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 is 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 Hg^{2+} 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.

Keywords: mercury, stable mercury isotopes, monomethylmercury, photo-reduction, photo-demethylation, mass-independent fractionation, Rayleigh fractionation factors

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 reported to result in large MIF (>0.5 ‰) are photochemical reduction of Hg^{2+} and MMHg (Bergquist and Blum, 2007; Malinovsky et al., 2010; Sherman et al., 2010; Zheng and Hintelmann, 2009; Zheng and Hintelmann, 2009, 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; Engel and Reid, 2006), 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, 2011). 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, 1997; Sellers et al., 1996; Poulain et al., 2004; O'Driscoll et al., 2006; Hammerschmidt and Fitzgerald, 2006; Lehnher & St. Louis, 2009; Black et al., 2012; Kim and Zoh, 2013; Fernández-Gómez et al., 2013; Tai et al., 2014; Qian et al., 2013), although the specific mechanisms operating in natural environments are elusive, in particular for MMHg. Hg^{2+} compounds can photolyse 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 photolysing at naturally available wavelengths (ex. Kern, 1952; Zepp et al., 1973; Kunkely and Vogler, 2001; 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 ($\cdot\text{OH}$, Chen et al., 2003, Kim and Zoh, 2013 and $^1\text{O}_2$, Zhang and Hsu-Kim, 2010) and reducing ($\text{H}\cdot$ and $\text{CO}\cdot$, Zheng et al., 2005, and 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, is thought to be a major control over photo-reduction rates (Krabbenhoft et al., 2002; Hammerschmidt & Fitzgerald, 2006; Lehnher & St. Louis, 2009; Li et al., 2010; Black et al., 2012; Kim and Zoh, 2013; Fernández-Gómez et al., 2013). The DOM type and amount (Xia et al., 1998; Ravichandran, 2004; O'Driscoll et al., 2004; Garcia et al., 2005; Zhang and 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; 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 (Harris et al, 2003) 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; Jackson et al., 2008; Gantner et al., 2009; Laffont et al., 2009; Gartner et al., 2009; Senn 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 Hintelman (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 MΩ). All sample containers and analytical vials were glass and were cleaned with both 10% HCl and 2% BrCl followed by 5 rinses with 18 MΩ 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), and two sets of three simultaneous photochemical reduction experiments each were carried out using a CH_3HgCl standard (Alfa Aesar). Photo-reduction took place under natural sunlight in Toronto, Canada (43° N, 79° W). Initial sets for each species were carried out in July, 2009, and replicate sets in September, 2009. Aqueous solutions of 2 mg/L Suwannee River Fulvic Acid Standard (International Humic Substance Society 1S101F; <http://ihss.gatech.edu/ihss2/>) were prepared in glass bottles, sampled to verify negligible mercury content, spiked to achieve a final concentration of Hg of approximately 30 µg/L for the Hg^{2+} experiments (using the $\text{Hg}(\text{NO}_3)_2$ standard) and approximately 25 µg/L for the MMHg experiments (using the CH_3HgCl standard), sub-sampled to determine initial Hg isotopic composition, and allowed to equilibrate overnight wrapped in aluminum foil. Experimental Hg concentrations were four to five orders of magnitude higher than in typical freshwaters, but were chosen to facilitate high precision Hg isotope analyses of the run products. The morning following preparation, the foil-wrapped solutions were transferred to a 1-L quartz reactor (as in Bergquist and Blum 2007, SI) and promptly covered with the UV filters where appropriate. Mercury vapor, Hg^0 , was continuously sparged from solutions with ambient air pulled through a 0.2 µm filter and gold trap to remove particles and Hg. The reservoir was sub-sampled immediately after set up and at intervals over the day as the reactions progressed. Sub-samples

were immediately preserved by spiking with concentrated BrCl to achieve a sample BrCl concentration of 2.5%.

UV light filters were boxes closed on five sides that were placed over the quartz reactors. Mylar sheets screened the UVB portion of the electromagnetic spectrum (93-95%), some of the UVA spectrum (43-45%), and a small amount of the visible spectrum (19-22%). Acrylic sheets covered with a 3M Scotchshield (Ultra S150) window film screened the UVB (96%) the UVA (98%) portions of the spectrum and a small amount of the visible spectrum when the sun was not directly overhead. Around mid-day, the intensity of visible light was higher under the acrylic box (by 30% or more) than the intensity of visible light under direct solar radiation. Measurements of the light reaching each reactor were taken with a Solar Light PMA2200 Radiometer fitted with detectors specific to the three spectral regions of interest: UVB (PMA2106), UVA (PMA2110) and Visible (PMA2130). Dark control experiments for Hg^{2+} and MMHg were performed in the laboratory with the same procedure except that the quartz reactors were covered with aluminum foil at all times.

Since the Hg speciation was not determined during the experiments as the reaction progressed in the reservoir, it was assumed that MMHg photo-degraded to Hg^0 without significant Hg^{2+} contamination in the reservoir. This is supported by high and consistent $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios for the MMHg experiments in this study (1.33 ± 0.14 , 2SE) along with other studies (Bergquist and Blum, 2007; Chandan et al., 2014), which likely would be significantly lowered if significant amounts of Hg^{2+} were present in the reservoir undergoing photo-reduction with a ratio of ~ 1 (for example, 0.98 ± 0.04 (2SE) in this study).

2.3. Hg concentration and isotope analysis

Concentrations of Hg in the aqueous samples were measured using a Tekran 2600 Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) following a modification of US EPA Method 1631, Revision E. The standard reference material NIST1641d was used to monitor accuracy and precision, and the error for Hg concentrations was $\pm 5\%$ (1SD). To avoid matrix effects during isotopic analysis, Hg was transferred from sample matrices to an aqueous acidic trapping solution of 10% (wt) H_2SO_4 and 1% (wt) KMnO_4 by SnCl_2 reduction, sparging and trapping. The aqueous acidic trapping solution was then reduced with SnCl_2 online and Hg^0 was

separated using a frosted glass tip gas-liquid separator. Inter-sample blanks were ~0.25 % of sample concentrations. Process standards using NIST 3133 reference mercury solution (concentration- and matrix-matched to samples) were run routinely at the beginning of each session and then throughout the day as needed. Sample recoveries after matrix transfer were always greater than 90% and usually greater than 95%. Method replicates were achieved by processing R0 (sampled before Hg-DOM equilibration) from each of the three experiments from both sets.

Isotopic compositions were measured on a Nu Instruments multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Department of Earth and Environmental Sciences, University of Michigan. Samples were introduced to the plasma by the online reduction cold vapor generation technique (Lauretta et al., 2001). Instrumental mass bias was corrected with a thallium internal standard (NIST 997; reported $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of 2.38714) and through matrix and concentration matched sample standard bracketing (SSB; NIST SRM 3133), as recommended in Blum and Bergquist (2007). The sample matrix (1% KMnO_4 in 10% H_2SO_4) was pre-reduced with NH_2OH a minimum of one hour before cold vapor generation. On-peak zero corrections were applied to all Hg and Pb masses by measuring a matrix matched blank solution prior to each sample after 10 to 12 minutes of washout. Blank correction on the Tl masses was not possible because Tl was continuously streamed throughout the analytical sessions. Isobaric interference of ^{204}Pb on ^{204}Hg was corrected by monitoring ^{206}Pb , but was always negligible. The Faraday cups were configured to collect masses of 196, 198, 199, 200, 201, 202, 203, 204, 205 and 206 atomic mass units.

Isotopic compositions are reported in delta notation as the permil (‰) deviation from the bracketing NIST SRM 3133 standards after blank and Tl corrections. It is determined through SSB as follows, where the $(^{XXX}\text{Hg}/^{198}\text{Hg})_{\text{NIST SRM 3133}}$ ratio in the denominator is the average ratio of the bracketing standards run prior to and after the sample:

$$\delta^X\text{Hg} = [(^X\text{Hg}/^{198}\text{Hg})_{\text{sample}} / (^X\text{Hg}/^{198}\text{Hg})_{\text{NIST3133 std}} - 1] \times 1000 \quad (1)$$

where XXX is the mass the Hg isotope of interest from 198 to 204 amu. Mass-independent fractionation is reported using capital delta notation ($\Delta^{XXX}\text{Hg}$) and is the deviation in isotope ratios from the theoretical values predicted by MDF, also in units of permil (‰). The theoretical isotope ratios are determined using the $^{202}\text{Hg}/^{198}\text{Hg}$ ratio (i.e. $\delta^{202}\text{Hg}$) and applying the kinetic

mass-dependent fractionation law derived by Bigeleisen (1949) and reviewed by Young et al. (2002) as follows:

$$\Delta^{199}\text{Hg} = 1000 \times \{ \ln[\delta^{199}\text{Hg}/1000 + 1] - 0.2520 \times \ln[\delta^{202}\text{Hg}/1000 + 1] \} \quad (2)$$

$$\Delta^{200}\text{Hg} = 1000 \times \{ \ln[\delta^{200}\text{Hg}/1000 + 1] - 0.5024 \times \ln[\delta^{202}\text{Hg}/1000 + 1] \} \quad (3)$$

$$\Delta^{201}\text{Hg} = 1000 \times \{ \ln[\delta^{201}\text{Hg}/1000 + 1] - 0.7520 \times \ln[\delta^{202}\text{Hg}/1000 + 1] \} \quad (4)$$

$$\Delta^{204}\text{Hg} = 1000 \times \{ \ln[\delta^{204}\text{Hg}/1000 + 1] - 1.493 \times \ln[\delta^{202}\text{Hg}/1000 + 1] \}. \quad (5)$$

External reproducibility was monitored with a secondary standard, UM-Almadén, of different isotopic composition than the bracketing standard. The data presented here were produced over 8 analytical sessions (October 2009 –July 2010). The mean Almadén values for the October through January sessions were $\delta^{202}\text{Hg} = -0.58 \pm 0.13 \text{ ‰}$ and $\Delta^{199}\text{Hg} = 0.00 \pm 0.07 \text{ ‰}$ (2SD, n = 12). The mean Almadén values for the June and July sessions were $\delta^{202}\text{Hg} = -0.58 \pm 0.09 \text{ ‰}$ and $\Delta^{199}\text{Hg} = -0.02 \pm 0.07 \text{ ‰}$ (2SD, n = 20).

2.4. Estimation of fractionation factors

Photo-reduction of both Hg^{2+} and MMHg appeared to follow a Rayleigh distillation model. Thus, kinetic fractionation factors were determined from the results of our experiments using the form of the Rayleigh distillation equation outlined by Mariotti et al., 1981:

$$(10^{-3} \varepsilon_{p/r}) \ln(f) = \ln(10^{-3} \delta^x\text{Hg}_t + 1) / \ln(10^{-3} \delta^x\text{Hg}_0 + 1) \quad (6)$$

where, $\varepsilon_{p/r}$ is the enrichment factor (‰), which is related to the fractionation factor using $\alpha_{p/r} = 1 + (\varepsilon_{p/r}/1000)$, f is the fraction of MMHg remaining in the reservoir, $\delta^x\text{Hg}_0$ is the initial isotopic composition of Hg where x = ^{199}Hg to ^{204}Hg , and $\delta^x\text{Hg}_t$ is the isotopic composition of Hg at time (t) where x = ^{199}Hg to ^{204}Hg . $\Delta^{199}\text{Hg}_0$ and $\Delta^{199}\text{Hg}_t$ were substituted for $\delta^x\text{Hg}_0$ and $\delta^x\text{Hg}_t$ respectively to estimate $\alpha_{\Delta 199}$. The slope of the best linear fit of the relation $\ln(\Delta^{199}\text{Hg})$ or $\ln(\delta^{202}\text{Hg})$ as a function of $\ln(f)$ represents the enrichment factor ($\varepsilon_{p/r}$), which was used to calculate kinetic fractionation factors $\alpha_{\delta 202}$ and $\alpha_{\Delta 199}$. The uncertainty in $\alpha_{\delta 202}$ and $\alpha_{\Delta 199}$ was estimated using the 2SE of the slope.

3. Results

3.1. Light intensities

Quartz reactors containing either Hg^{2+} or MMHg in aqueous solutions with dissolved organic matter were simultaneously exposed to three different light regimes. Initial sets of three replicates were carried out on July 19th (MMHg) and July 30th (Hg^{2+}), 2009, and additional replicate sets of three were carried out on September 1st (MMHg) and September 3rd (Hg^{2+}), 2009. Ultraviolet intensities in September were generally lower (**Table S1** in the Supporting Information, SI). For example, the maximum UVB intensities recorded near solar noon (approximately 1 pm) in September were ~30% lower than the corresponding July intensities. UVA intensities were ~20% lower in September than in July. Visible waveband intensities were not significantly different between September and July. Technical difficulties lead to the exposure of the September Hg^{2+} no UV experiment to the full solar spectrum (i.e., the filter box had to be removed for more than an hour); thus, this experiment was compromised and the data is not presented.

3.2. Hg^{2+} and MMHg concentration loss during photo-reduction

The amount of Hg^{2+} or MMHg lost via photo-reduction was estimated from the decreasing concentration of Hg in the substrate reservoir over time (**Figure 1**). Experimental ratios of Hg:DOM were far higher than are typically found in nature. This was necessary to allow for high precision isotopic analyses, but meant that chemical conditions, such as the profile of Hg-binding sites, are not typical of natural freshwaters and so kinetic reduction rates from this study are not directly applicable to natural systems.

In July, Hg^{2+} showed similar maximum losses of 80% in both the experiment exposed to full sun and the experiment with UVB blocked (**Figure 1a**). Blocking all UV suppressed most of the photo-reduction (only 10% loss). Maximum September loss (70%) was in the full spectrum experiment and blocking of UVB resulted in approximately 40% loss. In the September Hg^{2+} experiment with UVB removed (**Figure 1b**), the lowest reservoir Hg concentrations are recorded after approximately four hours and are followed by small concentration increases. This is likely a result of reservoir evaporation, as water vapor would have been pumped out of the reactor headspace along with the Hg^0 . It is likely that the UV

filtering boxes increased the ambient temperature compared to the uncovered, full sun experiment but the temperature contrast between experiments covered and uncovered was not monitored. Dark control experiments were carried out in the laboratory with the Hg^{2+} -organic matter solution shielded with aluminum foil at all times. They showed no detectable losses after 8.5 hours of sparging with Hg-free air (**Figure 1a**). Thus, we conclude that Hg loss due to non-photochemical reduction during the 6-7 hour light experiments was negligible.

In the July MMHg photoexperiments, neither blocking the UVB waveband only nor blocking all UV radiation had a significant effect on the total amount of MMHg lost (**Figure 1c**). All three experiments showed losses of approximately 20% after seven hours of exposure. In September, overall concentration losses were smaller. The experiments exposed to full sun and to UVA lost approximately 10% (**Figure 1d**), but the experiment blocking both UVB and UVA appears to have experienced less photo-degradation (4%) than its full spectrum counterpart. The smaller losses observed in September might be due to the lower intensity of sunlight in September (see **Table S1**). The uncertainty in the Hg concentration measurements ($\pm 5\%$) makes it difficult to determine whether loss in the September no UV trial is indeed significantly lower. The MMHg control experiment carried out under foil in the laboratory showed no detectable losses after 8.5 hours of sparging with Hg-free air. We therefore conclude that any losses due to non-photochemical reduction during the 6-7 hour UV filtration experiments were negligible.

3.3. Mass Dependent Fractionation of Hg

MDF was observed in all experiments where there was significant photo-reduction with the heavier isotopes preferentially retained in the reactor/reactant, which is consistent with kinetic isotope fractionation (see Figure 2). The Hg^{2+} experiments displayed much larger isotopic enrichment in the reactant, up to $\sim 2\%$ for $\delta^{202}\text{Hg}$, than the MMHg experiments, which is consistent with the larger extents of reaction for Hg^{2+} . The MMHg photo-degradation experiments had maximum enrichments of $\sim 0.3\%$ for $\delta^{202}\text{Hg}$ at $\sim 20\%$ loss of MMHg. Complete isotopic data are displayed in **Tables S2 and S3** in the SI and summarized in **Tables 1 and 2**.

3.4. Mass-independent isotope fractionation of Hg

MIF of Hg was observed for the odd isotopes only, with ^{199}Hg and ^{201}Hg being preferentially retained in the reactor as observed by Bergquist and Blum (2007) for all experiments displaying MIF. Complete MIF data are displayed in **Table S2 and S3** in the SI and summarized in **Tables 1 and 2**.

In July, the largest Hg^{2+} MIF signature was $2.45 \pm 0.14\text{‰}$ (2SE) for $\Delta^{199}\text{Hg}$ in the experiment exposed to full sun. Blocking the UVB waveband reduced MIF significantly by $50 \pm 10\%$ at a similar extent of reaction, and blocking all UV radiation suppressed most of the photo-reduction and MIF. Rayleigh models based on estimated MIF fractionation factors for July experiments are shown in **Figure 3a**. In September, the largest Hg^{2+} MIF signature, $0.69 \pm 0.14\text{‰}$ (2SE) for $\Delta^{199}\text{Hg}$, was also in the experiment exposed to full sun. Blocking the UVB waveband resulted in a significant decrease of $30 \pm 20\%$ (Figure 3b) at similar extent of reaction. Rayleigh models based on estimated MIF fractionation factors for July experiments are shown in **Figure 3b**. As no loss in Hg^{2+} was observed in the dark control, there was no opportunity for MDF or MIF.

In July, the largest MIF value for the MMHg photo-degradation experiments was $0.55 \pm 0.07\text{‰}$ for $\Delta^{199}\text{Hg}$ in the experiment exposed to full sun. Although blocking the UVB and UVA wavebands did not have an appreciable effect on total losses of MMHg through photo-degradation, MIF was suppressed in both the UVB-blocked experiment and the UVA&B-blocked experiment (**Figure 4a**). In September, the full sun experiment also displayed the largest MIF signature, $0.42 \pm 0.14\text{‰}$ for $\Delta^{199}\text{Hg}$. MIF was significantly reduced by blocking the UVB waveband with MIF suppressed up to $70 \pm 50\%$ compared to the full sun experiment at a similar extent of reaction (**Figure 4b**). The effect of blocking UV on MIF in the September experiments is more difficult to quantify, since photo-degradation was very low in these experiments, but the MIF expressed is lower than the full spectrum experiment. No change in MMHg concentration was observed in the dark control, providing no opportunity for MIF.

3.6. Relationship between $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$

$\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios were only calculated and used for samples with MIF greater than or equal to 4SE of the secondary standard, UM-Almadén; this was 0.07 for $\Delta^{199}\text{Hg}$ and 0.05 for $\Delta^{201}\text{Hg}$. Data that met this criteria are plotted in **Figure 6**. The $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope was 0.98 ± 0.04 (2SE) for the Hg^{2+} photo-reduction experiments and 1.33 ± 0.14 (2SE) for MMHg photo-demethylation experiments.

4. Discussion

4.1. Mass Dependent Fractionation

Despite the extent of MDF being much larger in the Hg^{2+} compared to the MMHg photo-reduction experiments due to the larger extents of reaction, $\delta^{202}\text{Hg}$ fractionation factors ($\alpha_{\delta 202}$) are similar for all Hg^{2+} and MMHg experiments that displayed significant MDF and range from 0.9977 to 0.9992. For most of the sets of experiments, there are no systematic variations in $\alpha_{\delta 202}$ with filtering of solar light wavelengths or with the higher UV intensities in July. Only in the Hg^{2+} July experiments is there larger fractionation for the UVB filtered experiment, $\alpha_{\delta 202} = 0.9988 \pm 0.0001$ (2SE), than for the full sun, $\alpha_{\delta 202} = 0.9992 \pm 0.0002$ (2SE). This effect is not observed in September, however, where the mass-dependent fractionation factors of the two experiments are indistinguishable. As noted above, higher temperatures under the UV-filtering boxes in September likely resulted in evaporation and slight increases in concentration towards the end of the experiments, possibly confounding the fractionation factors somewhat.

4.2. MIE as the cause of large MIF in Hg photo-reduction

The clear relationship between the magnitude of MIF and the wavelengths of light available for Hg^{2+} and MMHg photo-reduction experiments suggests that MIE is the dominant mechanism producing MIF during Hg photo-reduction. For Hg^{2+} , the largest MIF is observed in the experiments exposed to full sun in both the July and the September experiments. The July experiments were exposed to more intense ultraviolet radiation than the September experiments and show correspondingly larger MIF ($\alpha_{\Delta 199} = 0.9986 \pm 0.0001$, 2SE, for July and $0.9993 \pm$

0.0001, 2SE, for September). For both sets of experiments, UVB is a large contributor to MIF as its removal reduced MIF by up to $50 \pm 10\%$ in July and by $30 \pm 20\%$ in September. UVA seems to contribute significantly as well, but how much it contributes relative to visible radiation is not clear because blocking out both UVA and UVB in July reduced overall photo-reduction significantly and it was not possible to measure significant isotope fractionation. Thus, for Hg^{2+} it appears that both the UVB and UVA spectra are likely to be capable of producing MIF.

For MMHg, the most pronounced MIF is also in the experiments exposed to full sun in both the July and the September experiments. However, there was not a clear difference between July and September in the overall amount of MIF expressed in the full sun ($\alpha_{\Delta 199} = 0.9977 \pm 0.0011$, 2SE, for July and 0.9964 ± 0.0014 , 2SE, for September). The lower overall extents of reaction and smaller MIF magnitudes result in larger uncertainties in the estimates of fractionation factors. It appears that UVB is the major contributor to MIF during photo-degradation of MMHg, even more so than for Hg^{2+} . When UVB is blocked, most of the MIF ceases, although small amounts are still present in experiments exposed to UVA in September suggesting that some MIF occurs due to radiation in the UVA region.

4.3. Relationship between MIF and photo-reduction of Hg^{2+} and MMHg

For both Hg^{2+} and MMHg, there is no relationship between MIF and overall extent of photo-reduction for the experiments in this study. For example, in the Hg^{2+} July experiments, removing the UVB wavebands has a clear effect on MIF but no significant effect on total amount of photo-reduction. The same was observed for the July MMHg photo-degradation experiments where blocking the UVB waveband largely or completely suppressed MIF, but the amount of total photo-degradation was not significantly affected. This indicates that there are multiple pathways for photo-reduction and not all of them produce MIF in our experiments. As discussed in more detail in section 4.5, the results from the experiments in this study should not be extrapolated to natural systems 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. Different Hg-ligand species may have different sensitivities to the energy of radiation. 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 Hg. From our experiments, it is evident that the higher energy wavelengths (UVA and UVB) appear necessary to produce radical pairs and conditions favorable for allowing the expression of MIE. In support this conclusion, there are several studies that demonstrate direct photolysis of Hg complexes that have radical pair intermediates by UVA and UVB (Friswell and Gowenlock, 1965; Zepp et al. 1973; Inoko, 1981; Tossell, 1998; Gardfeldt and Jonsson, 2003; Lin and Ariya, 2008; Tai et al., 2014).

The disappearance of MIF does not, however, necessarily indicate the disappearance of direct photolysis of Hg species. Not all direct photolysis reactions with radical pair intermediates will have conditions favorable for expressing the MIE (Turro, 1983; Grissom, 1995; Buchachenko, 2001). For direct photo-reduction to result in MIF, the rate-limiting step needs to involve an excited radical pair intermediate where hyper-fine interactions (HFI) can influence the spin of the unpaired electrons and the fate of the radical pair intermediate. For example, the lifetime and coupling of the radical pair as well as the solvent cage are all important variables that may affect expression of MIE induced MIF (Turro, 1983; Buchachenko, 2001; Turro et al., 2009). If the lifetime of the radical pair is too short, then HFI induced spin conversion cannot compete with dissociation into free radicals (Turro, 1983; Turro et al., 2008). The distance (or coupling) of the radical pair is also important (Turro, 1983; Turro et al., 2008). In order for HFI to effectively induce spin conversion, the radical fragments must separate to a physical distance where the energy gap between the singlet and triplet states is of the same order or smaller than the hyperfine interaction (Turro et al., 2008). At such a distance, the original chemical bond will have completely dissociated and one or more solvent molecules may separate the radicals. The probability of the newly-singlet radical fragments re-encountering each other before separating completely is high because they will “bounce” against the surrounding solvent molecules and each other several times before finding avenues through the solvent to become fully separated (Turro et al., 2008).

The data in this paper shows no strong correlation between MIF and total photo-reduction. Therefore, we suggest that Hg photo-reduction reactions that lead to MIE in our experiments are likely only a small portion of multiple reactions that resulted in photo-reduction. Although not all direct photolysis reactions may lead to MIE, MIE may still be a good indication of the extent of direct photolysis since excited radical pairs require higher

energy radiation to be generated. If such high energy is available for direct photolysis leading to MIE, then it is also available for direct photolysis that does not lead to MIE. Thus the lack of correlation between MIF and total photo-reduction may be an indication that indirect photo-reduction is dominating in many of our experiments. This is especially true for the MMHg photo-degradation experiments where no significant suppression of photo-degradation is observed when blocking out UV radiation, with the exception of a slight suppression for the UVA and UVB filtered experiment in September. Since the Hg^{2+} experiments show suppression of total photo-reduction when all UV was blocked, direct photolysis was likely more important in those experiments.

Although the exact pathway of indirect photolysis is unclear from the current experiments, there are a number of studies that have investigated indirect pathways for photo-reduction of Hg by reactive photo-generated intermediates. Indirect photolysis leading to stepwise reduction of aqueous Hg^{2+} to Hg^0 with formic acid and visible light (Zheng et al., 2005) showed that formic acid decomposes to produce hydrogen and carbon monoxide under environmentally available wavelengths (Allmand and Reeve, 1926), and thus photo-generated reactive intermediates such as $\cdot\text{H}$ and $\text{CO}\cdot$ can be responsible for the Hg^0 production. In another study, other low molecular weight organic molecules (formaldehyde, methanol, acetic acid, glycerol, oxalic and malonic acid) also can reduce Hg^{2+} to Hg^0 in aqueous solution when exposed to light (Han et al., 2007). Hydroxyl radicals have also been shown to degrade MMHg (Chen et al., 2003), however, Zhang and Hsu-Kim (2010) point out that under natural conditions substrate abundance and pH do not always favor a concentration of $\cdot\text{OH}$ radicals high enough to account for the MMHg degradation rates reported for natural systems, and present a strong case for the role of singlet oxygen in the decomposition of MMHg.

4.4. $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$

In examining MIF during photo-reduction of Hg^{2+} , Bergquist and Blum (2007) observed that the ratio of $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ was very consistent (1.00 ± 0.02 , 2SE) and distinct from the ratio of $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ resulting from photo-degradation of MMHg (1.36 ± 0.02 , 2SE). The $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio produced by the nuclear volume effect (NVE) contrasts with these values and is now theoretically (Schauble, 2007; Wiederhold et al., 2010) and experimentally

constrained at $\sim 1.59 \pm 0.05$ (2SE) (Wiederhold et al., 2010; Zheng and Hintelmann 2010b, Ghosh et al., 2013). The $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios produced in this study agree well with Bergquist and Blum (2007), which is not surprising since both studies used the same source of DOM, natural sunlight and similar Hg/DOM ratios. The difference in the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ relationship between Hg^{2+} and MMHg photo-reduction indicates that the different reactions that lead to MIE-induced MIF for these two Hg species have different relative rates of spin conversion for ^{199}Hg and ^{201}Hg .

The $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio for all Hg^{2+} photo-reduction experiments in this work falls within error of 1.0. If the ratio is indeed indicative of the pathway, then the pathway resulting in MIF in our experiments may be constant even when higher energy radiation is filtered out and the amount of photo-reduction is reduced. Although there could also be multiple reactions that have a MIE slope of ~ 1 . The ratio in this study agrees well with natural samples containing inorganic Hg^{2+} , which have a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope of 0.98 ± 0.02 (2SE) (see review: Sonke, 2011). Although the $\square \Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ relationship observed in this study agrees well with Bergquist and Blum, 2007, and the inorganic Hg^{2+} dominated natural samples, it is different from ratios observed in experiments by Zheng and Hintelman (2009, 2010a). Under varying DOM amounts and types, and using an artificial light source, these authors observed ratios for Hg^{2+} photo-reduction varying from 1.0 to 1.3. The difference between Zheng and Hintelmann's results and the ratios observed by Bergquist and Blum (2007), this study, and natural samples still needs to be resolved, but may be related to the type and amount of organic matter used or the use of different light sources (i.e., natural sun versus artificial light).

The average ratio $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ for all MMHg experiments in this work was 1.35 ± 0.16 (2SE), which is similar to the value obtained by Bergquist and Blum (2007) (1.36 ± 0.02 , 2SE), also under natural sunlight. Chandan et al. (2014) found variable $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ for MMHg photo-degradation for different DOM types and amounts using an artificial light source. Experiments by Chandan et al. (2014) with low MMHg/DOM ratios had a consistent $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.38 ± 0.02 (2SE); whereas higher MMHg/DOM ratio experiments had more lower slopes of 1.17 ± 0.04 (2SE, $n = 7$) to 1.30 ± 0.02 (2SE). Malinkovsky et al., 2010, reported a slightly lower ratio (1.28 ± 0.03 , 1SD) for experimental photo-degradation of MMHg under UVC radiation. The causes of variable $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios with respect to the MIE are not completely understood and a more quantitative understanding of the MIE is needed.

4.5. Implications for natural samples and quantifying Hg photo-reduction with MIF

The results from our experiments should not be simply extrapolated to natural systems. Although the total extent of photo-reduction was found in this study to be decoupled from both MIF magnitude and energy of incident radiation, the experiments are not representative of the photo-reduction in natural freshwaters and did not use realistic Hg:DOM ratios. In this study the experiments were stirred exposing the entire reservoir to sunlight. In natural systems, the amount of solar radiation is attenuated with depth and the amount of the water column that can undergo photochemical reactions is limited (Morris et al., 1995; Williamson et al., 1996). Thus, the amount of both direct and indirect photo-reduction will be related to the penetration of solar radiation. As long as MIF is related to the depth of UV penetration, then it is likely that MIF will be related to the amount of direct photochemical reduction. However, based on our experiments, the relationships between MIF and total photo-reduction might depend on the relative depths of UV versus PAR penetration for lakes, which is dependent on type and amount of DOC (Morris et al., 1995; Williamson et al., 1996). Incident radiation as measured by photon flux is attenuated in fresh water predominantly by DOM. The depth of 90% attenuation can be as large as 5 m for UVB in low-DOC (clear) aquatic systems and as small as a few cm for high-DOC (humic) aquatic systems (Scully and Lean, 1994; Morris et al., 1995; Crump et al., 1999; Belmont et al., 2007). Depths of 90% attenuation for PAR are typically 4 or 5 times larger, with UVA at intermediate values (Scully and Lean, 1994; Morris et al., 1995, Crump et al., 1999, Belmont et al., 2007). Our data, therefore, suggest that in a clear, low DOC lake total photo-reduction will be far more important and dominated by a larger MIE MIF signature than in a darker high DOC lake. Thus, there is the potential for useful relationships to be developed between total photo-reduction and MIF.

5. Conclusions

Photo-reduction experiments of Hg^{2+} and MMHg in the presence of DOM were conducted with exposure to unfiltered full natural solar spectrum, 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 was a clear relationship between the expression and magnitude of MIF and the energy of incident radiation for both Hg^{2+} and MMHg in the experiments in this study. This supports the MIE as the mechanism behind large MIF in photo-reduction of mercury species. For Hg^{2+} , UVB radiation was a major contributor to MIF and UVA radiation seems to contribute significantly as well. For MMHg, UVB radiation was the major contributor to MIF with minor contributions from UVA. The lack of correlation observed between MIF and total photo-reduction may be an indication that indirect photo-reduction was dominating in many of the experiments. This was especially true for the MMHg photo-degradation experiments where no significant suppression of photo-degradation was observed when blocking out UV while MIF is significantly suppressed. Hg^{2+} experiments showed more suppression of total photo-reduction when UV is blocked and therefore direct photolysis was likely more important in these experiments. Ratios of $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ remained consistent for each of the species undergoing photo-reduction (0.98 ± 0.04 , 2SE for Hg^{2+} and 1.33 ± 0.14 , 2SE for MMHg) regardless of the energy of incident radiation. This is consistent with previous reports of MIF caused by the MIE and distinct from $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios attributed to the NV effect (~ 1.6). While total photo-reduction in the experiments in this study was decoupled from both MIF magnitude and energy of incident radiation, the clear relationship between MIF and energy of incident radiation and the fairly predictable relationships of UV radiation to PAR in natural systems still suggests that MIF signatures have a strong potential to constrain aspects of Hg photo-reduction. However, in order to use MIF preserved in natural samples more quantitatively, more work is needed to elucidate the relationship between MIF and photo-reduction in natural systems.

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Figure Captions:

Figure 1. Mercury concentration in the substrate reservoir over time for replicate photo-reduction experiments on two Hg species (Hg^{2+} and monomethylmercury, MMHg) in the presence of dissolved organic matter and under varying exposure to solar radiation. Maxima in solar irradiation were recorded at approximately 1 pm, Eastern Standard Time, coinciding with solar noon in Toronto, Ontario. Effective blocking of the UVB spectrum resulted in partial blocking of the UVA spectrum (by 30 to 52%). Complete radiation measurements are shown in Table S1 of the Supplemental Information. Dark controls were carried out with a foil-wrapped reactor.

Figure 2. Mass-dependent fractionation ($\delta^{202}\text{Hg}$) of the substrate reservoir as a function of Hg remaining for replicate photo-reduction experiments on Hg^{2+} and MMHg with dissolved organic matter under varying exposure to solar radiation. Rayleigh distillation models using estimated fractionation factors ($\alpha_{\Delta 202}$) are shown where there was significant loss in concentration. **Solid black lines:** full sun; **broken grey lines:** UVB spectrum blocked. Complete isotope data are given in Tables S2 and S3 of the Supplemental Information.

Figure 3. MIF, $\Delta^{199}\text{Hg}$, in odd isotopes as a function of substrate Hg^{+2} remaining during photo-reduction in the presence of DOM under varying exposure to solar radiation. Rayleigh distillation models based on estimated MIF factors ($\alpha_{\Delta 199}$) are shown for experiments with significant MIF. **Solid black lines:** full sun (July $\alpha_{\Delta 199} = 0.9986 \pm 0.0001$; Sept $\alpha_{\Delta 199} = 0.9993 \pm 0.0002$). **Broken grey lines:** UVB spectrum blocked (July $\alpha_{\Delta 199} = 0.9993 \pm 0.0001$; Sept $\alpha_{\Delta 199} = 0.9995 \pm 0.0001$). Complete isotope data are given in Tables S2 and S3 of the Supplemental Information.

Figure 4. MIF, $\Delta^{199}\text{Hg}$ in odd isotopes as a function of substrate MMHg remaining during photo-reduction in the presence of DOM under varying exposure to solar radiation. Rayleigh distillation models (**solid black lines**) based on an estimated MIF factors ($\alpha_{\Delta 199}$) are shown for experiments with significant MIF, which was only for the full sun experiments (July $\alpha_{\Delta 199} = 0.9977 \pm 0.0011$; September $\alpha_{\Delta 199} = 0.9964 \pm 0.0014$). Complete isotope data are given in Tables S2 and S3 of the Supplemental Information.

Figure 5. $\Delta^{201}\text{Hg}$ versus $\Delta^{199}\text{Hg}$ for photochemical reduction of Hg^{2+} and MMHg in the presence of dissolved organic matter under varying exposure to solar radiation. Only samples with significant MIF were plotted, so R0 (pre-exposure) and R1 (taken immediately after first exposure to solar radiation) do not appear for any experiment. For Hg^{+2} , the average $\Delta^{201}\text{Hg}/\Delta^{199}\text{Hg}$ is 0.98 ± 0.04 , 2SE, $n = 16$ (**black line**). For MMHg, the average $\Delta^{201}\text{Hg}/\Delta^{199}\text{Hg}$ is 1.33 ± 0.14 , 2SE, $n = 4$ (**broken line**).

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810

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table S1. Solar radiation measurements

Mercury Species	Hg ²⁺			
Date performed	July 29, 2009			
Photoexperiment exposure	full sun	no UVB	no UV	Time of Day
Spectrum	Radiation Measured (W/m ²)			
UVB (290-320 nm)	2.1	0.1	0.1	11:15
	2.5	0.1	0.1	12:25
	2.7	0.2	0.1	1:12
	1.7	0.1	0.1	3:38
	1.2	0.1	0.1	5:00
UVA (320-400 nm)	50.1	24.3	0.8	11:15
	53.8	29.8	1.4	12:25
	57.1	34.0	1.0	1:12
	41.8	25.4	0.7	3:38
	38.2	19.5	0.5	5:00
Photopic (400-700 nm)	164	150	177	11:15
	166	128	217	12:25
	163	142	172	1:12
	95	57	68	3:38
	145	109	113	5:00
Mercury Species	MMHg			
Date performed	July 19, 2009			
Photoexperiment exposure	full sun	no UVB	no UV	Time of Day
Spectrum	Radiation Measured (W/m ²)			
UVB (290-320 nm)	1.5	0.1	0.1	11:45
	2.2	0.2	0.1	12:15
	2.5	0.1	0.1	1:45
	1.0	0.1	0.1	5:00
UVA (320-400 nm)	43.9	25.3	0.7	11:45
	52.7	37.1	1.1	12:15
	54.4	28.3	1.4	1:45
	40.1	19.7	0.5	5:00
Photopic (400-700 nm)	145	114	136	11:45
	163	153	223	12:15
	156	134	248	1:45
	141	95	131	5:00

Hg ²⁺			
September 03, 2009			
full sun	no UVB		Time of Day
Radiation Measured (W/m ²)			
1.8	0.1		11:50
2.3	0.2		1:10
1.0	0.1		4:55
50.1	34.1		11:50
49.4	26.4		1:10
31.8	21.1		4:55
160	130		11:50
157	111		1:10
141	110		4:55
MMHg			
September 01, 2009			
full sun	no UVB	no UV	Time of Day
Radiation Measured (W/m ²)			
1.6	0.1	0.1	11:25
2.1	0.1	0.1	1:00
1.7	0.1	0.1	3:00
0.9	0.1	0.1	4:50
44.1	22.9	0.7	11:25
48.6	25.1	0.7	1:00
44.0	24.7	0.6	3:00
30.4	20.4	0.5	4:50
152	107	149	11:25
159	104	141	1:00
146	111	131	3:00
140	109	118	4:50

Note 1: Radiometer readings at a given time were taken in the absence of (perceptible) cloud cover and in rapid succession for the most accurate comparison possible.

Table 3.2. Isotopic Data for Hg(II) aqueous photo-reduction

sample name	f _R subst	MS n	ave δ ²⁰⁴ Hg (‰)	2SE	ave δ ²⁰² Hg (‰)	2SE	ave δ ²⁰¹ Hg (‰)	2SE	ave δ ²⁰⁰ Hg (‰)	2SE	ave δ ¹⁹⁹ Hg (‰)	2SE	ave δ ¹⁹⁸ Hg (‰)	2SE	Avg Δ ²⁰⁴ Hg (‰)	2SE	Ave Δ ²⁰¹ Hg (‰)	2SE	Avg Δ ²⁰⁰ Hg (‰)	2SE	Avg Δ ¹⁹⁹ Hg (‰)	2SE
Hg(II) July full sun																						
Ph30 R0	1.00	2	-1.00	0.19	-0.67	0.17	-0.50	0.10	-0.42	0.14	-0.20	0.12	-1.04	4.06	0.00	0.07	0.01	0.03	-0.08	0.23	-0.03	0.16
Ph30 R1	1.00	2	-0.92	0.04	-0.60	0.01	-0.46	0.04	-0.39	0.14	-0.19	0.11	-0.16	0.68	-0.03	0.03	-0.01	0.04	-0.09	0.14	-0.04	0.11
Ph30 R3	0.79	2	-0.49	0.03	-0.27	0.02	0.00	0.05	-0.12	0.01	0.15	0.05	-2.03	2.49	-0.08	0.05	0.21	0.06	0.02	0.01	0.22	0.05
Ph30 R4	0.64	2	-0.19	0.08	-0.12	0.05	0.43	0.04	-0.10	0.02	0.50	0.04	-1.01	0.02	-0.01	0.01	0.52	0.00	-0.05	0.01	0.53	0.06
Ph30 R5	0.27	2	0.36	0.04	0.21	0.03	1.97	0.02	0.14	0.09	1.89	0.06	0.40	1.64	0.04	0.01	1.81	0.00	-0.04	0.11	1.84	0.07
Ph30 R6	0.18	2	1.28	0.13	0.87	0.09	3.01	0.06	0.43	0.15	2.64	0.07	-0.62	1.55	-0.02	0.00	2.35	0.00	-0.01	0.19	2.42	0.09
Hg(II) July no UVB																						
Ph31 R0	1	2	-1.04	0.06	-0.69	0.06	-0.55	0.08	-0.23	0.06	-0.12	0.03	-0.36	0.01	0.00	0.03	-0.03	0.04	0.11	0.09	0.06	0.05
Ph31 R1	1.00	2	-1.02	0.01	-0.68	0.02	-0.54	0.04	-0.35	0.27	-0.15	0.22	-1.17	0.55	0.00	0.02	-0.03	0.03	0.00	0.26	0.02	0.22
Ph31 R3	0.78	2	-0.41	0.09	-0.26	0.02	-0.07	0.06	-0.20	0.02	0.04	0.05	-0.74	1.03	-0.02	0.06	0.12	0.04	-0.06	0.03	0.11	0.04
Ph31 R5	0.40	2	0.46	0.21	0.32	0.16	0.87	0.15	0.32	0.25	0.79	0.10	-0.66	2.11	-0.02	0.03	0.63	0.03	0.16	0.33	0.71	0.14
Ph31 R6	0.26	2	1.23	0.16	0.81	0.05	1.73	0.09	0.25	0.28	1.26	0.10	1.38	1.43	0.02	0.09	1.12	0.05	-0.16	0.31	1.05	0.11
Ph31 R7	0.23	2	1.71	0.18	1.19	0.08	1.89	0.04	0.28	0.31	1.17	0.22	0.54	1.40	-0.06	0.05	1.00	0.02	-0.32	0.35	0.87	0.24
Hg(II) July no UV																						
Ph32 R0	1	2	-1.22	0.06	-0.81	0.02	-0.64	0.02	-0.25	0.01	-0.13	0.05	-1.45	2.31	-0.01	0.09	-0.03	0.03	0.15	0.02	0.08	0.06
Ph32 R1	0.94	2	-1.12	0.09	-0.76	0.07	-0.58	0.01	-0.20	0.05	-0.11	0.01	-0.75	0.63	0.01	0.13	-0.01	0.06	0.18	0.01	0.08	0.05
Ph32 R4	0.89	2	-1.30	0.03	-0.86	0.00	-0.67	0.02	-0.33	0.14	-0.16	0.08	-0.37	1.53	-0.01	0.13	-0.02	0.02	0.10	0.14	0.06	0.08
Ph32 R7	0.86	2	-0.73	0.17	-0.46	0.13	-0.35	0.03	-0.18	0.42	-0.08	0.18	0.19	0.66	-0.05	0.13	-0.01	0.07	0.05	0.49	0.03	0.22
Ph32 R9	0.87	2	-0.81	0.02	-0.52	0.06	-0.42	0.03	-0.27	0.05	-0.11	0.00	-0.14	1.71	-0.03	0.13	-0.02	0.01	-0.01	0.02	0.02	0.01
Hg(II) September full sun																						
Ph44 R0	1	2	-0.94	0.12	-0.66	0.12	-0.50	0.07	-0.31	0.10	-0.15	0.02	-0.56	2.59	0.04	0.06	-0.01	0.02	0.02	0.04	0.02	0.01
Ph44 R2	0.66	2	-0.11	0.05	-0.09	0.01	0.17	0.03	-0.05	0.01	0.22	0.03	0.85	1.04	0.03	0.06	0.24	0.02	0.00	0.01	0.24	0.02
Ph44 R3	0.52	2	0.23	0.13	0.12	0.09	0.55	0.05	0.05	0.01	0.50	0.01	0.79	0.07	0.05	0.00	0.46	0.01	-0.01	0.04	0.47	0.04
Ph44 R5	0.38	2	0.98	0.04	0.67	0.05	1.25	0.02	0.35	0.01	0.91	0.00	1.37	2.94	-0.03	0.03	0.74	0.02	0.01	0.02	0.74	0.01
Ph44 R7	0.32	2	1.72	0.16	1.14	0.06	1.72	0.08	0.54	0.01	1.09	0.03	2.46	3.30	0.02	0.06	0.86	0.03	-0.04	0.02	0.81	0.01
Ph44 R9	0.31	2	2.01	0.01	1.37	0.06	1.72	0.03	0.67	0.01	1.03	0.01	0.87	0.52	-0.03	0.08	0.69	0.01	-0.02	0.04	0.68	0.03

Note 1: In graphs and calculations, 2SE of the sample replicates are used unless they are smaller than the 2SD of the secondary standard (UM-Almadén). In cases where 2SE of the sample is smaller (for both MDF and MIF) the 2SD of UM-Almadén is used (italicized entries).

Note 2: All Hg(II) photo-reduction experiments were carried out in 2 mg/l of Suwannee River Fulvic Acid Standard. Initial Hg²⁺(R0) concentrations in the reservoirs were all approximately 30 µg/l. Specific Hg RO concentrations for each experiment were 32.2 µg/l for the Hg(II) July full sun experiment, 31.2 µg/l for the Hg(II) July no UVB experiment, 30.3 µg/l for the Hg(II) July no UV experiment, 31.4 µg/l for Hg(II) September full sun experiment, 28.8 µg/l for the Hg(II) September no UVB experiment, and 28.9 µg/l for the Hg(II) September no UV experiment.

Table 3.2 continued

sample name	f _R subst	MS n	ave δ ²⁰⁴ Hg (‰)	2SE	ave δ ²⁰² Hg (‰)	2SE	ave δ ²⁰¹ Hg (‰)	2SE	ave δ ²⁰⁰ Hg (‰)	2SE	ave δ ¹⁹⁹ Hg (‰)	2SE	ave δ ¹⁹⁸ Hg (‰)	2SE	Avg Δ ²⁰⁴ Hg (‰)	2SE	Ave Δ ²⁰¹ Hg (‰)	2SE	Avg Δ ²⁰⁰ Hg (‰)	2SE	Avg Δ ¹⁹⁹ Hg (‰)	2SE
Hg(II) September no UVB																						
Ph46 R0	1	2	-1.17	0.08	-0.74	0.02	-0.59	0.04	-0.40	0.06	-0.20	0.01	-0.51	3.22	-0.07	0.05	-0.03	0.02	-0.03	0.07	-0.01	0.02
Ph46 R2	0.77	2	-0.48	0.06	-0.20	0.11	-0.10	0.06	-0.13	0.05	0.04	0.06	0.04	0.89	-0.18	0.22	0.05	0.14	-0.03	0.01	0.10	0.09
Ph46 R3	0.65	2	0.15	0.11	0.17	0.01	0.32	0.07	0.08	0.01	0.24	0.04	1.36	0.26	-0.11	0.13	0.19	0.08	-0.01	0.02	0.20	0.04
Ph46 R5	0.52	2	0.65	0.06	0.45	0.06	0.72	0.02	0.24	0.09	0.47	0.03	0.60	0.99	-0.03	0.15	0.38	0.02	0.01	0.06	0.36	0.02
Ph46 R7	0.42	2	1.18	0.01	0.79	0.06	1.08	0.06	0.38	0.08	0.64	0.07	-0.98	1.93	0.01	0.08	0.48	0.02	-0.01	0.05	0.44	0.05
Ph46 R9	0.55	2	0.43	0.19	0.26	0.03	0.47	0.04	0.13	0.08	0.28	0.00	-0.49	0.16	0.04	0.23	0.28	0.06	0.00	0.09	0.22	0.01
Hg(II) September no UV																						
Ph45 R0	1	2	-0.93	0.04	-0.61	0.02	-0.41	0.04	-0.30	0.05	-0.08	0.00	-1.41	1.06	-0.02	0.01	0.05	0.03	0.00	0.04	0.08	0.01
Ph45 R2	0.85	2	-0.59	0.18	-0.39	0.10	-0.23	0.12	-0.20	0.11	-0.01	0.06	0.59	0.38	-0.01	0.03	0.07	0.04	0.00	0.06	0.09	0.04
Ph45 R3	0.75	2	-0.18	0.23	-0.15	0.13	0.06	0.09	-0.08	0.10	0.14	0.07	-0.08	1.84	0.04	0.04	0.17	0.00	0.00	0.04	0.18	0.03
Ph45 R5	0.62	2	0.26	0.15	0.19	0.03	0.41	0.09	0.08	0.03	0.37	0.04	-1.00	0.46	-0.02	0.19	0.27	0.11	-0.01	0.05	0.32	0.05
Ph45 R7	0.55	2	0.30	0.03	0.19	0.00	0.48	0.00	0.08	0.04	0.41	0.00	-0.41	1.28	0.02	0.03	0.34	0.01	-0.01	0.04	0.36	0.01
Ph45 R9	0.59	2	0.10	0.07	0.03	0.02	0.20	0.05	0.02	0.02	0.19	0.03	1.01	0.46	0.05	0.03	0.18	0.06	0.01	0.01	0.18	0.03
Hg(II) Dark Control 2 Abiotic reduction with Suwannee R FAS sealed bottle no sparging																						
PDR4 R0	1.00	2	-0.87	0.01	-0.59	0.06	-0.49	0.09	-0.30	0.02	-0.14	0.04	-0.08	2.06	0.01	0.08	-0.05	0.04	-0.01	0.02	0.01	0.03
PDR4 R1	0.82	2	-0.84	0.02	-0.58	0.02	-0.48	0.01	-0.33	0.04	-0.17	0.04	-0.96	0.72	0.02	0.00	-0.05	0.02	-0.04	0.04	-0.02	0.04
PDR4 R3	0.61	2	-0.59	0.01	-0.39	0.03	-0.33	0.02	-0.19	0.04	-0.14	0.03	-0.12	2.40	-0.01	0.05	-0.04	0.04	0.00	0.06	-0.04	0.04
Bracketing Standard																						
NIST 3133 all sessions			-0.02	0.13	-0.02	0.09	-0.02	0.09	0.01	0.16	0.00	0.10	-0.13	2.75	0.00	0.10	0.00	0.05	0.02	0.15	0.00	0.10
External Standard																						
UM-Amadén July + Control		12	-0.89	0.17	-0.58	0.13	-0.49	0.11	-0.27	0.17	-0.14	0.08	-0.28	2.09	-0.03	0.11	-0.06	0.05	0.02	0.17	0.00	0.07
UM-Amadén September Expts		20	-0.87	0.15	-0.58	0.09	-0.46	0.08	-0.29	0.08	-0.17	0.08	-0.23	2.96	0.00	0.12	-0.02	0.05	0.00	0.06	-0.02	0.07

Note 1: In graphs and calculations, 2SE of the sample replicates are used unless they are smaller than the 2SD of the secondary standard (UM-Almadén). In cases where 2SE of the sample is smaller (for both MDF and MIF) the 2SD of UM-Almadén is used (italicized entries).

Note 2: All Hg(II) photo-reduction experiments were carried out in 2 mg/l of Suwannee River Fulvic Acid Standard. Initial Hg²⁺(R0) concentrations in the reservoirs were all approximately 30 µg/l. Specific Hg RO concentrations for each experiment were 32.2 µg/l for the Hg(II) July full sun experiment, 31.2 µg/l for the Hg(II) July no UVB experiment, 30.3 µg/l for the Hg(II) July no UV experiment, 31.4 µg/l for Hg(II) September full sun experiment, 28.8 µg/l for the Hg(II) September no UVB experiment, and 28.9 µg/l for the Hg(II) September no UV experiment.

Table 3.3. Isotopic Data for MMHg aqueous photo-reduction with UV filtration

sample name	f _R subst	MS n	ave $\delta^{204}\text{Hg}$ (‰)	2SE	ave $\delta^{202}\text{Hg}$ (‰)	2SE	ave $\delta^{201}\text{Hg}$ (‰)	2SE	ave $\delta^{200}\text{Hg}$ (‰)	2SE	ave $\delta^{199}\text{Hg}$ (‰)	2SE	ave $\delta^{198}\text{Hg}$ (‰)	2SE	Avg $\Delta^{204}\text{Hg}$ (‰)	2SE	Ave $\Delta^{201}\text{Hg}$ (‰)	2SE	Avg $\Delta^{200}\text{Hg}$ (‰)	2SE	Avg $\Delta^{199}\text{Hg}$ (‰)	2SE
MMHg July full sun																						
Ph25 R0	1.00	2	-1.74	0.03	-1.14	0.10	-0.81	0.05	-0.58	0.11	-0.21	0.03	-0.57	0.83	-0.04	0.11	0.05	0.02	0.00	0.16	0.08	0.05
Ph25 R1	0.94	2	-1.73	0.05	-1.12	0.01	-0.84	0.02	-0.70	0.13	-0.28	0.01	0.29	2.74	-0.06	0.07	0.00	0.01	-0.14	0.14	0.00	0.02
Ph25 R3	0.90	2	-1.60	0.17	-1.04	0.14	-0.68	0.14	-0.66	0.05	-0.19	0.04	0.72	1.31	-0.05	0.04	0.11	0.04	-0.14	0.12	0.08	0.01
Ph25 R6	0.83	2	-1.57	0.01	-1.00	0.11	-0.45	0.06	-0.50	0.06	0.18	0.09	-1.03	0.33	-0.07	0.17	0.30	0.02	0.00	0.00	0.44	0.06
Ph25 R7	0.79	2	-1.31	0.14	-0.84	0.09	-0.24	0.02	-0.44	0.07	0.24	0.00	-2.16	2.99	-0.06	0.02	0.39	0.04	-0.02	0.03	0.46	0.03
Ph25 R9	0.81	2	-1.31	0.13	-0.86	0.05	-0.21	0.06	-0.45	0.10	0.33	0.09	-0.16	1.88	-0.02	0.06	0.44	0.03	-0.02	0.12	0.55	0.10
MMHg July no UVB																						
Ph28 R0	1.00	2	-1.77	0.08	-1.20	0.04	-0.87	0.04	-0.46	0.06	-0.15	0.04	0.02	0.90	0.02	0.13	0.04	0.01	0.14	0.08	0.16	0.05
Ph28 R1	0.94	2	-1.69	0.12	-1.14	0.01	-0.83	0.12	-0.60	0.11	-0.22	0.04	0.51	0.63	0.01	0.13	0.03	0.11	-0.03	0.12	0.07	0.04
Ph28 R3	0.91	2	-1.71	0.00	-1.14	0.04	-0.82	0.01	-0.71	0.10	-0.28	0.08	-0.20	2.06	-0.01	0.13	0.03	0.04	-0.14	0.12	0.01	0.09
Ph28 R5	0.86	2	-1.67	0.12	-1.15	0.07	-0.79	0.10	-0.53	0.05	-0.18	0.06	-0.81	0.46	0.04	0.13	0.07	0.04	0.05	0.01	0.11	0.04
Ph28 R7	0.83	2	-1.57	0.12	-1.01	0.03	-0.72	0.05	-0.47	0.05	-0.14	0.00	-1.29	0.72	-0.06	0.13	0.04	0.03	0.03	0.03	0.11	0.01
Ph28 R8	0.83	2	-1.48	0.18	-1.00	0.04	-0.70	0.05	-0.39	0.06	-0.08	0.02	-0.50	0.32	0.02	0.13	0.06	0.02	0.12	0.04	0.17	0.00
MMHg July no UV																						
Ph29 R0	1	2	-1.86	0.17	-1.22	0.01	-0.91	0.05	-0.52	0.02	-0.21	0.04	-1.01	0.19	-0.03	0.15	0.01	0.04	0.09	0.03	0.09	0.04
Ph29 R1	0.94	2	-1.87	0.02	-1.27	0.08	-0.89	0.07	-0.40	0.18	-0.09	0.05	-3.40	1.73	0.03	0.10	0.07	0.01	0.24	0.22	0.23	0.07
Ph29 R3	0.91	2	-1.68	0.00	-1.07	0.10	-0.81	0.04	-0.45	0.01	-0.14	0.02	-0.32	1.16	-0.08	0.15	0.00	0.11	0.09	0.07	0.13	0.01
Ph29 R5	0.83	2	-1.38	0.14	-0.93	0.11	-0.61	0.09	-0.45	0.16	-0.14	0.13	-1.70	0.93	0.01	0.01	0.09	0.01	0.02	0.11	0.09	0.10
Ph29 R7	0.78	2	-1.46	0.11	-0.95	0.10	-0.61	0.04	-0.38	0.12	-0.06	0.10	-1.67	0.41	-0.03	0.03	0.11	0.04	0.09	0.17	0.18	0.12
Ph29 R8	0.79	2	-1.35	0.06	-0.90	0.02	-0.59	0.03	-0.50	0.03	-0.15	0.02	-1.17	1.33	-0.01	0.02	0.08	0.02	-0.05	0.02	0.08	0.02
MMHg September full sun																						
Ph41 R0	1	2	-1.71	0.14	-1.14	0.04	-0.84	0.03	-0.57	0.06	-0.23	0.01	-1.05	1.88	-0.02	0.07	0.01	0.00	0.00	0.04	0.05	0.00
Ph41 R1	1.00	2	-1.81	0.07	-1.21	0.17	-0.88	0.14	-0.60	0.07	-0.22	0.05	0.04	0.76	-0.01	0.19	0.03	0.01	0.00	0.01	0.08	0.00
Ph41 R3	0.98	2	-1.57	0.02	-1.03	0.06	-0.60	0.11	-0.51	0.01	-0.03	0.01	-1.09	0.29	-0.04	0.11	0.18	0.04	0.00	0.03	0.23	0.02
Ph41 R4	0.93	2	-1.58	0.10	-1.02	0.09	-0.60	0.03	-0.51	0.07	0.00	0.02	-1.71	3.55	-0.06	0.03	0.17	0.02	0.01	0.02	0.26	0.00
Ph41 R5	0.91	2	-1.49	0.07	-0.95	0.04	-0.53	0.02	-0.48	0.01	0.13	0.02	0.11	0.39	-0.08	0.02	0.18	0.01	0.00	0.01	0.37	0.00
Ph41 R6	0.92	2	-1.44	0.01	-0.93	0.05	-0.37	0.04	-0.46	0.05	0.23	0.00	-2.76	0.13	-0.05	0.07	0.33	0.00	0.01	0.03	0.47	0.01

Note 1: In graphs and calculations, 2SE of the sample replicates are used unless they are smaller than the 2SD of the secondary standard (UM-Almadén). In cases where 2SE of the sample is smaller (for both MDF and MIF) the 2SD of UM-Almadén is used (italicized entries).

Note 2: All MeHg photo-reduction experiments were carried out in 2 mg/l of Suwannee River Fulvic Acid Standard. Initial Hg (R0) concentrations in the reservoirs were all approximately 25 µg/l. Specific Hg RO concentrations for each experiment were 25.0 µg/l for the MeHg July full sun experiment, 25.8 µg/l for the MeHg July no UVB experiment, 26.0 µg/l for the MeHg July no UV experiment, 24.5 µg/l for MeHg September full sun experiment, 24.0 µg/l for the MeHg September no UVB experiment, and 23.0 µg/l for the MeHg September no UV experiment.

Table 3.3 continued

sample name	f _R subst	MS n	ave δ ²⁰⁴ Hg (‰)	2SE	ave δ ²⁰² Hg (‰)	2SE	ave δ ²⁰¹ Hg (‰)	2SE	ave δ ²⁰⁰ Hg (‰)	2SE	ave δ ¹⁹⁹ Hg (‰)	2SE	ave δ ¹⁹⁸ Hg (‰)	2SE	Avg Δ ²⁰⁴ Hg (‰)	2SE	Ave Δ ²⁰¹ Hg (‰)	2SE	Avg Δ ²⁰⁰ Hg (‰)	2SE	Avg Δ ¹⁹⁹ Hg (‰)	2SE
MMHg September no UVB																						
Ph42 R0	1.00	2	-1.73	0.07	-1.16	0.06	-0.84	0.05	-0.60	0.04	-0.23	0.05	-0.61	2.63	0.00	0.02	0.03	0.00	-0.02	0.01	0.06	0.07
Ph42 R1	1.01	2	-1.77	0.10	-1.19	0.11	-0.83	0.07	-0.60	0.03	-0.25	0.01	-0.88	0.33	0.01	0.07	0.06	0.02	0.00	0.03	0.05	0.04
Ph42 R2	0.97	2	-1.64	0.03	-1.08	0.05	-0.74	0.04	-0.52	0.01	-0.13	0.06	-1.25	2.73	-0.03	0.11	0.08	0.00	0.03	0.01	0.14	0.04
Ph42 R4	0.96	2	-1.07	0.03	-0.74	0.14	-0.38	0.18	-0.38	0.23	0.06	0.18	-2.30	4.52	0.03	0.18	0.18	0.08	0.00	0.16	0.24	0.14
Ph42 R5	0.89	2	-1.56	0.07	-1.03	0.05	-0.64	0.00	-0.51	0.01	-0.07	0.04	2.09	1.38	-0.02	0.00	0.14	0.04	0.01	0.03	0.19	0.05
Ph42 R6	0.89	2	-1.30	0.08	-0.87	0.06	-0.50	0.01	-0.43	0.02	0.00	0.02	0.41	0.96	0.01	0.00	0.16	0.03	0.01	0.05	0.23	0.04
MMHg September no UV																						
Ph43 R0	1.00	2	-1.79	0.12	-1.18	0.06	-0.80	0.03	-0.58	0.02	-0.15	0.05	-2.70	2.18	-0.03	0.03	0.09	0.07	0.01	0.05	0.15	0.04
Ph43 R2	0.96	2	-1.73	0.10	-1.18	0.02	-0.80	0.10	-0.57	0.06	-0.21	0.03	0.24	1.58	0.03	0.07	0.08	0.09	0.02	0.05	0.08	0.03
Ph43 R3	0.95	2	-1.66	0.15	-1.11	0.07	-0.75	0.04	-0.54	0.07	-0.14	0.04	-0.14	0.92	0.01	0.05	0.09	0.01	0.02	0.03	0.15	0.02
Ph43 R4	0.95	2	-1.72	0.04	-1.18	0.02	-0.83	0.03	-0.61	0.05	-0.21	0.05	-0.31	1.53	0.04	0.01	0.06	0.01	-0.01	0.04	0.09	0.04
Ph43 R5	0.96	2	-1.78	0.04	-1.20	0.10	-0.87	0.10	-0.60	0.07	-0.18	0.11	0.16	1.33	0.01	0.18	0.03	0.03	0.00	0.03	0.12	0.09
Ph43 R6	0.96	2	-1.71	0.00	-1.14	0.06	-0.79	0.05	-0.54	0.01	-0.15	0.04	-3.18	3.09	-0.01	0.09	0.07	0.09	0.03	0.02	0.14	0.05
sample name	f _R subst	MS n	ave δ ²⁰⁴ Hg (‰)	2SE	ave δ ²⁰² Hg (‰)	2SE	ave δ ²⁰¹ Hg (‰)	2SE	ave δ ²⁰⁰ Hg (‰)	2SE	ave δ ¹⁹⁹ Hg (‰)	2SE	ave δ ¹⁹⁸ Hg (‰)	2SE	Avg Δ ²⁰⁴ Hg (‰)	2SE	Ave Δ ²⁰¹ Hg (‰)	2SE	Avg Δ ²⁰⁰ Hg (‰)	2SE	Avg Δ ¹⁹⁹ Hg (‰)	2SE
Bracketing Standard																						
NIST 3133 all sessions			-0.02	0.13	-0.02	0.09	-0.02	0.09	0.01	0.16	0.00	0.10	-0.13	2.75	0.00	0.10	0.00	0.05	0.02	0.15	0.00	0.10
External Standard																						
UM-Amadén July + Control		12	-0.89	0.17	-0.58	0.13	-0.49	0.11	-0.27	0.17	-0.14	0.08	-0.28	2.09	-0.03	0.11	-0.06	0.05	0.02	0.17	0.00	0.07
UM-Amadén September Expts		20	-0.87	0.15	-0.58	0.09	-0.46	0.08	-0.29	0.08	-0.17	0.08	-0.23	2.96	0.00	0.12	-0.02	0.05	0.00	0.06	-0.02	0.07

Note 1: In graphs and calculations, 2SE of the sample replicates are used unless they are smaller than the 2SD of the secondary standard (UM-Almadén). In cases where 2SE of the sample is smaller (for both MDF and MIF) the 2SD of UM-Almadén is used (italicized entries).

Note 2: All MeHg photo-reduction experiments were carried out in 2 mg/l of Suwannee River Fulvic Acid Standard. Initial Hg (R0) concentrations in the reservoirs were all approximately 25 µg/l. Specific Hg RO concentrations for each experiment were 25.0 µg/l for the MeHg July full sun experiment, 25.8 µg/l for the MeHg July no UVB experiment, 26.0 µg/l for the MeHg July no UV experiment, 24.5 µg/l for MeHg September full sun experiment, 24.0 µg/l for the MeHg September no UVB experiment, and 23.0 µg/l for the MeHg September no UV experiment.