



# Mercury in Arctic snow: Quantifying the kinetics of photochemical oxidation and reduction



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## HIGHLIGHTS

- Mercury photochemical kinetics were studied in frozen and melted Arctic snow.
- UV-induced photoreduction and photooxidation rate constants were quantified.
- Chloride ion, iron, and DOC influence mercury photoreactions in snow.
- Frozen and melted snow have different mercury photoreduction characteristics.
- Kinetic information provided can be used to model mercury fate in the Arctic.

## ARTICLE INFO

### Article history:

Received 30 January 2014

Received in revised form 27 June 2014

Accepted 7 July 2014

Available online 3 August 2014

### Keywords:

Mercury  
Photochemistry  
Arctic  
Snow  
Kinetics  
Snowmelt

## ABSTRACT

Controlled experiments were performed with frozen and melted Arctic snow to quantify relationships between mercury photoreaction kinetics, ultra violet (UV) radiation intensity, and snow ion concentrations. Frozen ( $-10\text{ }^{\circ}\text{C}$ ) and melted ( $4\text{ }^{\circ}\text{C}$ ) snow samples from three Arctic sites were exposed to UV (280–400 nm) radiation ( $1.26\text{--}5.78\text{ W}\cdot\text{m}^{-2}$ ), and a parabolic relationship was found between reduction rate constants in frozen and melted snow with increasing UV intensity. Total photoreduced mercury in frozen and melted snow increased linearly with greater UV intensity. Snow with the highest concentrations of chloride and iron had larger photoreduction and photooxidation rate constants, while also having the lowest Hg(0) production. Our results indicate that the amount of mercury photoreduction (loss from snow) is the highest at high UV radiation intensities, while the fastest rates of mercury photoreduction occurred at both low and high intensities. This suggests that, assuming all else is equal, earlier Arctic snow melt periods (when UV intensities are less intense) may result in less mercury loss to the atmosphere by photoreduction and flux, since less Hg(0) is photoproduced at lower UV intensities, thereby resulting in potentially greater mercury transport to aquatic systems with snowmelt.

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## 1. Introduction

Mercury is a toxic contaminant that moves into aquatic ecosystems in many ways, including snowmelt in the spring, and can bioaccumulate and biomagnify in Arctic food webs (Atwell et al., 1998; Swanson and Kidd, 2010). The environmental behavior of mercury is dependent on its speciation. Elemental Hg (Hg(0)) has a high vapor pressure and is the primary form of Hg in the atmosphere (Lindqvist and Rodhe, 1985; Morel et al., 1998; Wängberg et al., 2007), in the air spaces of soils and snow (Dommergue, 2003; Fain et al., 2006; Ferrari et al., 2004b; Moore and Castro, 2012; Obrist et al., 2014; Sigler and Lee, 2006), and as dissolved gaseous mercury in water (O'Driscoll et al.,

2008). Oxidized forms of mercury (Hg(II), free or within organic complexes) predominate in condensed phases such as natural waters (Morel et al., 1998; Ullrich et al., 2001), sediments (Bloom et al., 1999), and the water-filled pores and solid phases of soils (Skjyllberg, 2011), and in snow (Ferrari et al., 2004a; Poulain et al., 2007). Methylmercury (MeHg) is the bioaccumulative form of Hg (Atwell et al., 1998; Bartels-Rausch et al., 2011), and the formation of MeHg in ecosystems depends on, among other factors, the presence of Hg(II) (Mason and Sheu, 2002). The Arctic is a region where mercury retention is of significant interest due to high Hg concentrations reported in Arctic biota (Carrie et al., 2010; Kirk et al., 2012; Muir et al., 1992), and a predicted 25% increase in atmospheric inputs by 2020 (AMAP, 2011). This presents potential problems to Arctic indigenous populations who rely heavily on higher trophic level wildlife such as marine mammals as a food source (Barrie et al., 1992; Kinloch et al., 1992). To predict

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increasing mercury loading to Arctic biota, it is necessary to develop predictive models incorporating reactions regulating mercury retention and movement between Arctic environmental media (snow, air, water).

Snow and snowmelt are important ways for Hg(II) to move within and between Arctic ecosystems. Snow is a complex environmental medium consisting of solid, gaseous and liquid phases, and it can scavenge mercury and particles from the atmosphere (Ebinghaus et al., 1999; Gardfeldt et al., 2001; Schroeder and Munthe, 1998). Mercury can also be deposited to snow via dry gaseous or dry particle deposition (Cobbett et al., 2007; O'Driscoll et al., 2005; Schroeder and Munthe, 1998). Once present in snow, mercury is labile, undergoing reactions and changing speciation (Lalonde et al., 2002; Poissant et al., 2008; Schroeder and Munthe, 1998). In Arctic and sub-Arctic regions, atmospheric mercury can be deposited to the snow surface by atmospheric mercury depletion events (AMDEs) (Ariya et al., 2004; Ariya et al., 2002; Kirk et al., 2006; Schroeder et al., 1998; Steffen et al., 2008), resulting in total mercury (THg) concentrations in snow as high as  $820 \text{ ng} \cdot \text{L}^{-1}$  (Douglas et al., 2005). Some research suggests that this is a transient effect, with snow THg concentrations falling to pre-AMDE levels within 24 to 48 h due to the labile nature of AMDE-deposited mercury, which is quickly reduced and lost from snow (Aspmo et al., 2006; Dommergue et al., 2010; Kirk et al., 2006). Still other research suggests that AMDEs represent a significant source of Hg to Arctic snow since some deposited mercury is retained and transported with snow melt (Dommergue et al., 2003; Hirdman et al., 2009; Johnson et al., 2008; Loseto et al., 2004; Steffen et al., 2005).

The environmental fate of Hg depends on its speciation and this is critical to the debate concerning deposition and retention processes in Arctic snow. Oxidized Hg, or Hg(II), is the form that will remain in the snowpack, and has the ability to be transformed into the bioaccumulative and toxic methylmercury, while reduced Hg, or Hg(0), is volatile and does not sorb appreciably to ice crystals (Bartels-Rausch et al., 2008), so it will tend to be removed from a snowpack, with wind pumping accelerating this removal (Faïn et al., 2013; Ferrari et al., 2005). This means that a greater fraction of Hg(II) and more photooxidation, or formation of Hg(II) from Hg(0), over photoreduction would make a snowpack a greater mercury source to aqueous environments upon melting.

Photochemical reactions have been identified by many researchers as critical mechanisms driving mercury oxidation and reduction in snow (Durnford and Dastoor, 2011; Lalonde et al., 2002; Poulain et al., 2004); however, limited data are available and often assume linear kinetics, that is, linear relationships between radiation and rates (Durnford and Dastoor, 2011). Lalonde et al. (2003) and Poulain et al. (2004) determined that mercury oxidation can occur in snow, but no kinetic rates were derived. Faïn et al. (2006) found the rate of Hg(0) oxidation in snow to be  $0.5\text{--}0.7 \text{ pmol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ , but did not report a rate constant. Dommergue et al. (2007) measured reduction rate constants of  $0.25 \text{ h}^{-1}$  or  $0.18 \text{ h}^{-1}$  by continuously monitoring the decrease in mercury in headspace above irradiated snow over time. Other groups have determined the rate of mercury reduction in snow to range between  $0.25 \text{ pmol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$  and  $1.60 \text{ pmol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ , but no rate constants have been reported, and these determinations were based on a limited number of available data points (Lalonde et al., 2003; Lalonde et al., 2002; Poulain et al., 2007; Poulain et al., 2004). This wide variation in reaction rates, up to a six-fold difference, makes the development of an accurate predictive model difficult (Dastoor et al., 2008; Durnford and Dastoor, 2011; Soerensen et al., 2010), and the assumption of linearity used to determine kinetics, while true over short time periods, may not necessarily hold true over longer time frames (e.g., daily or seasonally), meaning that the predicted rates may not be accurate. With this wide range in oxidation and reduction rates, it is difficult to say whether oxidation (maintenance or increase of Hg levels in snow) or reduction (potential loss of Hg from snow) in snow is dominant or faster, since reported oxidation rate constants are on the same order as the reported reduction rate constants.

The variability in reported reaction rates is likely due to differences in sampling and analytical techniques, combined with an inability to control the wide range of chemical and physical variables affecting in-situ measurements of mercury speciation and oxidation/reduction (Durnford and Dastoor, 2011; Mann et al., 2014). Sequestration of reactive mercury by dissolved organic carbon (DOC) and chloride ions ( $\text{Cl}^-$ ), or photosensitization of reactions by DOC, may be important in determining the balance of photoreduction and photooxidation in the snowpack. In natural waters, DOC is important to Hg photoreactions (Xiao et al., 1995; Zhang, 2006); it is important to note, however, that very little is known about DOC action in snow, and as such, relationships determined in natural water systems may not hold true in snow. Chloride has been found to enhance Hg photooxidation, or suppress Hg photoreduction in snow (Lalonde et al., 2003), thereby influencing the kinetics of Hg reaction. In addition, physical variables such as the energy and spectra of the incident radiation are also important (Bartels-Rausch et al., 2011; Lalonde et al., 2003; St. Louis et al., 2007). Several researchers have proposed ultraviolet-B (UVB) radiation (280–320 nm wavelengths) as a primary driver of mercury reduction in snow (Dommergue et al., 2007; Durnford and Dastoor, 2011; Lalonde et al., 2003). In contrast, Bartels-Rausch et al. (2011) found ultraviolet-A (UVA) radiation (320–400 nm) induced mercury reduction in ice film experiments, and Faïn et al. (2007) determined that UVA radiation plays an active role in mercury photochemical processes in snow. While there are few studies examining mercury photooxidation in snow, UVA radiation has been proposed as the driving variable (Durnford and Dastoor, 2011). Although the balance of photoreduction and oxidation processes is still unclear, studies suggest there is predominantly a net reduction effect with exposure to natural solar radiation (Ariya et al., 2004; Lalonde et al., 2002, 2003). However, the effects of UV irradiation intensity on the separate processes of mercury photochemical oxidation and reduction in snow have not been determined.

Currently, there are knowledge gaps surrounding the effects of irradiation intensity, irradiation quality,  $\text{Cl}^-$ , and DOC on the fundamental processes of mercury photochemical oxidation and reduction in frozen snow (reviewed in Durnford and Dastoor (2011) and Mann et al. (2014)). As such, accurate predictive models are difficult to develop and have limited our ability to predict the distribution of mercury in polar ecosystems affected by a changing climate. In this study, we used controlled experiments to examine the influence of these factors on Hg photoreduction in Arctic snow, and made the following hypotheses: (i) reduction of Hg(II) in Arctic snow, both frozen and melted, is related to UV radiation intensity, with greater photoreduction of Hg(II) occurring at greater radiation intensities; and (ii) chemical species present in the snowpack, specifically chloride ions and DOC, will influence the rate and/or extent of Hg photochemical reactions in the snow.

## 2. Methods

### 2.1. Field sampling

Surface snow (5–10 cm) was collected from three sites near the Polar Continental Shelf Program research base in Resolute Bay, NU, Canada (74.6975°N, 94.8322°W) from 8 to 12 of March 2012 in late morning (Table A.1). It should be noted that snow samples were more than 24 h old, and no snowfall was observed over the course of our sample collection. Site 1 was located near the shore of a small ice covered pond, Site 2 was on the shaded side of a hill and Site 3 was located nearest to Resolute; sites were chosen to cover the general variation in snowpack cover and depth, and sampling locations, (sunny, shaded or rocky) seen in the Resolute Bay area. Snow was stored in 2.2 L PTFE Teflon bottles (multiple Milli-Q water rinses) double bagged in Ziplocs® and sealed in dark coolers in a freezer ( $< -20 \text{ }^\circ\text{C}$ ) until analysis. At each site, seven bottles of frozen snow (snow collected, shipped and stored without melting) and six bottles of melted snow (snow collected then

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