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

Final Project Report – Event-Based Wet Deposition – 1/16/2009

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Event-based precipitation mercury concentration and deposition at Underhill, VT

Event-based wet deposition sampling at Underhill, VT was continued for the project duration and continues uninterrupted, maintaining the longest, continuous record of event-based atmospheric mercury deposition *in the world.* These measurements are currently being supported by a grant from NOAA through the Lake Champlain Research Consortium and now follow the NADP-MDN network protocol using event-based sampling. The Underhill site (VT99) is currently a full member of MDN.

A principal goal of the project was to continue event collection and analysis of mercury in wet deposition following the UMAQL protocols that had been in place since the initiation of sampling at Underhill in 1992 (Burke et al. 1995) and were used by EPA elsewhere in New England (Alter 2000). At the outset of the project the University of Michigan expressed reluctance to continue precipitation analysis at the available funding level. Thus, we agreed as a group to analyze archived samples at UMAQL while new samples were to be directed to the Dartmouth College Trace Element Analysis Facility. We conducted an inter-laboratory comparison study using blind analysis of split precipitation samples (described below). After establishing the capability of the local (Dartmouth) laboratory to perform precipitation analyses, the University of Michigan agreed to continue serving as the precipitation analysis laboratory, so the services of the Dartmouth Lab were not required for the duration of the project. This was a better result, as we were able to maintain a consistent laboratory and protocol as well as maintain the interest and involvement of Dr. Keeler in the project.

Mid-way through the project it was made clear to the investigators that future funding of mercury wet deposition at Underhill through NOAA channels (EPA could not commit to long-term funding) would only be possible through the NADP MDN network. The investigators (with input from the broader mercury research community) agreed to begin NOAA-funded mercury wet-deposition measurements following the NADP, MDN protocols. MDN accepted VT99 (an already established NTN and AIRMoN site) into the network as a weekly sample site in 2004. VT99 transitioned to an MDN event-basis site beginning in 2005. The investigators requested and received additional support from MDN, NOAA, USGS and this project to conduct a comparison of the relative performance of the University of Michigan modified MICB, NCON and ACM samplers.

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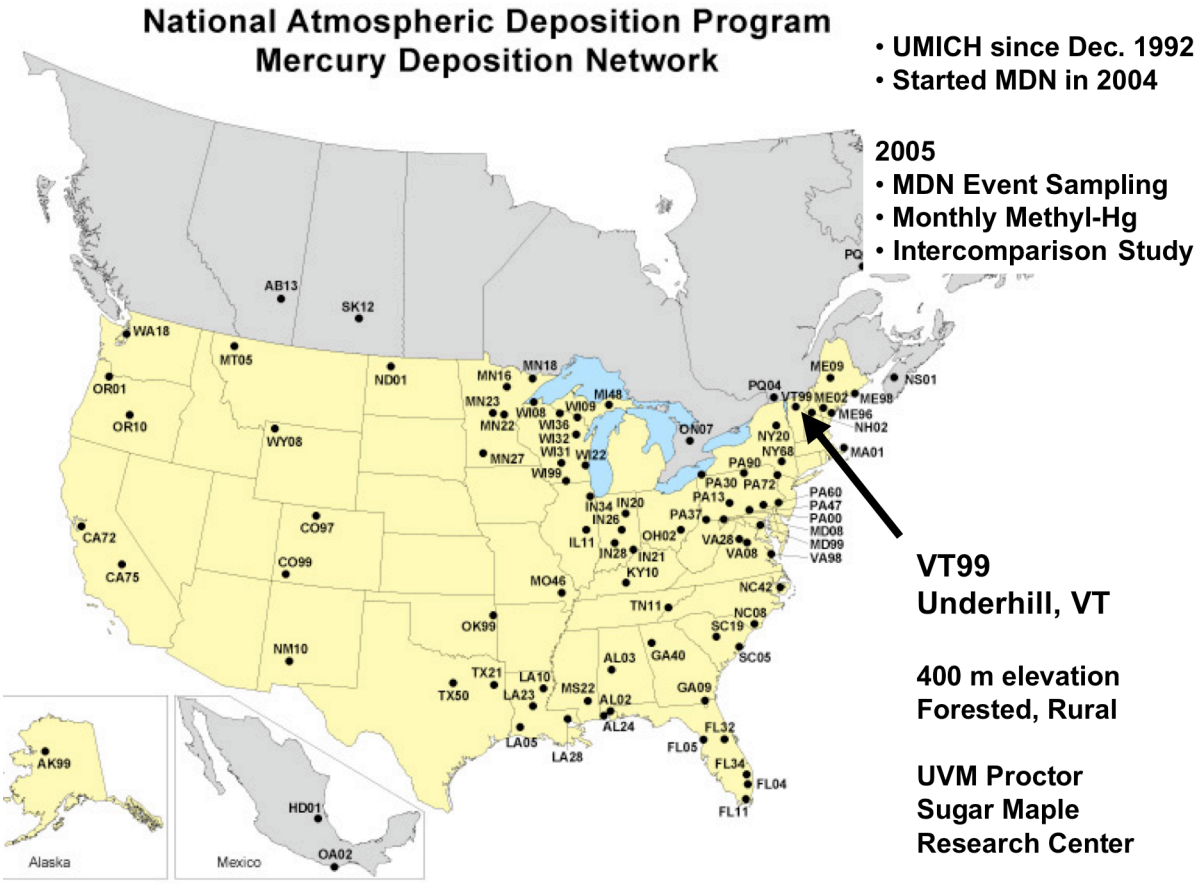
The collector-comparison project facilitated the successful transition from wet-deposition measurements using the University of Michigan modified-MICB collector and the University of Michigan Air Quality Laboratory to wet-deposition measurements using the NCON collector and the Frontier Geosciences Mercury Analytical Facility as part of the national NADP Mercury Deposition Network (MDN). There were considerable challenges to overcome in transitioning between collectors, protocols, laboratories, and networks. As part of this project and in conjunction with NOAA, USGS and MDN we conducted a 3-way wet-deposition collector comparison. This trial characterized the relative performance of the MICB, NCON and ACM collectors for mercury wet-deposition. We identified strengths and weaknesses of each collector and protocol which lead to changes in collector design and network practices. The results of this study have been used to improve the performance and reliability of the MDN-sanctioned systems. We developed transfer functions that can be used to combine wet-deposition records developed using the three different collectors. A supplemental study in we conducted in 2007 suggested the persistent bias between the MICB collector and University of Michigan Protocol and the MDN collectors and MDN protocol is due in large part to differential sample train performance and an approximately 6% laboratory bias.



MICB – MDN (NCON, ACM) Collector Comparison

In partnership with MDN, the USGS, and NOAA, we initiated (August 2005) a 1-year precipitation mercury collector inter-comparison study. 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. 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. A manuscript for peer-review was produced (included below) but submission has been held up pending receipt of data from University of Michigan from paired deployment of the MDN and University of Michigan sample trains in the MICB collector. The MICB can hold up to 4 sample trains. We exposed multiple pairs of each type of sample train and sent one of each to each laboratory for processing and analysis. This experiment was designed to identify and eliminate and 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.

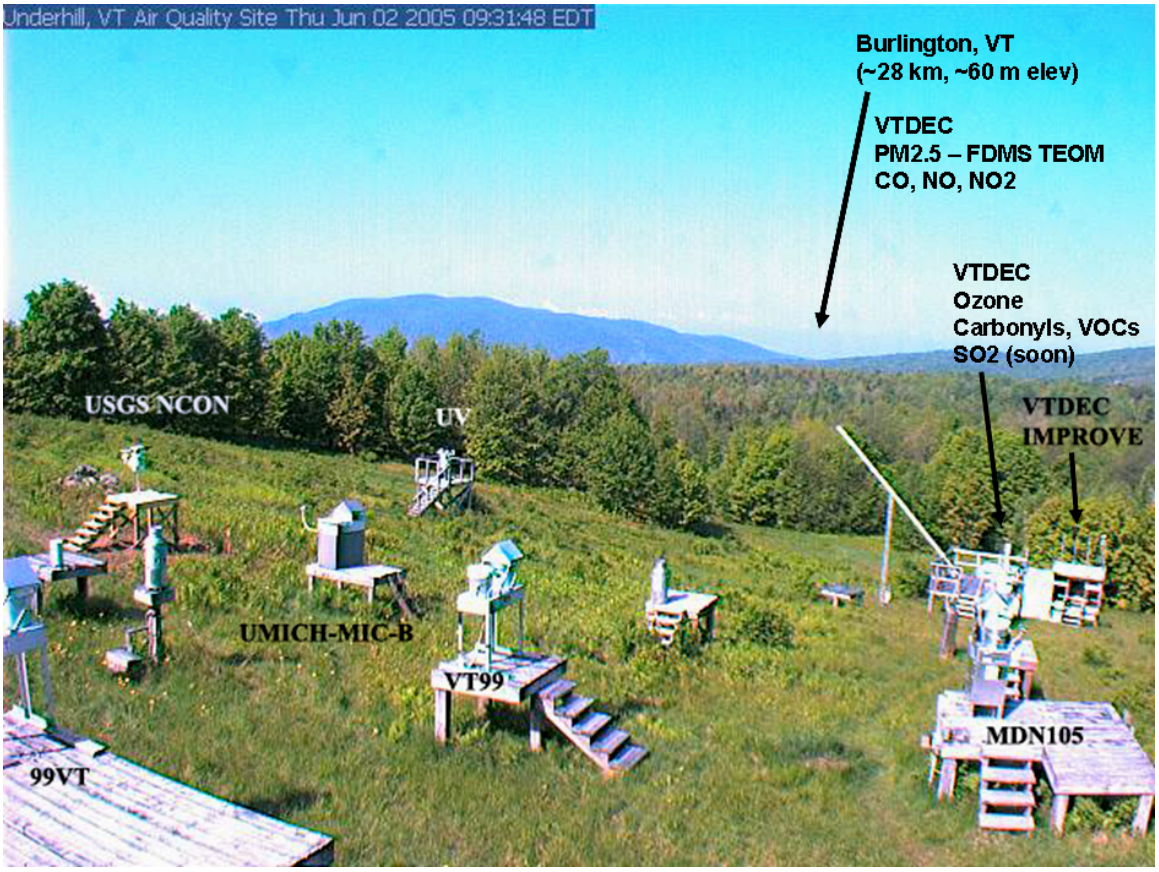


Figure 1. Location of mercury collectors for intercomparison study (left-to-right: USGS NCON, UMICH-MIC-B, MDN-ACM [MDN105]) at the Underhill, VT Air Quality Site. The locations of other air quality instrumentation are also noted.

PLEASE SEE THE SEPARATE DOCUMENT "FR-sec2b-Collector-Comparison-2009-01-16.pdf" FOR THE FULL REPORT ON THE COLLECTOR COMPARISON STUDY.

Dartmouth / University of Michigan Air Quality Laboratory Comparison

Ten precipitation samples spanning the range of generally observed concentrations at Underhill were split for analysis by both labs. There was good agreement between the two labs (Table and Figure 2, $r^2 = 0.97$, $p < 0.0001$). Individual samples showed a mean difference between the two labs of 0.42%, with a range of -10% to +17% [(Dartmouth – UMAQL) / (UMAQL) * 100]. There was no significant correlation of bias with concentration. There was no significant difference between the two labs as determined by a paired T-test. Dartmouth results were non-significantly higher (mean apparent bias +0.18 ng/L) while the median apparent bias was (0.08 ng/L). The maximum exhibited a deviation was 1.22 ng/L (Dartmouth higher) . Dartmouth was never lower than Michigan by more than 0.33 ng/L.

Table. UMAQL / DARTMOUTH Laboratory Comparison for Mercury in Precipitation

		DARTMOUTH				UNIVERSITY OF MICHIGAN				
Samp#	**Reps**	**Mean**	**Min**	**Max**	**SE**	**Mean**	**Min**	**Max**	**SE**	**%Diff**
335	3	6.73	6.55	6.89	0.0987	6.17	6.14	6.2	0.03	6.16
339	3	4.04	3.98	4.09	0.0318	4.35	4.29	4.41	0.06	-8.51
341	3	3.48	3.41	3.51	0.0333	3.775	3.73	3.82	0.045	-9.67
345	3	3.71	3.59	3.82	0.0664	3.62	3.61	3.63	0.01	-0.83
346	3	9.62	9.51	9.73	0.0636	9.215	9.14	9.29	0.075	3.20
348	3	4.88	4.85	4.93	0.0267	4.59	4.58	4.6	0.01	5.66
359	3	12.17	12.04	12.27	0.0681	12.105	12.08	12.13	0.025	-0.54
362	3	7.86	7.73	7.99	0.0751	6.58	6.51	6.65	0.07	17.48
363	3	3.87	3.82	3.93	0.0318	3.85	3.81	3.89	0.04	-0.78
364	3	4.18	4.15	4.21	0.0173	4.51	4.5	4.52	0.01	-7.98

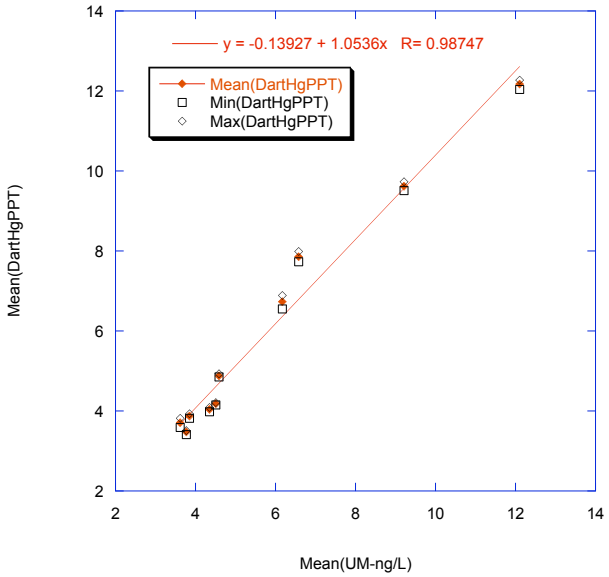


Figure 2. Correspondence between Dartmouth (Dart) and University of Michigan (UM) analyses of mercury in split precipitation samples.

Long-Term Record of Mercury Wet Deposition

The initial year of funding for this project allowed the University of Michigan to complete analysis of archived samples, extending the precipitation record through 2003. Keeler et al. (2005) analyzed the resulting ten-year record and determined that there had been no trend in average-annual mercury concentration (Fig. 3) or deposition (Fig. 4) over the period. The annual volume-wtd mean mercury concentration ranged from 7.8 – 10.5 ng/L during 1993 to 2003. Average annual deposition was 9.7 ug/m^2/y during 1993 to 2003. NOAA HYSPLIT model back trajectories of the highest-deposition events were predominantly from the southwest and south (Fig. 5).

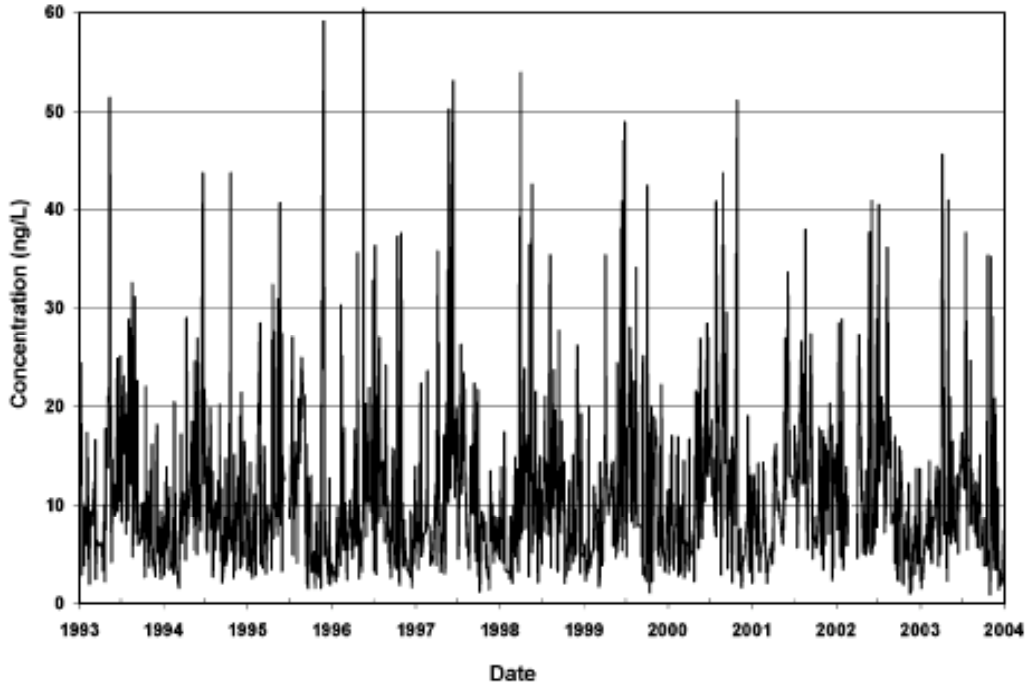


Figure 3. Mercury event precipitation concentrations 1993 thru 2003 from Keeler et al. 2005 – *Ecotoxicology*, **14**:71-83.

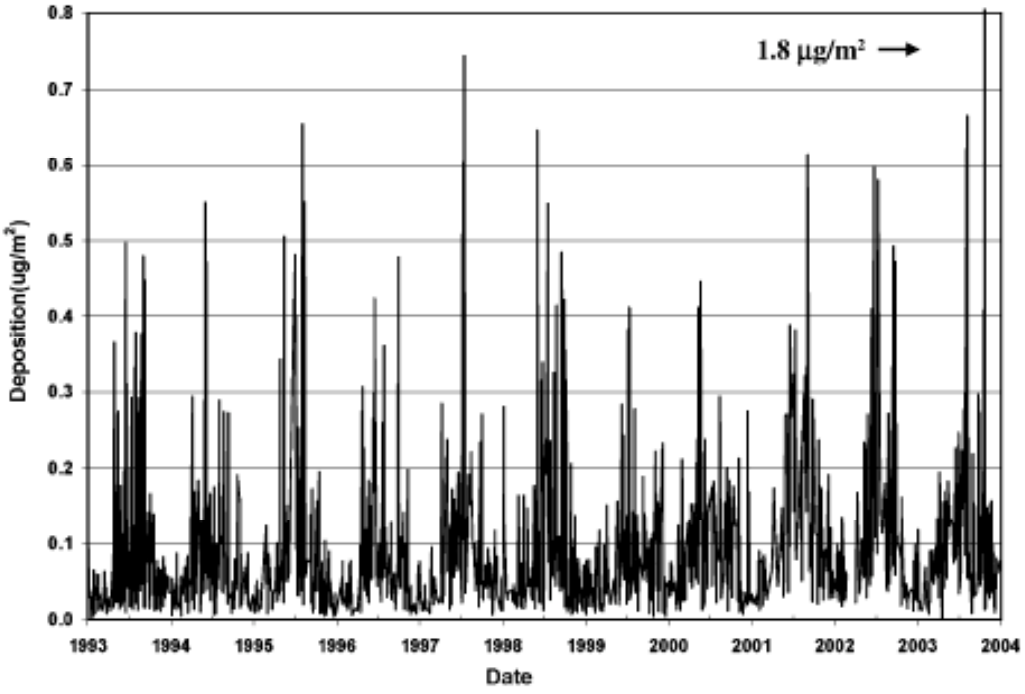


Figure 4. Mercury event wet-deposition 1993 thru 2003 from Keeler et al. 2005 – *Ecotoxicology*, **14**:71-83.

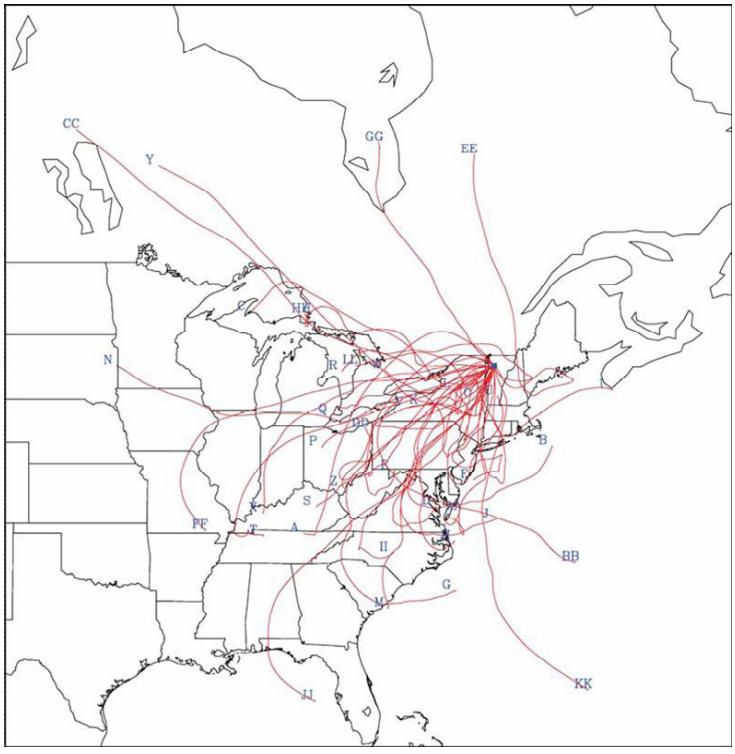


Figure 5. NOAA HYSPLIT Model 72-hour back-trajectories for high mercury deposition events from 1993-2003 from Keeler et al. 2005 – *Ecotoxicology*, **14**:71-83

An additional 3 years (2004, 2005, and 2006) of event data were collected with the MICB as part of this project. Years 2005 and 2006 provided overlap with the start up of the MDN sampler. The event record continued in 2007 using the MDN sampler, while operation of the MICB was discontinued at the end of the sample train comparison study.

The transfer functions described in section 2b were used to correct the low-biased MDN results to an "MICB-basis" for analysis and plotting in order to extend the long-term event record. There was good agreement of the annual volume-weighted mean Hg concentration between the MICB and corrected MDN records in both 2005 and 2006 (Figure 6). There was also good agreement between the annual wet mercury depositions determined using the MICB and corrected MDN values (Figure 7).

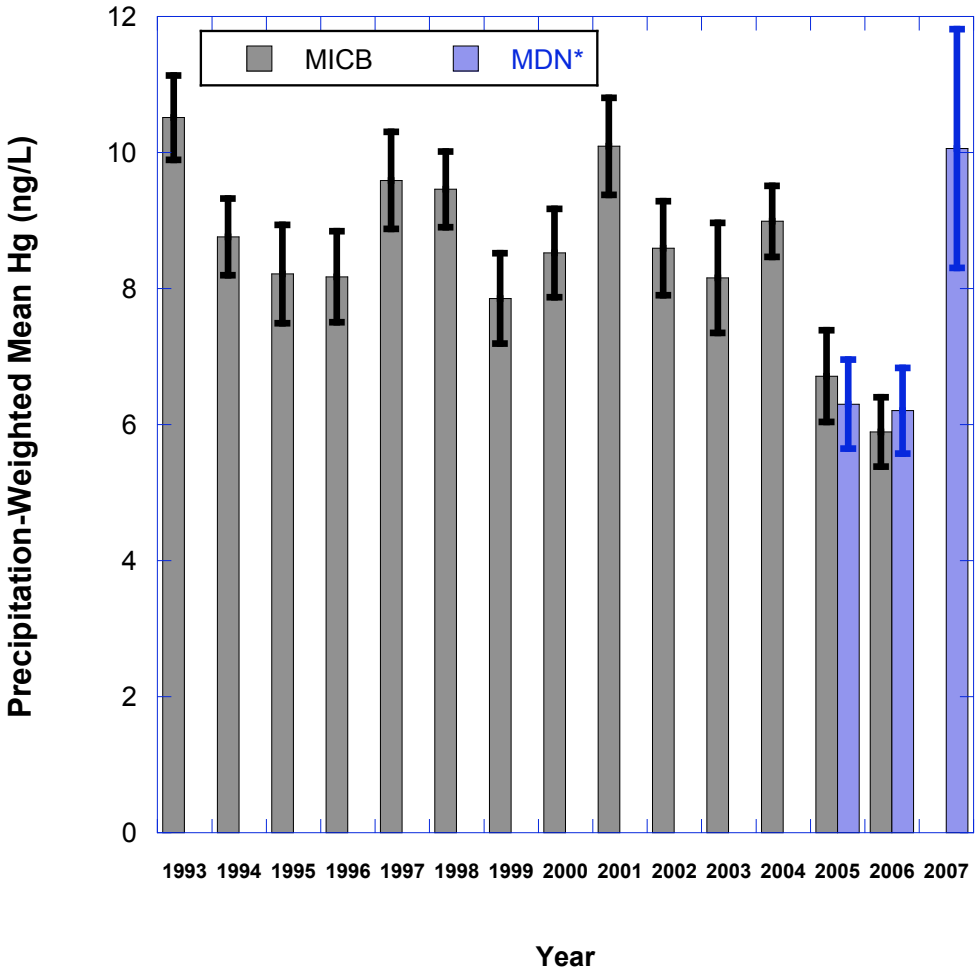


Figure 6. Annual precipitation-weighted mean Hg concentration at Underhill, VT as determined by the MICB collector operating the UMAQL protocol with analysis at UMAQL (1993-2006) and the MDN ACM collector operating the MDN event protocol with analysis at Frontier Geosciences. MDN concentration values were adjusted by a factor of 1.22 (MDN*) as established by a 1-year collector comparison study. This factor compensates for different collector and sample train performance as well as a persistent laboratory bias.

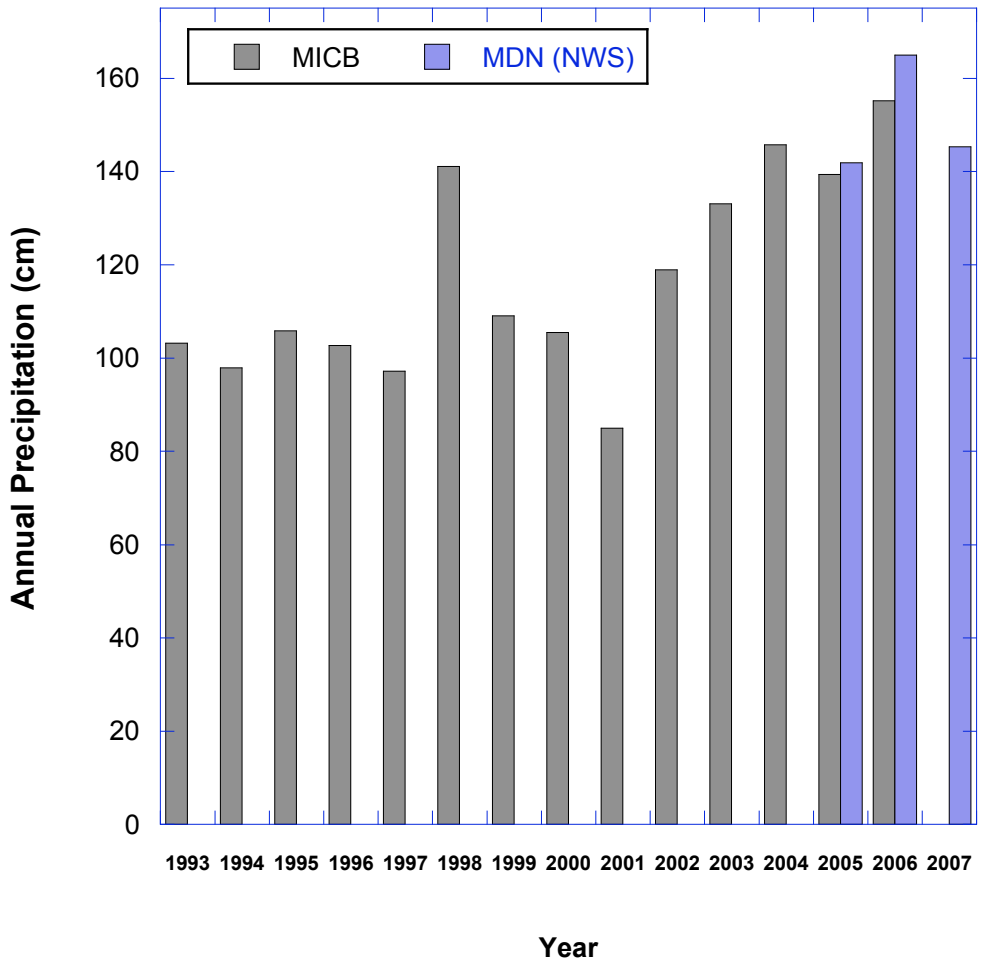


Figure 7. Annual precipitation at Underhill, VT as determined by the MICB collector (1993 – 2006) and the NWS 8-inch rain gage (2005 – 2007). As the result of the 1-year collector comparison study, it was determined that both the ACM collector and the Belfort recording precipitation gage used by MDN significantly under-report precipitation, while the MICB collector and the NWS gage agreed within 1%. Therefore, VT99 MDN reports precipitation amounts and wet-deposition based on the NWS gage precipitation readings.

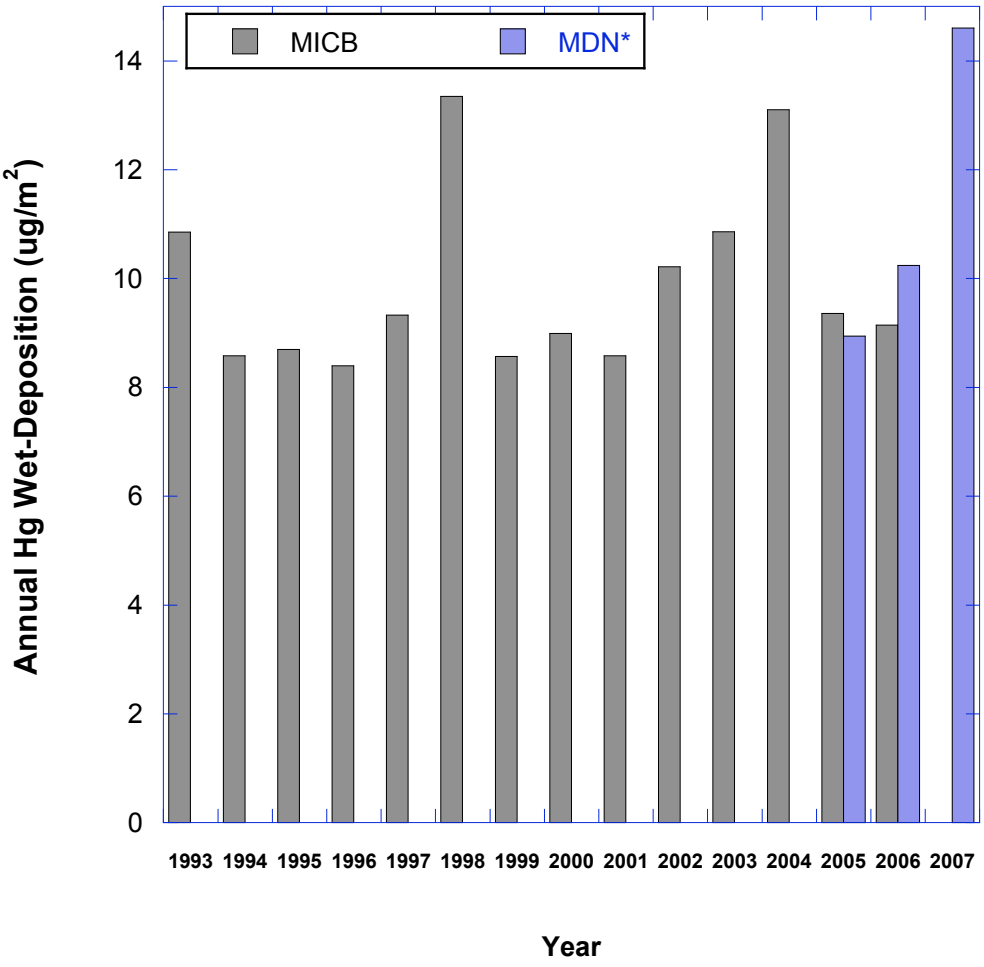


Figure 8. Annual wet-deposition of Hg at Underhill, VT as determined by the MICB collector operating the UMAQL protocol with analysis at UMAQL (1993 - 2006) and the MDN ACM collector operating the MDN event protocol with analysis at Frontier Geosciences (2005 – 2007). MDN concentration values were adjusted by a factor of 1.22 (ACM collector) as established by a 1-year collector comparison study. This factor compensates for different collector and sample train performance as well as a persistent laboratory bias. The MDN deposition values were calculated from the corrected MDN concentrations and precipitation recorded by the NWS rain gage.

A detailed analysis of the wet deposition data from the combined record and methyl-mercury measurements is presented in a separate document "FR-sec2c-Long-Term-Record-2009-01-16.pdf". Please see this document for additional information.

Continuing the Long-Term Record of Mercury Wet Deposition

Through this project, we have successfully transitioned from the UMAQL program the MDN program. We established and tested transfer functions enabling us to link the long historical record developed with the MICB collector to the ongoing record with either and ACM or NCON collector. Event-based precipitation sampling continues at Underhill (VT99) with the MDN NCON and ACM collectors under funding from the NOAA Lake Champlain Research Consortium Program.

References

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Burke, J., M. Hoyer, G. Keeler, and T. Scherbatskoy. 1995. Wet deposition of mercury and ambient mercury concentrations at a site in the Lake Champlain Basin. *Water Air and Soil Pollution* **80**:353-362.

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