# **2014 Quality Assurance Report Atmospheric Mercury Network**



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# Abbreviations

AMNet	Atmospheric Mercury Network
GEM	Gaseous Elemental Mercury (expressed in ng/m <sup>3</sup> )
GOM	Gaseous Oxidized Mercury (expressed in pg/m <sup>3</sup> )
MDN	Mercury Deposition Network
NADP	National Atmospheric Deposition Program
PBM2.5	Particulate-Bound Mercury less than 2.5 $\mu$ m in diameter (expressed in pg/m <sup>3</sup> )
QAP	Quality Assurance Program
SOP	Standard Operating Procedures

# **Units and Conversion Factors**

degrees Fahrenheit
degrees Celsius
centimeters
liters
microliter $(1 \ \mu l = 10^{-6} L)$
liters per minute
nanograms $(1 \text{ ng} = 10^{-9} \text{ g})$
nanograms per cubic meter
picograms $(1 \text{ pg} = 10^{-12} \text{ g})$
picograms per cubic meter

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### **1.0** Introduction

The Atmospheric Mercury Network (AMNet) started in 2009. In 2014 the network consisted of 19 sites across North America and one at Mt LuLin in Taiwan (Table 1). The concentrations of gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM<sub>2.5</sub>) are measured at each site following the AMNet Standard Operating Procedures (SOPs). The AMNet Site Liaison provides remote technical support to site operators in the operation of AMNet equipment, performs site performance and systems surveys, and reviews the data on a monthly basis to identify problems. Data review includes both manual and automated quality control checks. Site operators are notified whenever problems are discovered.

In 2014 fourteen sites were surveyed by the AMNet Site Liaison. Two sites (AK03 and ME97) were visited twice and 2 sites (FL96 and NU15) had multiple instruments evaluated. This report includes a summary of the findings from each of the surveys.

NADP Site ID	State	Table 1. AMN           Operating Agency	Start Date	End Date	Lapse
AK03	Alaska	National Park Service	2/5/2014	Current	
AL19	Alabama	ARA Inc.	1/1/2009	Current	
CA48	California	UC Santa Cruz	1/1/2010	12/31/2011	
FL96	Florida	ARA Inc.	1/1/2009	Current	
GA40	Georgia	ARA Inc.	1/1/2009	Current	
HI00	Hawaii	NOAA/EPA	12/30/2010	Current	
MD08	Maryland	University of Maryland	1/1/2008	Current	6/30/2011 - 1/12/2012
MD96	Maryland	NOAA	1/26/2007	Current	
MD97	Maryland	NOAA	11/7/2006	Current	
ME97	Maine	Micmac Tribe	12/3/2013	Current	
MS12	Mississippi	NOAA	9/29/2006	11/12/2012	
MS99	Mississippi	NOAA	10/18/2007	Current	
NH06	New Hampshire	University of New Hampshire	1/1/2009	11/29/2011	
NJ05	New Jersey	State of New Jersey	6/1/2009	4/30/2010	
NS01	Nova Scotia, Canada	Environment Canada	1/26/2009	Current	
NU15	Nunavut, Canada	Environment Canada	1/4/2002	Current	
NY06	New York	State of New York	8/27/2008	Current	
NY20	New York	SUNY ESF	11/21/2007	Current	
NY95	New York	State of New York	11/21/2007	Current	
OH02	Ohio	Ohio University	1/1/2007	Current	2/15/2012 - 9/24/2013
OH52	Ohio	Ohio State University	1/1/2012	Current	
OK99	Oklahoma	Cherokee Nation	10/20/2008	Current	
PA13	Pennsylvania	NOAA	4/1/2011	11/10/2011	
UT96	Utah	University of Utah	6/18/2009	6/30/2011	
UT97	Utah	State of Utah	11/23/2008	Current	
VT99	Vermont	University of Vermont	1/1/2008	Current	
W199	Wisconsin	State of Wisconsin	2/1/2012	Current	
WV99	West Virginia	NOAA	1/1/2007	10/14/2012	
TW01	Taiwan	EPA Taiwan	1/1/2010	Current	

Table 1. AMNet Sites

Changes in 2014 include the following:

AK03 initiated GEM analysis on August 7, 2014

Changes to data in 2014 include the following:

AL19 (Birmingham), GA40 (Yorkville) and FL96 (Pensacola) 2014 results for the entire year were multiplied by 1.087 standardizing the data from 25°C to 0°C.

OK99 (Stilwell) GOM and PBM<sub>2.5</sub> results from January 1 through May 14, 2014 were multiplied by 1.351 to adjust for reduced flow rates.

VT99 (Underhill) GOM and PBM<sub>2.5</sub> results from March 5 through June 6, 2014 were multiplied by 5.21 to adjust for incorrect scale factor.

### 2.0 Site Performance and Systems Surveys

Sites are surveyed at least once every two years by the AMNet Site Liaison. Normally, the site performance and systems surveys would be performed by an independent entity. This is true for the other four NADP networks. The expertise required to operate and troubleshoot the AMNet instrumentation prohibits an independent third party from providing this service. Field survey reports are completed to document problems that are discovered and their resolution. Site surveys evaluate both field and laboratory operations (including equipment operation), and siting criteria. Site surveys ensure data comparability within the network, resolve operational problems that may not be apparent in data review, and address training needs at each site.

Additional information regarding site surveys may be found in the document titled *Atmospheric Mercury Network: Site Performance and Systems Survey*. This document is available from the NADP website (<u>http://nadp.isws.illinois.edu/</u>).

### 2.1 AMNet Sites Surveyed in 2014

Site surveys were conducted at fourteen AMNet sites in 2014. Station ID's, survey dates and station names are presented in Table 2. The AK03 site was visited twice to help install the instrument then perform a site survey after 5 months of operation. The ME97 site was visited a second time due to elevated mercury concentrations in the shelter during the initial visit.

Site ID	Station Name	Survey Date
AK03	Denali	3/10/2014
AK03	Denali	8/7/2014
AL19	Birmingham	1/30/2014
FL96	Pensacola	1/31/2014
GA40	Yorkville	1/28/2014
ME97	Presque Isle	10/28/2014
ME97	Presque Isle	12/8/2014
MS12	Grand Bay NERR	1/25/2014
NU15	Alert	11/6/2014
NY20	Huntington Wildlife Forest	6/18/2014
OH02	Athens	5/6/2014
OH52	South Bass Island	5/8/2014
TW01	Mount LuLin	6/7/2014
UT97	Salt Lake City	9/22/2014
VT99	Underhill	6/9/2014
WI07	Horicon	9/29/2014

**Table 2.** AMNet Sites Surveyed in 2014.

### 2.2 Instrument Test Results

As part of the site survey, instrument sensitivity (i.e., response factor) and the internal calibration source are verified. Independent, third party calibration certificates for the survey test equipment are included in the appendix to this document.

Table 3 lists the serial numbers for the AMNet instruments at each site. Illegible serial numbers are listed as "n/a" (not available). Not present instruments are listed as "n/p"

Site ID	1102	2537	1130P	1130	1135	2505
AK03	n/p	51	n/p	n/p	n/p	n/p
AL19	73	320	87	9	n/a	144
FL96	74	86	9	n/a	n/a	28
FL96 II	n/a	93	55	n/a	4	28
GA40	5	KT4XF	118	n/a	n/a	104
ME97	125	5041	150	147	134	232
MS12	36	291	78	66	53	147
NU15	n/p	124	141	103	117	5
NY20	35	211	57	n/a	46	n/a
OH02	54	174	49	47	36	81
OH52	94	397	112	n/a	n/a	196
TW01	12	210	63	n/a	n/a	100
UT97	77	364	105	103	88	169
VT99	22	178	53	n/a	n/a	n/a
WI07	95	396	117	n/a	n/a	231

Table 3. Serial Numbers for Instruments at Surveyed Sites.

Table 4 lists the results [i.e., pass (p), fail (f)] for each test of the field instruments. Criteria for assigning pass/fail are defined in *Atmospheric Mercury Network: Site Performance and Systems Survey*. Significant deviation from the test criteria are indicated with an uppercase F. Parameters that were not tested are listed as "n/a."

			Air Flow and Leak Tests			Cartridge A and B Recoveries			
Site ID	Survey Date	Temps OK	Inlet Flow	2537 Flow	Leak Check	Response Factor	Low Level	High Level	Ambient Air
AK03	3/10/2014	р	р	р	р	р	р	р	р
AK03	8/7/2014	р	р	р	р	р	р	р	р
AL19	1/30/2014	р	р	р	р	р	f	f	р
FL96	1/31/2014	р	р	р	р	р	р	р	р
GA40	1/28/2014	р	р	р	f	р	р	р	р
ME97	10/28/2014	р	n/a	n/a	n/a	р	n/a	n/a	n/a
ME97	12/8/2014	р	р	р	р	р	р	р	р
MS12	1/25/2014	р	р	р	р	р	р	Р	р
NU15	11/6/2014	р	р	р	р	р	р	р	р
NY20	6/18/2014	р	р	р	р	р	р	р	р
OH02	5/6/2014	р	р	р	р	р	р	f	f
OH52	5/8/2014	р	р	р	р	р	р	р	р
TW01	6/7/2014	р	р	р	р	р	р	р	р
UT97	9/22/2014	р	р	р	р	р	р	р	р
VT99	6/9/2014	р	р	р	р	р	р	р	р
WI07	9/29/2014	р	р	р	р	р	р	р	р

Table 4. Survey Results.

# 2.3 Siting Criteria

Siting criteria is evaluated with regard to obstructions (>20°) in each of 8 directions (i.e., N, NE, E, SE, S, SW, W, and NW) from the instrument inlet. Inlet heights from the ground are also measured. Results are presented in Table 5. Obstructions are evaluated as pass (p)/fail (f). Deviations from the siting criteria are discussed with the operator during the site survey. Corrective action, when possible, is the responsibility of the site operator and the site supervisor. Site photos can be found at <u>http://nadp.isws.illinois.edu/data/sites/list/?net=AMNet</u>

Site	Inlet Height (m)	N	NE	Е	SE	S	SW	W	NW
AK03	3.2	р	р	р	р	р	р	р	р
AK03	3.2	р	р	р	р	р	р	р	р
AL19	5.2	р	р	р	р	р	р	р	р
FL96	5.2	р	р	р	р	р	р	р	р
GA40	5.2	р	р	р	р	р	р	р	р
ME97	3.4	р	р	р	р	р	р	р	р
ME97	3.4	р	р	р	р	р	р	р	р
MS12	10.0	р	р	р	р	р	р	р	р
NU15	5.4	р	р	р	р	р	р	р	р
NY20	4.9	р	р	р	р	р	р	р	р
OH02	2.5	р	р	р	р	р	р	р	р
OH52	1.9	f	f	f	f	f	f	р	р
TW01	8.0	р	р	р	р	р	р	р	р
UT97	8.2	р	р	р	р	р	р	р	р
VT99	5.9	р	р	р	р	р	р	р	р
WI07	4.8	р	р	р	р	р	р	р	р

**Table 5**. Siting Criteria Obstructions and Inlet Heights.

# 2.4 Instrument Repairs

In 2014, instruments at five sites (AK03, NY20, OH52, TW01 and VT99) required repairs in order to complete the survey. By comparison, in 2013, three instruments required repairs in order to complete the survey.

### 2.5 Test Equipment Calibration

Two Bios Definer 220 flow meters are used to verify analyzer and inlet flow rates. The high level meter (3-30 lpm) is used with the inlet flow. The medium level meter (0.5-5 lpm) is used with the analyzer. Each meter is certified annually by the manufacturer. Certification includes checking the thermocouple, the barometer and three flow rates across the range of the

instrument. Values are reported both pre- and post-calibration (i.e., as-received and as-shipped). Table 6 lists the calibration results for the two flow meters as reported in January 2014 (the start of the reporting year) and in January 2015 (the end of the reporting year).

Flow	Moton	Calibration Date			
Flow Meter		01/2014	01/2015		
medium level	as-received	battery-failure: cell board damaged, cell board faulty, needs replacement	Thermocoupler $1.4^{\circ}$ C low (tolerance $\pm 0.8^{\circ}$ C)		
(0.5 – 5.0 lpm) as-shipped		within tolerance for all parameters	within tolerance for all parameters		
high level (3 – 30 lpm)	as-received	barometer 15 mm Hg high (tolerance ± 3.5 mm Hg), flow rates 7% low (tolerance ± 1%) temperature within tolerance	flow rates 4% high (tolerance ± 1%) temperature within tolerance		
	as-shipped	within tolerance for all parameters	within tolerance for all parameters		

Table 6. Flow Meter Cal	ibration Results for 2013 and 2014.
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As part of the site survey, on-site flow meters are checked against AMNet test equipment flow meters. Throughout 2014, the AMNet test equipment high flow meter reported values that were higher than the on-site meters. Calibration of this flow meter in January 2015 indicated that it reported high by 4%. No inlet flows were adjusted in 2014

In order to identify problems with the AMNet test equipment sooner, two sets of test equipment will be calibrated and certified. One set will reside in the laboratory. The second set will be designated as travel equipment. Prior to each site survey, operation of the travel equipment will be verified against the laboratory equipment. This work will begin in 2015.

A Tekran 2505 Mercury Vapor Primary Calibration Unit and a certified Hamilton 25 uL syringe (model 1702RN) are used to validate instrument internal permeation sources. On December 31, 2013 and on April 16, 2014 the syringe was found to be within tolerance both as-received and as-shipped.

### 3.0 Training

There were no official AMNet training sessions held in 2014. Operator training is performed with each site visit, if required.

### 4.0 Data

AMNet data are evaluated using a series of automated checks and through manual inspection by the AMNet Site Liaison. Additional information on this process is available in the *Atmospheric Mercury Network Data Management Manual*. Table 7 lists the percent valid data for each site in 2014. Values are presented for each of the three forms of mercury that are measured including: GEM, GOM, and PBM<sub>2.5</sub>. Three sites did not meet data quality objectives ( $\geq$  75% data completeness on annual basis) for GEM in 2014. Seven sites did not meet data quality objectives for GOM and 8 sites for PBM<sub>2.5</sub>.

The frequency of the slow desorption invalidation flags increased for GOM and PBM<sub>2.5</sub>. This affected a large percentage of the data for some sites. This behavior was discussed at the Tekran User Group Meeting in September 2015. The decision was made to change the slow desorption flag from a control flag (i.e., QR=C) to a warning flag (i.e., QR=B). The change was approved at the fall 2015 NADP meeting, and is reflected in this report.

AL19 -50% of the invalid GOM and PBM<sub>2.5</sub> data was due to low flow or low response. Slow desorption accounted for 30% of the GOM and 25% of the PBM<sub>2.5</sub> invalid data.

FL96 - 48% of the invalid GOM and  $PBM_{2.5}$  data was due to high baseline deviation or incomplete load cycles. Slow desorption accounted for 44% of the GOM and 38% of the  $PBM_{2.5}$  invalid data.

GA40 - 34% of the invalid GOM and PBM<sub>2.5</sub> data was due to trap calibration bias or incomplete load cycles. Slow desorption accounted for 63% of the GOM and 70% of the PBM<sub>2.5</sub> invalid data.

HI00 - 25% of the invalid PBM<sub>2.5</sub> data was due to incomplete load cycles. Slow desorption accounted for 64% of the PBM<sub>2.5</sub> invalid data.

NY06 - Slow desorption accounted for 97% of the GOM and 96% of the PBM<sub>2.5</sub> invalid data.

NY20 - 69% of the invalid GOM and PBM<sub>2.5</sub> data was due to low response or calibration trap bias. Slow desorption accounted for 13% of the GOM and 3% of the PBM<sub>2.5</sub> invalid data.

OK99 – 70% of the invalid GOM and PBM<sub>2.5</sub> data was due to low response or calibration trap bias. Slow desorption accounted for 27% of the GOM and 21% of the PBM<sub>2.5</sub> invalid data.

UT97 - 73% of the invalid GOM and PBM<sub>2.5</sub> data was due to low response or calibration trap bias. Slow desorption accounted for 10% of the GOM and 2% of the PBM<sub>2.5</sub> invalid data.

Site ID	GEM	GOM	
			<b>PBM</b> <sub>2.5</sub>
AK03	93	n/a	n/a
AL19	74	75	71
FL96	88	79	79
GA40	82	85	85
HI00	85	79	75
MD08	n/a	n/a	n/a
MD98	89	94	94
MD99	90	80	80
ME97	93	92	92
MS12	92	91	89
NS01	97	96	96
NY06	85	84	70
NY20	71	66	66
NY43	82	82	74
OH02	89	90	87
OH52	90	86	85
OK99	9	9	9
UT97	54	44	46
VT99	94	92	91
WI07	97	94	93
Average	82	79	77

 Table 7. Percent Valid Data by Site for 2014.

# **Appendix – Test Equipment Calibration Documents**





### **Calibration Certificate**

Certificate No.	5053373	Sold to:	National Atmospheric Deposition Program- NADP - IL
Product	Definer 220 Medium Flow		1876 Lewis Road
Serial No.	119093		Mt. Hereb, WI 53572
Cal. Date	19-Jan-2015		USA

All calibrations are performed at Mesa Laboratories, Inc., 10 Park Place, Butler, NJ, 07405, an ISO 17025:2005 accredited laboratory through NVLAP of NIST. This report shall not be reproduced except in full without the written approval of the laboratory. Results only relate to the items calibrated. This report must not be used to claim product certification, approval, or endorsement by NVLAP, NIST, or any agency of the Federal Government.

#### As Received Calibration Data

Technician Lilianna Malinowska

Lab. Pressure 759 mmHg Lab. Temperature 22.6 °C

Instrument Reading	Lab Standard Reading	Deviation	Allowable Deviation	As Received
100.9 sccm	100.25 sccm	0.65 % %	1.00%	In Tolerance
1000.6 sccm	1000.2 sccm	0.04 % %	1.00%	In Tolerance
5011.1 sccm	5001.4 sccm	0.19 % %	1.00%	In Tolerance
21.5 °C	22.6 °C	-1.1 °C	±0.8°C	Out of Tolerance
759 mmHg	759 mmHg	0.0 mmHg	±3.5mmHg	In Tolerance

Mesa Laboratoires Standards Used

Description	Standard Serial Number	Calibration Date	Calibration Due Date
ML-800-24	100439	8-May-2014	8-May-2015
Precision Thermometer	305460	9-Sep-2014	9-Sep-2015
Precision Barometer	2981392	24-Jun-2014	24-Jun-2015

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#### As Shipped Calibration Data

Certificate No. 5053373 Technician Lilianna Malinowska

Lab. Pressure 746 mmHg Lab. Temperature 22.6 °C

Instrument Reading	Lab Standard Reading	Deviation	Allowable	As Shipped
101.75 sccm	101.225 sccm	0.52 %%	1.00%	In Tolerance
1004.2 sccm	1000.8 sccm	0.34 %%	1.00%	
5024.1 sccm	5001.5 sccm	0.45 %%	1.00%	In Tolerance
22.6 °C	22.6 °C	0.40 /0/0		In Tolerance
746 mmHg	746 mmHg	-	±0.8°C	In Tolerance
i to mining	740 mmng	-	±3.5mmHg	In Tolerance

#### Mesa Laboratories Standards Used

tandard Genal Number	Calibration Date	Calibration Due Date
100439	8-May-2014	8-May-2015
305460	9-Sep-2014	9-Sep-2015
2981392		24-Jun-2015
		100439 8-May-2014 305460 9-Sep-2014

#### **Calibration Notes**

The expanded uncertainty of flow, temperature, and pressure measurements all have a coverage factor of k = 2 for a confidence interval of approximately 95%.

Flow testing is in accordance with our test number PR18-13 with an expanded uncertainty of 0.18% using highpurity nitrogen or filtered laboratory air. Flow readings in sccm are performed at STP of 21.1°C and 760 mmHg.

Pressure testing is in accordance with our test number PR18-11 with an expanded uncertainty of 0.16 mmHg.

Temperature testing is in accordance with our test number PR18-12 with an expanded uncertainty of 0.04 °C.

Traceability to the International System of Units (SI) is verified by accreditation to ISO/IEC 17025 by NVLAP under NVLAP Code 200661-0.

Technician Notes:

JW.j

David W. Wilson, Chief Metrologist

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#### **Calibration Certificate**

Certificate No.	5053375	Sold to:	National Atmospheric Deposition Program- NADP - IL
Product	Definer 220 High Flow		1876 Lewis Road
Serial No.	119152		Mt. Hereb, WI 53572
Cal. Date	19-Jan-2015		USA

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#### As Received Calibration Data

Technician Lilianna Malinowska

#### Lab. Pressure 758 mmHg Lab. Temperature 23.1 °C

Instrument Reading	Lab Standard Reading	Deviation	Allowable Deviation	As Received
521.72 sccm	501.125 sccm	4.11 % %	1.00%	Out of Tolerance
5186.4 sccm	5001.5 sccm	3.70 % %	1.00%	Out of Tolerance
31367 sccm	30270.5 sccm	3.62 % %	1.00%	Out of Tolerance
22.6 °C	23.1 °C	-0.5 °C	±0.8°C	In Tolerance
758 mmHg	758 mmHg	0.0 mmHg	±3.5mmHg	In Tolerance

Mesa Laboratoires Standards Used

Description	Standard Serial Number	Calibration Date	Calibration Due Date
ML-800-44	101897	18-Nov-2014	18-Nov-2015
Precision Thermometer	305460	9-Sep-2014	9-Sep-2015
Precision Barometer	2981392	24-Jun-2014	24-Jun-2015

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#### As Shipped Calibration Data

ertificate No. 5053375 echnician Lilianna Malinowska		re 747 mmHg rature 23.1 °C		
Instrument Reading	Lab Standard Reading	Deviation	Allowable Deviation	As Shipped
504.81 sccm	500.765 sccm	0.81 %%	1.00%	In Tolerance
5002.2 sccm	5000.55 sccm	0.03 %%	1.00%	In Tolerance
30410 sccm	30214 sccm	0.65 %%	1.00%	In Tolerance
23.1 °C	23.1 °C	-	±0.8°C	In Tolerance
747 mmHg	747 mmHg	-	±3.5mmHg	In Tolerance

#### Mesa Laboratories Standards Used

Description	Standard Serial Number	Calibration Date	Calibration Due Date
ML-800-44	101897	18-Nov-2014	18-Nov-2015
Precision Thermometer	305460	9-Sep-2014	9-Sep-2015
Precision Barometer	2981392	24-Jun-2014	24-Jun-2015

#### **Calibration Notes**

The expanded uncertainty of flow, temperature, and pressure measurements all have a coverage factor of k = 2 for a confidence interval of approximately 95%.

Flow testing is in accordance with our test number PR18-13 with an expanded uncertainty of 0.18% using highpurity nitrogen or filtered laboratory air. Flow readings in sccm are performed at STP of 21.1°C and 760 mmHg.

Pressure testing is in accordance with our test number PR18-11 with an expanded uncertainty of 0.16 mmHg.

Temperature testing is in accordance with our test number PR18-12 with an expanded uncertainty of 0.04 °C.

Traceability to the International System of Units (SI) is verified by accreditation to ISO/IEC 17025 by NVLAP under NVLAP Code 200661-0.

**Technician Notes:** 

) Wil

David W. Wilson, Chief Metrologist

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