in the future as Arctic sea ice thins due to climate change, allowing the release of active iodine to the Arctic atmosphere. Therefore, the polar iodine paradox is probably one of the remaining major open questions in the chemistry of the polar troposphere.

References


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