

2015

Stability of Monomethylmercury in Water

Sarah Elyse Harvey
Wright State University

Follow this and additional works at: https://corescholar.libraries.wright.edu/etd_all



Part of the [Earth Sciences Commons](#), and the [Environmental Sciences Commons](#)

Repository Citation

Harvey, Sarah Elyse, "Stability of Monomethylmercury in Water" (2015). *Browse all Theses and Dissertations*. 1301.
https://corescholar.libraries.wright.edu/etd_all/1301

This Thesis is brought to you for free and open access by the Theses and Dissertations at CORE Scholar. It has been accepted for inclusion in Browse all Theses and Dissertations by an authorized administrator of CORE Scholar. For more information, please contact corescholar@www.libraries.wright.edu, library-corescholar@wright.edu.

STABILITY OF MONOMETHYLMERCURY IN WATER

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

SARAH ELYSE HARVEY
B.S., Wright State University, 2012

2015
Wright State University

WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

May 12, 2015

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Sarah Elyse Harvey ENTITLED Stability of Monomethylmercury in Water BE ACCEPTED IN PARTIAL FULFILLMENT OF THEREQUIREMENTS FOR THE DEGREE OF Master of Science.

Chad R. Hammerschmidt, Ph.D.
Thesis Director

David F. Dominic, Ph.D.
Chair, Department of Earth &
Environmental Science

Committee on
Final Examination

Chad R. Hammerschmidt, Ph.D.

Carl H. Lamborg, Ph.D.

Christopher Barton, Ph.D.

Robert E. W. Fyffe, Ph.D.
Vice President for Research and Dean of Graduate School

ABSTRACT

Harvey, Sarah E. M.S. Department of Earth and Environmental Sciences, Wright State University, 2015. Stability of Monomethylmercury in Water.

Monomethylmercury (MMHg) bioaccumulates in aquatic food webs, leading to concentrations in fish that increase health risks for humans who consume fish. As a result of processes that produce and decompose it, MMHg concentrations are notoriously unstable in many natural waters. I examined the stability of MMHg in both filter-sterilized ($< 0.1 \mu\text{m}$) reagent-grade water and $0.22\text{-}\mu\text{m}$ filtered sediment pore water from Grand Lake St. Marys, Auglaize and Mercer Counties, Ohio, each at three MMHg treatment concentrations (1, 5, and 50 ng/L). Reagent-grade water samples were incubated under both light and dark conditions at either 5 or 26 °C for 112 days. Pore water samples were incubated in the dark at 26 °C, mimicking environmental conditions, for a period of 98 days. Decay constants ($\pm 95\%$ CI) for solutions containing either 1 or 5 ng/L MMHg in reagent-grade water ranged from 0.0009 ± 0.0013 to $0.1225 \pm 0.0150 \text{ d}^{-1}$, with greater decay constants at higher temperature and no significant effect of light exposure. In contrast, decay constants for 50 ng/L MMHg in reagent-grade water were much less than those in more dilute solutions, ranging from 0.0018 ± 0.0015 to $0.0055 \pm 0.0023 \text{ d}^{-1}$, with both light and temperature influencing MMHg decomposition. Decay constants of MMHg in pore water were found to be independent of initial concentration of MMHg; however, decay constants in pore water samples were 3-fold higher than those in reagent-grade water amended with the same initial concentration ($p = 0.007$). These results suggest that natural constituents in pore water accelerate MMHg decay reactions.

TABLE OF CONTENTS

	Page
I. INTRODUCTION.....	1
II. OBJECTIVE.....	4
III. METHODS AND MATERIALS	
Stability in reagent-grade water.....	5
Stability in pore water.....	7
MMHg analysis.....	8
Statistical analysis.....	10
IV. RESULTS	
Reagent-grade water.....	11
Pore water.....	15
V. DISCUSSION	
Reagent-grade water.....	18
Pore water.....	19
VI. CONCLUSION.....	20
VII. LITERATURE CITED.....	22

LIST OF FIGURES

Figure	Page
1. Decay curves of time zero normalized MMHg for 1ng/L spike (a), 5 ng/L spike (b), and 50 ng/L spike (c). Filled blue = dark, 5 °C; filled red = dark, 26 °C; open blue = light, 5 °C; open red = light, 26 °C. Horizontal lines show the detection limit of 0.04 ng/L.....	13
2. Decay constants of MMHg in filtered pore water for 1 ng/L (a), 5 ng/L spike and negative control (b), 50 ng/L (c), and native control (d) solutions. Samples were and incubated in the dark at 26 °C to mimic the field conditions.....	16

LIST OF TABLES

Table	Page
1. Design of experiment to examine MMHg stability in reagent-grade water. Each treatment and time point included three independent samples, for a total of 384 samples.....	6
2. Design of experiment to examine MMHg stability in filtered pore water. Each treatment and time point included three independent samples, for a total of 144 samples.....	9
3. MMHg decomposition rate constants k_d (\pm 95% CI) in reagent-grade water and p -values for the slope of the regression line shown in figure 1.....	14
4. Decay constants (\pm 95% CI) for each pore water treatment. All treatments had a calculated p -value of <0.005 , indicating k_d is significantly different from zero.....	17

I. INTRODUCTION

Natural and anthropogenic sources introduce mercury (Hg) to the atmosphere (Pirrone et al., 2010), which is then deposited into aquatic systems. Once in aquatic systems, microorganisms, such as sulfate-reducing bacteria, can transform inorganic forms of Hg (Hg(II)) to monomethylmercury (MMHg; Compeau and Bartha, 1985; Gilmour et al., 2013). MMHg is passively bioconcentrated from water by benthic and pelagic primary producers (Mason et al., 1996; Hammerschmidt and Fitzgerald, 2006a) and subsequently biomagnified in aquatic food webs (Wiener et al., 2003), resulting in potentially harmful concentrations in fish that humans consume (Mergler et al., 2007). Accordingly, and among many ecological factors, concentrations of MMHg dissolved in water can be an important control on levels in aquatic organisms (Chen et al., 2014).

The concentration of MMHg in water is a balance between processes that add and remove it. Methylation of Hg in the water column, sediments, and watershed (particularly wetlands) are important sources of MMHg in aquatic systems (Drott et al., 2008; Hammerschmidt and Fitzgerald, 2006c; Sellers and Kelly, 2001; Yan et al., 2013; Marvin-DiPasquale et al., 2014), and considerable effort has been made to quantify its rates of production (Hammerschmidt and Fitzgerald, 2004; Heyes et al., 2006; Lehnher et al., 2011; Yu et al., 2012) and the mechanism of the process (Parks et al., 2013). Comparatively much less is known about losses of MMHg from aquatic systems, particularly its decomposition in the water column.

MMHg is known to be decomposed in aquatic ecosystems by both microbial and photochemical processes. Decomposition of MMHg in natural surface waters is a first-order reaction related to light intensity (Sellers et al., 1996; Hammerschmidt and

Fitzgerald, 2006d; Black et al., 2012). Lehnherr and St. Louis (2009) found that UV-A radiation (315–400 nm) accounted for about half (42–58%) of the MMHg that was photochemically decomposed in surface waters, while UV-B (280–315 nm) was responsible for 12–18% and visible light (380–750 nm) for the other 24–46%. Photolysis of MMHg in natural systems is thought to be by an indirect mechanism (Hammerschmidt and Fitzgerald, 2010; Zhang and Hsu-Kim, 2010). Intermediate pathways of photochemical MMHg decomposition are hypothesized to include attack by hydroxyl radical generated by either the photo-Fenton reaction (Hammerschmidt and Fitzgerald, 2010) or nitrate photolysis (Chen et al., 2003), and singlet oxygen resulting from solar irradiation of dissolved organic matter (Zhang and Hsu-Kim, 2010); however, Black et al. (2012) suggest that singlet oxygen production does not cause a significant change in demethylation rates in natural surface waters.

Demethylation of MMHg is also known to occur by oxidative and reductive microbial pathways (Marvin-DiPasquale et al., 2000; Moore et al., 1990; Robinson and Touvinen, 1984; Oremland et al., 1991; Oremland et al., 1995). MMHg can be decomposed by the oxidative pathway to Hg(II) and CO₂ (Marvin-DiPasquale et al., 2000), presumably by methylotrophic microorganisms for energy. Oxidative pathways are suspected to dominate in natural systems; however, reductive demethylation has been observed in highly contaminated systems (Marvin-DiPasquale et al., 2000). Reductive microbial demethylation occurs as a result of the organomercurial lyase (MerB) and mercuric reductase (MerA) enzymes, yielding CH₄ and elemental Hg (Moore et al., 1990; Robinson and Touvinen, 1984; Schaefer et al., 2004). MerA and MerB proteins are transcribed from the *merA* and *merB* genes located on the cosmopolitan *mer* operon,

hypothesized to be an ancient gene sequence (Osborne et al., 1997). As little as 80,000 ng/L of Hg(II) has been found to be sufficient for inducing transcription of *mer* genes (Schaefer et al., 2004).

As a result of known, and more likely unknown, decomposition reactions, MMHg concentrations are notoriously unstable in natural water samples. In both unpreserved and acidified water samples, MMHg can be lost to adsorption to the wall of sample containers (Parker and Bloom, 2005). Container material also appears to influence concentration stability: more MMHg was lost from solutions stored in polyethylene (PE) as opposed to polytetrafluoroethylene (PTFE) containers (Ahmend and Stoeppler 1986).

Sample preservation methods also can affect MMHg stability. Parker and Bloom (2005) recommend sample preservation by acidification to 0.5% with HCl, because MMHg concentrations in freshwater samples (presumably unfiltered) were maintained at $90 \pm 10\%$ of initial concentrations for over 200 days. The same authors recommend acidification of seawater with 0.2% H₂SO₄ because HNO₃ appeared to accelerate demethylation of MMHg (Parker and Bloom, 2005). Preservation of normally circumneutral natural waters with acid to pH < 2 halts most microbial activity and limits adsorption to container walls (Leermakers et al., 1990; Yu and Yan 2003). The maximum recommended holding time of water samples for MMHg analysis range from six to 12 months (*Method 1630*; Parker and Bloom, 2005). However, even acidified samples stored in light at room temperature experienced ~15% MMHg loss over a 1-month period (Parker and Bloom 2005).

II. OBJECTIVE

The objective of this study was to examine the stability of MMHg in filter-sterilized ($< 0.1 \mu\text{m}$) reagent-grade water (nominal resistivity $> 18 \text{ M}\Omega\text{-cm}$) and determine if the loss kinetics were influenced by either the initial concentration of MMHg, temperature, or light exposure. Additionally, I examined the loss of MMHg from lake sediment pore water and determined if the kinetics of loss were related to the initial concentration of MMHg and different from those in reagent-grade water.

III. METHODS AND MATERIALS

MMHg stability in reagent-grade water. The stability of MMHg in filter-sterilized reagent-grade water was examined by storing water samples under different light and temperature conditions (Table 1). Each sample consisted of 20 mL of filter-sterilized ($<0.1 \mu\text{m}$), reagent-grade water (nominal resistivity $> 18 \text{ M}\Omega\text{-cm}$) containing added MMHg (as CH_3HgCl) in a new, sterile 50-mL polypropylene centrifuge tube. Water samples initially containing either 1, 5, or 50 ng/L of MMHg were incubated at either $5 \text{ }^\circ\text{C}$ or $26 \text{ }^\circ\text{C}$ and either without (tubes wrapped in Al foil) or with continuous exposure to light from incandescent bulbs in the respective incubation chambers. Light exposure was measured to be $1.05 \pm 0.01 \mu\text{mol m}^{-2} \text{ s}^{-1}$ for $\lambda = 400\text{--}700 \text{ nm}$ with a Li-Cor PAR meter. Water samples were prepared with clean and aseptic techniques, including use of the clean-hands, dirty-hands technique (Lamborg et al., 2012), inside a Class 100 laminar flow hood to minimize potential biological and chemical contamination. A three-factor experimental design was implemented with factors of light (two treatments), temperature (two treatments), and MMHg concentration (three factors). Water storage periods were sacrificed at eight time points up to 112 d by freezing the samples until analysis. Each treatment and time point was performed and analyzed in triplicate to allow for statistical comparison among treatments and over time (Table 1). In addition to the three MMHg concentrations, a triplicate set of method blanks, consisting of only reagent-grade water (MMHg concentration less than detection limit), was included to control for potential contamination or in-growth of MMHg. Measured MMHg concentrations in the initial samples (Day 0) were used as a reference to which the subsequent samples were compared .

Table 1. Design of experiment to examine MMHg stability in reagent-grade water. Each treatment and time point included three independent samples, resulting in a total of 384 samples.

Treatment	[MMHg] (ng/L)	Incubation (d)							
		0	1	3	7	14	28	56	112
Light, 5 °C	0	3n	3n	3n	3n	3n	3n	3n	3n
	1	3n	3n	3n	3n	3n	3n	3n	3n
	5	3n	3n	3n	3n	3n	3n	3n	3n
	50	3n	3n	3n	3n	3n	3n	3n	3n
Light, 26 °C	0	3n	3n	3n	3n	3n	3n	3n	3n
	1	3n	3n	3n	3n	3n	3n	3n	3n
	5	3n	3n	3n	3n	3n	3n	3n	3n
	50	3n	3n	3n	3n	3n	3n	3n	3n
Dark, 5 °C	0	3n	3n	3n	3n	3n	3n	3n	3n
	1	3n	3n	3n	3n	3n	3n	3n	3n
	5	3n	3n	3n	3n	3n	3n	3n	3n
	50	3n	3n	3n	3n	3n	3n	3n	3n
Dark, 26 °C	0	3n	3n	3n	3n	3n	3n	3n	3n
	1	3n	3n	3n	3n	3n	3n	3n	3n
	5	3n	3n	3n	3n	3n	3n	3n	3n
	50	3n	3n	3n	3n	3n	3n	3n	3n

Stability in pore water. The stability of MMHg in lake sediment pore water was examined with three concentrations of MMHg added to filtered pore fluid: 1, 5, and 50 ng/L (Table 2). The 5 and 50 ng/L treatments are greater than concentrations observed in most natural pore waters (Hammerschmidt and Fitzgerald, 2004; He et al., 2007; Jeremiason et al., 2007) but were used in this study so that a statistically significant change in concentration might be observed over time.

Pore water was obtained from Grand Lake St. Marys, Ohio, in September 2013. This lake was selected because of the high porosity of the sediment, allowing for an efficient collection of pore water from sediment cores. Thirty-eight cores of undisturbed sediment and overlying water were collected with polycarbonate tubes (30 cm × 6.5 cm diameter), capped, and promptly transported to Wright State University, where overlying water was removed with a siphon. The upper 6 cm of sediment was transferred to new, sterile 50 mL polypropylene centrifuge tubes and centrifuged at 3000 rpm for 10 minutes to separate the pore water from the sediment. Supernatant pore fluids were filtered through a 0.22 µm membrane and stored for 12 hours in a 2-L polycarbonate bottle in the dark at 5 °C until it was transferred to incubation tubes. Filtered pore water in the storage bottle was sparged with ultra-high purity N₂ before storage to minimize oxidation of pore water constituents.

As with tests of reagent-grade water, 20 mL of filtered pore water containing one of three concentrations of MMHg (as CH₃HgCl) was added to sterile 50 mL polypropylene centrifuge tubes (Table 2). The test of MMHg stability in pore water also included: 1) a native control consisting of only pore water (no added MMHg) to measure any changes in the ambient concentration of MMHg within the matrix, 2) method blanks

consisting of reagent-grade water to observe potential contamination, and 3) negative controls consisting of reagent-grade water amended with MMHg to 5 ng/L to compare with pore water containing the same concentration (Table 2). The tubes were wrapped in Al foil (dark) and incubated at 26 °C to mimic the field conditions from which the pore water was obtained. To examine the stability of MMHg over time, water incubations were terminated at multiple time points up to 98 d. Incubations were terminated by freezing the samples until analysis. Three samples from each treatment, including native and negative controls and blanks, were analyzed at each time point to allow for statistical comparison among treatments and over time (Table 2).

MMHg analysis. Samples were analyzed for MMHg by flow-injection gas-chromatographic cold vapor atomic fluorescence spectrometry (GC-CVAFS; Bloom, 1989; Tseng et al., 2004). Frozen samples were thawed at 4 °C for 24 hours and then acidified to 1% with high-purity H₂SO₄ (J.T. Baker Instra Analyzed) at least six hours prior to analysis (Bowman and Hammerschmidt, 2011). Immediately before analysis, the acid was neutralized by addition of 12M KOH. Sample solutions were quantitatively transferred to a customized blown-glass UConn Bubbler (Lamborg et al., 2012) containing ~100 mL of reagent-grade water, adjusted to pH = 4.9 with acetate buffer, and derivatized with sodium tetraethylborate. Ethylated mercury derivatives were sparged from solution with high-purity N₂, concentrated on Tenax, and quantified by GC-CVAFS. The estimated detection limit was about 0.04 ng/L for a 20-mL sample.

Table 2. Design of experiment to examine MMHg stability in filtered pore water. Each treatment and time point included three independent samples, resulting in a total of 144 samples.

Treatment	Incubation period (d)							
	0	1	3	7	14	28	56	98
Native								
Control	3n	3n	3n	3n	3n	3n	3n	3n
1 ng/L	3n	3n	3n	3n	3n	3n	3n	3n
5 ng/L	3n	3n	3n	3n	3n	3n	3n	3n
50 ng/L	3n	3n	3n	3n	3n	3n	3n	3n
Blank	3n	3n	3n	3n	3n	3n	3n	3n
-Control	3n	3n	3n	3n	3n	3n	3n	3n

Statistical Analysis. SigmaPlot was used to calculate three-way ANOVA (analysis of variance) to compare the effect of light, temperature, and initial MMHg concentration on decay rates of reagent-grade water samples. Two-way ANOVA was used to compare the effects of light and temperature within initial MMHg concentration subsets. One-way ANOVA was used to compare the effect of initial MMHg concentration on decay rates of pore water samples. Linear regression models were fit to natural log transformed normalized data from each treatment to calculate the rate constant of decay and the 95% confidence interval. Student's *t*-tests were used to compare decay constants. Statistical significance of Type 1 errors was determined using a significance threshold of $\alpha=0.05$.

IV. RESULTS

Reagent-grade water. Monomethylmercury concentrations in reagent-grade water detectably decreased over time under all experimental conditions with the exception of the 1 ng/L treatment stored in the dark at 5°C (Figure 1, Table 3). Slopes of the least-squares linear regressions between time zero normalized MMHg concentration (equation 1) and time were used as the best estimate of the decay constant, with $\rho \leq 0.05$ indicating that the slope of the line was significantly different than horizontal. To normalize the data, the measured value at a give time point, given as $[\text{MMHg}]_t$ is divided by the initial measured value at time point zero, given as $[\text{MMHg}]_o$.

$$\frac{[\text{MMHg}]_t}{[\text{MMHg}]_o} \quad \text{eq. 1}$$

No MMHg was detected any of the method blanks, indicating that all of the MMHg in samples of reagent-grade water resulted from known additions and not contamination.

Three-way ANOVA results of reagent-grade water samples indicate that light ($\rho = 0.007$), temperature ($\rho < 0.001$), and initial MMHg concentration ($\rho < 0.001$) had significant effects on MMHg decay constants among all samples (Table 3). The impact of light on decay rates depended on initial MMHg concentration ($\rho = 0.010$). Additionally, the impact of temperature on decay rates depended on initial MMHg concentration ($\rho < 0.001$). However, the impact of light on decay rates was independent of temperature ($\rho = 0.465$). Two-way ANOVA of results from 1 ng/L samples indicate that temperature had a significant effect on decay rates ($\rho < 0.001$), but light did not ($\rho = 0.204$). Decay constants of MMHg in water stored at 26 °C were about 10-fold greater than those in water stored at 5 °C. Two-way ANOVA of results from 5 ng/L samples were similar to

those of the 1 ng/L samples in that decay constants were significantly increased by greater temperature ($p < 0.001$), but light had no effect ($p = 0.644$). In contrast, decay constants of 50 ng/L MMHg were increased significantly by both temperature ($p = 0.029$) and light ($p = 0.037$).

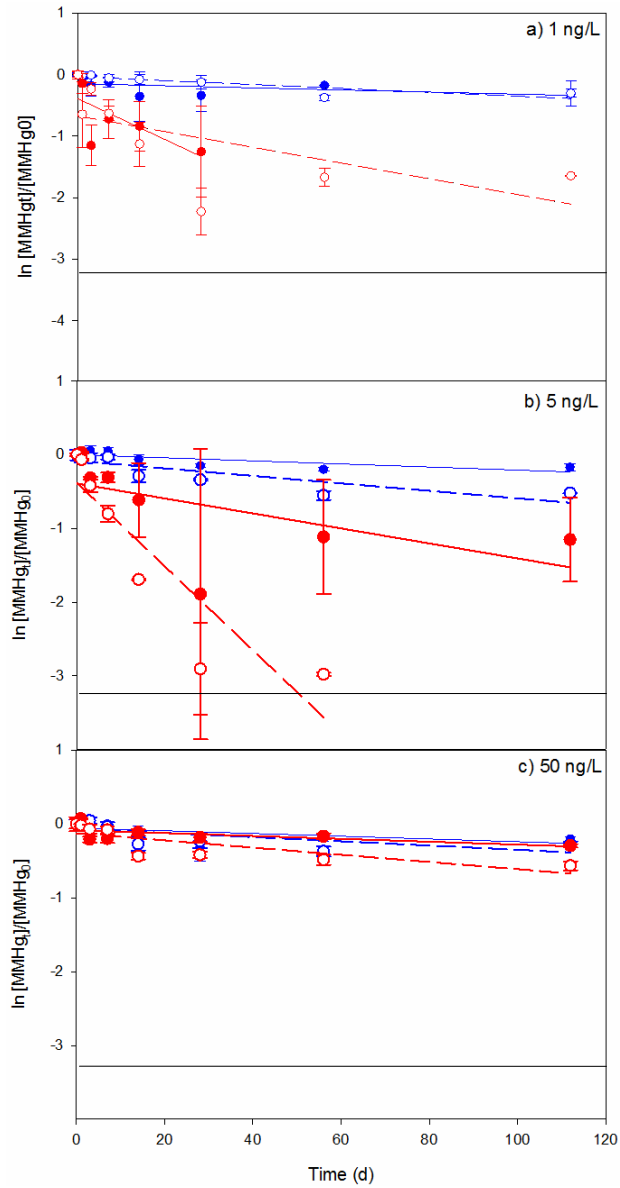


Figure 1. Decay curves of time zero normalized MMHg for 1ng/L spike (a), 5 ng/L spike (b), and 50 ng/L spike (c). Filled blue = dark, 5 °C; filled red = dark, 26 °C; open blue = light, 5 °C; open red = light, 26 °C. Horizontal lines show the detection limit of 0.04 ng/L.

Table 3.MMHg decomposition rate constants k_d (\pm 95% CI) in reagent-grade water and p -values for the slope of the regression line shown in figure 1.

Treatment		k_d (d ⁻¹)	p
1 ng/L	Dark, 5 °C	0.0009 \pm 0.0013	0.1680
	Dark, 26 °C	0.0363 \pm 0.0263	0.0097
	Light, 5 °C	0.0063 \pm 0.0029	0.0003
	Light, 26 °C	0.0541 \pm 0.0324	0.0025
5ng/L	Dark, 5 °C	0.0023 \pm 0.0010	0.0002
	Dark, 26 °C	0.0272 \pm 0.0165	0.0030
	Light, 5 °C	0.0087 \pm 0.0031	<0.0001
	Light, 26 °C	0.1225 \pm 0.0150	<0.0001
50 ng/L	Dark, 5 °C	0.0019 \pm 0.0015	0.0154
	Dark, 26 °C	0.0018 \pm 0.0015	0.0136
	Light, 5 °C	0.0037 \pm 0.0021	0.0022
	Light, 26 °C	0.0055 \pm 0.0023	<0.0001

Pore water. Monomethylmercury concentrations decreased over time in pore water samples (Figure 2, Table 4). Slopes of the least-squares linear regressions between normalized MMHg concentration (equation 1) and time were used as the best estimate of the decay constant, with $p \leq 0.05$ indicating that the slope of the line was significantly different from zero. The native control samples, consisting of pore water with no added MMHg, contained a relatively low concentration of native MMHg (0.70 ng/L); however, the reagent-grade water blanks analyzed with the pore waters had no detectable MMHg. Therefore, the MMHg measured in the native control samples represents environmental concentrations of MMHg in pore water in Grand Lake St. Marys. By day 28, MMHg in the native control samples was below the detection limit of 0.04 ng/L. One-way ANOVA results of pore water samples indicate that initial MMHg concentration did not have a significant impact on decay constants ($p=0.731$). Decay constants of 5 ng/L and negative control samples were significantly different (t -test, $p = 0.007$), with MMHg being decomposed three-fold faster in pore water than in reagent grade water.

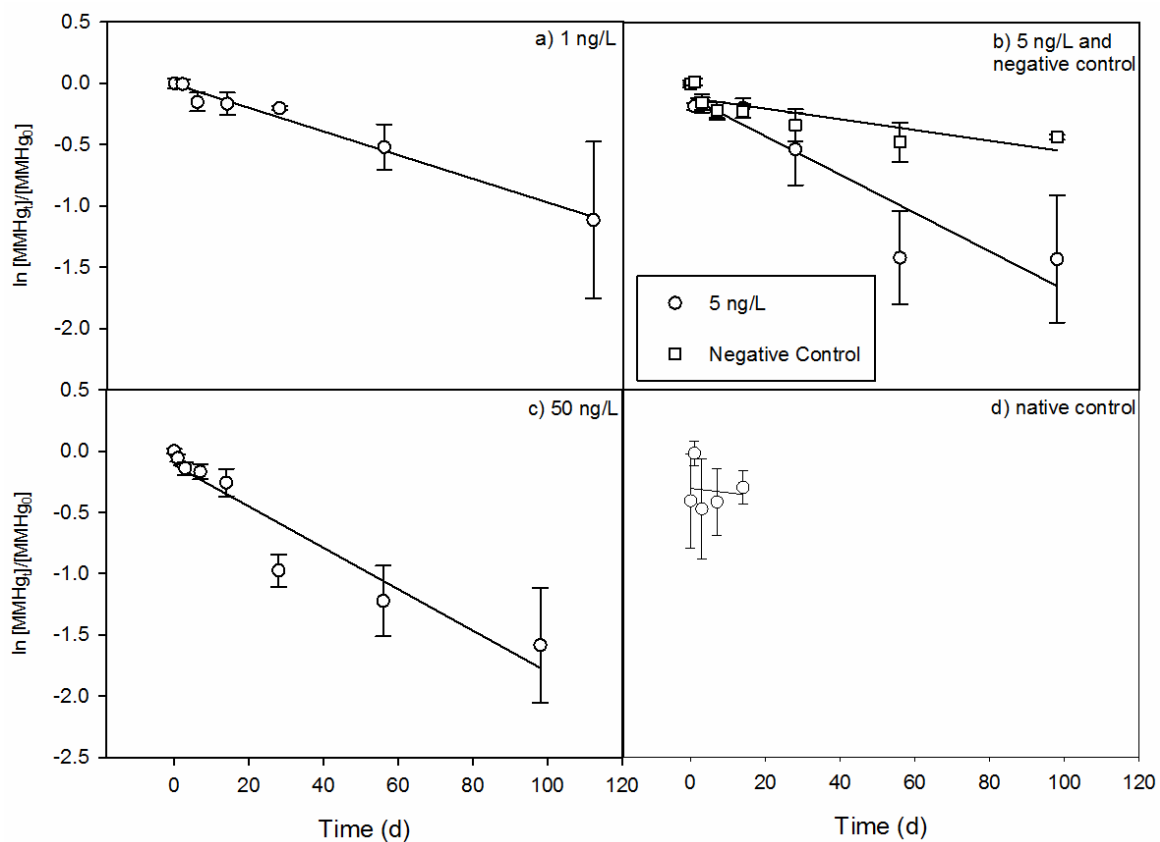


Figure 2. Decay constants of normalized MMHg for pore water 1 ng/L spike (a), pore water 5 ng/L spike and negative control (b), pore water 50 ng/L spike (c), and native control (d). Samples were and incubated in the dark at 26 °C to mimic the field conditions.

Table 4. Decay constants (\pm 95% CI) for each pore water treatment. All treatments had a calculated p -value of <0.005 , indicating k_d is significantly different from zero.

Treatment	k_d (d^{-1})
1 ng/L	0.0178 ± 0.005
5 ng/L	0.0154 ± 0.005
50 ng/L	0.0212 ± 0.005
-Control	0.0044 ± 0.002

V. DISCUSSION

Reagent-grade water. Thermal decomposition appears to be the primary mechanism for MMHg loss from reagent-grade water at the two lowest MMHg concentrations used in this study. For water amended with MMHg to 1 and 5 ng/L, decay constants were much greater when stored at 26 °C as opposed to 5 °C. The low light exposure had no detectable impact on MMHg loss from solutions containing either 1 or 5 ng/L of MMHg. A greater rate of MMHg decomposition with increased temperature could be attributed to microbial demethylation (Marvin-DiPasquale et al., 2000; Moore et al, 1990; Robinson and Touvinen, 1984; Oremland et al., 1991; Oremland et al., 1995). However, the presence and activity of microbes in the samples, should have been extremely low as a result of using sterile tubes, filter-sterilized (<0.1 µm) reagent-grade water, the techniques that were used to avoid microbial contamination, and the unavailability of electron donors other than MMHg. Wall losses could be another potential source of MMHg loss related to temperature increase. However, acidifying the sample prior to analysis ensures that no MMHg is bound to container walls. Another possible mechanism for thermal decomposition is chemical reactions with other constituents present in the matrix. Iron(III) hydroxide has been shown to reduce detectable MMHg concentrations by as much as 50% (Bloom 1989). Dissolved organic matter has also been shown to reduce MMHg yield by 60-70% (Bloom 1989). However, these constituents are not present in MilliQ water. The mechanism for thermal decomposition of MMHg in MilliQ water is unknown.

In contrast to 1 ng/L and 5 ng/L samples, both thermal decomposition and photodecomposition mechanisms appear to be responsible for MMH loss at 50 ng/L. One explanation for this increased significance of light in regards to increased levels of MMHg is that MMHg has a higher affinity for the thermal decomposition mechanism than it does for the photo-decay mechanism. Increasing MMHg concentration increases the amount of MMHg available for the less preferable photo-decay mechanism and increases detectability of photo-decay.

Pore water. The k_d of -Control was lower than all pore water samples by at least a factor of three (Table 4). Decay constants of the 5 ng/L pore water samples were higher than the -Control by a factor of three, which points to natural constituents in pore water having a significant impact on decay constants of MMHg in natural systems. Dissolved organic matter decreases MMHg recovery analyzed by CVAFS by 60-70% (Bloom 1989). Additionally, Fe(III) hydroxide can decrease MMHg concentration by 50% (Bloom 1989).

VI. CONCLUSION

No previous studies have been done to examine MMHg decay in filter sterilized pore water. Studies have examined flux of MMHg from lake sediments (He et al., 2007; Marvin-Dipasquale et al., 2009; Hammerschmidt and Fitzgerald, 2006b), however, my study removes biogeochemical interactions, resulting in decay constants for pore water only. The results of this study indicate that MMHg is decomposed in pore water in the absence of both microbial activity and photo-decay. Additionally, the natural dissolved constituents in a pore water matrix accelerate MMHg decomposition compared to a reagent-grade water matrix. My results point to an unidentified mechanism of MMHg loss. To identify said mechanism, a detailed chemical analysis of pore water should be performed. Selective addition of individual constituents could identify constituents that have greater impacts on MMHg loss.

I observed that decay constants for MMHg in reagent-grade water were dependent on temperature, light, and initial MMHg concentration. At all MMHg concentrations used in this study, thermal appeared to be responsible for MMHg decay. This disagrees with the finding of Devai et al. (2001), who concluded that temperature had no significant impact on MMHg losses; however, the test concentration of MMHg used by Devai and colleagues was three orders of magnitude greater than those used in this study. Additionally, a matrix of methylene chloride was used in Devai et al., which could indicate that matrix composition could impact MMHg susceptibility to storage conditions. The mechanism by which thermal decomposition of MMHg occurs is unknown. Adding a mercury isotope form of MMHg to MilliQ water and measuring all

mercury species could help identify if the MMHg is being demethylated or being lost elsewhere. Digesting and analyzing the containers after use could help identify if interactions between the container and MMHg that are not controlled by 1% H₂SO₄ could be contributing to thermal loss. At higher concentrations (50 ng/L), both thermal decomposition and photodecomposition are significant drivers of MMHg decay. This partially supports Ahmed and Stoeppler (1987) who found that MMHg decomposed in light, but increased temperature had no effect. The difference in the importance of temperature could be attributed to a difference in matrices between the studies. Ahmed and Steoppler used a methylene chloride matrix while I used a water matrix. An important point to note is that my study used incandescent bulbs to simulate light. However, both in the natural environment and labs with windows, samples are exposed to natural sunlight, which supplies much higher fluxes of PAR than an incandescent light bulb. Therefore, exposure to natural sunlight may have a greater impact than exposure to incandescent bulbs. Repeating my study with more powerful bulbs to better simulate sunlight may reveal potentially higher decay rates.

VII. LITERATURE CITED

- Ahmed, R.; Stoeppler, M. Decomposition and stability studies of methylmercury in water using cold vapour atomic adsorption spectrometry. *Analyst* **1986**, *111*, 1371–1374.
- Black, F. J.; Poulin, B. A.; Flegal, A. R. Factors controlling the abiotic photo-degradation of monomethylmercury in surface waters. *Geochim. Cosmochim. Acta* **2012**, *84*, 492–507.
- Bloom, N. Determination of pictogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Can. J. Fish. Aquat. Sci.* **1989**, *46*, 1131–1140.
- Chen, C. Y.; Borsuk, M. E.; Bugge, D. M.; Hollweg, T.; Balcom, P. H.; Ward, D. M.; Williams, J.; Mason, R. P. Benthic and pelagic pathways of methylmercury bioaccumulation in estuarine food webs of the northeast United States. *Plos One* **2014**, *9*, 1–11.
- Chen, J.; Pehkonen, S. O.; Lin, C-J. Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters. *Water Res.* **2003**, *37*, 2496–2504.
- Compeau, G. C.; Bartha, R. Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. *Appl. Environ. Microbiol.* **1985**, *50*, 498–502.
- Drott, A.; Lamertsson, L.; Bjorn, E.; Skyllberg, U. Do potential methylation rates reflect accumulated methyl mercury in contaminated sediments? *Environ. Sci. Technol.* **2008**, *42*, 153–158.

- Gilmour, C. C.; Podar, M.; Bullock, A. L.; Graham, A. M.; Brown, S. D.; Somehahally, A. C.; Johs, A.; Hurt, R. A.; Bailey, K. L.; Elias, D. A. Mercury methylation by novel microorganisms from new environments. *Environ. Sci. Technol.* **2013**, *47*, 11810–11820.
- Hammerschmidt, C. R.; Fitzgerald, W. F. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* **2004**, *38*, 1487–1495.
- Hammerschmidt, C. R.; Fitzgerald, W. F. Bioaccumulation and trophic transfer of methylmercury in Long Island Sound. *Arch. Environ. Contam. Toxicol.* **2006a**, *51*, 416–424.
- Hammerschmidt, C. R.; Fitzgerald, W. F. Biogeochemical cycling of methylmercury in lakes and tundra watersheds of arctic Alaska. *Environ. Sci. Technol.* **2006b**, *40*, 1204–1211.
- Hammerschmidt, C. R.; Fitzgerald, W. F. Methylmercury cycling in sediments on the continental shelf of southern New England. *Geochim. Cosmochim. Acta* **2006c**, *70*, 918–930.
- Hammerschmidt, C. R.; Fitzgerald, W. F. Photodecomposition of methylmercury in an arctic Alaskan lake. *Environ. Sci. Technol.* **2006d**, *40*, 1212–1216.
- Hammerschmidt, C. R.; Fitzgerald, W. F. Iron-mediated photochemical decomposition of methylmercury in an arctic Alaskan lake. *Environ. Sci. Technol.* **2010**, *44*, 6138–6143.

- He, T.; Lu, J.; Yang, F.; Feng, X. Horizontal and vertical variability of mercury species in pore water and sediments in small lakes in Ontario. *Sci. Total Environ.* **2008**, *386*, 53–34.
- Heyes, A.; Miller, C.; Mason, R. P. Mercury and methylmercury in Hudson River sediment: impact of tidal resuspension on partitioning and methylation. *Mar. Chem.* **2004**, *90*, 75–89.
- Jeremiason, J. D.; Engstrom, D. R.; Swain, E. B.; Nater, E. A.; Johnson, B. M.; Almendinger, J. E.; Monson, B. A.; Kolka, R. K. Sulfate addition increases methylmercury production in an experimental wetland. *Environ. Sci. Technol.* **2006**, *40*, 3800–3806.
- Karagas, M. R.; Choi, A. L.; Oken, E.; Horvat, M.; Schoeny, R.; Kamai, E.; Cowell, W.; Grandjean, P.; Korric, S. Evidence on the human health effects of low-level methylmercury exposure. *Environ. Health Perspect.* **2012**, *120*, 799–806.
- Lamborg, C. H.; Hammerschmidt, C. R.; Gill, G. A.; Mason, R. P.; Gichuki, S. An intercomparison of procedures for the determination of total mercury in seawater and recommendations regarding mercury speciation during GEOTRACES cruises. *Limnol. Oceanogr.–Methods* **2012**, *10*, 90–100.
- Leermakers, M.; Lansens, P.; Baeyens, W. Storage and stability of inorganic and methylmercury solutions. *J. Anal. Chem.* **1990**, *336*, 655–662.
- Lehnherr, I.; St. Louis V. L. Importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater ecosystems. *Environ. Sci. Technol.* **2009**, *43*, 5692–5698.

- Lehnherr, I.; St. Louis, V. L.; Hintelmann, H.; Kirk, J. L. Methylation of inorganic mercury in polar marine waters. *Nat. Geosci.* **2011**, *4*, 298–302.
- Mahaffey, K. R.; Clickner, R. P.; Jeffries, R. A. Adult women's blood mercury concentrations vary regionally in the United States: Association with patterns of fish consumption (NHANES 1999–2004). *Environ. Health Perspect.* **2009**, *117*, 47–53.
- Marvin-DiPasquale, M.; Agee, J.; McGowan, C.; Oremland, R. S.; Thomas, M.; Krabbenhoft, D.; Gilmour, C. C. Methyl-mercury degradation pathways: A comparison among three mercury-impacted ecosystems. *Environ. Sci. Technol.* **2000**, *34*, 4908–4916.
- Marvin-DiPasquale, M.; Lutz, M. A.; Brigham, M. A.; Krabbenhoft, D. P.; Aiken, G. R.; Orem, W. H.; Hall, B. D. Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment-pore water partitioning. *Environ. Sci. Technol.* **2009**, *43*, 2726–2732.
- Marvin-DiPasquale, M.; Windham-Myers, L.; Agee, J. L.; Kakouros, E.; Kieu, L. H.; Fleck, J. A.; Alpers, C. N.; Stricker, C. A. Methylmercury production in sediment from agricultural and non-agricultural wetlands in the Yolo Bypass, California, USA. *Sci. Total Environ.* **2014**, *484*, 288–299.
- Mason, R. P.; Reinfelder, J. R.; Morel, F. M. M. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Environ. Sci. Technol.* **1996**, *30*, 1835–1845.
- Matsunaga, K.; Konishi, S.; Nishimura, M. Possible errors caused prior to measurement of mercury in natural waters with special reference to seawater. *Environ. Sci. Technol.* **1979**, *13*, 63–35.

- Mergler, D.; Anderson, H. A.; Chan, L. H. M. ; Mahaffey, K. R.; Murray, M.; Stern, A. H. Methylmercury exposure and health effects in humans: a worldwide concern. *Ambio* **2007**, *36*, 3–11.
- Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*; EPA-821-R-02-019; United States Environmental Protection Agency: Washington D.C., 2001; 1–46.
- Moore, M. J.; Distefano, M. D.; Zydowsky, L. D.; Cummings, R. T.; Walsh, C. T. Organomercuriallyase and mercuric ion reductase: nature's mercury detoxification catalysts. *Acc. Chem. Res.* **1990**, *23*, 301–308.
- Oremland, R. S.; Culbertson, C. W.; Winfrey, M. R. Methylmercury decomposition in sediments and bacterial cultures: Involvement of methanogens and sulfate reducers in oxidative demethylation. *Appl. Environ. Microbiol.* **1991**, *57*, 130–137.
- Oremland, R. S.; Miller, L. G.; Dowdle, P.; Connell, T.; Barkay, T. Methylmercury oxidative degradation potentials in contaminated and pristine sediments of the Carson River, Nevada. *Appl. Environ. Microbiol.* **1995**, *61*, 2745–2753.
- Osborn, A. M.; Bruce, K. D.; Strike, P.; Ritchie, D. A. Distribution, diversity, and evolution of the bacterial mercury resistance (*mer*) operon. *FEMS Microb. Rev.* **1997**, *19*, 239–262.
- Parker, J. L.; Bloom, N. S. Preservation and storage techniques for low-level aqueous mercury speciation. *Sci. Total Environ.* **2005**, *337*, 253–263.
- Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R. B.; Friedli, H. R.; Leaner, J.; Mason, R.; Mukherjee, A. B.; Stracher, G. B.; Streets, D. G.; Telmer, K. Global mercury

- emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* **2010**, *10*, 5951–5964.
- Robinson, J. B.; Touvinen, O. H. Mechanisms of microbial resistance and detoxification of mercury and organomercury compounds: physiological, biochemical, and genetic analyses. *Microbiol. Rev.* **1984**, *48*, 95–124.
- Rodríguez Martín-Doimeadios, R. C.; Tessier, E.; Amouroux, D.; Guyoneaud, R.; Duran, R.; Caumette, P.; Donard, O. F. X. Mercury methylation/loss and volatilization pathways in estuarine sediment slurries using species-specific enriched stable isotopes. *Mar. Chem.* **2004**, *90*, 107–123.
- Schaefer, J. K.; Yagi, J.; Reinfelder, J. R.; Cardona, T.; Ellickson, K. M.; Tel-Or, S.; Barkay, T. Role of bacterial organomercurylase (MerB) in controlling methylmercury accumulation in mercury-contaminated natural waters. *Environ. Sci. Technol.* **2004**, *38*, 4304–4311.
- Sellers, P.; Kelly, C. A. Fluxes of methylmercury to the water column of a drainage lake: The relative importance of internal and external sources. *Limnol. Oceanogr.* **2001**, *46*, 623–631.
- Tseng, C., Hammerschmidt, C. R., Fitzgerald, W. F. Determination of methylmercury in environmental matrixes by on-line flow injection and atomic fluorescence spectrometry. *Anal. Chem.* **2004**, *76*, 7131–7136.
- Whalin, L.; Kim, E-H.; Mason, R. Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. *Mar. Chem.* **2007**, *107*, 278–294.

- Wiener, J. G.; Krabbenhoft, D. P.; Heinx, G. H.; Scheuhammer, A. M. Ecotoxicology of mercury. In *Handbook of Ecotoxicology*; Hoffman, D. J., Rattner, B. A., Burton, G. A., Jr., Cairns, J., Jr., Eds.; Lewis Publishers: Boca Raton, FL, 2003; pp 409–463.
- Yan, H.; Li, Q.; Meng, B.; Wang, C.; Feng, X.; He, T.; Dominik, J. Spatial distribution and methylation of mercury in a eutrophic reservoir heavily contaminated by mercury in Southwest China. *Appl. Geochem.* **2013**, *33*, 182–190.
- Yu, R.; Flanders, J. R.; Mack, E. E.; Turner, R.; Mirza, M. B.; Barkay, T. Contribution of coexisting sulfate and iron reducing bacteria to methylmercury production in freshwater river sediments. *Environ. Sci. Technol.* **2012**, *46*, 2684–2691.
- Zhang, T.; Hsu-Kim, H. Photolytic degradation of methylmercury enhanced by binding to natural organic ligands. *Nat. Geosci.* **2010**, *3*, 473–476.