MERCURY DEPOSITION IN PENNSYLVANIA: STATUS REPORT

James A. Lynch
Professor of Forest Hydrology
School of Forest Resources

Kevin S. Horner
Senior Research Technologist
Environmental Resources Research Institute

Jeffrey W. Grimm
Research Assistant
Environmental Resources Research Institute

The work upon which this report is based was supported by funds from the Pennsylvania Department of Environmental Protection through Contract Number ME94583.

Environmental Resources Research Institute
The Pennsylvania State University
University Park, Pennsylvania 16802

October 1999

Introduction

Mercury (Hg) exhibits varying toxicity levels in the environment depending on its chemical form. The three predominant chemical species are elemental mercury (Hg°), divalent ionic mercury (Hg-ll) and mono-methylmercury (MMHg). Elemental mercury exists as a gas in the atmosphere and is removed very slowly. Because of its slow rate of removal, it is a major component of the global circulation of atmospheric mercury (Schroeder and Munthe, 1998). Mono-methylmercury can be emitted directly to the atmosphere by combustion sources. Oxidation processes in the atmosphere and in cloud water can also convert Hg° to Hg-ll. Reactive mercury in the form of Hg-ll is less volatile and more water-soluble than Hg°. It may be found in the gas phase or bound to airborne particles. Both gas-phase and particulate Hg-ll are readily removed from the atmosphere by precipitation. Mono-methylmercury is the most toxic of the mercury species. While some MMHg is found in precipitation, most of the MMHg occurring in lakes and other surface waters is generated by microbially mediated transformation of Hg-ll in water and sediments (Schroeder and Munthe, 1998). This process seems to be accelerated in acidic lakes (Driscoll, et al., 1995). MMHg is a neurotoxin and teratogen, which bioaccumulates up the food chain by a factor of a million or more. Human and wildlife exposure to Hg is due primarily from the consumption of contaminated fish (U.S. EPA, 1996)

Mercury in the atmosphere can come from natural sources (geology, oceans, forest fires, volcanoes, etc.) or anthropogenic sources (incinerators, coal combustion, industrial emissions, etc.). In its ***Mercury Study: Report to Congress,*** the United States Environmental Protection Agency (U.S. EPA, 1996) found that "a plausible link exists between past and present, human-induced atmospheric emissions of Hg in the United States and increased concentrations of Hg that have been found in the environment and in freshwater fish". However, the U.S. EPA goes on to say that an apportionment between Hg sources and Hg in environmental media and biota cannot be described in quantitative terms with the current scientific understanding of the environmental fate and transport of the pollutant. Currently, 39 states (including Pennsylvania) and five Canadian provinces have issued advisories about the dangers of eating fish contaminated with Hg taken from surface waters within their boundaries. This problem is most severe in the Great Lakes and Northeast regions of the U. S., in the Canadian Maritime Provinces, and in South Florida. Many lakes and streams in these areas contain fish with Hg levels above state (0.5 to 1.0 ppm) and U.S. Food and Drug Administration (1.0 ppm) action levels for human consumption (U.S. EPA, 1996).

The Mercury Deposition Network (MDN), coordinated through the National Atmospheric Deposition Program (NADP), is designed to study and quantify spatial and temporal trends in the fate and deposition of mercury in the atmosphere. The NADP began monitoring trace chemicals in precipitation in 1978 in order to describe and study "acid rain" related problems. It has grown to a network of more than 200 sites throughout the U.S. In 1995, following a year of field testing (Vermette et al., 1995), the NADP began "transition phase" mercury monitoring at 17 sites in preparation for the acceptance of MDN into NADP, which occurred in January, 1996. Between 1996 and 1998, 35 MDN sites were in operation across the U.S. and Canada for at least part of the period. MDN data will be an important input to atmospheric and multi-media models and will provide feedback to better assess the trends in mercury deposition. Plans are to continue operation of the MDN for at least 5 to 10 years. Thus, the MDN database will be particularly useful to help evaluate the effectiveness of any state or federally mandated controls on mercury emissions to the atmosphere. This report summaries the results of mercury monitoring at two MDN sites located in Pennsylvania for1997 and 1998. The results are compared to similar data collected at other MDN sites throughout the U.S. and Eastern Canada.

Network Design and Operation

Both wet and dry deposition 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 movement of mercury to water bodies (Lamborg et al., 1995; Mason et al., 1997; Scherbatskoy et al., 1997). Since the primary environmental problem associated with mercury deposition is fish contamination, wet deposition is probably the most important atmospheric deposition process for assessing mercury's environmental impact.

Sampling Locations

Sites in the MDN are designed to evaluate regional wet deposition patterns. They were selected using an established set of siting criteria (Bloom and Crecelius, 1983). Most of the sites are in rural areas at least 10 to 20 km away from major air pollution sources and at least 100 m away from local sources. All sites are in open, grass-covered areas well away from overhanging vegetation and buildings. About half of the MDN sites are collocated with NADP acid rain collectors. One of the MDN sites is in a residential area in Seattle (WA18); deposition at this site may not be exactly comparable to the other sites in the network in terms of regional representativeness. The site locations are shown in Figure 1. Site names and full descriptions are available on the NADP WEB site (http://nadp.sws.uiuc.edu). Two sites are currently located in Pennsylvania, one at Hills Creek State Park (PA90) in Tioga County and the other at The Allegheny Portage National Historic Railroad Site (PA13) near Cresson in Cambria County. Both sites were operational in January, 1997. Both sites are supported by the Pennsylvania Department of Environmental Protection, Bureau of Air Quality Control in cooperation with the Pennsylvania Bureau of State Parks (PA90) and the National Park Service (PA13). A third Pennsylvania site was established in 1999 in the extreme southwest corner of the state (Figure 1, PA37). This site is supported by the U.S. Department of Energy.

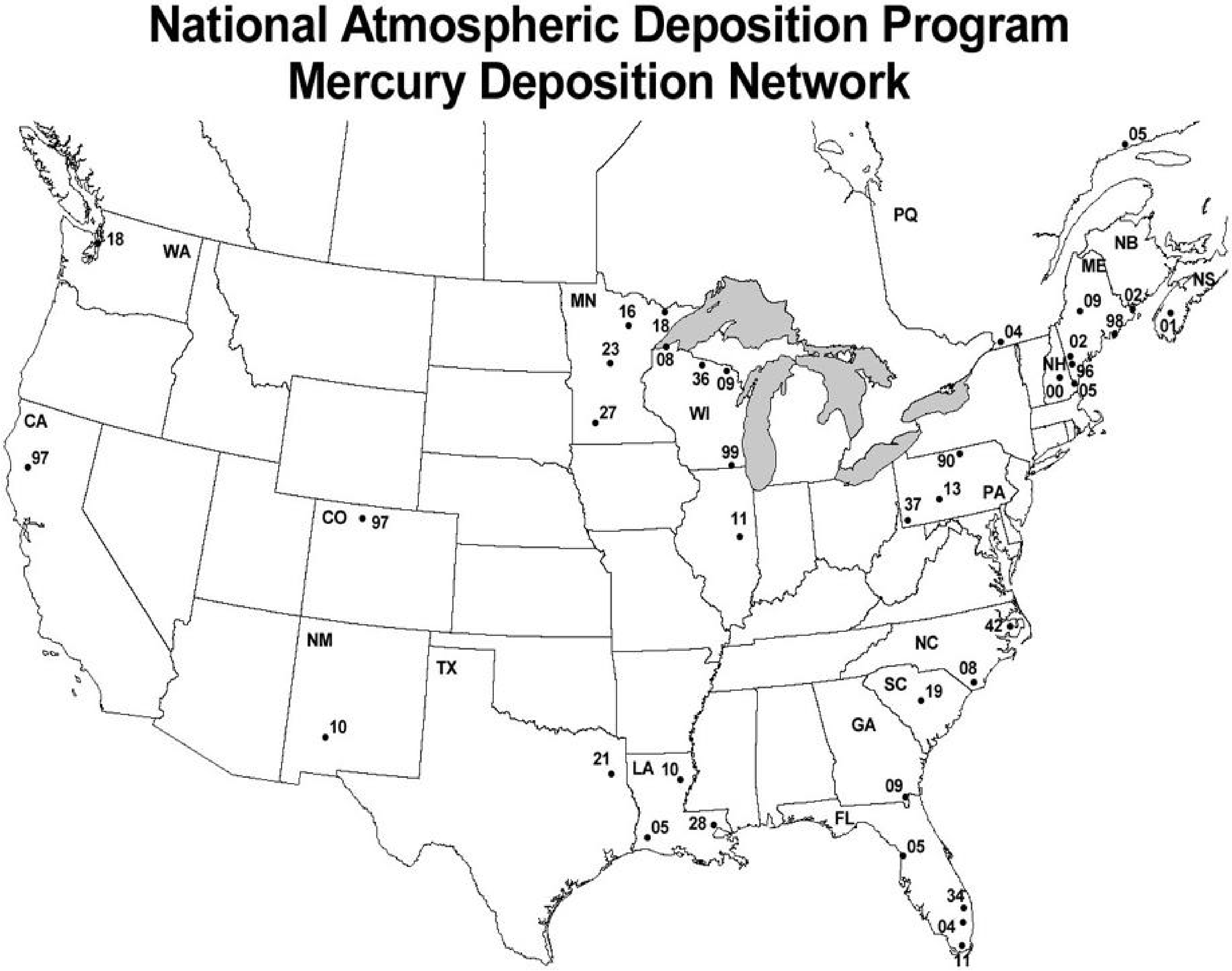

Figure 1. Sampling Locations for Mercury Deposition Network (MDN) sites.

Sampling Methods

In establishing the MDN, the National Atmospheric Deposition Program (NADP) has sought to ensure uniformity in commitment, in sampling protocol, 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 has 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 types 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 of total mercury and other metals. *If not needed, the precipitation collected in the second orifice drains out the bottom of the collector.* The sampling train is designed so that the sample will contact only glass surfaces to minimize trace metal 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 bottle to prevent microbial action. The two-liter bottle hold a maximum volume equivalent to 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 the capillary tube and between the capillary tube and the sample bottle are not air tight, the sampling train effectively inhibits evaporation during the 1-week sampling period. Additional modifications include: Teflon-coated lid supports and Teflon-wrapped lid sealing 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. Materials collected in the dry-side bucket are not analyzed by 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. 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 deposition for the entire sampling period. This can occur when the sampler motor fails and the lid is "stuck" in the open position for the whole sampling period.

Undefined Sample: Any Wet-Side or Dry-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 lab (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 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. Pennsylvania MDN sites are also equipped with standard non-recording funnel-type rain gauges. Rainfall increments 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 properly 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 gage is used as a back-up. In the unlikely event that volume measurements from both rain gauges are not available, the "bottle catch" rainfall amount is used as a substitute.

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 HCI, 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 HCI 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 HCI (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 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 sealed around the openings. The funnel and capillary tube are placed in separate new polyethylene bags and packed in the 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, Washington, for total mercury and methyl mercury 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 the clean air station, and low-Hg (< 0.05 ng/mL), 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 Hg present in the sample to Hg(ll). The caps are replaced, and the bottles are shaken for at least four hours to remove adsorbed Hg 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 for 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 Hg(ll) back to Hg°, 300 µL of 25% $SnCl_2$ are added, and the sample is purged with ultra-pure nitrogen onto a gold-coated, silica trap. The traps are then analyzed for Hg 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 (3 standard deviations of the reagent blanks).

The Standard Sampling Period

The 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 midnight 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 (53 some years) 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, which 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 events. 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 amount for at least 90% of the year; 3) there must be valid samples representing at least 75% of the precipitation amount 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.

RESULTS AND DISCUSSION

Seasonal and annual volume-weighted mean concentrations of total mercury in precipitation samples collected at the two DEP, Bureau of Air quality Control sponsored MDN sites in 1997 and 1998 are shown on Table 1. Weekly concentrations and deposition measurements at these sites for 1997 and 1998 are listed in the Appendix. For comparative purposes, volume-weighted mean annual mercury concentrations for all sites in the MDN in 1998, that met data completeness criteria, are shown in Figure 2. Annual volume-weighted mean concentrations of total mercury in precipitation in 1998 at the 30 MDN sites ranged from 3.7 ng/L to 23.0 ng/L. The volume-weighted average concentration for all sites in 1998 was 9.5 ng/L. Average concentrations were lowest at the Northeast and West Coast sites and highest in Florida and at a New Mexico site (NM1O), which recorded the highest mean annual concentration in 1998. The Hills Creek State Park site in Pennsylvania (PA90) averaged 8.9 ng/L in 1998; the average concentration at the Allegheny Portage NHS site (PA13) was 10.2 ng/L. Total mercury concentrations in Pennsylvania tend to be higher than those found in New England and along the West Coast and somewhat lower than those reported around the Great Lakes region and in the Southeastern U.S. The mean annual concentration of total mercury in precipitation at the two Pennsylvania sites in 1997 was slightly lower than observed in 1998 (Table 1).

Annual wet deposition of mercury in the U.S. for 1998 is shown in Figure 3. Wet deposition across the 30 MDN sites ranged from 4.0 $\mu g/m^2$ to 26.1 $\mu g/m^2$. These values include zero deposition (no rainfall) weeks and estimated deposition for weeks with valid precipitation amounts but no mercury concentration measurements. In the latter cases, the seasonal, volume-weighted average concentration is used to estimate mercury deposition. The average annual deposition across the network was 10.2 $\mu g/m^2$. It is important to keep in mind that mercury deposition is the product of

Table 1. Annual seasonal concentration and deposition of mercury at MDN monitoring sites in Pennsylvania during 1997-98. Seasonal estimates were based on Dec.-Feb., Mar.-May, June-Aug., and Sep.-Nov. quarters. Annual estimates were based on normal calendar years (i.e., Jan.-Dec.).

Site	Season	Year	Volume-Weighted Mean Concentration (ng/L)	Quarterly Deposition (µg/m2)	Mean Weekly Deposition (µg/m2)	Precip. (Inches)
ALLEPORT (PA13)	Winter	1997*	10.52	0.9296	0.1328	3.48
	Spring	1997	12.65	4.5218	0.3230	14.07
	Summer	1997	11.41	2.9456	0.2266	10.16
	Fall	1997	4.21	1.7875	0.1375	16.71
	Annual	1997	9.20	10.8710	0.2132	46.54
	Winter	1998	7.61	1.9203	0.1477	9.93
	Spring	1998	8.68	3.0847	0.2374	13.99
	Summer	1998	14.09	3.3961	0.2612	9.49
	Fall	1998	13.04	1.7557	0.1351	5.30
	Annual	1998	10.19	9.7824	0.1881	37.80
HILLSCRK (PA90)	Winter	1997*	11.50	0.6661	0.0952	2.28
	Spring	1997	10.65	1.9864	0.1419	7.34
	Summer	1997	13.40	3.1561	0.2428	9.27
	Fall	1997	5.09	1.2148	0.0934	9.39
	Annual	1997	9.61	7.2592	0.1423	29.73
	Winter	1998	5.34	1.1792	0.0907	8.69
	Spring	1998	9.15	2.7551	0.2119	11.86
	Summer	1998	14.15	2.6685	0.2053	7.42
	Fall	1998	7.95	1.0849	0.0835	5.38
	Annual	1998	8.98	7.5027	0.1443	32.91

* Only two months of data were used (Jan. and Feb. 1997).

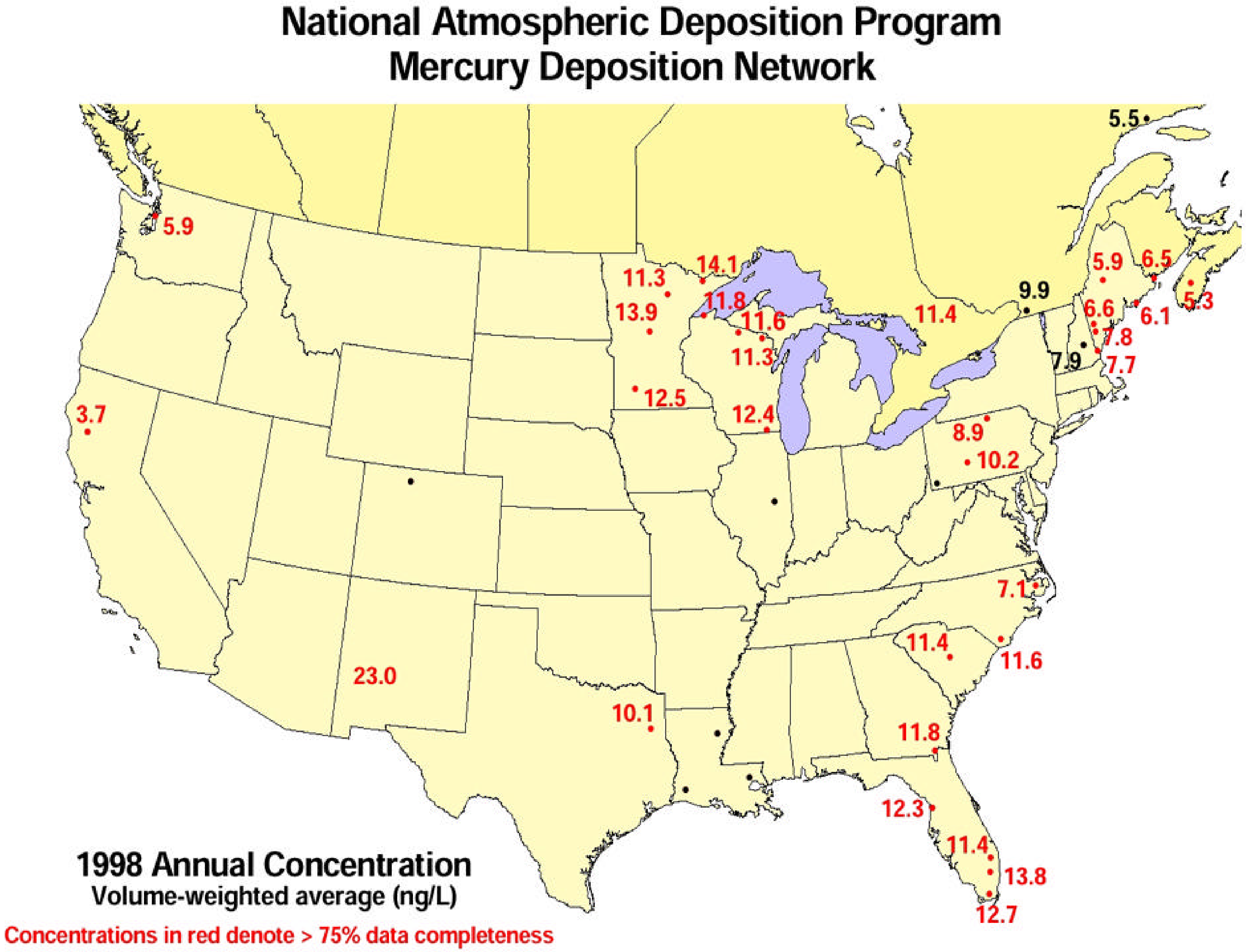

Figure 2. Volume-weighted mean total mercury concentrations (ng/L) at MDN sites in 1998.

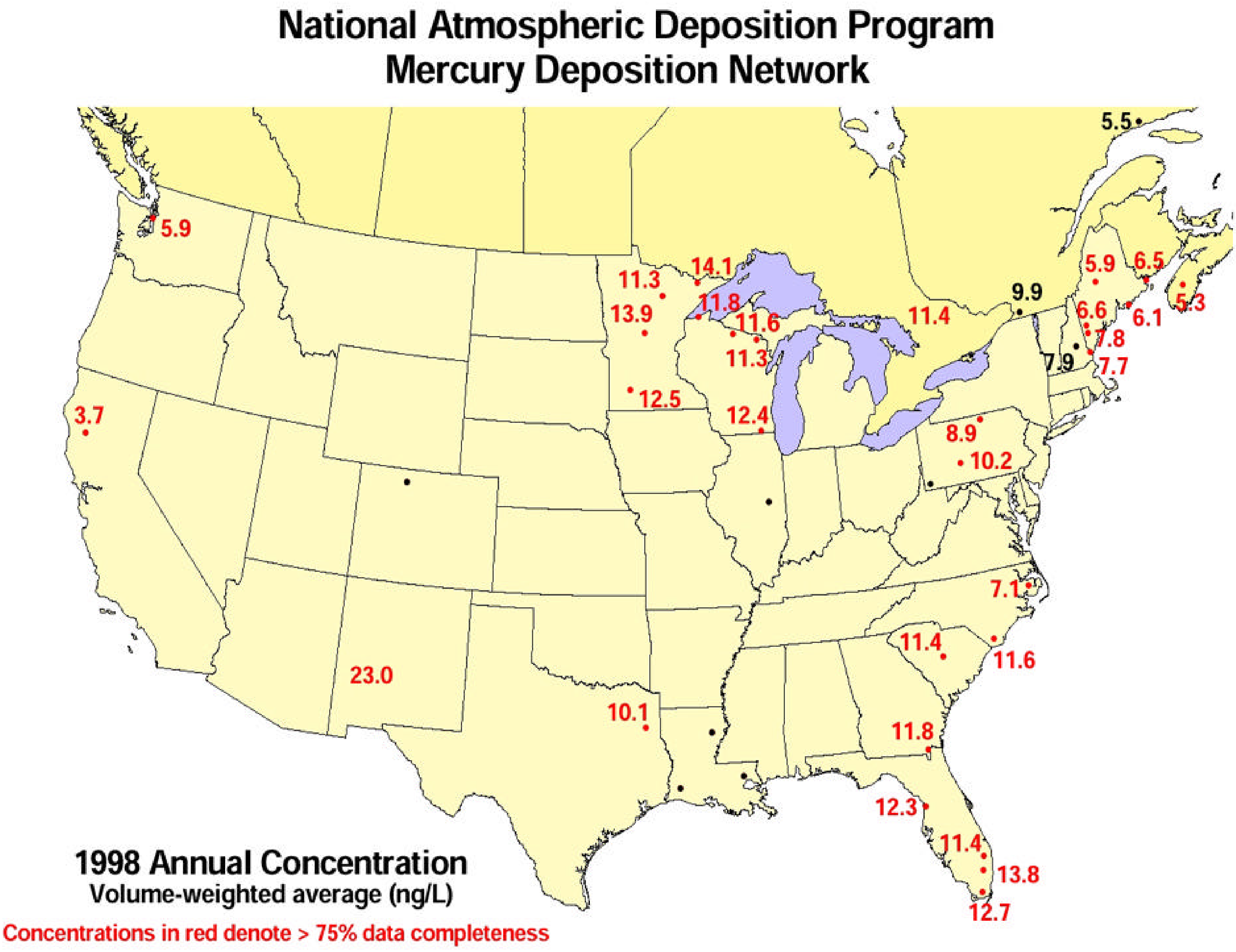

Figure 3. Annual wet deposition of mercury (µg/m^2) at MDN sites in 1998.

concentration and the amount of precipitation. Sites with high average mercury concentrations in rainfall are not necessarily the sites with the highest wet deposition of mercury. For example, NM1O had the highest average concentration of total mercury (23.0 ng/L); but with only 17.4 cm (6.8 inches) of rainfall, this site had the lowest wet deposition of mercury in the MDN Network for 1998. Annual wet deposition of mercury at Hills Creek State Park in 1998 totaled 7.5 µg/m^2 (Table 1); the Allegheny Portage site received 9.8 µg/m^2. These values are generally comparable to wet deposition levels reported in the New England and Great Lakes regions, but lower than observed in the Southeast (Figure 3).

In the eastern half of North America, concentrations of total mercury in precipitation and mercury wet deposition amounts show a definite seasonal pattern. The data in Figure 4 show that average summer (June - August) mercury concentrations are more than double winter concentrations (December - February), and average summer deposition values are almost three times higher than the comparable winter period. Spring and Fall averages for both concentration and deposition are in between the summer and winter values. Higher deposition of mercury in the summer months is a function of both higher concentrations of mercury in rainfall and higher summer rainfall amounts at most of the sites. Strong seasonal concentration patterns are also evident at the two Pennsylvania sites (Figure 5, PA90 and Figure 6, PA13). Seasonal concentration patterns at Hills Creek (PA90) are particularly strong, with summer (June - August) concentrations nearly twice as high as Fall and Winter concentrations. Seasonal concentration patterns are not quite as strong at the Allegheny Portage site (PA13). Wet deposition also exhibits seasonal patterns in Pennsylvania, although the seasonal differences are not as large as for concentrations (Figures 5-6) and reflects to a great extent, seasonal differences in precipitation patterns between the two sites.

Table 2 gives the annual wet deposition and average concentration of total mercury at 18 selected sites for the period between 1995 and 1998. Eleven of these sites have data records extending back to 1995. Even though MDN was a pilot program still under development in 1995, the field and laboratory procedures were essentially the same as those used in the official NADP/MDN network, which began in 1996. The sites in Table 2 are grouped by geographic region. Concentrations are relatively consistent across each region and range from 5 ng/L to 7 ng/L in Maine and eastern Canada to between 11 ng/L and 15 ng/L in south Florida. Annual deposition is somewhat more variable ranging from 6 µg/m^2 to 9 µg/m^2 in Maine and eastern Canada to between 17 µg/m^2 and 27 µg/m^2 in south Florida. Some of site-to-site and year-to-year variations in wet deposition of mercury are due simply to differences in precipitation amount. Year-to-year values for concentration and deposition are fairly consistent for each region with no obvious trends. An exception to this is WA18, which recorded a large decline in both concentration and deposition in 1998 compared to 1997. As indicated earlier, WA18 (Seattle) is the only urban site in the MDN. The decline seen here in 1998 may reflect changes in mercury emissions from nearby sources.

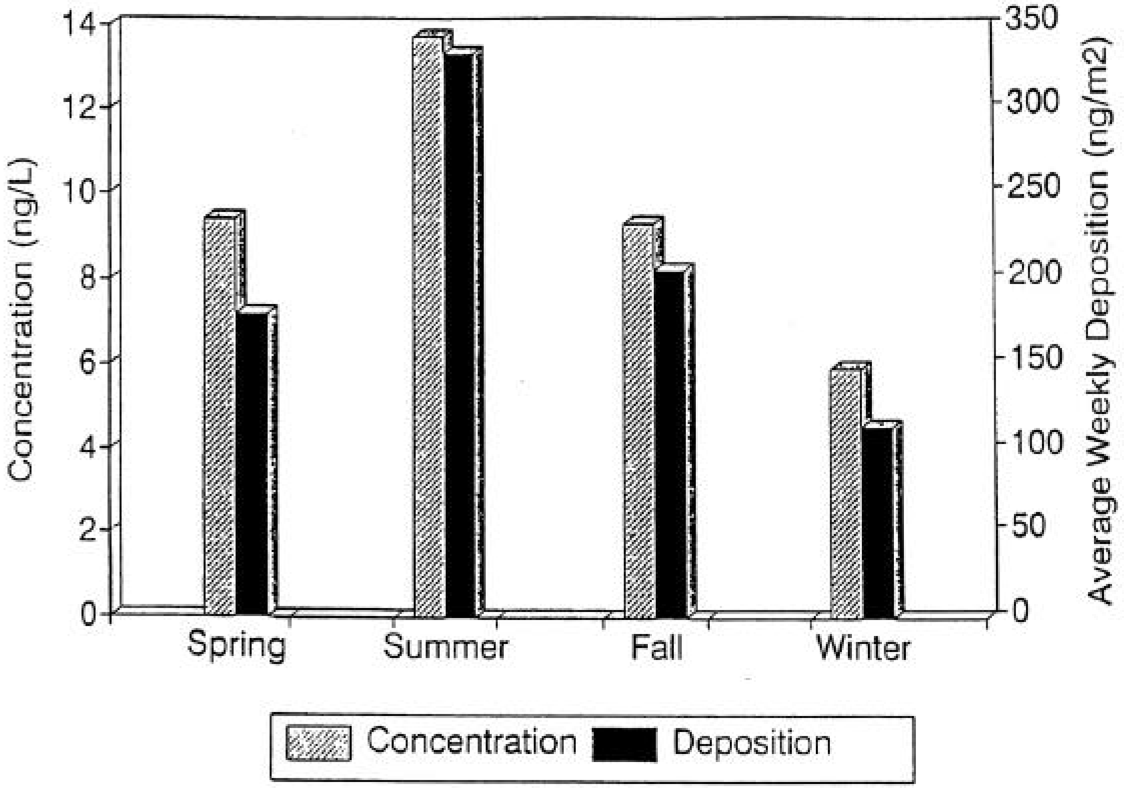

Figure 4. Seasonal variation of total mercury concentrations and wet deposition at MDN sites in the eastern North America in 1998.

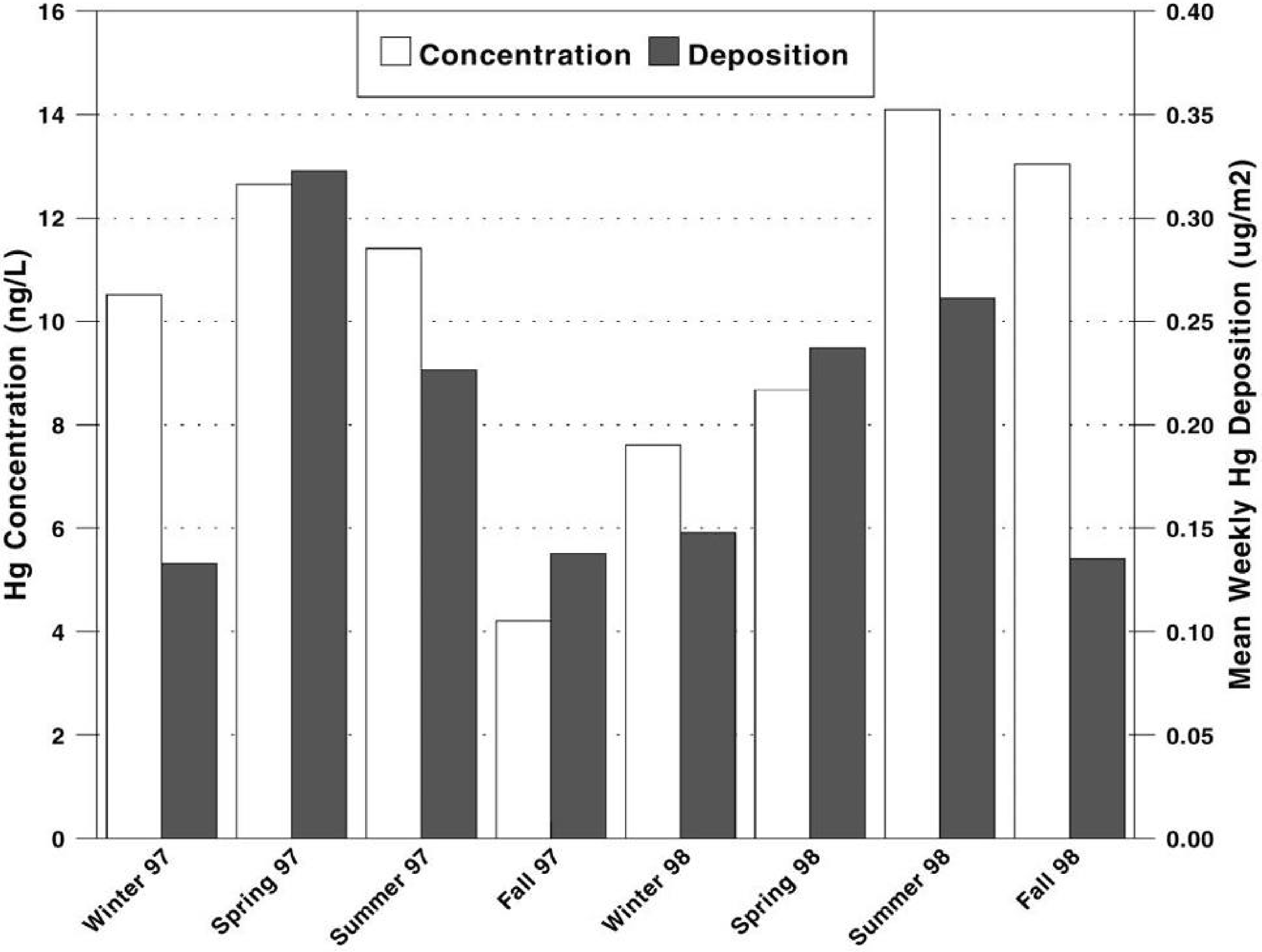

Figure 5. Seasonal mercury concentrations and depositions at the Hills Creek State Park MDN site (PA90) in Tioga County during 1997 and 1998.

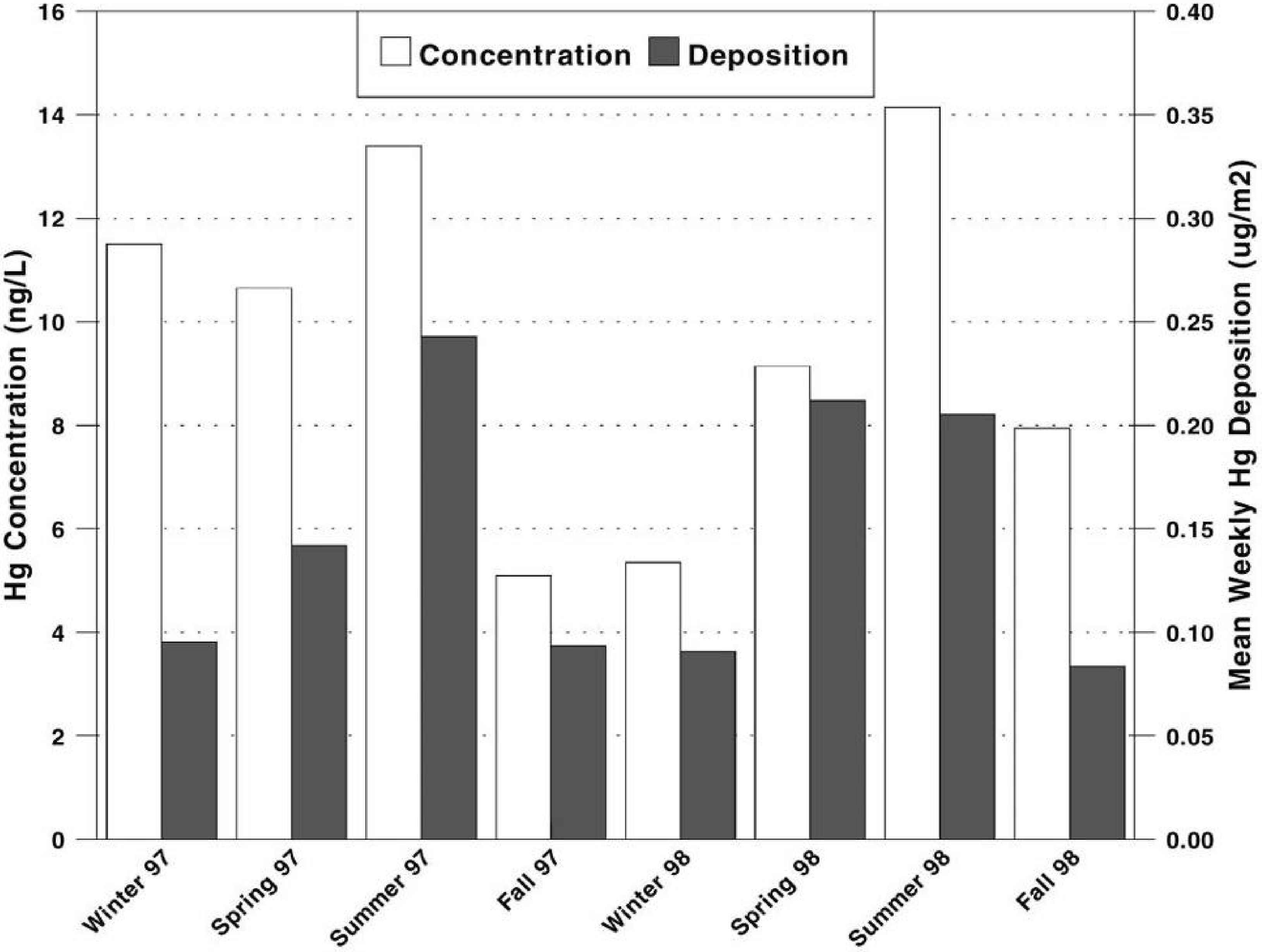

Figure 6. Seasonal mercury concentrations and depositions at the Allegheny Portage NHS Railroad MDN site (PA13) in Cambria County during 1997 and 1998.

Table 2. Wet deposition (μg/m^2/yr) and volume-weighted average concentration (ng/L) of total mercury in precipitation at selected Mercury Deposition Network (MDN) sites in 1995 through 1998[a].

SITE ID	**1995**	**1995**		**1996**		**1997**		**1998**
	Dep.	Conc.	**199** Dep.	Conc.	**199** Dep.	Conc.	**1998** Dep.	Conc.
MN16	6.4	8.4	7.6	10.2	7.6	11.3	8.8	11.3
MN18	4.0	9.0	*(11.1)*	*(14.2)*	4.2	10.4	9.2	14.1
WI08	5.2	10.0	6.3	10.0	6.6	12.5	9.0	11.7
WI09	10.0	10.5	6.7	9.6	5.6	10.1	5.8	11.3
WI36	9.3	12.5	8.2	9.4	8.3	11.2	7.5	11.6
ME98	*(5.2)*	*(3.6)*	8.4	6.0	7.7	6.8	9.0	6.1
ME09			*(5.5)*	*(4.0)*	5.7	6.1	6.7	5.9
NBO1			*(11.6)*	*(7.7)*	5.7	7.1	7.3	6.5
NSO1			*(11.7)*	*(7.5)*	7.6	6.5	6.4	5.3
NCO8	11.5	9.2	13.3	11.8	11.2	10.6	15.8	11.6
NC42	9.7	8.8	12.3	9.3	9.9	9.5	9.9	7.1
SC19	11.3	12.8	*(10.2)*	*(11.4)*	13.5	10.7	12.8	11.4
FL11	*(32-0)*	*(7.9)*	17.2	14.1	27.2	14.7	20.3	12.7
FL34					*(^4)*	*(18.7)*	26.1	11.4
FL04							20.1	13.8
TX21	*(4.0)*	*(8.1)*	9.8	10.8	12.3	9.0	12.7	10.6
WA18			(19.8)	*(22.0)*	18.9	18.3	5.4	5.9
PA13					10.9	9.2	9.8	10.2
PA90					7.3	9.6	7.5	9.0

a. Values in parentheses indicate that NADP completeness criteria were not met for this year. Other values are based on valid samples for at least 75% of the time and 75% of the precipitation amount for the year.

Conclusions

Annual wet deposition of total mercury at 30 MDN sites in the U.S. and eastern Canada in 1998 ranged from 4 µg/m^2 and 26 µg/m^2. Wet mercury deposition in Pennsylvania in 1998 ranged from 9.8 µg/m^2 in Cambria County to 7.5 µg/m^2 in Tioga County. The volume-weighted mean annual concentration of mercury in precipitation in the U.S. ranged from 4 ng/L to 23 ng/L. The volume-weighted average annual mercury concentration measured in the MDN Network in 1998 was 9.5 ng/L. The volume weighted mean concentration of total mercury in Pennsylvania ranged from 9.0 ng/L in Tioga County to 10.2 ng/L in Cambria County. At most sites, mercury concentrations and depositions were similar within geographic regions and between 1997 and 1998. At MDN sites in the Eastern U.S., wet deposition of mercury was highest in the summer and lowest in the winter. This seasonal pattern was also evident at the two Pennsylvania sites. Wet deposition was also lower in New England and Eastern Canada and higher in south Florida. In general, mercury deposition in Pennsylvania falls in the middle of values reported throughout the country. Wet deposition of mercury depends on both the mercury concentration in precipitation and the amount of precipitation. Both of these factors are higher during the summer months in Eastern North America and have an impact on the amount of mercury deposited on this region.

Mercury deposition will continue in Pennsylvania in 1999. The number of sites in the state will increase to four. A site in extreme southwestern Pennsylvania was activated this past summer (PA37). This site is supported by the U.S. Department of Energy. A fourth site will be added to the network in October, 1999. This site will be located at the Valley Forge National Historic Park in Montgomery County. This site will be supported by the Pennsylvania Department of Environmental Protection, Bureau of Air Quality Control.

Contact Information:

Mercury Lab (HAL)
Bob Brunette
Frontier Geosciences Inc.
414 Pontius Av. North
Seattle, WA 98109
206-622-6960 (voice)
206-622-6870 (fax)
bobb@frontier.wa.com

NADP Program Office
Clyde Sweet
Illinois State Water Survey
2204 Griffith Dr.
Champaign, IL 61820
217-333-7191 (voice)
217-333-6540 (fax)
csweet@sws.uiuc.edu

PA Site Supervisor
James A. Lynch
Penn State University
311 Forest Resources Lab
University Park, PA 16802
(814) 865-8830 (voice)
(814) 863-9173 (FAX)
jal@psu.edu

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APPENDIX

Table 1A. Weekly mercury concentration and deposition observations at MDN sites in Pennsylvania

Site	Date Off	Pptrec	Hg Conc. ng/L	Hg Dep. ng/m2	Quality Rating Code	Sample Protocol Code	Screening Level Code	Invalidation Code
PA13	970114	0.31	9.82	76.09	A	w		v
PA13	970121	0.20	7.28	36.99	A	w		
PA13	970128	1.00	7.80	197.83	A	w		
PA13	970204	0.10	13.73	34.86	A	w		
PA13	970211	0.93	6.42	151.60	A	w		
PA13	970218	0.74	18.71	351.60	A	w		
PA13	970225	0.20	15.55	78.99	A	w		
PA13	970304	1.48	11.77	442.49	A	w		
PA13	970311	0.98	18.81	465.73	A	w		
PA13	970318	0.71	12.40	223.70	A	w		
PA13	970325	0.18	22.70	100.91	A	w		
PA13	970401	1.20	6.11	186.14	A	w		
PA13	970408	0.00	----	0.00	A	w		n
PA13	970415	0.54	13.92	189.17	A	w		
PA13	970422	0.00	2.27	0.00	B	w		h
PA13	970429	0.63	9.60	152.42	A	w		
PA13	970506	0.65	19.17	316.49	A	w		
PA13	970513	0.35	17.54	155.93	A	w		
PA13	970520	2.25	15.39	879.63	B	w		h
PA13	970527	3.05	9.36	725.03	A	w		
PA13	970603	2.05	12.98	675.76	A	w		
PA13	970610	0.38	20.95	202.23	A	w		
PA13	970617	1.28	19.82	644.53	A	w		
PA13	970624	0.38	19.03	183.72	A	w		
PA13	970701	0.06	10.23	16.89	A	w		
PA13	970707	0.59	7.01	105.46	A	w		p
PA13	970715	0.50	13.06	165.86	A	w		
PA13	970722	0.27	38.95	267.13	A	w		
PA13	970729	1.00	8.84	224.42	A	w		
PA13	970806	0.05	35.91	45.61	A	w		
PA13	970812	0.00	----	0.00	A	w		n
PA13	970819	4.54	7.44	857.38	B	w		hr
PA13	970826	1.01	6.65	170.73	A	w		
PA13	970902	0.10	24.80	62.99	A	w		
PA13	970909	0.20	5.86	29.78	A	w		
PA13	970916	1.51	4.48	171.73	A	w		
PA13	970923	0.33	20.84	174.71	A	w		
PA13	970930	2.58	2.16	141.48	B	w		x
PA13	971007	0.35	6.79	60.40	A	w		
PA13	971015	0.09	3.66	8.37	B	w		r
PA13	971021	0.00	----	0.00	A	w		n
PA13	971029	0.97	6.84	168.62	A	w		
PA13	971104	2.04	2.79	144.62	B	w		h
PA13	971112	6.38	2.59	418.95	A	w		
PA13	971118	0.72	5.35	97.77	A	w		
PA13	971125	0.35	5.00	44.42	A	w		
PA13	971202	1.19	10.78	327.07	A	w		

Table 1A (Continued)

Site	Date Off	Pptrec	Hg Conc. ng/L	Hg Dep. ng/m2	Quality Rating Code	Sample Protocol Code	Screening Level Code	Invalidation Code
PA13	971209	0.39	7.03	70.50	A	w		
PA13	971216	0.58	5.16	75.97	A	w		
PA13	971223	0.31	48.47	384.77	A	w		
PA13	971230	0.84	7.46	158.29	A	w		
PA13	980106	0.48	12.06	147.00	A	W		
PA13	980113	1.28	9.57	311.05	A	W		
PA13	980120	0.55	4.13	57.76	B	W		hn
PA13	980127	1.01	2.94	75.48	A	W		
PA13	980203	0.40	6.84	69.52	A	W		
PA13	980210	0.85	6.34	136.84	A	W		
PA13	980217	0.32	9.01	74.37	A	W		
PA13	980225	2.39	3.35	203.29	A	W		
PA13	980303	0.53	11.77	158.47	A	W		
PA13	980310	0.85	6.95	150.03	A	W		
PA13	980317	0.10	20.56	52.22	A	W		
PA13	980324	1.50	8.39	319.49	B	W		x
PA13	980331	0.01	100.05	10.50	A	W		v
PA13	980407	1.18	3.65	108.87	A	W		
PA13	980414	1.44	6.97	254.86	B	W		x
PA13	980421	2.15	9.08	495.71	B	W		x
PA13	980428	2.00	14.24	723.30	B	W		x
PA13	980504	0.97	5.56	136.98	B	W		x
PA13	980512	3.06	5.01	389.75	B	W		x
PA13	980519	0.23	30.99	181.07	B	W		x
PA13	980526	0.16	7.77	31.56	A	W		
PA13	980602	0.35	25.93	230.47	B	W		x
PA13	980609	0.14	18.61	68.54	A	W		
PA13	980616	2.42	11.61	713.74	B	W		x
PA13	980623	0.74	16.75	314.77	B	W		x
PA13	980630	0.50	19.21	244.01	A	W		
PA13	980707	0.55	12.07	168.61	A	W		
PA13	980714	1.31	10.11	335.84	B	W		x
PA13	980721	0.60	18.82	286.83	A	W		
PA13	980728	0.38	23.26	221.53	B	W		h
PA13	980804	0.30	17.34	132.13	A	W		
PA13	980811	0.54	14.85	205.60	B	W		x
PA13	980818	1.30	9.60	317.00	A	W		
PA13	980825	0.14	26.93	92.34	A	W		
PA13	980901	0.57	20.39	295.22	A	W		
PA13	980908	0.89	16.84	380.58	A	W		
PA13	980916	0.19	11.97	57.77	A	W		
PA13	980922	0.25	25.12	159.51	A	W		
PA13	980929	0.28	28.24	204.43	A	W		
PA13	981006	0.70	6.65	117.32	A	W		
PA13	981013	1.90	9.19	443.59	A	W		
PA13	981020	0.19	6.82	32.91	A	W		
PA13	981027	0.02	9.17	5.82	A	W		
PA13	981103	0.05	50.57	64.22	A	W		
PA13	981110	0.35	13.09	116.37	A	W		
PA13	981117	0.25	8.43	53.56	A	W		
PA13	981124	0.08	38.26	72.88	A	W		
PA13	981201	0.15	12.25	46.68	A	W		
PA13	981208	0.09	13.70	31.33	B	W		r
PA13	981215	0.19	2.80	13.52	A	W		
PA13	981222	0.88	11.44	254.27	A	W		

Table 1A (Continued)

Site	Date Off	Pptrec	Hg Conc. ng/L	Hg Dep. ng/m2	Quality Rating Code	Sample Protocol Code	Screening Level Code	Invalidation Code
PA13	981229	0.05	10.19	12.95	A	W		
PA90	970114	0.22	----	----	C	w	F	f
PA90	970121	0.23	11.14	65.09	A	w		
PA90	970128	0.66	7.08	118.72	A	w		
PA90	970204	0.03	69.87	44.37	A	w		v
PA90	970211	0.53	----	----	C	w	C	rc
PA90	970218	0.57	----	----	A	Q		v
PA90	970226	0.04	42.76	48.87	A	w		v
PA90	970304	0.90	14.85	339.47	A	w		
PA90	970311	0.85	1.67	36.04	A	w		
PA90	970318	0.56	7.68	109.22	A	w		
PA90	970325	0.16	11.68	47.47	A	w		
PA90	970401	0.75	4.03	76.72	A	w		
PA90	970408	0.04	----	----	A	w		n
PA90	970415	0.25	6.42	40.77	A	w		
PA90	970422	0.20	6.02	30.57	A	w		
PA90	970429	0.41	10.51	110.76	A	w		
PA90	970506	0.63	14.17	226.78	A	w		
PA90	970513	0.38	7.66	73.94	B	w		h
PA90	970520	0.87	13.58	300.09	B	w		h
PA90	970527	0.25	25.28	160.53	A	w		
PA90	970603	1.09	15.33	424.53	A	w		
PA90	970610	0.06	35.85	50.08	A	w		
PA90	970617	0.12	6.42	19.56	B	w		zr
PA90	970624	0.78	16.23	321.58	A	w		
PA90	970701	1.55	16.00	629.84	A	w		
PA90	970708	0.05	13.81	17.54	A	w		
PA90	970715	1.02	15.34	397.42	A	w		
PA90	970722	0.78	13.98	276.95	A	w		
PA90	970729	0.93	10.55	249.15	A	w		
PA90	970805	0.31	5.73	45.45	A	w		
PA90	970812	0.11	28.96	80.91	A	w		
PA90	970819	1.89	11.69	562.57	A	w		
PA90	970826	0.69	11.79	208.05	B	w		hpr
PA90	970902	0.98	11.87	295.80	A	w		p
PA90	970909	0.16	15.93	65.14	B	w		pr
PA90	970916	0.74	5.42	101.67	A	w		p
PA90	970923	0.46	10.95	128.47	A	w		p
PA90	970930	1.50	5.09	194.02	A	w		
PA90	971007	0.33	18.25	153.01	A	w		
PA90	971014	0.00	----	0.00	A	w		n
PA90	971021	0.00	----	0.00	A	w		n
PA90	971028	0.82	3.50	72.97	B	w		h
PA90	971104	2.17	2.24	123.38	A	w		
PA90	971110	1.44	5.44	198.89	A	w		
PA90	971118	1.13	3.40	97.70	A	w		
PA90	971125	0.23	6.82	38.98	A	w		
PA90	971203	0.41	3.90	40.59	A	w		
PA90	971209	0.19	9.72	48.17	A	w		
PA90	971216	0.80	8.37	170.10	B	w		h
PA90	971222	0.02	28.92	14.69	A	w		v
PA90	971229	0.44	6.13	67.70	A	w		
PA90	980106	1.33	3.61	121.90	B	W		h
PA90	980113	1.41	7.01	251.18	A	W		
PA90	980120	0.62	1.75	27.32	A	W		

Table 1A (Continued)

Site	Date Off	Pptrec	Hg Conc. ng/L	Hg Dep. ng/m2	Quality Rating Code	Sample Protocol Code	Screening Level Code	Invalidation Code
PA90	980127	0.53	4.75	63.88	A	W		
PA90	980203	0.06	11.14	16.98	B	W		vh
PA90	980210	0.13	11.84	39.11	B	W		h
PA90	980217	0.40	4.99	50.71	A	W		
PA90	980224	2.01	4.89	249.87	A	W		
PA90	980303	0.75	3.06	58.26	A	W		
PA90	980310	0.89	3.41	77.18	A	W		
PA90	980317	0.13	9.63	31.81	A	W		
PA90	980324	1.35	6.36	218.22	B	W		h
PA90	980331	0.04	25.08	25.48	A	W		
PA90	980407	0.48	6.01	73.33	B	W		x
PA90	980414	1.66	4.39	185.06	B	W		x
PA90	980421	1.83	7.19	334.18	C	W	F	nf
PA90	980428	0.73	4.81	89.11	A	W		
PA90	980505	0.58	10.30	151.74	B	W		x
PA90	980512	2.64	5.53	370.84	B	W		x
PA90	980519	0.72	35.27	645.00	B	W		x
PA90	980526	0.18	11.18	51.12	A	W		
PA90	980601	0.63	25.70	411.22	B	W		x
PA90	980609	0.48	17.55	213.94	B	W		x
PA90	980616	1.45	9.04	332.95	A	W		
PA90	980623	0.15	14.05	53.53	B	W		h
PA90	980630	1.68	15.34	654.60	B	W		hx
PA90	980707	0.65	13.34	220.17	B	W		hx
PA90	980714	0.55	21.93	306.42	B	W		h
PA90	980721	0.46	11.11	129.78	A	W		
PA90	980728	1.05	4.73	126.09	B	W		h
PA90	980804	0.04	18.83	19.13	A	W		
PA90	980811	0.30	19.66	149.83	B	W		x
PA90	980818	0.09	23.68	54.14	B	W		x
PA90	980825	0.18	28.94	128.64	A	W		
PA90	980901	0.35	31.40	279.11	B	W		x
PA90	980908	0.69	9.39	164.64	B	W		x
PA90	980915	0.16	4.37	17.21	A	W		
PA90	980922	0.13	15.56	51.39	B	W		h
PA90	980929	0.39	15.95	158.04	A	W		
PA90	981006	0.17	8.28	34.18	A	W		p
PA90	981013	2.64	6.38	428.02	B	W		x
PA90	981020	0.07	40.36	71.76	B	W		hxz
PA90	981027	0.15	5.10	19.43	A	W		
PA90	981103	0.10	0.78	1.89	A	W		
PA90	981110	0.05	13.32	18.93	A	W		
PA90	981117	0.40	7.03	70.50	A	W		
PA90	981124	0.22	3.70	21.13	B	W		h
PA90	981202	0.22	5.22	28.50	B	W		x
PA90	981208	0.07	13.25	23.55	B	W		r
PA90	981217	0.08	3.94	8.00	A	W		
PA90	981222	0.87	4.16	91.69	B	W		s
PA90	981229	0.00	----	0.00	A	W		v

Quality Control Code Description for MDN Data

QR Quality rating code. A code indicating the relative quality of the sample:

A	Valid samples with no problems; contained only water; all sampling and laboratory protocols were followed; all required equipment was installed and operating properly.
B	Valid samples with minor problems; may have contaminants such as insects of plant debris; there may be an exception to approved sampling or laboratory methods; required equipment may be lacking or not operating properly. The quality codes for specific problems are listed for each B sample. The laboratory does not consider these problems sufficient to invalidate the data, but there is more uncertainty than for A data. These data are used along with A data to calculate average concentrations and deposition.
C	Invalid samples; major problems occurred; the laboratory does not have confidence in the data. These data are not reported in the database, but the quality codes for the problems are listed.

SP Sample protocol code. A code indicating departures from standard sample collection procedures that may have compromised sample integrity:

(blank)	No identifiable departures
U	Undefined sample type
B	Bulk sample
Q	Quality assurance sample

SL Screening level code. A code indicating departures from field or laboratory standard operating procedures.

(blank)	No identifiable departures
F	Field error
L	Laboratory error
C	Contaminated sample

Invalcode A series of codes assigned to samples which describe problems. If the problems are minor, the samples may receive a quality rating of "B", but they are still considered valid by NADP/MDN. Problems serious enough to invalidate the sample result in a quality rating of "C". C samples are not used in the calculation average concentrations, deposition, or data completeness.

b	Bulk sample. (Collector was open continuously).
u	Undefined sample. (Collector was open for > 6 hours and less than the entire sampling interval when no precipitation was occurring.

f	Major field protocol departure.
c	Contaminated sample.
v	Low volume sample.
s	Short sampling interval < 6 days).
e	Extended sampling interval (> 8 days).
l	Lab error.
i	Incomplete chemical analysis.
n	No sample, no analysis, or volume < 1.0mL.
p	Precipitation amount unknown.
x	Debris present.
r	No event recorder.
h	Handling protocol problems.
z	Site operations problems.