

# **Aqueous Phase Methylation as a Potential Source of Methylmercury in Wet Deposition**

Chad R. Hammerschmidt\*<sup>a</sup>, Carl H. Lamborg<sup>a</sup>, William F. Fitzgerald<sup>b</sup>

*<sup>a</sup>Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic  
Institution, Woods Hole, MA, USA*

*<sup>b</sup>Department of Marine Sciences, University of Connecticut, Groton, CT, USA.*

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\*Corresponding author. Department of Marine Chemistry and Geochemistry, Woods  
Hole Oceanographic Institution, MS #51, Woods Hole, MA, USA 02543.

*E-mail:* methylhg@whoi.edu (C. R. Hammerschmidt)

*Tel:* 508-289-3551

*Fax:* 508-457-2075

**Abstract**

The source of monomethylmercury (MMHg) in wet deposition is unknown.

Volatilization of gaseous MMHg, evasion and demethylation of dimethylmercury, and methylation of  $\text{Hg}^0$  have been either proposed or tested unsuccessfully as potential sources. Here, we show that MMHg in precipitation, sampled across a wide geographical range in North America, is related positively to an operationally defined and measured reactive Hg species ( $\text{Hg}_R$ ), but connected weakly to total Hg. The mean molar ratio of MMHg: $\text{Hg}_R$  measured in continental precipitation ( $0.025 \pm 0.006$ ) is comparable to the MMHg: $\text{Hg}(\text{II})$  ratio estimated from first-order rate constants for acetate-mediated Hg methylation and MMHg photolysis ( $0.025 \pm 0.002$ ). This suggests MMHg may be formed in the atmosphere through a reaction between labile Hg(II) complexes and an unknown methylating agent(s), potentially acetate or similar molecules. Availability of Hg(II) appears to limit the reaction, and accordingly, increased atmospheric loadings of Hg could lead to enhanced MMHg in precipitation.

**Keywords:** mercury; abiotic; atmosphere; precipitation; photodecomposition

## 1. Introduction

Precipitation often contains trace quantities of monomethylmercury (MMHg), the toxic and bioaccumulative form of Hg; however, the source of the MMHg in wet deposition is unknown (Downs et al., 1998). Most MMHg in the environment is presumed to result from methylation of inorganic Hg complexes (Hg(II)) by microorganisms, notably sulfate-reducing (Benoit et al., 2003) and iron-reducing bacteria (Fleming et al., 2006). Given that the atmospheric environment is relatively inhospitable for anaerobic bacteria, mechanisms other than *in situ* microbial production have been either proposed or tested as potential sources of MMHg in precipitation. These include volatilization of CH<sub>3</sub>Hg complexes from surface waters (Mester and Sturgeon, 2002) and landfills (Lindberg et al., 2001), oceanic evasion and subsequent demethylation of dimethylmercury (DMHg; Bloom et al., 1996; St. Louis et al., 2005), gas-phase methylation of elemental Hg (Hg<sup>0</sup>) by methyl carbonium and/or methyl radical donors (Hall et al., 1995), and aqueous-phase methylation of Hg(II) in the atmosphere (Gårdfeldt et al., 2003).

Laboratory studies have shown a considerable potential for abiotic methylation of Hg(II) exists in the environment. These include observations of artifact MMHg formation from Hg(II) during extraction or analysis of sediments, biota, and natural waters (Bloom et al., 1997; Holz et al., 1999; Hammerschmidt and Fitzgerald, 2001), and positive results for wet-chemical Hg(II) methylation tests with acetate (Akagi and Takabatake, 1973; Bloom et al., 1997; Gårdfeldt et al., 2003), organic acids with a methyl group in the  $\gamma$ -position (Falter, 1999), other methylated metals (Howell et al., 1986; Cerrati et al., 1992), and humic substances (Weber, 1993). It has been hypothesized that

labile Hg(II) complexes, commonly assayed as reactive Hg ( $Hg_R$ ), are a substrate for abiotic and biological reactions that produce both  $Hg^0$  and methylated forms of Hg in aquatic systems (Mason and Fitzgerald, 1990; Fitzgerald et al., 1991).  $Hg_R$  is an operationally defined fraction of Hg that is reduced readily with  $SnCl_2$  at low pH, and includes weak organic associations, inorganic complexes, and labile particulate Hg (Mason and Fitzgerald, 1990). While the thermodynamic and kinetic interpretation of the  $Hg_R$  determination can vary among environmental matrixes (Bloom, 1994; Lamborg et al., 2003), we have observed positive relationships between  $Hg_R$  and both  $Hg^0$  in estuarine water (Rolfhus and Fitzgerald, 2001) and MMHg produced abiotically in extracts of marine sediment (Hammerschmidt and Fitzgerald, 2001). We submit that levels of strong Hg-binding organic ligands are low enough in aqueous environments of the atmosphere (cloudwater, liquid phases, or aerosols) so that all Hg(II) present in solution will be associated with complexing agents that are kinetically facile, and therefore able to exchange rapidly with other ligands in accordance with dynamic equilibrium. Thus, solid–solution partitioning of Hg(II) in atmospheric water should be the primary control on Hg “reactivity” (Mason et al., 1997). Accordingly, and if aqueous methylation of labile Hg(II) complexes were an important source of MMHg, then a positive relationship would be expected between MMHg and  $Hg_R$  in precipitation.

## **2. Hg Speciation in Precipitation**

Figure 1 shows that mean concentrations of MMHg and  $Hg_R$  in wet deposition are correlated strongly among a variety of locations spanning North America. This relationship is based on values reported in the peer-reviewed literature (Table 1), which

contains limited information on  $\text{Hg}_R$  in precipitation. However, and although average levels of MMHg and  $\text{Hg}_R$  vary widely within and among locations/studies (Table 1), there is a relatively constant degree of proportionality between mean concentrations of the two Hg species (Fig. 1). The mean molar ratio of MMHg: $\text{Hg}_R$  is  $0.025 \pm 0.006$  among continental locations (Table 1). The relatively consistent ratio between MMHg and  $\text{Hg}_R$  suggests that either these two Hg species have comparable atmospheric behavior or that  $\text{Hg}_R$  is a substrate for MMHg and a molar ratio of about 0.025 represents a steady-state condition between competing methylation and demethylation reactions.

If  $\text{Hg}_R$  were a substrate for MMHg, then one would not expect MMHg to be related to total Hg (sum of all Hg species including  $\text{Hg}_R$ ) in precipitation, given that the fraction of total Hg as  $\text{Hg}_R$  in wet deposition is highly variable, ranging from 14% to 95% (Table 1). Figure 2 shows a weak relationship ( $r^2 = 0.26$ ,  $p = 0.09$ ) between mean concentrations of MMHg and total Hg in precipitation among the same samples shown in Figure 1, as well as several other studies that did not assay  $\text{Hg}_R$ . It appears that MMHg in precipitation is more a function of  $\text{Hg}_R$  (Fig. 1) than of total Hg (Fig. 2). Sorption to particles plays a major role in determining the “reactivity” of Hg in precipitation (Mason et al., 1997), and thereby, may control the fraction of total Hg that is available for methylation reactions.

### **3. Potential Sources of MMHg**

If volatilization and dissolution of gaseous  $\text{CH}_3\text{Hg}$  species, including those derived from oceanic evasion and atmospheric demethylation of DMHg, were the primary source of MMHg in precipitation, then, on average, these processes must

proceed at rates that are proportional to those affecting the formation and removal of  $Hg_R$  in order to explain the relationship between MMHg and  $Hg_R$  in Figure 1.  $Hg_R$  in precipitation, largely ionic Hg(II) (Mason et al., 1992), is emitted from natural and anthropogenic sources (Nacht et al., 2004; Lee et al., 2006) and produced by atmospheric oxidation of  $Hg^0$  (Fogg and Fitzgerald, 1979), the rate of which varies spatially depending on the strength and abundance of atmospheric oxidants (Fitzgerald and Lamborg, 2003). Hg(II) is scavenged by particles (Lamborg et al., 2000), and as noted, levels of  $Hg_R$  in precipitation are highly dependent on the concentration and nature of particulate material. Accordingly, it is unlikely that gas-phase concentrations and dissolution of MMHg complexes are comparable to unrelated processes affecting  $Hg_R$ , especially given the heterogeneity of Hg(II) emissions,  $Hg^0$  oxidation, and Hg(II) scavenging. However, and although accurate measurements of gaseous MMHg species in the atmosphere limit our understanding of its distribution and equilibrium with precipitation (Bloom and Watras, 1989), the potential significance of this process can be evaluated in oceanic upwelling regions where atmospheric concentrations of DMHg should be greatest.

DMHg appears to be produced throughout the oceanic water column. Enhanced DMHg levels, for example, have been observed in low-oxygen subsurface waters of the equatorial Atlantic and Pacific Oceans as well as in recently formed deep waters of the Atlantic (Mason and Fitzgerald, 1990; Mason and Sullivan, 1999). Levels in the surface mixed layer usually are not measurable ( $< 0.005\text{--}0.015$  pM; Mason and Fitzgerald, 1990; Mason et al., 1995; Mason and Sullivan, 1999), and this has been attributed principally to demethylation in surface water rather than atmospheric evasion (Mason and Fitzgerald,

1993). Thus, DMHg must be transported rapidly to the surface for it to escape to the atmosphere. If DMHg from subsurface waters were an important source of MMHg in precipitation, then the concentrations should be elevated near the equator, where rates of upwelling are substantial and DMHg, as noted, is enhanced in sub-thermocline waters (Mason et al., 1990; Mason and Sullivan, 1999). However, no detectable amounts of MMHg ( $< 0.05$  pM) were present in equatorial Pacific rain (Mason et al., 1992), and only one of five rain samples from the equatorial Atlantic had levels exceeding a detection limit of 0.04 pM (Table 1; Lamborg et al., 1999). MMHg in equatorial oceanic rain is much less than that in precipitation over the North American continent (Table 1), and these results suggest that DMHg evasion is not an important source of MMHg in wet deposition at most locations. Moreover, and if MMHg in precipitation results from methylation of  $Hg_R$  (Figure 1), then it is possible that the responsible methylating agent(s) may be terrestrially derived. Although all oceanic rain samples contained ample  $Hg_R$  (Table 1), only one, as noted, had a detectable quantity of MMHg, and the composition of this sample was influenced by continental air from western Africa, as evidenced by the amounts of Al and Fe (Lamborg et al., 1999). An alternative explanation for exceedingly low levels of MMHg in oceanic rain is that its decomposition is enhanced in the marine troposphere, potentially by reactive halogens (Sheu and Mason, 2004) that readily demethylate MMHg (Hammerschmidt and Fitzgerald, 2001).

The mean MMHg: $Hg_R$  molar ratio of 0.025 in continental precipitation (Table 1) is consistent with results from kinetic experiments of MMHg photochemical decomposition (Gårdfeldt et al., 2001) and production from acetate (Gårdfeldt et al.,

2003) in simulated natural waters. We hypothesize that MMHg in precipitation results from competing methylation and demethylation reactions with Hg(II) such that

$$\frac{dMMHg}{dt} = k_{meth}[Hg(II)][MA] - k_{demeth}h\nu[MMHg] \quad (1)$$

where  $k_{meth}$  and  $k_{demeth}$  respectively are methylation and demethylation rate constants,  $h\nu$  is solar radiation, and  $MA$  is a methylating agent(s). Gårdfeldt and colleagues (2003) have shown that acetate is a prolific methylator of Hg(II) in simulated rainwater (i.e., dilute, pH 4.9), and that the gross rate of MMHg production is pseudo-first order with respect to Hg(II) concentration and independent of light. Accordingly, and assuming that 1)  $MA$  is available in excess relative to Hg(II), which is reasonable given that levels of acetate in the atmospheric aqueous phase (1–10  $\mu\text{M}$ ; Chebbi and Carlier, 1996; Kieber et al., 2002) are  $10^5$ – $10^6$  greater than  $\text{Hg}_R$  (Table 1), and 2) demethylation is mostly a function of MMHg concentration (Gårdfeldt et al., 2001; Hammerschmidt and Fitzgerald, 2006), then Equation 1 can be simplified to a steady-state expression where  $[MMHg]_{ss}/[Hg(II)]_{ss} = k_{meth}/k_{demeth}$ . Gårdfeldt and co-workers (2001) determined  $k_{demeth} = 2.2 (\pm 0.2) \times 10^{-4} \text{ s}^{-1}$  in synthetic rainwater irradiated with filtered light ( $\lambda > 290 \text{ nm}$ ) from a collimated 450 W Xe lamp at 0.45 m (Katarina Gårdfeldt, personal communication). The shortwave (300–5000 nm) light exposure of samples in these tests ( $\sim 140 \text{ W m}^{-2}$ ) is comparable to the average shortwave solar insolation at Earth's surface ( $165 \text{ W m}^{-2}$ ; Rossow and Zhang, 1995) and within a factor of two of the flux into the top of the atmosphere ( $230 \text{ W m}^{-2}$ ; Rossow and Zhang, 1995). Thus, and with a laboratory-measured  $k_{meth}$  of  $5.4 \times 10^{-6} \text{ s}^{-1}$  for Hg(II) and acetate in artificial rainwater (Gårdfeldt et al., 2003), the expected steady-state MMHg:Hg(II) ratio in precipitation would be 0.025

$\pm 0.002$ . The uncertainty associated with this estimate results from variability in the  $k_{demeth}$  determination only; no uncertainty was reported for  $k_{meth}$ . The estimated steady-state MMHg:Hg(II) molar ratio is comparable to that approached after 325 min incubation of Hg(II) in the presence of acetate under irradiation from the Xe lamp (about 0.025; Fig. 4 in Gårdfeldt et al., 2003), and most noteworthy, similar to the average MMHg:Hg<sub>R</sub> concentration ratio measured in North American precipitation ( $0.025 \pm 0.006$ ; Table 1).

#### 4. Conclusions

MMHg in North American precipitation is related to Hg<sub>R</sub>, an operationally defined fraction of Hg that includes mostly labile Hg(II) complexes. Mean MMHg:Hg<sub>R</sub> molar ratios in wet deposition are similar among sampling locations and periods on the continent, and comparable to the steady-state condition predicted from laboratory-determined rate constants for sunlight-mediated MMHg photodecomposition and Hg(II) methylation by acetate. This suggests that MMHg in precipitation may be formed by an aqueous phase methylation reaction involving Hg(II), although it is unknown whether acetate is the responsible methylating agent. Levels of acetate far exceed those of Hg<sub>R</sub> in both continental and marine atmospheres, implying that Hg(II) should limit the methylation reaction and a positive relationship between MMHg and Hg<sub>R</sub> might be expected. Solid–solution partitioning of Hg may be the primary control on Hg<sub>R</sub> in aqueous environments of the atmosphere, given that dissolved Hg(II) will be associated with complexing agents that are kinetically facile, and therefore able to exchange rapidly with other ligands ( $t_{1/2} < 3$  h; Lamborg et al., 2003), relative to the methylation reaction

( $t_{1/2} = 36$  h; Gårdfeldt et al., 2003), in accordance with dynamic equilibrium. Thus, and if MMHg in precipitation were produced from  $Hg_R$  in the atmosphere, then changes in atmospheric Hg and/or particle loadings should result in a corresponding increase or decline in the net synthesis and deposition of MMHg.

### **Acknowledgments**

We are grateful to Katarina Gårdfeldt for helpful comments on an earlier draft of the manuscript. This study was supported by a grant from the National Science Foundation-Office of Polar Programs (0425562) and the Postdoctoral Scholar Program at the Woods Hole Oceanographic Institution, with funding from the Doherty Foundation.

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### Figure captions

**Figure 1.** Relation between mean concentrations of MMHg and reactive Hg ( $Hg_R$ ) in wet deposition at locations in North America: closed circle, rain in Washington state (Bloom and Watras, 1989); closed triangle up, Maryland rain and snow (Mason et al., 1997); closed triangle down, Connecticut rain and snow (Balcom et al., 2004); open circle, Wisconsin snow (Bloom and Watras, 1989); open square, Wisconsin snow (Lamborg et al., 1995); open triangle up, Wisconsin snow (Fitzgerald et al.,

1991); open triangle down, Wisconsin rain (Lamborg et al., 1995); open diamond, snow in Washington state (Bloom and Watras, 1989).

**Figure 2.** MMHg versus total Hg in wet deposition at locations in North America: closed circle, rain in Washington state (Bloom and Watras, 1989); closed square, northwest Ontario rain and snow (St. Louis et al., 2001); closed triangle up, Maryland rain and snow (Mason et al., 1997); closed triangle down, Connecticut rain and snow (Balcom et al., 2004); closed diamond, northwest Ontario rain (St. Louis et al., 1995); closed hexagon, northwest Ontario snow (St. Louis et al., 1995); open circle, Wisconsin snow (Bloom and Watras, 1989); open square, Wisconsin snow (Lamborg et al., 1995); open triangle up, Wisconsin snow (Fitzgerald et al., 1991); open triangle down, Wisconsin rain (Lamborg et al., 1995); open hexagon, Ellesmere Island snow (St. Louis et al., 2005).

Figure 1.

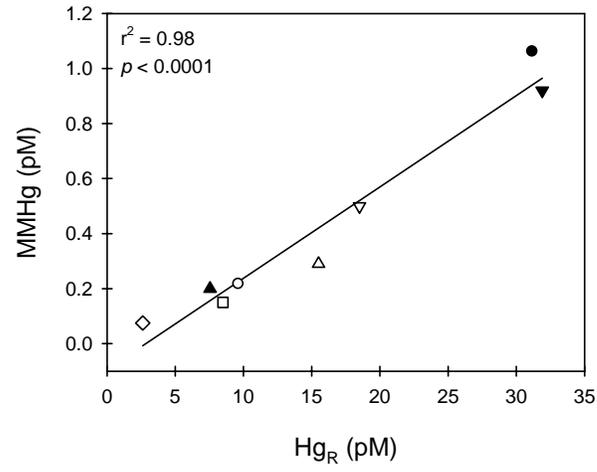
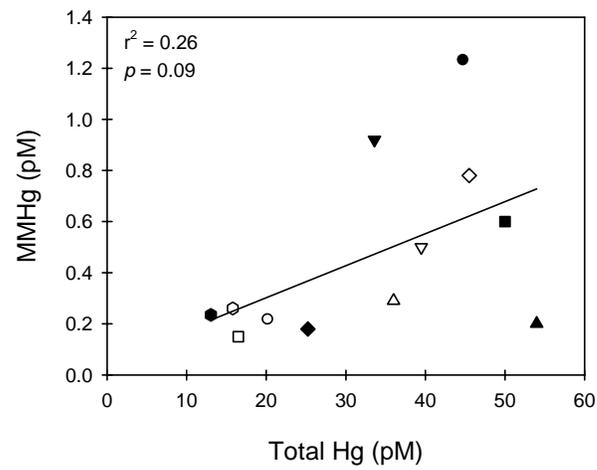


Figure 2.



**Table 1.** Monomethylmercury (MMHg), reactive Hg (Hg<sub>R</sub>), and total Hg (Hg<sub>T</sub>) in precipitation samples examined in this study.

Values in parentheses are  $\pm 1$  SD of the mean.

Sample, location	MMHg (pM)	Hg <sub>R</sub> (pM)	Hg <sub>T</sub> (pM)	Hg <sub>R</sub> :Hg <sub>T</sub>	MMHg:Hg <sub>R</sub>	Reference
Rain, Washington state	1.06 (0.60)	31.2 (21.8)	–	–	0.034	Bloom & Watras (1989)
Snow, Washington state	0.08	2.62	–	–	0.029	Bloom & Watras (1989)
Snow, Wisconsin	0.22 (0.08)	9.65 (1.30)	20.3 (3.45)	0.48	0.022	Bloom & Watras (1989)
Snow, Wisconsin	0.15 (0.15)	8.50 (8.50)	16.5 (10.5)	0.52	0.018	Lamborg et al. (1995)
Snow, Wisconsin	0.29 (0.11)	15.5 (11.0)	36.0 (14.0)	0.43	0.019	Fitzgerald et al. (1991)
Rain, Wisconsin	0.50 (0.50)	18.5 (19.5)	39.5 (34.0)	0.47	0.027	Lamborg et al. (1995)
Rain & snow, NW Ontario	0.60 (0.30)	–	50.0 (35.0)	–	–	St. Louis et al. (2001)
Rain, NW Ontario	0.18 (0.12)	–	25.2 (14.9)	–	–	St. Louis et al. (1995)
Snow, NW Ontario	0.24 (0.30)	–	13.1 (6.3)	–	–	St. Louis et al. (1995)
Snow, Ellesmere Island	0.26 (0.10)	–	15.8 (15.5)	–	–	St. Louis et al. (2005)
Rain & snow, Maryland	0.20 (0.21)	7.55 (6.50)	54.0	0.14	0.026	Mason et al. (1997)
Rain & snow, Connecticut	0.92 (0.26)	31.9 (8.70)	33.6 (9.2)	0.95	0.029	Balcom et al. (2004)
Rain, equatorial Pacific	< 0.05 <sup>a</sup>	8.9 (4.5)	14.4 (6.5)	0.62	< 0.006	Mason et al. (1992)
Rain, equatorial Atlantic	< 0.04 <sup>b</sup>	20.2 (24.9)	22.9 (12.1)	0.88	< 0.002	Lamborg et al. (1999)

Mean<sup>c</sup> = 0.025 (0.006)

<sup>a</sup>All samples had less than the detection limit of 0.05 pM.

<sup>b</sup>Only one (0.095 pM) of five samples had more than the detection limit of 0.035 pM.

<sup>c</sup>Average MMHg:Hg<sub>R</sub> ratio in continental precipitation; excludes the two ocean rain studies.