the Great Lakes, the Northeast, in the Gulf States, and in South Florida. Many lakes and streams in these areas contain fish with mercury levels above state (0.5 to 1.0 mg/L) and U.S. Food and Drug Administration action level (1.0 mg/L) for human consumption (U.S. EPA, 1997 and 2004).

The Mercury Deposition Network

The Mercury Deposition Network (MDN), coordinated through the National Atmospheric Deposition Program (NADP), was designed to study and quantify spatial and temporal trends in the deposition and fate of mercury in the atmosphere. The NADP began monitoring trace chemicals in precipitation at 18 sites in 1978 in order to describe and study "acid rain" related problems. It has since grown to a network of more than 270 sites located throughout the United States and Canada. (More information on the NADP is available at http://nadp.sws.uiuc.edu). In 1995, following a year of field testing (Vermette et al., 1995), the NADP began "transition phase" mercury monitoring at 26 sites in preparation for the acceptance of the MDN into NADP which occurred in January 1996. Since 1996, the MDN has grown to more than 100 active sites in the USA and Canada (Figure 3).

Mercury deposition data from the MDN will be an important input to atmospheric and multi-media models designed to assess the fate and consequences of mercury emissions and will provide feedback to better assess trends in mercury deposition. Thus, the MDN database will be particularly useful in the evaluation of the effectiveness of EPA and/or state mandated controls on mercury emissions to the atmosphere (U.S. EPA, 2000). Summarized in this report are the results of mercury monitoring at eight MDN sites located in Pennsylvania from January 2005 through December 2006. The results are discussed in relationship to similar data collected at sites throughout the United States and southern Canada.

Network Design and Operation

Both wet and dry depositions are important processes for the movement of mercury from the atmosphere to land and water surfaces. The Mercury Deposition Network (MDN) is a wet deposition network and does not attempt to measure dry deposition of mercury. The main reason for this is that dry deposition methods are based on indirect measurements that are largely experimental and difficult to implement at isolated sites using personnel with a wide variety of backgrounds. Wet deposition measurements, on the other hand, are based on direct collection techniques that use standardized methods and equipment that are relatively easy to implement and operate at remote sites. Although dry deposition of mercury is very important in terrestrial systems (Lindberg et al., 1992) other studies have estimated that wet deposition is the most important atmospheric process for the movement of mercury to water bodies (Lamborg et al., 1995; Mason et al., 1997; Scherbatskoy et al., 1997). Since the primary environmental problems associated with mercury deposition are fish contamination and human health risks associated with the consumption of contaminated fish (U.S. EPA 1997), wet deposition is probably the most

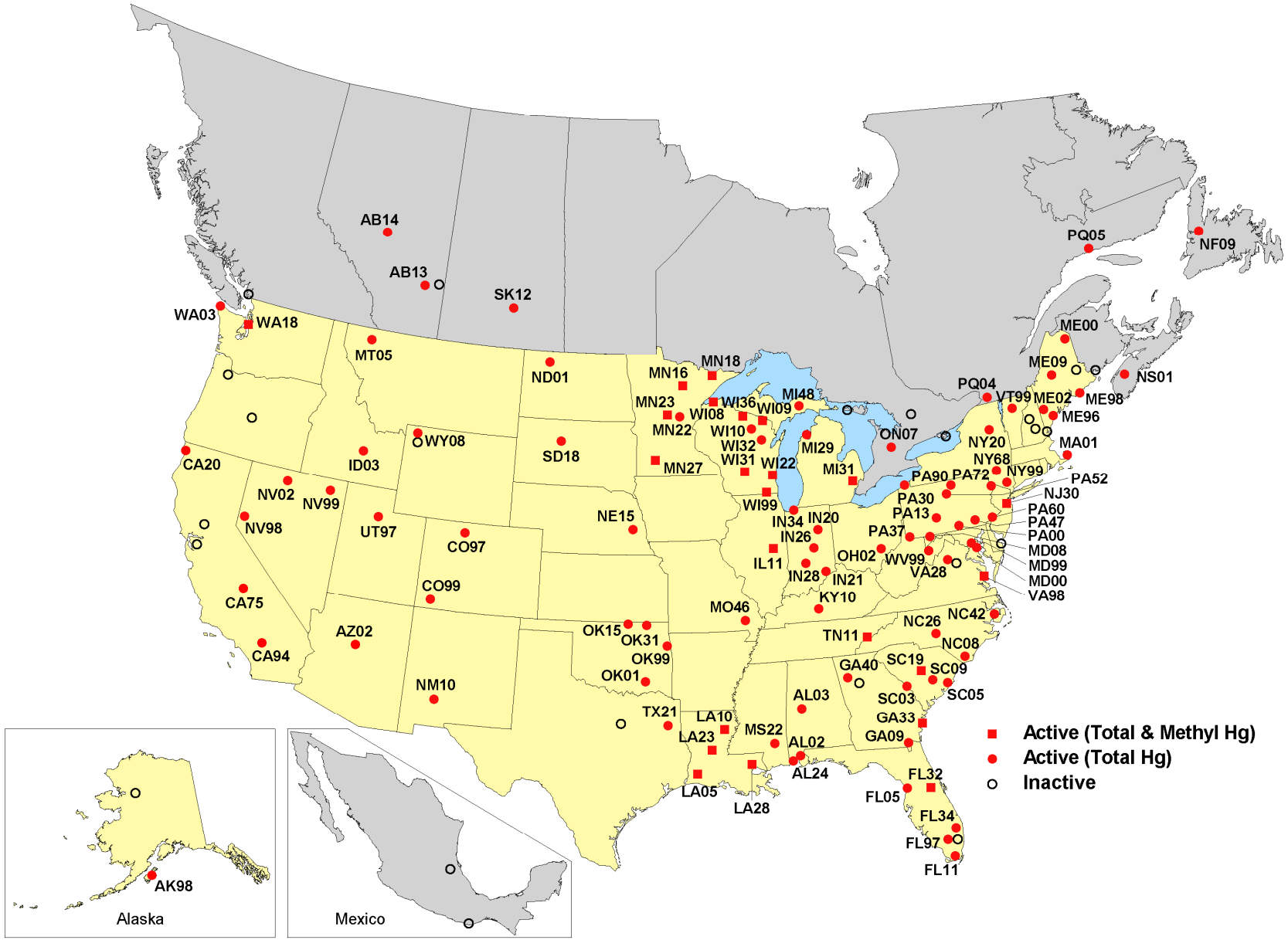

Figure 3. Location of active and inactive National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) sites in the United States and southern Canada as of November 2007.

important atmospheric deposition process for assessing mercury's environmental and human health impacts.

Sampling Site Locations

The Mercury Deposition Network was designed to evaluate regional concentration and wet deposition patterns of total mercury in precipitation. Sites were selected using an established set of criteria (Bloom and Crecelius, 1983). Most of the sites are in rural areas at least 10 to 20 kilometers from major air pollution sources and at least 100 meters from local sources. Most sites are in open, grass-covered areas well away from overhanging vegetation and buildings. About half of the MDN sites are collocated with NADP/NTN acidic deposition collectors. The locations of active (as of November 2007) MDN sites are shown in Figure 3. Site names and descriptions are available on the NADP/MDN web site: (http://nadp.sws.uiuc.edu). Eight sites were in operation in Pennsylvania in 2005 and 2006 (Table 1, Figure 4). These sites are located in Tioga County (PA90) near Wellsboro, in Cambria County (PA13) near Cresson, in Erie County (PA30) near Erie, in Greene County (PA37) near Holbrook, in Adams County (PA00) near Arendtsville, in Montgomery County (PA60) near Valley Forge, in Pike County (PA72) near Milford, and in Lancaster County (PA47) near Millersville. The latitude, longitude,

Table 1. Location of National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) sites in Pennsylvania in 2005 and 2006.

Site No.	Latitude	Longitude	County	Elevation Meters	Sampling Started
PA00	39.9231	-77.3078	Adams	269	11/16/2000
PA13	40.457	-78.56	Cambria	739	01/07/1997
PA30	42.1558	-80.1134	Erie	177	06/20/2000
PA37	39.8161	-80.285	Greene	347	05/27/1999
PA47	39.99	-76.3862	Lancaster	85	11/26/2002
PA60	40.1166	-75.8833	Montgomery	46	11/23/1999
PA72	41.3275	-74.8203	Pike	212	09/15/2000
PA90	41.8043	-77.1903	Tioga	476	01/07/1997

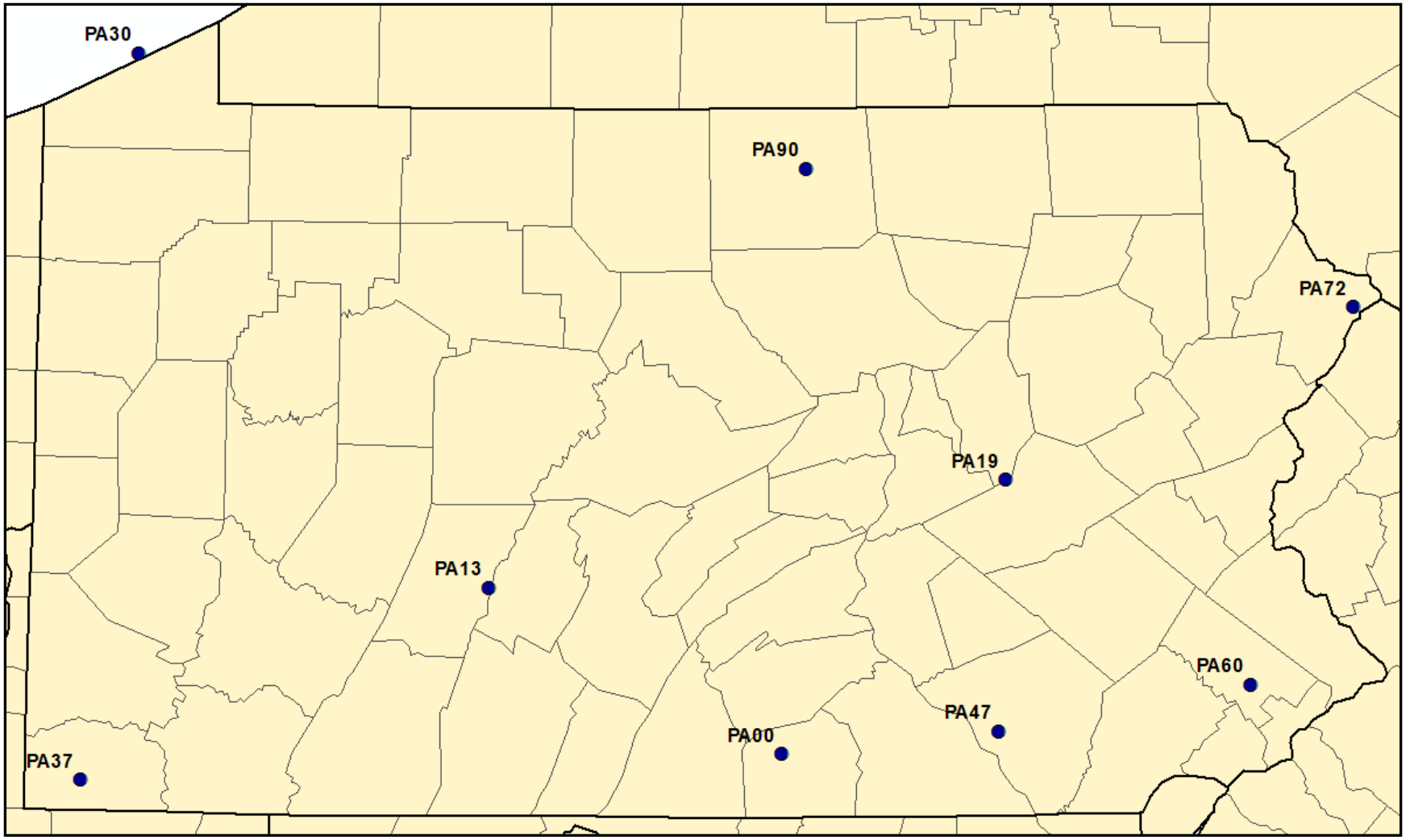

Figure 4. Location of active National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN) sites in Pennsylvania in 2005 and 2006.

elevation and date sampling was initiated at each of the Pennsylvania NADP/MDN sites are shown in Table 1. Seven of the Pennsylvania MDN sites are supported by the Pennsylvania Department of Environmental Protection, Bureau of Air Quality Control in cooperation with The Pennsylvania Bureau of State Parks (PA30 and PA90), The National Park Service (PA13 and PA60), The U.S. Forest Service, Northeast Forest Experiment Station (PA72), The Pennsylvania State University, Fruit Research and Extension Center (PA00), and Millersville University (PA47). The eighth site in the Pennsylvania Network (PA37) is supported by The U.S. Department of Energy/Federal Energy Technology Center and is operated by Advanced Technology Systems, Inc. For more information on each of the sites the reader is referred to the MDN web site http://nadp.sws.uiuc.edu/mdn

Sampling Protocols

In establishing the MDN, The National Atmospheric Deposition Program (NADP) sought to ensure uniformity in commitment, in sampling protocols, and in analytical techniques and procedures. These are the ingredients essential to a successful network design and operation. To this end the NADP/MDN monitoring program designated specific precipitation collection equipment to be used throughout the network which allows precipitation to be recorded, collected and verified. A strict weekly sampling protocol and a clear definition of sample type further makes comparisons between sites possible.

A modified Aerochem Metrics Model 301 Automatic Sensing Wet/Dry Precipitation Collector used in the NADP/MDN was designed to sample precipitation for mercury and (potentially) other trace metals, simultaneously. Modifications include the downsizing of the original orifice to a 128 mm diameter and the addition of a second wet-side orifice of the same diameter. The two wet-side orifices (a glass sampling train for mercury collection and a Teflon or Polyethylene/Teflon sampling train for the collection of other metals) allows for the simultaneous sampling for total mercury and other metals. *If not needed, the precipitation collected in the second orifice drains out the bottom of the collector.*

The mercury sampling train is designed so that the sample will contact only glass surfaces to minimize contamination. Precipitation is caught in a glass funnel and stored in a two-liter glass bottle, previously charged with 20 mL of dilute hydrochloric acid (0.12 M) used as a preservative. This is sufficient acid to maintain a pH of less than 2 in the sample collection bottle to prevent microbial activity. The two-liter bottle holds a maximum volume equivalent to 12.7 cm (five inches) of precipitation. The sampling train for total mercury consists of a 124 mm (inner diameter) borosilicate glass funnel, a thin (3 mm inner diameter) capillary tube, and a 2-liter borosilicate glass bottle. Even though connections between the funnel and capillary tube and between the capillary tube and sample collection bottle are not air tight, the sampling train effectively inhibits evaporation during the weekly sampling period. Additional modifications include: Teflon-coated lid supports and Teflon-wrapped lid seal foam pads; flexible sleeves at the base of the lid arms; an insulated enclosure around the collector base; and a thermostatically controlled heater and fan to maintain a given temperature range within the enclosure and to melt snow collected in the funnels.

Sample Types

Between precipitation events the mercury wet deposition sampling train is covered by a motor-activated lid. When precipitation occurs, a sensor activates the motor which moves the lid from the wet deposition side to a dry-side plastic bucket. In the discussion that follows, samples will be referred to as ***Wet-Side*** for the mercury deposition samples or ***Dry-Side*** for the dry-side bucket. Material collected in the dry-side bucket is not analyzed by the MDN. Definitions of sample types are as follows:

Wet-Deposition-Only Sample: A Wet-Side sample that has been exposed only to precipitation and that has been protected from dry-fall during rain-free periods. Dry deposition exposures of less than 6 hours in any sampling period and less than 30 minutes at the end of any single event are considered insignificant. This is the type of sample normally collected in MDN.

Bulk Sample**:** A Wet-Side sample that has been exposed continuously to both wet and dry depositions for the entire sampling period. This can occur when the sampler motor fails and the lid remains in the open position for the whole sampling period.

Undefined Sample: Any Wet-Side sample that does not meet one of the above definitions *(i.e.,* part-week or unknown duration of exposure to dry deposition).

Field operators receive a pre-cleaned sampling train each week. Every Tuesday, the exposed sampling train is removed and returned to the Mercury Analytical Lab at Frontier Geosciences, Inc., Seattle, WA, along with the sample bottle containing any collected precipitation. All operators wear plastic gloves when handling the sampling train and follow special procedures to avoid contaminating the sample. Any overflow from the bottle is collected and measured but it is not included with the sample sent to the lab. Each site is also equipped with a Belfort weighing-bucket rain gauge (Belfort Instruments, Baltimore, MD) that provides a weekly chart with rainfall amounts and distribution. MND sites in Pennsylvania that are supported by the Bureau of Air Quality Control are also equipped with a standard non-recording funnel-type rain gauge. Rainfall volumes, as small as one mm, can be measured. The recording rain gauge has an "event recorder" that marks the chart each time the lid on the Aerochem Metrics sampler opens and closes. This indicates whether the sampler was open during wet periods and closed during dry periods. The precipitation amount measured by the recording rain gauge is used to calculate wet deposition. If no rain gauge chart is available, the volume from the non-recording gauge is used as a back-up. In the unlikely event that volume measurements from both rain gauges are not available, the "bottle catch" is used to calculate the amount of precipitation.

Glassware Preparation

Precipitation samples are collected and stored in 1-liter borosilicate glass bottles with Teflon-lined, phenolic resin caps. Initial cleaning is by heating to 70 °C for 48 hours in 4 M HCL, followed by a thorough rinsing in low-Hg (< 1 ng/L) distilled deionized water (DDW). The caps are cleaned by soaking for 48 hours in 0.1 M HCL at room temperature. Before use, bottles are filled with DDW containing 5 mL of BrCl in concentrated HCL, capped, and placed in a low-Hg

(< 15 ng/m^2), Class-100 clean air station for 24 hours. Bottles are then emptied, thoroughly rinsed with DDW, and allowed to dry for several hours in the clean air station. Each bottle receives 20 ± 0.5 mL of 0.12 M HCL (Hg < 0.5 ng/L), and the lids are tightly fastened. While still at the clean air station, the bottles are enclosed in new polyethylene bags and packed into polyethylene foam-lined shipping containers.

The funnels and capillary tubes are cleaned by rinsing in nitric acid (HNO_3) followed by rinsing in DDW. The openings to the funnel and tube are wrapped in aluminum foil and the glassware placed in a muffle furnace at 500°C for 4 hours. After cooling, the aluminum foil is removed and the funnel and capillary tube are placed in separate new polyethylene bags and packed in a shipping container.

Laboratory Analysis

Every precipitation sample collected by the MDN is analyzed at a single laboratory, the Mercury Analytical Laboratory (HAL), operated by Frontier Geosciences, Inc., Seattle, WA, for total mercury and methylmercury, if desired by a site sponsor. The analytical methods used are those given in U.S. EPA Method 1631 and are described in detail by Liang and Bloom (1993). Briefly, upon arrival at the laboratory, the bottles are unpacked in a clean air low-Hg (< 0.05 ng/mL) station where 0.2 N BrCl in HCL reagent is added to each bottle to give a final concentration of 1%. This reagent oxidizes all of the mercury present in the sample to Hg(ll). The caps are replaced, and the bottles are shaken for at least four hours to remove adsorbed mercury from the bottle walls and to fully oxidize any suspended particles. Weighed sample aliquots (50-100 mL) are poured into 125 mL Teflon bottles prior to analysis. Two-hundred mL of 20% hydroxylamine-hydrochloride is added to each aliquot to eliminate free halogens; the aliquot is then poured into a purge vessel. To reduce the conversion of Hg(ll) back to Hg^0, 300 µL of 25% $SnCl_2$ are added to the sample, and the sample is purged with ultra-pure nitrogen onto a gold-coated, silica trap. The traps are then analyzed for total mercury by thermal desorption, dual gold trap amalgamation, and cold vapor atomic fluorescence. Peaks are quantified by peak height. The method detection limit for a 100 mL sample is about 0.1 ng/L or 3 standard deviations of the reagent blanks.

The Standard Sampling Period

The standard sampling period is the interval between sampling train installation and sampling train removal. Typically, samples accumulate for one week. The sampling train is removed from the collector and replaced at or about 9 AM (0900 local time) each Tuesday. If it is raining or snowing at collection time the sampling train is changed after the precipitation stops, but in no case later than 5:00 PM on Tuesday. The wet-side sampling train is replaced weekly and sent to the HAL, even if no precipitation was collected during the sampling period. This standard sampling protocol results in 52 samples (some years 53 samples) submitted for analysis per year.

Quality Assurance Samples

Quality assurance samples include: ***travel blanks, field blanks, and system blanks***. The ***travel blanks*** are bottles that are shipped with the regular sampling train and stored unopened in the enclosure during the sample period. They are returned to HAL unopened after the specified period. ***Field blanks*** are samples from dry weeks where all equipment has operated perfectly and there is no indication of precipitation. In other words, the sampler is operating properly on inspection, the enclosure temperature is in the proper range, and the rain gauge and event recorder worked properly and showed no indication of any precipitation. Even a single trace event disqualifies a sample from being a ***field blank***.

About once a year, site operators receive a 500 mL bottle labeled ***system blank*** containing pre-analyzed deionized water. This bottle is stored in the enclosure until a dry week occurs. At the end of the next sampling period with no precipitation, the operator opens the lid by wetting the sensor. The operator then pours half of the deionized water from the 500 mL bottle into the funnel in circular motions, wetting the sides of the funnel. The rinse water goes into the sample bottle. The sampling train and sample bottle are then collected according to the procedures for weekly sampling. The 500 mL bottle with the unused portion of the rinse water is capped and returned to HAL in the sample cooler with the sample bottle and sampling train.

Data Completeness Criteria

NADP/MDN criteria for data completeness include the following: 1) at least 75% of the year (or other summary period) is represented by valid samples; 2) there must be information on precipitation amounts for at least 90% of the year; 3) there must be valid samples representing at least 75% of the precipitation measured for the year; and, 4) total precipitation measured from the sample volume (bottle catch) must be at least 75% of the amount measured by the rain gage for the year. Data completeness criteria are used to assure uniformity in the comparison of data collected at all MDN sites.

Summary Periods

Total mercury concentrations and depositions are summarized into annual and seasonal periods. Annual summaries are presented for each calendar year (January-December) as well as each climatic year (December-November) since mercury monitoring began in Pennsylvania in 1997. Seasonal periods are defined as winter (December-February), spring (March-May), summer (June-August) and fall (September-November). These seasons were selected because they closely match seasonal climatic patterns observed in Pennsylvania. Eight MDN sites were in operation in Pennsylvania for all of 2005 and 2006 (Figure 3, Table 1). Weekly concentrations and wet deposition estimates for each site from January 2005 through April 17, 2007 are included in Appendix I of this report. However, most of the following analyses have been based on data collected 2005 and 2006 when all eight MDN sites were in operation simultaneously.