Photodecomposition of Methylmercury in Atmospheric Waters

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ABSTRACT

Experiments were conducted to empirically examine net changes in methylmercury concentration of atmospheric waters as function of irradiance. Methods were developed to allow experiments to be conducted at atmospherically relevant concentrations using trace metal clean techniques, over a range of aqueous matrices. Rain water was collected at Devil's Lake State Park, WI, and simulated cloud water was created by water extraction of particulate matter collected at the same site. These waters were spiked with methyl mercury chloride and mercuric chloride and exposed to sunlight on the roof of a building. Experiments were conducted during typical summer conditions with respect to temperature, sunlight intensity and sunlight duration. For all cases, exposure to sunlight resulted in net loss of methylmercury: -0.022 ± 0.002 1/hr in rainwater at a total UVB flux of 8 kWhrs/m^2; -0.008 ± 0.001 1/hr in simulated cloud water at a total UVB flux of 5.5 kWhrs/m^2. For dark cases, no statistically significant formation in methylmercury from inorganic mercury was detected. Furthermore, laboratory experiments to form methylmercury from mercuric-acetate complexes did not give detectable yields. Given the results of this study, and the results of studies cited in this article, it is unlikely that homogeneous MeHg formation is fast enough to lead to the net formation of MeHg in atmospheric waters exposed to sunlight.

Keywords: Cloud; Fog; Rain; Formation; Methylmercury.

INTRODUCTION

Methylmercury (MeHg) can be found in freshwater and marine fish as a consequence of atmospheric deposition of inorganic mercury. This deposited mercury is subsequently methylated by bacteria in anoxic regions of surface waters and sediments (Bloom, 1992; Westcott and Kalff, 1996; Schroeder and Munthe, 1998; Munthe *et al.*, 2001; USEPA, 2004; Hammerschmidt and Fitzgerald, 2006; Wiener *et al.*, 2006). Although relatively low levels of MeHg are found in most natural waters, MeHg has the ability to bioaccumulate in the aquatic food chain, resulting in levels of MeHg in fish consumed by humans that exceed health guidelines (Sellers *et al.*, 1996; Lin and Pehkonen, 1999; Munthe *et al.*, 2001; Sellers *et al.*, 2001; USEPA, 2004). This is a human health concern because MeHg is a neurotoxin and has been linked to: i) neurological and developmental abnormalities in infants born to mothers with high blood levels of MeHg (Clarkson, 1993; Grandjean *et al.*, 1997; Goldman and Shannon, 2001); and, ii) subclinical health effects in individuals with high consumptions of sport and commerciall fish (Knobeloch *et al.*, 1995; Salonen *et al.*, 1995; Sorensen *et al.*, 1999;

Knobeloch *et al.*, 2006). There has been extensive study of *in situ* formation of MeHg in natural waters and their sediments through biotic and abiotic pathways (Wood, 1968; Jensen and Jernelov, 1969; Gilmour *et al.*, 1992; King *et al.*, 1999; King *et al.*, 2000; Kainz *et al.*, 2006). However, wet deposition has also been shown to be a contributing source of MeHg to natural waters (Sellers *et al.*, 1996; Rolfhus *et al.*, 2003; Hall *et al.*, 2005). MeHg has been directly measured in rain water in remote locations in the Great Lakes Region of the United States and Canada, and in Sweden (St Louis *et al.*, 1995; Munthe *et al.*, 2001; Hall *et al.*, 2005), but the potential source of MeHg in rain water is yet to be determined.

MeHg in rain water could be due to direct emissions from natural and anthropogenic sources (Soar *et al.*, 1999; Lindberg *et al.*, 2001; Hall *et al.*, 2005), decomposition of volatile dimethylmercury (Munthe *et al.*, 2001), or it could be formed in the atmosphere. The focus of this study is on the potential for the atmospheric formation and photodecomposition of MeHg. One possible pathway for atmospheric formation of MeHg was proposed by Gardfeldt *et al.* (2003), who reported MeHg formation under dark and light conditions using solutions of acetic acid and Hg(II). This reaction was proposed to progress via the mercuric acetate complex. However, the chemical speciation of Hg (II) and MeHg in atmospheric waters are not extensively understood and has been found to be

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complex in rainwater (Kieber *et al.*, 2008). Decomposition of MeHg by photodegradation has been shown to take place in surface waters and has been reported in several publications (Sellers *et al.*, 1996; Liu *et al.*, 2000; Sellers *et al.*, 2001). However, Krabbenhoft *et al.* (1998) observed little or no photodegredation of MeHg in water from the Everglades in Florida, while Lean and Siciliano (2003) reported production of MeHg due to solar radiation in surface waters. This range of results demonstrates the complexity of aqueous MeHg chemistry. Furthermore, understanding of MeHg formation and decomposition in natural waters may not directly translate to atmospheric waters because the composition of cloud and fog water is usually very different than water found in lakes and wetlands in terms of inorganic composition, dissolved organic carbon, pH and biota. This means that the chemistry of the reaction systems may be very different. Kieber *et al.* (2008) observed both increases and decreased in methylmercury in filtered rainwater during 6 hour photolysis experiments across samples collected during multiple rain events.

MeHg concentrations in rain water may be determined by a variety of competing processes: 1) abiotic formation in fog and cloud droplets; 2) heterogeneous formation of methylmercury on particles suspended in atmospheric waters; 3) dissolution of methylmercury from particles suspended in atmospheric waters; 4) photo-degradation in fog and cloud droplets; 5) gas-droplet partitioning ; and, 6) scavenging of gases and particulate matter by precipitation during rain events (Gardfeldt *et al.*, 2003; Hammerschmidt *et al.*, 2007; Kieber *et al.*, 2008)

The objective of this study was to determine if there was either formation or photodecomposition of MeHg in matrices of natural rain water or simulated cloud water under summer temperature and sunlight conditions. Sunlight exposure experiments, similar to those done previously (Sellers *et al.*, 1996; Krabbenhoft *et al.*, 1998; Sellers *et al.*, 2001; Lean and Siciliano, 2003), were conducted using rain water and simulated cloud water.

METHODS

Laboratory Experiments of MeHg Formation

Experiments were conducted to investigate the formation of MeHg from Hg(II) acetate complexes presented by Gardfeldt *et al.* (2003). Batch reactions were performed using closed 125 mL wide-mouth Teflon® bottles. All Teflon parts used in the experiments were cleaned in a hot bath of concentrated nitric acid overnight as described in EPA method 1631 revision E. Since MeHg would be measured, there was an additional step of baking overnight with 10% HCl acid to prevent demethylation by halogen gases trapped in the pores of the Teflon after acid cleaning. All bottles were thoroughly rinsed in Millipore MilliQ water (18.2 Mohms) prior to use. Reagent grade chemicals and Millipore MQ water were used in the preparation of all reagent solutions. Hg(II) solutions were diluted from a stock solution of 1000 mg/L preserved in nitric acid and further diluted for each experiment. MeHg spikes were taken from a

stock solution of 100 ng/L. Hg(T) was measured by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) following EPA method 1631 revision E. MeHg analysis was done by gas chromatography CVAFS after distillation and then derivatization by ethylation as per EPA Method 1630, Bloom (1989), and Hall *et al.* (2005).

Distillation prior to derivatization was done in an effort to prevent under-measurement of MeHg due to binding to ligands within the sample matrix. This was especially important for natural water samples that may have contained high levels of dissolved organic carbon (DOC).

Blanks were analyzed for each of the experimental matrices to be used (Table 1). In addition to the matrices for MeHg formation experiments, blank levels were measured in the MQ water, acids, and sodium hydroxide used for preservation and pH manipulation, respectively. The average blank concentration was 0.008 ng/L with a standard deviation of 0.016 ng/L. The average and standard deviation of the measured blanks were used to help estimate the uncertainty of the MeHg measurements. The upper limit of the standard deviation (0.016 ng/L) was taken as the nominal detection limit.

The experimental conditions were similar to those used by Gardfeldt *et al.* (2003). Acetic acid concentrations were varied from 0.33 mM to 33 mM and Hg(II) concentrations from 60 ng/L to 180 ng/L. Solution pH was varied from 3 to 5 by the addition of NaOH, since the pH for MeHg formation reported by Gardfeldt *et al.* (2003) was between 3.0 and 5.1, with the optimal pH at 3.7. The MeHg formation experiments were done at room temperature for 24 and 72 hours. The Teflon bottles were sealed in opaque, brown bags to prevent exposure to light. Upon completion of the reaction period, samples were acidified with 1% HCl by volume and refrigerated until analysis. Samples were analyzed for Hg(T) and MeHg. In addition to varying acetic acid and Hg(II) concentrations, pH, and duration of reaction, different speciations of Hg(II) were also used to determine if there was any matrix effect due to the counter ions in the preservative acid of the Hg(II) solution. Solutions in nitric, hydrochloric and sulfuric acids were used. Finally, some experiments were analyzed by direct ethylation rather than by first distilling the samples to determine if MeHg was being lost in the distillation process. The recoveries of four

Table 1. Summary of blank measurements for MeHg formation experiment method development and validation. Each entry represents an individual measurement.

Blanks	MeHg Concentration (ng/L)
matrix, 33 mM acetic acid	0.009
matrix, 33 mM acetic acid	0.018
MQ water	0.002
66 mM acetic acid	0.004
NaOH	–0.022[*]
50% HCl 1	0.018
50% HCl 2	0.028
Average	0.008
Standard Deviation	0.016

[*] sample not statistically different than zero

matrix spikes of MeHg added to samples were also analyzed: there were three spikes of 600 pg/L and one of 300 pg/L. The spiked samples were treated the same as the unspiked samples and analyzed for MeHg by direct ethylation. The matrix spike recovery averaged 83% with a range of 71% to 103%.

The MeHg system was calibrated as defined my EPA Method 1630, where calibrations were performed at the start of each analysis session which usually included 30 samples, and was checked with matrix spikes every tenth sample. Relative standard deviations of the calibration factors (slope of calibration curve at each data point) had to be less than 15% for the curve to be used to calculate sample contents.

Rain and Simulated Cloud Water Experiments

Rain water was collected at Devil's Lake, Wisconsin (43°26′05″N, 89°40′48″W) for the investigation of reactions in rain exposed to sunlight. The Devil's Lake site was chosen because it is part of the National Atmospheric Deposition Program Mercury Deposition Network. The rain used in the MeHg formation experiments was collected in a single rain event on July 9, 2004. Rain was collected in Teflon bags which were used to line polyethylene bins. The Teflon bags were cleaned using the same nitric acid bath techniques discussed earlier for the Teflon bottles. The rain water was immediately transferred into acid cleaned Teflon bottles and frozen for preservation until it was needed for the irradiation experiments. The event was sampled from beginning to end and no other events were included in the collection on that day. The composition of the rainwater presented in the supplemental materials (bulk composition; Fig. S1) and Figs. 2 and 3 (mercury species) provide a basis for comparison between other event samples. The rain water was characterized for MeHg concentrations, sulfate, nitrate, ammonium, chloride, total dissolved solids (TDS), suspended particulate matter (SPM), total organic carbon (TOC), dissolved organic carbon (DOC), and soil derived cations.

To simulate cloud water, total suspended particulate matter (TSP) was collected over 24 hour collection periods at the Devil's Lake site every day from June 15 through June 26, 2004. The TSP was collected by a General Metal Works Hi-Volume sampler (GMWL 2000; Thermo Andersen, Smyrna, GA, USA) with quartz fiber filters. The particulate matter was collected for 24 hours periods on pre-baked 8 in. × 10 in. filters (QFF; TISSUQUARTZ 2500QAO-UP; Gelman Sciences, Ann Arbor, MI). The filters were pre-and post-weighed in a temperature and humidity controlled atmosphere. Sections from the 10 filters selected (see below for selection criterion) were composited and the particulate matter was extracted in MQ water by shaking overnight and then filtering the extract to remove remnants of the filter.

By the nature of precipitation versus cloud water, it is expected that concentrations of total dissolved solids (TDS; Fig. S1) in clouds are equal or slightly higher than in rain (Malcolm *et al.*, 2003). The mass of particulate matter extracted was made to match the TDS measured in the rain water collected at Devil's Lake State Park in order to

provide a similar concentration for both matrices. To account for the insoluble fraction of particulate matter on the filters, the target mass for the extraction was 3-4 times the intended concentration in order to ensure enough soluble material to meet or exceed the concentration in the rain water. There was not enough rainwater collected in the July, 2004 event used for this study to perform the experiments, and to determine the amount of TDS. Therefore we used systematic collections of rainwater and TSP made during the summer of 2003 to understand average rainwater and aerosol compositions at the site. The average TDS in the 2003 rainwater was 5.8 mg/L, and this measurement directed the mass of TSP collected in 2004 that was used to achieve the target concentration of TDS for the extraction. Taking into consideration the mass of insoluble material on the filter, and the potentially higher concentrations measured in cloud and fog water, the target extract concentrations were set at 20 mg/L. Measurements of the average TSP mass collected on each filter were used to direct the filter area to be excised from 10 filters collected on the days leading up to the July, 2004 rain event.

For the MeHg formation experiments in which rain water was used as the reaction matrix, the rain water was used as collected for one third of the samples. Hg(II) was spiked to a final concentration of 50 ng/L for another third of the samples and MeHg was spiked to a final concentration of 800 pg/L for the final third of the samples. The rainwater was not filtered before use in the experiments. Each group of samples was also divided between exposure to sunlight and darkness. Triplicate samples of the rain water were exposed at each irradiance and spike condition, and one set of triplicates was not spiked and measured at the start of the experiment, constituting a blank. The MeHg formation experiments were done in 125 mL wide-mouth Teflon bottles. Teflon has been shown to transmit visible and UV light (Amyot *et al.*, 1994; Sellers *et al.*, 1996). For the dark experiments the bottles were covered in aluminum foil. Sunlight exposures were performed on the roof of a building adjacent to the Environmental Chemistry and Technology Laboratories in Madison, WI (43.077236°N, 89.402947°W). Portions of the samples exposed to light were preserved immediately after preparation, after one day of reaction, and after five days of reaction. Portions of the dark samples were preserved immediately after preparation and after five days of reaction. To minimize variations in temperatures between samples, they were placed in an unheated, shallow water bath. The temperature was continuously monitored by a HOBO® Water Temp Pro temperature logger (Onset, Pocasset, MA) at an interval of one reading per minute. The temperature logger was covered in aluminum foil to prevent inaccurate temperature measurements due to direct sunlight. Air temperature measurements were downloaded from National Environmental Satellite, Data and Information Service (NESDIS), operated by the National Oceanic and Atmospheric Association (NOAA), which were collected at Madison International Airport (~3 miles from EC&T Labs). In addition to monitoring water and air temperature, UVB (290 nm–320 nm) measurements were provided by the

Integrated Surface Irradiance Study Network, operated by NOAA at Madison, WI (43.13°N, 89.33°W).

For the MeHg formation experiments conducted using the simulated cloud water, the same protocol was used for the no-spike, Hg(II)-spike, and MeHg-spike splits as was used in the rain water experiments. The same splits of exposure to sunlight and darkness were also used, except an unspiked solution was not subjected to UV exposure, since the amounts of native Hg(II) and MeHg present were too low to detect any potential formation or degradation of MeHg. Triplicate samples of the simulated cloud water were used to follow MeHg concentrations during exposure, while duplicate samples were used to follow the Hg(II) concentrations. Two unspiked samples were analyzed at the start of the experiment, one in which MeHg was measured, the other in which Hg(II) was measured.

The rainwater MeHg formation experiments were performed in August, 2004, while the simulated cloud water experiments were conducted in June, 2005. All of the MeHg analysis used the distillation, derivatization, and CVAFS measurement methods described in the previous section.

RESULTS AND DISCUSSION

Laboratory Experiments of MeHg Formation

Attempts were made to replicate the results presented by Gardfeldt *et al.* (2003) which suggested that MeHg can be formed via the mercuric acetate complex. The formation of MeHg reported could not be replicated using the experimental conditions presented by the authors. Table 2 is a list of the conditions under which MeHg formation was attempted; the acetic acid concentrations used in these experiments were the same concentrations used by Gardfeldt *et al.* (2003a). A review of published measurements for acetic acid in cloud and fog water is presented by Bittrich *et al.* (2011), and shows the concentrations used by the Gardfeldt (0.33–33 mM) to be higher than those measured in the atmosphere (0.01–0.118 mM). For each of the experimental conditions there was no significant formation of MeHg. Furthermore, thermodynamic modeling of

mercury speciation in the aqueous component of cloud and fog water indicated that mercuric acetate is not an important complex in atmospheric waters, due to the low concentration of acetate ion in atmospheric waters and the high affinity of reactive mercury for the chloride ion (Bittrich *et al.*, 2011). Given the results of the thermodynamic modeling study, the lack of MeHg formation in these experiments is reasonable.

### *Rain and Simulated Cloud Water Experiments*

Experiments using both rain water and simulated cloud water were used to investigate the potential for formation or decomposition of MeHg in atmospheric waters under summer conditions.

Figs. 1(a) and 1(b) show the air and water temperature profiles and UVB exposure profiles of the rain water (1(a)) and simulated cloud water (1(b)). Because the exposures were performed outside, the temperature and UVB light vary diurnally, as would be the case for cloud droplets being transported in the atmosphere. Air temperatures ranged between 6.7°C and 27.2°C during the rain water exposures, and between 17.8°C and 13.7°C during the simulated cloud water exposures. Water temperatures ranged between 8.1°C and 29.9°C during the rain water exposures. The water temperature monitor failed on the first day during the simulated cloud water experiments. Air temperature data provide a basis for estimating the water temperature given the relationship seen between the air and water temperature data in the rain water experiments (Fig. 1(a)). Measurements of UVB flux were available every 3 minutes throughout the experiment and flux maxima were consistently 0.2 W/m^2 on each day during both experiments. Intermittent cloud cover was observed in the UVB data as a disruption in the expected smooth, sinusoidal curves. The total UVB fluxes for the rain water experiments were 8 $kWhrs/m^2$ in the rain water expts (Fig. 1(a)), and 5.5 $kWhrs/m^2$ in the simulated cloud water experiments. The lower flux during the August 2004 experiment was due to greater cloud cover.

Decomposition of MeHg was observed in the rainwater and simulated cloud water that had been spiked and irradiated before analysis at day 1 (Fig. 2). This

Table 2. Experimental conditions for mercuric acetate complex methylation reactions.

pH	acetic acid (mM)	Hg(II) (ng/L)	Counter Ion	Sunlight exposure	MeHg Analysis	number of replicates	MeHg formation
3	33	60	nitrate	no	distilled	3	NO
4	33	60	nitrate	no	distilled	1	NO
4	3.3	60	nitrate	no	distilled	1	NO
4	0.33	60	nitrate	no	distilled	1	NO
5	0.33	60	nitrate	no	distilled	1	NO
5	3.3	60	nitrate	no	distilled	1	NO
5	33	60	nitrate	no	distilled	1	NO
3.4	33	180	chloride	no	distilled	3	NO
3.2	33	180	sulfate	no	distilled	3	NO
3.2	33	180	nitrate	no	distilled	3	NO
3.5	33	180	nitrate	no	distilled	3	NO
3.2	33	180	nitrate	no	direct ethylation	3	NO
3.5	33	180	nitrate	no	direct ethylation	3	NO
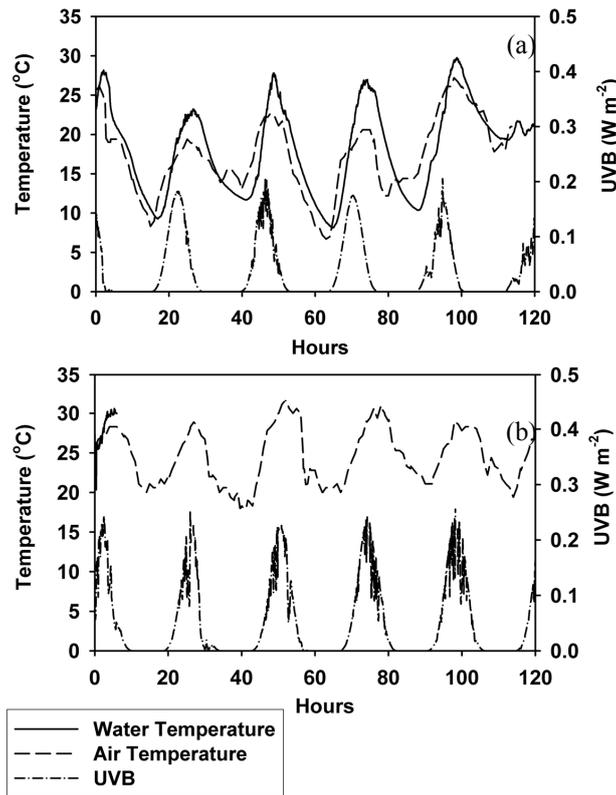
Fig. 1. (a) Air temperature, sample water temperature, and UVB flux for the sunlight exposures rain water collected at Devil's Lake State Park; (b) air temperature, sample water temperature, and UVB flux for the simulated cloud water sunlight exposures. Simulated cloud water was made from dissolving TSP collected at Devil's Lake State Park in MilliQ water.
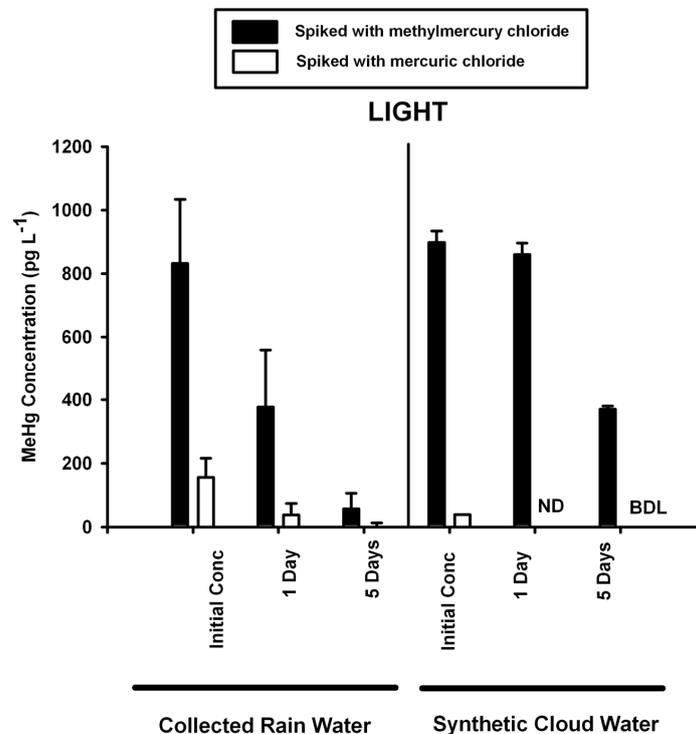
Fig. 2. Changes in MeHg concentration in samples of rain water and simulated cloud water during 5 day sunlight exposure experiments. Samples were either left unamended, or spiked with MeHg or Hg(II). ND means "No Data", and BDL means "Below Detection Limit". Uncertainties are represented by the standard deviation of replicate samples and blank concentrations.

decomposition had progressed further by day 5. By contrast, no statistically significant MeHg formation was observed in the samples spiked with 55 ng/L of Hg(II) or in the samples spiked with 900 pg/L of MeHg. This interpretation stems from the overlap of the uncertainty bars on in each of the individual data points in Figs. 2 and 3. The uncertainty bars represent the quadrative summation of standard deviations from replicate and blank measurements for conditions with two or more replicate bottles. For conditions with only one measurement no error bars were given, but the measurement uncertainty should be estimated from the uncertainties reported for the other samples. Even if the apparent increase in MeHg concentrations observed in the darkened samples in Fig. 3 are real, the dominant behavior in samples exposed to both light (day) and dark (night) conditions in Fig. 3 is net decomposition. It is our interpretation that these samples are a reasonable representation of the net changes in MeHg concentration in atmospheric waters as they are transported.

Native MeHg levels in the unspiked solutions were too low (i.e. too close to blank concentrations) to observe any statistically significant decrease in concentration in the irradiated experiments, although a decreasing trend was suggested (Fig. 2). In the darkened experiments, no statistically significant change in native MeHg was observed in the darkened samples over the course of the experiments although an increasing trend was suggested (Fig. 3).

The results of this study clearly demonstrated that MeHg was decomposed in our samples of rain water and simulated cloud water when spiked with large concentrations of MeHg, and that no statistically significant formation of MeHg was observed when the samples were spiked with large concentrations of Hg(II). This implied that decomposition reactions of MeHg dominated when concentrations were elevated above 100–200 pg/L. The lack of MeHg formation in the samples spiked with Hg(II) show the absence of a mechanism that could compete with MeHg decomposition to produce steady state MeHg concentrations, or photo-associated increases in MeHg as has been proposed in other studies (Hammerschmidt *et al.*, 2007; Kieber *et al.*, 2008). The experiments were conducted in closed batch reactions meaning that they did not allow for replenishing of the removed MeHg by gas-particle partitioning of atmospheric gaseous MeHg to the cloud or fog droplet.

Estimates of methylmercury photodecomposition rates (Table 3) were made using first order reaction model fits for rainwater (-0.022 ± 0.002 1/hr), and the synthetic cloud water (-0.008 ± 0.001 1/hr) presented in Fig. 2. The uncertainties in these rates of decomposition were the standard errors calculated from the least squares linear regression. The rates were measured at total UVB fluxes of 8 kWhrs/m^2 and 5.5 kWhrs/m^2, respectively (Figs. 1(a) and 1(b)). The average $\pm$ 1 standard deviation, the minimum, and the maximum air temperatures measured during each experiment were as follows: i) rainwater experiment, avg $\pm$ 1 sdv = 24 $\pm$ 3°C, min = 17.8°C, max = 31.7°C; for the simulated cloudwater experiments avg $\pm$ 1 sdv = 17.4 $\pm$ 5°C, min = 6.7°C, max = 27.2°C (Figs. 1(a) and 1(b)). Removal of MeHg was slower in the simulated cloud water
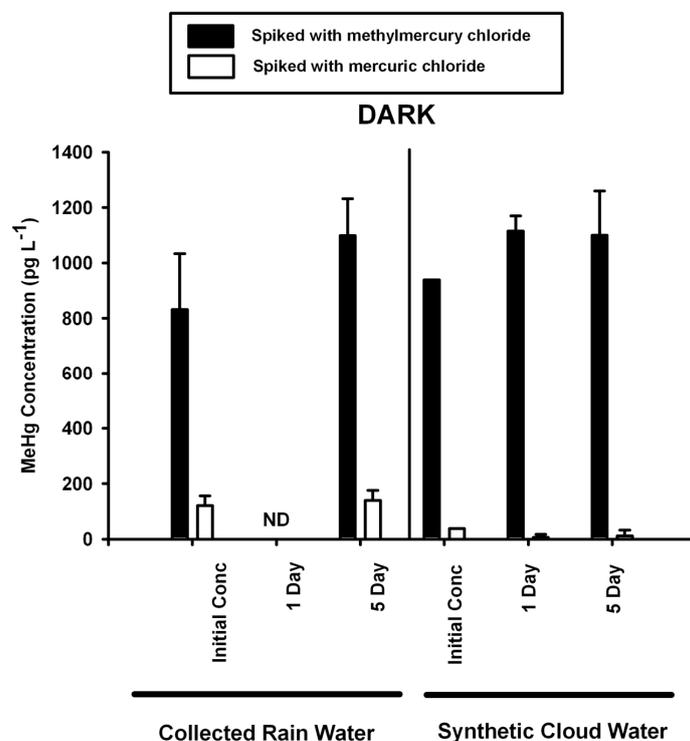
Fig. 3. Changes in MeHg concentration in samples of rain water and simulated cloud water during 5 day darkness exposure experiments. Samples were spiked with MeHg or Hg(II). BDL means "Below Detection Limit". Uncertainties are represented by the standard deviation of replicate samples and blank concentrations.

Table 3. Estimates of methylmercury production and photodecomposition rates in rainwater and simulated cloud water.

Matrix	Dark k (1/hr)	Light k (1/hr)
Collected Rainwater	0.001 ± 0.001	-0.022 ± 0.002
Simulated Cloudwater	0.002	-0.008 ± 0.001

experiment, probably due to the increased cloud cover and a lower UVB flux (Fig. 1(b)), although differences in the chemistry and suspended particulate loadings between the rain water (unfiltered) and simulated cloud water (filtered) may have also played a role.

Gardfeldt *et al.* (2001) estimated MeHg photodecomposition to be -0.8 ± 0.07 1/hr using a simplified reaction system based on MilliQ water spiked with Hg, MeHg, NO_3^-, and a phosphate buffer to test the effects of ligand binding. The reaction mixture was irradiated with a 450W Xe arc lamp with a filter to remove wavelengths less than 290 nm. Kieber *et al.* (2008) also measured MeHg decreases in a subset of rainwater samples from event collections when they were irradiated with a Xe arc lamp. Analysis of the data reported by Kieber for these events gave an average photodecomposition rate of -0.11 ± 0.07 1/hr, the lower uncertainty range of which is close to the photodecomposition rate measured in rainwater in this study. However, the irradiances of UV that the samples were exposed to in the Garfeldt and Kieber studies were not reported, meaning that direct comparisons to outdoor exposure experiments cannot be made since the reaction rate is dependent on photon flux. Furthermore, the Garfeldt study used simplified experimental matrices to allow a very pure observation of the MeHg photodecomposition reaction. In contrast, Bittrich *et al.* (2011) revealed that the use of more environmentally realistic experimental matrices gave rise to different MeHg speciations than were used by Gardfeldt *et al.* (2001), and the results reported in this article demonstrate that when these realistic matrices were combined with authentic exposures to sunlight different decomposition rates were measured than those observed by the Kieber and Garfeldt studies. The photodecomposition rates measured in our study compare reasonably well with photodemethylation rates between -0.01 and -0.04 /1hr observed in lakes (Sellers *et al.*, 1996).

CONCLUSIONS

Photodecomposition of MeHg was observed in rain water and simulated cloud water following the additions of high concentration MeHg spikes and exposure to sunlight. No statistically significant decreases or increases in MeHg concentrations were observed in darkened control experiments, despite apparent increases in the MeHg spiked samples in both experiments and the Hg(II) spiked rainwater. MeHg was not formed in laboratory experiments using Hg(II) and acetate as per Gardfeldt *et al.* (2003), and Gardfeldt showed that dark formation of MeHg was effectively counterbalanced by photodecomposition when the samples were irradiated with UV. Furthermore, a

modeling study by Bittrich *et al.* (2011) suggested that mercuric-carboxylate complexes would not be concentrated enough to lead to significant homogeneous formation of MeHg in the aqueous phase in fog and cloud water. However, Kieber *et al.* (2008) observed both increases and decreases in methylmercury concentrations during 6h irradiances of unfiltered rainwater samples, indicating that both photo induced formation and decomposition were occurring to different degrees in samples collected during different events. If we consider the results presented here, in conjunction with the observations and results of Gardfeldt *et al.* (2001), Gardfeldt *et al.* (2003), Kieber *et al.* (2008) and Bittrich *et al.* (2011), it seems that even if abiotic homogeneous MeHg formation does occur in atmospheric waters, it is unlikely to be important enough to lead to the net formation of MeHg by the homogeneous aqueous pathway observed by Gardfeldt *et al.* (2003): it would appear that the photodecomposition reaction is faster than the homogeneous formation pathway. It is possible that increases in MeHg observed in rainwater by Kieber on exposure to light were due to reactive formation on particle surfaces, or photo-mediated releases from suspended particulate which were not consistently active in all rain events, perhaps due to the chemistry of the rainwater and its suspended particulate. Photomediated release from particles in rainwater was observed by Kieber for total mercury, but more research is needed to determine whether such heterogeneous pathways are important for methylmercury in fog and cloud water.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES

Amyot, M., Mierle, G., Lean, D.R.S. and McQueen, D.J. (1994). Sunlight-Induced Formation of Dissolved Gaseous Mercury in Lake Waters. *Environ. Sci. Technol.* 28: 2366–2371.

Bittrich, D.R., Chadwick, S.P., Babiarz, C.L., Manolopoulos, H., Schauer, J.J., Armstrong, D.E., Collett, J. and Herckes, P. (2011). Speciation of Mercury (Ii) in Cloud and Fog Water. *Aerosol Air Qual. Res., In Press.*

Bloom, N., (1989). Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas-Chromatography with Cold Vapor Atomic Fluorescence Detection. *Can. J. Fish. Aquat. Sci.*

46: 1131–1140.

Bloom, N.S. (1992). On the Chemical Form of Mercury in Edible Fish and Marine Invertebrate Tissue. *Can. J. Fish. Aquat. Sci.* 49: 1010–1017.

Clarkson, T.W. (1993). Mercury - Major Issues in Environmental-Health. *Environ. Health Perspect.* 100: 31–38.

Gardfeldt, K., Munthe, J., Stromberg, D. and Lindqvist, O. (2003). A Kinetic Study on the Abiotic Methylation of Divalent Mercury in the Aqueous Phase. *Sci. Total Environ.* 304: 127–136.

Gardfeldt, K., Sommar, J., Stromberg, D. and Feng, X.B. (2001). Oxidation of Atomic Mercury by Hydroxyl Radicals and Photoinduced Decomposition of Methylmercury in the Aqueous Phase. *Atmos. Environ.* 35: 3039–3047.

Gilmour, C.C., Henry, E.A. and Mitchell, R. (1992). Sulfate Stimulation of Mercury Methylation in Fresh-Water Sediments. *Environ. Sci. Technol.* 26: 2281–2287.

Goldman, L.R. and Shannon, M.W. (2001). Technical Report: Mercury in the Environment: Implications for Pediatricians. *Pediatrics* 108: 197–205.

Grandjean, P., Weihe, P., White, R.F., Debes, F., Araki, S., Yokoyama, K., Murata, K., Sorensen, N., Dahl, R. and Jorgensen, P.J., (1997). Cognitive Deficit in 7-Year-Old Children with Prenatal Exposure to Methylmercury. *Neurotoxicol. Teratol.* 19: 417–428.

Hall, B.D., Manolopoulos, H., Hurley, J.P., Schauer, J.J., St Louis, V.L., Kenski, D., Graydon, J., Babiarz, C.L., Cleckner, L.B. and Keeler, G.J. (2005). Methyl and Total Mercury in Precipitation in the Great Lakes Region. *Atmos. Environ.* 39: 7557–7569.

Hammerschmidt, C.R. and Fitzgerald, W.F. (2006). Methylmercury in Freshwater Fish Linked to Atmospheric Mercury Deposition. *Environ. Sci. Technol.* 40: 7764–7770.

Hammerschmidt, C.R., Lamborg, C.H. and Fitzgerald, W.F. (2007). Aqueous Phase Methylation as a Potential Source of Methylmercury in Wet Deposition. *Atmos. Environ.* 41: 1663–1668.

Jensen, S. and Jernelov, A. (1969). Biological Methylation of Mercury in Aquatic Organisms. *Nature* 223: 753–754.

Kainz, M., Telmer, K. and Mazumder, A. (2006). Bioaccumulation Patterns of Methyl Mercury and Essential Fatty Acids in Lacustrine Planktonic Food Webs and Fish. *Sci. Total Environ.* 368: 271–282.

Kieber, R.J., Parler, N.E., Skrabal, S.A. and Willey, J.D. (2008). Speciation and Photochemistry of Mercury in Rainwater. *J. Atmos. Chem.* 60: 153–168.

King, J.K., Kostka, J.E., Frischer, M.E. and Saunders, F.M. (2000). Sulfate-Reducing Bacteria Methylate Mercury at Variable Rates in Pure Culture and in Marine Sediments. *Appl. Environ. Microbiol.* 66: 2430–2437.

King, J.K., Saunders, F.M., Lee, R.F. and Jahnke, R.A. (1999). Coupling Mercury Methylation Rates to Sulfate Reduction Rates in Marine Sediments. *Environ. Toxicol. Chem.* 18: 1362–1369.

Knobeloch, L., Steenport, D., Schrank, C. and Anderson, H. (2006). Methylmercury Exposure in Wisconsin: A Case Study Series. *Environ. Res.* 101: 113–122.

Knobeloch, L.M., Ziarnik, M., Anderson, H.A. and Dodson, V.N. (1995). Imported Sea-Bass as a Source of Mercury Exposure - A Wisconsin Case-Study. *Environ. Health Perspect.* 103: 604–606.

Krabbenhoft, D.P., Hurley, J.P., Olson, M.L. and Cleckner, L.B. (1998). Diel Variability of Mercury Phase and Species Distributions in the Florida Everglades. *Biogeochemistry* 40: 311–325.

Lean, D.R.S. and Siciliano, S.D. (2003). Production of Methymercury by Solar Radiation. *J. Phys. IV* 107: 743–747.

Lin, C.J. and Pehkonen, S.O. (1999). The Chemistry of Atmospheric Mercury: A Review. *Atmos. Environ.* 33: 2067–2079.

Lindberg, S.E., Wallschlager, D., Prestbo, E.M., Bloom, N.S., Price, J. and Reinhart, D. (2001). Methylated Mercury Species in Municipal Waste Landfill Gas Sampled in Florida, USA. *Atmos. Environ.* 35: 4011–4015.

Liu, J., Wang, W. and Peng, A. (2000). The Photochemical Reduction of Divalent Mercury and Methyl-Mercury. *J. Environ. Sci. Health* 35: 1859–1867.

Malcolm, E.G., Keeler, G.J., Lawson, S.T. and Sherbatskoy, T.D. (2003). Mercury and Trace Elements in Cloud Water and Precipitation Collected on Mt. Mansfield, Vermont. *J. Environ. Monit.* 5: 584–590.

Munthe, J., Kindbom, K., Kruger, O., Petersen, G., Pacyna, J. and Iverfeldt, A. (2001). Examining Source-Receptor Relationships for Mercury in Scandinavia. *Water Air Soil Pollut. Focus* 1: 299–310.

Rolfhus, K.R., Sakamoto, H.E., Cleckner, L.B., Stoor, R.W., Babiarz, C.L., Back, R.C., Manolopoulos, H. and Hurley, J.P. (2003). Distribution and Fluxes of Total and Methylmercury in Lake Superior. *Environ. Sci. Technol.* 37: 865–872.

Salonen, J.T., Seppanen, K., Nyyssonen, K., Korpela, H., Kauhanen, J., Kantola, M., Tuomilehto, J., Esterbauer, H., Tatzber, F. and Salonen, R. (1995). Intake of Mercury from Fish, Lipid-Peroxidation, and the Risk of Myocardial-Infarction and Coronary, Cardiovascular, and Any Death in Eastern Finnish Men. *Circulation* 91: 645–655.

Schroeder, W.H. and Munthe, J. (1998). Atmospheric Mercury - An Overview. *Atmos. Environ.* 32: 809–822.

Sellers, P., Kelly, C.A. and Rudd, J.W.M. (2001). Fluxes of Methylmercury to the Water Column of a Drainage Lake: The Relative Importance of Internal and External Sources. *Limnol. Oceanogr.* 46: 623–631.

Sellers, P., Kelly, C.A., Rudd, J.W.M. and MacHutchon, A.R. (1996). Photodegradation of Methylmercury in Lakes. *Nature* 380: 694–697.

Sommar, J., Feng, X.B. and Lindqvist, O. (1999). Speciation of Volatile Mercury Species Present in Digester and Deposit Gases. *Appl. Organomet. Chem.* 13: 441–445.

Sorensen, N., Murata, K., Budtz-Jorgensen, E., Weihe, P. and Grandjean, P. (1999). Prenatal Methylmercury Exposure as a Cardiovascular Risk Factor at Seven Years of Age. *Epidemiology* 10: 370–375.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A. and Barrie, L.A. (1995). Wet Deposition of Methyl Mercury in

Northwestern Ontario Compared to Other Geographic Locations. *Water Air Soil Pollut.* 80: 405–414.

USEPA (2004). National Listing of Fish Advisories Fact Sheet, EPA Doc. EPA-823-F-04-016

Westcott, K. and Kalff, J. (1996). Environmental Factors Affecting Methyl Mercury Accumulation in Zooplankton. *Can. J. Fish. Aquat. Sci.* 53: 2221–2228.

Wiener, J.G., Knights, B.C., Sandheinrich, M.B., Jeremiason, J.D., Brigham, M.E., Engstrom, D.R., Woodruff, L.G., Cannon, W.F. and Balogh, S.J. (2006). Mercury in Soils, Lakes, and Fish in Voyageurs National Park (Minnesota): Importance of Atmospheric Deposition and Ecosystem Factors. *Environ. Sci. Technol.* 40: 6261–6268.

Wood, J. (1968). Synthesis of Methyl-Mercury Compounds by Extracts of a Methanogenic Bacterium. *Nature* 220: 173.