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External Quality Assurance Programs Managed by the U.S. Geological Survey in Support of the National Atmospheric Deposition Program/Mercury Deposition Network

Open-File Report 2007–1170

U.S. Department of the Interior
U.S. Geological Survey

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By Natalie E. Latysh and Gregory A. Wetherbee

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Suggested citation:
Latysh, N.E., and Wetherbee, G.A., 2007, External quality assurance programs managed by the U.S. Geological Survey in support of the National Atmospheric Deposition Program/Mercury Deposition Network: U.S. Geological Survey Open-file Report 2007-1170, 33 p.

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Conversion Factors and Datums

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
liter (L)	1.057	quart
milliliter (mL)	0.03381	ounce, fluid

Abbreviations

Abbreviation	Full name
ACM	Aerochem Metrics Model 301
AIRMoN	Atmospheric Integrated Research Monitoring Network
DI	Ultrapure (>16.7 megohm) deionized water
FORF	Field observer report form
FGS	Frontier GeoSciences, Inc.
HAL	Mercury Analytical Laboratory
HCl	Hydrochloric acid
HDPE	High density polyethylene
Hg	Mercury
HPS	High-Purity Standards, Inc.
MDN	Mercury Deposition Network
Me-Hg	Methylmercury
MOF	MDN observer form
MP	Mercury precipitation
MPV	Most probable value
MRL	Minimum reporting limit
NADP	National Atmospheric Deposition Program
NIST	National Institute of Standards and Technology
NOS	Network Operations Subcommittee
NTN	National Trends Network
PDF	Portable document format
QA	Quality assurance
SAS	SAS Institute Inc.
SP	Synthetic precipitation
USGS	U.S. Geological Survey

The following terms and abbreviations also are used in this report:

gram (g)
grams per mole (g/mol)
microgram (μg)
micrograms per liter (μg/L)
milligrams per gram (mg/g)
milligrams per liter (mg/L)
moles per liter (mol/L)
nanograms per liter (ng/L)

External Quality Assurance Programs Managed by the U.S. Geological Survey in Support of the National Atmospheric Deposition Program/Mercury Deposition Network

By Natalie E. Latysh and Gregory A. Wetherbee

Abstract

The U.S. Geological Survey (USGS) Branch of Quality Systems operates external quality assurance programs for the National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN). Beginning in 2004, three programs have been implemented: the system blank program, the interlaboratory comparison program, and the blind audit program. Each program was designed to measure error contributed by specific components in the data-collection process. The system blank program assesses contamination that may result from sampling equipment, field exposure, and routine handling and processing of the wet-deposition samples. The interlaboratory comparison program evaluates bias and precision of analytical results produced by the Mercury Analytical Laboratory (HAL) for the NADP/MDN, operated by Frontier GeoSciences, Inc. The HAL's performance is compared with the performance of five other laboratories. The blind audit program assesses bias and variability of MDN data produced by the HAL using solutions disguised as environmental samples to ascertain true laboratory performance. This report documents the implementation of quality assurance procedures for the NADP/MDN and the operating procedures for each of the external quality assurance programs conducted by the USGS. The USGS quality assurance information provides a measure of confidence to NADP/MDN data users that measurement variability is distinguished from environmental signals.

Introduction

In March 1995, a transition Mercury Deposition Network (MDN) was initiated, with seventeen collection sites (Clyde Sweet, Illinois State Water Survey, written commun., 2006), to monitor weekly concentration and temporal flux of total mercury (Hg) in precipitation (*http://nadp.sws.uiuc.edu/mdn/*; accessed April 26, 2007). The MDN became an official network in the National Atmospheric Deposition Program (NADP) in 1996. As of fall 2006, precipitation for Hg analysis was being collected from 89 sites in the United States, Canada, and Mexico (fig. 1). The NADP comprises three networks: the MDN, the National Trends Network (NTN), and the Atmospheric Integrated Research Monitoring Network (AIRMoN).

The U.S. Geological Survey (USGS) Branch of Quality Systems has been conducting external quality assurance (QA) programs for the NTN since the network's inception in 1978 and began QA monitoring for the MDN in 2004. The MDN QA programs are designed after the QA activities conducted for the NTN, incorporating methodologies acquired through many years of QA data acquisition.

Since 2004, the USGS has operated three external QA programs for the NADP/MDN. The aim of these QA programs is to identify and quantify sources of variability in total Hg concentration and deposition data collected by the NADP/MDN. Beginning in 2004, the USGS system blank program has assessed the effects of sample handling, shipping, and processing along with the effects of field exposure on MDN sample chemistry. The Mercury Analytical Laboratory (HAL) for the NADP/MDN is operated by Frontier GeoSciences, Inc., located in Seattle, Wash. The HAL analyzes all weekly precipitation samples collected by the NADP/MDN. The USGS interlaboratory comparison program, also initiated in 2004, evaluates the performance of the HAL.

Beginning in 2006, the blind audit program has assessed the variability and bias of analytical results produced by the HAL by disguising QA samples as weekly precipitation samples from MDN sites. The USGS collaborates with the HAL and the NADP Program Office in designing, implementing, and monitoring QA programs for the MDN.

Purpose and Scope of Report

This report documents methods used by the USGS for administering the external QA programs in support of the NADP/MDN. The external QA programs for the MDN evolved during the years 2004–2006. Procedural changes occurred as needed to improve data quality and to study

Figure 1. Map showing National Atmospheric Deposition Program/Mercury Deposition Network site locations, fall 2006 (Mercury Deposition Network, 2006).

different influences on Hg data quality. In each section of this report describing a QA program, a brief history is presented which describes the methods used to develop the program. Subsequently, methods used for solution preparation, sample processing, and data analysis are presented.

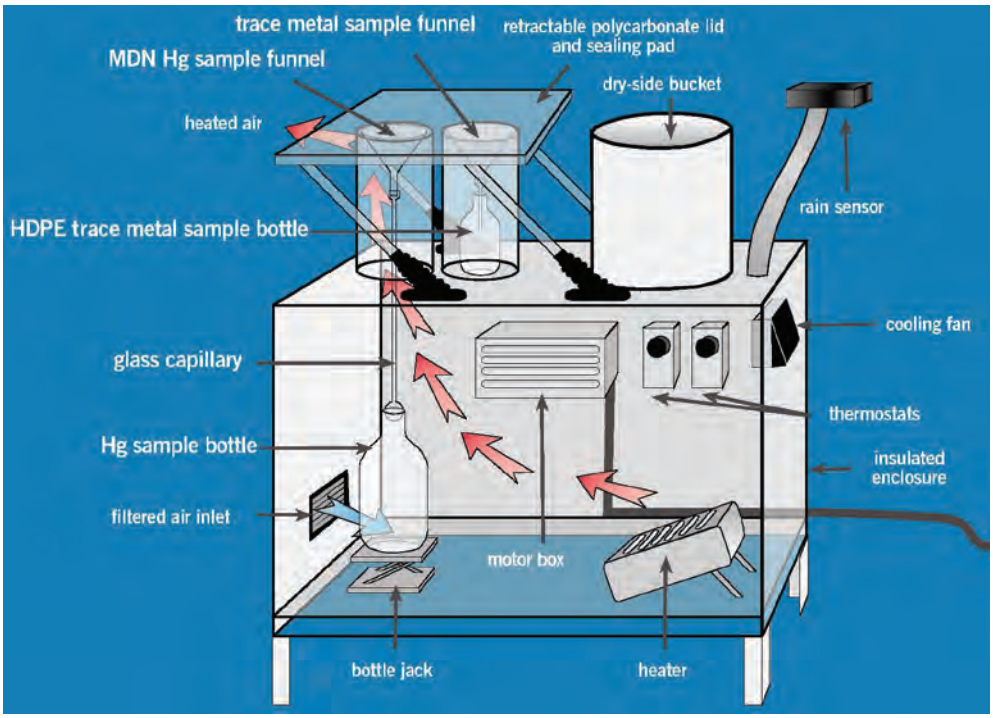

Figure 2. Schematic showing the sampling train in the National Atmospheric Deposition Program/Mercury Deposition Network precipitation collector manufactured by Loda Electronics.

Mercury Analytical Laboratory Internal Quality Assurance Activities

The HAL conducts its own QA investigations focusing on field activities and laboratory practices. The HAL field blank program assesses the influence of field exposure on Hg concentration during weeks with no precipitation. All MDN sample collection bottles are precharged with 20 mL of hydrochloric acid (HCl) preservative prior to field installation in the precipitation collector. The HAL continuously measures Hg concentrations in randomly selected precharged MDN bottles. These samples are called "bottle blanks." An MDN sample returned from the field to the HAL after a dry week is called a "field blank," which contains only the HCl precharge. Differences in Hg concentrations between field blanks and bottle blanks can indicate influences of field exposure resulting in Hg contamination. The HAL monitors laboratory practices to ensure acceptable data variability resulting from laboratory analysis by routinely analyzing preparatory blanks, ongoing calibration blanks, ongoing calibration standards, matrix duplicates, matrix spikes, and reference materials (Gerard Van der Jagt, Frontier GeoSciences, Inc., written commun., 2006). The USGS does not evaluate HAL's internal quality control data, but the internal quality control results may be used to help explain potential issues with the USGS external QA results.

Sample Collection in the NADP/MDN

For sample collection, the MDN uses (1) a modified Loda Electronics Model 2001 Precipitation Collector (*www.lodaelectronics.com*; accessed April 26, 2007), modeled after the Aerochem Metrics Model 301 (ACM) precipitation collector (Aerochem Metrics, Inc., Bushnell, Fla.) used by the NTN, and (2) an N-CON Systems MDN Sampler (N-CON Systems Co., Inc., 2004), which the NADP approved for precipitation collection by the MDN in 2006. The MDN site sponsors can choose either the Loda Electronics collector or the N-CON Systems collector for use at their site. The availability of multiple precipitation collectors to MDN sites promotes competition among manufacturers, which minimizes cost and prevents monopolism.

Figure 2 shows the sample collection train installed in the Loda Electronics MDN precipitation collector. The MDN collector is modified from the original NTN collector: in place of the wet-side bucket two smaller cylindrical inlets (known as chimneys), each with a 128-cm diameter, collect precipitation. The high density polyethylene (HDPE) collection bucket used by the NTN can be a source of contamination and is not suitable for the collection of Hg (Vermette and others, 1995). One of the chimneys, containing HDPE sampling train, collects precipitation for trace metal analysis, an option offered to MDN sites. However, these data are not reported by the NADP.

The primary chimney collects precipitation for total Hg analysis and holds a borosilicate glass funnel at the collection orifice. The funnel drains to an attached thin glass capillary tube, which empties into the 2-L glass sample collection bottle that has been precharged with 20 mL of 1 percent (volume/volume) hydrochloric acid (HCl). The sample collection bottle is contained in an overflow bucket. The HCl keeps Hg ions in solution, preventing them from volatilizing and from adhering to the glass walls of the sample bottle (Bob Brunette, Frontier GeoSciences, Inc., personal commun., 2004). During precipitation, a precipitation sensor activates the opening of a

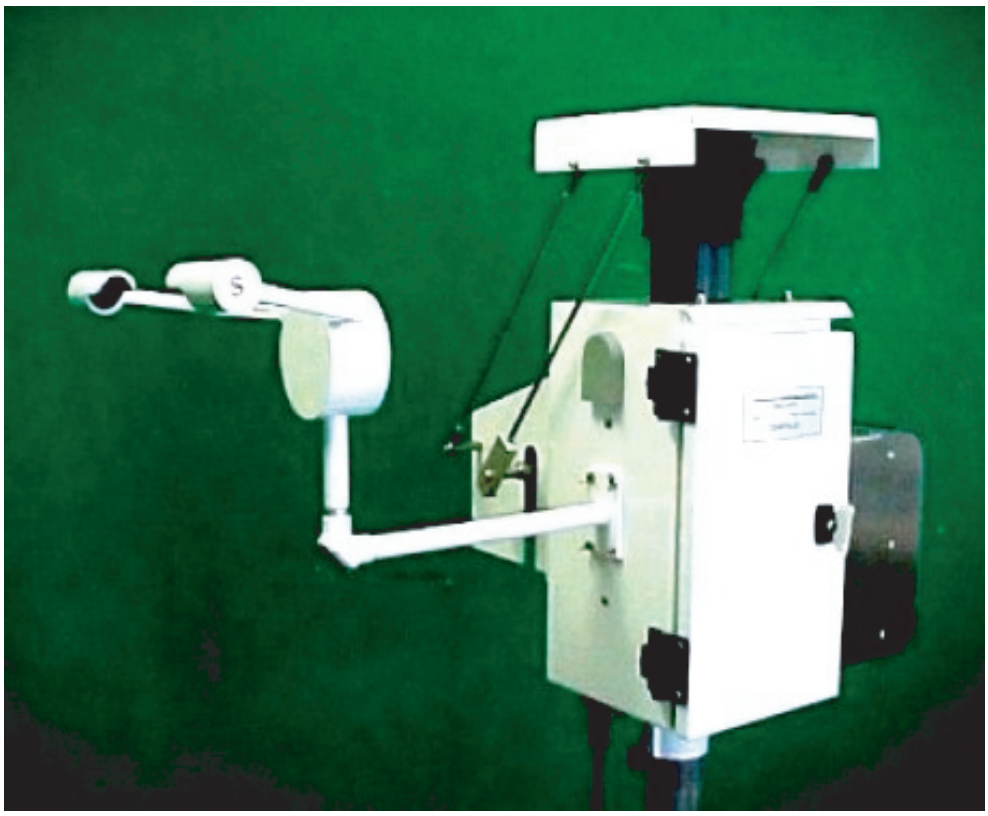

Figure 3. Photograph showing the National Atmospheric Deposition Program/Mercury Deposition Network precipitation collector manufactured by N-CON Systems (N-CON Systems Co., Inc., 2004).

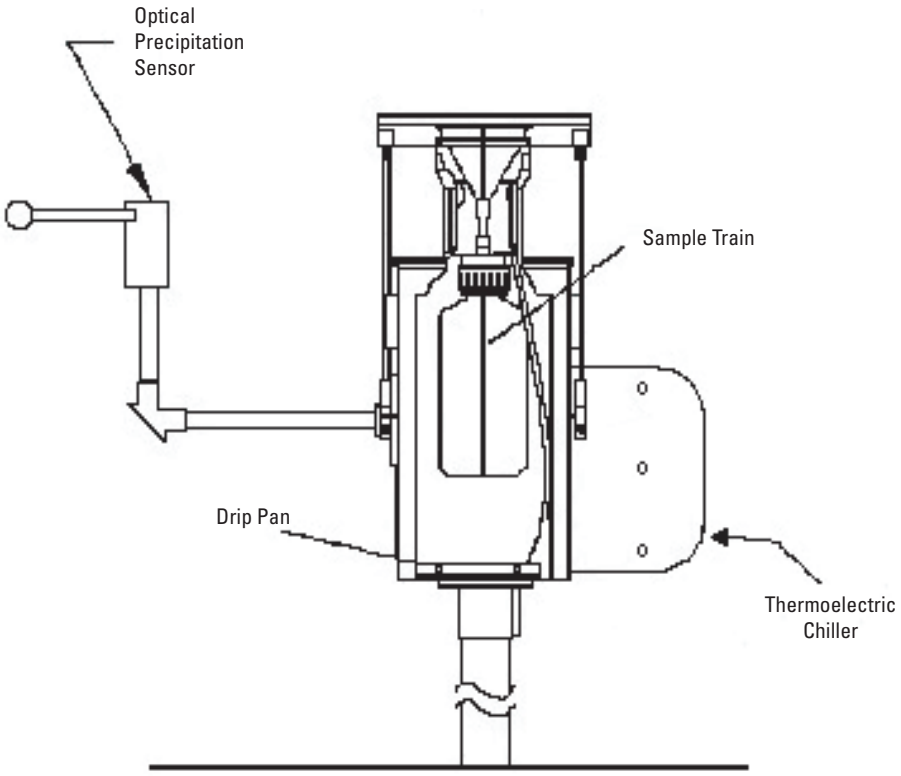

Figure 4. Schematic showing the sampling train in the National Atmospheric Deposition Program/Mercury Deposition Network precipitation collector manufactured by N-CON Systems (N-CON Systems Co., Inc., 2004).

lid, thus uncovering the chimneys and allowing for sample collection. When the precipitation ceases, the heated sensor dries and triggers the lid to close and cover the chimneys.

Figure 3 shows a photograph of the N-CON collector and figure 4 shows a schematic of the sample collection train installed in the N-CON collector. Identical sample collection apparatus (glass funnel, capillary tube, 2-L sample bottle) are installed in the Loda Electronics collector and the N-CON collector for precipitation collection. The N-CON collector has one opening for collection of wet deposition for Hg analysis and relies on an infrared precipitation sensor to trigger the opening of the lid for sample collection.

The collection apparatus is replaced with a clean glass sample train every Tuesday at each MDN site during the weekly site visit. The weekly precipitation sample and used glass sample train are mailed to the HAL. The glassware is cleaned and acid-leached in 30 percent HCl before being returned to a site for sample collection.

System Blank Program

The system blank program was initiated in 2004 to assess the effects of sample handling, shipping, processing, and field exposure on sample chemistry. The program evaluates the entire system of MDN sample collection. The system blank program mimics the field audit program operated for the NTN by the USGS (Wetherbee and others, 2006). Different solution volumes and mercury concentrations are used in the program to assess mercury contamination and loss resulting from sample collection.

Sample Processing

All MDN sites are supplied with a system blank sample to process annually. A dry week is required for processing the sample. If a dry week does not occur, the site operator is asked to return their unprocessed sample to the HAL for total Hg analysis and to participate again the following year. In December, prior to the beginning of the first quarter in January, all active MDN sites are scheduled to participate during a designated annual quarter of the following year. The number of active MDN sites is divided into four groups of 22 to 25 sites. Site operators are asked to process their system blank samples within six months of receiving the sample because experimental studies performed by the HAL confirm the stability of Hg for up to six months (Bob Brunette, Frontier GeoSciences, Inc., personal commun., 2004). Operators process the system blank sample on a Tuesday, to coincide with the weekly site visit when they collect the previous week's precipitation sample and replace the glass sample collection train.

For processing a system blank sample, the site operator is shipped a 125-, 500-, or a 1,000-mL solution along with a cover letter (appendix 1), instructions for processing the system blank sample (appendix 2), two MDN observer forms (MOFs) (appendix 3), and a stamped postcard addressed to the USGS for reporting sample processing and shipping information (appendix 4).

During a weekly site visit, prior to processing the system blank sample, the site operator must verify that no precipitation occurred during the preceding week for which the weekly sample is being collected. The rain gage chart is checked to ensure the collector lid did not open and uncover the sample train. Exceptions are made for sites located in areas with high humidity. For these sites, samples may be processed if the collector lid opened, as long as no precipitation was recorded and the operator is sure the lid opened solely as a result of high humidity. This exception allows the participation of more sites in the system blank program. Otherwise, some MDN sites would never meet the dry-week criteria. The operator must also verify that the collector worked properly during the preceding week, with no clock stoppages or pen skips on the event recorder chart.

To begin sample processing, the site operator, wearing a clean pair of laboratory gloves to avoid contaminating the sample, triggers the collector lid to open and expose the sample collection orifice. The site operator removes the system blank sample bottle from the plastic bag in which it was shipped and pours 50 percent of the solution into the glass precipitation collection funnel. The bottom of a line drawn on the solution bottle marks the 50-percent portion of the solution that should remain in the bottle. The glass precipitation collection funnel is located in the chimney that collects precipitation for total Hg analysis. The solution passes through the funnel and glass capillary tube into the sample collection bottle, entraining potential contaminants adhering to the glass walls as well as potentially losing Hg ions as they adhere to the sampling equipment. The portion of the solution that passes through the sample collection train is known as the system sample, while the portion of the system blank solution remaining in the original bottle is known as the bottle sample (Wetherbee and others, 2006). The site operator closes the system blank sample bottle with the screw lid and places the bottle in the original plastic bag in which it was shipped. The operator screws the cap onto the sample collection bottle which contains the 50 percent of the transferred system sample and the HCl preservative. This bottle is removed from the overflow bucket, placed into a sample bottle bag, and transferred to a shipping cooler.

The site operator completes two MOFs: one for the bottle sample and one for the system sample, listing sample processing and shipping dates. The same information is included in the postcard mailed to the USGS. The MOFs, the system sample, the bottle sample, and the rain gage chart are packaged in a shipping cooler that is routinely used to ship precipitation samples and mailed to the HAL. The postcard is mailed to the USGS, indicating the sample has been processed and mailed. A flowchart of the system blank program is shown in figure 5.

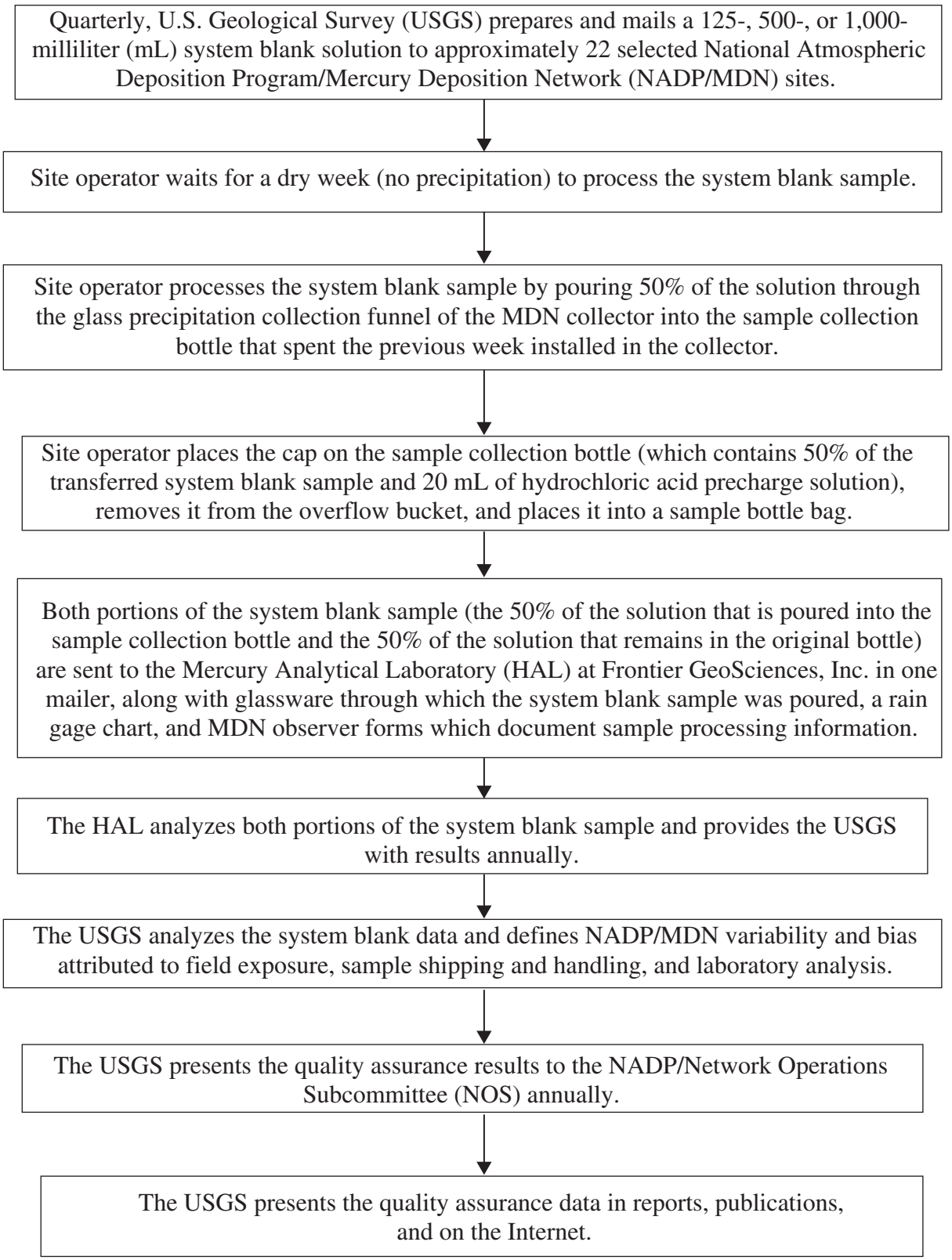

Figure 5. Flowchart for the National Atmospheric Deposition Program/Mercury Deposition Network system blank program.

System Blank Solution Preparation

The Hg concentrations in the solutions used in the system blank program are intended to represent the range of concentrations measured in precipitation samples collected by the NADP/MDN. At the start of the program, 2004–2006, solutions spiked with Hg were used in the system blank program. Three solutions, with different Hg concentrations, and three sample volumes are used in the system blank program to assess how sample-handling affects sample chemistry in solutions with different Hg concentrations and volumes. A description of the solutions and chemical compositions for the standard reference solutions used in the USGS system blank program is provided in table 1.

Solutions used in the system blank program have included (1) low-concentration standard reference samples, prepared by High-Purity Standards, Inc. (HPS; Charleston, S.C.) and diluted by the USGS, (2) low-concentration standard reference samples, prepared by HPS, and diluted and spiked with Hg by the USGS, and (3) Ultrapure deionized water with a measured resistivity greater than 16.7 megohm (DI). System blank data are used to determine influences of the sampling process on Hg concentrations as precipitation passes through the glass sample train. Therefore, system blank solutions are not preserved with HCl, which could leach Hg ions from the sampling glassware and not replicate natural conditions.

In 2004, diluted low-concentration standard reference samples and DI were used to make system blank solutions. In 2005, the USGS began spiking the diluted low-concentration standard reference samples with Hg and continued to spike solutions through the second quarter of 2006. The USGS-designated mercury precipitation (MP) spikes, MP3 and MP4 Hg spikes with target Hg concentrations of 14.3 and 20.0 ng/L respectively, were used for the system blank samples.

Hg spiking of the system blank samples was discontinued during the third quarter of 2006. Large discrepancies in Hg concentrations between the system samples and the corresponding bottle samples raised concerns that samples were being mishandled or that the analytical data were being misinterpreted. Measured Hg concentrations in the system samples were lower than Hg concentrations in the bottle samples. Analysis of the data showed that Hg spike recovery may not be possible with unpreserved system blank sample aliquots. Without an HCl preservative, Hg ions in the original system blank container were assumed to have adsorbed to the container walls and Hg was not uniformly transferred to the sample collection bottle. As of the third quarter of 2006, only low-concentration standard reference solutions and DI solutions, with no additional Hg, are used in the system blank program to monitor contamination from field exposure, sample handing and shipping, and laboratory analysis.

During 2004, the first year of the system blank program, ultraclean glass sample bottles, manufactured by I-CHEM (*http://www.ichembrand.com/*; accessed April 26, 2007) and guaranteed to meet the U.S. Environmental Protection Agency's performance-based specifications for metals analysis, were used to store the system blank samples. Despite stringent shipping methods, the glass bottles were often damaged or leaked during transit from the USGS to the MDN sites. Teflon® bottles replaced the glass bottles in 2005, eliminating the disqualification of many damaged samples and resulting loss of data. Teflon bottles are used for collection of natural waters because they have been proven to contribute the least contaminants to the sample (Moody and Lindstrom, 1977). Teflon bottles are reused by the USGS for the MDN system blank and MDN interlaboratory comparison programs. The HAL receives Teflon bottles from site operators participating in the system blank program and from laboratories participating in the interlaboratory comparison program. The HAL cleans the Teflon bottles with HCl to leach Hg and other contaminants and returns the cleaned bottles to the USGS for reuse.

A DI sample is collected prior to system blank sample preparation, and a second DI sample is collected after all system blank sample bottles are filled. The DI is the same water matrix used to dilute the standard reference solutions for the system blank samples. The DI samples are collected in the same Teflon bottles used to bottle the system blank samples. The HAL analyzes these two DI samples for total Hg a week prior to system blank sample mailing to ensure the system blank samples are not contaminated with Hg. This procedure was initiated in 2004 after system blank samples had higher than expected Hg concentrations resulting from the use of contaminated DI.

Solutions used for the system blank program were changed in 2006. Solutions provided by HPS are used for both the MDN and NTN external QA programs. The solution chemistry used for the NTN QA programs was re-evaluated for 2006 and the solution matrices were changed to reflect the current precipitation chemistry collected by NADP/NTN sites. The change in solution types provided by HPS affected the solutions used for the MDN system blank program: solutions SP-97 and SP-98 were replaced by solutions SP-2 and SP-3. The MDN sites are randomly assigned a specific volume and solution type for the system blank program. Distribution of the solutions and their respective volumes used in the system blank program during 2006 are listed in table 2.

Data Analysis

Each quarter, the USGS records a description of the system blank solutions and corresponding volumes sent to each participating site in the MDN logbook and a Microsoft Excel workbook. Site operators mail the pre-addressed postcards to the USGS after processing the system blank samples. The USGS personnel transfer information from the postcards to the system blank program database, enter the date the card was returned to the USGS in the MDN logbook, and file the postcard for record. Card submission is evidence that the system blank sample has been submitted to the HAL.

The HAL supplies the USGS with analytical results from the system blank program on a yearly basis. The USGS makes

Table 1. Mercury concentration values for solutions used in the U.S. Geological Survey system blank program for the National Atmospheric Deposition Program/Mercury Deposition Network.

[all units are mercury concentration values in nanograms per liter; ng/L, nanograms per liter; Hg, mercury; SP, synthetic precipitation; Q1, 25th percentile; Q3, 75th percentile]

Solution	Agency preparing the solution	Description	Q1	Median	Q3	Year used
Ultrapure, 1% hydrochloric acid blank[a]	U.S. Geological Survey	Deionized water with a measured resistivity greater than 16.7 megohm, preserved with hydrochloric acid.	0.50	0.77	1.10	2004–2006
SP-2[b]	High-Purity Standards, Inc	National Institute of Standards and Technology certified reference solutions prepared by High-Purity Standards, Inc. and diluted by the U.S. Geological Survey.	0.03	0.03	0.05	2004,
SP-3[b]	U.S. Geological Survey		0.01	0.02	0.05	July–Dec. 2006
SP-97[c]	High-Purity Standards, Inc.,	National Institute of Standards and Technology certified reference solutions prepared by High-Purity Standards, Inc. and diluted by the U.S. Geological Survey.		0.36		2004
SP-98[d]	U.S. Geological Survey			0.02		
SP-97+14.3 ng/L Hg spike[e]	High-Purity Standards, Inc.,	National Institute of Standards and Technology certified reference solutions prepared by High-Purity Standards, Inc., diluted and spiked with Hg, preserved with 1% hydrochloric acid by the U.S. Geological Survey.				2005
SP-98+20.0 ng/L Hg spike[e]	U.S. Geological Survey					
SP-2+20.0 ng/L Hg spike[e]						Jan.– June 2006
SP-3+20.0 ng/L Hg spike[e]						

[a] Concentrations calculated using Mercury Deposition Network interlaboratory comparison data submitted by six laboratory participants from 2004 through July 2006.

[b] Concentrations calculated using Mercury Deposition Network system blank data for 2004.

[c] Concentration is derived for one system blank sample analyzed during 2004.

[d] Concentration is the average of the only two available system blank samples analyzed during 2004.

[e] Concentrations for system blank solutions spiked with mercury were not considered accurate and were not calculated for these.

Table 2. Solution names, sample volumes, and approximate number of samples used in U.S. Geological Survey system blank program for the National Atmospheric Deposition Program/Mercury Deposition Network during 2006.

[mL, milliliters; HCl, hydrochloric acid; SP, synthetic precipitation]

Solution name	Sample volume (mL)	Number of samples
Ultrapure, 1% HCl blank	125	10
Ultrapure, 1% HCl blank	500	10
Ultrapure, 1% HCl blank	1,000	10
SP-2	125	10
SP-2	500	10
SP-2	1,000	10
SP-3	125	10
SP-3	500	10
SP-3	1,000	10

statistical interpretations of analytical data, which are published in annual reports (Wetherbee and others, 2004; Wetherbee and others, 2006), posted on the Internet (*http://bqs.usgs.gov/precip/new/frontpage_home.htm*; accessed April 26, 2007), and presented to the NADP/Network Operations Subcommittee (NOS). All system blank data are archived in SAS datasets and Microsoft Access databases, which are stored on a USGS file server.

The HAL analyzes both the system sample and the bottle sample for total Hg, and provides two sets of analyses for each system blank sample to the USGS for statistical data analysis and reporting. The USGS calculates system-minus-bottle differences. Paired concentration differences between the system sample and the bottle sample may indicate network bias due to possible contamination or Hg loss during standard handling and processing of precipitation samples. Positive system-minus-bottle differences indicate Hg contamination of the system sample during its handling and exposure to sampling equipment. Quantifying differences in Hg concentration between the system sample and the minimally-handled bottle sample provides information for deducing Hg concentration in precipitation samples prior to their exposure to sources of sampling variability. Selected statistics (from SAS software) used for reporting the system-minus-bottle differences include median and other quartile values, the f-pseudosigma, and upper confidence limits. Examples of these statistics are presented in the annual reports for the USGS QA programs (Wetherbee and others, 2006).

Interlaboratory Comparison Program

The purposes of the MDN interlaboratory comparison program are to (1) quantify the uncertainty of chemical analyses determined by the HAL through comparison of the results with those produced by participating laboratories, (2) evaluate the analytical precision and accuracy of data produced by participating laboratories, and (3) enable comparison of laboratory data produced by other wet-deposition monitoring networks. The program requires participating laboratories to analyze DI solutions spiked with Hg or unspiked DI samples using U.S. Environmental Protection Agency Method 1631 (U.S. Environmental Protection Agency, 2002) or an equivalent atomic fluorescence spectrometry method. A flowchart of the MDN interlaboratory comparison program is provided in figure 6.

The MDN interlaboratory comparison program was initiated in January 2004, with four participating laboratories: (1) HAL; (2) IVL Swedish Environmental Research Institute in Göteborg, Sweden (IVL); (3) North Shore Analytical, Inc., in Duluth, Minn. (NSA); and (4) USGS Wisconsin Mercury Research Laboratory in Middleton, Wis. (WML). Two additional laboratories joined the program in July 2004: (1) ACZ Laboratories, in Steamboat Springs, Colo. (ACZ), and (2) Northern Lake Service, Inc., in Crandon, Wis. (NLS).

Single-blind samples are those that are identified to the laboratories as QA samples but whose chemical characteristics are not known to the laboratories. From 2004 through June 2006, HAL, NSA, and NLS received four single-blind samples from the USGS every 2 weeks for chemical analysis; ACZ, IVL, and WML received two single-blind samples every month. As of July 2006, HAL, NSA, and NLS receive four single-blind samples every month; ACZ, IVL, and WML continue to receive two single-blind samples every month. Results submitted by the participating laboratories are compiled, analyzed, posted on the Internet (*http://bqs.usgs.gov/precip_2/mdn/index.html*; accessed April 26, 2007), published in annual reports, and presented to the NADP/NOS at semiannual meetings.

Preparation of Samples and Solutions

Samples for the interlaboratory comparison program are shipped by the USGS to the participating laboratories. Each laboratory receives samples derived from the same solutions for each mailing. Solutions that have been used in the program consist of (1) natural precipitation collected in Arvada, Colo., using an NTN Aerochem Metrics precipitation collector, (2) DI solutions spiked with Hg in a 1 percent HCl matrix, (3) DI solutions in 1 percent HCl, and (4) USGS standard reference water sample P41 (used for two sample mailings during 2004) (*http://bqs.usgs.gov/srs/SRS_Fall03/P.xls*; accessed April 26, 2007). As of July 2006, only the synthetic DI solutions spiked with Hg in a 1 percent HCl matrix and DI solutions in 1 percent HCl are used in the program.

Solutions are made in 4-L flasks. These flasks are stored in a fume hood and filled with 10 percent HCl storage solution when not in use. Prior to solution preparation, the storage solution is emptied into an approved waste receptacle for proper neutralization and disposal and the flask is rinsed 3 times with DI. For each sample mailing, an attempt is made to minimize

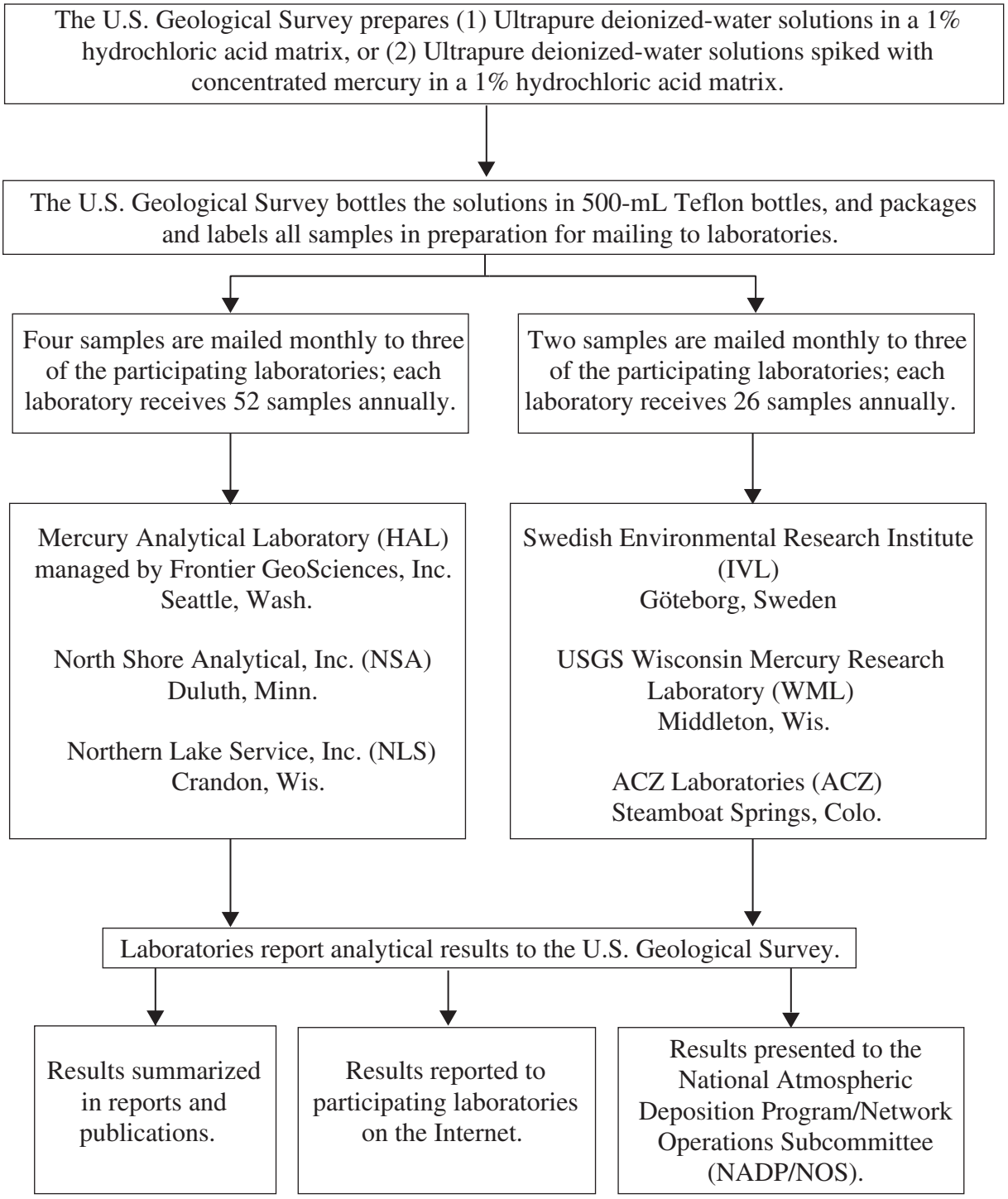

Figure 6. Flowchart for the National Atmospheric Deposition Program/Mercury Deposition Network interlaboratory comparison program.

solution volume to minimize storage solution waste. Three solutions are prepared for each mailing to the six laboratories. The same solution distributed to each laboratory in a monthly mailing must be derived from the same well-mixed solution in a flask, as the use of different batches of the same solution imparts variability on the results that cannot be differentiated from laboratory performance.

All interlaboratory comparison samples are labeled with a unique 10-digit sample number assigned by the USGS. The 10-digit sample identification is assigned as follows: the first 4 digits of the 10-digit sample number represent the year during which the study is conducted, followed by the 3-digit Julian date of sample mailing, and the unique 3-digit identification of the sample, ranging from 001 to 018. Each laboratory receives samples with the same last 3-digit identifications for each sample mailing. For example, four interlaboratory comparison samples mailed to the HAL on June 26, 2006, would have the following identifications: 2006177001 through 2006177004.

A random schedule of the monthly solution distribution is generated annually. An example solution distribution schedule is included in tables 3 and 4, for laboratories receiving four monthly samples and for laboratories receiving two monthly samples, respectively. Annually, 52 samples are distributed to each laboratory receiving four monthly samples. Of the 52 samples, the USGS prepares 8 DI solutions and 44 DI solutions spiked with Hg. Laboratories receiving two monthly samples analyze 26 samples annually. Of the 26 samples, the USGS prepares 6 DI solutions and 20 DI solutions spiked with Hg. Table 5 lists descriptions, including Hg concentration values, of solutions that have been used in the USGS interlaboratory comparison program for the MDN.

Natural Precipitation Solutions

Natural precipitation solutions, known as HALNAT solutions, were used in the MDN interlaboratory comparison program from September 2004 through May 2006. The USGS selected weekly natural precipitation samples collected in Arvada, Colo., using an NADP/NTN Aerochem Metrics wet-deposition collector for use in the interlaboratory comparison program. Weekly precipitation samples were composited to obtain sufficient volume of a homogeneous solution for sample mailing to all laboratory participants. The precipitation solutions were combined in a volumetric flask and mixed on a magnetic stirrer with a Teflon-coated magnetic stir bar. Quantities of HCl and Hg were not added to these natural matrix solutions. The USGS bottled the precipitation aliquots in 500-mL Teflon containers. The USGS did not analyze the samples for target values prior to shipping the samples to the

Table 3. Example of sample mailing schedule for U.S. Geological Survey interlaboratory comparison program participants: Mercury Analytical Laboratory, North Shore Analytical, Inc., and Northern Lake Service, Inc.—each receiving four monthly samples.

[MP, mercury precipitation]

Mailing number	Sample mailing date	MP1	MP2	MP3	MP4	Blank
1	January 9	1	1			2
2	February 6	2	1	1		
3	March 6		2		1	1
4	April 3	1		2	1	
5	May 1			1	2	1
6	May 29	2		1	1	
7	June 26	1	2	1		
8	July 24		1	2		1
9	August 21	1	1		2	
10	September 18			2	1	1
11	October 16	1	1		2	
12	November 13		2	1		1
13	December 11	2			1	1
Sample total		11	11	11	11	8

Table 4. Example of sample mailing schedule for U.S. Geological Survey interlaboratory comparison program participants: ACZ Laboratories, U.S. Geological Survey Wisconsin Mercury Research Laboratory, and IVL Swedish Environmental Research Institute—each receiving two monthly samples.

[MP, mercury precipitation]

Mailing number	Sample mailing date	MP1	MP2	MP3	MP4	Blank
1	January 9	1	1			
2	February 6		1	1		
3	March 6				1	1
4	April 3	1			1	
5	May 1			1		1
6	May 29			1	1	
7	June 26	1		1		
8	July 24		1			1
9	August 21	1	1			
10	September 18				1	1
11	October 16	1	1			
12	November 13			1		1
13	December 11				1	1
Sample total		5	5	5	5	6

participating laboratories. Natural precipitation samples were kept refrigerated before being used in the program.

The use of HALNAT solutions was discontinued in June 2006 because analytical results for these solutions were highly variable among the participating laboratories. Windborne contaminants and bugs can be entrained in NADP precipitation samples and the HALNAT solutions were not filtered prior to being sent to the laboratories. Even though particulates were not observed in the solutions, variable laboratory results may have been due to the presence of particulate-bound Hg, heterogeneously distributed in the solutions. Natural precipitation samples may be reintroduced to the interlaboratory comparison program, however the bulk solutions will have to be filtered and acidified prior to splitting the solutions to ensure homogenous composition.

Spiked Mercury Solutions

Four solutions with specific Hg concentrations are used in the MDN interlaboratory comparison program. The USGS prepares solutions with approximate Hg concentrations that span the interquartile range (25th percentile to 75th percentile of concentrations) in precipitation collected by the MDN. For precipitation collected by the MDN from 1995 through 2004, the Hg concentration interquartile range is 5.8 to 15.0 ng/L. For QA sample preparation, USGS spikes DI with a diluted National Institute of Standards and Technology (NIST) Hg standard to produce target concentrations between 5.7 and 20.0 ng/L. The target Hg concentrations will change as needed to reflect Hg concentrations in precipitation collected by the MDN.

Hydrochloric acid is added to Hg-spiked solutions, keeping Hg in solution by preventing Hg from volatilizing and adhering to the glass flasks and Teflon bottles. The USGS prepares two HCl solutions diluted to 10 percent (volume/volume). The HCl storage solution, purchased from the USGS supply, is used to fill flasks and beakers during storage when they are not being used to prevent contaminants from adhering to the glass walls. The storage HCl has a certified Hg content less than 500 parts per trillion. The HCl, with a certified Hg content less than 100 parts per trillion (certificate of analysis for Baseline® HCl obtained from Seastar Chemicals, Vancouver, British Columbia, Canada, *http://www.seastarchemicals.com/cgi-bin/sci.exe?sproduct=BL04_ HydrochloricAcid*; accessed April 26, 2007), is added to the diluted Hg standards, Hg-spiked solutions, and blank solutions to yield a final HCl concentration of 1 percent.

In 2003, the USGS purchased Standard Reference Material 3133, Lot Number 991304, with a gravimetric certified Hg value of 10.00 mg/g ± 0.02 mg/g from NIST (*https://srmors.nist.gov/view_detail.cfm?srm=3133*; accessed April 26, 2007) for preparing Hg-spiked solutions. The Hg standard was diluted to ease regularly scheduled preparation of low-concentration Hg-spiked synthetic wet-deposition samples. First, an intermediate standard with an Hg concentration of 125.25 mg/L in 1 percent Baseline® HCl was prepared by pipetting 12.525 g of the standard stock solution into a 1-L flask and bringing to volume with DI and 100-mL of 10 percent (volume/volume) Baseline® HCl. Then, after thorough mixing, 1 mL of this intermediate standard was further diluted in a 1-L flask with DI and 100-mL of 10 percent (volume/volume) Baseline® HCl to yield the final standard with a calculated Hg concentration of 125.25 µg/L preserved in 1 percent Baseline® HCl. The additional dilution was required to enable the USGS to accurately formulate solutions with Hg concentrations in the parts per trillion range (ng/L). In October 2003, HAL analyzed the final standard and reported an Hg concentration of 121 µg/L. This value was used to determine target concentrations of prepared solutions spiked with the Hg standard.

Periodically, the HAL analyzes the Hg standard for the USGS because the Hg concentration decreases slightly with time, probably through volatilization. This ensures the target Hg concentrations in prepared QA samples are well known to the USGS. The measured Hg concentration of the standard was 114.5 µg/L in May 2005, suggesting an approximate negative monthly Hg difference of 0.3 µg/L since the previous analysis in October 2003. The Hg standard has been used for preparing spiked Hg samples for the interlaboratory comparison program, the system blank program, and the blind audit program.

For spiking solutions, a microliter-range pipette is used to measure the small volumes of Hg standard. Prior

Table 5. Mercury concentration values for solutions used in the U.S. Geological Survey interlaboratory comparison program for the National Atmospheric Deposition Program/Mercury Deposition Network.

[all units are mercury concentration values in nanograms per liter; ng/L, nanograms per liter; Hg, mercury; MP, mercury precipitation; Q1, 25th percentile; Q3, 75th percentile; HALNAT, natural precipitation solution collected by the U.S. Geological Survey in Arvada, Colo.]

Solution	Agency preparing the solution	Description	Q1	Median	Q3	Year used
HALNAT[a]	U.S. Geological Survey	Natural wet-deposition collected using an Aerochem Metrics collector at a U.S. Geological Survey experimental site located in Arvada, Colo., and bottled by the U.S. Geological Survey.	2.03	3.91	6.20	2004–June 2006
Ultrapure, 1% hydrochloric acid blank[a]	U.S. Geological Survey	Deionized water with a measured resistivity greater than 16.7 megohm, preserved with hydrochloric acid.	0.50	0.77	1.10	2004–2006
MP1 (5.7 ng/L Hg spike)[a]	U.S. Geological Survey	Deionized water with a measured resistivity greater than 16.7 megohm, spiked with Hg, preserved with 1% hydrochloric acid.	6.10	6.52	7.04	2004–2006
MP2 (8.6 ng/L Hg spike)[a]			8.90	9.38	10.00	
MP3 (14.3 ng/L Hg spike)[a]			14.90	15.72	17.00	
MP4 (20.0 ng/L Hg spike)[a]			20.00	21.32	23.00	
P41	U.S. Geological Survey	USGS standard reference water sample.	0.30	0.55	1.56	2004

[a] Concentrations calculated using Mercury Deposition Network interlaboratory comparison data submitted by six laboratory participants from 2004 through July 2006.

to use, the pipette is checked for calibration by weighing known volumes of reagent water and recording the measurements in a logbook. Five gravimetric measurements are recorded for each volume between 100 µL and 1,000 µL, in increments of 100 µL. The average of the five measurements for each volume is plotted and a least-squares regression equation is generated which can be used to estimate the appropriate pipette settings to use for specific volumes. Table 6 lists the volumes of Hg standard required to prepare spiked Hg solutions with specific target values used in the interlaboratory comparison program, the system blank program, and the blind audit program. The solution Hg concentrations listed in tables 1, 5, and 7 are median values for numerous analyses of the solutions, and thus are considered the most probable values (MPVs). The target Hg concentration values listed in table 6 are considered approximate, as they are calculated by the USGS during sample preparation.

Table 6. Required volumes of diluted mercury standard for preparing 4-L batches of spiked solutions used for U.S. Geological Survey external quality assurance programs for the National Atmospheric Deposition Program/ Mercury Deposition Network.

[mL, milliliters; ng/L, nanograms per liter; MP, mercury precipitation]

Solution name	Diluted mercury standard volume (mL)[a]	Target value (ng/L)
MP1[b,c]	0.200	5.7
MP2[b]	0.300	8.6
MP3[b,c,d]	0.500	14.3
MP4[b,d]	0.700	20.0

[a] Volume is calculated for samples made with a standard having a mercury concentration of 114.5 micrograms per liter.
[b] Solution used in the interlaboratory comparison program.
[c] Solution used in the blind audit program.
[d] Solution used in the system blank program.

For preparing an Hg-spiked solution, a 4-L volumetric flask is filled approximately 75 percent full with DI and then 400 mL of 10 percent (volume/volume) Baseline® HCl is added. Finally, the appropriate volume of Hg standard is added, and the flask is diluted to volume with DI. The solution is mixed for approximately 15 minutes on a magnetic stirrer with a Teflon-coated magnetic stir bar. The USGS bottles the solution aliquots in 500-mL Teflon containers and mails them to laboratory participants.

Ultrapure Deionized Water Solutions

Ultrapure deionized water solutions are used for samples in the interlaboratory comparison program to detect low-level laboratory contamination. The 4-L volumetric flask used for preparing blank solutions is stored filled with 10 percent (volume/volume) HCl storage solution. This flask is only used to make blank solutions for the MDN QA programs and Hg is never added to this flask. The DI blanks are prepared in the 4-L volumetric flask by combining 3.6 L of DI with 400 mL of 10 percent HCl Baseline® solution to yield a DI solution preserved with 1 percent HCl.

Sample Mailing to Laboratory Participants

Interlaboratory comparison samples are mailed biweekly to participating laboratories on a Tuesday morning in Teflon sample bottles which have been acid-washed and dried by the HAL and mailed to the USGS. These bottles are not conditioned with the solution prior to being filled. The QA solutions are poured directly into the bottles.

A USGS label is affixed to each 500-mL sample bottle, identifying the sample as an interlaboratory comparison solution, listing the laboratory recipient name and the assigned 10-digit USGS identification number. Each bottle is sealed in two Ziploc® bags. Because the cardboard boxes in which the samples are shipped to the laboratories can be a source of Hg (Chris Geske, Northern Lake Service, Inc., personal commun., 2005), the double bags help protect the samples from contamination. The USGS attempted to place identification labels on the Ziploc bags instead of the bottles to ease the effort of bottle cleaning, making label-removal unnecessary. A laboratory participant expressed disapproval citing the ease of separating unmarked bottles from their corresponding bags and sample identifications. Therefore, identification labels are placed directly on each bottle.

For each monthly mailing, four samples are placed into a cardboard shipping container and mailed to the HAL, NSA, and NLS; while WML, ACZ, and IVL receive two samples in a padded envelope. The samples are not chilled with ice packs, like NTN QA solutions, because they are preserved with HCl, and MDN precipitation samples are not kept cold during shipment. A cover letter is included with each set of samples listing the sample identification numbers and the requested analyte determinations (appendix 5). Upon completion of analysis, laboratories are asked to mail the empty Teflon bottles to the HAL where they are acid-rinsed and returned to the USGS for reuse in the interlaboratory comparison program. Instructions for returning the Teflon bottles to the HAL and a preaddressed, postage-paid padded envelope are included with the interlaboratory comparison samples.

Data Records

Participating laboratories provide analytical results to the USGS in electronic format including Microsoft Excel and portable document format (PDF). Data are compiled in a Microsoft Access database, processed, and graphically displayed using SAS Institute Inc. (SAS) software. The data are presented in control charts on the Internet (*http://bqs.usgs.gov/precip/new/mdninterlab_frontpage_data.htm*; accessed April 26, 2007), an example of which is included in appendix

Table 7. Mercury concentration values for solutions used in the U.S. Geological Survey blind audit program for the National Atmospheric Deposition Program/Mercury Deposition Network.

[all units are mercury concentration values in nanograms per liter; ng/L, nanograms per liter; Hg, mercury; SP, synthetic precipitation; Q1, 25th percentile; Q3, 75th percentile]

Solution	Agency preparing the solution	Description	Q1	Median	Q3	Year used
Ultrapure, 1% hydrochloric acid blank[a]	U.S. Geological Survey	Deionized water with a measured resistivity greater than 16.7 megohm, preserved with hydrochloric acid.	0.50	0.77	1.10	2006
SP-2+5.7 ng/L Hg spike SP-2+14.3 ng/L Hg spike[b]	High-Purity Standards, Inc., U.S. Geological Survey	National Institute of Standards and Technology certified reference solutions prepared by High-Purity Standards, Inc., diluted and spiked with Hg, preserved with 1% hydrochloric acid by the U.S. Geological Survey.	2.93	4.25 14.05	6.0	2006

[a] Concentrations calculated using Mercury Deposition Network interlaboratory comparison data submitted by six laboratory participants from 2004 through July 2006.

[b] Concentration is the mean of the only two available blind audit samples spiked with 14.3 ng/L of Hg analyzed during 2006.

6. Each laboratory's data are only accessible by the individual laboratory and the USGS by way of password-protected web pages.

Results for laboratories participating in the interlaboratory comparison program are posted on the Internet as analyses are received. The frequency of data reporting throughout the year varies for the individual laboratories. The data are posted on the Internet within one week of receipt of the data. Median concentrations for each solution are calculated as data are reported throughout the year. The USGS does not assign calculated target values based on the dilution of known Hg spike concentrations because the low-concentration solutions are difficult to prepare precisely. Median values calculated for each solution from submitted results are considered a more accurate measure of the MPVs of the solutions.

Two kinds of bias are investigated in the interlaboratory comparison program. Interlaboratory bias (bias among participating laboratories) is determined by systematic differences of reported values from the median values determined from all participating laboratories. Intralaboratory bias (bias within a single laboratory) is identified by a systematic difference between the reported and expected values, at least as a preliminary indication.

Interlaboratory results are graphically presented on control charts. The control charts are used to identify potential systematic error that might affect the quality of a laboratory's data. Consistent, acceptable laboratory performance is indicated when the data remain within the control limits on the control charts. Positive and negative bias is indicated when data consistently exceed or are less than the control limits. Results for detected total Hg in the DI solutions are displayed in a plot showing the distribution of Hg concentrations reported by each laboratory; a line is graphed at the median Hg concentration for the DI solutions calculated from all reported results (appendix 7). For a complete explanation of statistical methods used to interpret USGS external QA program data, see Wetherbee and others (2004).

Blind Audit Program

The blind audit program for the MDN was initiated to assess the variability and bias of laboratory analysis of precipitation samples. The blind audit samples, whose Hg concentrations are known to the USGS, are disguised to the HAL as environmental precipitation samples. Differences between Hg concentrations reported for the blind audit samples and target values, determined by the USGS using interlaboratory comparison data, provide an insight into variability and bias resulting from laboratory analysis. A pilot MDN blind audit study was conducted in June 2005 to identify and remedy problems, and the program was implemented in January 2006.

Sample Processing

Approximately 20 MDN sites are chosen to process a blind audit sample annually. During 2006, the MDN collectors had to be co-located with NTN sampling equipment to be considered for blind audit participation. The co-located NTN and MDN precipitation samplers share a precipitation rain gage whose chart shows the precipitation depth, along with two event records for the NTN and the MDN collector lid openings. The original weekly rain gage chart from a co-located site is mailed to the Central Analytical Laboratory along with the NTN precipitation sample, and a copy of the rain gage chart is mailed to the HAL in the same cooler containing the MOF and MDN precipitation sample. During 2006, USGS personnel thought that an authentic rain gage chart could not be created in the laboratory, consequently exposing the QA identity of the sample to the HAL personnel. The submittal of a photocopied and therefore, less legible weekly rain gage chart to the HAL with the QA sample helped disguise a USGS laboratory-created rain gage chart. Beginning in 2007, sites will not have to be co-located with NTN equipment to participate in the blind audit program because the USGS has refined the production of laboratory-created rain gage charts and now are less likely to be distinguishable from real rain gage charts.

In 2006, experimental fake rain gage charts were prepared using several methods. Laboratory-created rain gage charts were made using Adobe Photoshop. A blank rain gage chart was scanned and saved in a graphic format. Event recorder and precipitation depth lines, consistent with sample volume, were drawn on the graphic file and printed. The site operator was asked to fill in the pertinent weekly information on the laboratory-created rain gage chart, including site identification, time on, time off, and precipitation depth. The site operator copied this chart and shipped the copy along with the blind audit sample to the HAL. While this method produced believable laboratory-created rain gage charts, problems arose when the number of participants in the blind audit program had to be increased. The MDN sites without co-located NTN equipment now had to be included. These MDN sites send in original rain gage charts, so photocopying could not be relied upon to help disguise the laboratory-created charts; photocopies would no longer be believable. Believable event records and precipitation depths had to be transcribed to original Belfort charts to avoid raising suspicions at the HAL as to the identity of the QA samples. The USGS attempted to produce laboratory-created rain gage charts using a Belfort precipitation recording drum attached to the base mechanism, which had been removed from the rain gage's housing and placed on a laboratory workbench. A specified volume of water was poured into the collection bucket and the depth was recorded on the rain gage chart. These charts were mailed to site operators, who were asked to fill in the weekly information and mail the chart with the blind audit sample to the HAL. Unfortunately, using the Belfort mechanism to make the laboratory-created rain gage charts took a long time and it was difficult to regulate the water flow over a specified duration to produce

believable precipitation depth. Consequently, the USGS attempted to draw the event record and precipitation depth, using the same color of ink as that used by Belfort rain gages. This procedure produced the most believable laboratory-created rain gage charts and was used to produce fake rain gage charts for blind audit samples mailed to site operators during 2007. However, purposeful splotches of ink and ruffling of the chart were necessary to replicate the wear that paper charts experience under field conditions. The laboratory-created rain gage charts, recording depth corresponding to blind audit sample volumes, are mailed with the blind audit samples to MDN sites.

In December each year, samples are prepared and mailed to sites chosen to participate in the blind audit program during the following year. Sites are asked to process the sample within a year of receiving the sample. Operators process the blind audit sample on a Tuesday, to coincide with the weekly site visit when they collect the previous week's precipitation sample and replace the sample collection glassware. A dry week, when no precipitation occurs and the collector lid does not open to expose the sample train (figs. 2 and 4), is required for processing a blind audit sample. If a dry week does not occur during the year, the site is asked to return their unprocessed sample to the HAL and the site is asked to participate again the following year.

The unprocessed sample is analyzed by the HAL to determine if Hg concentrations change during storage. It is suspected that Hg concentrations decrease through volatilization. The Hg concentrations are closest to the target value for blind audit samples that are processed soon after receipt by the site operator. The Hg concentrations generally decrease for samples that are stored for longer durations. If these preliminary interpretations are correct, the blind audit program will have to be modified to ensure that laboratory performance alone is being evaluated, without influences of Hg concentration decreases resulting from extended sample holding times.

The Hg concentrations in the solutions used in the blind audit program are intended to represent the range of concentrations measured in precipitation samples collected by the NADP/MDN. Every two years, the USGS evaluates Hg concentrations measured by the MDN and confirms that the QA solution target values are representative of precipitation concentration ranges. Three solutions, with different Hg concentrations, and two sample volumes are used in the blind audit program to assess how laboratory analysis affects sample chemistry in solutions with different Hg concentrations and volumes. A description of the solutions and a summary of target values for solutions used in the blind audit program are provided in table 7. Distribution of the solutions and their respective volumes used in the 2006 blind audit program are listed in table 8.

For processing a blind audit sample, the site operator is shipped a 75- or 150-mL solution along with a cover letter (appendix 8), instructions for processing the sample (appendix 9), and a postcard addressed to the USGS for reporting sample processing and shipping information (appendix 10). The USGS personnel transfer information from the postcard to the blind audit program database, enter the date the card is returned to the USGS in the MDN logbook, and file the postcard for record. Card submission is evidence that the blind audit sample has been submitted to the HAL.

In December, the HAL mails shipping coolers containing 2-L sample collection bottles precharged with 20 mL of HCl to the USGS for use in the blind audit program. The USGS pours prepared blind audit solutions into the sample collection bottles, encloses the bottles in protective plastic bags, and ships the samples in HAL-supplied coolers to sites chosen to participate in the blind audit program. The HAL has the capability to track shipping coolers by using identification numbers inscribed on the container and lid of the cooler. Therefore, to avoid unveiling the identity of a blind audit solution to the HAL through recognition of a cooler tracking number, site operators are asked to transfer the blind audit sample to a different cooler out of their stock.

Site operators are asked to fill in weekly information on the laboratory-created rain gage chart, recording dates for the dry week and time when the sample collection bottle was installed and removed from the field, along with precipitation depth indicated by the laboratory-created rain gage chart corresponding to solution volume of the QA sample. If the participating site is co-located with an NTN site, the site operator photocopies the rain gage chart to mail to the HAL with the blind audit sample and the original rain gage chart is mailed to the Central Analytical Laboratory with the NTN sample. If the site is not co-located with an NTN site, the original USGS-created rain gage chart is mailed to the HAL with the blind audit sample. The site operator fills out the MOF recording site information for the dry week but modifies the precipitation record by recording depth measurements drawn on the laboratory-created rain gage chart. The site operator mails the sampling train funnel and capillary tube that were installed in the collector during the previous dry week, the completed MOF and rain gage chart with the blind audit solution to the HAL, as if it were an actual precipitation sample.

Site operators are instructed to place the sample collection bottle and rain gage chart that were installed in the field during the dry week, along with the MOF documenting the dry week's sample collection, into the shipping cooler that was mailed to them by the USGS. They are asked to retain this cooler until the blind audit sample has been processed at the HAL and the data are reported to the USGS. Then, the USGS notifies the site operator to ship the actual dry-week sample to the HAL. The MDN precipitation samples are typically analyzed within three weeks of sample collection. The USGS compiles the returned blind audit postcards and notifies the HAL that blind audit samples have been processed in the previous month. The HAL grants the USGS access to its database to retrieve blind audit data and the USGS discloses the identity of sites that processed a blind audit sample to the HAL. The HAL identifies the QA sample data in its database and excludes them from monthly summary reports provided to MDN sites. Then, the USGS notifies participating sites to mail

Table 8. Solution names, sample volumes, and approximate number of samples used in the U.S. Geological Survey blind audit program for the National Atmospheric Deposition Program/Mercury Deposition Network during 2006.

[mL, milliliters; ng/L, nanograms per liter; SP, synthetic precipitation]

Solution name	Sample volume (mL)	Number of samples
Ultrapure deionized water	75	3
Ultrapure deionized water	150	3
SP-2 + 5.7 ng/L mercury spike	75	4
SP-2 + 5.7 ng/L mercury spike	150	3
SP-2 + 14.3 ng/L mercury spike	75	3
SP-2 + 14.3 ng/L mercury spike	150	4

coolers containing the actual dry week sample bottle, MOF, and rain gage chart to the HAL.

For individual MDN sites requesting methylmercury (Me-Hg) analysis, the HAL extracts aliquots from weekly precipitation samples. These aliquots are analyzed individually for MDN sites requesting weekly Me-Hg analysis or, the weekly aliquots are composited and analyzed monthly for MDN sites requesting monthly Me-Hg analysis. In September 2006, the USGS discovered that it had unknowingly asked several sites that determine Me-Hg to process blind audit samples. Since the identity of QA samples is not revealed to the HAL until after analysis, the processed blind audit samples were split for Me-Hg analysis. The splits were blended with precipitation samples and analyzed as part of monthly composite Me-Hg samples. This oversight corrupted several Me-Hg samples, the data for which had to be corrected. In the future, sites chosen for the blind audit program must not submit samples for Me-Hg analysis or for any other special analysis requiring the splitting and compositing of solutions. This mistake is documented herein to help avoid similar oversights in the future.

Data Records

The HAL supplies the USGS with analytical results for the processed blind audit samples on a yearly basis. Solutions used in the blind audit program are also analyzed by six laboratories participating in the interlaboratory comparison program. The MPVs are determined for each solution from the median Hg concentrations calculated using interlaboratory comparison program data. Statistical analysis of the differences between the reported Hg concentrations and the MPVs for the blind audit solutions quantify bias and variability in analytical data produced by the HAL. The USGS makes statistical interpretations of blind audit data, which are published in annual reports (Wetherbee and others, 2006) and presented to the NADP/NOS. All blind audit data are archived in SAS and Microsoft Access databases, which are stored on a USGS file server. A flowchart of the blind audit program is provided in figure 7.

Summary

Over the past 25 years, the USGS has been conducting external QA programs to quantify data variability for the NADP/NTN, and that expertise has been applied to implement programs for the MDN. The external QA programs conducted by the USGS in support of the NADP/MDN provide an ongoing assessment of data quality, quantify influences from most sources of contamination, and provide useful information for interpreting NADP/MDN data. Since 2004, three programs have been implemented: the system blank program, the interlaboratory comparison program, and the blind audit program.

The QA programs assess possible influences on data quality for precipitation samples collected by the NADP/MDN. The system blank program quantifies Hg contamination of precipitation samples contributed by field exposure of sampling equipment and by routine sample handling and processing. The interlaboratory comparison program evaluates bias and variability of Hg data produced by the HAL by comparing HAL results with five other laboratories. The blind audit program assesses bias and variability of Hg data produced by the HAL using USGS-prepared solutions disguised as NADP/MDN precipitation samples which are submitted to the HAL by NADP/MDN site operators.

Preparing MDN QA solutions with specific Hg concentrations is more challenging than preparing solutions for the NTN because Hg concentrations in precipitation are very low and Hg can volatilize or adsorb to container surfaces. The use of HCl and Hg requires stringent safety and waste-disposal protocols. Preparation, processing, and storage methods for QA solutions and samples are continually being evaluated and modified when necessary. The QA evaluations of NADP/MDN sample collection help data users to differentiate between environmental indicators and sample collection influences.

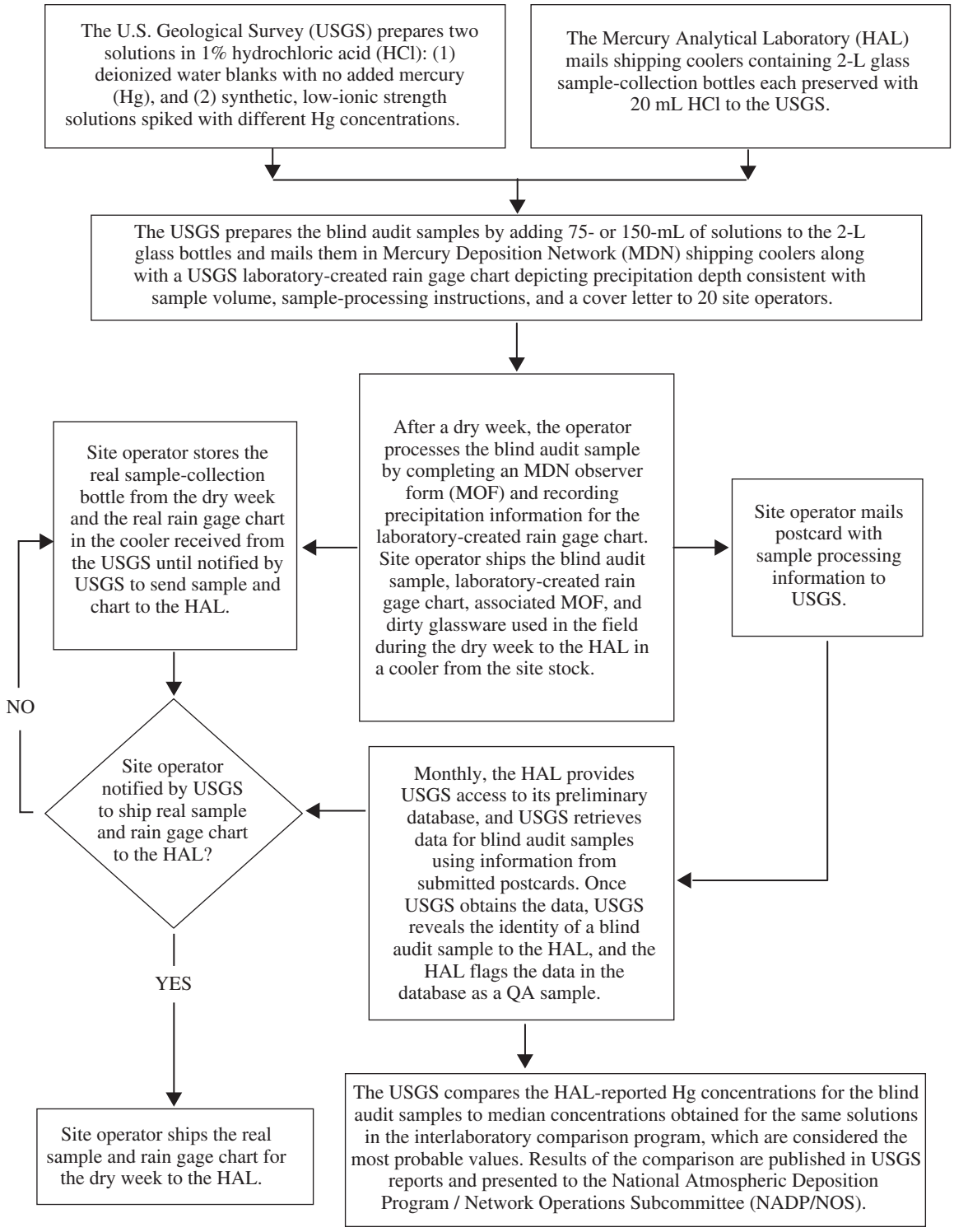

Figure 7. Flowchart for the National Atmospheric Deposition Program/Mercury Deposition Network blind audit program.

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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, 62 p.

Appendices

United States Department of the Interior

U. S. GEOLOGICAL SURVEY
Box 25046, M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

Site Operator Address

Dear Site Operator Name,

Your site has been chosen to participate in the NADP/MDN System Blank Program during the specified quarter of year. This quality assurance program, conducted jointly by the U.S. Geological Survey and Frontier Geosciences, Inc., is intended to measure the effects of field exposure, handling, and processing on the chemistry of NADP/MDN precipitation samples. We appreciate your participation in this mandatory NADP/MDN quality assurance program.

Please refer to the enclosed instructions for the exact steps that need to be followed to ensure that the System Blank sample is submitted correctly. Enclosed please find the System Blank sample, instructions and forms for your participation in the program. The samples used in the program consist of deionized water (blanks) and synthetic rainwater (reference materials).

Fifty percent of the enclosed solution must be poured into the Aerochem Metrics collector, through the wet side sample collection train, and into the "sample collection bottle" that was installed in the field for an **entire week with no precipitation**. Please process the sample as soon as you have a dry week. If a dry week does not occur prior to deadline date please: 1) mail the sample to Frontier Geosciences, Inc. (it will be analyzed even though it was not processed) and 2) mail the enclosed postcard to the U.S. Geological Survey, stating that there was no dry week prior to deadline date.

If you have any questions or concerns regarding the submission of the System Blank sample please call me at: (303) 236-1837, or e-mail: nlatysh@usgs.gov. Thank you in advance for your participation in the System Blank Program.

Sincerely,

Greg Wetherbee

Appendix 1. Cover letter mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators participating in the U.S. Geological Survey system blank program. Highlighted text indicates fields customized for each site participating in the system blank study.

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/MERCURY DEPOSITION NETWORK
Instructions for submitting a system blank sample from your site to Frontier Geosciences, Inc.

ONLY SUBMIT A SYSTEM BLANK SAMPLE AFTER A WEEK WITH NO PRECIPITATION AT YOUR SITE

The sample you have been sent should be submitted prior to deadline date (6 months after sample mailing).

If this time period passes without a **full dry week**, please mail the sample to Frontier Geosciences, Inc. in the original box in which it was sent and mail the enclosed post card to the U.S. Geological Survey explaining that there were no dry weeks prior to **deadline date (6 months after sample mailing).**

Please verify that you have a 3-hole cooler for mailing all items to Frontier Geosciences Inc. If you do not have a 3-hole cooler, please contact Gerard Van der Jagt at Frontier Geosciences, Inc. (toll free: 877-622-6960).

Step 1: Verify that no precipitation occurred

- Make sure that not even a trace of precipitation was measured by the rain gage.
- Verify the collector worked properly and there were no clock stoppages or pen skips on the event recorder chart. If equipment malfunctioned during the preceding week, please do not process the system blank sample.
- If a lid opening occurred, ensure that no precipitation was recorded. Explain any lid openings due to humidity, dew or fog in the remarks section (Block 10) of the observer form.

Step 2: Transfer half of the system blank sample into the collection bottle

- Wet the sensor with MilliQ water to expose the sample train.
- Pour 50% of the system blank sample (down to the line marked on the bottle) into the collection funnel of the MDN collector. The sample will pass through the funnel and thistle tube, into the "sample collection bottle". Wear clean gloves and be careful not to contaminate the sample. Replace the cap on the system blank bottle and seal it in its original ziploc bag. Screw the cap onto the "sample collection bottle" (which contains 50% of the transferred system blank sample and the pre-charge preservative) and remove it from the overflow bucket. Place this sample bottle into a sample bottle bag.
- Please do not write anything on the bottles for identification purposes. The bag for the original system blank sample is labeled with sample information useful to Frontier Geosciences Inc.
- Place both the bagged 2-L "sample collection bottle" and the bagged system blank bottle inside a standard cooler for shipping samples to Frontier Geosciences, Inc. Once both samples are capped and bagged you can begin the normal Tuesday field sampling procedures.

Step 3: Fill out 2 MDN Observer Forms (MOFs) for the System Blank samples

A) MOF for system blank sample bottle containing 50% of the original solution is labeled "System Blank Sample Bottle" in the Remarks section. Please fill in the following:
1) Station. 2) Observer.

Appendix 2. Sample-processing instructions mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators participating in the U.S. Geological Survey system blank program. Highlighted text indicates fields customized for a system blank study.

3) Bottle-Off Date and Time when you poured the system blank sample into the collection bottle (it is the off date because the process occurs the day you are taking the sample off the collector).
4) Site Operations–all equipment should have worked properly during the previous dry week in order to process the system blank sample.
5) Enclosure Temperature.

B) MOF for the "sample collection bottle" that was installed in the collector for a full dry week is labeled "Sample Collection Bottle" in the Remarks section. Please fill in the following:

1) Station. 2) Observer.
3) Bottle Id and the On and Off Dates and Times the collection bottle spent installed inthe collector. (The On Date should be previous Tuesday's date and Off Date should be Tuesday's date when you process the system blank sample).
4) Analysis Type-please check the 'System Blank' box.
5) Observations-all should be checked 'No' since the bottle was covered by the lid all week and should not have been exposed to contamination.
6) Site operations–all equipment should have worked properly during the previous dry week in order to process the system blank sample.
7) Precipitation Record–please check the rain gage chart; precipitation values should all be zero.
8) Overflow–should be 'No'.
9) Enclosure Temperature.
10) Please state the following in the Remarks section:
Poured system blank sample into the sample collection bottle on 'date'.

Step 4: Fill out the enclosed pre-addressed post card and mail it to the U.S. Geological Survey.

Step 5: Ship the system blank samples to Frontier Geosciences, Inc.

Please send the following items to Frontier Geosciences, Inc. in the standard 3-hole shipping cooler:

- The 2-L sample collection bottle containing 50% of the system blank sample plus pre-charge preservative
- The 1-L system blank bottle containing the remaining 50% of the solution placed into the cooler's smaller opening normally used for trace metal samples
- Observer form for the sample collection bottle
- Observer form for the system blank bottle
- Rain gage chart
- The dirty funnel and thistle tube

Please place the paper work, including the rain gage chart, into a ziploc bag and lay it on top of the samples inside the cooler.

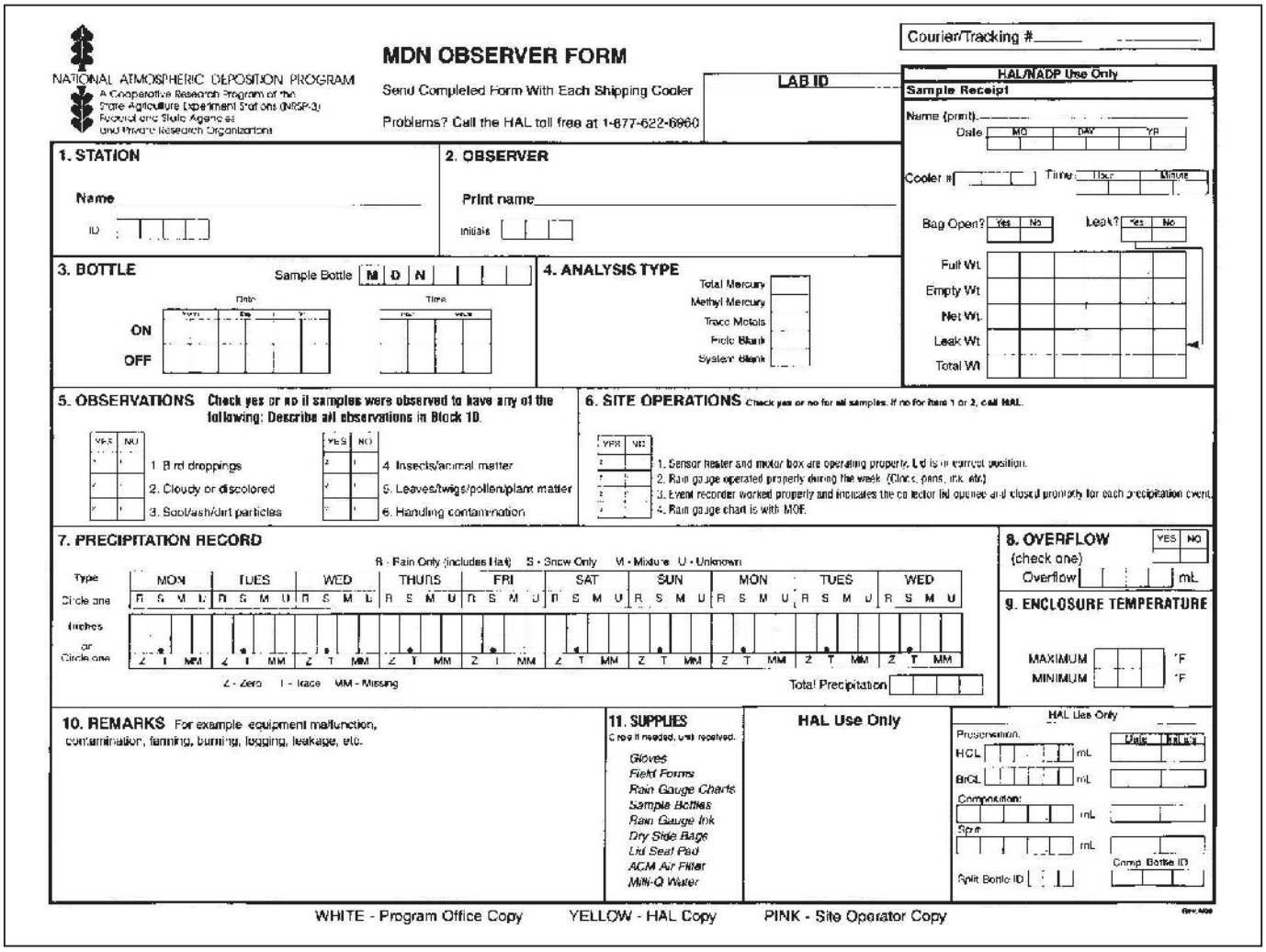
****

Thank you for participating in the System Blank Program. We appreciate your time.

If you have questions please contact Natalie Latysh at (303) 236-1874 or e-mail: nlatysh@usgs.gov

****

Appendix 2. Sample-processing instructions mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators participating in the U.S. Geological Survey system blank program. Highlighted text indicates fields customized for a system blank study.—Continued



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Program of the State Agriculture Experiment Stations (NRSP-3), Federal and State Agencies and Private Research Organizations

MDN OBSERVER FORM

Send Completed Form With Each Shipping Cooler

Problems? Call the HAL toll free at 1-877-622-6960

Courier/Tracking #

LAB ID

HAL/NADP Use Only
Sample Receipt
Name (print)
Date MO DAY YR
Cooler # Time: Hour Minute
Bag Open? Yes No Leak? Yes No
Full Wt
Empty Wt
Net Wt.
Leak Wt
Total Wt

1. STATION
Name
ID

2. OBSERVER
Print name
Initials

3. BOTTLE
Sample Bottle M D N
ON
OFF
Date
Time

4. ANALYSIS TYPE
Total Mercury
Methyl Mercury
Trace Metals
Field Blank
System Blank

5. OBSERVATIONS Check yes or no if samples were observed to have any of the following; Describe all observations in Block 10.
YES NO
1. Bird droppings
2. Cloudy or discolored
3. Soot/ash/dirt particles
4. Insects/animal matter
5. Leaves/twigs/pollen/plant matter
6. Handling contamination

6. SITE OPERATIONS Check yes or no for all samples. If no for item 1 or 2, call HAL.
YES NO
1. Sensor heater and motor box are operating properly, Lid is in correct position.
2. Rain gauge operated properly during the week. (Check, pans, ink, etc.)
3. Event recorder worked properly and indicates the collector lid opened and closed promptly for each precipitation event.
4. Rain gauge chart is with MOF.

7. PRECIPITATION RECORD
R - Rain Only (includes Hail) S - Snow Only M - Mixture U - Unknown
Type
Circle one
MON TUES WED THURS FRI SAT SUN MON TUES WED
R S M U
Inches or Circle one
Z T MM
Z - Zero T - Trace MM - Missing
Total Precipitation

8. OVERFLOW YES NO
(check one)
Overflow mL

9. ENCLOSURE TEMPERATURE
MAXIMUM °F
MINIMUM °F

10. REMARKS For example: equipment malfunction, contamination, farming, burning, logging, leakage, etc.

11. SUPPLIES
Circle if needed, and received.
Gloves
Field Forms
Rain Gauge Charts
Sample Bottles
Rain Gauge Ink
Dry Side Bags
Lid Seal Pad
ACM Air Filter
Milli-Q Water

HAL Use Only

HAL Use Only
Preservation:
Date Initials
HCL mL
BrCL mL
Composition: mL
Spike mL
Comp. Bottle ID
Split Bottle ID

WHITE - Program Office Copy YELLOW - HAL Copy PINK - Site Operator Copy

Appendix 3. Mercury Deposition Network observer form used by the National Atmospheric Deposition Program/ Mercury Deposition Network site operators for recording sample information.

MDN –RECORD OF SYSTEM BLANK SAMPLE SUBMISSION

PLEASE FILL IN THE BLANKS BELOW AND MAIL TO THE USGS.
THIS INFORMATION SHOULD MATCH WHAT IS LISTED ON
THE MDN OBSERVER FORM

SITE ID ☐☐☐☐ SITE NAME _____

SITE OPERATOR _____ ☐☐☐
Initials

SAMPLE PROCESSING DATE _____

DATE SAMPLE SENT TO FRONTIER GEOSCIENCES _____

MS 401
U.S. Dept. of the Interior
Geological Survey
Box 25046 Federal Center
Denver CO 80225-0046

U.S. Geological Survey
WRD / BQS
Bldg. 95 / MS 401
Box 25046 Denver Federal Center
Denver CO 80225

Appendix 4. Front and back sides of the postcard mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators for reporting system blank sample processing and shipping information to the U.S. Geological Survey.

United States Department of the Interior
U. S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

Laboratory contact address

Dear Contact:

Enclosed are four samples for the Interlaboratory Comparison Program for the National Atmospheric Deposition Program / Mercury Deposition Network (NADP/MDN). This program is a component of the NADP/MDN External Quality Assurance (QA) Program, which is managed by the U.S. Geological Survey (USGS).

The identification numbers for the enclosed samples are:

Sample identification 1
Sample identification 2
Sample identification 3
Sample identification 4

Each sample should be analyzed for total mercury concentration in the same way that your laboratory would analyze an ordinary environmental sample. If possible, these samples should be processed immediately. Each sample is in a 1% hydrochloric acid matrix. Your laboratory identification code is "Laboratory". Please email your data to us, preferably in an Excel spreadsheet or ASCII text file using the following example format:

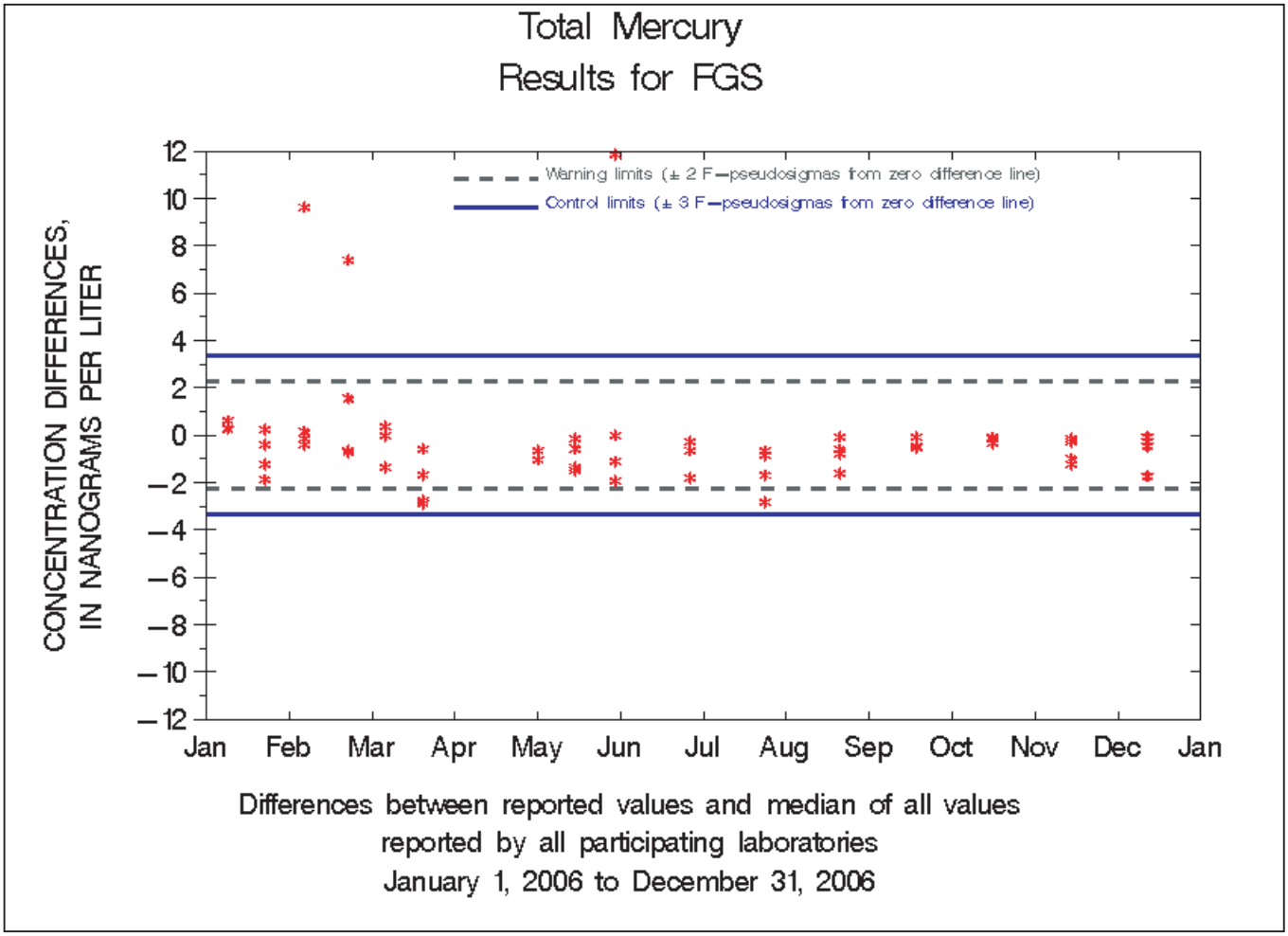
Sample Identification Number (shown above)	Laboratory Identification Code	**Date of Analysis**	Total Mercury Concentration, in nanograms / Liter (ng/L)	Minimum Reporting Limit (ng/L)
Sample identification	Laboratory	Date	##.####	##.####

Please direct any questions regarding the program to us at 303-236-1837 (Greg) or 303-236-1874 (Natalie) or via e-mail at *wetherbe@usgs.gov* or *nlatysh@usgs.gov*. We appreciate your participation in this important quality assurance program for the NADP/MDN.

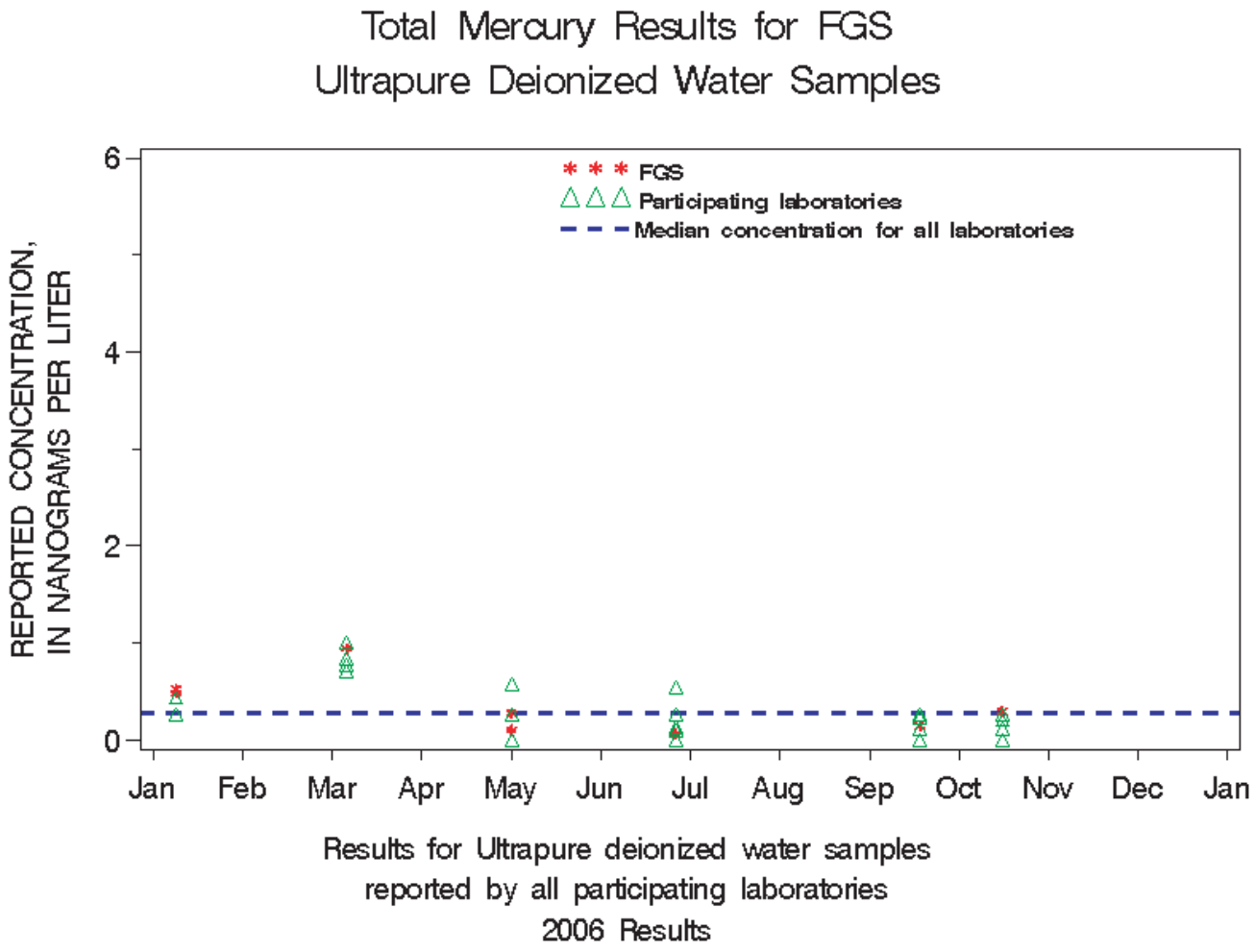
Best Regards,

Natalie Latysh

Appendix 5. Cover letter mailed to laboratories participating in the U.S. Geological Survey interlaboratory comparison program for the National Atmospheric Deposition Program/Mercury Deposition Network. Highlighted text indicates fields customized for each participating laboratory.



Appendix 6. Example of control chart posted on the Internet (*http://bqs.usgs.gov/precip_2/mdn/index.html/*) displaying a participating laboratory's results for spiked mercury solutions used in the U.S. Geological Survey interlaboratory comparison program for the National Atmospheric Deposition Program/Mercury Deposition Network.



Appendix 7. Example of control chart posted on the Internet (*http://bqs.usgs.gov/precip_2/mdn/index.html/*) displaying a participating laboratory's results for deionized water solutions used in the U.S. Geological Survey interlaboratory comparison program for the National Atmospheric Deposition Program/Mercury Deposition Network.

United States Department of the Interior
U. S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

Site contact address

Re: MDN BLIND-AUDIT PROGRAM

Dear Site Operator,

Please read this letter and the enclosed Mercury Deposition Network (MDN) Blind Audit Instructions carefully. Enclosed you will find the materials needed to process a MDN blind-audit sample. Please let us know if this package is missing any of the following items.

- ☐ MDN Blind-Audit sample
- ☐ Illustrated instruction sheet
- ☐ Self-addressed, stamped, MDN Blind-Audit postcard
- ☐ FedEx shipping label and plastic sleeve

You have been selected as a participant for blind-audit quality assurance program. The MDN blind audit is designed to measure the variability and bias in the HAL analytical data. It is very important that you take great care to disguise the blind-audit sample so that the HAL will not know that it is a quality assurance sample. Please submit your blind-audit sample(s) the next time your site has a dry week before study deadline date. If you are waiting for a dry week to submit a MDN system-blank sample, please submit the system-blank sample first, and then wait for the next dry week to submit the blind-audit sample.

MINIMIZE BLIND-AUDIT SAMPLE HANDLING!! DO NOT OPEN THE ZIPLOCK BAG CONTAINING THE BLIND-AUDIT SAMPLE BOTTLE NOR THE BOTTLE ITSELF.

If a dry week does not occur prior to study deadline date please ship the cooler containing the blind-audit materials to the HAL, using the enclosed FedEx shipping label and plastic sleeve. Since there is no specified submission date, it is important that you mail the self-addressed, stamped postcard to the USGS on the day you ship the blind-audit sample to the HAL.

If you have any questions or concerns regarding the submission of the blind-audit sample please call Greg Wetherbee at 303-236-1837 or Natalie Latysh at 303-236-1874, or e-mail: nlatysh@usgs.gov. Thank you in advance for your participation in this program.

Sincerely,
Greg Wetherbee, Chemist, Project Chief

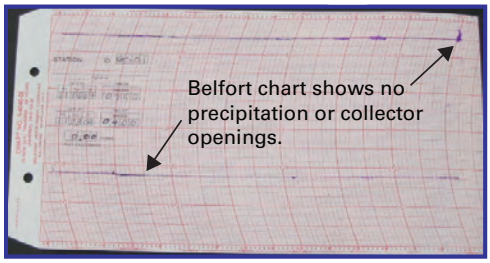
Appendix 8. Cover letter mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators participating in the U.S. Geological Survey blind audit program. Highlighted text indicates fields customized for each site participating in the blind audit study.

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

MDN BLIND-AUDIT INSTRUCTIONS

USGS science for a changing world

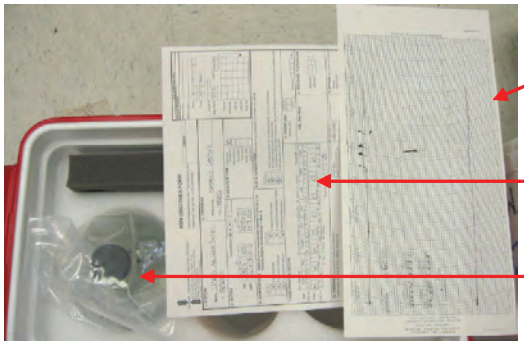
The intent of the blind-audit program is to assess the variability and bias in the analytical results produced by the Mercury Analytical Laboratory (HAL) by disguising a quality assurance sample as a weekly precipitation sample from your site.



STEP 1

Service MDN collector and rain gage. If no precipitation occurred and the collector did not open during the preceding week, then you can process the blind-audit sample. Please **DO NOT** process the blind-audit sample if the collector lid opened even once.

Store in USGS cooler

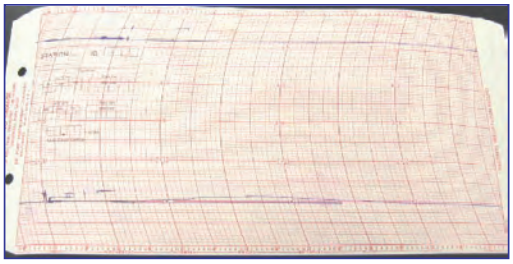


STEP 2

Transfer the blind-audit sample from the USGS cooler to an extra cooler in your stock. This is **IMPORTANT!** It helps to disguise the blind-audit sample as a precipitation sample from your site since the coolers can be tracked by the HAL.

Complete a MOF for the field bottle that spent a dry week installed in the collector. Store the MOF, field bottle and the rain gage chart that you just retrieved from the field in the cooler that you received from the USGS until you are notified by the USGS to send it to the HAL.

Fill out USGS-created raingage chart



STEP 3

Read and fill out the USGS-created rain gage chart just as you would for any raingage chart from your site. Fill in: site id, date-on, date-off, time-on, time-off, and precipitation total. Make sure that the time-on and time-off match the data from the real chart for the dry week. Make a small mark at the time-on and time-off with a pen. If you typically photocopy the rain gage chart to mail to the HAL, photocopy the USGS-created chart and mail it to the HAL with the blind audit sample. Then, you may discard the original USGS-created chart. If you send the original rain gage chart to the HAL with your weekly samples, send the original USGS-created chart to the HAL with the blind audit sample.

GO TO REVERSE SIDE

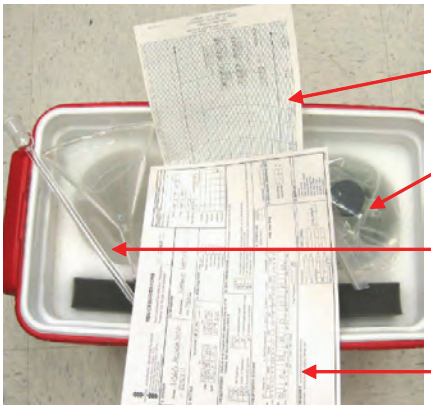
Appendix 9. Sample-processing instructions mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators participating in the U.S. Geological Survey blind audit program.

BLIND-AUDIT INSTRUCTIONS–Continued

STEP 4

Complete a second MOF for the blind-audit sample with information for a typical precipitation sample. Fill in all fields on the MOF, except for field #7 Precipitation Record. For this field, use information from the USGS-created rain gage chart (See step 3). Fill in the daily and weekly precipitation data on the blind-audit MOF per the USGS-created rain gage chart. **PLEASE DO NOT INDICATE ON THE BLIND-AUDIT MOF THAT THIS IS A QUALITY ASSURANCE SAMPLE IN ANY WAY!**

Mail to the HAL in a cooler from your stock



STEP 5

Make sure that the cooler that you obtained from your stock (not the USGS cooler) sent to the HAL contains: blind-audit sample, USGS-created rain gage chart, blind-audit MOF, and the used funnel and thistle tube. Use standard shipping methods to mail the cooler to the HAL. **DO NOT** USE THE ENCLOSED FEDEX LABEL.

STEP 6

You will be notified in a few months to ship the actual field bottle, that spent a dry week installed in the collector, to the HAL in the USGS cooler. Use the enclosed FedEx label to ship the USGS cooler to the HAL. All fields have already been completed, please place the label in the plastic sleeve and affix it to the USGS cooler.

Mail postcard to USGS

MDN – RECORD OF BLIND-AUDIT SAMPLE SUBMISSION
PLEASE FILL IN THE BLANKS BELOW AND MAIL TO THE USGS.
THIS INFORMATION SHOULD MATCH WHAT IS LISTED ON THE MDN OBSERVER FORM

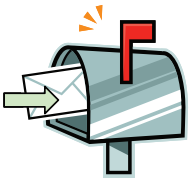
SITE ID ☐☐☐☐ SITE NAME _____ ☐☐☐

SITE OPERATOR _____ Initials

DATE ON: _____
TIME ON: _____

DATE SHIPPED
TO FRONTIER GEOSCIENCES
_____

DATE OFF: _____
TIME OFF: _____



Fill out the stamped, pre-addressed postcard provided with the blind-audit sample and mail to the USGS.

You Have Completed the MDN Blind Audit for Your Site! Thank You!
For more information, call Natalie Latysh at 303-236-1874 / e-mail: nlatysh@usgs.gov

Appendix 9. Sample-processing instructions mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators participating in the U.S. Geological Survey blind audit program.—Continued

MDN- RECORD OF BLIND-AUDIT SAMPLE SUBMISSION

PLEASE FILL IN THE BLANKS BELOW AND MAIL TO THE USGS.
THIS INFORMATION SHOULD MATCH WHAT IS LISTED ON
THE MDN OBSERVER FORM

SITE ID ☐☐☐☐ SITE NAME _____

SITE OPERATOR _____ ☐☐☐
Initials

DATE ON: _____
TIME ON: _____

DATE OFF: _____
TIME OFF: _____

DATE SHIPPED
TO FRONTIER GEOSCIENCES
_____

MS 401
U.S. Dept. of the Interior
Geological Survey
Box 25046 Federal Center
Denver CO 80225-0046

U.S. Geological Survey
WRD / BQS
Bldg. 95 / MS 401
Box 25046 Denver Federal Center
Denver CO 80225

Appendix 10. Front and back sides of the postcard mailed to National Atmospheric Deposition Program/Mercury Deposition Network site operators for reporting blind audit sample processing and shipping information to the U.S. Geological Survey.