Investigation of the Accuracy of Monomethyl Mercury Measurements in Rainwater in the Presence of Increased Inorganic Mercury

Kate McPeek
Frontier GeoSciences, Inc.
414 Pontius Avenue N
Seattle, WA 98109 USA

Lucas Hawkins
Eric Prestbo PhD*
Frontier GeoSciences, Inc.

Abstract

Measurements of mercury in rainwater are an important tool used to assess deposition rates into watersheds and other sensitive environments. Monomethyl mercury (MMHg) is of special concern due to its known toxicity to living organisms. For eight years MMHg has been measured at many National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) sites. This study investigates standard NADP/MDN sampling protocol for potential enrichment of wet MMHg deposition that could arise from *in situ* methylation of inorganic mercury (Hg^{2+}). For this experiment Hg^{2+} was added to rain collectors prior to deployment to test for a positive MMHg bias. Each collection event consisted of three samples spiked with 10 ng of Hg^{2+} and three control samples containing no Hg^{2+} spike. All samples were analyzed for total and monomethyl mercury via cold vapor atomic fluorescence spectrometry (CVAFS). A total of six weeklong sampling events resulting in 36 samples were collected in Seattle, WA from June 2006 to July 2007. The outside temperature during collection events ranged from 40-70˚F. Results were evaluated using a two tailed paired t-test (mean delta=0.008 ng/L, *p*=0.413). These data indicate that there is not enrichment of MMHg.

Experimental Design

The experiment was designed to simplistically mimic rain collection at MDN sites. Six sample collection shells made from PVC pipe were set-up on the roof of Frontier Geosciences (FGS) in Seattle, Washington in January 2006 (Figure 1). During weeks with forecasted rain, acid-cleaned MDN glassware (Figures 2 and 3) consisting of a funnel, thistle tube, and half gallon bottle were deployed to the sampling shells using ultra-clean handling techniques (Figure 4). All six bottles contained 20 mL of 1% HCl, while three bottles were also pre-spiked with 10 ng of Hg^{2+}. During rain events the funnels were opened to collect precipitation (Figure 5). The date, time and temperature were noted each time the funnels were opened and closed. Funnels remained covered when it was not raining (Figure 1). Glassware stayed on the roof for seven days. Sample bottles were then stored in coolers for two days to mimic transportation time before being received by FGS staff for splitting and preservation in accordance with MDN protocol.

Splits for total mercury (THg) analysis were preserved with 0.2N BrCl to a level of 1% (v/v) and were stored at room temperature prior to analysis via CVAFS. Splits for MMHg analysis were preserved to 0.4% HCl and kept dark and refrigerated prior to distillation and analysis via gas chromatography CVAFS (GC-CVAFS).

Figure 1: Sample collection shells with covered funnels

Figure 3: Sample bottle during collection

Figure 5: Funnels open for sample collection

Table 1: Mean % Recovery of Inorganic Hg from Spiked Samples

Sampling Event	Sampling Date	Mean % Recovery
1	June 2006	100.8
2	June 2006	125.1
3	November 2006	97.0
4	November 2006	102.3
5	November 2006	113.9
8	July 2007	109.0

Results and Discussion

Each seven day collection resulted in a group of six samples: three unspiked or control samples and three spiked samples. All were analyzed for THg and MMHg. Average ambient levels of mercury in the controls ranged from 8.577-36.275 ng/L for THg and 0.093-0.212 ng/L for MMHg. Average recoveries of inorganic mercury from the spiked samples ranged from 97-125% (Table 1).

For the purpose of comparing MMHg concentrations, the mean concentration of the controls and the mean concentration of the spikes were paired together for each sampling event. Six collection events resulted in six mean control/mean spike pairs (Table 2). One control data point from the first event was excluded due to analytical problems. This sample was later reanalyzed but was determined to be an outlier using the Grubbs' method.

Results from sampling events six and seven were not included in any of the data presented in this poster. These two events resulted in minimal rain collection (approximately 50 mL). Due to volume limitations, THg and MMHg analysis could not be conducted on every sample. Furthermore, the MMHg data for these events was compromised due to analytical issues. No sample volume remained for reanalysis.

Mean MMHg concentrations between controls and spikes were examined through a paired t-test. This analysis indicates that there is not enrichment of MMHg in the presence of increased inorganic mercury. The mean delta between controls and spikes (control - spike) is 0.008 ng/L. This is well below the method detection limit of 0.019 ng/L. The two tailed paired t-test results in a *p*-value of 0.413 (Figure 6). To demonstrate statistical significance, the *p*-value must be 0.05 or less.

Figure 2: Funnel and thistle tube

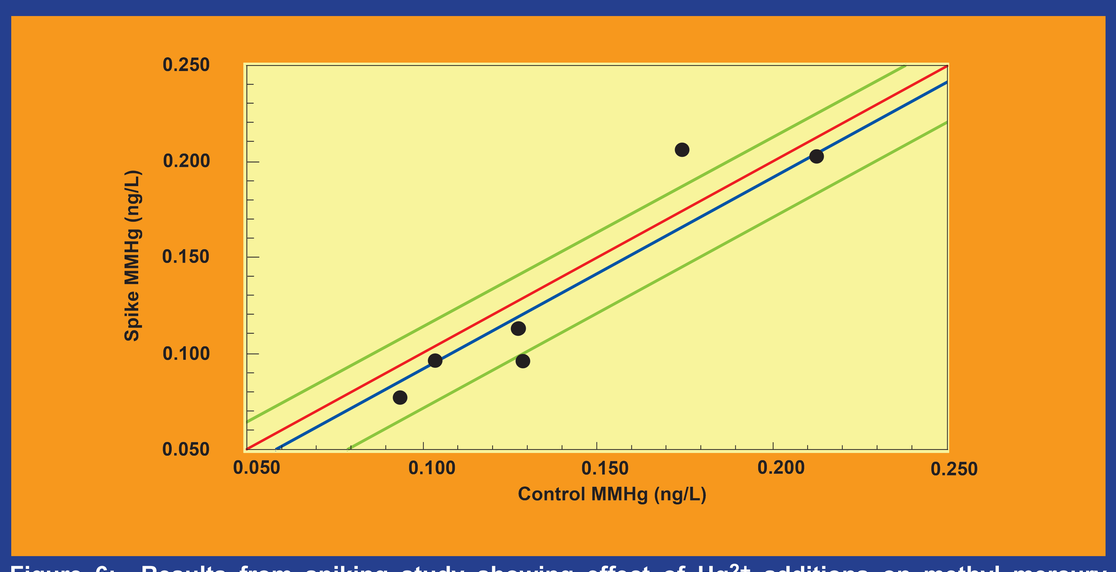

Figure 6: Results from spiking study showing effect of Hg^{2+} additions on methyl mercury concentrations measured in wet deposition. Red line - 1:1 agreement; blue line - least squares regression line with fixed slope of 1; green lines - 95% confidence interval from the mean difference.

Table 2: Mean MMHg Concentrations per Event

Sampling Event	Mean [MMHg] Controls ng/L	Mean [MMHg] Spikes ng/L
1	0.129	0.097
2	0.212	0.204
3	0.103	0.096
4	0.127	0.113
5	0.174	0.205
8	0.093	0.077

Figure 4: Glassware deployment and ultra-clean handling

Conclusion and Further Study

These data indicate that there is not enrichment of MMHg in the MDN rainwater collection method. Given the relatively small number of events sampled, however, a larger set of data is preferred and sample collection continues. Of particular interest is examining data from warmer months to investigate possible enrichment of MMHg at higher temperatures due to an increase in biomethylation and/or the presence of free radicals.

*Eric Prestbo is now with Tekran Canada R&D Facility, 330 Nantucket Blvd., Toronto, ON M1P2P4, Canada.