LONG-TERM ATMOSPHERIC MERCURY TRENDS IN EASTERN NORTH CAROLINA: RELATIONSHIPS BETWEEN LOCAL SOURCE ACTIVITIES AND AMBIENT AIR MERCURY CONCENTRATIONS

J. Hayward*, K. Clevenger and T. Crawford

North Carolina Department of Environment and Natural Resources,
Division of Air Quality, Raleigh, NC

ABSTRACT

Mercury is a naturally occurring substance that is present at very low levels in ambient air as a result of both natural and anthropogenic processes. In recent years, ultra-sensitive techniques have been developed to measure and speciate mercury in ambient air and rainwater, allowing for the determination of temporal and spatial trends in atmospheric mercury levels. In this paper, we present the results of a multi-year study characterizing trends in ambient air mercury in eastern North Carolina, an area impacted by elevated levels of methylmercury in fish and fish-consuming humans. We present data on total gaseous mercury (TGM) levels in ambient air at several sampling locations, as well as shorter-term measurements of reactive gaseous mercury (RGM) at one location. We also illustrate associations between atmospheric mercury concentrations and wind direction, suggesting local source impacts. Additionally, regional wet deposition data collected in support of the National Atmospheric Deposition Program's Mercury Deposition Network are presented. We submit that historical trends in atmospheric mercury in these areas reflect regional anthropogenic activities involving mercury use.

INTRODUCTION

Concern over mercury emissions originating from a variety of man-made sources has been increasing in the United States due in part to the identification of widespread contamination of fish with methylmercury, a potent neurodevelopmental toxin. While considerable uncertainty remains, it is generally agreed that some fraction of mercury emitted from local or regional sources will enter into nearby aquatic ecosystems through wet and dry deposition mechanisms. Thus, it may be beneficial to identify and reduce airborne emissions near aquatic systems that efficiently move atmospheric inputs of mercury into the aquatic food chain.

The eastern coastal plain of North Carolina is characterized by elevated levels of methylmercury in several species of freshwater fish consumed by recreational and subsistence fishermen. An epidemiological survey conducted in the early 1990s involving area residents identified some of the highest levels of mercury in human hair and blood ever recorded in the U.S. – confirming that both high rates of fish consumption and high levels of methylmercury in fish were contributing to excessive exposures. This focused attention on identifying contributions to the mercury burden in these ecosystems, including atmospheric inputs.

For several years, the North Carolina Division of Air Quality has operated two ambient air monitoring stations in eastern North Carolina, collecting continuous data on atmospheric concentrations of TGM. The first site, at Pettigrew State Park in northeastern North Carolina, collected data on TGM levels during the summer of 1996. The second site, at Lake Waccamaw State Park in southeastern North Carolina, has collected data since December of 1997. Both locations are situated in rural/remote areas at least 25 kilometers from any significant source of mercury emissions. However, the Waccamaw site is situated approximately 50 kilometers west of Wilmington, NC and may also be affected by major release points in the area, including waste incinerators, coal-fired utility boilers and a mercury cell chlor-alkali operation.

Following the analysis of early data from the Waccamaw and Pettigrew sites, additional monitoring locations were established in Riegelwood, NC, an industrial area located between Lake Waccamaw and Wilmington, NC. Measurement of RGM was initiated at one of these sites in March of 2000.

In this paper we describe the results from these atmospheric monitoring studies, as well as results from measurement of mercury in rainwater collected at Lake Waccamaw and Pettigrew State Parks in support of the national Mercury Deposition Network. We also discuss our experiences with relatively new techniques to continuously measure atmospheric RGM in ambient air over long time periods. Finally, we attempt to relate notable changes in ambient air mercury trends to significant changes in local and regional use patterns.

EXPERIMENTAL

Ambient air TGM was measured using Tekran Model 2537A mercury vapor analyzers (Tekran, 1999a). These instruments allow for sub-ng/m^3 analysis of mercury in air by first trapping mercury vapor passed over an ultra-pure gold adsorbent, then thermally desorbing the trapped mercury for measurement by Cold Vapor Atomic Fluorescence Spectrometry. The dual cartridge design allows for continuous monitoring by alternating mercury sampling and desorption/measurement. The instruments were housed in temperature-controlled enclosures, maintained between 20^0C and 30^0C. Ambient air was drawn through ¼ inch heated Teflon tubing containing two 0.2 μm particulate filters in the sample line. The instruments were programmed to initiate automatic calibrations by way of an internal injection from a mercury vapor permeation source every 25 hours. Data are not presented if the area difference between internal calibrations exceeded 5 percent. The instruments were programmed to measure mercury levels every 5 or 15 minutes, depending on the location, using a flow rate of 1.5 L of air per minute. Ambient air mercury was measured continuously, except under unusual circumstances such as instrument failure, power outages or hurricane conditions.

Ambient air RGM was measured using a Tekran Model 1130 Mercury Speciation Unit, a front-end accessory for the Tekran 2537A (Tekran, 1999b). The system uses an annular denuder coated with potassium chloride that traps RGM while allowing elemental mercury vapor to pass through to the detector unit. RGM is then released to the sample line as mercury vapor by heating the denuder to 500^0C for 15 minutes, once every two hours. The denuder inlet was placed at a height of 5 m above ground level for all sampling. Denuder assemblies were replaced on a weekly basis.

Meteorological stations were erected at the Waccamaw and Riegelwood locations. All sites were equipped to continually measure temperature, wind speed and wind direction during time periods simultaneous with mercury collection. Conditions were monitored at a height of 6 m at the Riegelwood sites and 20 meters at the Waccamaw site. Data were downloaded weekly by the site operator. The initial calibration was carried out by the manufacturer and performance and system audits carried out quarterly. Meteorological data were further validated after downloading at the laboratory using EPA guidance (USEPA, 1987).

Rainwater collection was performed consistent with guidance from the National Atmospheric Deposition Program (MDN). Weekly composite rainwater samples were collected using a modified Aerochem Metric sampler with a motor-activated lid that opened in response to precipitation events. All samples were retrieved using clean techniques and shipped to Frontier Geosciences for measurement of mercury using EPA Method 1631. Precipitation amount and temperature were recorded at the sites. Data are presented as cumulative wet deposition (ng/m^2) and volume-weighted mercury concentration (ng/L) for each weekly composite sample.

Estimated source mercury emission rates were compiled from the most recent available State of North Carolina air permit databases, unless more recent, reliable estimates could be found. Estimated emission quantities were verified against state air quality permits, whenever possible. Sources reporting annual releases less than 10 pounds were not included in this analysis.

RESULTS

Total Gaseous Mercury: TGM measurements at Waccamaw State Park are summarized in table 1 and presented graphically in figure 1. Data are derived from 15-minute average TGM measurements. Results from the Riegelwood Flynn and Ballpark data are presented in tables and figures 2 and 3, respectively. All Riegelwood data are generated from 5-minute average TGM concentrations.

Simultaneous on-site meteorological data are available for significant periods at all sampling locations. Figure 4 illustrates the relationship between wind direction and TGM readings at Lake Waccamaw for several time periods appearing in figure 1. Figures 5 and 6 present data from the Riegelwood sites.

Reactive Gaseous Mercury: Sampling for atmospheric RGM was conducted at the Riegelwood Ballpark site beginning in March of 2000. Figure 7 illustrates RGM and TGM levels recorded between March 7 and March 18. TGM values in figure 7 represent 2-hour averages, based on 24 consecutive 5-min periods. RGM values represent concurrent 2-hour average concentrations. Each sampling period was interrupted for 40 minutes for denuder desorption and RGM measurement.

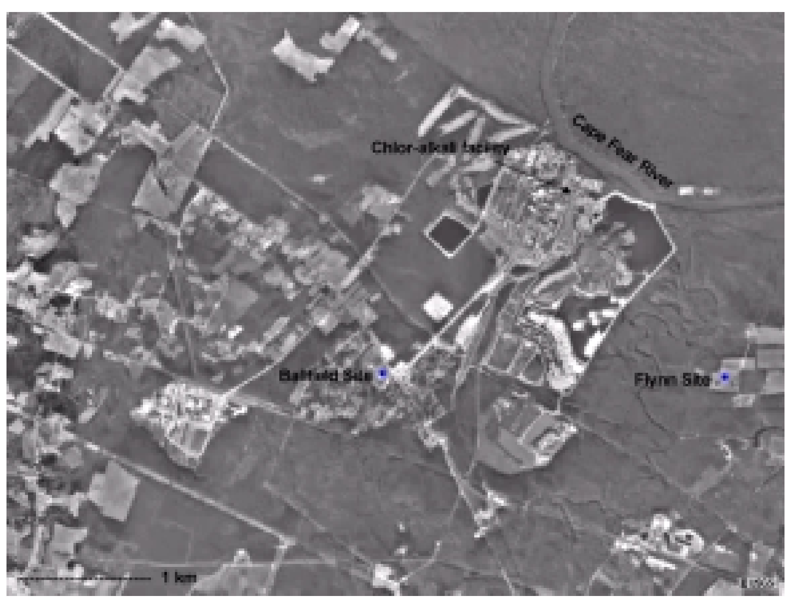
Mercury in Rainwater: Data on mercury in rainwater collected from Pettigrew and Waccamaw State Parks for various periods between 1996 and 1999 are presented in table 4 and figures 8 and 9. All data in table 4 are based on annual figures. Volume-weighted average mercury concentration is calculated by dividing the annual sum of weekly deposition rates (ng/m^2) by annual precipitation (mm). Wet deposition data for 1999 are preliminary and have not been fully quality-assured by the MDN program office.

DISCUSSION

Total Gaseous Mercury: Data reported as TGM are believed to be representative of vapor-phase elemental mercury, Hg^0. Although reactive gaseous species of mercury such as $HgCl_2$ exist in air, they are typically present at less than 5% of Hg^0 levels and are unlikely to reach the gold traps in the mercury analyzers due to the high degree of water solubility for these species (Lindberg; Stevens, personal communication). Data from ambient air monitoring efforts at Pettigrew State Park are not presented here but were remarkable only for exhibiting uninterrupted northern hemisphere "background" conditions for TGM (EPA, 1997a). During the summer of 1996, the average 15-minute reading for TGM at this location was 1.54 ng/m^3 (max = 6.01 ng/m^3, SD = 0.24, n=4664). In contrast, early sampling results from Lake Waccamaw State Park highlighted frequent fluctuations in TGM exceeding an order of magnitude above background conditions (see figure 1). Initially, these results were considered puzzling given the relative remoteness of both sites and reported data on atmospheric TGM at remote or rural locations (EPA, 1997a).

Both Pettigrew and Waccamaw State Parks are situated in very similar areas characterized by flat marshy or sandy terrain with sparse development and little industrial activity within 20 to 25 kilometers. However, while the closest reported point source of mercury emissions to Pettigrew is a large pulp and paper mill approximately 30 kilometers away in Plymouth, NC (1996 reported emissions, 131 lbs.), the Waccamaw site could be affected by several large regional mercury emission sources. These include two coal-fired utility boilers, a municipal waste incinerator and a mercury cell chlor-alkali facility (see table 5). In order to determine whether a directional component existed for elevated TGM values a meteorological station was erected at Waccamaw State Park with a wind sensor placed at 20 meters above ground level. Overlapping wind direction and TGM concentration data are available for limited periods during 1998, including several weeks that included significantly elevated TGM readings (see figures 1 and 4). The majority of elevated readings during these periods appear associated with winds originating from the east-northeast.

Two monitoring stations were erected in the area surrounding Riegelwood, NC in early 1999 to provide additional regional sampling locations. These sites were situated approximately 1 kilometer southeast and south-southwest of the chlor-alkali operation and a large pulp-and-paper mill. TGM results from the Riegelwood sites show patterns similar to those seen at Waccamaw State Park (figures 2 and 3). Mercury concentration roses suggest a relationship between wind direction and elevated TGM readings (figures 5 and 6) consistent with a source of mercury



located to the north of both monitoring stations. However, there is a greater degree of scatter in these data and several of the events appear to occur when winds are light and variable.

Soon after the initiation of TGM monitoring at the Riegelwood Flynn site, the chlor-alkali plant announced plans to cease mercury cell chlorine production and convert to a membrane process that would eliminate the active use of mercury. Shipment of mercury to off-site locations continued during the spring and summer of 1999 with residual clean-up extending into 2000.

Average levels of TGM have declined at all three monitoring stations through 1999 and early 2000. This pattern is most pronounced at Lake Waccamaw, where TGM levels are now consistent with “background” rural/remote locations. Short-term elevations in TGM continue to arise at the Riegelwood sites, but the frequency and magnitude of these phenomena are greatly reduced relative to earlier time periods.

<u>Reactive Gaseous Mercury</u>: Water-soluble forms of mercury in air include $HgCl_2$ and other compounds incorporating mercury in the mercuric (Hg^{2+}) oxidation state. In the atmosphere these species may exist as gases or associated with particulate matter (Lindberg). The atmospheric residence time for RGM emitted from point sources is likely much shorter than that for TGM which is known to persist in the atmosphere for months or years. Due to the high degree of water-solubility it is believed that these species are subjected to atmospheric removal processes involving wet or dry deposition. Thus, it is important to gain an understanding of the chemical speciation of mercury in point source emissions and ambient air to better predict the impact on nearby aquatic systems.

In March of 2000, we initiated ambient air monitoring for RGM at Riegelwood, NC using a speciation method that employs an annular denuder system for collection of water-soluble forms of mercury. Our primary goal was to determine whether any consistent pattern existed between fluctuations in TGM and observed concentrations of RGM. In figure 7 we present preliminary data on levels of RGM and TGM simultaneously measured at Riegelwood Ballpark between March 7 – 18, 2000. From this limited data set, no consistent pattern appears to emerge. On two occasions, 2-hour average TGM levels rose above 4 ng/m^3, but while RGM was increased during the event on March 18, it was depressed during the March 14 event. This could suggest that elevated TGM levels are unrelated to RGM fluctuations or that variable atmospheric conditions were differentially affecting the various mercury species. Rain events are known to depress RGM levels in air while leaving TGM levels unchanged (Lindberg). It is conceivable that precipitation during the March 14 sampling event scavenged RGM from the air while still allowing the TGM plume to reach the sampling device. Future studies will incorporate more thorough site-specific information on precipitation and humidity levels.

It is worth noting that an intermittent pattern of depressed TGM readings appeared during this and subsequent RGM monitoring efforts. On many occasions the first several 5-minute TGM readings immediately following the denuder desorption cycle appeared artificially depressed down to levels as low as 0 ng/m^3. Recovery to expected levels (~1.5 ng/m^3 or higher) would generally be achieved before the end of the 2-hour analysis period. Suspect readings are represented in figure 7 as white columns. We have not yet determined the cause of these anomalies but suspect that they may be related to the release of material from the denuder assembly during heating and desorption that interferes with the collection efficiency of the gold traps. We are currently evaluating methods to improve analytical performance, including the attachment of a soda-lime trap to the sample line.

Mercury in Rainwater: Rainwater samples were collected on a weekly basis at Lake Waccamaw and Pettigrew State Parks in support of the national Mercury Deposition Network. Data on rainwater mercury concentrations and cumulative deposition rates are presented here to supplement atmospheric data (see table 4 and figures 8 & 9). Wet deposition rates are dependent on precipitation levels as well as mercury concentration in rainwater. Annual wet deposition rates in North Carolina are generally higher than rates in western and northern states but lower than areas such as south Florida. Annual volume-weighted mercury concentrations are comparable to other MDN network locations (Sweet).

Several intriguing patterns can be seen in the data from these two rural locations. As evidenced in table 4, both mercury concentration and wet deposition rates are consistently higher at Lake Waccamaw than Pettigrew State Park. It is conceivable that this pattern could be a result of local source influences. However the substantial variability in the week-to-week deposition totals and the composite sampling approach make it difficult to draw any meaningful conclusions on this relationship at this time. It will be interesting to note whether any consistent reductions in rainwater mercury concentration appear in the years ahead as local and regional sources reduce mercury use.

A seasonal pattern of rainwater mercury concentration appears when the data are separated into summer (April – September) and winter (October – March) months. The seasonal effect on rainwater mercury concentration has been described elsewhere (Sweet, Mason). While snow is believed to be less efficient at scavenging particles from the atmosphere, little or no frozen precipitation would be expected at these sites, even during winter months. Other potential reasons for seasonal variability could include a temperature effect on atmospheric or cloud-water reactions or seasonal shifts in air mass movement.

CONCLUSIONS

Historical results from long-term ambient air monitoring at Lake Waccamaw State Park suggest the possibility of regional source impacts on TGM levels. Recent improvements occurred coincident with a substantial reduction in mercury use at a chlor-alkali facility located approximately 25 kilometers to the east-northeast. At monitoring stations located within a mile of the former mercury-cell operation, fluctuations in TGM continue to be seen although with diminishing magnitude and frequency. A clear relationship between atmospheric TGM and RGM in this area has not yet been established. Methods to continuously monitor atmospheric RGM have encountered complications that may be resolved by making minor sampling modifications. Composite rainwater sampling and analysis suggests that wet deposition rates in eastern North Carolina are comparable to other areas along the east coast of the United States. Annual cumulative wet deposition and rainwater mercury concentration are slightly, but consistently, higher at Lake Waccamaw than at Pettigrew State Park.

Table 1
Quarterly statistics for ambient air TGM measured at Lake Waccamaw. Values were calculated using 15-minute average TGM concentrations. All values in ng/m^3.

Lake Waccamaw (TGM)	1998[1]			1999[2]				2000[3]
	1st Q	**3rd Q**	**4th Q**	**1st Q**	**2nd Q**	**3rd Q**	**4th Q**	**1st Q**
10th percentile	1.53	1.21	1.35	1.54	1.50	1.08	1.33	1.56
25th percentile	1.69	1.44	1.58	1.71	1.64	1.36	1.54	1.67
50th percentile (median)	1.87	1.62	1.77	1.86	1.77	1.54	1.67	1.79
75th percentile	2.08	1.81	1.94	1.99	1.87	1.65	1.78	1.90
90th percentile	2.50	2.82	2.24	2.15	1.98	1.73	1.90	1.99
95th percentile	4.02	7.02	4.96	2.26	2.09	1.82	2.01	2.07
99th percentile	11.47	22.07	21.15	3.80	2.58	2.43	2.39	2.30
Maximum	33.31	44.42	60.97	7.67	6.75	7.17	5.12	4.08
Arithmetic mean	2.23	2.44	2.40	1.88	1.75	1.49	1.65	1.78
Standard deviation	1.85	3.66	3.53	0.42	0.29	0.35	0.26	0.20
Count (n)	6056	2986	7102	6566	5829	6351	8410	6550

[1]Missing data: 1/21 - 2/3, 3/3 - 6/23, 7/14 - 8/11, 8/18 - 9/24, 12/15 - 1/17/99.
[2]Missing data: 2/11- 2/15, 5/17 - 5/20, 5/24 - 6/3, 6/26 - 7/5, 9/15 - 9/21.
[3]Missing data: 2/14-2/24.

Table 2
Quarterly statistics for TGM measured at Riegelwood Flynn site. Values are calculated using 5-minute average TGM concentrations. All values in ng/m^3.

Riegelwood Flynn (TGM)	1999[1]			
	1st Q	**2nd Q**	**3rd Q**	**4th Q**
10th percentile	1.92	1.51	1.36	1.42
25th percentile	2.08	1.62	1.51	1.55
50th percentile (median)	2.31	1.76	1.65	1.72
75th percentile	2.87	1.98	1.79	2.14
90th percentile	4.43	2.43	2.06	2.40
95th percentile	6.36	3.77	2.75	3.31
99th percentile	28.70	20.83	15.11	15.23
Maximum	338.32	247.29	203.64	60.54
Arithmetic mean	3.76	2.55	2.17	2.23
Standard deviation	10.72	5.94	4.84	2.80
Count (n)	3484	20595	15281	7973

[1]Missing data: 3/8 - 3/24, 4/11 - 4/13, 4/19 - 5/5, 8/11 - 8/14, 8/28 - 9/3, 9/14 - 11/30, 12/7 - 12/21.

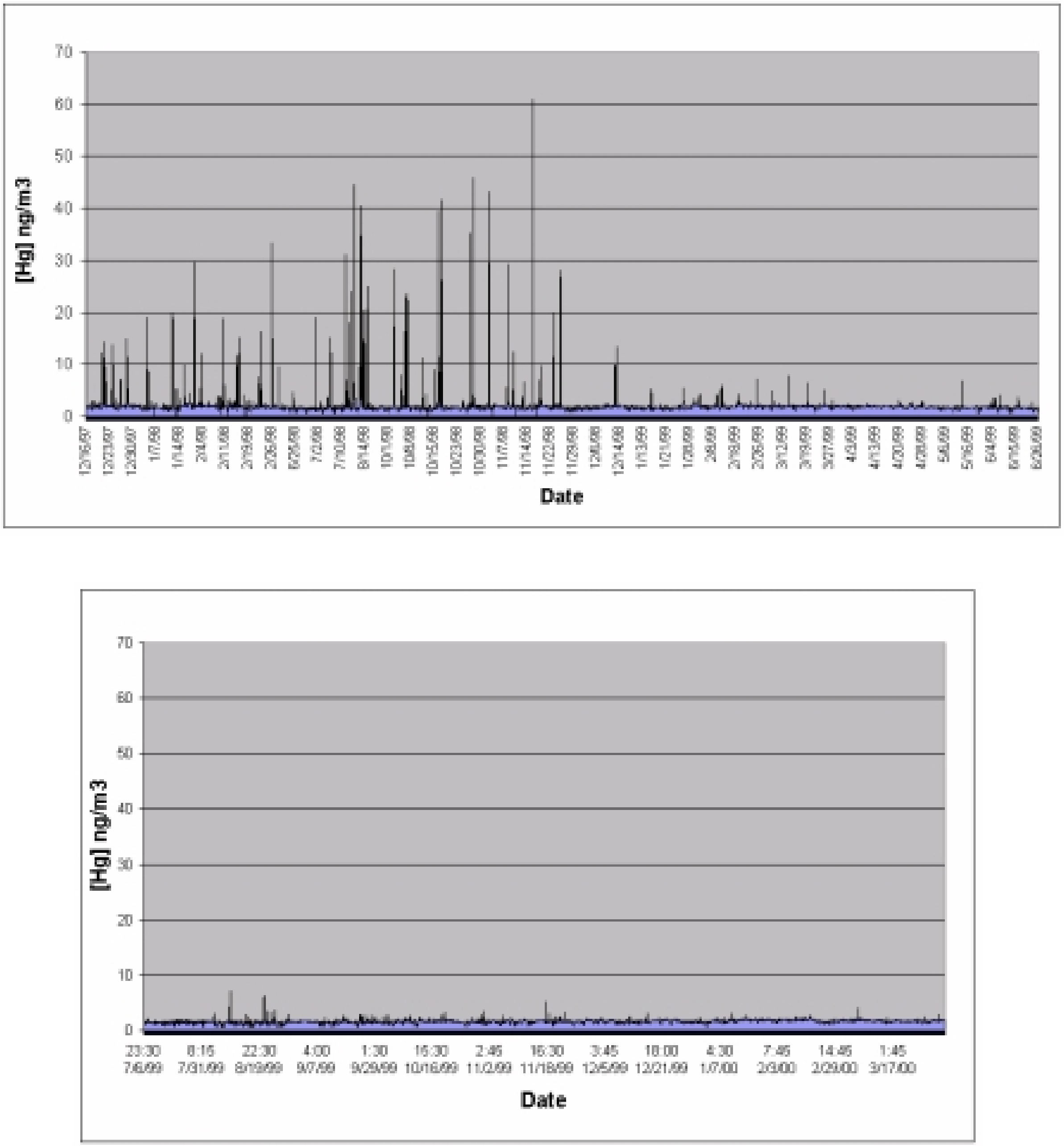


Fig. 1. Lake Waccamaw TGM concentration profile, December 1997 – March 2000. All individual data points represent 15-minute average concentrations.

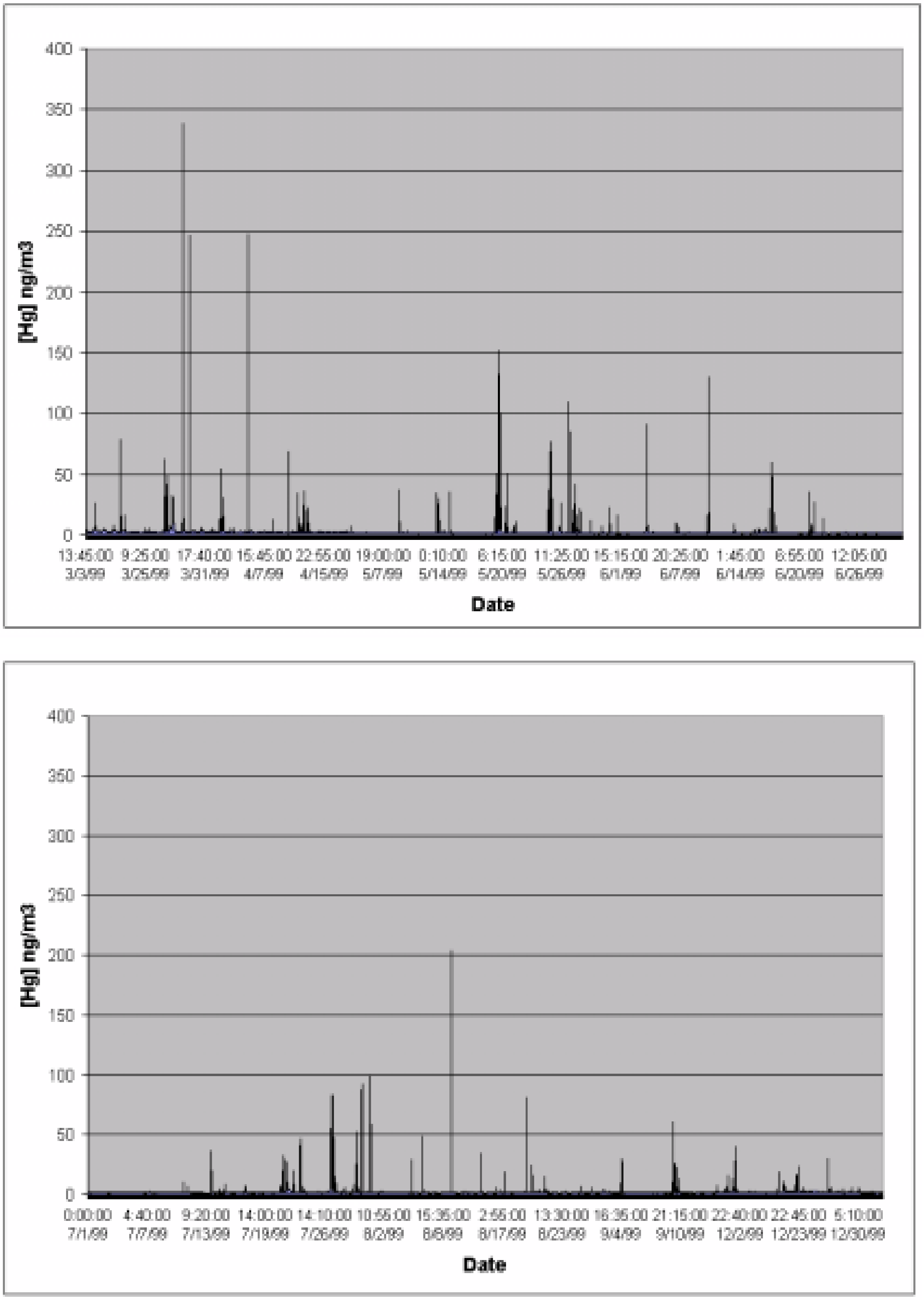


Fig. 2. Riegelwood Flynn TGM concentration profile, March – December 1999. All data points represent 5-minute average concentrations.

Table 3
Quarterly statistics for TGM measured at Riegelwood Ballpark site. Values are calculated using 5-minute average TGM concentrations. All values in ng/m^3.

Riegelwood Ballpark (TGM)	1999[1]		
	2nd Q	**3rd Q**	**4th Q**
10th percentile	2.18	1.86	1.78
25th percentile	2.56	2.10	1.96
50th percentile (median)	3.05	2.38	2.16
75th percentile	4.01	2.74	2.62
90th percentile	6.47	3.59	6.65
95th percentile	10.42	6.51	10.61
99th percentile	31.03	19.73	19.95
Maximum	240.94	101.35	33.83
Arithmetic mean	4.66	3.09	3.34
Standard deviation	2.13	2.18	3.50
Count (n)	9881	18200	3507

[1]Missing data: 6/16 - 6/18, 6/28 - 7/1, 7/6 - 7/9, 7/24 - 7/27, 8/27 - 9/8, 9-14 - 9/22.

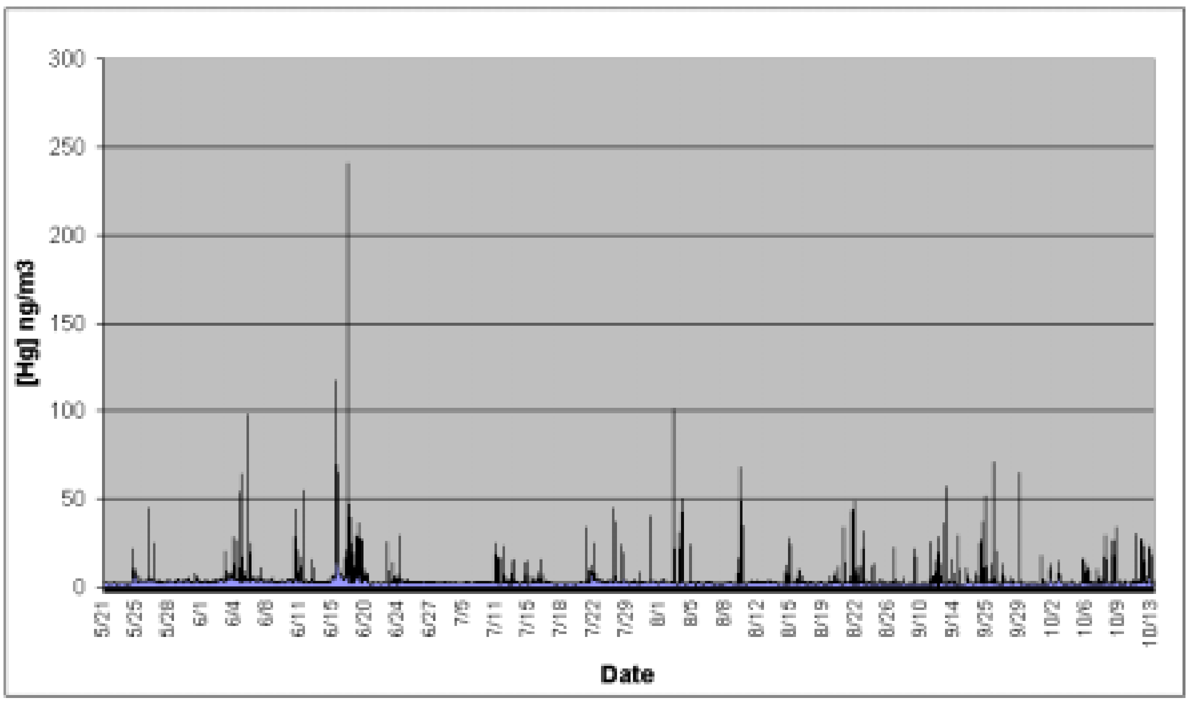


Fig. 3. Total gaseous mercury concentration profile at Riegelwood ballpark site, May – October 1999. All individual data points represent 5-minute average concentrations. Only fully quality-assured data are presented.

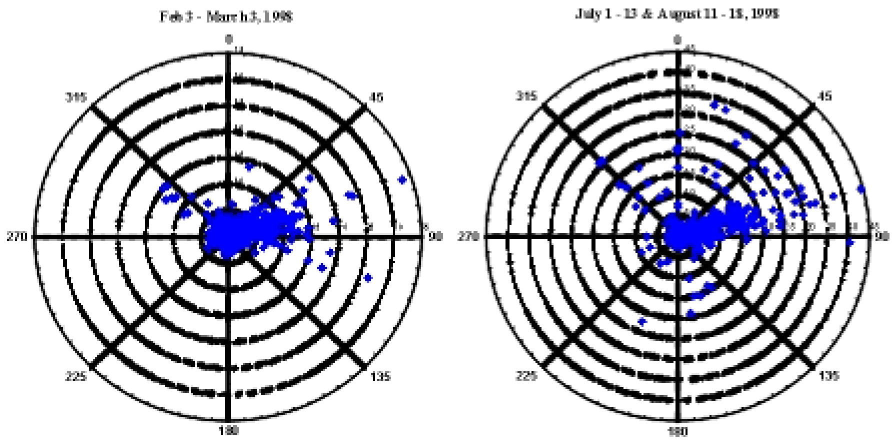


Fig. 4. Profile of TGM vs. wind direction for three time periods at Lake Waccamaw S.P. Both TGM concentration and wind direction values represent 15-minute averages.

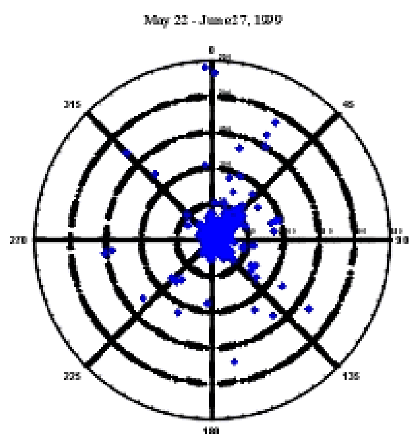


Fig. 5. TGM vs. wind direction, Riegelwood Ballpark. 5-minute averages.

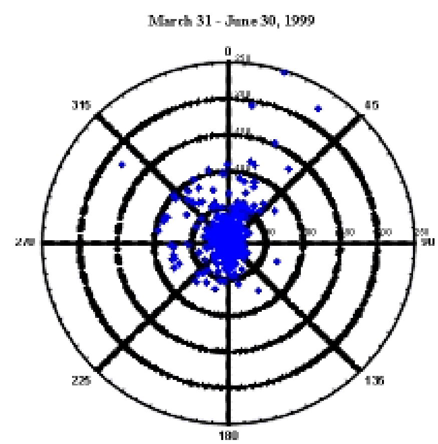


Fig. 6. TGM vs. wind direction, Riegelwood Flynn. 5-minute averages.

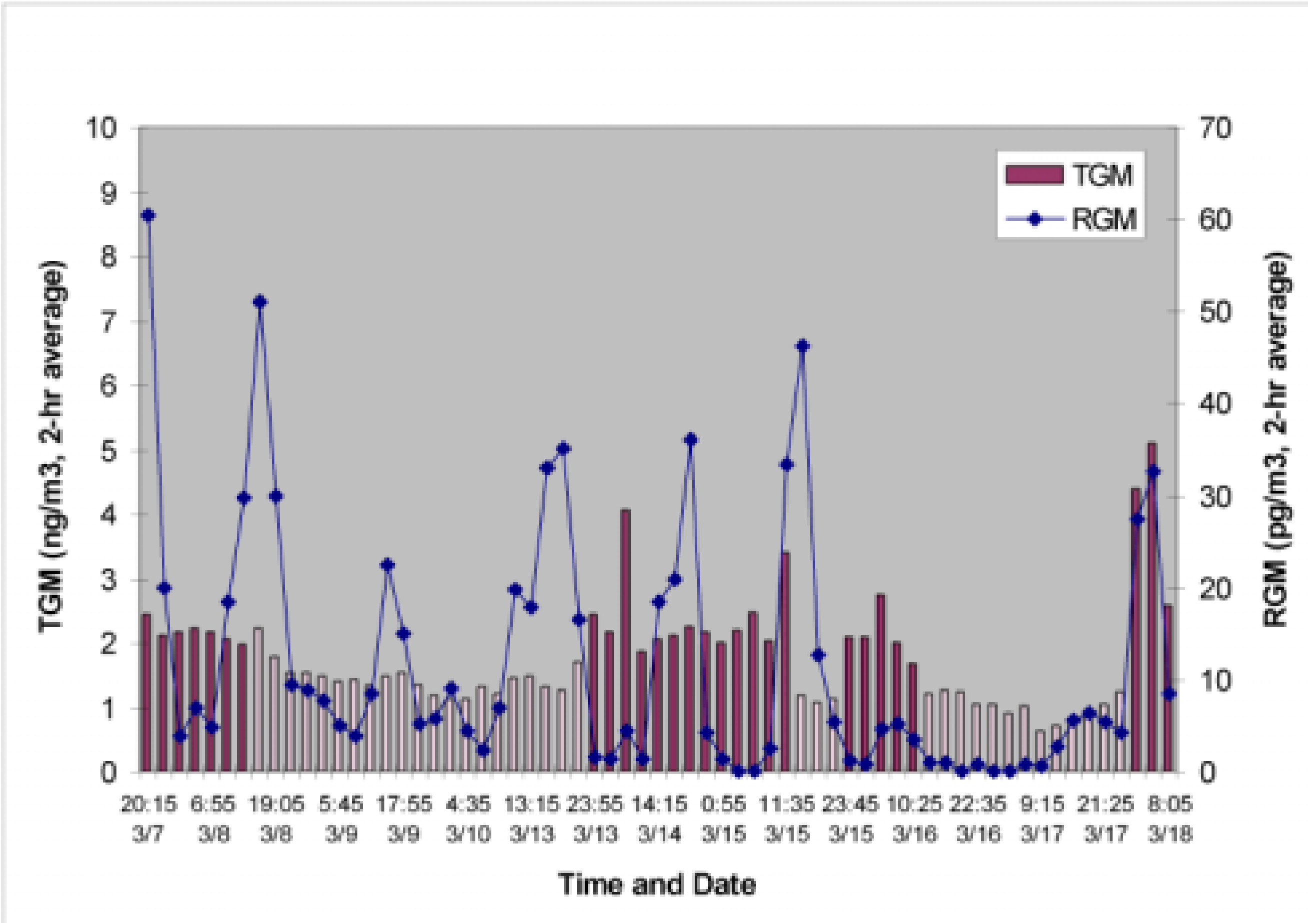


Fig. 7. Concurrent measurement of atmospheric reactive and total gaseous mercury at Riegelwood Ballpark, March 7 – 18, 2000. White columns represent questionable TGM data (refer to discussion).

Table 4
Annual wet deposition of mercury at Pettigrew and Waccamaw State Parks, 1996-1998.

Year	Waccamaw			Pettigrew		
	Cumulative Wet Deposition ($ng/m^2/yr$)	Precipitation (mm/yr)	Volume-weighted concentration (Hg, ng/L)	Cumulative Wet Deposition ($ng/m^2/yr$)	Precipitation (mm/yr)	Volume-weighted concentration (Hg, ng/L)
1996	12821	1087.6	11.8	12361	1336.0	9.3
1997	10430	996.0	10.5	9321	985.6	9.5
1998	15830	1265.7	11.6	9939	1395.5	7.1
1999 (prelim)	14832	1854.5	8.0	7684	1139.7	6.7

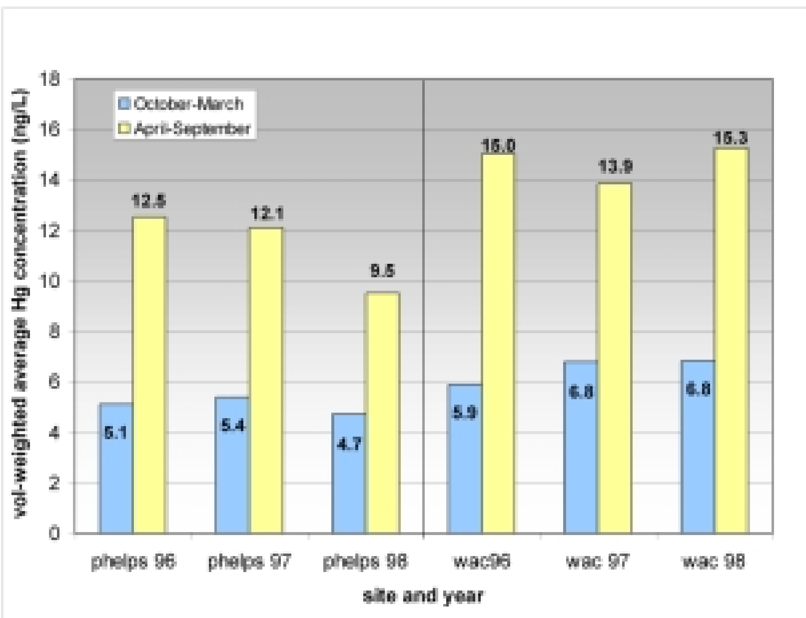


Figure 8: Seasonal trends in rainwater mercury concentration.

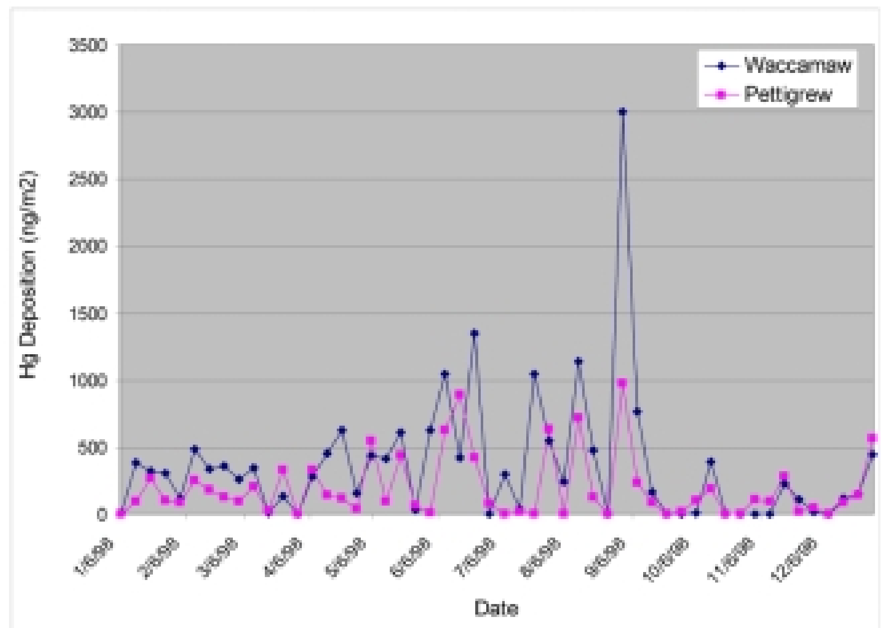


Figure 9: Weekly wet deposition rates, 1998 (ng/m^2).

Table 5
Major mercury emission sources within 75 kilometers of Waccamaw S.P.

Source (category)	1998 reported Hg emissions (lbs)[1]	Distance and direction from Waccamaw S.P. (km)
Chlor-alkali	1276	25, ENE
Municipal waste incinerator	362	50, E
Coal-fired utility boiler	354	45, E
Pulp and paper mill	93	25, ENE
Coal-fired utility boiler	90	70, WNW
Chemical manufacturer	60	45, E
Chemical manufacturer	29	55, SE
Chemical manufacturer	9	55, SE

[1]Reported emissions from state air quality permit database, self-reported values or 1998 TRI.

REFERENCES

Lindberg SE, Stratton WJ, 1998. Atmospheric Mercury Speciation: Concentrations and Behavior of Reactive Gaseous Mercury in Ambient Air. *Environ. Sci. Technol.* **32**, 49-57.

Mason RP, Lawson NM and Sheu GR, 2000. Annual and seasonal trends in mercury deposition in Maryland. *Atmospheric Environment*, **34**, 1691-1701.

MDN Standard Operating Procedure Manual, Frontier Geosciences, Inc., 414 Pontius North, Suite B, Seattle, WA 98109.

Sweet CW and Prestbo E. 1999. Wet deposition of Mercury in the U.S. and Canada. Mercury in the Environment, Proceedings of a Specialty Conference. AWMA, 306-315.

Stevens RK, USEPA, personal communication.

Tekran, Inc. 1999a. Model 2537A Mercury Vapour Analyzer User Manual. Tekran, Inc. Toronto, Canada.

Tekran, Inc. 1999b. Model 1130 Mercury Speciation Unit User Manual. Tekran, Inc. Toronto, Canada.

USEPA, 1987. On-site Meteorological Program Guidance for Regulatory Applications. Office of Research and Development. RTP, NC. EPA-450/4-87-013.

USEPA, 1987a. Mercury Study Report to Congress. OAQPS, ORD. EPA-452/R-97-003.