Atmospheric Mercury in Vermont and New England:
Measurement of deposition, surface exchanges and assimilation in terrestrial ecosystems

Final Project Report – Wet-Deposition Collector Comparison – 1/16/2009

PI:	Melody Brown Burkins, University of Vermont (UVM)
Co-PIs:	Eric K. Miller[1], Ecosystems Research Group, Ltd.; Gerald J. Keeler, University of Michigan; and Jamie Shanley, US Geological Survey
Collaborators:	Sean Lawson, VTANR-VMC; Jen Jenkins, Mim Pendelton, Carl Waite and Alan Strong, UVM; Rich Poirot, VTANR-APCD; Alan VanArsdale, USEPA; Mark Cohen, NOAA;
Project Officer:	Eric Hall, USEPA

MICB – MDN (NCON, ACM) Collector Comparison

In partnership with NOAA, MDN, the USGS, and EPA, we conducted a 1-year precipitation mercury collector inter-comparison study. We conducted a short-term follow on direct comparison of MDN and UMICH sample trains in 2007. This experiment was designed to identify and eliminate laboratory bias as well as to test the relative performance of each sample train when deployed in the same collector. The experimental design allowed us to separate the overall collector-protocol-laboratory bias into components of 1) collector, 2) sample-train, and 3) laboratory bias. We also analyzed laboratory quality assurance data provided by MDN and USGS. This study was the first to make scientific comparisons of the MIC-B (UMICH), MDN and NCON (USGS) collectors for event-based assessment of precipitation mercury deposition. All three types of collectors were in use in the Northeastern US at the start of the project. Data from these different collectors and networks could not readily be pooled and coordinated. We identified and quantified substantial uncertainties the must be taken into account when mercury wet-deposition data are used together with mercury measurements in other media (e.g. water, sediment, fish) in ecosystem studies and modeling.

This project developed transfer functions allowing data from the three collector types to be merged for regional analyses. This study also informed mercury researchers about of the strengths and weaknesses of each collection system, guiding long-term mercury monitoring and upgrade efforts throughout the country. Most-probable value or "best-estimate" functions were developed to adjust data from different labs and collectors to a common sampling efficiency and NIST-referenced basis.

A manuscript for peer-review was produced (draft included below). Submission of the manuscript is pending discussions by the authors and their institutions. You are receiving this draft as part of your role in reviewing EPA-ORD's Vermont Atmospheric Mercury Program. ***Please do not cite or distribute this manuscript without permission from the corresponding author.***

[1] Corresponding author for the final project report. Email: ekmiller at ecoystems-research.com Voice: 802-649-5550

Comparison of the MDN Standard Aerochem, proposed MDN NCON, and University of Michigan Air Quality Lab modified MICB precipitation collectors for mercury deposition.

Eric K. Miller*, David Gay, Mark Nilles, Gerald Keeler, Clyde Sweet, Rick Artz, Sean Lawson, Mim Pendleton, and James Barres

*Corresponding Author ekmiller@ecosystems-research.com

Note: Bob Brunette and Gerard Van der Jagt of Frontier Geosciences made significant contributions to this study by generating and providing data as well as contributing to the discussion of results. The authors have extended the opportunity for co-authorship to both scientists and hope they will join the paper after institutional review.

Abstract

We conducted a 1-year study (August 2005 – July 2006) of the event-based relative collection performance of the MDN modified Aerochem (ACM) sampler, the University of Michigan modified MICB sampler, and the NCON Systems mercury deposition sampler. The samplers were deployed at the Underhill, VT Air Quality Research Facility (VT99). The study was designed to assess the effects of differential rain sensor performance, sampling trains, and collector geometry on sampled mercury concentrations and deposition. Extensive data on collector lid status and meteorological conditions including rainfall rate, surface wetness, and humidity were collected. National Weather Service standard 8-inch precipitation gages were monitored as the reference for precipitation amount. Samples from the MICB were analyzed at the University of Michigan Air Quality Laboratory. Samples from the ACM and NCON were analyzed at the MDN HAL.

All three collectors experienced mechanical and other failures during the study. Drive systems failures compromised the results from each of the samplers at one time or another. The MICB collector overflowed during 3 rain events. Heater problems and collector geometry resulted in poor snow collection performance for the ACM and NCON collectors. Approximately 20% of precipitation events and ~24% of precipitation volume were either disqualified or classified as questionable results for each of the samplers. All 3 collectors simultaneously functioned satisfactorily (according to respective protocol QA standards) during 69% of events and 68% of the precipitation measured by the NWS gage during the study period. Because failures occurred more frequently during the colder months, lower fractions of observed snow (33%) and mixed precipitation (62%) were represented in the valid comparison data set than rain (74%).

Compared to the NWS gage, all three collectors under collected snow (NCON < ACM < MICB). The ACM and NCON collectors under collected mixed precipitation (ACM < NCON). The MICB was within 1% of the NWS gage catch for mixed events. All three samplers collected +/- 2.7% of the NWS gage catch for rain events. Part of the observed difference in collection efficiency can be attributed to the precipitation sensing logic of each collector. The MICB lid cycled 3302 times, the NCON 3186 times, and the ACM only 1190 times during the valid comparison period. The NCON lid was open for 1248 hours, the MICB for 789.6 hours, and the ACM for 617 hours during the valid comparison period. The NCON opened immediately in response to any rain shower activity. The MICB was slightly less responsive and did not open for all minor shower events detected by the NCON and an independent wetness sensor. The ACM was often delayed in opening relative to the NCON and MICB for light precipitation and did not stay open as long. The NCON and ACM collectors frequently failed to melt snow rapidly enough to prevent "blow-out" or "knock-off" (when lid closing displaced snow accumulated on the funnel).

The MICB and the NCON collected more Hg than the ACM during the comparison period. Differences in MDN and University of Michigan sample train performance as well as a 6% bias between the laboratories contribute to the discrepancies between measurements obtained by the different collectors.

Background

Three different types of automated wet-only precipitation samplers have been widely used for the collection of mercury in precipitation in North America. Previous studies have identified that there can be substantial differences in the estimates of mercury concentrations and deposition made with each type of collector (Miller et al. 2005). This study was undertaken in order to simultaneously assess the relative performance of 3 collector types in a rural location in Northeastern North America which experiences considerable snow and mixed precipitation. A primary objective of the study was to identify the most suitable collector for long-term monitoring of mercury in precipitation in the Lake Champlain Basin. Secondary objectives were to identify reasons for differences in collector performance that could lead to improved collector designs and to develop transfer functions for normalizing data obtained from the different collector types and laboratories.

Description of Collectors

In 1992, the University of Michigan (UM) developed a modified version of the Canadian MIC-B sampler for simultaneous collection of mercury and trace metals in precipitation (MICB). UM selected the MIC-B platform due to the superior performance of its heated, conductivity/ wetness sensing grid relative to other collectors available at that time (Landis and Keeler 1997). The UM version of the MICB (Figure 1a) uses a borosilicate glass, nominally 199-cm^2 area, straight-sided, 18.5-cm deep collection funnel for the mercury sampling train (Figure 2a). Precipitation is collected in a 1-liter Teflon® bottle precharged with 20 ml of ultra-pure HCl. The funnel and sample bottle are connected by means of a Teflon® adaptor that contains a glass vapor lock. The chamber holding the sample bottle is heated with a 1500-watt thermostatically controlled ceramic heater. Conduction of heat upward through the sample train rapidly melts frozen precipitation accumulated at the base and on the sides of the funnel. The UM-MICB has been deployed at more than 25 sites in the upper Midwest, New England States, Maryland, and Florida.

In 1995 Frontier Geosciences developed a modified version of the Aerochemetrics precipitation sampler for collection of mercury and trace elements in precipitation for use in the NADP Mercury Deposition Network (MDN). The ACM sampler (Figure 1b) was selected because it was widely deployed as the standard wet-only precipitation sampler for the NADP network monitoring major ions in precipitation. The ACM also uses a heated, conductivity/wetness sensing grid; however, the grid is much coarser than the one found on the MICB. The MDN-ACM uses a glass, 120.2-cm^2 area, 10-cm deep, conical funnel. The sample is collected in a 2-liter glass bottle precharged with 20-ml of ultra-pure HCl. The funnel and sample bottle are connected by means of a glass thistle tube which, by virtue of its length and small diameter, prevents substantial vapor loss (Figure 2b). The chamber holding the sample bottle is heated with a 1500-watt thermostatically controlled ceramic heater. Conduction of heat upward through the thistle tube and chimney is intended to melt frozen precipitation accumulated in the funnel. The MDN-ACM has been deployed at 95 sites as part of the international NADP/MDN.

Recently, Frontier Geosciences and the USGS jointly developed a modified version of the NCON Systems automated precipitation sampler for collection of mercury in precipitation (NCON). The NCON sampler (Figure 1c) was selected by USGS because of its superior screw-type lid motor drive which was expected to be more durable than the ACM sampler's motor drive. In contrast to the MICB and ACM samplers, the NCON sampler uses an infrared-scattering optical precipitation sensor to control lid opening and closing. This sensor has a more immediate response to changes in precipitation than conductivity sensing grids. The NCON sampler uses the same sample train as the MDN-ACM with the exception of a slightly shorter thistle tube to accommodate the collector geometry. The chamber holding the sample bottle is heated with a combination of a 500-watt plate heater and a 200-watt fan heater. Conduction of heat upward through the thistle tube and chimney is intended to melt frozen precipitation accumulated in the funnel. The NCON mercury sampler has been deployed at 8 sites as part of USGS investigations of mercury deposition and cycling.

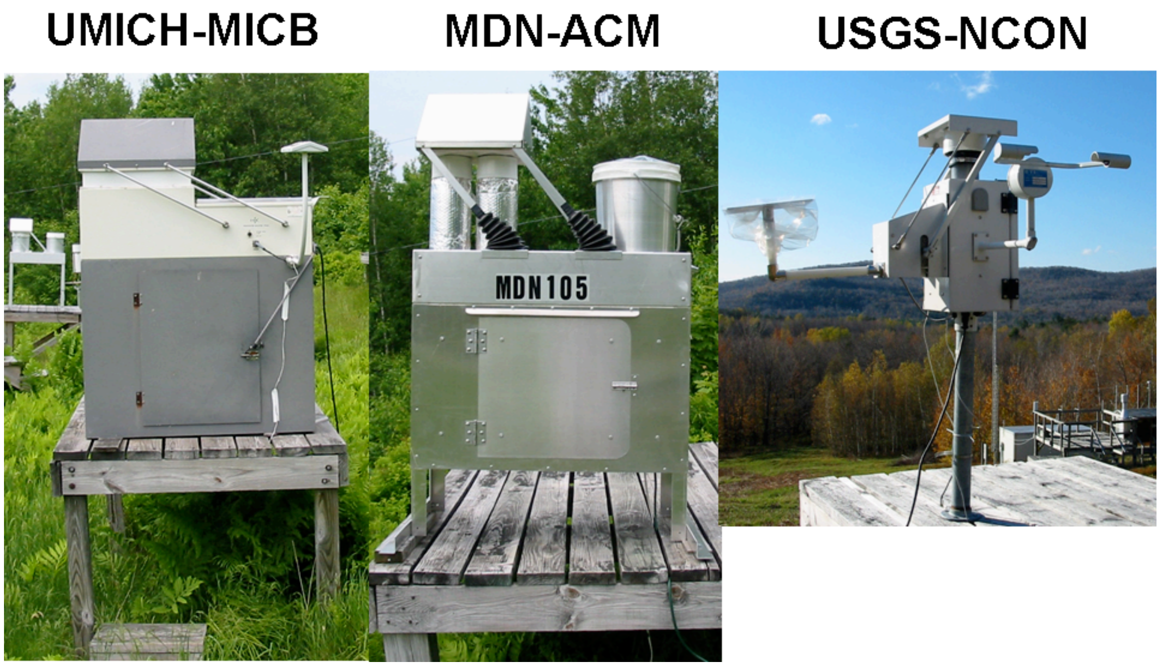
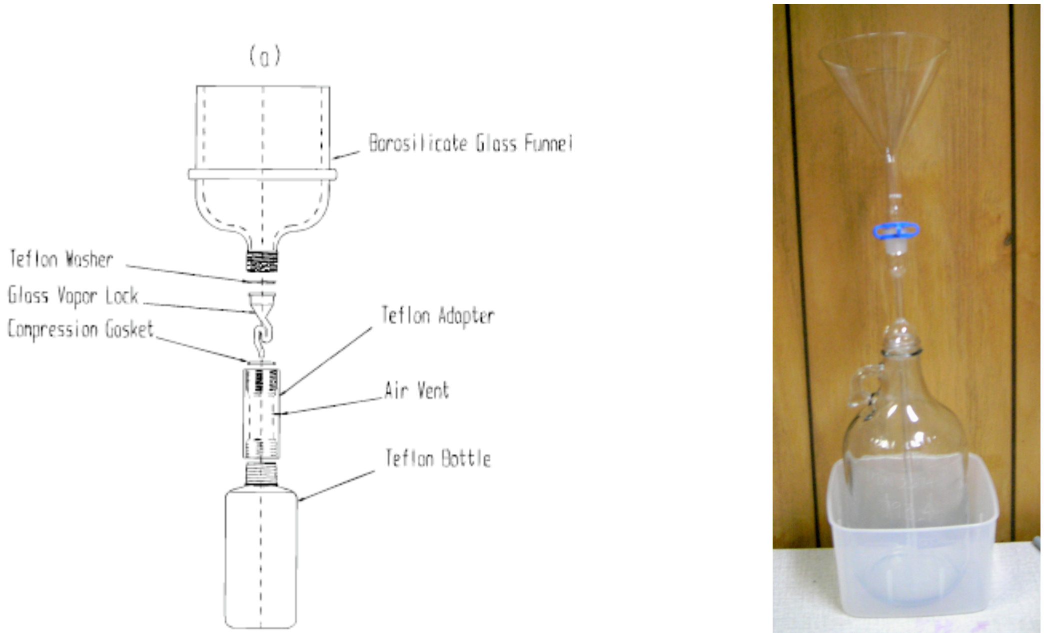


Figure 1. a) University of Michigan modified MIC-B collector, b) MDN modified Aerochem collector, and c) USGS NCON collector.



a) MICB   b) ACM and NCON

Figure 2. a) MICB, b) ACM and NCON sample trains.

Methods

The three automated collectors were deployed at the Underhill, VT Air Quality Research Facility (VT99) following standard NADP criteria. Figure 3 shows the locations of the samplers, recording rain gages and tipping bucket rain gage. A National Weather Service (NWS) standard 8-inch gage located just to the north of the ACM was monitored throughout the study as the "gold standard" for precipitation amount. Two additional NWS 8-inch gages were deployed east of the MICB and NCON samplers in May 2006 to provide an estimate of the variance in NWS precipitation amount. All samplers and gages were on the same contour with orifice heights +/- 1 meter. The automated samplers were fitted with reed switches to allow recording of lid opening and closing times. A tipping bucket rain gage was located east of the MICB. Temperature, RH, global solar radiation, and surface wetness sensors were located on a tower at the northeast corner of the collector field. The time of each tip of the TBRG or change in status of lid positions was recorded with a data logger. The signal from the surface wetness sensor was also recorded at the time of a lid status change.

The sample trains of the automated collectors were changed on an event basis following the protocol in use at VT99 since 1993. The site is visited daily between 8:30am and 10am. If a precipitation event has concluded in the past 24 hours, the sample trains are changed. If precipitation is occurring, but expected to stop before 3pm, the site operator returns after the end of precipitation to change the sample trains. When precipitation continues steadily or lightly for more than 48 hours, the operator attempts to change sample trains during periods of minimal precipitation in conjunction with air mass changes or to prevent overflow of the MICB collector. Sample trains are changed after 7 days without precipitation. MICB sample trains were prepared and samples analyzed at the University of Michigan Air Quality Laboratory. ACM and NCON sample trains were prepared and samples analyzed at the MDN Mercury Analytical Lab (HAL), Frontier Geosciences, Seattle, WA.

A standard definition of collector area was adopted for all collectors based on the measurement of funnel diameters from mid-rim to mid-rim of the funnel. Recent measurements of funnels were used to calculate funnel areas.

Data, flags, and notes from the two laboratories for the 3 collectors were compiled along with notes and flags from the site operator's log into a common data set. Each record in the data set represented a common deployment period for all 3 sample trains. Field and laboratory QA flags were used to disqualify records where any one of the 3 samplers experienced failures or QA exceptions. A second category of "questionable" records was identified where either the laboratory or field notes identified potential problems with samples such as leaks during shipment, but the responsible laboratory had not disqualified the sample. Additional screening of the remaining records was conducted to uncover QA problems that were missed by the laboratories.

A follow-on comparison of the MDN and University of Michigan sample trains deployed simultaneously in the MICB collector was conducted from May through October of 2007. Due to funding limitations, this study could only address the relative performance of the sample trains for rain events.

Laboratory quality-assurance data provided by the HAL for 2004-2006 as well as data from a multi-laboratory blind sample exchange coordinated by USGS were analyzed to constrain the potential for stable laboratory-laboratory bias within performance standards of EPA Method 1631.

Linear regression, ANOVA, and paired t-tests were employed to test hypotheses about relative collector performance. All statistical analyses were conducted with JMP 4.04 (SAS Institute).

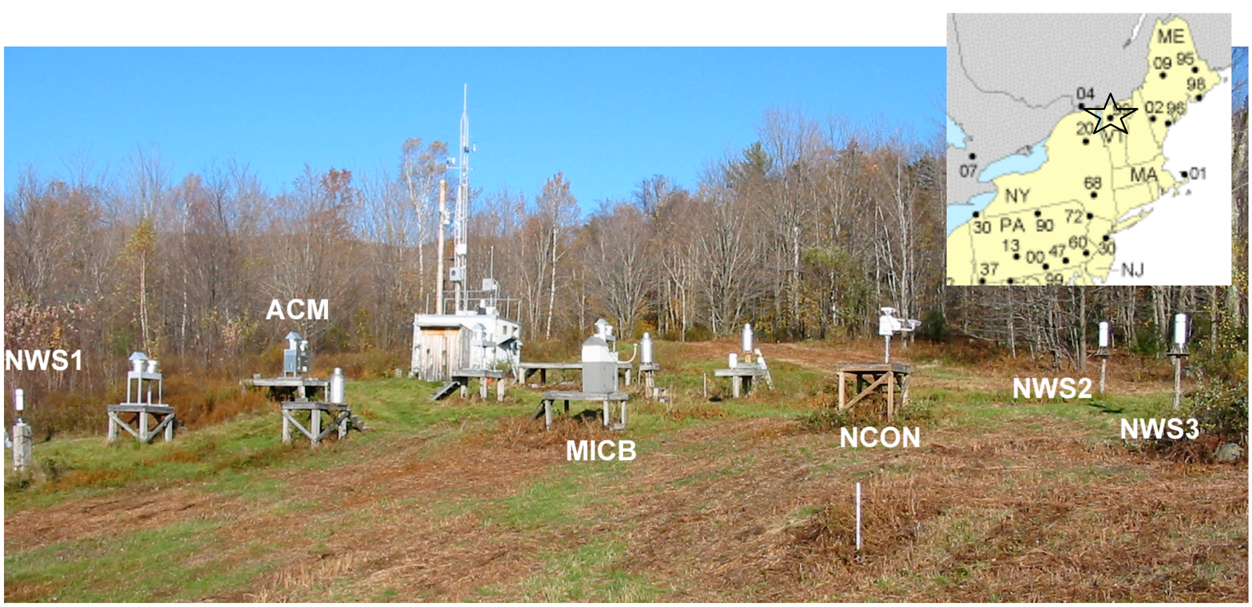


Figure 3. Locations of precipitation samplers at the VT99 NADP site (inset) in Underhill, VT. The NCON is farthest right (south). The MIC-B is in the center of the field. The ACM is on the left (north). The primary NWS 8-inch gage is just slightly downhill (west) of the ACM. Two additional NWS 8-inch gages were located

to the right (south) of the NCON and MICB samplers. The site's 3 Belfort recording rain gages are visible. Two tipping bucket rain gages are located on the platform to the right and behind the MICB.

Results

NWS gage variance

The variance in precipitation sampled by the NWS standard 8-inch gages is summarized in Table 1. On an event basis, we consider the differences between collector catch and NWS gage catch to be meaningful when the difference is > 22% for low volume events (showers), >2.6% for rain, > 3% for intense rain such as in thunderstorms, and > 4% for heavy rain events (>40 mm). NWS gage number 1 (NWS1), used as the standard for the full year of the study, was not significantly different from the mean of the 3 gages or from either of the two other gages when compared gage to gage using paired t-tests. For the sum of the period (May – September 2006), NWS1 = 769.42 mm, NWS2 = 769.74 mm, NWS3 = 762.90 mm, and mean = 767.35. The difference in precipitation measured over the observation period ranged +0.3% to -0.6% compared to the mean. The much lower percent range for the period compared to the percent range on an event basis indicates that event-to-event differences between gages were random and cancelled out.

Table 1. Summary Results for NWS 8-inch rain gages May 2006 – September 2006.

Type	N Rows	Mean(NWSmean(mm))	Mean(StdDev(mm))	Mean(%CV)	Mean(Range(mm))	Mean(%range)
showers	9	3.55	0.11	12.16	0.21	21.99
rain	18	15.09	0.20	1.58	0.33	2.63
tstorm	7	18.73	0.22	1.60	0.42	3.00
heavy-rain	6	55.46	1.10	2.08	2.12	3.97

Collector performance and QA exceptions

There were 96 sample train deployments (95 with precipitation) during the 1-year comparison period. Equipment malfunctions and QA exceptions compromised the automated collector results for about 20% of the events sampled for each collector (Table 2). Mechanical failures were greatest for the ACM and least for the MICB. It should be noted that the motor drive failure that occurred in the MICB collector was the first such failure since the collector was deployed at Underhill in December of 1992. There were 9 events where the NCON and 3 events where the ACM collectors failed to completely melt all of the snow captured in the funnels (Figure 3). These records were retained in the data set as they represent the performance of the collectors during snow. The ACM and NCON sample bottles were prone to leakage during shipment (Table 2). These records were retained in the data set because they were not disqualified by the HAL. There were no leaks of the MICB sample bottles during shipment. The MICB sample bottle overflowed during 3 large rain events, including during the passage of the remnants of hurricane Katrina over New England. These records were excluded from the data set because they should have been identified as incomplete samples during standard QA. Additional screening detected an apparent sample contamination for the NCON where debris was noted, but the sample was not disqualified by the HAL. This record was removed from the data set. The remaining “valid comparison set” represents 66 (69%) sample train changes and 1158.5 mm (68%) of the total precipitation observed during the study period (Table 3). Collector performance for capture of precipitation was evaluated with this set of samples.

Additional samples with QA problems were detected by tertiary screening during analysis of collector performance for capture of mercury. Two extremely low-volume (NWS1 < 2.1 mm) snow samples from the MICB were identified as exhibiting mercury concentrations greater than any other snow sample previously analyzed by the UMAQL. These records had been flagged as questionable by the lab and were excluded from the analysis of Hg concentrations and deposition. One low volume rain sample (NWS1 = 2.29 mm) from the ACM exhibited a mercury concentration greater than two times the concentrations measured in samples collected by the NCON and MICB samplers. The ACM exhibited extremely poor collection efficiency for this event (27% of NWS1) while the other two collectors sampled within +/- 3% of the NWS1 gage. The ACM appears to have failed to sample the more dilute portion of the event. This record was excluded from analysis of Hg concentrations and deposition.

Collector openings

During the valid comparison period the NCON sampler was the most responsive to changes in precipitation – opening and closing first and remaining open for the largest number of hours (Table 4). However, there was no statistically significant difference in the number of openings per event between the NCON and MICB collectors (2-sided paired t-test, p=0.859). The ACM collector opened significantly fewer times per event compared to the NCON (-63%, p=0.0009) and the MICB (-64%, p<0.0001) as assessed by 1-sided, paired t-tests. The NCON sampler was open a significantly greater number of hours per event than both the MICB (+58%, p<0.0001) and the ACM (+103%, p<0.0001) as assessed by 1-sided, paired t-tests. The ACM collector was open for significantly fewer hours per event (-22%) than the MICB (1-sided paired t-test, p=0.002).

Table 2. Summary of equipment and QA exceptions.

VT99 Sampler Comparison	**Precipitation Sampled (mm)**						**Number of Precipitation Events**				
(8/1/2005 - 7/31/2006)	**snow**	**mixed**	**rain**	**all**	**%all**		**snow**	**mixed**	**rain**	**all**	**%all**
NWS Standard 8" Gage	**124.7**	**426.5**	**1159.0**	**1710.1**	100.0%		**18**	**22**	**55**	**95**	100.0%
	Precipitation NOT Sampled (mm)						**Number of Events NOT Sampled**				
ACM	**snow**	**mixed**	**rain**	**all**	**%all**		**snow**	**mixed**	**rain**	**all**	**%all**
Mechanical Failure*	42.7	106.4	6.6	155.7	9.1%		3	3	1	7	7.4%
Sample Train Failure*			9.1	9.1	0.5%				1	1	1.1%
Power Failure*			14.5	14.5	0.8%				1	1	1.1%
Leak DQed by HAL*			30.2	30.2	1.8%				1	1	1.1%
Shipping Leak NOT DQed by HAL**	10.4	50.8	138.4	199.6	11.7%		1	2	4	7	7.4%
Snow not melted**	7.9	66.6		74.4	4.4%		1	2		3	3.2%
All Disqualified*	42.7	106.4	60.5	209.5	**12.3%**		3	3	4	10	**10.5%**
All DQ* + Questionable**	61.0	223.8	198.9	483.6	**28.3%**		5	7	8	20	**21.1%**
	48.9%	52.5%	17.2%				27.8%	31.8%	14.5%		
	Precipitation NOT Sampled (mm)						**Number of Events NOT Sampled**				
NCON	**snow**	**mixed**	**rain**	**all**	**%all**		**snow**	**mixed**	**rain**	**all**	**%all**
Mechanical Failure*	50.9	30.7	29.7	111.3	6.5%		4	3	2	9	9.5%
Sample Train Failure*	8.9			8.9	0.5%		1			1	1.1%
Power Failure*		83.8	14.5	98.3	5.7%			1	1	2	2.1%
Debris Contam. Missed by HAL*			25.4	25.4	1.5%				1	1	1.1%
Shipping Leak NOT DQed by HAL**		85.1	104.9	190.0	11.1%			3	3	6	6.3%
Snow not melted**	22.1	86.9		109.0	6.4%		3	3		6	6.3%
All Disqualified*	59.8	114.6	69.6	243.9	**14.3%**		5	4	4	13	**13.7%**
All DQ*+ Questionable**	81.9	286.5	174.5	542.9	**31.7%**		8	10	7	25	**26.3%**
	65.7%	67.2%	15.1%				44.4%	45.5%	12.7%		
	Precipitation NOT Sampled (mm)						**Number of Events NOT Sampled**				
MICB	**snow**	**mixed**	**rain**	**all**	**%all**		**snow**	**mixed**	**rain**	**all**	**%all**
Mechanical Failure*	20.8	48.5	6.6	75.9	4.4%		5	5	1	11	11.6%
Overflow*			198.1	198.1	11.6%				3	3	3.2%
Power Failure*		83.8	14.5	98.3	5.7%			1	1	2	2.1%
Operator Error*			9.1	9.1	0.5%				1	1	1.1%
Possible Contam. noted by lab**	3.3			3.3	0.2%		2			2	2.1%
All Disqualified*	20.8	132.3	228.3	381.5	**22.3%**		5	6	6	17	**17.9%**
All DQ*+ Questionable**	24.1	132.3	228.3	384.8	**22.5%**		7	6	6	19	**20.0%**
	19.3%	31.0%	19.7%				38.9%	27.3%	10.9%		
Notes											
All single asterisk "*" items reflect samples that normal QA at the site or lab level either did disqualify or should have disqualified.											
All double asterisk "**" items reflect samples that normal QA at the site or lab level did or should have identified as questionable.											
The final line in each table combines all of the disqualified "DQ" and questionable samples.											
The amount of precipitation not sampled is the NWS measured precip corresponding to the disqualified or questionable samples.											

Figure 3. NCON sampler with unmelted snow in funnel. A portion of the snow extending above the funnel rim was knocked off when the lid closed.

Precipitation collection efficiency

Data were available for the NWS1 and Belfort gages for the full year comparison period. The NWS1 gage recorded 1710.11 mm of precipitation for the year. The Belfort gage (charts interpreted by the site operator) recorded 1632.7 mm or 4.5% less (1-sided t-test, $p < 0.0001$) than the NWS gage for the year.

During the valid comparison period the precipitation catches of the MICB and NCON samplers were not significantly different from the NWS1 catch (paired t-tests) and both differed from the NWS gage less than the percent difference noted between the 3 NWS gages (- 0.6 to +0.3%). The precipitation catch of the ACM was biased significantly lower (-5.0%) than the NWS1 gage (1-sided paired t-test, p=0.016). When analyzed by precipitation type, all collectors were significantly biased low (1-sided paired t-tests: MICB, -46% p=0.046; NCON, -66% p=0.021; ACM, -46% p=0.007) compared to the NWS1 gage for collection of snow (Table 3). The ACM was significantly biased low (1-sided paired t-test: -10.6% p=0.054) compared to NWS1 for mixed precipitation. There was no significant difference in precipitation catch between any of the collectors and NWS1 for rain events. Because snow and mixed precipitation are severely underrepresented in proportion to their occurrence relative to rain in the valid comparison set (Table 2), it is possible that all 3 collectors could be biased low on annual basis if these precipitation types were fully represented in the data set.

The frequency distributions of event collection efficiencies (%CE, Figure 4) show that there can be substantial departures from the NWS1 gage catch on an event basis for all 3 collectors. The standard deviations of the distributions of event errors (mm) were 3.8 mm for the NCON, 3.3 mm for the ACM, and 2.9 mm for the MICB. The errors (mm) were strongly positively correlated between the NCON and ACM samplers ($r^2= 0.7$, $p<0.0001$) and weakly positively correlated between the MICB and the other two collectors ($r^2= 0.2$, $p<0.0001$).

Relative performance for collecting mercury

For the 63 sample train deployments valid for comparison of mercury concentrations, the 3 samplers collected significantly different amounts of mercury as determined by paired t-tests. The ACM sampler collected significantly less mercury than the NCON (-7.3%, 1-sided t-test, p = 0.023) and the MICB (-21.4%, 1-sided t-test, p < 0.0001). The NCON sampler also collected significantly less mercury than the MICB (-15.3%, 1-sided t-test, p = 0.002). Mercury concentrations were well correlated (p < 0.0001) among all three samplers with coefficients of determination ranging from 0.8 to 0.86.

Precipitation type had a profound influence on the relative collection of mercury between the collectors. There were smaller, but significant differences between collectors for rain-only events (ACM -6.0% of NCON, p = 0.037; NCON -14.5% of MICB, p = 0.006; ACM -19.7% of MICB, p = 0.0001) than for all snow events (ACM -46% of NCON, p = 0.059; NCON -23% of MICB, ns; ACM -59% of MICB, p = 0.050). Mixed precipitation events produced mixed results with the NCON and ACM (+/- 1.5%, ns) sampling similar amounts of mercury but about 15% less than the MICB (p = 0.081 and 0.037, respectively). The degrees of freedom were much lower (4) for the analyses of all snow events than for the analyses of mixed (12) or rain (44) events.

Table 3. Summary of precipitation catch relative to NWS 8-inch gage by precipitation type.

	ACM	NCON	MICB
snow	-48.3%	-66.0%	-46.4%
mix	-10.6%	-7.3%	-0.5%
rain	-1.2%	2.4%	2.7%
all	-5.0%	-2.2%	0.2%

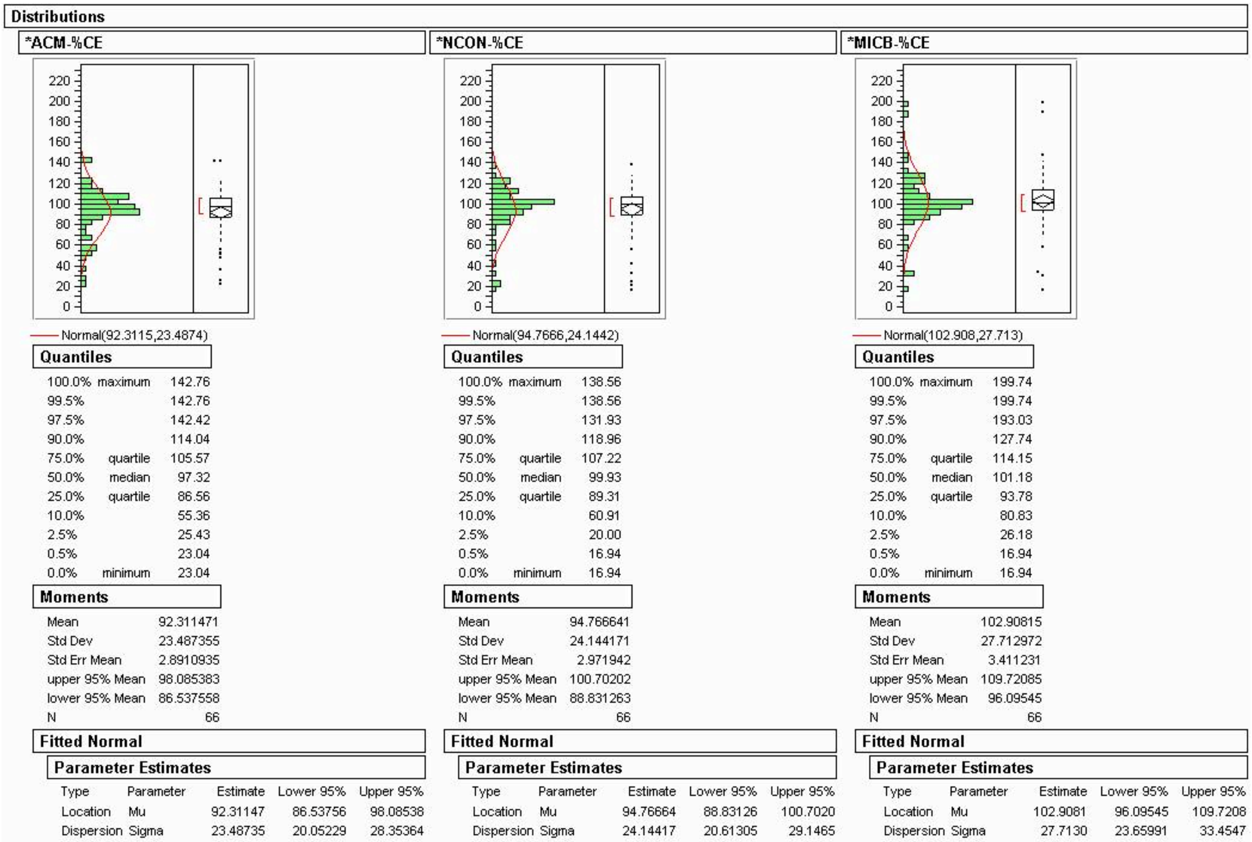


Figure 4. Frequency distributions of event precipitation collection efficiency compared to the NWS1 gage.

Table 4. Summary of collector lid openings.

Number of Collector Openings and Closings				
	Snow	**Mixed**	**Rain**	**All Valid**
ACM	363	300	527	1190
NCON	155	642	2389	3186
MICB	786	765	1751	3302
Number of Hours Collector was Open				
	Snow	**Mixed**	**Rain**	**All Valid**
ACM	51.3	145.3	420.5	617.0
NCON	247.4	301.0	699.5	1248.0
MICB	57.8	186.7	545.1	789.6

Paired deployment of replicate MDN and UMICH sample trains in the MICB collector

A total of 16 paired-deployments were achieved. For 8 events a pair of MDN sample trains were deployed along side a University of Michigan (UMICH) sample train. Frontier Geosciences analyzed one of the MDN sample trains while the UMICH sample train and one MDN sample train were shipped for analysis by the UMAQL. For an additional 8 events a duplicate UMICH sample train was deployed with one of the duplicates analyzed by Frontier Geosciences and one by UMAQL. This design allowed comparison of sample train performance (e.g. catch, evaporation) as well as a comparison of laboratory processing of the sample trains. Due to funding limitations, data were only returned by the UMAQL for the UMICH sample trains, partially limiting the laboratory comparison. For the data reported below the reference UMICH sample train was always analyzed by UMAQL (UMAQL-UMICH: LAB-SAMPLETRAIN) while the replicate MDN or UMICH sample trains were always analyzed by Frontier Geosciences (Frontier-MDN, or Frontier-UMICH).

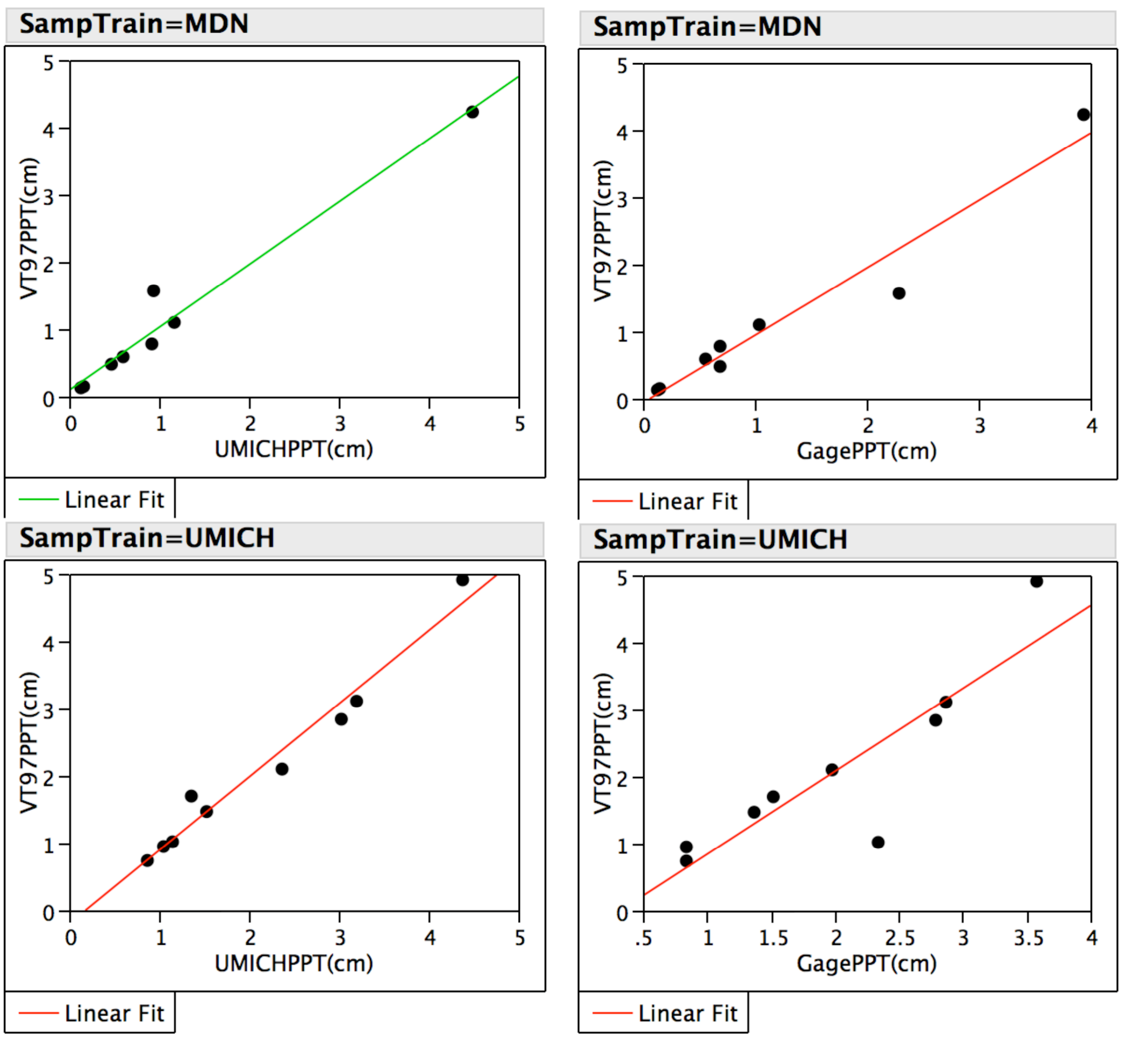


Figure 5. Correlations between redundant co-deployed sample trains (VT97 = MDN at top or UMICH at bottom) and the reference co-deployed UMICH sample train (left-side) and the Belfort rain gage (right-side).

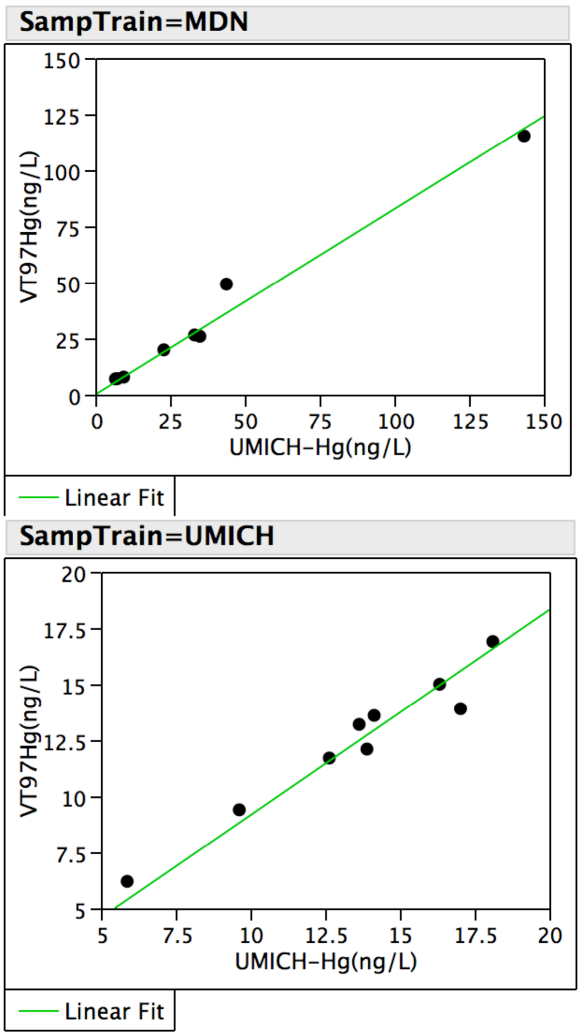


Figure 6. Correspondence between mercury concentrations measured in samples collected by redundant co-deployed sample trains (VT97 = MDN at top or UMICH at bottom) and the reference co-deployed UMICH sample train.

Precipitation amounts sampled during the sample-train comparison ranged from 0.13 to 3.94 cm as measured by the Belfort gage and were distributed over nearly this full range for each sample train. Precipitation sampled by both redundant sample trains correlated well with the co-deployed reference UMAQL-UMICH sample train (Frontier-MDN r^2=0.96 or Frontier-UMICH r^2=0.96) and somewhat less well with the Belfort gage (Frontier-MDN r^2=0.94 or Frontier-UMICH r^2=0.75) (Figure 5). Best-fit lines constrained to an intercept of zero produced slopes of 0.97+/-0.05 for the Frontier-MDN vs. UMAQL-UMICH; 1.02+/-0.04 Frontier-UMICH vs. UMAQL-UMICH; 0.98+/-0.06 Frontier-MDN vs. Belfort; and 1.07+/-0.10 Frontier-UMICH vs. Belfort.

Mercury concentrations ranged from 5.9 to 143 ng/l as measured by the normally deployed reference UMICH sample train and analyzed by UMAQL (UMAQL-UMICH). Mercury sampled by both redundant sample trains correlated well with the co-deployed UMAQL-UMICH sample train (Frontier-MDN r^2=0.98 or Frontier-UMICH r^2=0.95, Figure 6). Best-fit lines constrained to an intercept of zero produced slopes of 0.83+/-0.03 for the Frontier-MDN vs. UMAQL-UMICH and

0.92+/-0.02 Frontier-UMICH vs. UMAQL-UMICH. The apparent mercury concentration bias with respect the reference UMICH sample train analyzed by UMAQL averaged -10.6% (median -15.6%) for the MDN sample train ([Frontier-MDN – UMAQL-UMICH] / UMAQL-UMICH) and averaged -6.2% (median -5.3%) for the UMICH sample train ([Frontier-UMICH – UMAQL-UMICH] / UMAQL-UMICH).

Laboratory Quality Assurance Data

EPA Method 1631 performance data from Frontier Geosciences (HAL) for 2004-2006 are summarized in Table 5. The HAL demonstrated excellent performance with respect to the Method 1631 criteria. Mean recovery of the CRM by the HAL was 95.2% with an RSD of 4.1%.

The USGS conducted a multi-laboratory blind sample analysis program (Gregory Wetherbee, U.S. Geological Survey, written communication, 2008). Data from 6 participating labs with adequate numbers of samples were analyzed to assess the relative bias observed between laboratories when all laboratories meet the Method 1631 performance criteria. There were adequate data for 4 dilutions of NIST CRM prepared by USGS. Because of anticipated error in the method of preparation of the NIST dilutions to rain water levels, USGS did not report an expected concentration for the dilutions (Gregory Wetherbee, U.S. Geological Survey, personal communication, 2008). Dilutions were prepared and shipped to the laboratories monthly. Periodic batch-to-batch preparation variability was detected by ANOVA. Batches that were significantly different in mean concentration from the majority of batches were eliminated from further analysis. A small number of outlier values beyond Method1631 performance criteria were also removed. The means, 95% confidence intervals about the means, and median values for each of the 4 solutions are presented in Table 6.

There were significant differences among laboratories as indicated by ANOVA[2] for all 4 solutions. Means comparisons using the Tukey-Kramer Highly Significant Difference test indicated that the HAL was consistently biased low (average – 5.2%) relative to other laboratories and the Northern States Analytical Laboratory was consistently biased high (average +3.9%). The spread (stable bias) between these two EPA 1631 performance-compliant laboratories was 9.1%. Taking the mean value of all analyses for all laboratories as a good estimate of the true value of each solution, then the mean percent recovery of blind USGS-prepared NIST CRM dilutions indicated for the HAL (94.8%) is consistent with the HAL's own internal NIST performance data (mean recovery 95.2%).

[2] While only one of the 4 solutions produced a normal distribution as determined by the Shapiro-Wilk test, normal quantile plots indicated that the measurements of each solution were nearly normally distributed with only minor tailing. In a normal distribution the median and mean are equal. The observed median values were typically within about 1% of the mean for the 4 solutions. In all cases the medians were within the 95% confidence envelope of the means. Thus, it is reasonable and appropriate to use parametric techniques such as ANOVA to investigate these data.

Table 5. HAL CRM (NIST1641d) recovery 2004-2006.

EPA Method 1631 Minimum	71.0%
HAL Minimum	75.0%
HAL 2.5% Quantile	86.5%
HAL 10% Quantile	90.0%
HAL 25% Quantile	93.3%
HAL Mean	**95.2%**
HAL Median	**95.7%**
HAL 75% Quantile	97.5%
HAL 90% Quantile	99.7%
HAL 97.5% Quantile	104.9%
HAL Maximum	106.4%
EPA Method 1631 Maximum	125.0%
HAL Precision (CV)	4.1%
HAL Inter-Quartile Range	4.5%
HAL 95%-Probability Range	18.4%
HAL Range	33.0%
HAL Number of Samples	1073

Table 6. Summary table of the current study's interpretation of USGS Inter-lab comparison data for 2004-2007. Data for Northern States Analytical Laboratory (NSA) are provided to illustrated the possible spread (bias) between the HAL and another EPA Method 1631 – compliant laboratory.

	QA Solution Most Probable Value Estimates						Individual Lab Performance				
Solution	**N**	**L95%CI**	**Median**	**Mean**	**U95%CI**	**Med-Mean%**	**HAL Mean**	**HAL Bias**	**HAL CV**	**NSA Bias**	**NSA CV**
MP1	134	6.36	6.40	6.47	6.59	-1.1%	6.10	-5.72%	9.2%	+2.8%	7.3%
MP2	122	9.06	9.10	9.19	9.32	-1.0%	8.94	-2.70%	7.2%	+3.5%	7.9%
MP3	113	15.1	15.4	15.4	15.8	0.0%	14.2	-7.80%	12.3%	+5.2%	9.5%
MP4	122	21.4	21.4	21.7	22.0	-1.4%	20.7	-4.61%	4.7%	+4.1%	6.4%

Discussion

Multiple working hypotheses were developed that might explain the observed differences in collector performance for sampling of precipitation and mercury. Below we review information gathered in this study and others that either supports or refutes each working hypothesis.

1. Differences between precipitation sensors were responsible for the -5% bias of the ACM as compared to the NCON and MICB collectors which were not significantly different in precipitation catch from the NWS gage.

The significantly lower number of lid openings and significantly lower time open for the ACM compared to the NCON and MICB are consistent with this hypothesis.

2. Rain splash from the large surface area pan, lid, or lid screen of the MICB collector augmented the precipitation collected by the MICB.

If rain splash was augmenting the collector catch of the MICB we might expect the following conditions to be true [result is provided in brackets]:

- Mean MICB %CE > 100% [not significantly different (nsd) from 100% by t-test]
- Mean MICB %CE significantly greater than both NCON and ACM [nsd from NCON]
- Mean MICB %CE positively correlated with average rainfall intensity (mm/hr) [ns]
- Mean MICB %CE > ACM and NCON for the top-5 rainfall intensity events [nsd]
- Mean MICB %CE positively correlated with maximum event rain intensity (mm/hr) [ns]

Landis and Keeler (1997) reported that the MICB collector under collected (98%) a co-located MICB sample train that was manually exposed on event basis on a simple ring stand which had no opportunity for sample splash.

3. Differing heater efficiencies lead to different collection efficiencies for snow and mixed precipitation events among the 3 collectors.

The ACM and MICB both had 1500 W heaters while the NCON had only 700 W of combined plate and fan-type heating capacity. The sample funnel is farthest from the heated area in the ACM and closest in the MICB. The NCON had the lowest %CE for snow but is similar to the ACM for mixed precipitation. The MICB had the highest %CE for both snow and mixed precipitation. There were multiple observations of unmelted precipitation in the NCON (6) and ACM (3) at the time of collection (Figure 3).

4. Differences in funnel geometry are responsible for different precipitation collection efficiencies among the 3 collectors.

The MICB funnel was the widest and had deep (18.5 cm), straight sides making it most similar to the geometry of the NWS 8-inch gage. A deep, cylindrical catch basin would be expected to be more efficient at preventing wind-entrainment of deposited snow and bounce out of high kinetic energy rain drops. If wind-entrainment were a significant problem, we might expect to see an inverse relationship between average or peak wind speeds and the %CE of the NCON and ACM The mean %CE for snow events was markedly lower for the NCON (48%) and the ACM (55%) than for the MICB (80%). If bounce-out of high-energy rain droplets were a problem for the shallow funnels, we might expect the %CE of the NCON and ACM to be negatively correlated to average or instantaneous rainfall intensity (mm/h) [contrary result, see below]. The mean %CE of the 5 most intense rain events was not significantly different (paired t-tests) between the NCON (99%), ACM (98%), and MICB (96%) collectors. The NCON had the lowest %CE for snow but was similar to the ACM for mixed precipitation. The MICB had the highest %CE for all precipitation types. Thus it seems likely that funnel geometry may influence collection efficiency for snow. The effect is less clear for rain (see #8 below).

5. Laboratory differences were responsible for a portion of the difference in mercury concentrations among samplers.

Processing of field samples for this study was conducted similarly by UMAQL and Frontier Geosciences following EPA Method 1631. Both laboratories demonstrated compliance with the Method 1631 performance criteria. Unfortunately, there were no direct comparisons between the laboratories during the time period of this study. Sample exchanges between Frontier Geosciences and the University of Michigan Air Quality Laboratory (UMAQL) in 1999 demonstrated that laboratory differences in analyses of pre-digested samples should not exceed 5% (Keeler, personal communication). The duplicate sample-trains analyzed at the two different laboratories were consistent with this earlier study, yielding an average difference between the laboratories of 6.2% (median 5.3%). The internal NIST recovery data for the HAL and the USGS multi-laboratory comparison indicate the HAL is biased low on average by 4.8% and 5.2%, respectively. The apparent 6.2% spread between the laboratories is less than the spread observed between the HAL and NSA (9.1%) in the USGS 6-lab comparison data. In a recent (2006) exchange of pre-digested samples between the UMAQL and the Dartmouth College Trace Element Research Facility agreement averaged 5.4% (slope of linear regression = 1.054, intercept=ns, r^2= 0.97, $p<0.0001$, Dartmouth biased high). The available information suggests that laboratory results from the HAL are generally 5% below NIST values while UMAQL results may be ~1.2% above NIST values. Therefore, it is reasonable to attribute 6.2% of the 22% difference between the MICB and ACM collector and 6.2% of the 13% difference between the MICB and NCON collector in this study to laboratory bias that is permitted to exist within the EPA Method 1631 performance criteria.

6. Rain splash from the large surface area pan, lid, or lid screen of the MICB collector contaminated the MICB samples leading to the observed greater Hg amount collected by the MICB relative the NCON and ACM samplers.

In the discussion of hypothesis 2 (above) we have explained why it is unlikely that rain splash makes a significant contribution to the MICB samples. Even if rain splash does not add significant volume to the sample, dry-deposited mercury on collector surfaces could still be picked up and added to the sample by minor rain splash. If this were the case, we would expect to observe the following:

- The difference in Hg collection between the MICB and NCON should increase with increasing rainfall amount [ns]
- The difference in Hg collection between the MICB and NCON should increase with increasing average rainfall intensity [ns]
- The difference in Hg collection between the MICB and NCON should increase with increasing peak rainfall intensity [ns]

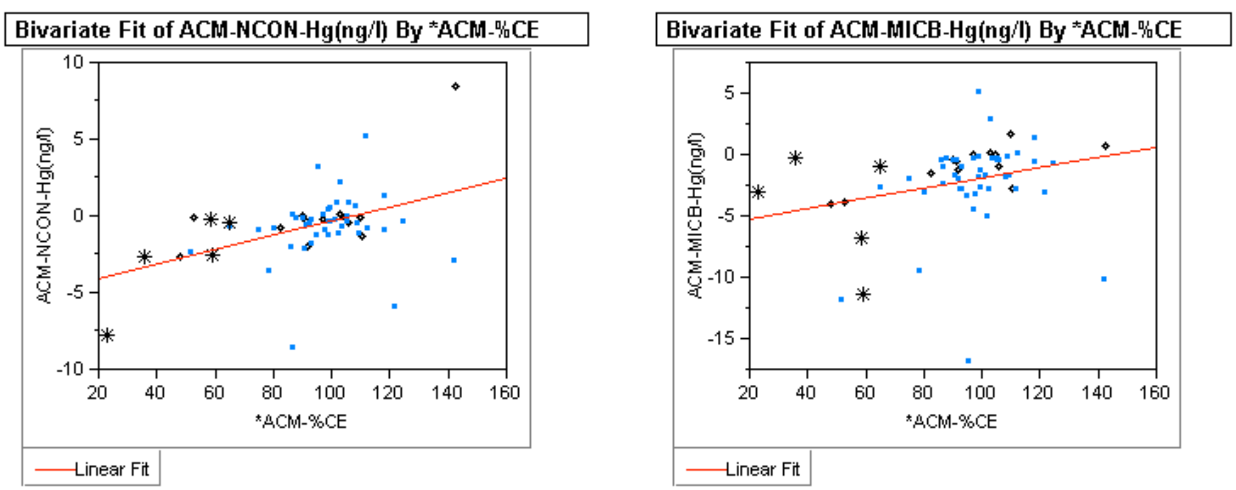
- The difference in Hg collection between the MICB and NCON should be larger for the top-5 rainfall intensity events than for the bottom-5 intensity rainfall events [ns]

Landis and Keeler (1997) reported no statistically significant difference between the concentration of mercury collected using the UM-MICB automated system and a manual system consisting of the same sample train, deployed on an event basis with no possibility of splash contamination (15.8 ng/l and 15.9 ng/l, respectively).

7. The lower precipitation collection efficiency of the ACM sampler relative to the NCON and MICB samplers resulted in lower mercury concentrations being measured in samples from the ACM.

There was a weak but significant positive correlation between the ACM vs. NCON Hg bias and the ACM %CE (r^2=0.19, p=0.0003, Figure 5a). The Hg bias between the ACM and NCON for all samples with ACM % CE < 100% (mean -1.1 ng/l) was significantly less than the bias (+0.16 ng/l) for all samples with ACM %CE >= 100%.

There was also a weak but significant positive correlation between the ACM vs. MICB Hg bias and the ACM %CE (r^2=0.07 p=0.0364, Figure 5 b). The Hg bias between the ACM and MICB for all samples with ACM % CE < 100% (mean -2.73 ng/l) was significantly less than the bias (-1.10 ng/l) for all samples with ACM %CE >= 100%.



a) b)

Figure 5. a) The difference in Hg concentration between the ACM and NCON samples was positively correlated with ACM % collection efficiency for precipitation. **b)** The difference in Hg concentration between the ACM and MICB samples was positively correlated with ACM % collection efficiency for precipitation. Stars = snow, diamonds = mixed precipitation, blue squares = rain.

8. Differences in collection efficiency of the NCON sampler relative to the MICB sampler resulted in lower mercury concentrations being measured in samples from the NCON.

Despite the lack of a significant difference between either the NCON or the MICB and the NWS1 gage for the collection of precipitation when analyzed over all 65 samples, there was a significant difference between the %CE of the NCON and MICB collectors for the 62 samples with valid Hg concentrations. The mean %CE for the NCON (95.5 %) was significantly different (1-sided, paired t-test, p=0.0024) from the %CE for the MICB (102.3%) including samples of all precipitation types. Mercury concentrations measured in samples of all precipitation types from the NCON were significantly less (t-test, p = 0.05) than in samples from the MICB when the %CE of the NCON was <100% (mean -2.45 ng/l) than when NCON %CE was >= 100% (-0.55 ng/l). There was no significant difference (t-test, p=0.88) in mercury bias between the two collectors as a function of the MICB %CE with a mean bias of -1.48 ng/l for samples of all precipitation types.

The mean %CE for the NCON (100.4 %) was also significantly different (1-sided, paired t-test, p=0.0024) from the %CE for the MICB (104.9%) for rain-only samples. Mercury concentrations measured in samples of rain-only events from the NCON were significantly less (t-test, p = 0.03) than in samples from the MICB when the %CE of the NCON was <100% (mean -2.99 ng/l) than when NCON %CE was >= 100% (-0.38 ng/l) (Figure 6a). There was no significant difference (t-test, p=0.74) in mercury bias between the two collectors as a function of the MICB %CE with a mean bias of -1.60 ng/l for samples of rain-only events (Figure 6b).

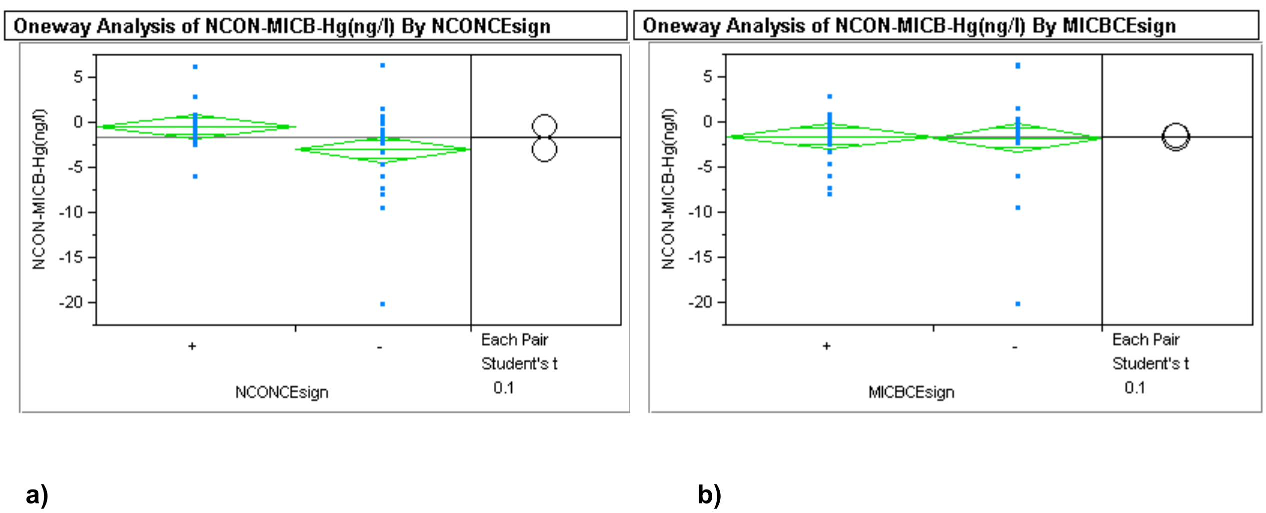


Figure 6. a) The difference in Hg concentration measured in samples from the NCON and MICB collectors was significantly different (t-test, p = 0.03) for events where the NCON over (+) or under (-) sampled precipitation relative to the NWS1 gage. The mean difference (NCON-MICB) was -0.38 ng/l for events where the NCON over sampled NWS1 and -2.99 ng/l for events where the NCON under sampled the NWS1 gage. **b)** The difference in Hg concentration measured in samples from the NCON and MICB was not significantly different (t-test, p = 0.88) as function of MICB over (+) or under (-) collection relative to the NWS1 precipitation gage.

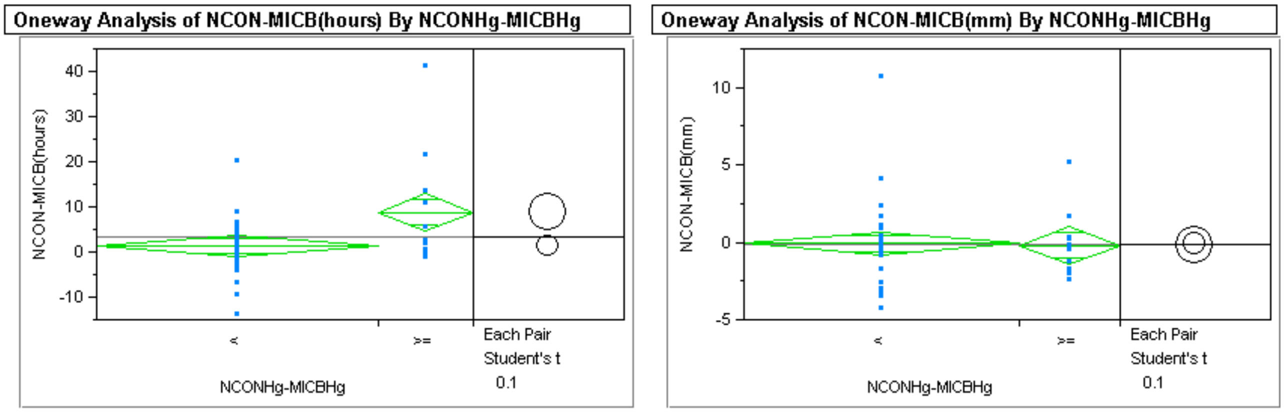
These relationships suggest that the observed differences in mercury concentration between the MICB and NCON collectors could, in part, be the result of the collection of slightly less precipitation by the NCON sampler than by the MICB sampler during rain, snow, and mixed precipitation. This small difference in collection is not enough to be significantly different from the

NWS1 gage collection, but is large enough to produce a significant and meaningful bias in the mercury concentrations measured in samples from the two collectors. However, it is difficult to square this interpretation of the results with lid opening data. The NCON and MICB lid openings were not significantly different and the NCON was consistently open for many more hours than the MICB, thus apparently offering more opportunity to collect precipitation and mercury than the MICB. The NCON was open on average 1.5 hours more than the MICB when measured mercury concentrations were less in the NCON samples than MICB samples. The NCON was open 9 hours longer than MICB on average when concentrations measured in the NCON samples were higher than the MICB. This difference in duration of opening was significant (t-test, $p = 0.010$, Figure 7a). There was no significant difference in the amount of precipitation collected as a function of mercury concentration bias (Figure 7b) or as a function of difference in time open (linear regression, $p = 0.827$). This may suggest that the additional time of lid opening for the NCON (average +9 hours) allowed dry deposition of Hg to be collected on the funnel that was subsequently incorporated into the sample with continuing rainfall resulting in higher concentrations compared to the MICB for these conditions. Dry deposition appears to be greater than potential volatile losses (see below).

Conversely, the additional amount of time the NCON was open compared to the MICB (average 1.5 hours, Figure 7a) when mercury concentrations measured in samples from the NCON were lower than those measured in samples from the MICB may have lead to a portion of the collected precipitation and mercury volatilizing and escaping from the NCON collector. It is possible that the thistle tube vapor restrictor is less effective than a water trap for preventing evaporation and volatile Hg loss. For the rain events where the measured Hg concentration in samples from the NCON were lower than those from the MICB there was a weak (r^2=0.13) but significant (p=0.037) positive correlation with the amount of precipitation measured by the NWS1 gage (Figure 8a). This relationship supports the idea of evaporative/volatile loss as an explanation for the lower %CE (Figure 8b) and lower Hg concentrations (Figure 8a) measured in these events relative to the MICB. Smaller volume samples would be more susceptible to evaporative/volatile loss than larger volume samples. It is hard to explain how more hours open would lead to a lower opportunity to catch precipitation. There was no significant correlation (p=0.44) between the MICB %CE for precipitation and NWS1 precipitation amount for the same events.

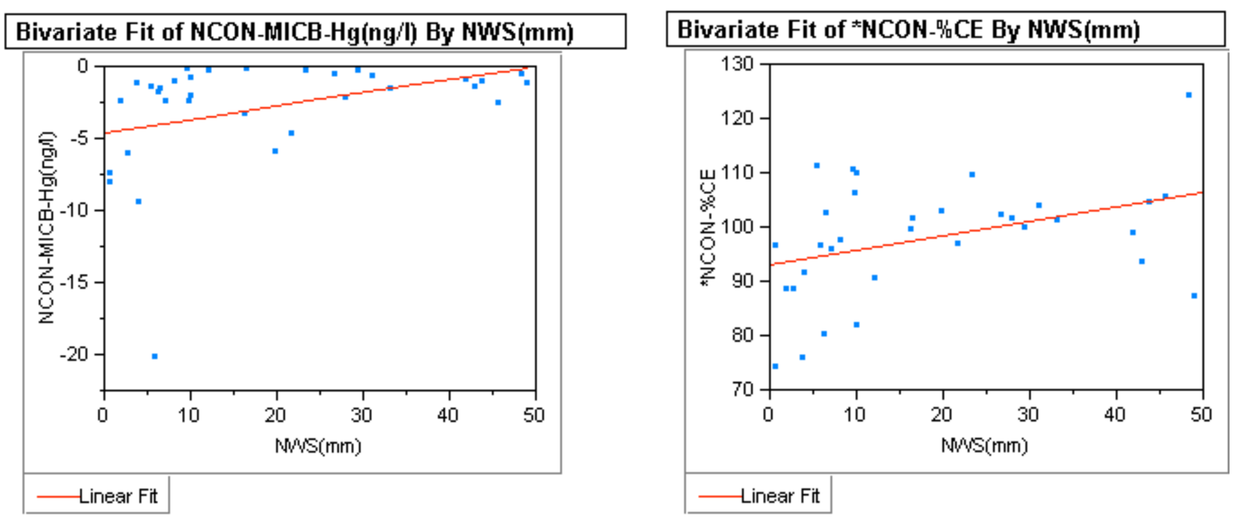
Another possible explanation for both lower %CE and lower Hg concentrations in the NCON collector for smaller precipitation events might be aerodynamic differences between the smaller funnel and chimney of the NCON, relative to the larger funnel and pan of the MICB. In windy conditions it might be possible for small droplets to escape capture by the smaller funnel, while the larger MICB pan and funnel create more drag, stalling airflow enough to allow small droplets to sediment into the collector.

The paired sample-train comparison data suggest the possibility of a sample train bias (MDN 5-6% lower than UMICH). The sample train bias was only evaluated for rain samples. The sum of bias indicated for laboratory and sample-train effects approaches the total bias observed in the 1-year collector comparison. However, sample-train bias could be higher for mixed precipitation and snow (see above). The collector opening performance differences effects on collection efficiency could reasonably account for the remaining bias.



a) **b)**

Figure 7. a) The difference in time open for the NCON and MICB collectors was significantly greater (t-test, p=0.010, + 9 hours) for events where the Hg concentrations measured in samples from the NCON were greater (>=) than the Hg concentration in samples from the MICB compared to events where Hg concentrations from the NCON were less (<) than from the MICB (+ 1.5 hours). Rain-only events are shown in this figure, but a similar significant difference (t-test, p=0.027) was observed for all precipitation types. **b)** The significant difference in time open was not accompanied by a significant difference in precipitation captured by the NCON relative the MICB as a function of mercury concentration bias.



a) **b)**

Figure 8. a) Linear correlation (r^2=0.13, p=0.037) between mercury concentration bias (NCON-MICB) and the amount of precipitation (equivalent to sample volume). The bias was more negative (lower concentrations from the NCON sampler) for lower volume events. This might be suggestive of evaporative/volatile loss. **b)** Linear correlation (r^2=0.16, p=0.022) between NCON percent precipitation collection efficiency and rainfall amount (equivalent to sample volume).

Mechanical failures of the collectors and sample trains

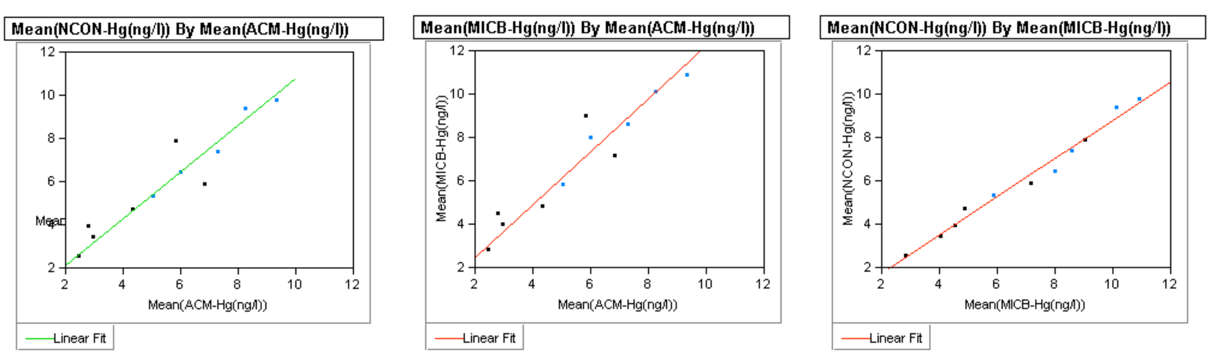
Each of the collectors had performance problems that compromised samples. The combination of large funnel diameter with a small sample bottle resulted in overflows for the MICB collector during 3 events. Overflow is a serious performance issue because large amounts of the annual deposition are included in large storm events. The MICB failed to sample 11.6% of the total precipitation for the year due to overflows. While mechanical failure of the MICB resulted in the loss of samples for 4.4% of the precipitation during the study period, this was an anomalous situation. The same MICB collector has been deployed at Underhill since 1993 with no prior mechanical failure. The ACM failed to sample 9.1% of the total precipitation for the year due to various mechanical failures. The NCON failed to sample 6.5% of the total precipitation due to mechanical failures. Additional samples from the ACM (17.9% of precipitation) and NCON (17.5% of precipitation) were compromised by sample bottle leaks during shipping and the failure to completely melt snow.

Transfer functions

Transfer functions were developed so that data acquired using each of the three collector types can be directly compared with each of the others. The correlations between collectors on an event basis are too low (only 80 to 86% of variance explained) to produce transfer functions with acceptable error rates (< 10%). However, the correlations between the monthly precipitation-weighted means of the different collectors are suitable for normalizing the data obtained with one collector to the reference frame of another. The NCON-MICB transfer function is very strong (98% of variance explained). The NCON-ACM and MICB-ACM transfer functions are satisfactory (90% of variance explained).

Using monthly precipitation-weighted means where the precipitation amount is on an NWS 8-inch gage basis for all collectors, the transfer functions are as follows:

1. NCON-basis = 1.0789 * ACM %variance explained = 90% (Figure 9a)
2. NCON-basis = 0.8813 * MICB %variance explained = 98%
3. MICB-basis = 1.2232 * ACM %variance explained = 90% (Figure 9b)
4. MICB-basis = 1.1320 * NCON %variance explained = 98% (Figure 9c)



a) b) c)

Figure 9. Transfer functions for NWS precipitation-weighted mean monthly mercury concentration.

Additional transfer functions were developed to correct each of the collector types to the best collective estimate of mercury concentration. Following the discussion above, MICB concentrations are reduced 1.2% and MDN (NCON or ACM) concentrations increased 5% to bring them a common NIST-referenced basis that is consistent with the mean performance of 6 laboratories. Thus, accounting for the sampling deficiencies discussed above:

1. Best Estimate = 0.988 * MICB
2. Best Estimate = 1.209 * ACM
3. Best Estimate = 1.116 * NCON

Accounting for the 95% NIST-recovery normalization for the MDN samplers the effective difference between collector systems is 16% between the MICB and ACM sampler and 6.6% between the MICB and NCON sampler. As noted above, the difference between the NCON and ACM sampler is 7.9%. These differences in relative collector performance approximate the expected performance of duplicate ACM samplers (Wetherbee et al. 2008) of 8.6% to 13%. However, the precipitation regimes sampled by Wetherbee et al. (2008) may not be representative of the precipitation regime at VT99. In the discussion above we have demonstrated how differences in collector performance of this magnitude can be explained and accounted for, suggesting corrections that may be applied to account for systematic differences in estimates of precipitation and mercury by different sampling systems.

Summary

Lab-to-lab bias of 6.2% plus performance differences of sample-trains (6%), and collectors (sensors/heaters) explain differences in mercury collection of the NCON sampler with respect to the MICB sampler in rain and mixed precipitation events dominated by rain. Based on the observations in this study, it seems possible that evaporative/volatile losses from the NCON sample train and/or aerodynamic differences in the capture of small droplets between the two types of collectors may account for a portion of the observed difference in precipitation collection efficiencies and Hg concentration bias.

An additional -8% difference (total -23%) in mercury collection observed for the NCON with respect to the MICB during snowfall events is likely due to the demonstrated under sampling of snow by the version of the NCON sampler evaluated here. Under sampling of snow by the NCON is most likely due to a combination of funnel geometry and inadequate heating capacity. Heating capacity has been improved in current models.

Differences in the response of the rain sensors is most likely responsible for the under sampling of precipitation by the ACM relative to the NWS gage and the two other collectors. The under sampling of mercury by the ACM compared to both the NCON and MICB samplers appears to be related to failure to capture complete precipitation samples (fewer hours open, fewer lid openings, lower CE). The laboratory and sample-train differences noted above contribute to the difference between the ACM and the MICB collector as well. A modern rainfall sensor, a deep straight-sided funnel, additional heating of the sample funnel, and an improved motor-drive would significantly improve the performance of the ACM sampler.

Because of its larger funnel area and smaller sample bottle the original UM-MICB is prone to overflow potentially causing the loss of valid mercury data for a meaningful portion (~10%) of annual precipitation. The 2nd-generation UM-MICB sampler with multiple collection bottles addresses this problem.

Precipitation collector designs undergo constant modification and new designs for all three collectors emerged during this study. It is possible that the next generation ACM sampler may overcome some of the problems experienced in this study due to more durable screw-type motor drive and improved conductivity/wetness sensing grid. Current versions of the UM-MICB include the option to split event samples into multiple bottles under computer control or to sample multiple events without operator intervention. We propose modifications to the NCON sampler (larger, deeper, and straight-sided funnel, water trap, and a heated chimney) that may combine the advantages of the original UM-MICB and the NCON sampler designs to produce a low-cost and effective sampler for mercury suitable for wide deployment in North America.

Additional studies could be conducted to clearly identify the factors contributing to the 15% difference in mercury deposition measured by previous and current generation collectors. These investigations might include modifications to each of the collectors (heater, water-trap, straight-sided funnels), and triggering all collectors with a common precipitation sensor, wind-tunnel evaluations, and modeling. Additional raw and prepared sample exchanges between laboratories would be helpful. Because mechanical and power failures caused the amount of precipitation collected as snow or mixed precipitation to be severely underrepresented in this study, additional cold-season sampling should be conducted to better quantify collector limitations and performance differences.

Mercury concentrations estimated using the MICB and NCON collectors are extremely well correlated on a monthly precipitation-weighted mean basis with a consistent ~ 12-13% difference. Modelers and other users of MDN data should know that existing measurements based on the ACM are at least 8% low relative to an NCON collector and potentially as much as 18% low relative to an MICB collector on a monthly precipitation-weighted mean basis. The observed 6.2% difference between the two laboratories is within the range of commonly accepted agreement for trace-level analysis with EPA Method 1631 and within the demonstrated stable spread between the HAL and another laboratory. Thus, data from the two laboratories can be corrected to common NIST-referenced basis. Modelers should consider correcting data from multiple laboratories to a common NIST-referenced basis prior to combined analysis (e.g. atmospheric deposition and lake-water concentrations used in an ecosystem model). Atmospheric modelers should account for both the laboratory and sampler systematic biases prior to comparison of simulation results with wet-deposition observations. Unless these corrections are undertaken, data users should assign significant uncertainty envelopes (up to 54% allowed by EPA Method 1631, plus the additional uncertainty associated with differential collector performance) to the observational data used to drive or evaluate models. End-users of MDN data should also realize that apparent differences in mercury concentrations between locations and over time might be explained, in part, by differences in the amount of snow, rain, and mixed precipitation due to the strong bias of the ACM collector for frozen precipitation. Site operators should be required to provide information on precipitation type for each sample, and this information should be included in the web distribution of MDN data.

Acknowledgements

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References

Landis, M.S. and G. J. Keeler (1997) Critical Evaluation of a Modified Automatic Wet-Only Precipitation Collector for Mercury and Trace Element Determinations. *Environmental Science and Technology* 31:2610-2615.

Miller, E.K., VanArsdale, A., Keeler, G.J., Chalmers, A., Poissant, L., Kamman, N., and Brulotte, R. (2005) Estimation and Mapping of Wet and Dry Mercury Deposition across Northeastern North America. *Ecotoxicology* 14, 53-70.”

Wetherbee, G.A., Latysh, N.E., and Greene, S.M. (2006) External quality-assurance results for the National Atmospheric Deposition Program/National Trends Network and Mercury Deposition Network, 2004, U.S. Geological Survey Scientific Investigations Report 2006-5067, 52 p.

Wetherbee, G.A., Gay, D.A., Brunette, R.C., and Sweet, C.W. (2008) Estimated Variability of National Atmospheric Deposition Program/Mercury Deposition Network Measurements Using Collocated Samplers. *Environ. Monit. Assess*. DOI 10.1007s10661-006-9456-6.