



Effects of ultraviolet radiation on mercury isotope fractionation during photo-reduction for inorganic and organic mercury species



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ABSTRACT

Photo-reduction of mercury (Hg) is an important mechanism for removal of both Hg²⁺ species and monomethylmercury (MMHg) from surface waters. Large mass independent fractionation (MIF) signatures of Hg isotopes preserved in natural samples are thought to reflect MIF produced during aqueous photo-reduction by the magnetic isotope effect (MIE). Recently, Hg MIF signatures in natural samples are being used to quantify photochemical reduction in aquatic systems. However, the fractionation factors used are from laboratory experiments that did not investigate many of the environmental parameters that may affect MIF during photo-reduction. In this study, the effects of different regions of the solar spectrum on the expression of MIF caused by the MIE during Hg²⁺ and MMHg photo-reduction were investigated to assess how the type of radiation affects the extent and signature of MIF. Photo-reduction in the presence of DOM was carried out through exposure to the full natural solar spectrum unfiltered, with the ultraviolet B (UVB; 290–320 nm) portion removed and with both the UVB and the ultraviolet A (UVA; 320–400 nm) removed. There is a clear relationship between the expression and magnitude of MIF and the energy of incident radiation for both Hg²⁺ and MMHg photo-reduction. The experiments indicate that MIF produced during photo-reduction of Hg²⁺ is significantly influenced by both UVB and UVA radiation. For MMHg photodemethylation, however, UVB radiation is mostly responsible for the MIF with minor contributions from UVA. Overall, there is a lack of correlation between the observed MIF and total photo-reduction in the experiments conducted in this study, which indicates that indirect and other non-MIF producing pathways of photo-reduction are the dominant pathways by which Hg species are being photo-reduced. Extrapolating these experimental results to natural systems is difficult as the experiments were not performed at realistic Hg/DOM ratios and the distribution of ligands that Hg is bound to in the experiments likely differs from natural systems. However, the strong relationship between MIF and energy of incident radiation in this study supports Hg MIF signatures as promising tools for helping to quantify photochemical cycling of mercury, but this study also highlights the need to understand the link between MIF and total photo-reduction before this tool can be fully utilized.

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1. Introduction

Mercury is toxic in all of its forms, but it is monomethylmercury (MMHg) that bioaccumulates in aquatic food webs and is the major pathway for human and wildlife exposure through fish consumption (see review: Fitzgerald and Lamborg, 2014). Mercury is introduced to the environment from anthropogenic activities such as combustion of fossil fuels, waste incineration, mining and industrial manufacturing, and also from natural emissions including volcanoes, hydrothermal activity and biomass burning. Once in the environment, Hg goes through complex redox, biological and phase transformations and is

frequently re-emitted to the atmosphere after deposition to soil and water surfaces. Many of its pathways and transformations in the environment are still not completely understood and are poorly quantified (see review: Fitzgerald and Lamborg, 2014). Recent advances in cold vapor multicollector inductively coupled plasma mass spectrometry (CV–MC–ICP–MS, Lauretta et al., 2001) allow precise determination of the relative abundances of the stable isotopes of Hg and has proved to be a useful tool in understanding sources and transformations of Hg in nature (see review: Blum, 2012). Mercury is unique in that it not only displays mass-dependent fractionation (MDF), but also large mass-independent fractionation (MIF) (Bergquist and Blum, 2007). The reported range of isotopic values in natural materials is now up to ~10‰ for both MDF and for MIF of the odd isotopes (Blum, 2012). While many environmental transformations induce MDF (see reviews: Bergquist and Blum, 2009; Sonke, 2011; Blum, 2012), the only processes

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reported to result in large MIF (>0.5‰) are photochemical reduction of Hg^{2+} and MMHg (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009; Malinovsky et al., 2010; Sherman et al., 2010; Zheng and Hintelmann, 2010a). Constraining the processes that cause MIF signatures and the environmental factors that affect them is necessary if MIF signatures are to be useful for tracing and quantifying specific Hg sources and transformations.

Two mechanisms are currently thought to produce odd isotope mass-independent anomalies in Hg isotopes: the nuclear volume effect (NVE) and the magnetic isotope effect (MIE). Of these, it is thought that MIE is responsible for the large MIF observed in photochemical reactions (Bergquist and Blum, 2007; Malinovsky et al., 2010). This effect is a result of hyperfine coupling interactions (HFI) between the magnetic moments of odd nuclei (even isotopes have nuclear magnetic moments of zero) and the spin magnetic moments of unpaired electrons. The HFI are small and have no effect on the equilibrium characteristics of chemical systems (Turro, 1983; Bigeleisen, 1996), but can produce a kinetic effect by allowing isotopes with different nuclear spins to react at different rates when paramagnetic intermediates such as radical pairs are involved. The MIE is observed when the magnetic and non-magnetic nuclei are distributed differently among the reaction products (see reviews: Turro, 1983; Buchachenko, 2001). For example, if photolysis of a mercury compound generates radical pairs in a triplet state, they are spin-forbidden from recombining. The unpaired electron of an odd isotope, ^{199}Hg or ^{201}Hg , can undergo spin conversion faster to a singlet state allowing the odd nuclei to preferentially recombine and be enriched in the starting material (ex. Bergquist and Blum, 2007; Zheng and Hintelmann, 2009; Malinovsky et al., 2010). Alternatively, if photolysis conditions result in a singlet state radical pair, the odd nuclei can preferentially undergo spin conversion to a triplet state and be enriched in the product species (ex. Buchachenko et al., 2007; Zheng and Hintelmann, 2010a). The MIE to explain MIF is frequently adopted by investigators to explain MIF during the photochemical reduction of aqueous Hg species in the presence of dissolved organic matter (DOM) and MIF observed in natural samples. However, the only direct proof of the MIE mechanism during photochemical reduction of Hg so far has been by Malinovsky et al. (2010). The authors report suppression of MIF by addition of radical scavengers during photodemethylation of MMHg in solutions with ascorbic acid and with ammonia, and attribute it to suppression of radical pair formation or to scavenging of the radical pair during decomposition.

Photo-reduction of Hg species is known to be a significant process for removal of both Hg^{2+} species and MMHg in surface waters (Amyot et al., 1994; Sellers et al., 1996; Amyot et al., 1997; Poulain et al., 2004; Hammerschmidt and Fitzgerald, 2006; O'Driscoll et al., 2006; Lehnher and Louis, 2009; Black et al., 2012; Fernández-Gómez et al., 2013; Kim and Zoh, 2013; Qian et al., 2014; Tai et al., 2014), although the specific mechanisms operating in natural environments are elusive, in particular for MMHg. Hg^{2+} compounds can photolyze readily at very short wavelengths, generally due to ligand-to-metal charge transfer (LMCT; see review, Kunkely et al., 1997), and there have also been laboratory demonstrations of Hg^{2+} bonds photolyzing at naturally available wavelengths (ex. Kern, 1952; Zepp et al., 1973; Horvath et al., 2004). More work is needed to establish whether the C–Hg bond in MMHg can be excited by wavelengths longer than 290 nm, although this is predicted to be possible for certain species (ex. Tossell, 1998). Photo-reduction of Hg compounds by radical species that are both oxidizing (OH , Chen et al., 2003; Kim and Zoh, 2013 and $^1\text{O}_2$, Zhang and Hsu-Kim, 2010) and reducing (H and CO , Zheng et al., 2005; Han et al., 2007) are also proposed. There are many environmental factors known to affect Hg^{2+} and MMHg photo-reduction rates in nature. Light intensity and frequency, with higher rates associated with shorter wavelengths, are thought to be a major control over photo-reduction rates (Krabbenhof et al., 1998; Hammerschmidt and Fitzgerald, 2006; Lehnher and Louis, 2009; Li et al., 2010; Black et al., 2012; Fernández-Gómez et al., 2013; Kim and Zoh, 2013). The DOM

type and amount (Xiao et al., 1995; Xia et al., 1999; Ravichandran, 2004; O'Driscoll et al., 2004; Garcia et al., 2005; Zhang and Hsu-Kim, 2010; Tai et al., 2014; Qian et al., 2014) and the presence of other metals such as Fe in solution (Zhang and Lindberg, 2001; Hammerschmidt and Fitzgerald, 2010; Kim and Zoh, 2013) can also be important variables.

Because it is thought that Hg MIF in natural samples is dominantly caused by photo-reduction, it was proposed that Hg MIF signatures could be used to quantify photochemical reduction in nature and to put constraints on the Hg biogeochemical cycle (Bergquist and Blum, 2007; Sonke, 2011). For example, Bergquist and Blum (2007) postulated that MIF signatures in fish were due to photo-demethylation of MMHg in the water column prior to incorporation in the food web. This was largely based on >90% of Hg in fish muscle being MMHg (Bloom, 1992) and on the similar extents and ratios of MIF ($\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$) for MMHg photo-demethylation experiments and for freshwater fish muscle ($\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ of ~1.3 for both). Photo-reduction of Hg^{2+} yielded a significantly different ratio (~1.0). Using experimentally determined fractionation factors, and MIF signatures preserved in freshwater fish, the authors estimated the corresponding photodemethylation of bulk MMHg for several locations. This approach has been used several times subsequently (Bergquist and Blum, 2007; Gantner et al., 2009; Laffont et al., 2009; Senn et al., 2010; Perrot et al., 2010; Gehrke et al., 2011; Sherman and Blum, 2013; Blum et al., 2013; Tsui et al., 2014; Kwon et al., 2014) even though the only published fractionation factors for photo-demethylation with natural dissolved organic matter (DOM) were obtained at unrealistic MMHg to DOM ratios and with only one type of organic matter (Bergquist and Blum, 2007). There is only limited information on how environmental variables will affect fractionation factors. Zheng and Hintelmann (2009, 2010a) demonstrated that DOM type and amount significantly affected the expression of Hg^{2+} MIF during photo-reduction and the same has recently been demonstrated for MMHg photodemethylation (Chandan et al., 2014). The effects of type and amount of solar radiation as well as aqueous matrix composition remains unexplored for both Hg^{2+} and MMHg. Sonke (2011) presented a global model of mass independent Hg isotopes, but conceded that many fractionation factors were poorly known if at all and that much more work is needed to constrain MIF of Hg before a model could truly represent the Hg cycle.

The primary objective of this study was to assess the effect of limiting the energy spectrum of electromagnetic radiation on the expression of MIF during photo-reduction of both inorganic and organic mercury species. Photo-reduction of both Hg^{2+} and MMHg in the presence of DOM was carried out through exposure to (1) the full natural solar spectrum unfiltered, (2) with the ultraviolet B (UVB; 290–320 nm) portion removed and (3) with both the UVB and the ultraviolet A (UVA; 320–400 nm) removed. As the shorter wavelengths were removed, it was hypothesized that radiation remaining would be less effective at producing radical species. The MIE cannot be expressed in the absence of unpaired electrons, therefore we expected MIF to be suppressed as higher energy radiation was screened from the reaction vessels. Additional goals were to assess how MIF is related to total photo-reduction and whether MIF can be used to quantify photo-reduction.

2. Materials and methods

2.1. Materials

All acids were of trace metal grade and water used was deionized Millipore (18 M Ω). All sample containers and analytical vials were glass and were cleaned with both 10% HCl and 2% BrCl followed by 5 rinses with 18 M Ω water.

2.2. Photo-reduction experiments

Two sets of three simultaneous photochemical reduction experiments each were carried out using a $\text{Hg}(\text{NO}_3)_2$ standard (J.T. Baker),

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