Atmospheric Mercury Network Data Management Manual



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Abbreviations

U.S. EPAUnited States Environmental Protection AgencyUSGSUnited States Geological Survey	AIRMoN AMNet AMoN CAMD CAMD CAMNet CASTNET CVAFS DFU DQO GEM GOM Hg MDE MDN MSDS NADP NED NIST NTN NYSDEC PBM2.5 PO QA QAAG QC RespFctr RGM SAES SOP TGM UHP	Atmospheric Integrated Research Monitoring Network Atmospheric Mercury Network Ammonia Monitoring Network Clean Air Markets Division Canadian Atmospheric Mercury Network Clean Air Status and Trends Network Cold Vapor Atomic Fluorescence Spectroscopy Dry Filter Unit Data Quality Objective Gaseous Elemental Mercury (expressed in ng/m ³) Gaseous Oxidized Mercury (expressed in ng/m ³) Gaseous Oxidized Mercury (expressed in pg/m ³) Mercury Mercury Deposition Event Mercury Deposition Network Material Safety Data Sheet National Atmospheric Deposition Program Network Equipment Depot National Institute of Standards and Technology National Institute of Standards and Technology National Institute of Standards and Technology National Trends Network New York State Department of Environmental Conservation Particulate-Bound Mercury less than 2.5 µm in diameter (expressed in pg/m ³) Program Office Quality Assurance Quality Assurance Quality Assurance Advisory Group Quality Control Response Factor Reactive Gaseous Mercury (expressed in pg/m ³) State Agricultural Experiment Stations Standard Operating Procedures Total Gaseous Mercury (expressed in ng/m ³) Ultra-High Purity
USGS United States Geological Survey	U.S. EPA	United States Environmental Protection Agency
	USGS	

Units and Conversion Factors

0	degrees
°C	degrees Celcius
cm	centimeters
L	liters
lpm	liters per minute
mm	millimeters $(1 \text{ mm} = 10^{-3} \text{ m})$
ng	nanograms $(1 \text{ ng} = 10^{-9} \text{ g})$
ng/m ³	nanograms per cubic meter
pg	picograms $(1 \text{ pg} = 10^{-12} \text{ g})$
pg/m ³	picograms per cubic meter
psi	pounds per square inch
μm	micrometer (1 μ m = 10 ⁻⁶ m)
V	volts

Introduction

This document, the *NADP AMNet Data Management Manual*, details the data practices within the Atmospheric Mercury Network (AMNet). It considers what data is captured, how that data is processed and stored, where the data will be made available, and when the data will be available. These processes ensure consistent data operations across the network and over time, and help ensure that the data quality objectives (DQOs) of the network are met.

Network Data

Table 1 lists the types of data products that are collected for use in the network, the frequency with which these products are collected and/or updated, and the individual(s) responsible for the data product. All data products will be maintained indefinitely at the National Atmospheric Deposition Program (NADP) Program Office (PO).

Data Product	Frequency	Responsible Party	
Tekran instrument data, raw data	Collect: 5 minute averages Submit to PO: monthly	Site Operator	
Tekran data, processed and quality-assured	Process: 60 minute, or 120 minute averages, based on instrument cycle Post: within 6 months of data submission	NADP Program Office	
Site Report A Each Visit/Weekly Activities*	Complete: each visit Submit to PO: monthly		
Site Report B Glassware Change-out/Monthly Activities*	Complete: as needed Submit to PO: monthly	Site Operator	
Site Report C Quarterly Activities*	Complete: as needed Submit to PO: quarterly		
Site Report D Annual/As-Needed Activities*	Complete: as needed Submit to PO: when completed		
Preliminary Data Reports to site Site Liaison logs (e.g., phone, Email)	Monthly As needed	Site Liaison	
Site Information Worksheet (SIW)	Submit to PO: prior to site start-up Update: as needed	Site Operator	
Site sketch	Submit to PO: prior to site start-up Update: every 2 years	Site Operator,	
Site photos	Submit to PO: prior to site start-up Update: every 2 years	NADP Program Office	
Site Performance and Systems Survey reports	Once every 2 years	NADP Program Office	

 Table 1. AMNet Data Products.

* Site Reports A-D are discussed in separate Standard Operating Procedure documents.

Data and Site Report Submission

Tekran instrument raw data files and the completed Site Reports should be uploaded to the NADP PO via the following URL: <u>http://nadp.isws.illinois.edu/upload/amn</u>. As indicated in Table 1, instrument data should be submitted monthly. Completed Site Reports should be submitted according to the report schedule. Questions and/or problems relating to the submission of these files should be directed to the AMNet Site Liaison (608-335-4232, <u>amnet@isws.illinois.edu</u>).

Measurement of Mercury Species

The Tekran 2537 system measures mercury concentration using cold vapor atomic fluorescence spectroscopy (CVAFS). Mercury sampling and measurement occurs for 2 out of every 3 hours of operation. During the first 2 hours of operation, the Tekran 2537 measures the concentration of gaseous elemental mercury (GEM). These measurements are made directly and are presented as 5-minute averages. Each average results from the operation (i.e., collection and analysis) of one of two cartridges that operate in alternating fashion. As alternating cartridges are used for the measurements, cartridge bias is evaluated as part of data validation.

Throughout the entire 2 hour sampling period, two other mercury species are concentrated for analysis at the end of the period. These species include gaseous oxidized mercury (GOM), and particulate-bound mercury of mean diameter less than or equal to $2.5 \,\mu\text{m}$ (PBM_{2.5}). The concentration of these species in ambient air is low, hence the need to concentrate them during the first two hours of instrument operation. Analysis for GOM and PBM_{2.5} requires an hour to complete, and occurs during the third hour of instrument operation. No sampling occurs during this third hour of instrument operation, and GEM is not measured. The resulting concentrations for GOM and PBM_{2.5} correspond to the first two hours of instrument operation, when sampling occurred.

Concentrations for GOM and PBM_{2.5} are calculated using the equations listed below. The Cycle IDs used in the equations represent the cycles of operation of the Tekran 2537 instrumentation as identified in Table 2. Table 2 also includes the associated Event Flags and the cartridge used for the measurement, assuming normal start-up of the instrumentation. Event Flags appear in the untitled column to the right of the *Stat* column in the Tekran 2537 output, and are numeric values from 1 to 4. Figure 1 illustrates sample data from the Tekran 2537 and identifies the corresponding Event Flags and cycles of operation. Table 3 identifies the column names that are used with the Tekran 2537 output data. It should be noted that the cycles apply to the third hour of operation of the instrumentation, and do not include sampling or measurement of GEM.

PBM_{2.5} (pg/m³):Cycle(E) + Cycle(F) + Cycle(G) - 3*Cycle(C)**GOM** (pg/m³):Cycle(H) + Cycle(I) + Cycle(J) - 3*Cycle(C)

The majority of PBM_{2.5} and GOM that were captured during the 2 hour sampling period is expected to be released (and measured) during cycles E and H, respectively. Values for cycles F, G, I, and J are expected to be much smaller by comparison, and in many cases will be 0 pg/m³. Cycle(C) is also expected to have a value of 0 pg/m³. It measures the concentration of mercury in the final system flush prior to measurement of PBM_{2.5} and GOM. As indicated in Table 2, Cycle(E) and Cycle(H) are measured using different cartridges. Again, evaluation of cartridge bias is necessary as part of data validation.

Cycle ID	Cycle Description	Event Flags	Cartridge*
A	Flush	1	А
В	Flush	1	В
С	Flush	1	А
D	Pyrolyzer heating	2	В
Е	PBM _{2.5} heating	3	А
F	PBM _{2.5} heating	3	В
G	PBM _{2.5} heating	3	А
Н	GOM heating	4	В
Ι	GOM heating	4	А
J	GOM heating	4	В
K	Cooling	1	А
L	Cooling	1	В

Table 2. Tekran 2537 Cycles of Operation for Measurement of GOM and PBM_{2.5}.

* Assumes normal startup of the Tekran instrumentation with Cartridge A.

Date	Time	Тур С	Stat	AdTim	Vol Bl	BlDev Ma	xV Area	a pg/m	3
10-07-02	2 07:10:01	CONT	B OKF	1 300	5.00 0.130	.061 0.131	3658	0.401	: A
10-07-02	2 07:15:01	CONT	A NPF	1 300	4.99 0.130	.068 .000	0	.000	: B
10-07-02	2 07:20:01	CONT	B NPF	1 300	4.99 0.130	.069 .000	0	.000	: C
10-07-02	2 07:25:01	CONT	A OKF	2 300	4.99 0.129	.066 0.132	8497	0.899	: D
10-07-02	2 07:30:01	CONT	B OKF	3 300	4.99 0.129	.078 0.159	111421	12.217	: E
10-07-02	2 07:35:01	CONT	A NPF	3 300	4.99 0.129	.047 .000	0	.000	: F
10-07-02	2 07:40:01	CONT	B NPF	3 300	4.99 0.130	.095 .000	0	.000	: G
10-07-02	2 07:45:01	CONT	A OKF	4 300	5.00 0.130	.067 0.160	105635	11.177	: H
10-07-02	2 07:50:01	CONT	B NPF	4 300	4.99 0.130	.056 .000	0	.000	: I
10-07-02	2 07:55:01	CONT	A NPF	4 300	4.99 0.130	.070 .000	0	.000	: J
10-07-02	2 08:00:01	CONT	B NPF	1 300	4.99 0.131	.078 .000	0	.000	: K
10-07-02	2 08:05:01	CONT	A NPF	1 300	4.99 0.131	.057 .000	0	.000	: L

Figure 1. Sample output from the Tekran 2537 with Cycle IDs (far right column).

Column Header	Meaning	Units	Value
Column Header	ð	Units	Value
Date	start date of the		MM:DD:YY
Date	measurement		
Time	start time of the		HH:MM:SS
Time	measurement		(24-hr clock)
Τ	mode of operation		CLN, CONT, SPAN,
Тур	-		ZERO
С	channel		A or B
Stat*	instrument status		M#, M#F, NP, NPF, OK,
Stat*			OKF, OL, OLF
AdTim	Sampling time	seconds	
Vol	sample volume	liters	
Bl	baseline voltage	volts	
BlDev	standard deviation of the	volts	
Bibev	baseline voltage	voits	
MaxV	peak voltage	volts	
	Area under the curve		
Area	recorded by CVAFS		
	analysis		
pg/m3	measured concentration	pg/m ³	

Table 3. Column Headers Used With Tekran 2537 Output Data.

* "#"identifies the number of peaks (1-9),

"F" means a scaling factor has been applied to the measured concentration,

"M" means multiple peaks detected,

"NP" means no peak detected,

"OK" means a single peak was detected and that everything is ok,

"OL" means overload i.e., the peak height is out of range.

Data Validation

As indicated in Figure 2, validation of the Tekran instrument raw data is a three-step process. This process includes:

- 1. automated quality assurance (QA) checks,
- 2. manual inspection by the AMNet Site Liaison, and
- 3. approval by the Site Operator and/or Site Supervisor at each site

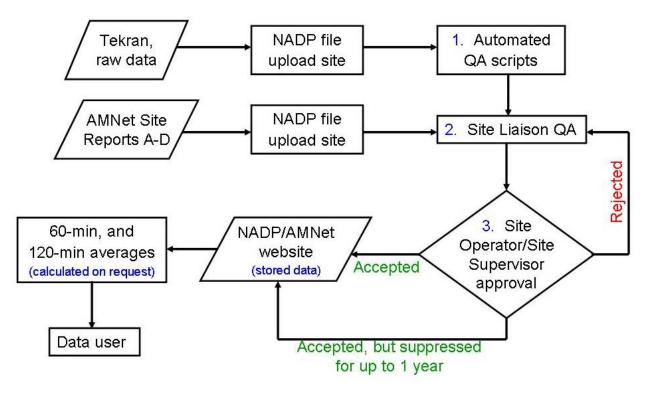


Figure 2. AMNet Quality Assurance and Data Flow Process.

Upon receipt at the NADP PO, the raw data files from the Tekran 2537 are imported into the AMNet SQL Server database. As part of the data import, quality assurance screening criteria are applied to the data. Validation flags are assigned to qualify data from the Tekran instrumentation. The flags used to validate the data are listed in Table 4.

Data Flag*	AMNet Data Flags Assigned by Quality Assurance Scree Description	Mercury Species		
null	Data meets criteria used in the automated scripts	All		
A1	$ (Air cartridge bias_i - Air cartridge bais_{i+1})/Air cartridge bias_i > 0.10 for 24 consecutive hours$	GEM		
A2	$\begin{array}{l} (Air \ cartridge \ bias_i - Air \ cartridge \ bias_{i+1})/Air \ cartridge \ bias_i \\ > 0.15 \ for \ 24 \ consecutive \ hours \end{array}$	0EM		
B0	Baseline voltage < 0.01V			
B1	Baseline voltage < 0.05V, or Baseline voltage > 0.25V			
B2	$ Baseline voltage_i - Baseline voltage_{i+1} > 0.01V$			
B3	Baseline deviation > 0.10 V for 5 consecutive readings			
B5	Baseline deviation > 0.15V	All		
C0	$ (Calibration_i - Calibration_{i+1})/Calibration_i > 0.10$			
C1	$ (Calibration cartridge bias_i - Calibration cartridge bias_{i+1})/Calibration cartridge bias_i > 0.10$			
C2	$ (Calibration cartridge bias_i - Calibration cartridge bias_{i+1}) /Calibration cartridge bias_i > 0.20$			
C5	$ (Calibration_i - Calibration_{i+1})/Calibration_i > 0.05$			
E0	First GEM from each cartridge			
E1	$GEM < 1.00 \text{ ng/m}^3$ for same cartridge	GEM		
E5	$ (GEM_i - GEM_{i+1})/GEM_i > 0.50$ for same cartridge			
F1	72 hours < Time between calibrations < 144 hours	All		
F2	Time between calibrations > 144 hours	All		
G0	$GOM = 0 \text{ pg/m}^3$ for more than 24 hours			
G1	Cycle(H) < 0.70 x GOM, or Cycle(I) > 0.20 x GOM, or Cycle(J) > 0.10 x GOM	GOM		
G2	$GOM < 0 \text{ pg/m}^3$			
L1	GEM cycles < 24 before desorption	GOM		
L2	GEM cycles $>$ GEM cycles _{historical}	PBM _{2.5}		
M2	Status = M2 (multiple peaks) All			
M3	Status > M2 (multiple peaks)			
NP	Status = NP (no peak)	GEM		
OL	Status = OL (overload) * Data Flags in Red indicate invalid data.	All		

Table 4. AMNet Data Flags Assigned by Quality Assurance Screening Criteria.

* Data Flags in Red indicate invalid data.

Data Flag*	Description	Mercury Species
PO	$PBM_{2.5} = 0 \text{ pg/m}^3$ for more than 24 hours	
P1	Cycle(E) < 0.70 x PBM _{2.5} , or Cycle(F) > 0.20 x PBM _{2.5} , or Cycle(G) > 0.10 x PBM _{2.5}	PBM _{2.5}
P2	$PBM_{2.5} < 0 \text{ pg/m}^3$	
R1	RespFctr $< 6x10^6$ units, or RespFctr $> 12x10^6$ units	All
R2	RespFctr $< 4x10^6$ units	
RS	Instrument restart	
SO	$Cycle(C) > 1.67 \text{ pg/m}^3$	GOM PBM _{2.5}
S 1	$Cycle(C) > 10 \text{ pg/m}^3$	1 DIVI2.5
V5	$ (Volume_{measured} - Volume_{expected})/Volume_{expected} > 0.05$	
V7	$ (Volume_{measured} - Volume_{expected})/Volume_{expected} > 0.07$	All
Z1	Zero > 1500 Peak Area units	All
Z2	Zero > 1%SPAN	

Table 4 - continued. AMNet Data Flags Assigned by Quality Assurance Screening Criteria.

* Data Flags in Red indicate invalid data.

The second step in the processing of AMNet data requires the AMNet Site Liaison to inspect the quality-assured data resulting from step 1. The purpose of this step is to validate the flags that were assigned to the data by the QA script, to incorporate field notes as recorded in the Site Reports, and to identify other periods of anomalous data. Data flags assigned by the Site Liaison are defined in Table 5.

Data Flag*	Description	Mercury Species
I1	Pre-injection verification	
I2	Injection source verification	
I3	Matrix spike	
Q1	Soda-lime changed	
Q2	Glassware changed	All
Q3	Flow check	
RM	Routine maintenance	
V1	Valid data	
XV	Invalid data	

 Table 5. AMNet Data Flags Assigned by Site Liaison and Site Operator.

* Data Flags in Red indicate invalid data.

Upon completion of these activities for a month of data from a site, a Data Report will be generated and sent to the Site Operator and Site Supervisor. The Data Report will include a list

of all time periods for which the data was invalidated with associated explanations. The Report should be generated within 4 weeks of receipt of the raw, instrument data and Site Reports for a site.

The third step in the processing of AMNet data requires the Site Operator and/or Site Supervisor to approve the Data Report. The AMNet Site Liaison should be notified of approval of the Data Report within 4 weeks of receipt of the Report. Questions regarding the validation of data should be discussed with the Site Liaison. Data flags assigned by the Site Operator are the same as those used by the Site Liaison and are defined in Table 5.

Following approval of the Data Report by the Site Operator and/or Site Supervisor, data is released for posting to the NADP website.

Data Posting

All processed, quality-assured, non-sequestered AMNet data will be freely available via the NADP AMNet website. That site may be accessed at <u>http://nadp.isws.illinois.edu/amn</u>. Registration is required to access the data. Registration is also free. Processed data will be posted to the AMNet website within 6 months of submission of the raw, instrument data to the PO.

60-minute and 120-minute averages are calculated automatically from all valid records at the time the database is queried. These values are not stored in the database.

Averaging periods correspond to the operating cycles of the Tekran instruments. These instruments may be configured to start operation on the hour, or at the next 5 minute interval. In the case of the latter configuration, the operating cycle and the associated averages would not align with the hour. This difference in instrument configuration is important with regard to unattended start-up following a power outage. For instance, GEM has an averaging period of 60 minutes. If the instrument loses power and restarts 15 minutes after the hour, then the corresponding average will also start 15 minutes after the hour. PBM_{2.5} and GOM have a sampling period of 120 minutes. Sample collection for PBM_{2.5} and GOM will start at the same time as the first GEM measurement. As such, average concentrations for PBM_{2.5} and GOM will also start 15 minutes after the hour. With instruments configured to start operation at the next 5 minute interval the timestamps contained in both the 60-minute and the 120-minute average archives can vary, depending on when the instrument was started.

To determine an average value for GEM, more than half the total records for the averaging period must be valid. For instance, there are 12 possible records for GEM during the 60-minute cycle. At least 7 of these records must be valid to generate an average. If no average is generated for GEM, then values for GOM and $PBM_{2.5}$ for the same period will be considered invalid.

At the request of the Site Operator and/or Site Supervisor data for the site may be sequestered for up to 12 months. Sequestered data will be made available on the NADP AMNet website within a year of its submission.

Raw, instrument data is not available from the NADP AMNet website. That data is available solely from the Site Operator and/or Site Supervisor for a site, at their discretion.

Appendix A: Terms

accuracy – the closeness of agreement between the result of a measurement and its true value.

- ANSI/ASQC E4-2004 "Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs."
- **assessment** the evaluation process to measure the performance or effectiveness of a system and its elements; this all-inclusive term denotes evaluations, audits, or reviews.
- **atmospheric deposition** removal of particles and gases from the atmosphere via fallout or precipitation.
- **audit** a systematic and independent examination to determine whether practices comply with documented **QAPs** and **SOPs**, and that these practices are implemented effectively and are suitable to achieve stated objectives.
- **bias** systematic or persistent distortion of a measurement process that causes errors in one direction.
- **chemisorption** chemical adsorption. Adsorption at an exposed surface with the adsorbate surface undergoing a chemical change. That is, a new chemical species results at the surface.
- **comparability** a measure of the confidence with which one data set can be compared to another.
- **completeness** a measure of the amount of valid data obtained from a measurement system compared to the amount that was possible when **SOPs** are followed.
- **data quality assessment** scientific and statistical evaluations of validated data to determine if they are of the right type, quality, and quantity to support their intended use.
- **Data Quality Indicator (DQI)** quantitative statistics and qualitative descriptors used to interpret the degree of acceptability or utility of data to the user: principally **bias/accuracy, precision, comparability, completeness**, and **representativeness**.
- **Data Quality Objective (DQO)** qualitative and quantitative statements that specify the technical characteristics of data that are required to support the intended purposes and uses of the data. May include tolerances on the **Data Quality Indicators.**

deposition - see atmospheric deposition.

environmental data – any measurements or information that describe environmental processes, location, or conditions; ecological or health effects and consequences; or the performance of environmental technology. Environmental data include information collected directly from measurements, produced from models, and compiled from other sources such as databases or the literature.

- **Gaseous Elemental Mercury (GEM)** gas phase mercury in its ground electronic state with the chemical formula Hg⁰. It is a mono-atomic gas.
- **Gaseous Oxidized Mercury (GOM)** oxidized gas phase compounds of mercury. It is sometimes called reactive gaseous mercury (RGM). GOM is believed to be the more accurate term as the term "reactive" can be misleading and imprecise.
- **metadata** data and other information about another related data set (e.g., instrument maintenance logs as metadata for direct instrument readings).
- **method detection limit (MDL)** the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is based on protocols in 40CFR Appendix B to part 136.
- $PBM_{2.5}$ mercury that is bound to particles of mean aerosol diameter less than or equal to 2.5 μ m. Mercury is bound to the particle by means of physiosorption, chemisorption, or entrainment during aerosol production.
- **peer review** a critical review of a specific scientific and/or technical product to corroborate scientific defensibility, which may include an in-depth assessment of assumptions, calculations, extrapolations, alternative interpretations, methodology, acceptance criteria, and conclusions pertaining to the specific scientific and/or technical products and of the supporting documentation.
- **performance evaluation** a quantitative test to determine whether a measurement system can obtain results that meet tolerance limits.
- **physioadsorption -** physical adsorption. Adsorption at an exposed surface with the adsorbate surface remaining intact. No chemical reaction takes place.
- **precision** a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of the standard deviation.
- **Quality Assurance (QA)** an integrated system of management activities involving planning, implementation, documentation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the necessary type and quality expected by the client; generally implemented before an activity has occurred.
- **Quality Assurance Plan (QAP)** a formal document describing in comprehensive detail the necessary QA, QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy stated performance criteria.
- **Quality Control (QC)** the overall system of technical activities to measure the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality; generally implemented while activities are being performed.

- **quality improvement** a management program to improve the quality of operations using a formal mechanism to encourage worker recommendations, timely management evaluation, and feedback or implementation.
- **Quality Management Plan (QMP)** a document that describes the quality system in terms of the organizational structure, functional responsibilities of management and staff, lines of authority, and required interfaces for those planning, implementing, and assessing all activities conducted.
- **Quality Management System (QMS)** the overall management system of the organization that determines and implements the quality policy. Includes strategic planning, allocation of resources, and other systematic activities (e.g., planning, implementation, documentation, and assessment) pertaining to the quality system.
- **record** a completed document that provides objective evidence of an item or process. Records may include photographs, drawings, magnetic tape, and other data recording media.
- **representativeness** a measure of the degree to which data accurately and precisely represent the characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Reactive Gaseous Mercury (RGM) - see gaseous oxidized mercury.

- specifications a document stating requirements and that refers to or includes drawings or other relevant documents. They should indicate the means and criteria for determining conformance.
- **Standard Operating Procedure (SOP)** a written document that details the method for an operation, analysis, or action with thoroughly prescribed techniques and steps. The officially approved method for performing certain routine or repetitive tasks.
- **Statement of Work (SOW)** a written document detailing the procedures and deliverables required to meet contract obligations.

wet deposition – removal of particles and gases from the atmosphere via precipitation.

Appendix B: References

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