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Mercury photoreduction and photooxidation in lakes: Effects of filtration and dissolved organic carbon concentration

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ABSTRACT

Mercury is a globally distributed, environmental contaminant. Quantifying the retention and loss of mercury is integral for predicting mercury-sensitive ecosystems. There is little information on how dissolved organic carbon (DOC) concentrations and particulates affect mercury photoreaction kinetics in freshwater lakes. To address this knowledge gap, samples were collected from ten lakes in Kejimkujik National Park, Nova Scotia (DOC: 2.6–15.4 mg/L). Filtered (0.2 μm) and unfiltered samples were analysed for gross photoreduction, gross photooxidation, and net reduction rates of mercury using pseudo first-order curves. Unfiltered samples had higher concentrations ($p = 0.04$) of photoreducible divalent mercury ($Hg(II)_{RED}$) (mean of 754 ± 253 pg/L) than filtered samples (mean of 482 ± 206 pg/L); however, gross photoreduction and photooxidation rate constants were not significantly different in filtered or unfiltered samples in early summer. DOC was not significantly related to gross photoreduction rate constants in filtered ($R^2 = 0.43$; $p = 0.08$) and unfiltered ($R^2 = 0.02$; $p = 0.71$) samples; DOC was also not significantly related to gross photooxidation rate constants in filtered or unfiltered samples. However, DOC was significantly negatively related with $Hg(II)_{RED}$ in unfiltered ($R^2 = 0.53$; $p = 0.04$), but not in filtered samples ($R^2 = 0.04$; $p = 0.60$). These trends indicate that DOC is a factor in determining dissolved mercury photoreduction rates and particles partially control available $Hg(II)_{RED}$ in lake water. This research also demonstrates that within these lakes gross photoreduction and photooxidation processes are close to being in balance. Changes to catchment inputs of particulate matter and DOC may alter mercury retention in these lakes and could partially explain observed increases of mercury accumulation in biota.

Introduction

Mercury is a toxic metal that is present in the environment in several forms. Elemental mercury (Hg(0)) is highly volatile, and is the dominant form in the atmosphere due to its low solubility in water and high vapour pressure. Divalent mercury (Hg(II)) is highly soluble and is the primary form deposited to freshwater ecosystems. Once in these ecosystems, Hg(II) can readily bind to

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particles and dissolved ligands (such as dissolved organic matter (DOM)) in lake water (Allard and Arsenie, 1991; Garcia et al., 2005a; Xiao et al., 1995). Some of the available Hg(II) in a lake may be subsequently converted to organic mercury compounds, primarily methyl mercury ($CH_3Hg(I)$) which can bioaccumulate in food webs and cause neurotoxic effects in upper trophic level organisms (Schroeder and Munthe, 1998).

Dissolved gaseous mercury (DGM) is thought to be primarily comprised of Hg(0) formed from *in situ* Hg(II) reduction reactions (O'Driscoll et al., 2004; Schroeder and Munthe, 1998). DGM can volatilise from water to air and thus be removed from aquatic ecosystems (Fig. 1; O'Driscoll et al., 2005). Some studies have shown that DGM volatilisation can equal the mass of mercury input from wet deposition in many freshwater systems (Amyot et al., 1994; O'Driscoll et al., 2005), and volatilisation from the world's oceans may account for approximately 30% of total global mercury emissions to the atmosphere (Mason et al., 1994). Although several mercury cycling models, such as the Regional Mercury Cycling Model (Harris et al., 1996), have been produced, there are still large sources of error in the mercury flux values produced by these models, particularly when comparing between ecosystems (Schroeder and Munthe, 1998). One reason for the large errors in mercury flux values may be that the specific processes and fundamental reaction rates governing mercury photoreduction and photooxidation have neither been quantified, nor related to lakewater characteristics (Lalonde et al., 2001).

Atmospheric mercury is globally distributed and can be deposited through rainfall and other deposition processes to remote ecosystems with no point sources (Fitzgerald et al., 1998; O'Driscoll et al., 2005). While deposition patterns vary, there is no clear explanation as to why some remote lakes have elevated levels of mercury while other similar lakes do not (Lavoie et al., 2013). Research by the METAALICUS mercury research network and others has shown that substantial amounts of Hg(II) deposited to lakes are quickly reduced to Hg(0) by solar radiation-driven reactions, and this volatilises back to the atmosphere (38%–59% after eight weeks) (Amyot et al., 1997; Orihel et al., 2007). Orihel et al. (2007) also suggest that the remaining mercury that is not volatilised is more efficiently incorporated into the food web than previously present mercury; however, recent work by Luo et al. (2017) found that with time, the reactivity and bioavailability of mercury deposited to aquatic environments decrease, potentially through the formation of mercury (II) sulphide (HgS) by photoreactions of mercury and DOM. Therefore, the higher the efficiency of photoreduction, and the greater the time elapsed since deposition, the less likely it is that mercury will be retained in a lake and subsequently methylated to the bioaccumulative form. We know from previous work that ultraviolet (UV) radiation (280–400 nm) is key to both photoreduction and photooxidation reactions of mercury in freshwater systems (Amyot et al., 1994; O'Driscoll et al., 2006).

The lakes in Kejimkujik National Park (KNP), Nova Scotia, Canada are an especially suitable system for this study not

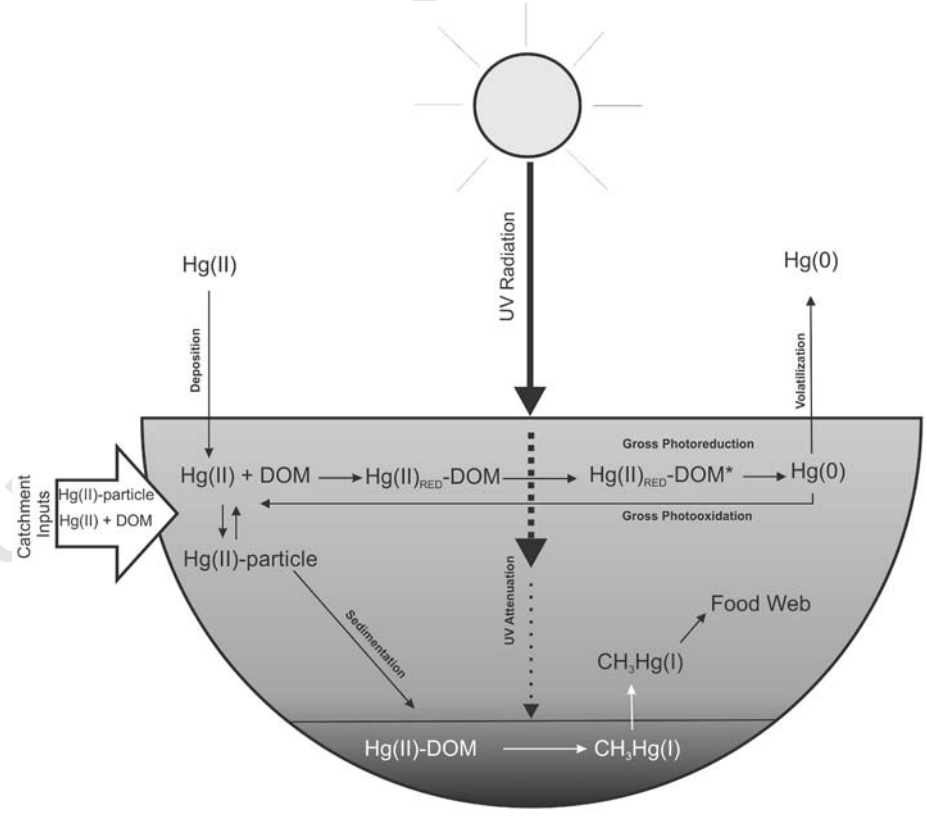

Fig. 1 – Conceptual diagram showing relationships between mercury gross photoreduction, gross photooxidation, $Hg(II)_{RED}$, DOM and particles in a typical freshwater lake. Intramolecular DOM facilitated mercury photoreaction is proposed (adapted from Vost et al. (2011)). $Hg(II)_{RED}$: photoreducible divalent mercury; DOM: dissolved organic matter.

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