First Interim Report

Mercury Emissions and Mercury Controls For Coal-fired Electrical Utility Boilers

Volume Two Of Two
September 1, 2003

North Carolina
Department of Environment and Natural Resources
Division of Air Quality

Requirement For This Report

Excerpted from the *North Carolina Clean Smokestacks Act*

[**Title**: An Act to Improve Air Quality in the State by Imposing Limits on the Emission of Certain Pollutants from Certain Facilities that Burn Coal to Generate Electricity and to Provide for Recovery by Electric Utilities of the Costs of Achieving Compliance with Those Limits]

SECTION 12. The General Assembly anticipates that measures implemented to achieve the reductions in emissions of oxides of nitrogen (NOx) and sulfur dioxide (SO2) required by G.S. 143-215.107D, as enacted by Section 1 of this act, will also result in significant reductions in the emissions of mercury from coal-fired generating units. The Division of Air Quality of the Department of Environment and Natural Resources shall study issues related to monitoring emissions of mercury and the development and implementation of standards and plans to implement programs to control emissions of mercury from coal-fired generating units. The Division shall evaluate available control technologies and shall estimate the benefits and costs of alternative strategies to reduce emissions of mercury. The Division shall annually report its interim findings and recommendations to the Environmental Management Commission and the Environmental Review Commission beginning 1 September 2003. The Division shall report its final findings and recommendations to the Environmental Management Commission and the Environmental Review Commission no later than 1 September 2005. The costs of implementing any air quality standards and plans to reduce the emission of mercury from coal-fired generating units below the standards in effect on the date this act becomes effective, except to the extent that the emission of mercury is reduced as a result of the reductions in the emissions of oxides of nitrogen (NOx) and sulfur dioxide (SO2) required to achieve the emissions limitations set out in G.S. 143-215.107D, as enacted by Section 1 of this act, shall not be recoverable pursuant to G.S. 62-133.6, as enacted by Section 9 of this act.

GENERAL ASSEMBLY OF NORTH CAROLINA - SESSION 2001 – (SENATE BILL 1078)
Ratified the 19th day of June 2002. (Ch. SL 2002-4 S.13)
Marc Basnight - President Pro Tempore of the Senate
James B. Black - Speaker of the House of Representatives
Michael F. Easley- Governor

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Preface

This report has been produced by a working group within the North Carolina Division of Air Quality. Stakeholders from industry, environmental and other organizations were also invited to provide their insights, comments and other input. The Division appreciates the efforts of all the stakeholders and other individuals who committed their time and effort to the development of this preliminary report. This open process will continue in the development of subsequent and final reports on this topic.

Many portions of this document were taken directly from other government (non-copyrighted) documents in the interest of time and completeness. Some of these sections may have only minor wording changes from the original documents. Quotations are not strictly used to identify these parts, but a strong effort has been made to reference these documents and acknowledge them. The purpose has not been to claim credit for original work of others, but to provide as much detail and accuracy as possible within a limited time.

This report consists of two volumes. Volume Two includes technical and scientific reports with background information. Volume One contains broader and more general information about mercury emissions and potential air pollution control devices.

The objective of this first interim report is to provide a technical background and to define the scope of efforts to address and respond to the legislative requirement. The purpose of this report is not to defend or promote particular conclusions regarding the consequences of emissions of mercury to the atmosphere, but to provide results or summaries of investigations and information as defined by the Clean Smokestacks Act. The underlying presumption is that it is prudent to undertake efforts to reduce these emissions, with the extent of reductions to be determined later based on the information to be provided.

CONTENTS OF VOLUME TWO

List of Acronyms Used in This Report

BAF - Bioaccumulation factors
CAPA – Clean Air Planning Act – Carper Bill
DAQ – NC Division of Air Quality
DEHNR - Former NC Department of Environment, Health, and Natural Resources, now DENR and DHHS
DENR – NC Department of Environment and Natural Resources
DHHS - NC Department of Health and Human Services
DMF - Division of Marine Fisheries
DWQ - Division of Water Quality
EPA – US Environmental Protection Agency
Hg(0) – elemental mercury
Hg(2+) – reactive mercury
$HgCl_2$ – mercury chloride
MDN - Mercury Deposition Network
MERAU - Medical Evaluation and Risk Assessment Unit
NC – North Carolina
NHANES -National Health and Nutrition Examination Survey
NOx – Oxides of Nitrogen, including NO_2, the primary nitrogen species from combustion.
RGM - Reactive Gaseous Mercury
SO_2 – Sulfur Dioxide
TGM - Total Gaseous Mercury
TMDL - Total Maximum Daily Load

MERCURY CONCERNS SPECIFIC TO NC

HISTORY: MERCURY IN NORTH CAROLINA

Biologists suspected for many years that freshwater fish in the black water systems of eastern North Carolina would be prone to mercury contamination as found in other parts of the country sharing similar environmental conditions. In 1970 the Federal Water Quality Administration issued a report on mercury pollution that mentioned mercury contamination found in fish caught in the lower Cape Fear River basin. Industrial discharges of mercury to local waterways and mercurial pesticide use were scrutinized at that time, but no mention was made of atmospheric contributions. Past studies of mercury levels in eastern North Carolina peat deposits discussed the possible contribution of atmospheric deposition of mercury to local waterways. However, no information was available on atmospheric mercury trends in the areas surrounding eastern North Carolina's sensitive waterways

Mercury in Fish Tissue

The rate and degree to which mercury bioaccumulates within a system is dependent on a number of factors. The most significant of these includes the water's pH, food chain length and composition (productivity), water temperature, water body chemistry, and the form and structure of the organisms present. Methyl mercury, the toxic and most bioaccumulative form of mercury in fish, can be concentrated in top predator species.

The Environmental Sciences Branch (fisheries programs) of the North Carolina Division of Water Quality (DWQ) conducts fish community assessments, fish tissue monitoring, fish kill data assessment, and supports special projects. In the early 1990s, DWQ division fell under the North Carolina Department of Environment, Health, and Natural Resources (NCDEHNR). In 1992, the DWQ conducted an intensive fish mercury survey in the vicinity of Lake Waccamaw, situated in the Lumber River Basin of southeastern North Carolina (Figure 1-1). In that study, 60% of largemouth bass samples from Big Creek and the Waccamaw River were found to contain mercury levels above 1 ppm, the threshold level for issuance of fish consumption advisories at that time by NCDEHNR.

Figure 1-1

Southeastern North Carolina

Including Lake Waccamaw and Surrounding Environs

The DWQ's efforts from 1995 to 1999 consisted of monitoring for mercury and other contaminants under basin-wide assessments, sampling statewide, verification of the high levels of mercury in eastern piscivores (fish-eaters), and the king mackerel mercury survey (1998-1999) with the Department of Marine Fisheries (DMF). From 1998 to 1999, DWQ assisted with the analyses of 112 king mackerel and Spanish mackerel samples that were collected by the DMF from recreational and commercial sources. The fish tissues were collected from a range of fish sizes and seasonal populations.

The Spanish mackerel samples contained low mercury levels. However, regression models using king mackerel tissue data demonstrates a strong relationship exists between king mackerel size and mercury concentration. From these regression curves, a mercury level over 1ppm is predicted for king mackerel over 13 pounds or 37 inches.

After characterizing the mercury problems in fish in North Carolina for about seven years, DWQ was forced to remove mercury assessment from routine statewide sampling due to budget limitations. Basin-wide surveys of mercury in fish tissue were discontinued in 1999 due to limited resources in "clean" watersheds. Present surveys target mercury trouble spots, such as the coastal plain, requests for surveys by regions and agencies, and sites where data are absent or suspect.

Since 1992, results of mercury concentrations in fish sampled have been shared with the Department of Health and Human Services (DHHS). In turn, DHHS posted site or basin specific advisories based on 1.0 ppm standard. They also posted the first North Carolina ocean advisory for king mackerel.

In 2001, the DHHS revaluated their methylmercury advisory protocols and decided to establish statewide fish eating guidelines based on 0.4 ppm level of concern. The new methylmercury guideline of 0.4 ppm from 1.0 ppm guideline was based on recent federal recommendations and also a need for consistency with our bordering states, which were already using the 0.4 ppm guideline.

DHHS currently recommends that women of childbearing age (15-44 years), pregnant or nursing women, and children under 15 not eat shark, swordfish, tilefish, king mackerel, blackfish (bowfin), largemouth bass, jack fish (chain pickerel) caught in North Carolina waters south and east of Interstate 85. Other women, men, and children 15 years and older are advised to eat no more than one meal per week of shark, swordfish, tilefish, or king mackerel; or blackfish (bowfin), largemouth bass, or jack fish (chain pickerel) caught in North Carolina waters south and east of Interstate 85. A meal is considered to be 6 ounces of cooked fish for adults, or 2 ounces of cooked fish for children under 15.

More information regarding fish advisories can be found on the web at this address: http://www.schs.state.nc.us/epi/fish/

Human Mercury Burden

The 1992 fish mercury survey findings sparked interest in determining the extent of ongoing exposure to local fish consumers. In 1993, the NC DEHNR Environmental Epidemiology Section, in conjunction with Brunswick and Columbus County Health Departments, conducted a study to determine body burdens of mercury in individuals residing in Brunswick and Columbus Counties near the Waccamaw River. The data revealed a direct relationship between the extent of consumption of local fish and mercury body burdens. The more fish consumed, the greater the chance of human samples indicating a mercury burden. The average hair mercury level of 3.4 parts per million (ppm) for consumers of freshwater fish was over ten times the average level of 0.3 ppm for those that did not eat freshwater fish. In addition, a wide distribution of hair and blood mercury concentration levels, with values as high as 33.5 ppm in hair, suggested that both elevated fish consumption rates and elevated fish tissue mercury levels were present in this study population.

Monitoring For Atmospheric Mercury

Mercury, in it's various forms, is transported into and out of the atmosphere by several different means. Mercury can be absorbed by cloud formations and deposited to the earth's surface in rainwater or as dew. This is known as "wet deposition". Mercury can also adhere to particulate matter and settle out onto vegetation and the earth's surface. This mechanism is known as "dry deposition". Levels of mercury in rainwater and adhered to particulate matter can both be measured. North Carolina has been measuring mercury in rainwater since 1996. However, the State has never had, nor does it does currently have the capability to measure particulate mercury. Mercury that is not deposited out of the atmosphere remains suspended in the ambient air and exists either in its elemental form, Hg(0), or its reactive form, Hg(2+), which is referred to as Reactive Gaseous Mercury, or RGM. Together these two forms of mercury comprise what is referred to as Total Gaseous Mercury, or TGM. North Carolina has the ability to measure these two forms of mercury while still suspended in the air and can distinguish one from the other.

MERCURY WET DEPOSITION

Mercury wet deposition involves the transfer of mercury from the atmosphere to land or surface waters in precipitation or condensation of water vapor. Water-soluble species of gaseous or particulate mercury may be scavenged from the atmosphere by cloud water, rain, snowfall or water vapor. For many surface waters, atmospheric deposition is the most significant route of mercury loading. Dry deposition of particulate mercury or RGM also contributes to the overall rate of atmospheric deposition, although wet deposition is believed to play a larger role in the eastern United States where precipitation rates are higher than in arid western states. Together, these phenomena contribute to raise methylmercury levels in fish residing in mercury-sensitive waters.

Wet deposition is most strongly influenced by two factors: the amount of precipitation received and the concentration of mercury in the rainwater when it reaches the earth's surface. In areas impacted by high levels of atmospheric gaseous or particulate mercury, wet deposition rates would be higher than comparable areas with lower levels of atmospheric mercury. Areas that experience relatively higher rates of precipitation would also experience higher rates of mercury wet deposition than more arid environments if atmospheric mercury levels were comparable between sites. In reality, the relationship between precipitation and wet deposition is much more complex. In arid environments, infrequent precipitation may allow gaseous mercury species to build up in the atmosphere, resulting in much higher mercury concentrations in subsequent precipitation events. Alternately, prolonged or frequent precipitation events may result in low rainwater mercury concentrations as the atmosphere is cleansed of water-soluble mercury species.

Other factors that affect rainwater mercury levels are not completely understood. They could include local source emissions, unique meteorology, terrain features or the presence of additional atmospheric pollutants. Areas influenced by local or regional

emissions of particulate mercury or RGM might be expected to record higher average rainwater mercury levels. Additionally, the existence of high levels of oxidative pollutants such as ozone and reactive chlorine species in air or cloud water could contribute to the oxidation of elemental mercury into RGM, which would subsequently increase local deposition rates (Lin and Pehkonen). Monitoring sites located in heavily polluted areas might exhibit the effect of these considerations.

Meteorological phenomena, including temperature, humidity, and cloud formations, may influence wet deposition rates. Temperature could play a role in facilitating oxidation reactions that form water-soluble RGM species. Similarly, the amount and intensity of sunlight could also affect mercury deposition by facilitating photochemical reactions. Cloud formation and cloud chemistry are also recognized as important factors in mercury deposition. Many of the most plausible atmospheric reactions involving mercury are believed to take place in the aqueous phase; that is in cloud water or precipitation. Dvonch, et al. speculated that the tall, cumulonimbus clouds of south Florida would be more effective at scrubbing atmospheric mercury from a larger area, possibly explaining the relatively high wet depositions rates in these environments. The aforementioned variables all contribute to significant geographical variability in both the concentration of mercury in rainwater and cumulative wet deposition rates.

The Mercury Deposition Network

The National Atmospheric Deposition Program's Mercury Deposition Network (MDN) was designed to identify geographical and temporal trends in mercury deposition across North America. As of 2002 more than 50 sites were operating in more than 20 states and Canadian provinces (Figure 1-2). At all sites, precipitation samples are collected weekly and sent to a contract laboratory for analysis of total mercury content. Precipitation levels, total mercury concentration, and mercury wet deposition rate are reported weekly. Volume-weighted mercury concentration is calculated on a quarterly and annual basis.

Mercury Wet Deposition Sites

Shortly after the discovery of widespread mercury contamination in Lumber River basin fish, the Division of Air Quality (DAQ) stationed air monitoring instruments at Lake Waccamaw and Pettigrew State Parks to measure mercury levels in rainfall. Measurement of mercury in rainwater can provide an estimated rate of atmospheric deposition and loading to local waters. Lake Waccamaw is situated approximately 50 kilometers (31 miles) to the west of Wilmington, NC and 50 kilometers southeast of Lumberton, NC. This site was chosen to represent general atmospheric conditions in the lower Lumber River Basin. The area surrounding Lake Waccamaw is typical of the region: flat terrain with ubiquitous wetlands and waterways. Very little commercial or industrial activity takes place in the area surrounding the park. The population density is relatively low and roadways are lightly traveled. The nearest town is Whiteville, NC, located approximately 15 kilometers (9 miles) to the west-northwest of Lake Waccamaw.

Pettigrew State Park is in northeastern North Carolina, just south of the Albemarle Sound. The area immediately surrounding this site is similar to the environment around Lake Waccamaw: very lightly populated and devoid of significant industrial activities with flat terrain primarily used for agricultural purposes. On the basis of population density, commercial and industrial activity and distance to urban activities, Pettigrew qualifies as a more remote site than Lake Waccamaw.

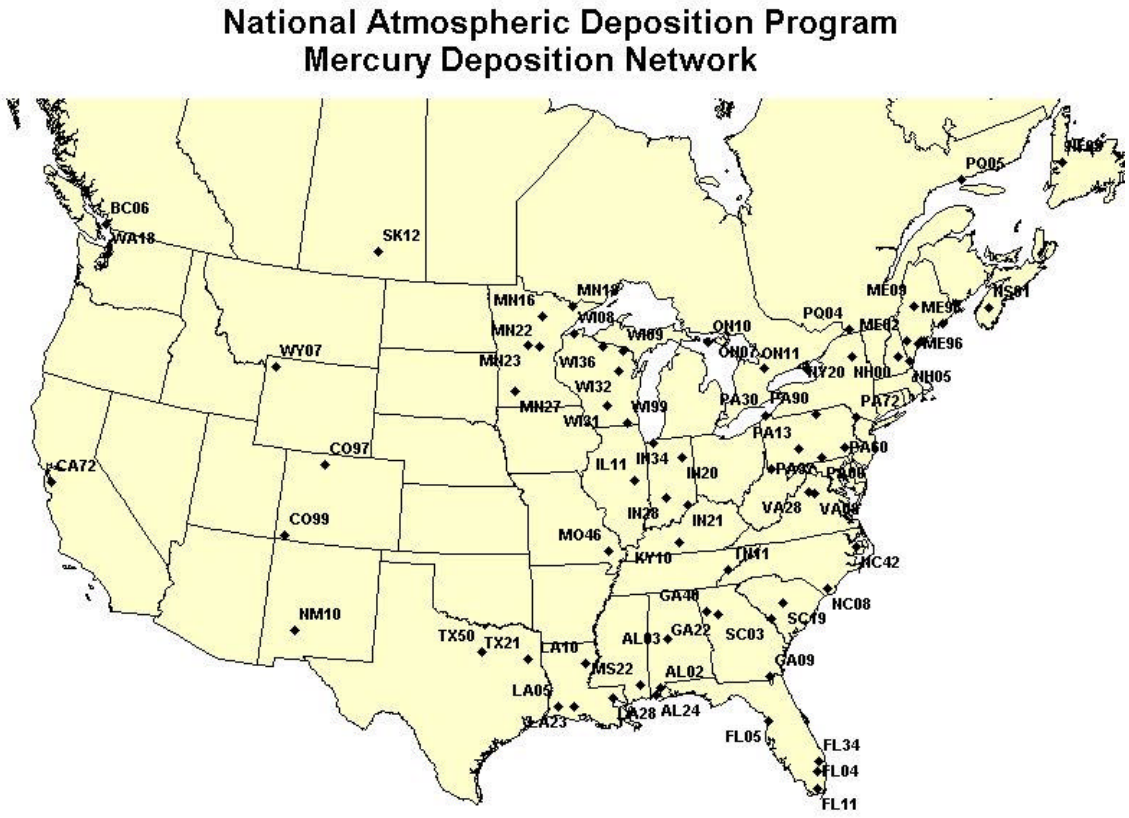
The Waccamaw and Pettigrew stations were amongst the earliest sites in the National Atmospheric Deposition Network's Mercury Deposition Network (MDN) (Figure 1-2). Composite rainwater samples were collected and analyzed weekly for total mercury content beginning in late 1995.

Mercury levels in samples of rainwater in eastern North Carolina vary greatly from week to week but are comparable to MDN data from sites across the United States. However, volume-weighted average levels of mercury in rainwater are consistently higher at Lake Waccamaw than at Pettigrew State Park, which is 150 miles north.

Figure 1-2

Map Of Current MDN Sites

(NC-08 corresponds to the Lake Waccamaw site)
(NC-42 corresponds to the Pettigrew State Park (Phelps) site)



Recent data from both sites during 1999 and 2000 suggested that mercury levels in precipitation may be declining in these areas. The most dramatic drop occurred between 1998 and 1999 at Lake Waccamaw State Park, when levels declined to values typical of the more remote location at Pettigrew State Park. Since 1998 however, the levels have crept back up. The current theory of cause and effect for mercury levels increasing may be cleanup activities at the closed chlor-alkali facility. Operations during the cleanup may have generated a considerable amount of fugitive emissions. It is possible these "cleanup" emissions are to blame for the rise in mercury levels following the drop that was observed after the plant shut down in 1999, as cleanup activities were not initiated immediately after plant closure. Continued sampling throughout the cleanup process and beyond should help to answer that question.

Results from wet deposition monitoring at the North Carolina sites are presented in Table 1-1, and Figures 1-3 and 1-4. Data recovery between 1996 and 1999 for both sites was greater than 98 percent. Sample handling problems and system blanks were the main causes of data loss, which occurred twice at Lake Waccamaw during 1996 and twice at Pettigrew State Park during 1996 and 1997. During 2000, some difficulties were encountered at both sites related to inconsistencies between the tipping rain gage and bucket precipitation samplers. A site audit performed during December of 1999 found that the tipping rain gage at the Lake Waccamaw site was prone to underreporting precipitation amount. However, subsequent estimates of rainwater mercury levels were based on the volume of rainwater collected in the volumetric flask; thus, estimated mercury levels were not consistently biased by erroneous information on rainwater amount. Improvements to the site instruments were made in June of 2000.

Table 1-1 shows a reduction in mercury deposition (a 30 percent drop compared to the previous three year average) at the Waccamaw site starting in 1999 (this reduction coincides with the closure of the HoltraChem mercury cell chlor-alkali plant). However, concentrations increase in 2000 and 2001. The weighted concentration levels in 2000 and 2001 do not reach the magnitude of pre-1999 concentrations. Data from the Pettigrew site generally follow the same curve, but with lower weighted concentrations. Figure 1-3 compares the annual amount of mercury in rainwater over a finite area (per square meter [m^2] in one millionth of a gram (microgram [µg]) increments each year). For example, in 1998, 18.7 $\mu g/m^2$ was captured. Figure 4-4 graphically compares the annual volume-weighted concentration (an average concentration) of mercury in billionth of a gram per liter (nanograms per liter = ng/L).

Discussion of NC Mercury Wet Deposition Network Data

Annual wet deposition rates in North Carolina are generally near the upper end of the range for all mercury wet deposition network (MDN) sites while annual volume-weighted mercury concentrations are close to the median value. Grasping the meaning of site-to-site variability in these parameters is difficult because the factors that influence mercury wet deposition are not completely understood. In general, the network sites that experienced the greatest rates of annual wet deposition also experienced higher annual

precipitation rates. These sites are also primarily situated in the southern reaches of the network. The relatively lower rates of annual wet deposition in northern states could be due in part to the decreased scavenging efficiency of snow during winter months.

Table 1-1

Annual wet deposition of mercury at Pettigrew and Waccamaw State Parks

1996 – 2001

Year	Cumulative Wet Deposition ($ng/m^2/yr$)	Precipitation (mm/yr)	Volume-weighted concentration (mercury, ng/L)
Waccamaw			
1996	12821	1087.6	11.8
1997	10429	996.0	10.5
1998	18655	1265.7	11.7
1999	17205	1854.5	7.8
2000	12083	1337.8	9.6
2001	9197	884.2	10.4
Pettigrew			
1996	12361	1336.0	9.3
1997	9321	985.6	9.5
1998	9943	1395.5	7.1
1999	7907	1139.7	6.6
2000	10829	1302.7	8.2
2001	6114	770.8	7.9

Eastern North Carolina has moderate precipitation rates, and during winter months, precipitation is primarily in the form of rain. On the other hand, winter temperatures are significantly lower than those experienced in south Florida. If lower temperatures act to suppress atmospheric conversion of elemental mercury to water-soluble RGM, then lower rates of deposition might be expected in colder environments. This relationship is supported by seasonal trends in mercury deposition. If the North Carolina data are split into summer months (April to September) and winter months (October to March), mercury levels are clearly lower in winter versus summer months

(see Fig 1-5). This phenomenon has been documented at many MDN sites, including those at lower latitudes where snow is not encountered and wintertime temperatures

Figure 1-3

Annual Cumulative Wet Deposition Of Mercury 1996 – 2001

Recorded At Lake Waccamaw And Pettigrew (Phelps) State Parks
Reported In Millionth of a Gram per Square Meter (mg/M^2)

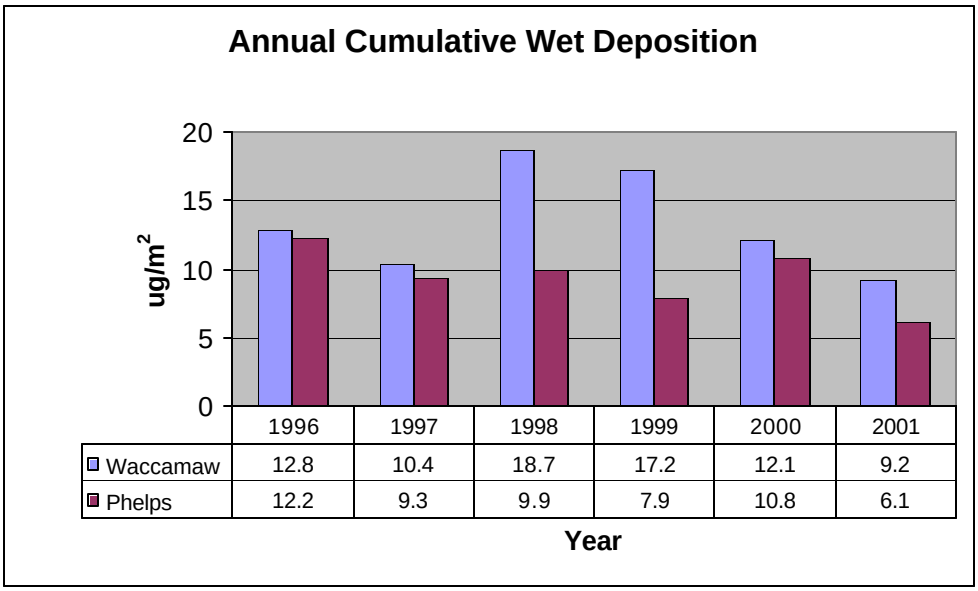
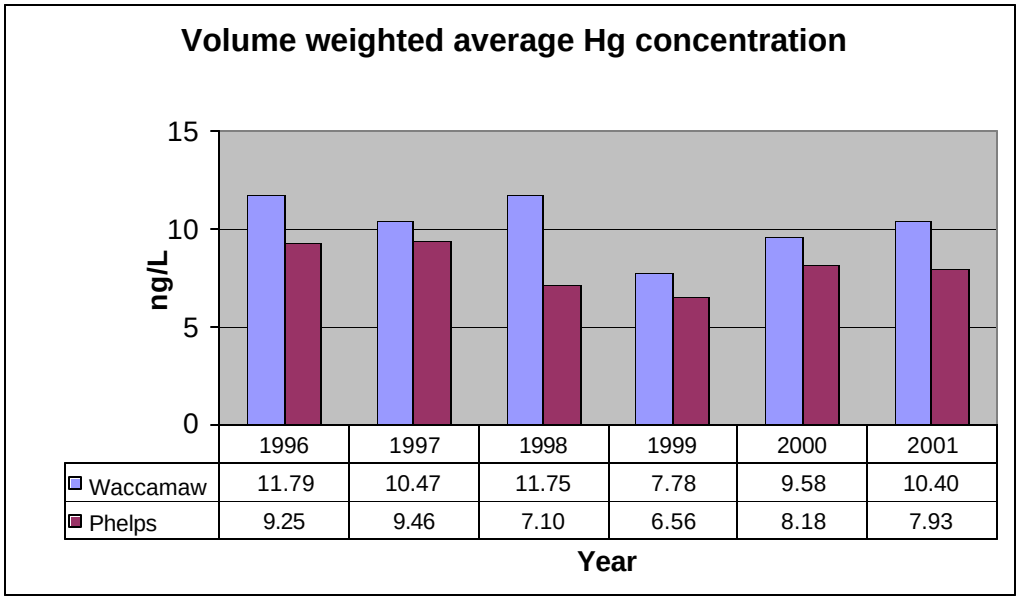


Figure 1-4

Annual Volume-Weighted Concentration Of Mercury 1996 – 2001

Recorded At Waccamaw And Pettigrew (Phelps) State Parks
Reported In Billionth of a Gram per Liter (ng/L)



are relatively warm. Other potential causes for the seasonal disparity might include air mass movement, which would tend to be northerly during the winter and southwesterly during the summer; cloud formation dynamics; and the amount and intensity of sunlight. Clearly, seasonal and regional meteorological patterns are critical factors affecting mercury wet deposition.

Additional factors affecting mercury deposition include local mercury emissions, unique terrain features, and the presence of additional atmospheric pollutants. Although MDN citing characteristics are meant to minimize the influence of emissions from local sources, invariably some network sites will be impacted. Sites influenced by local or regional emissions of RGM might be expected to record higher average levels of mercury in rainwater. Similarly, the existence of high levels of oxidative pollutants such as ozone and reactive chlorine species in air or cloud water could contribute to the oxidation of elemental mercury into RGM, which would subsequently increase local rainwater concentration and deposition rates.

While the aforementioned variables would clearly play a large role in the variability between national MDN sites located in diverse environments, they seem to serve as less plausible explanations for the differences seen between North Carolina's two MDN sites. As mentioned previously, surrounding features are very similar and the sites are only 200 kilometers apart. Annual precipitation rates between sites were similar between 1996 and 2000, with the exception of 1999 when the Waccamaw site experienced a disproportionately greater quantity of rainfall as a result of Hurricane Floyd. Other meteorological phenomena including temperature, prevailing winds and sunlight intensity should be similar.

Despite the overwhelmingly similar characteristics at the two sites, some consistent differences in mercury deposition patterns have been noted between them. Wet deposition rates have been higher at Waccamaw every year of sampling. This difference is primarily a reflection of different mercury concentration in rainwater because annual precipitation rates are comparable between sites. The magnitude of difference ranged from 10 percent during 1997 (11.5 ng/L vs. 10.5 ng/L) to over 60 percent during 1998 (11.6 ng/L vs. 7.1 ng/L). This relationship could also be observed if weekly data from each site were examined (Figure 1-6).

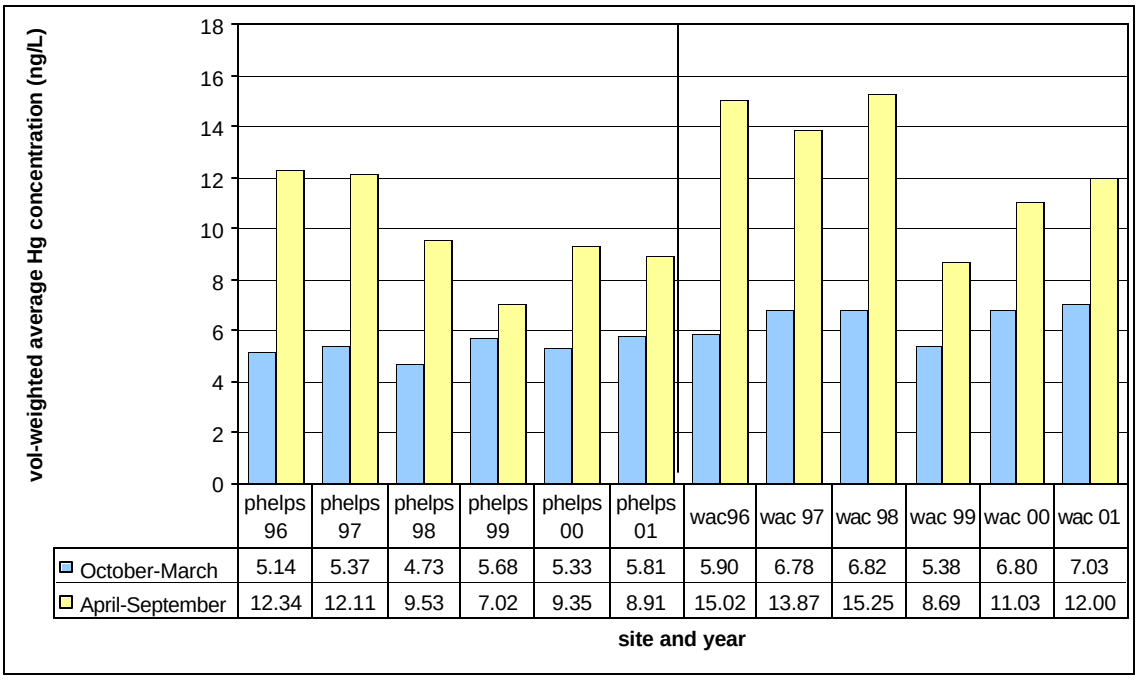
The consistency of this pattern suggests an additional influence on rainwater mercury levels. One important variable is regional levels of atmospheric mercury. Only limited information is available on atmospheric total gaseous mercury vapor levels in the vicinity of Pettigrew State Park, but those data indicated background conditions were present.[1] In stark contrast, total gaseous mercury levels at Lake Waccamaw were shown to fluctuate wildly during and before 1998, which suggests that local air masses may have contained higher mercury levels (Figure 1-8). Higher atmospheric mercury levels could contribute to higher mercury levels in precipitation if significant atmospheric scavenging of water-soluble mercury species is taking place.

A substantial decrease in mercury concentration in rainwater between 1998 and 1999 at the Lake Waccamaw site occurred at the same time as a sudden decrease in atmospheric mercury levels at this site. The decrease in total gaseous mercury between 1998 and 1999 (28 percent) was somewhat less than the decrease in rainwater mercury concentration over that same time (45 percent). Additional influences, such as the unusually high precipitation rate during 1999, could also have acted to decrease average mercury levels in rainwater through dilution.

Figure 1-5 Mercury Wet Deposition

(Expressed as volume-weighted average mercury concentration (ng/L)

and separated by season, site and year)

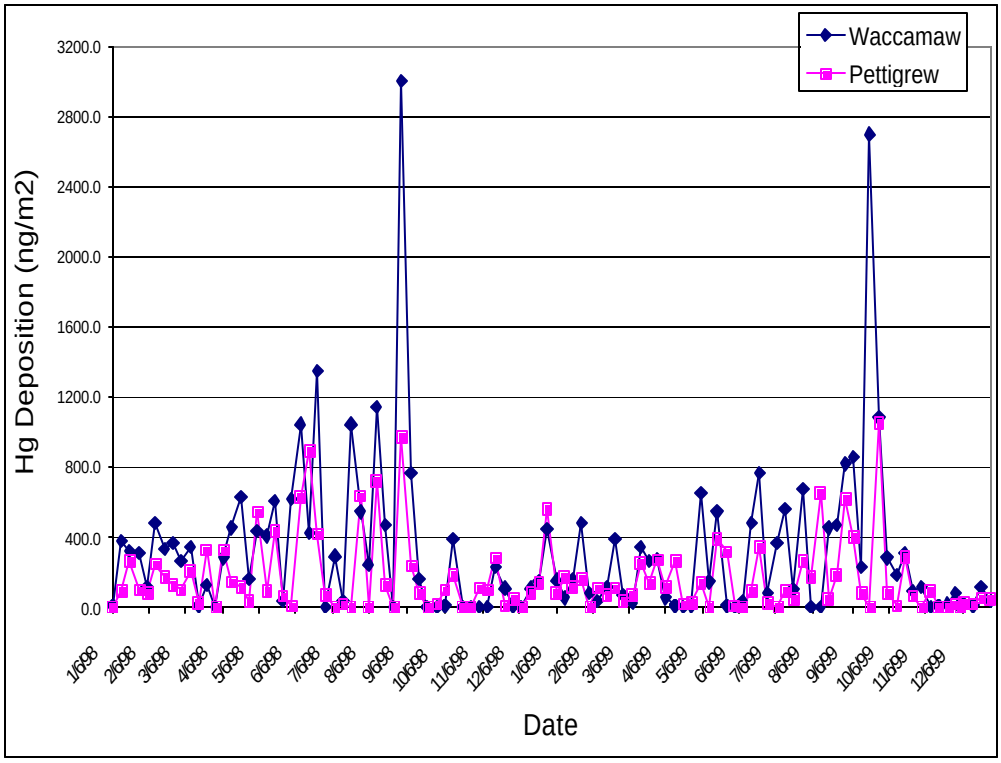


	phelps 96	phelps 97	phelps 98	phelps 99	phelps 00	phelps 01	wac96	wac 97	wac 98	wac 99	wac 00	wac 01
October-March	5.14	5.37	4.73	5.68	5.33	5.81	5.90	6.78	6.82	5.38	6.80	7.03
April-September	12.34	12.11	9.53	7.02	9.35	8.91	15.02	13.87	15.25	8.69	11.03	12.00

Figure 1-6

Coincident Weekly Deposition Data

From Waccamaw And Pettigrew State Parks, 1998 - 1999



Mercury in Ambient Air

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. Beginning in 1997, an automated mercury vapor analyzer was added to the Lake Waccamaw monitoring site. This instrument measured and recorded TGM levels in ambient air in 15-minute increments. Mercury vapor analyzers are not dependent on precipitation events. They collect and record mercury concentrations 24-hours per day. The vast majority of these readings showed total gaseous mercury levels at or below 2 ng/m^3, which is in the range of concentrations considered "background" for this type of site. However, fluctuations of mercury vapor concentrations, up to twice background values, were periodically seen. Mercury data were matched to concurrent wind direction data to illustrate an association between elevated total gaseous mercury and winds originating from the east-northeast. This evidence suggested a fixed upwind source might be impacting atmospheric mercury levels at Lake Waccamaw State Park.

In 1999 DAQ expanded its monitoring study to understand better the factors affecting atmospheric mercury levels and the relationship between mercury emissions and air quality in southeastern North Carolina. With assistance from the EPA, two additional sites were established in Riegelwood, NC, an industrial area located approximately 25 kilometers to the east-northeast of Lake Waccamaw and home to several mercury emission sources including a large pulp and paper operation and a mercury cell chlor-alkali plant.

The operation of a chlor-alkali plant is heavily dependent on the availability of huge quantities of direct-current electrical power, usually obtained from a high voltage source of alternating current. Chlor-alkali plants produce sodium hydroxide (caustic soda), chlorine, sodium carbonate (soda ash), potassium hydroxide (caustic potash), and hydrochloric acid. The process requires the electrolysis of sodium or potassium chloride. Mercury cells use a pool of mercury at the bottom of the cell to act as the cathode. Mercury is pumped into the cell during the process as an amalgam of sodium mercury and then is pumped out to a decomposer where the mercury is purified and recycled back to the cell. Hydrogen gas from mercury cell operation contains significant amounts of mercury, which is removed by scrubbing with sodium hypochlorite or sodium persulfate.[2]

Mercury cells were the original process equipment used throughout the country. However, two newer processes (the diaphragm cell and the membrane cell) have replaced the mercury cell process. These new process use less electrical power during the electrolysis (mercury cell requires 7 to 10 kilo-amperes per square meter (kA/m^2) while the diaphragm cell requires 1.5 to 4 kA/m^2).

By far the largest source of mercury emissions was the HoltraChem mercury cell chlor-alkali operation located in Riegelwood, NC, which was approximately 25 kilometers (16 miles) east-northeast of Lake Waccamaw. The facility reported almost 1,300 pounds of mercury emissions in 1998, over three times the amount of the second largest source, the New Hanover Waste-to-Energy municipal waste incinerator near Wilmington (1998 emissions: 362 pounds). The location and quantity of mercury released suggested that the HoltraChem plant in Riegelwood was significantly influencing regional levels of atmospheric mercury, and caused dramatic changes even at a distance of 25 kilometers from the source. However, with only the Lake Waccamaw data, other regional emission sources could not be ruled out as contributors.

Atmospheric monitoring for total gaseous mercury was carried out concurrently at the Riegelwood and Lake Waccamaw locations during 1999 and 2000. The study, known as the Waccamaw Atmospheric Mercury Study, also involved chemical speciation of elemental and reactive gaseous mercury during 2000 at one of the Riegelwood sites. In addition, mercury was measured in weekly rainwater samples collected from Lake Waccamaw and a second location in northeastern North Carolina, in support of the national Mercury Deposition Network.

As previously mentioned, historical data on total gaseous mercury from Lake Waccamaw strongly suggested regional source impacts. If the relationship between regional atmospheric total gaseous mercury levels and levels of mercury in rainwater are true, then it raises the possibility that local source mercury emissions are having an identifiable impact on regional mercury wet deposition rates. To properly analyze this relationship, rain event-based sampling would have to occur concurrently with analysis of trace signature pollutants and an analysis of micrometeorological conditions. The sampling method used in the MDN network blends together multiple precipitation events into one weekly composite sample, making it impossible to distinguish single precipitation events arising from different weather systems. Precipitation occurring at the sampling site after passing over an upwind emission source cannot be distinguished from other precipitation events that contribute to that week's sample. Despite these limitations, the local and regional MDN data does provide a useful accompaniment to data on atmospheric mercury and a possible indicator of the effect of anthropogenic releases of mercury.

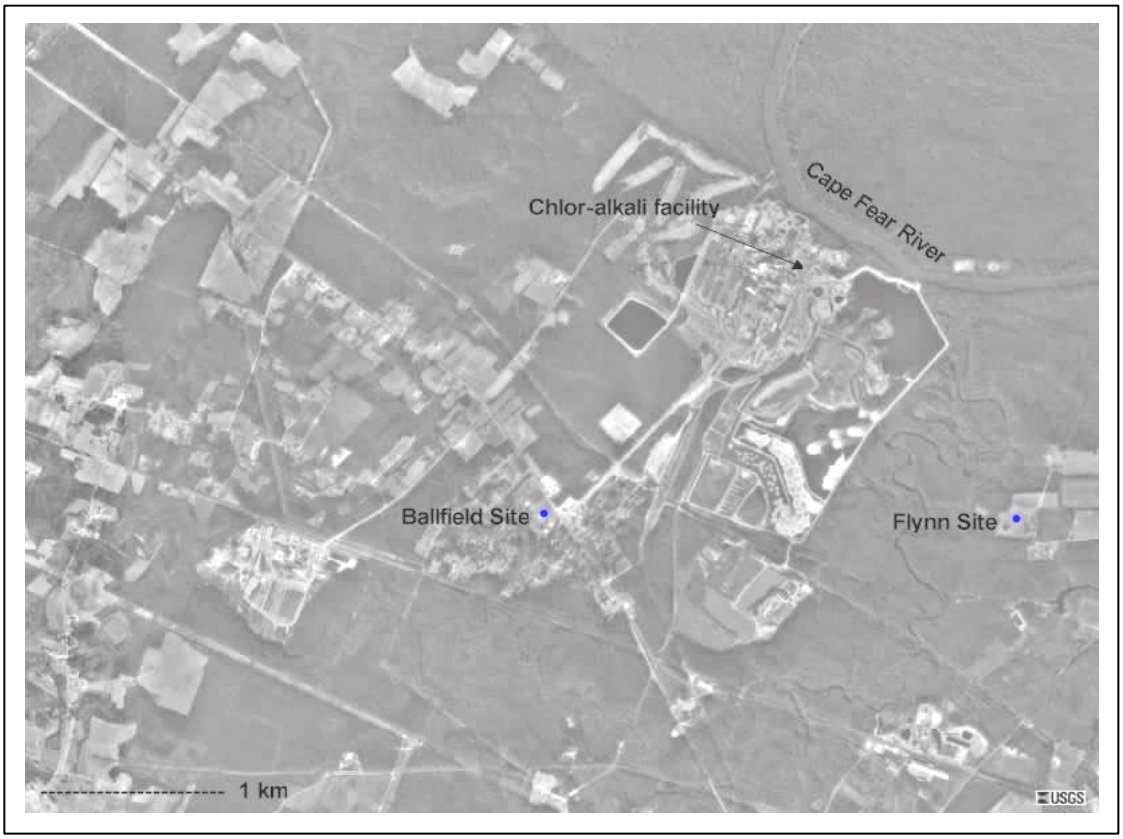
WACCAMAW ATMOSPHERIC MERCURY STUDY:

This study was successful in identifying long-term trends in atmospheric mercury in a rural/remote environment that is home to several mercury emission sources. All lines of evidence seem to suggest that significant improvements in regional ambient air mercury levels were most closely associated with the closing of a mercury cell chlor-alkali operation in Riegelwood, North Carolina. Conditions at Lake Waccamaw State Park appeared to represent typical mid-latitude northern hemisphere terrestrial "background" conditions for total gaseous mercury upon the conclusion of this study. Conditions in the industrial area of Riegelwood, NC, had also improved substantially but continued to show periodic elevations in both elemental and reactive gaseous mercury that suggested ongoing mercury emissions to the air, and increased atmospheric loading of mercury to local waterways.

STUDY DESIGN AND PURPOSE

To better define the cause of spikes in atmospheric mercury at the Lake Waccamaw State Park site, the DAQ proposed to expand its study to include several additional monitoring locations in the Cape Fear River Basin. The objective was to generate data from these sites that would help to better define the role of multiple sources and determine the magnitude of effect at shorter distances from a major source of mercury emissions.

In 1998 the chlor-alkali plant reported plans to convert its mercury cell chlorine production process to a membrane process. The membrane process is preferable because it is more energy efficient and eliminates the use of mercury (USEPA, 1997b). Representatives from the DAQ and the North Carolina Department of Health and Human Services (DHHS) contacted plant representatives to request permission to situate mercury vapor monitors on facility property during the conversion process. DHHS representatives were concerned that the processing and removal of immense quantities of mercury might lead to releases of mercury vapor sufficient to cause toxic exposures for workers or nearby residents. Plant officials declined to allow monitoring instruments on-site but the



DAQ subsequently identified suitable monitoring locations in the immediate vicinity of the chlor-alkali and pulp and paper mill industrial complex, and in early 1999 set up two monitoring stations within one mile to the southeast and southwest of the chlor-alkali plant (Fig 1-7). Despite the close proximity, the sites differed substantially. The Riegelwood Ballpark site was located in a clearing at the edge of a county park, just beyond the right-field fence of a baseball field at the intersection of NC 87 and Riegelwood Plant Road. The site was located directly across from the main entrance to the pulp and paper mill and provided a relatively unimpeded view to the industrial complex. To the east, west and south of this area are residential and open spaces. Some commercial structures were located near the site at the same intersection, including a gas station across NC Highway 87. Traffic near the site was moderate to heavy and

continuous. The Riegelwood Flynn site was placed in a fallow plot of agricultural land, surrounded by open space and a thick stand of trees 100 meters to the north, west and south. The surrounding area is rural and very sparsely populated. Access to the site was provided by a dirt road that received little or no daily traffic. No view of the industrial complex was provided due to the trees surrounding this site.

The instruments stationed at the Riegelwood sites were identical to the instrument at Lake Waccamaw and were capable of providing continuous monitoring of TGM. Both sites were also equipped with sufficient instrumentation to provide on-site meteorological information including wind speed and direction, temperature and humidity. The original mercury vapor monitor at the Riegelwood Flynn site was provided on loan from USEPA Region 4 but had to be returned in January of 2000, leaving only one Riegelwood site operational. In late 1999 the DAQ petitioned the USEPA for funding under the Persistent Bioaccumulative and Toxic (PBT) Chemical Program to help support a long-term study of atmospheric and fish mercury trends in the Lumber River Basin. In May of 2000, the EPA committed $47,900 in PBT funds to allow for procurement of atmospheric monitoring instrumentation and supplies for air and fish monitoring. This allowed for reinstatement of total gaseous monitoring at the Riegelwood Flynn site in the third quarter of 2000 and freed up Department funds for the purchase of an annular denuder-based mercury speciation unit to be stationed at Riegelwood Ballpark. The speciation system allowed for continuous concurrent monitoring of both Hg(0) and RGM, providing important information on the speciation of mercury during both "background" and highly elevated readings. This type of information could then be used to assess the extent to which spikes in TGM could be contributing to off-site deposition of mercury into the surrounding environment.

DAQ's objectives for the expanded study included: 1) assuring that the public was not being exposed to dangerously high levels of mercury in ambient air, 2) determining the impact of the conversion process on local atmospheric conditions, and 3) determining whether the chlor-alkali operation or another source was responsible for atmospheric mercury fluctuations in the Lumber River Basin. It was envisioned that this effort would last throughout the chlor-alkali conversion process. The DAQ also committed to maintain mercury vapor monitoring at Lake Waccamaw for the duration of this study. The continued collection of data from this site was deemed critical to gain a full understanding of the "before and after" effect of the conversion process at the chlor-alkali plant. If in fact that facility was responsible for the historical peaks in TGM at Lake Waccamaw then halting the active use of mercury might result in a return to background conditions at this site. Alternatively, if another source was primarily responsible or if documented levels represented normal variability for this region, then those conditions might be expected to persist.

Additionally, the DAQ committed to continue rainwater measurements at both North Carolina MDN sites. Data from previous years showed that rainwater mercury levels at Lake Waccamaw were consistently higher than at Pettigrew State Park. It is plausible that some of the same phenomena that had been contributing to significant fluctuations in gaseous mercury at Lake Waccamaw could also be contributing to greater

concentrations of mercury in local rainwater. If so, changes that might result in decreased atmospheric levels of mercury might also contribute to decreased levels in rainfall.

This section presents information on atmospheric mercury levels collected over a three-year period between 1997 and 2000. Parameters include: 1) continuous measurement of TGM at Lake Waccamaw between 1997 and 2000, 2) measurement of TGM at both Riegelwood monitoring locations during extended periods of both 1999 and 2000, and 3) speciation of atmospheric mercury at the Ballpark site during 2000. Many of the monitoring instruments chosen for this study are cutting edge and as such a considerable amount of time and effort was spent refining methods to improve instrument performance. We will discuss these methods and their bearing on future studies. In addition, we provide observations on the behavior of atmospheric mercury, including the relationship between elemental and reactive gaseous mercury species. Finally, we present the results of an analysis of regional mercury emission patterns that explores possible relationships between industrial activities and regional atmospheric mercury levels. Meaningful findings include:

Total Gaseous Mercury:

- Data collected during 1998 at Lake Waccamaw State Park suggested that periodic spikes of total gaseous mercury exceeding 50 ng/m^3 were typical for this area during this time, but atypical for such a remote/rural location.
- On-site meteorology identified a relationship between elevations in total gaseous mercury and winds originating from the east-northeast.
- Beginning in early 1999, levels of atmospheric mercury at Lake Waccamaw State Park returned to typical "background" levels (1.5 – 2.0 ng/m^3).
- Reduced atmospheric levels of total gaseous mercury were observed simultaneous with the cessation of chlorine production at a mercury cell chlor-alkali plant located approximately 25 kilometers to the east-northeast of Lake Waccamaw State Park.
- In Riegelwood, NC, measurements of atmospheric mercury included periodic spikes in total gaseous mercury throughout 1999 and 2000.
- Quarterly average total gaseous mercury levels during 1999 and 2000 were up to 166% higher at the Riegelwood monitoring locations versus coincident readings from Lake Waccamaw State Park. However, average values appeared to decline in Riegelwood over the course of this study and at one site decreased by roughly 40% between 1999 and 2000.
- Total gaseous mercury levels did not exceed 300 ng/m^3 (NC Acceptable Ambient Level and EPA inhalation RfC) at the Riegelwood sites for an extended period of time, suggesting that health risks from non-occupational inhalation of mercury were minimal for local citizens during the study period.
- Long-term continuous measurement of atmospheric mercury can be successfully achieved, even at the exquisitely low levels found in the atmosphere. Data from these types of studies can be used in combination with on-site meteorological data to identify possible source-receptor relationships.

Reactive Gaseous Mercury:

- Levels of atmospheric reactive gaseous mercury fluctuated significantly in the Riegelwood area throughout the last half of 2000.
- Short-term increases in reactive gaseous mercury frequently occurred in tandem with increases in elemental mercury when the monitoring site was downwind of the chlor-alkali plant and pulp and paper mill, suggesting that mercury emissions included both elemental and reactive gaseous mercury.
- In addition to source-related increases in reactive gaseous mercury, smaller scale increases also frequently occurred during afternoon hours, particularly on low humidity days, suggesting a natural diel cycle for reactive gaseous mercury.
- Meteorological conditions such as wind direction, precipitation, humidity and temperature appear to affect ambient air reactive gaseous mercury levels.
- New methods to measure and distinguish reactive gaseous mercury and elemental mercury performed well over extended periods of time; however, some modifications to the instrument assembly may be needed to maintain gold trap integrity over extended sampling periods.

WACCAMAW STUDY RESULTS & DISCUSSION

In the following pages we present an enormous database of information on levels of TGM, Hg(0) and RGM along the eastern coastal plain of North Carolina. We then attempt to highlight and explain trends in the data and on occasion speculate as to causative factors behind those trends. There are several areas that deserve additional attention, including the relative influence of meteorology and local emissions on RGM levels at Riegelwood Ballpark. Many of these questions may be answered through in-depth statistical analysis of existing data.

TOTAL GASEOUS MERCURY: RESULTS

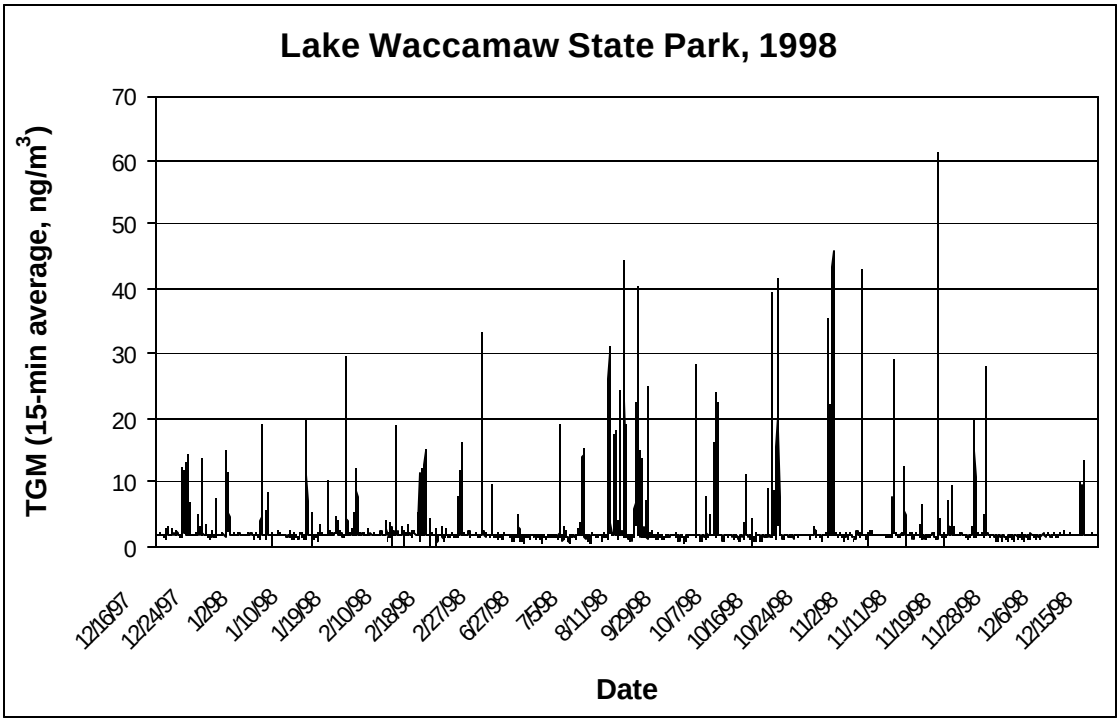
Waccamaw State Park

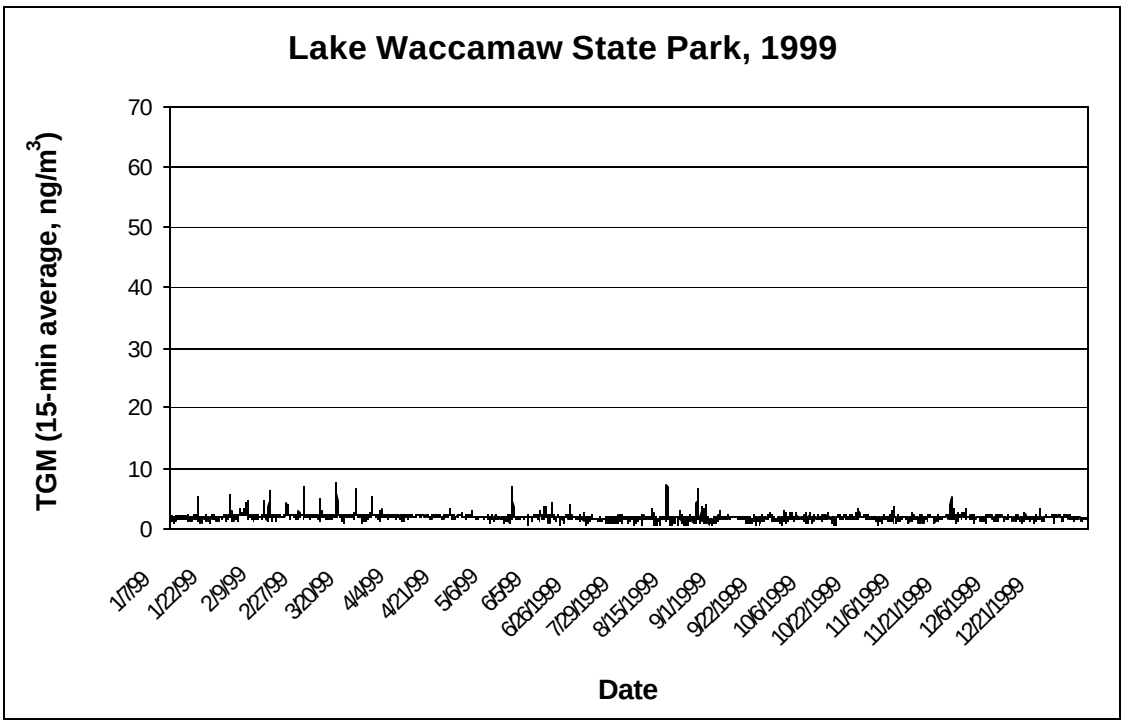
Continuous monitoring for TGM was carried out at Waccamaw State Park from December 1997 through December 2000. All data from this site represent 15-minute average TGM concentration (ng/m^3) except for a brief period between July 17 and August 1, 2000 when measurements were made on a 5-minute basis. Monitoring data are summarized in Table 1-2 and presented graphically in Figure 1-8.

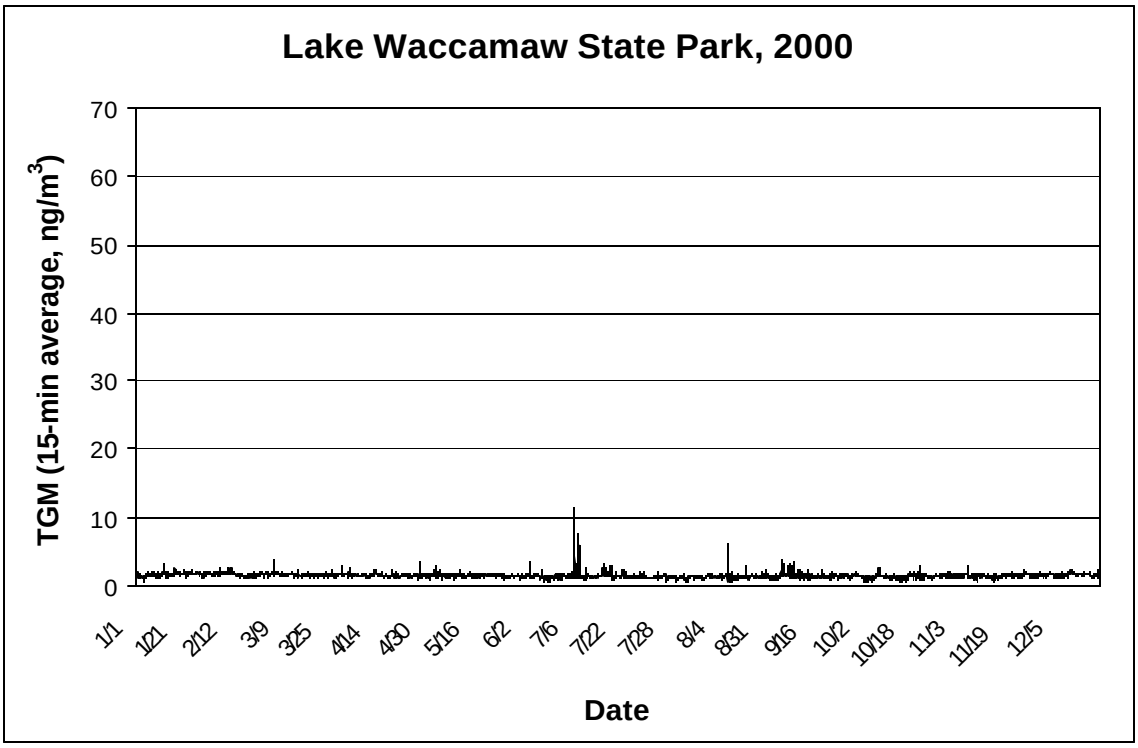
Table 1-2: *Quarterly statistics for ambient air TGM measured at Lake Waccamaw S.P. Values were calculated using 15-minute average TGM concentrations. All values in ng/m^3.*

Lake Waccamaw (TGM)	1998*			1999				2000			
	st Q	**rd Q**	**th Q**	**st Q**	**nd Q**	**rd Q**	**th Q**	**st Q**	**nd Q**	**rd Q**	**th Q**
10th percentile	.53	.21	.35	.54	.50	.08	.33	.56	.35	.07	.19
25th percentile	.69	.44	.58	.71	.64	.36	.54	.67	.55	.34	.47

50th percentile (median)	.87	.62	.77	.86	.77	.54	.67	.79	.65	.50	.64
75th percentile	.08	.81	.94	.99	.87	.65	.78	.90	.74	.62	.79
90th percentile	.50	.82	.24	.15	.98	.73	.90	.99	.81	.80	.87
95th percentile	.02	.02	.96	.26	.09	.82	.01	.07	.87	.01	.95
99th percentile	1.47	2.07	1.15	.80	.58	.43	.39	.30	.21	.77	.16
Maximum	3.31	4.42	0.97	.67	.75	.17	.12	.08	.48	1.41	.03
Arithmetic mean	.23	.44	.40	.88	.75	.49	.65	.78	.62	.50	.59
Standard deviation	.85	.66	.53	.42	.29	.35	.26	.2	.24	.46	.29
Count (n)	056	986	102	566	829	351	410	550	727	983	411


Lake Waccamaw State Park, 1998
TGM (15-min average, ng/m3)
70
60
50
40
30
20
10
0
12/16/97
12/24/97
1/2/98
1/10/98
1/19/98
2/10/98
2/18/98
2/27/98
6/27/98
7/5/98
8/11/98
9/29/98
10/7/98
10/16/98
10/24/98
11/2/98
11/11/98
11/19/98
11/28/98
12/6/98
12/15/98
Date


Lake Waccamaw State Park, 1999
TGM (15-min average, ng/m3)
70
60
50
40
30
20
10
0
1/7/99
1/22/99
2/9/99
2/27/99
3/20/99
4/4/99
4/21/99
5/6/99
6/5/99
6/26/1999
7/29/1999
8/15/1999
9/1/1999
9/22/1999
10/6/1999
10/22/1999
11/6/1999
11/21/1999
12/6/1999
12/21/1999
Date

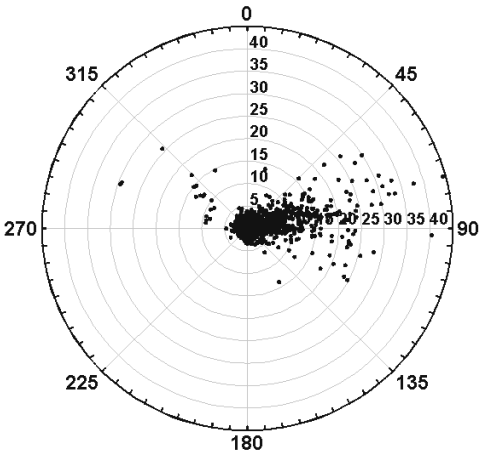


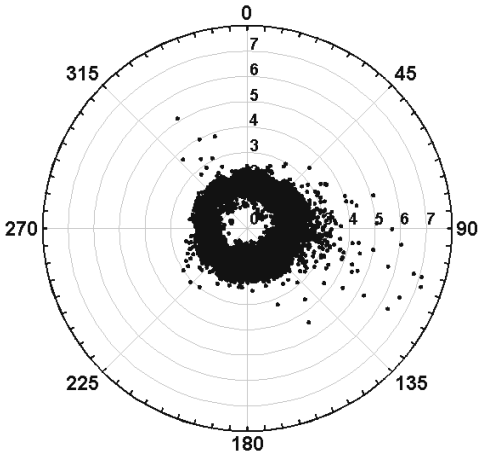
*Data from the 2nd quarter of 1998 did not meet this study's quality control standards and are not presented.

The average mercury level at Lake Waccamaw State Park during the entire study period was 1.84 ng/m^3. The annual average declined between consecutive years, from 2.34 ng/m^3 in 1998 to 1.68 ng/m^3 in 1999 and 1.61 ng/m^3 in 2000. Median mercury levels remained consistent throughout the entire length of the study, as did values in the lower percentile ranges and up through the 90th percentile. It is only in the upper end of the distribution (95th percentile and higher) that levels varied substantially between 1998 and subsequent periods. This is also reflected in quarterly standard deviations, which decreased substantially between 1998 and 1999, reflecting the absence of large deviations in mercury levels beginning in 1999. Over 133,000 individual samples passed QA tests and are presented for the 3-year period, representing over 30,000 hours of data.

Data recovery for 1998 was approximately 45%.[3] The primary reason for the relatively greater rate of data loss during this time is failed system calibrations. These data were collected before quality assurance and quality control methods described in the Quality Assurance Project Plan were implemented, thus the data have been scrutinized closely resulting in the removal of questionable results. We believe there is no valid reason to reject 1998 data with passing calibrations and remain confident in the results presented here. Data recovery is approximately 90% for calendar years 1999 and 2000. The primary reason for data loss was failed calibrations, channel disagreements and power outages related to severe weather events.

Analysis of mercury data with concurrent information on wind direction unearthed a clear association between wind conditions and elevations in TGM during 1998 (Figure 1-9). With very few exceptions, spikes in TGM were accompanied by winds arriving from the east-northeast. No clear pattern emerged during the remainder of 1999 or during 2000. The diminished events detected during this period were associated with winds arriving from various directions (Figure 1-10).[4]



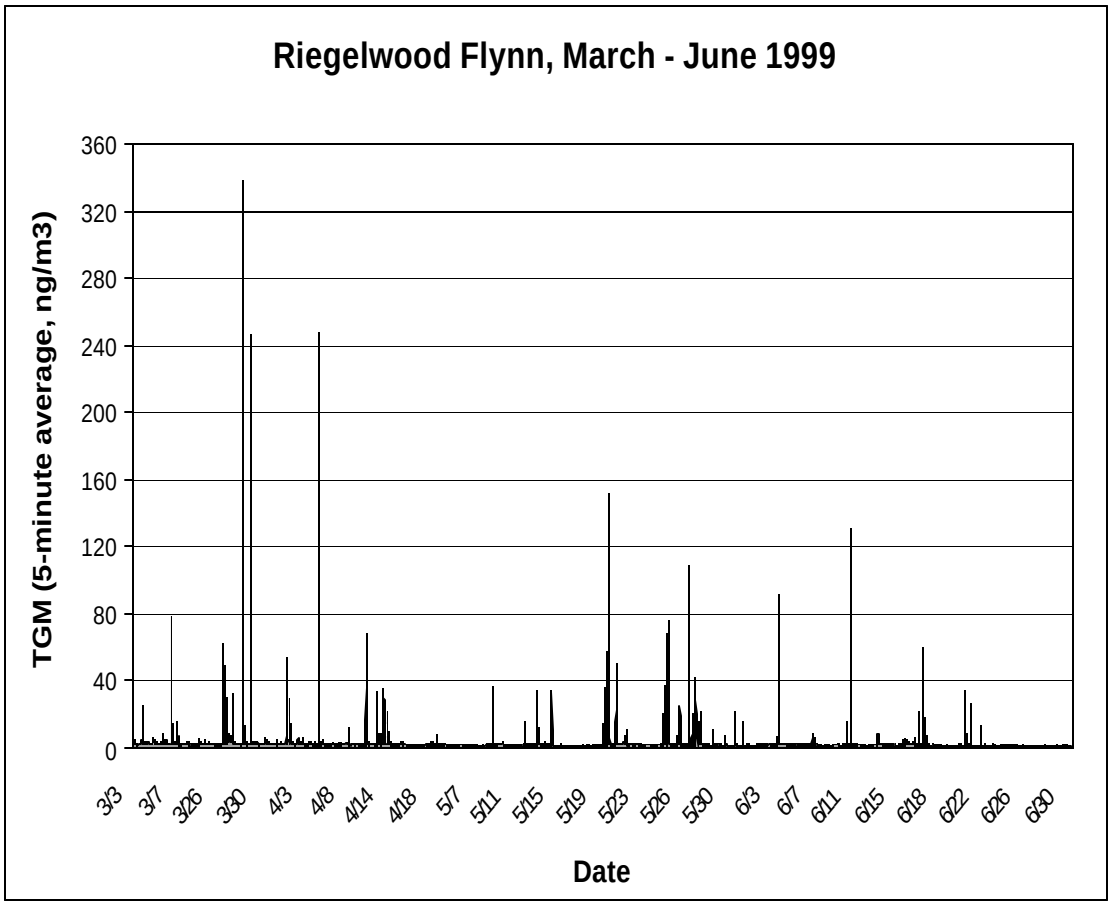


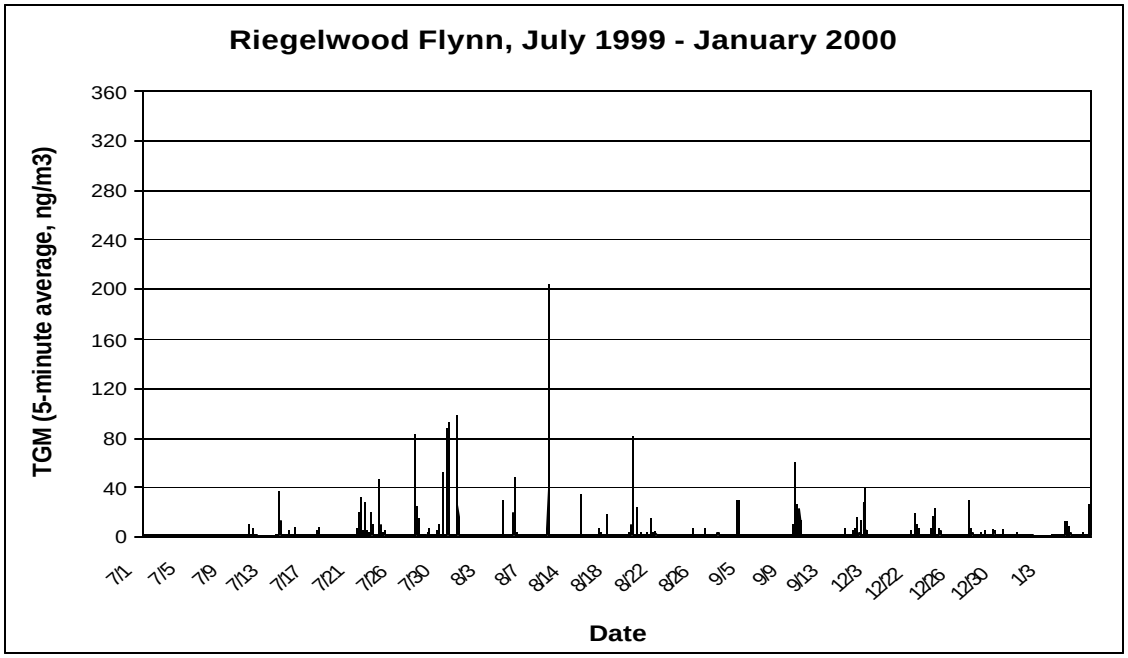
Riegelwood Flynn

The initial phase of TGM measurement began in March 1999 and continued into January 2000. A second phase of monitoring began in August of 2000 and continued through November 2000. All measurements presented in Table 1-3 and Figures 1-11 and 1-12 represent 5-minute average values in ng/m^3

Table 1-3: *Quarterly statistics for TGM measured at Riegelwood Flynn site. Values were calculated using 5-minute average TGM concentrations. All values in ng/m^3.*

Riegelwood Flynn (TGM)	1999				2000		
	1st Q	**2nd Q**	**3rd Q**	**4th Q**	**1st Q**	**3rd Q**	**4th Q**
10th percentile	1.92	1.51	1.36	1.42	0.85	1.10	1.31
25th percentile	2.08	1.62	1.51	1.55	1.13	1.24	1.45
50th percentile (median)	2.31	1.76	1.65	1.72	1.34	1.40	1.58
75th percentile	2.87	1.98	1.79	2.14	1.48	1.55	1.80
90th percentile	4.43	2.43	2.06	2.40	1.62	1.73	2.86
95th percentile	6.36	3.77	2.75	3.31	1.73	2.16	4.49
99th percentile	28.70	20.83	15.11	15.23	6.96	5.95	13.82
Maximum	338.32	247.29	203.64	60.54	26.76	32.29	111.30
Arithmetic mean	3.76	2.55	2.17	2.23	1.42	1.54	2.16
Standard deviation	10.72	5.94	4.84	2.80	1.09	1.05	3.06
Count (n)	3484	20595	15281	7973	1892	6617	12553


Riegelwood Flynn, March - June 1999
TGM (5-minute average, ng/m3)
360
320
280
240
200
160
120
80
40
0
3/3
3/7
3/26
3/30
4/3
4/8
4/14
4/18
5/7
5/11
5/15
5/19
5/23
5/26
5/30
6/3
6/7
6/11
6/15
6/18
6/22
6/26
6/30
Date


Riegelwood Flynn, July 1999 - January 2000
TGM (5-minute average, ng/m3)
360
320
280
240
200
160
120
80
40
0
7/1
7/5
7/9
7/13
7/17
7/21
7/26
7/30
8/3
8/7
8/14
8/18
8/22
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12/3
12/22
12/26
12/30
1/3
Date

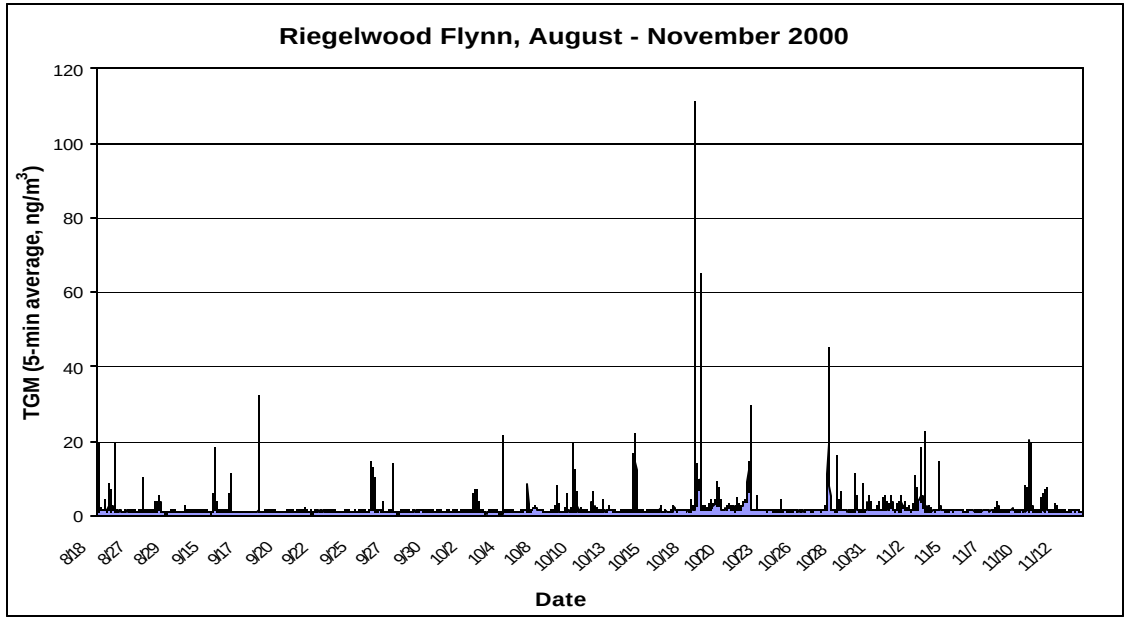
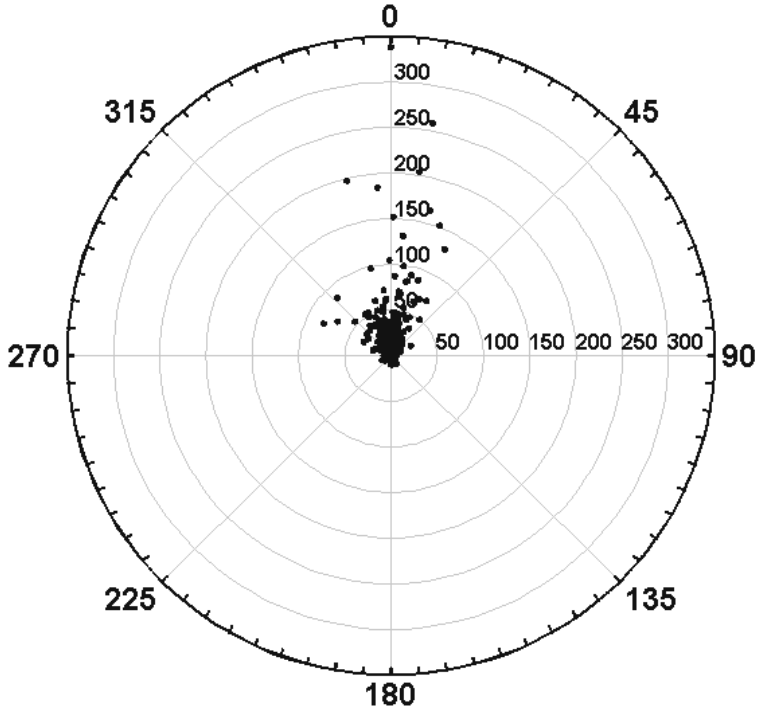
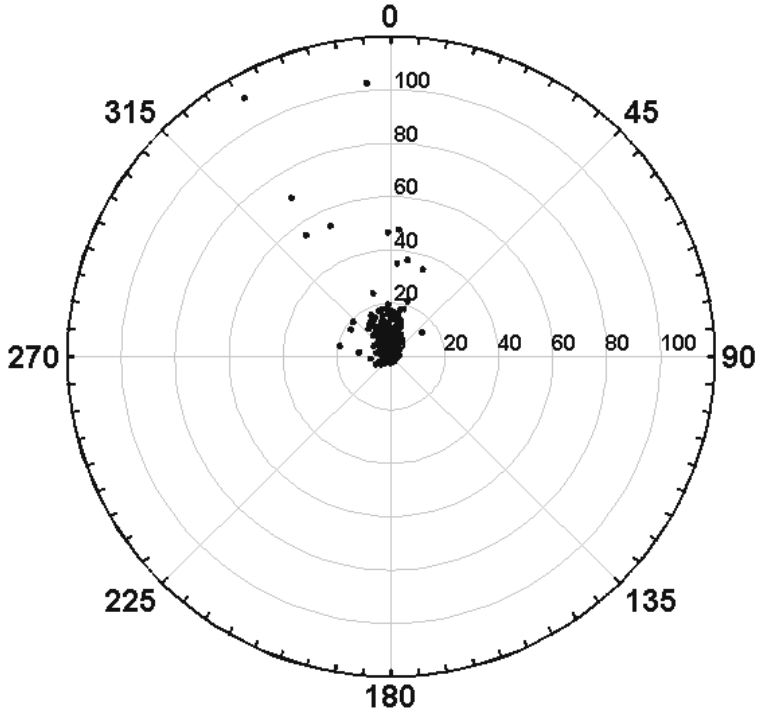

Riegelwood Flynn, August - November 2000
TGM (5-min average, ng/m3)
120
100
80
60
40
20
0
8/18
8/27
8/29
9/15
9/17
9/20
9/22
9/25
9/27
9/30
10/2
10/4
10/8
10/10
10/13
10/15
10/18
10/20
10/23
10/26
10/28
10/31
11/2
11/5
11/7
11/10
11/12
Date

Figure 1-11 (this and previous page): *Total gaseous mercury measured at Riegelwood Flynn during Phase 1 (1999 – 2000, first 2 figures) and Phase 2 (2000, 3rd figure).*

10th percentile	1.92	1.51	1.36	1.42	0.85	1.10	1.31
25th percentile	2.08	1.62	1.51	1.55	1.13	1.24	1.45
50th percentile (median)	2.31	1.76	1.65	1.72	1.34	1.40	1.58
75th percentile	2.87	1.98	1.79	2.14	1.48	1.55	1.80
90th percentile	4.43	2.43	2.06	2.40	1.62	1.73	2.86
95th percentile	6.36	3.77	2.75	3.31	1.73	2.16	4.49
99th percentile	28.70	20.83	15.11	15.23	6.96	5.95	13.82
Maximum	338.32	247.29	203.64	60.54	26.76	32.29	111.30
Arithmetic mean	3.76	2.55	2.17	2.23	1.42	1.54	2.16
Standard deviation	10.72	5.94	4.84	2.80	1.09	1.05	3.06
Count (n)	3484	20595	15281	7973	1892	6617	12553


0
45
90
135
180
225
270
315
300
250
200
150
100
50
50
100
150
200
250
300


0
45
90
135
180
225
270
315
100
80
60
40
20
20
40
60
80
100

The mean mercury level at this site for the entire duration of the study was 2.29 ng/m^3. The mean levels for the first (3/99 – 1/00) and second (8/00 – 11/00) phases of sampling were 2.42 ng/m^3 and 1.95 ng/m^3, respectively. Quarterly mean values and extreme values declined throughout the first phase of monitoring, reflecting the decreasing frequency and intensity of mercury fluctuations. Similarly, quarterly standard deviations declined between each quarter during the first phase of sampling and remained low during the second phase of sampling. Despite the apparent improvement in conditions at this site, occasional excursions in atmospheric mercury were encountered during all sampling periods. Most measurement statistics including mean and standard deviation were increased slightly between the 3rd and 4th quarter of 2000. Elevated TGM was generally associated with winds arriving from the north-northwest (Figures 1-12a-b).

Approximately 60% data recovery was achieved during the first phase of monitoring at Riegelwood Flynn. Loss of coverage resulted from site start-up problems and lack of closing calibrations during site malfunctions. However, the greatest loss of data occurred during Hurricane Floyd and its aftermath. Damage to this area was catastrophic, severely hindering access to the site during September and October of 1999. Monitoring was reestablished in late November 1999 following repairs to the site. Only two disruptions were encountered during the second phase of sampling, however a 2-week period was lost due to a computer malfunction at the site. Data recovery during this period was approximately 80%. It is not believed that any event leading to loss of data at this site adversely affected those data that were successfully obtained.

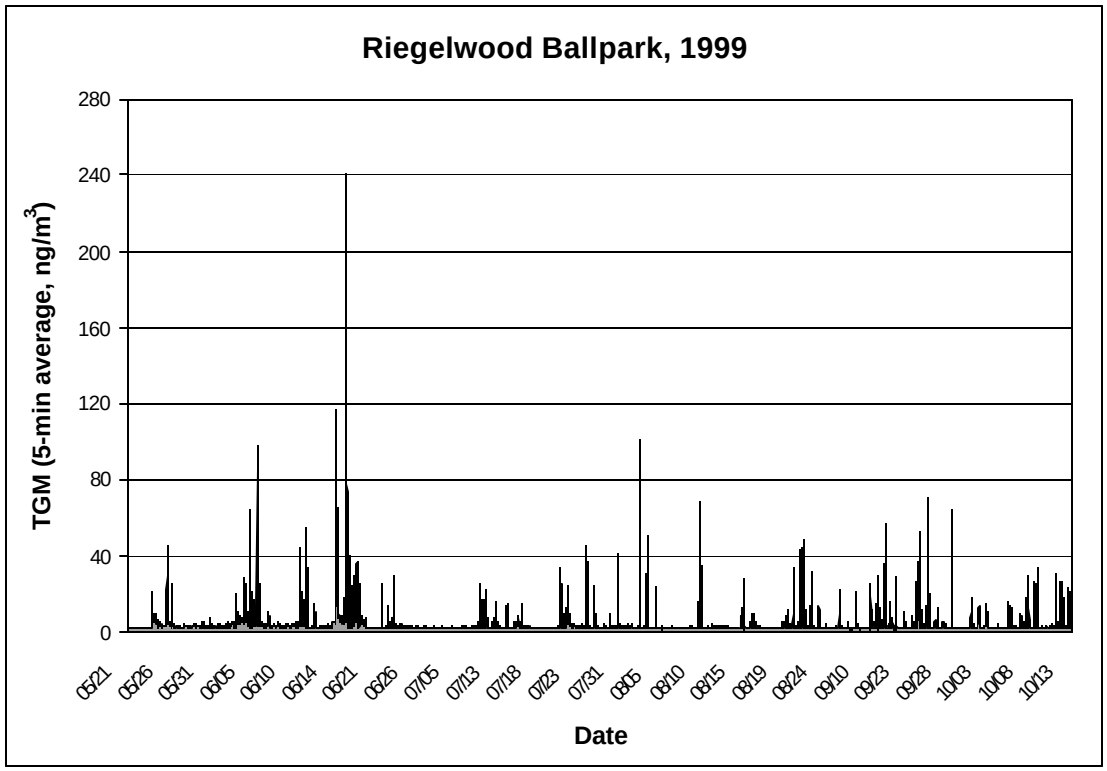
Riegelwood Ballpark

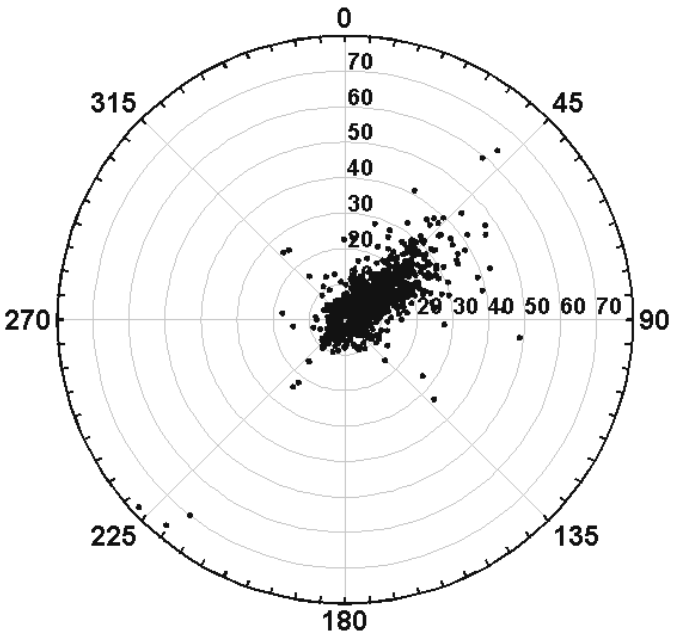
Two phases of mercury measurements were carried out at Riegelwood Ballpark. Between May and October of 1999, measurements of TGM were made every 5 minutes using the Tekran 2537A mercury vapor analyzer (Figure 1-13). A second phase of monitoring carried out during 2000 involved measurement and speciation of atmospheric mercury using the Tekran 1130 mercury speciation unit. These analyses, which produced separate measurements of RGM and Hg(0), are discussed in greater detail below in the sections on mercury speciation measurements; however, for comparison purposes we present here the 5-minute data on Hg(0) collected during August through November of 2000. Hg(0) represents greater than 95% of TGM in ambient air in virtually all circumstances, which validates comparisons between TGM data from 1999 using the Tekran 2537A and Hg(0) data from 2000 generated with the Tekran 1130 speciation unit. The comparability of speciated and non-speciated data is discussed further, below.

Table 1-4: *Quarterly statistics for TGM measured at Riegelwood Ballpark site. Values represent 5-minute average concentrations (ng/m^3).*

Riegelwood Ballpark (TGM)	1999			2000
	2nd Q	**3rd Q**	**4th Q**	**3rd/4th Q**[5]
10th percentile	2.18	1.86	1.78	1.28
25th percentile	2.56	2.10	1.96	1.40
50th percentile (median)	3.05	2.38	2.16	1.54
75th percentile	4.01	2.74	2.62	1.72
90th percentile	6.47	3.59	6.65	2.32
95th percentile	10.42	6.51	10.61	4.26
99th percentile	31.03	19.73	19.95	12.30
Maximum	240.94	101.35	33.83	52.46
Arithmetic mean	4.66	3.09	3.34	1.99
Standard deviation	2.13	2.18	3.50	2.10
Count (n)	9881	18200	3507	17797

The average TGM concentration throughout the first monitoring phase was 3.61 ng/m^3. The most significant fluctuations were encountered during May and June of 1999, with large mercury peaks encountered during several periods lasting up to a week. During subsequent months mercury peak events were generally diminished in magnitude. Elevated mercury measurements encountered during 1999 were related to winds originating from the northeast (Figure 1-14). Data in Table 1-4 are presented as stratified by calendar quarter. However, caution must be used in interpreting these data given that 4th quarter data only represent a 2-week period in October.


Riegelwood Ballpark, 1999
TGM (5-min average, ng/m3)
280
240
200
160
120
80
40
0
05/21
05/26
05/31
06/05
06/10
06/14
06/21
06/26
07/05
07/13
07/18
07/23
07/31
08/05
08/10
08/15
08/19
08/24
09/10
09/23
09/28
10/03
10/08
10/13
Date


0
45
90
135
180
225
270
315
70
60
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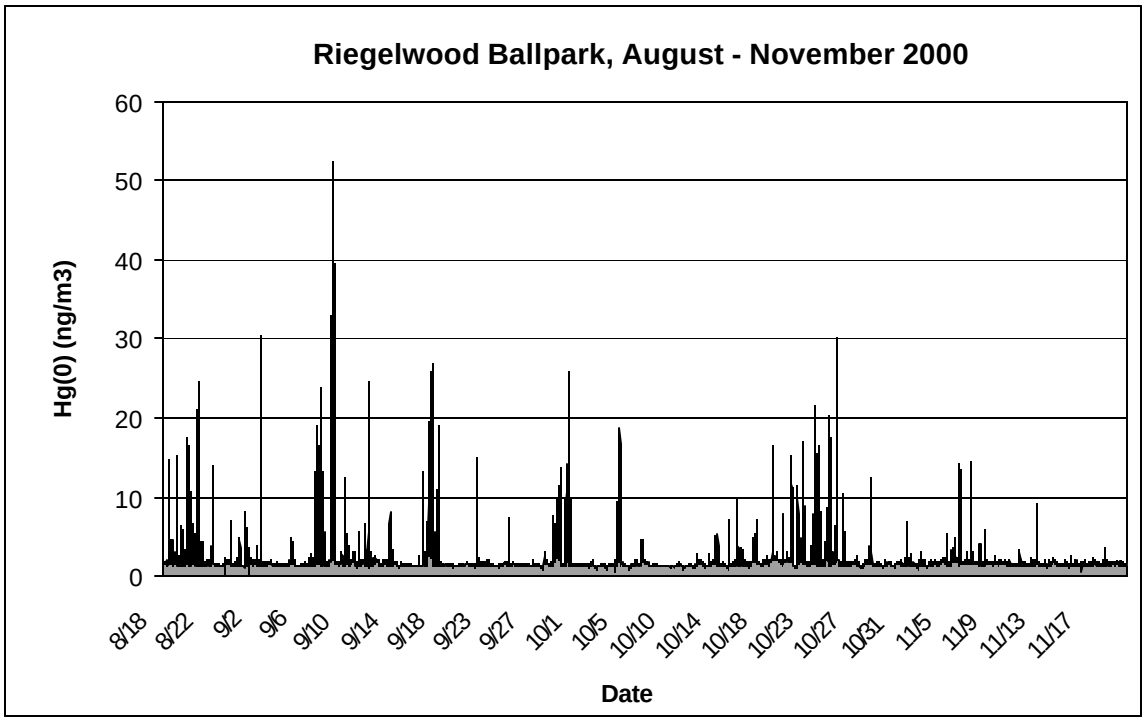
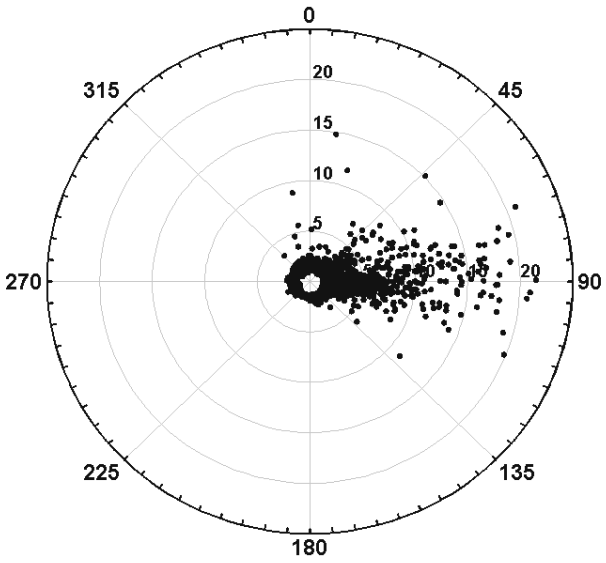
40
30
20
20 30 40 50 60 70



showed that the direction was being misreported. The difference was +38.3 degrees at 0 degrees and +26.95 degrees at 90 degrees, indicating that values reported as 90 degrees



were in all probability over-reported by between approximately 25 to 40 degrees. Correcting for this inaccuracy would provide a range of directional data very similar to that seen for TGM in Figure 1-14, with elevated TGM primarily associated with winds arriving from the northeast.

Over 30,000 measurements of mercury were taken during 1999 at this site, representing over 2,500 hours of coverage. Gaps in coverage were primarily due to early problems with water contamination of sample lines and resulting effects on sample volumes. Substantial loss of data also occurred during the aftermath of hurricanes Dennis and Floyd during August and September of 1999. Overall, 77% coverage was achieved between May and October of 1999 at this site. Sample recovery during speciation measurements was intermittent. This subject is discussed in more detail in the RGM results and discussion section.

TOTAL GASEOUS MERCURY: DISCUSSION

General Characteristics of Atmospheric Mercury

Mercury is a naturally occurring trace contaminant of ambient air. In rural and remote areas TGM levels typically range between 1.5 and 2.0 ng/m^3 (EPA 1997a). Atmospheric levels may vary substantially depending on the proximity to local anthropogenic emission sources (Lindberg; Keeler - as summarized in EPA 1997a). The USEPA recently chose 1.6 ng/m^3 to represent modern day terrestrial "background" conditions in a multi-media fate and transport model for mercury (EPA 1997a). TGM is almost entirely comprised of vapor phase Hg(0), although much smaller quantities of particulate mercury and RGM are also present in ambient air at pg/m^3 levels. Chemical and photochemical reactions may facilitate conversion between the various forms of mercury, thus affecting atmospheric residence time. Gaseous or aqueous phase oxidation of Hg(0) could lead to production of water-soluble RGM species that may contribute to localized deposition. Alternatively, atmospheric reduction of RGM species could lead to the formation of Hg(0) vapor, and reduced regional wet and dry deposition rates.

Variability in atmospheric TGM may be related to both point source releases and natural causes. Mercury's natural geochemical cycle involves migration between earth, water and air. Mercury that settles to the earth's surface through atmospheric deposition will likely undergo re-evasion to the atmosphere. Natural processes that involve addition of mercury to the air include continuous evasion from mercury-enriched surficial soils and freshwater and marine environments (Schroeder and Munthe). Periodic events such as geothermal venting, forest fires and volcanic eruptions can also result in concerted releases of mercury to the air. In general, natural releases of mercury occur over prolonged periods of time and are comprised predominantly of Hg(0) (Gustin).

Some have also suggested that TGM may be susceptible to a natural diel cycle under certain meteorological conditions (Schroeder and Munthe). Temperature and solar radiation may enhance volatilization from snowpack, surface waters, soils and wetlands, leading to enhanced flux rates during daylight hours (LaLonde, Poissant, Lindberg and

Zhang, Lindberg and Meyers). Although this may affect flux rates and measured mercury vapor concentrations at the water:air and soil:air interfaces, it is unclear whether similarly detectable deviations in atmospheric mercury would be expected at heights of a meter or greater above surface level where the air is more well-mixed. Long-term monitoring data collected to date does not support the argument that a natural diurnal pattern exists for TGM. Instead, it has been suggested that point source influences are the predominant cause of both short- and long-term measurable fluctuations in TGM at lower latitude terrestrial sites (Lindberg, Iverfeldt). Some data seem to suggest that seasonal variability in TGM levels is present, with highest levels in March and lowest levels between October and December at northern hemisphere monitoring sites (Iverfeldt). During 2000, a relatively undisturbed period at Lake Waccamaw, we observed our highest background TGM readings during the December through March timeframe and the lowest baseline readings between July and October. Whether this variability relates to natural phenomena or seasonal changes in anthropogenic emissions of mercury has not yet been determined.

Recently, dramatic changes in atmospheric mercury were noted in the Arctic region (Schroeder 1998). Atmospheric mercury was depleted from 1.5 ng/m^3 to 0.2 ng/m^3 just before the polar sunrise and during Arctic snowmelts. It was suggested that the decrease in TGM is due to chemical conversion of Hg(0) to RGM that then undergoes deposition to the earth's surface. The ready availability of reactive halide species could be contributing to this chemical reaction. To date no similar pattern has been described at lower latitudes although some have speculated that similar phenomena may occur to a lesser extent in lower latitude coastal regions (Mason, personal communication).

Historical Data on Atmospheric Mercury in North Carolina

Very few data are available describing typical atmospheric mercury levels in North Carolina. Stopford anecdotally reported levels between 1.7 and 8.9 ng/m^3 in Durham, NC in 1978, with a short-term peak of approximately 400 ng/m^3 during a plume fumigation event arising from a nearby coal-fired power plant (Stopford). Between 1998 and 2001, periodic measurements of TGM taken at a site in Research Triangle Park, NC indicated that levels rarely exceeded 2 ng/m^3, with values typically in a range between 1.4 - 1.7 ng/m^3 (Stevens). TGM was measured over a 3-month period between June and August of 1996 at Phelps Lake, a remote site in northeastern North Carolina; 15-minute readings were consistently between 1 and 2 ng/m^3 and never exceeded 6 ng/m^3.

Total Gaseous Mercury at Lake Waccamaw

At Lake Waccamaw, the vast majority of readings for TGM fell below 2 ng/m^3. Transient spikes in TGM helped raise the annual average concentration to 2.34 ng/m^3 during 1998, somewhat higher than expected for such a remote location but generally lower than levels documented in urban areas or sites immediately adjacent to point sources of mercury emissions. Spikes in TGM occurred on a regular basis and peak

values frequently exceeded an order of magnitude above background. This trend remained in place throughout 1998. Beginning in spring of 1999, mercury readings stabilized below 2 ng/m^3. This pattern persisted throughout 1999 and 2000. Annual average mercury levels were approximately 28% and 31% lower than 1998 values, respectively.

Total Gaseous Mercury at Riegelwood, NC

Qualitatively, results from Riegelwood, NC appear very similar to early data from Lake Waccamaw. The majority of readings were below 2 ng/m^3 but transient spikes would occasionally reach levels exceeding 300 ng/m^3. This pattern was seen at both sites, throughout 1999 and 2000.

Long-term average TGM levels at Riegelwood Flynn declined between 1999 and 2000. The highest individual readings were encountered during the first several weeks of monitoring; however, peaks did continue to appear during subsequent months, suggesting the possibility of continued local source impacts. While mercury levels declined throughout 1999, they appeared to remain relatively stable during the latter half of 2000. A comparison between 4th quarter data from 1999 and 2000 shows that mercury levels remained relatively consistent in terms of both average levels (2.23 ng/m^3 vs. 2.16 ng/m^3) and the magnitude and frequency of mercury spikes. This may suggest a "leveling-off" of atmospheric mercury levels in this area.

The profile for TGM at the Ballpark site was very similar to that encountered at Riegelwood Flynn. Baseline conditions were punctuated with periodic elevations as high as 240 ng/m^3 TGM. Monitoring was not initiated until mid-May 1999; thus measurements were not made during normal mercury cell chlor-alkali operating conditions. Although the quarterly statistics presented in Table 1-4 seem to suggest that average values declined between the 2nd quarter and subsequent quarters, conditions actually appear to have remained relatively stable. Data from the entire sampling period (May - October) illustrates consistent, but highly variable, atmospheric mercury levels at this site.

It should be noted that values encountered at the lower end of the range (10th - 50th percentiles) were consistently higher at this site relative to similar data from the Flynn and Waccamaw sites. This could reflect higher baseline levels of TGM due to site contamination or it could reflect an effect of instrument configuration. The Ballpark site provides a relatively unobstructed view of the nearby industrial complex and might be more susceptible to downwind migration of mercury from on-site waste ponds. However, this factor seems an unlikely explanation given the variability in wind direction. Alternatively, enhanced historical deposition of mercury to local soils could lead to greater rates of Hg(0) volatilization. If true, intraday variability might be expected with higher readings associated with elevated temperatures and solar radiation. Another possible explanation is performance of the mercury vapor monitor. Instrument configuration and operating conditions were identical to those at the other two sites, and the inlet to the sample line was positioned at a similar height. The instrument at Ballpark

was housed in a mobile trailer rather than a freestanding shelter, but conditions inside the structures were similarly maintained. None of these factors is a satisfactory explanation for the higher baseline readings of TGM observed at this site. This observation could warrant further study.

During 2000, the Ballpark instrument was modified to include a denuder assembly for speciation of gaseous mercury. Estimates for TGM can be generated by combining 2-hour average values for Hg(0) and RGM or by using Hg(0) alone as a surrogate measurement. The former calculation would theoretically be a more accurate representation of atmospheric TGM but would present data on a completely different time frame than those collected during 1999 and would "smooth over" short-term elevations in atmospheric mercury. Comparing 5-minute Hg(0) measurements to historical TGM data avoids this conflict but introduces additional complicating factors. First, dedicated measurement of TGM is a nearly continuous process with a single interruption for instrument calibration only taking place over 40 minutes once every 25 hours. By contrast, measurement of Hg(0) during mercury speciation is interrupted every 2 hours for a 40-minute denuder desorption and analysis cycle. While data were closely scrutinized to assure that the desorption/analysis cycle had no effect on flanking measurements of Hg(0) it could be argued that the loss of such a substantial fraction of daily coverage might limit the effectiveness of this type of comparison by excluding such a substantial portion of the sampling time. However given the large volume of measurements and the random nature of the timing on the desorption/analysis cycles it is doubtful that these periodic interruptions would contribute to any meaningful or consistent bias in the measurement of atmospheric mercury. A more challenging question concerns the comparability of Hg(0) and TGM readings, as Hg(0) is only one component of TGM. The Tekran 2537A is described as an instrument that "performs continuous measurement of TGM in ambient air" (Tekran). However, given that the instrument configuration involves several convoluted sample lines and filter assemblies it could be argued that the RGM component is lost through adherence to the instrument parts before it can reach the gold cartridge traps. If this assumption is true then Tekran 2537A data on "total gaseous mercury" may in fact represent only Hg(0). In fact, the point is nearly made moot by the fact that RGM appears to be a very small component of TGM in ambient air. During the course of this study RGM levels were less than 1% of TGM levels in over 90% of speciated mercury measurements and even in the most extreme situation did not exceed 7% of TGM. As evidenced in Table 1-5, a statistical comparison of Hg(0) and TGM shows that ambient levels are nearly identical. We believe that these data support the conclusion that a meaningful comparison can be made between measurements of TGM from 1999 and measurements of Hg(0) from 2000.

Using this technique, it appears that atmospheric mercury levels declined substantially between 1999 and 2000 at the Ballpark site. The average level for Hg(0) measured between August 24 and October 13 of 2000 was 1.9 ng/m^3, compared to 3.2 ng/m^3 for TGM during the period in 1999 – a 40% reduction. This reflects, in part, a reduction in the intensity of short-term elevations in atmospheric mercury, but mercury levels also appear to have fallen throughout the entire distribution of values. During 1999 even the values in the low end of the range were predominantly above 2.0 ppm while

low-end readings in 2000 were generally below 1.5 ng/m^3. It is not immediately clear why baseline conditions at this site would have improved during this period.

Table 1-5: *Comparative statistics for TGM and Hg(0) at the Riegelwood Ballpark site, Aug 24 – Oct 13, 1999 vs. 2000. All values are 5-minute readings in ng/m^3.*

	1999 TGM	2000 Hg(0)
10th percentile	1.66	1.24
25th percentile	1.91	1.36
50th percentile (median)	2.14	1.48
75th percentile	2.48	1.65
90th percentile	5.46	2.15
95th percentile	9.77	4.01
99th percentile	22.58	12.93
max	70.78	52.46
mean	3.24	1.94
n	8539	9113

In general, all monitoring sites provide a similar picture for atmospheric TGM in this region of southeastern North Carolina. TGM levels appear to be declining at both Riegelwood and Lake Waccamaw. At Lake Waccamaw the dramatic improvement in atmospheric conditions beginning in early 1999 and lasting throughout the duration of this study are consistent with rural or remote readings for TGM. Improvements were also noted at both Riegelwood sites, although periodic fluctuations in TGM continue to be detected in this area, and may warrant further study.

Concurrent measurements from all three sites illustrate geographic variability in TGM. Overlapping measurements are available between May and September of 1999 and August and November of 2000 (Table 1-6). These data illustrate a reduction in long-term mercury levels at both Riegelwood sites but also illustrate that TGM levels remain higher at these sites relative to corresponding data from Lake Waccamaw.

Table 1-6: *Concurrent total gaseous mercury levels measured at all three study monitoring sites during 1999 and 2000 (mean, ng/m^3)*

Period	**Lake Waccamaw**	**Riegelwood Flynn[6]**	**Riegelwood Ballpark**
May 21 - Sept 14, 1999	1.52 ng/m^3	2.21 ng/m^3	3.67 ng/m^3
Aug 18 - Nov 20, 2000	1.52 ng/m^3	1.94 ng/m^3	1.99 ng/m^3

Total Gaseous Mercury and Wind Direction

Establishment of a relationship between TGM levels and wind direction may help to identify potential fixed sources of TGM emissions. This relationship was examined in the present study using data from on-site meteorological equipment. Regional wind characteristics are illustrated in Figure 1-17 using a 5-year wind rose diagram with data collected at Wilmington, NC. Winds in this area are predominantly southwesterly during the summer months and north to northeasterly during the winter months.

Data from 1998 suggested a positive relationship between elevated mercury levels at Lake Waccamaw and winds arriving from the east-northeast. During 1999, elevated mercury at Riegelwood Flynn was associated with winds arriving from the northwest while winds from the north and northeast were most strongly associated with elevated mercury at Riegelwood Ballpark.

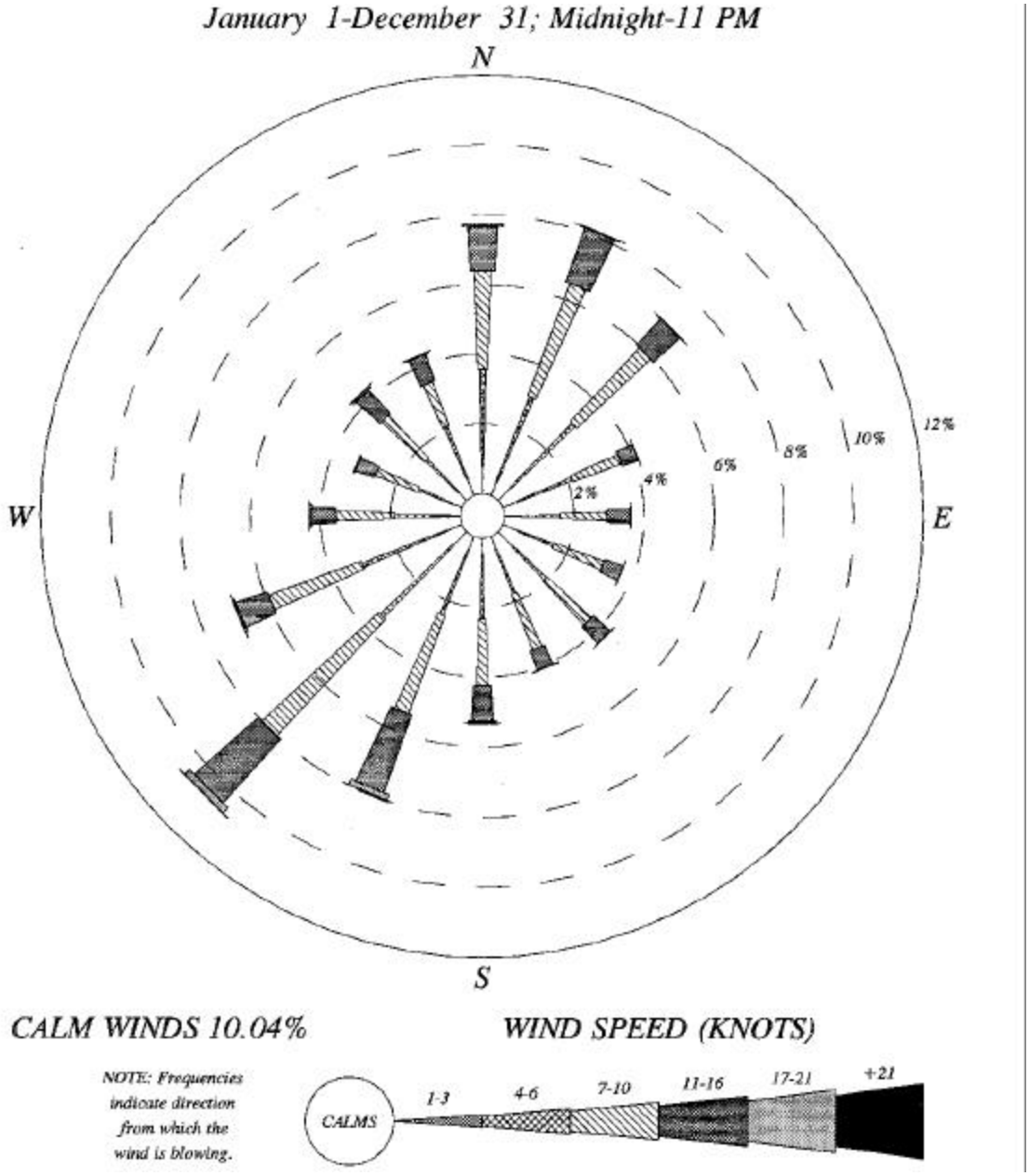


Figure 1-17: *Regional wind pattern for Wilmington, NC, 1986 – 1990.*

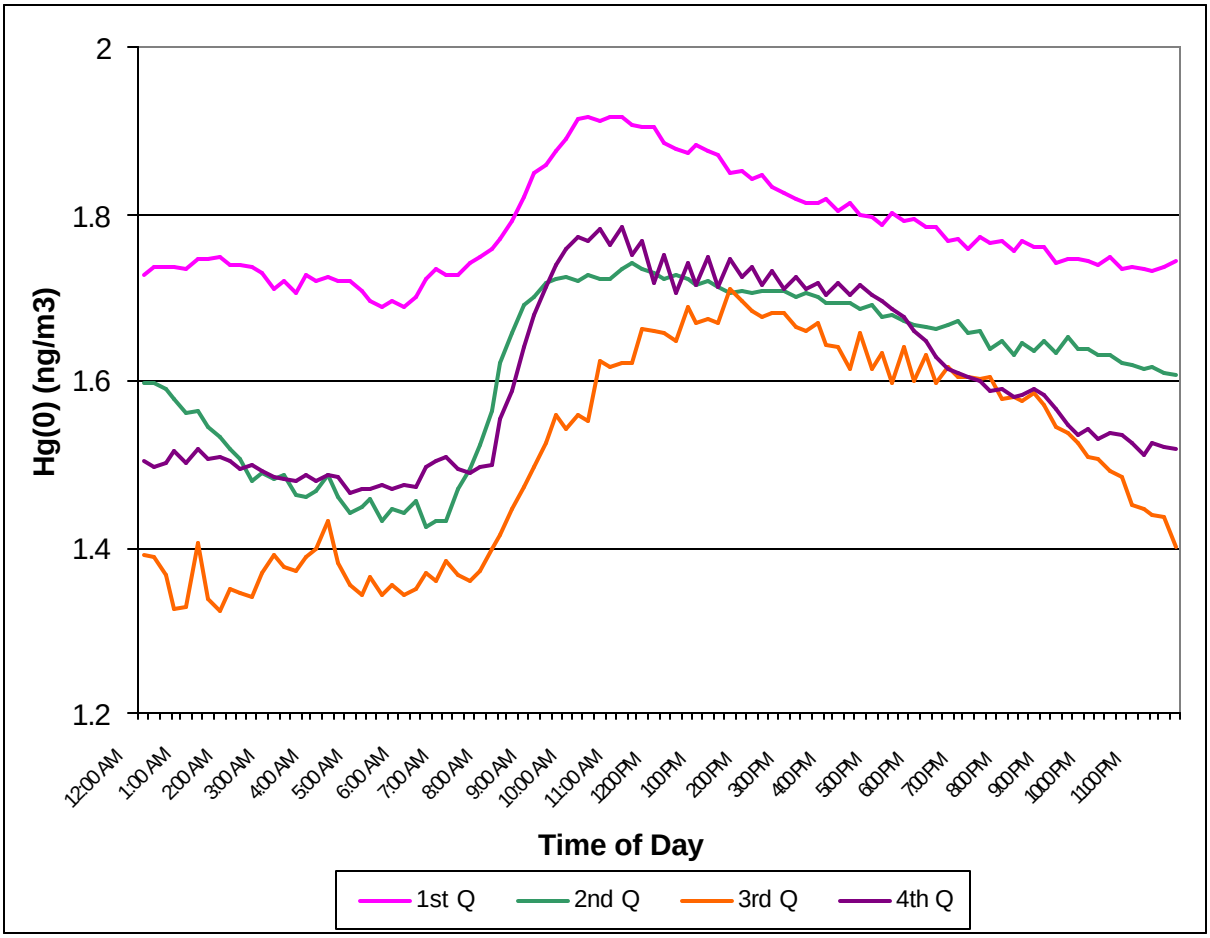
The combined data from all three sites provide an opportunity for "triangulation" of wind and mercury data. Early data from Lake Waccamaw was insufficient for distinguishing the most likely responsible source because several sources of mercury emissions lay to the east of this site. However, subsequent data from the Flynn site suggested that sources to the east of Riegelwood (i.e. in the vicinity of Wilmington, NC) played little role in affecting ground-level TGM in the Riegelwood area during the study period.

In our analyses, we removed data associated with wind speeds below 3 miles per hour. Wind direction data collected during periods of light and variable winds tends to be scattered and rarely provided meaningful information on relationships between mercury levels and wind direction. In addition, the calculation of an "average" 5-minute value for wind direction under these conditions might be misleading since it would represent the

product of highly variable, shifting winds. Elevated mercury readings were more frequently associated with calm winds at the Riegelwood sites as compared to Lake Waccamaw data from 1998. This phenomenon could be related to slow outward ground-level migration of a pollution plume from a nearby source as might be encountered during calm conditions. The magnitude and frequency of this type of phenomenon should be greater if ground-level monitoring stations are positioned immediately adjacent to pollution sources, thus minimizing dispersion of the pollution plume. Data from the Riegelwood sites, as such, might be suggestive of a nearby mercury emissions source.

Total Gaseous Mercury and Other Meteorological Variables

Determining a relationship between TGM levels and other meteorological parameters including temperature and humidity was complicated by the apparent influence on TGM levels by local sources; however, data from Lake Waccamaw during 2000 appear to exhibit minimal source influence and were thus analyzed closely. No clear relationship between TGM levels and temperature or humidity was identified, though possible seasonal differences were unearthed. The average TGM level during December through March was 1.8 ng/m^3, while during the warmer months levels typically averaged 1.5 ng/m^3. A diel pattern was seen during the course of the day with a bottoming out of mercury levels in pre-dawn hours followed by a rapid rise to maximal daily concentrations by late morning and a gradual descent in levels throughout the day (Fig 1-18). We are not aware of this relationship having been previously identified but believe it may warrant further examination. Possible explanations for this pattern could include photochemical reactions resulting in reduction of surficial Hg(2+) to Hg(0) and subsequent volatilization to the atmosphere. Several groups have identified enhanced flux rates from surface waters and contaminated soils following sunrise; however, the likelihood that this effect would be detectable at a 3 to 4 meter elevation seems small since atmospheric mixing is normally very efficient. Atmospheric turbulence, as represented by average wind speed, follows a similar diurnal pattern. The mid-morning rise in TGM occurs at approximately the same time of day that the wind speeds pick up and decreases to its lowest levels around nightfall. This turbulence could help to facilitate movement of deposited mercury or mixing with air masses that contain higher concentrations of gaseous mercury. It may be worth noting that virtually all mercury readings in the lowest 10^{th} percentile of values were confined to periods when the average wind speed was less than 5 mph. Figure 14 also illustrates the apparent seasonal effect on TGM levels, as the entire spectrum of 1^{st} quarter (Jan – Mar) readings are obviously elevated above 3^{rd} quarter (July - September) values. It has been speculated that this pattern might be related to wintertime atmospheric phenomena such as lower mixing heights, seasonal changes in energy demand or variable rates of atmospheric oxidation of Hg(0) which might relate to ambient temperature or sunlight intensity (Sheu and Mason).



If the diel pattern for TGM at Lake Waccamaw is a true atmospheric phenomenon and not an artifact of instrument design or operator error, then an obvious question arises concerning the fate of the depleted TGM during the late evening and early morning hours. Oxidation of Hg(0) to Hg(2+) might serve to explain a daily depletion event but atmospheric mercury speciation studies conducted to date have not shown a diel pattern for Hg(2+) that is consistent with this phenomenon. Another explanation could include adsorption of Hg(0) onto particulate matter and subsequent dry deposition, with revolatilization to the lower atmosphere during the subsequent day's warming period.

Data loss was significant during several study periods but spread out randomly during 1999 and 2000. The most frequent reason for data loss, a lack or failure of instrument calibration, was randomly encountered and should not impart any consistent bias on the data. On several other occasions, data from all sites were lost due to weather phenomena such as hurricanes. These events tended to be seasonal and occurred most frequently during late summer and early fall. Data from Lake Waccamaw are missing for significant periods during 1998 including an extended period between March 4 and June 22. These patterns of missing data could bias comparisons of annualized mercury data if significant seasonal variability exists in the data; however, the data do not support the existence of this type of relationship. We noted no seasonal trends in the available data from the Riegelwood sites and visually, the fluctuations in atmospheric mercury encountered during 1998 at Lake Waccamaw appear evenly spread out across the year. Quarterly statistics are consistent between the 1st, 3rd and 4th quarters of 1998. However, because of the previously noted relationship between mercury and wind direction, bias could be introduced through the exclusion of extended periods from one portion of the year. Winds during the fall and spring tend to be variable and unpredictable, shifting between southwesterly and northerly or northwesterly (C Buckler, DAQ meteorologist, personal communication). Because of the significant variability in wind direction and the relative lack of comparable data, it is nearly impossible to assess the nature or magnitude of the bias introduced by missing data.

Another elusive potential source of bias is the relationship between catastrophic weather events and the likely disruption of industrial activities during this time. If industrial activity was interrupted during these periods, and those activities were associated with spikes in atmospheric mercury, then monitoring data from these periods may be influenced by the lack of source impacts.

SPECIATION OF ATMOSPHERIC MERCURY: RESULTS AND DISCUSSION

Our attempt at long-term speciation of atmospheric mercury was a challenging experience. At the time we initiated this study, there were no published studies documenting experiences with newly developed denuder methods for speciation of atmospheric mercury. Unexpected challenges in the field led to the loss of a large amount of data collected during the first few months of sampling. These initial failures led to the removal of the speciation instruments from the Riegelwood Ballpark site for laboratory method development. Subsequently, modifications to the analytical system were made and a successful second phase of sampling was carried out in fall of 2000.

During the second monitoring phase we were able to distinguish trends in RGM that at times mimicked changes in Hg(0) and at other times seem to behave independently. Much more data will be needed under a variety of conditions to better understand the meaning of the data we present here. It remains uncertain whether ambient fluctuations of RGM represent pollution plume impacts or normal environmental

processes. However, these data do improve the understanding of the characteristics of atmospheric mercury adjacent to this contaminated industrial site and improve our understanding of the potential impacts of atmospheric mercury on regional environmental conditions.

All mercury speciation measurements were carried out at the Riegelwood Ballpark site. Two phases of monitoring took place during 2000: the first between March and June and the second beginning in mid-August and ending in mid-November. A two-month period of method development and testing was carried out between monitoring periods.

Phase 1 (March - June) Results

During the first monitoring phase, over 600 two-hour measurements of RGM and over 13,000 five-minute measurements of Hg(0) were made. Visually, the 5-minute data for Hg(0) appear very similar to the data on TGM collected during 1999, with baseline conditions punctuated by periodic spikes exceeding an order of magnitude above background. A considerable degree of variability was also seen in the RGM data. Two-hour measurements ranged from 0 to 96 pg/m^3. Concurrent two-hour measurements of Hg(0) and RGM are presented in Figure 15. Values for Hg(0) were calculated by averaging all 5-minute readings within each 2-hour sampling period.

On many occasions, 5-minute readings for Hg(0) as low as 0 ng/m^3 were seen. This type of pattern was not seen during previous measurements of TGM at any of our sites and is not considered possible given the steady-state background concentration of Hg(0) (~ 1.6 ng/m^3) that has been consistently documented at terrestrial ambient monitoring locations. It was determined that these depressed reading were most likely caused by contaminants that reduced the instruments collection efficiency. As a result, all data collected during this period have been flagged as questionable. This problem was addressed and solved during the two-month period between sampling phases, allowing for the collection of reliable data during Phase 2.

Phase 2 (Aug - Nov) Results

Between August and November of 2000, over 600 two-hour measurements of RGM and over 13,000 five-minute readings for Hg(0) were collected. Concurrent 2-hour values for Hg(0) and RGM are presented in Figure 1-19, and in Table 1-7. Short-term increases in Hg(0) were relatively common and reached levels as high as 52 ng/m^3 (refer to Table 1-4). The average value for Hg(0) over the entire sampling period was 2.0 ng/m^3. Significant variability in RGM was also seen. Levels were typically very low, with a majority of readings below 1 pg/m^3, but periodic excursions were evident. The average value[7] for RGM over the entire sampling period was 7.81 pg/m^3; the median value was 0.87 pg/m^3.

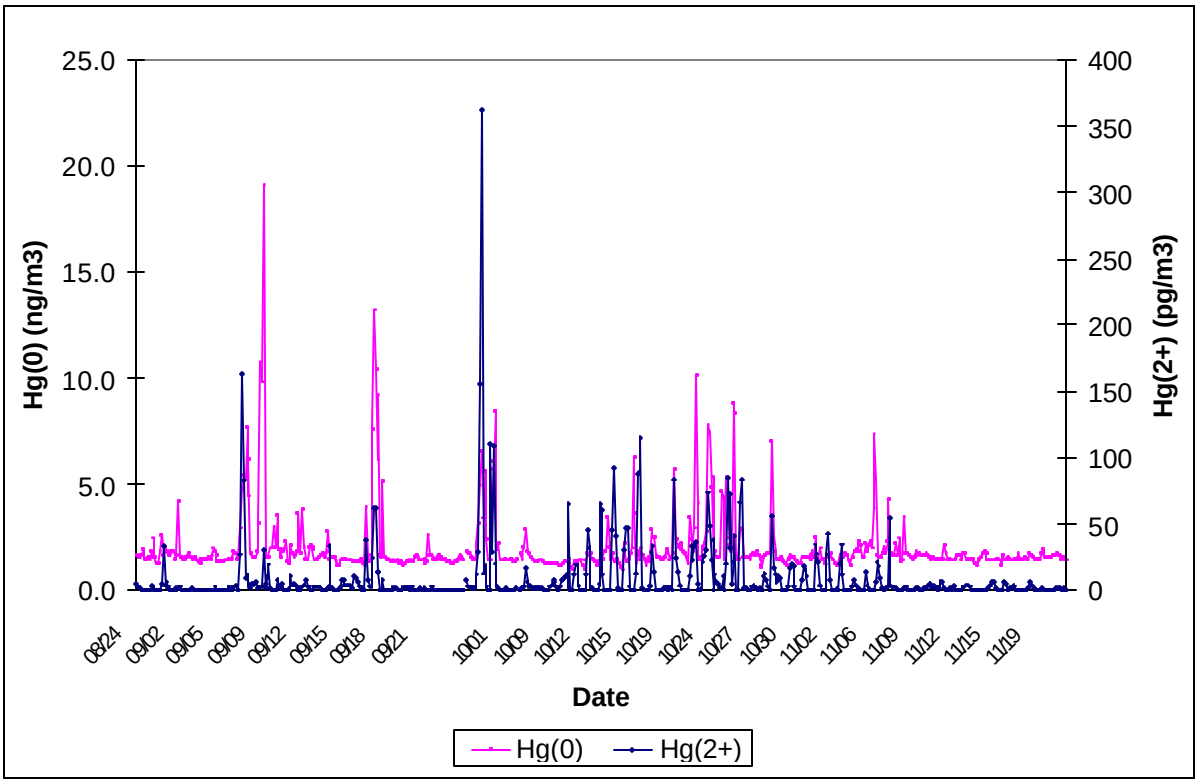


Table 1-7: *Statistics for 2-hour measurements of Hg(0), RGM and TGM from the Riegelwood Ballpark site, Aug 24 – Nov 21, 2000.*

	RGM (pg/m^3)	Hg(0) (ng/m^3)	TGM (ng/m^3)	RGM/Hg(0) (%)
10th percentile	0.00	1.32	1.32	0.00
25th percentile	0.00	1.43	1.44	0.00
50th percentile (median)	0.87	1.57	1.57	0.05
75th percentile	4.20	1.76	1.78	0.23
90th percentile	20.41	2.78	2.80	0.89
95th percentile	39.30	4.90	5.02	1.51
99th percentile	91.76	9.15	9.16	3.90
max	362.40	19.10	19.13	6.70
mean	7.81	1.99	2.00	0.32
standard deviation	23.22	1.56	1.57	0.0078
n	611	611	611	611

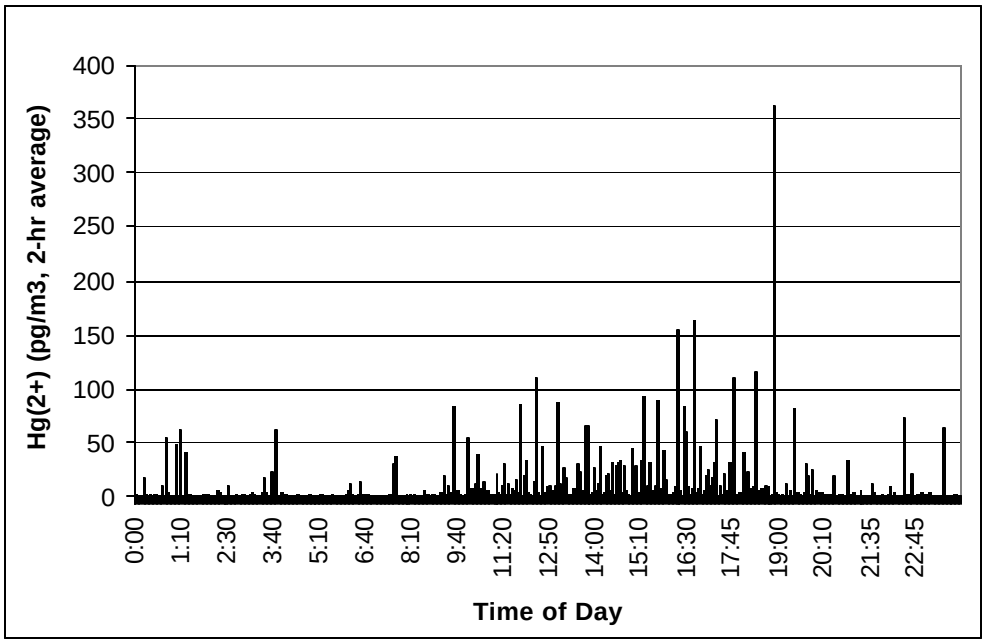
The values in the TGM column in Table 1-7 were derived by adding concurrent two-hour readings for Hg(0) and RGM. Data on TGM exhibits a pattern similar to that seen during prior sampling events at this site; however, both average and peak values were diminished relative to earlier results. In over 90% of measurements, RGM was present at less than one-one hundredth the level of TGM, and in fact, RGM never comprised more than 7% of TGM over any 2-hour period. Thus, spikes in TGM were primarily a result of increased levels of Hg(0) rather than RGM.

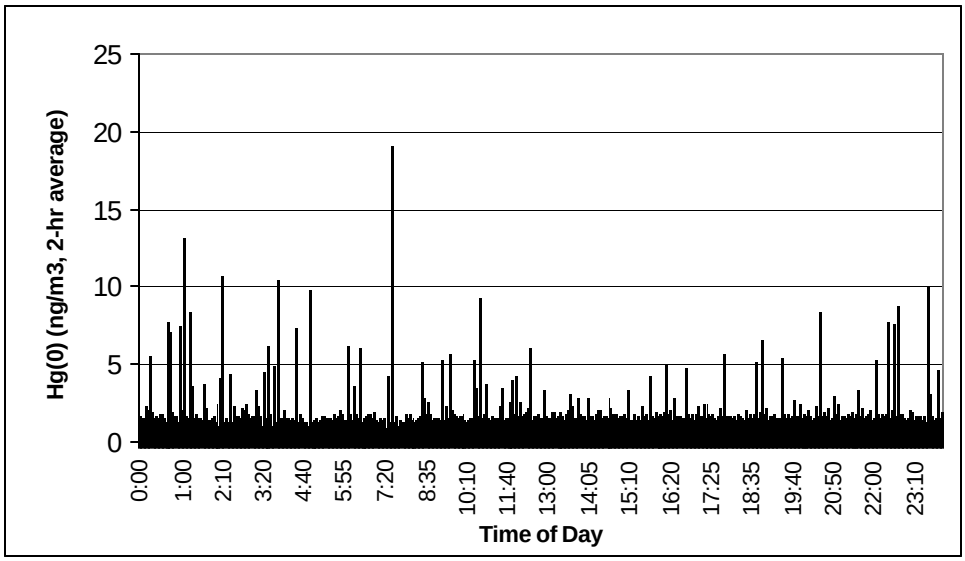
The behavior of RGM could not always be predicted by changes in Hg(0). In many cases a concordance between short-term increases in Hg(0) and RGM was seen, but at other times Hg(0) and RGM behaved independently.

Several possible relationships between atmospheric mercury levels and variables such as meteorology were identified and explored in further detail:

Mercury and Time of Day

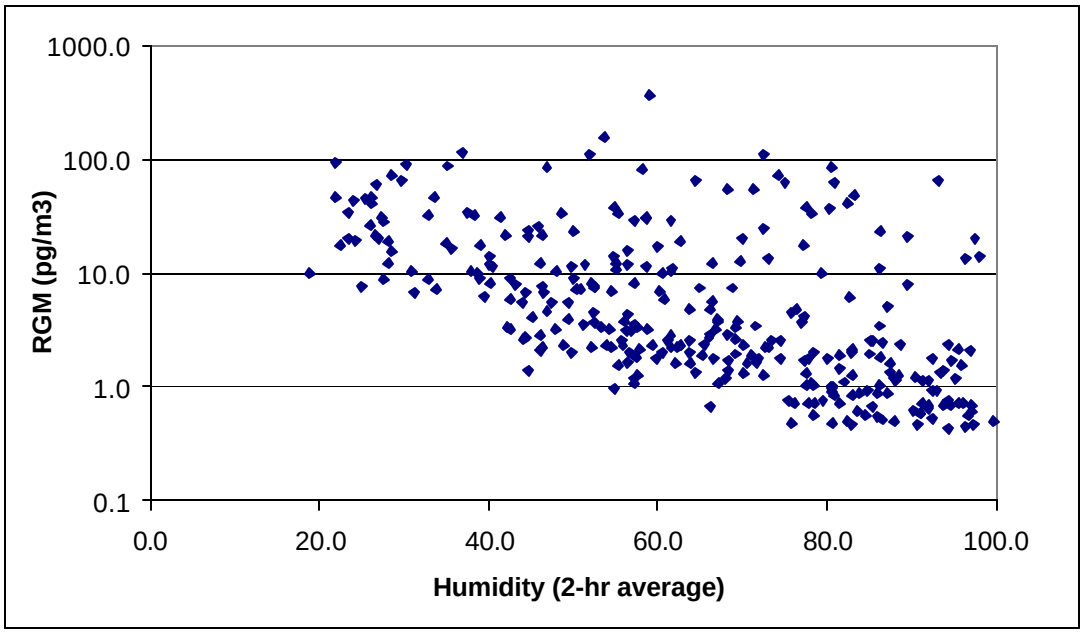
Figure 1-20 presents RGM data by time of collection. Most elevated readings for RGM arose during daylight hours, although some events were scattered throughout nighttime and early morning hours. No obvious pattern was identified for spikes of Hg(0) (Fig 1-21), but examination of 5-minute data sorted by time of day of collection revealed a diel pattern similar to that seen in Figure 14 when non-background values (>2.15 ng/m^3) were removed (data not shown).

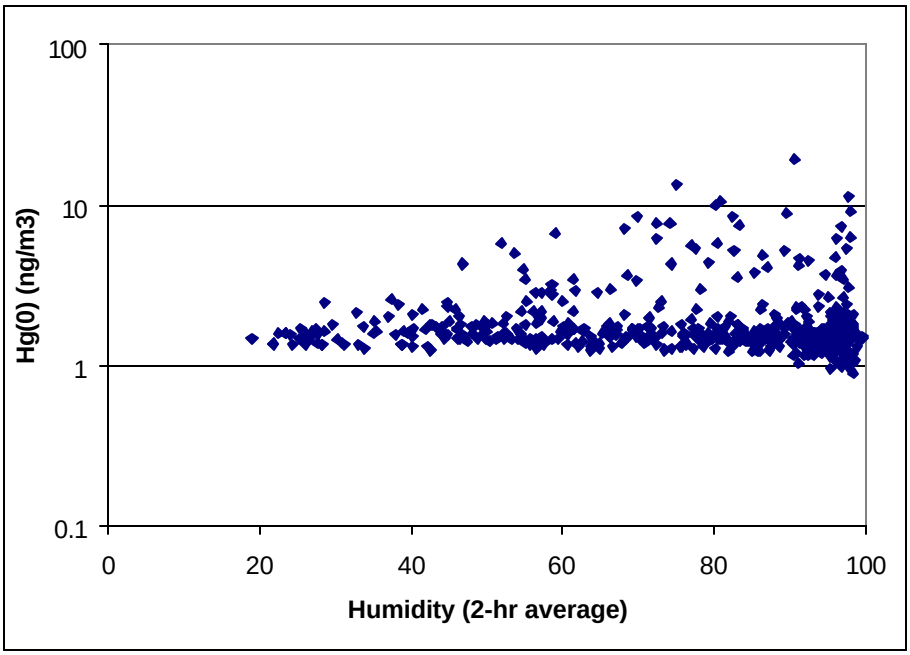

Hg(2+) (pg/m3, 2-hr average)
400
350
300
250
200
150
100
50
0
0:00
1:10
2:30
3:40
5:10
6:40
8:10
9:40
11:20
12:50
14:00
15:10
16:30
17:45
19:00
20:10
21:35
22:45
Time of Day


Hg(0) (ng/m3, 2-hr average)
25
20
15
10
5
0
0:00
1:00
2:10
3:20
4:40
5:55
7:20
8:35
10:10
11:40
13:00
14:05
15:10
16:20
17:25
18:35
19:40
20:50
22:00
23:10
Time of Day

Mercury and Humidity

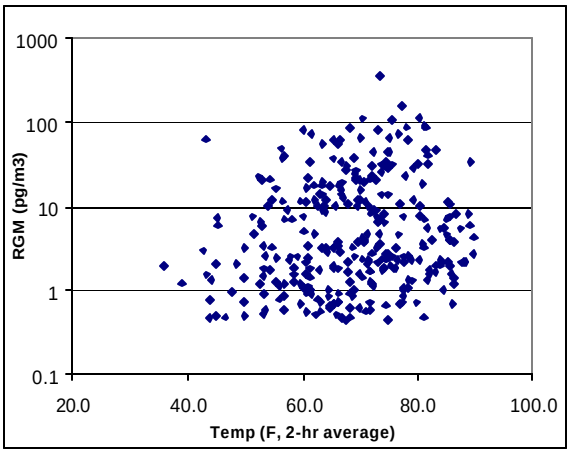
Figure 1-22 presents data on humidity levels during quantifiable measurements of RGM. Elevated RGM readings were detected under a wide range of conditions; however, the lowest readings for RGM appear to be confined to highly humid conditions. Most instrument non-detects (< 0.4 pg/m^3) were encountered under highly humid conditions. The average humidity level during instrument non-detects was 92.5% (s.d. = 6.56) vs. 64.2% (s.d. = 20.6) during quantifiable readings. The relationship between Hg(0) and relative humidity is illustrated in Figure 1-23. Most elevated Hg(0) readings occurred under moderate to high humidity conditions. Closer inspection of the data suggests that depressed readings at or below 1 ng/m^3 were almost exclusively affiliated with conditions of extreme humidity.

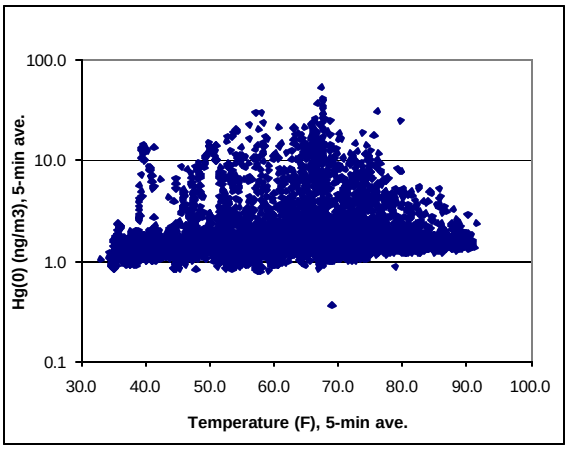



100
10
1
0.1
Hg(0) (ng/m3)
0
20
40
60
80
100
Humidity (2-hr average)

Mercury and Temperature

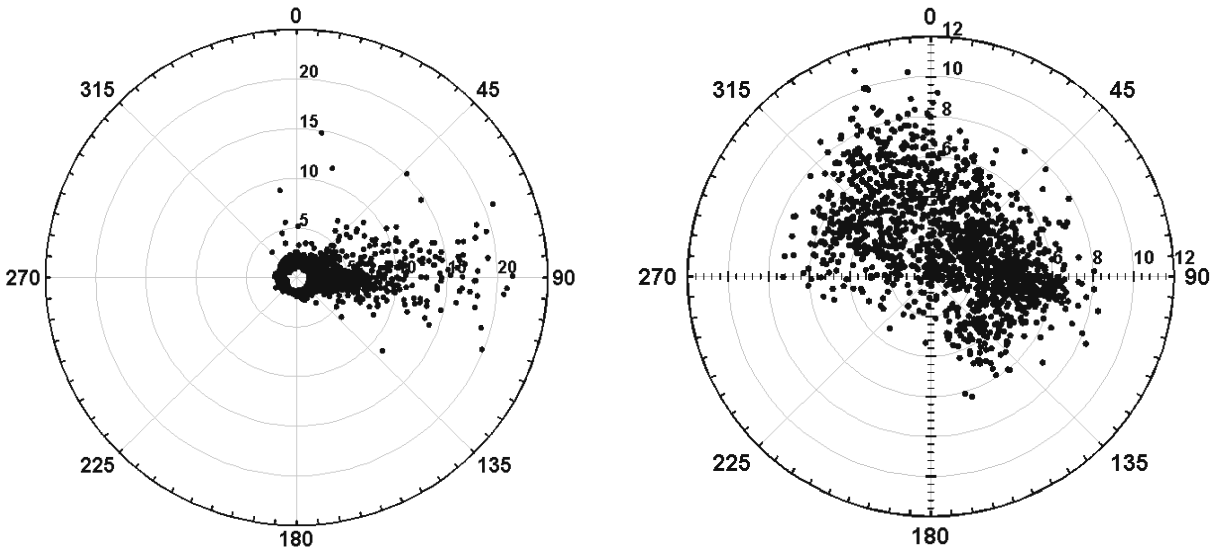
Daily average temperature decreased during this study period with the transition from late summer to fall and early winter. No related trend in the frequency or intensity of mercury spikes was seen during this period. Neither RGM nor Hg(0) appeared to exhibit a consistent relationship with temperature (Figures 1-24 and 1-25).





Mercury and Wind Conditions

Elevated Hg(0) was predominantly associated with winds arriving from the east-northeast. Figure 1-26 illustrates the consistent relationship between Hg(0) level and wind direction. As we noted previously, a closing site audit indicated wind direction was inaccurately measured at this site during this period. Actual wind direction was probably 25 to 40 degrees lower than the data presented in Figure 1-26, but the exact amount of offset is impossible to assess. The weather station at the Riegelwood site was not equipped to calculate average wind direction every 2 hours making it difficult to establish a clear relationship between RGM and wind direction over that time frame. Individual 5-minute data points on wind direction and wind speed correlating to 2-hour periods of elevated RGM are presented in Figure 1-27. It should be noted that variability in wind direction within each 2-hour sample collection period could confound our attempts to identify any relationship between elevated RGM and wind direction, especially if the majority of RGM was brought to the sampler during a fraction of a sampling period with highly variable winds. In the discussion section below we present wind direction data as a range based on individual 5-minute values generated within each 2-hour RGM sample collection period.



The following table summarizes the observed relationships between Hg(0) and RGM levels and the above mentioned variables:

Table 1-7: *Summary of observed relationships between reactive gaseous mercury, elemental mercury and several measured variables, August – November, 2000.*

Variable	Reactive Gaseous Mercury	Elemental Mercury
Time of Day	Elevated readings primarily confined to daylight hours	No clear pattern, elevated readings occurred during both daylight and nighttime hours
Humidity	High readings encountered under a wide variety of humidity levels, but lowest readings confined to highly humid conditions	Highest readings under moderate to highly humid conditions, depressed readings at extreme humidity levels
Temperature	No apparent relationship	No apparent relationship
Wind Direction	No clear relationship	Highest readings with winds from N-NW to E

Phase 2 (Aug - Nov) Discussion

Instrument Performance

The soda lime system modification appeared to have been successful at reducing or eliminating artificially low readings for TGM. However, on rare occasion 5-minute Hg(0) values below 1 ng/m^3 were encountered. These values were sporadic and generally confined to a 3-week period between September 28 and October 15, 2000.

Hg(0) levels below 1 ng/m^3 were frequently associated with extremely humid conditions. This could suggest that Hg(0) levels are lower during extremely humid conditions or that instrument readings reflect some degree of impairment in the capture or measurement of Hg(0). Hg(0) is not water-soluble and not predicted to undergo significant atmospheric removal during humid conditions or precipitation events. Others have shown that TGM levels do not decrease during or following rain events (Lindberg). Another more speculative theory is that the presence of atmospheric water vapor could enhance the rate or extent of mercury oxidation, resulting in a depletion of Hg(0). Several atmospheric oxidation reactions involving mercury occur most rapidly in the aqueous phase (Lin and Pehkonen). Many of these oxidizing agents are likely to exist at elevated levels in regional ambient air due to nearby industrial emissions. However, the likelihood that this phenomenon would give rise to a measurable change in TGM levels is very small given that only a minute fraction of Hg(0) in the air would be predicted to enter into the aqueous phase where oxidation reactions would take place. The most likely scenario involves interference with instrument performance by water vapor. Water vapor could condense on sample lines or saturate particulate filters, inhibiting the passage of Hg(0). It could also overwhelm the soda lime traps, allowing moisture to reach the gold traps which might affect mercury capture efficiency. Finally, it is also conceivable that other meteorological conditions associated with high humidity (e.g. precipitation, wind or temperature) could be impacting atmospheric mercury levels or instrument performance.

TGM measurements below 1.0 ng/m^3 were not confined to this site during the study. Interestingly, these values appeared periodically during the July through September timeframe at other sites. For example, the lowest 10% of readings for TGM taken at Lake Waccamaw from the third quarter of 1998, 1999 and 2000 were consistently lower than similar values from other periods during the year (Table 1-1). During these periods warm humid air masses arrive from the Gulf of Mexico; unfortunately, concurrent information on humidity and Hg(0) are not available from these sites, preventing the establishment of a similar relationship between humidity and TGM at this site.

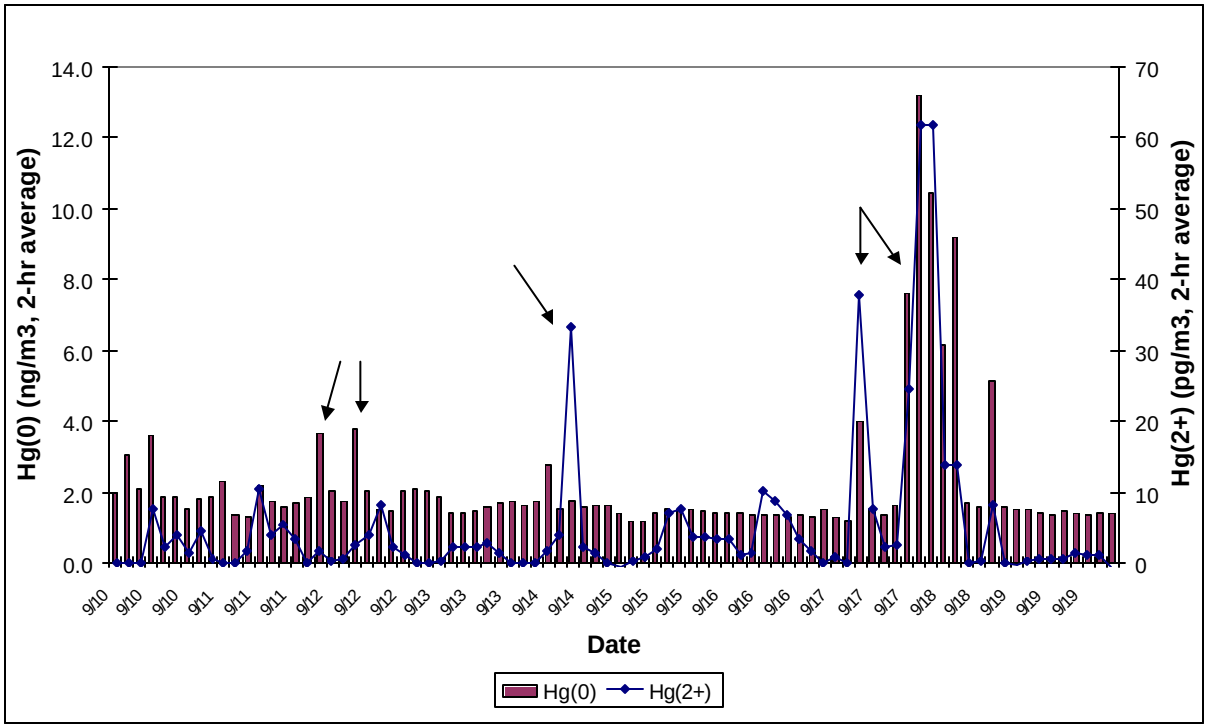
Despite the periodic appearance of low values for Hg(0) it does appear that system modifications improved the detection of Hg(0). It remains possible that some recorded values are lower than actual atmospheric levels, especially during periods of extreme humidity. However, because there were no clear indications of compromised instrument performance during these periods, data on Hg(0) and RGM are included in summary statistics and figures for this sampling period.

Total Gaseous Mercury, RGM and Elemental Mercury

TGM levels fluctuated significantly between August and November of 2000 in a pattern similar to that seen during the previous year. Average levels declined significantly relative to the same time period during 1999, reflecting the decreased frequency and diminished magnitude of spikes in TGM.

Our study confirmed that TGM is comprised overwhelmingly of Hg(0). Although increases in both Hg(0) and RGM were seen on a frequent basis during this study, it was Hg(0) fluctuations that were primarily responsible for changes in TGM. RGM levels were typically two to three orders of magnitude lower than Hg(0). Even in those cases where RGM increased without concurrent changes in Hg(0), levels never exceeded one-tenth those of Hg(0). These data are consistent with findings reported in previous studies (Lindberg, Sheu and Mason).

Our data suggest that RGM and Hg(0) levels may be differentially susceptible to various outside influences. As illustrated in Figure 1-28, changes in one form of gaseous mercury would often, but not always, occur independent of changes in the other mercury species. RGM is comprised of water-soluble species such as mercuric chloride ($HgCl_2$). It is believed that these species undergo atmospheric removal mechanisms involving both wet and dry deposition. It has been shown using continuous monitoring techniques that RGM levels in ambient air fall dramatically following a rain event (Lindberg). Theoretically, these same wet deposition removal mechanisms would be enhanced by the presence of high levels of water vapor in the air, such as might exist during the extremely humid conditions periodically documented during our study. This phenomenon is a likely explanation for the pattern of RGM non-detects during periods of high humidity. During dry periods (humidity < 50%) all readings for RGM were above the instrument limit of detection. However, elevated RGM was detected under conditions of low and high humidity, suggesting that while water vapor might be an effective tool for removing low levels of RGM, its removal efficiency is less than 100% at higher atmospheric concentrations.



Except for the lower baseline readings encountered under highly humid conditions, Hg(0) readings did not appear to be dramatically affected by humidity levels. Hg(0) is not water-soluble and thus not predicted to undergo significant atmospheric removal by wet deposition. Measurable changes in Hg(0) concentrations in temperate climates are more likely to be affiliated with impacts from nearby emission sources.

Elevated readings for RGM appeared most frequently during daylight hours.[8] Sunrise and sunset ranged from 5:40 a.m. to 6:48 p.m. EST on August 24 to 6:51 a.m. to 5:04 p.m. EST on November 21. Lindberg and Stratton also reported daytime increases in RGM and speculated that photochemical production might enhance RGM levels during the day while nighttime deposition acts as a removal mechanism, depleting atmospheric RGM trapped below the stable boundary layer (Lindberg). Sheu and Mason reported varying diurnal trends for RGM at a site near the Chesapeake Bay (Sheu and Mason). While nighttime depletion and daytime increases were noted on at least one occasion during a weeklong sampling period, other patterns were also noted. The authors speculated that these increases could be related to source impacts or variability in RGM levels between different air masses moving across their sampling site. During our study some isolated RGM peaks were noted during nighttime and early morning hours,

suggesting additional factors may have been impacting RGM levels during these periods (Fig 21). RGM levels were more highly correlated with Hg(0) levels during nighttime rather than daytime hours ($r^2 = 0.63$ vs. $r^2 = 0.54$). Peaks in Hg(0) were seen at all times of day, while background Hg(0) values appeared to conform to a diel pattern similar to that seen in Figure 29, with lowest values in the pre-dawn hours and the highest background values occurring during the middle of the day.

No correlation was identified between Hg(0) or RGM levels and temperature during this study period. Higher ambient temperatures could, in theory, facilitate several of the atmospheric reactions that could affect RGM levels; however, any association may be confounded by several simultaneous variables. During the summer months, warmer air arriving from the Gulf of Mexico is typically very humid, and the negative relationship between humidity and RGM levels may overwhelm any positive association involving temperature. Associations between wind direction and temperature could also hamper the identification of a relationship between temperature and atmospheric mercury levels, especially if mercury emission sources that are upwind during a significant portion of the year become downwind with seasonal shifts in wind direction. A more thorough statistical analysis involving analysis of variance might unearth a relationship between temperature and RGM or Hg(0) levels but is beyond the scope of this report.

The strongest historical indicator of emission source impacts on regional atmospheric mercury levels was illustrated through the consistent relationship between wind direction and elevated TGM readings at the Lake Waccamaw and Riegelwood monitoring sites. During speciation measurements, elevated RGM was most commonly associated with winds arriving from various directions, including the northwest, north and east. A wind rose plot summarizing 5-minute wind data collected in conjunction with elevated RGM shows a significant degree of variability but a notable absence of data points in the third quadrant (i.e. between south and west). Predominating winds during this period would be expected to range between southwesterly during August and September to northerly and northeasterly during October and November. In contrast, elevated readings for Hg(0) were bound to a fairly tight distribution between east-northeast and east-southeast. This suggests that increases in Hg(0) at this site may be related to a fixed upwind mercury emissions source.

Identifying Relationships between RGM and Elemental Mercury

Our data indicate that a variety of factors influenced atmospheric mercury levels at the Riegelwood Ballpark site. The single strongest line of evidence implicating point source effects is the correlation between wind direction and increases in Hg(0). Natural variability is most clearly illustrated through the relationships between RGM, and humidity and time of day. Although data for Hg(0) and RGM appear very similar - exhibiting a predominance of background or baseline readings punctuated by periodic spikes in concentration for both species – short-term changes were periodically isolated to one species of mercury. To better understand the distinct behaviors of Hg(0) and RGM and the influence of natural variability versus anthropogenic impacts we defined three types of scenarios for further study:

- Scenario A: RGM and Hg(0) increase concurrently.
- Scenario B: RGM increases without simultaneous increase in Hg(0).
- Scenario C: Hg(0) increases without simultaneous increase in RGM.

Figure 1-28 illustrates a brief period during which several of these events appeared.[9] Once these events had been categorized, coincident data on mercury concentration, time period sampled, temperature, humidity, and wind speed and direction were compiled. Wind speed, temperature, humidity and Hg(0) concentrations were calculated by taking the arithmetic average of 24 separate five-minute readings within each 2-hour sampling period. Wind direction data were compiled from 5-minute readings. Summary statistics for temperature, humidity and wind speed are presented in the following table.

Table 1-8: *Observed meteorological conditions during periods of elevated gaseous mercury and during the complete study period, September – November, 2000.*

Scenario	Temperature mean (sd)	Relative Humidity mean (sd)	Wind Speed mean (sd)	# Events
A: Both RGM and Hg(0) increase simultaneously	64.6 (7.6)	74.0 (16.3)	3.44 (1.87)	24
B: RGM increases while Hg(0) remains at baseline	71.3 (9.5)	34.9 (15.1)	4.12 (2.02)	43
C: Hg(0) increases while RGM remains depressed	55.9 (13.6)	92.2 (7.6)	1.33 (1.70)	10
Complete Study Period[10]	*65.7 (12.4)*	*75.7 (21.5)*	*2.80 (2.60)*	

Scenarios A and C include elevated readings for Hg(0). We initially suspected that short-term increases in Hg(0) would primarily be due to local or regional industrial emissions. Natural causes of short-term peaks in Hg(0) such as forest fires, volcanic activity or nearby geological deposits of mercury were absent and would not be expected to contribute substantially. Variability in RGM is possibly related to natural phenomena but may also reflect transport of local or regional emissions of RGM. Elevated readings for RGM were encountered under scenarios A and B.

An obvious difference between scenarios A and C is the accompanying humidity level. While atmospheric conditions in the former case very closely mimicked conditions encountered throughout the duration of the study, humidity levels were substantially higher in the latter scenario. High humidity may contribute to the removal of RGM from the air. It is conceivable that the monitoring instrument was measuring the impact of pollution plumes containing mercury during these periods but any RGM that may have been present was scavenged through wet deposition mechanisms as the plume moved away from the source. It is notable that wind speed was also substantially lower in the latter case. Slow winds might further inhibit the lateral movement of RGM and enhance the likelihood of atmospheric removal on short distance scales. If these atmospheric removal mechanisms are in place and are affecting measured RGM levels while leaving Hg(0) levels unchanged, then it is entirely plausible that scenarios A and C represent pollution plume impacts under differing meteorological conditions.[11]

Under scenario B, increases in RGM were unaccompanied by changes in Hg(0). This could arise from several situations including plume impacts from point source releases of RGM, local formation of RGM through oxidation of available Hg(0), RGM releases from natural sources, or variable levels of RGM in different air masses. Wind direction associated with these events was highly variable, decreasing the likelihood of plume impacts from a single point source. Humidity levels were frequently very low, reflecting favorable conditions for the existence of RGM in ambient air. Although we cannot rule out the possibility that increases in RGM without concurrent increases in Hg(0) were caused by point source releases of mercury, there also remains a strong possibility that these peaks in RGM levels reflect a natural diel cycle.

If elevated readings for Hg(0) are used to identify plume fumigation events, then the concurrent presence or absence of RGM appears to be most significantly tied to local atmospheric conditions. Closer examination of the data shows that a negative correlation exists between humidity levels and the ratio of RGM to TGM during plume fumigation events (Table 1-9). During the most highly humid conditions (> 90%) no RGM was measured, despite markedly elevated levels of TGM. This suggests that extremely humid conditions were able to influence the chemical speciation of mercury reaching the monitoring station during plume fumigation events by removing RGM on a very short (< 1 mile) distance scale. The resulting increase in mercury wet deposition over a relatively small area might significantly impact runoff to surrounding surface waters. It is worth noting that on occasion, increases in RGM were seen even under conditions of greater than 90% humidity. However, the ratio of RGM to TGM was low, suggesting some degree of removal may have been taking place.

Table 1-9: *Description of meteorological conditions during suspected plume fumigation events (scenarios A & C), September – November, 2000.* [12,13]

# Events	Rel. Humidity	RGM/TGM	Correlation (RGM/RH)
34	Mean: 79.4% Range: 38% – 98%	Mean: 0.46% Range: 0.00% - 1.45%	-0.812

Although we have used the combined effect of increased Hg(0) and wind direction to highlight suspected local plume fumigation events it also remains possible that pollution impacts are responsible for some of the increases in RGM alone. Lindberg, et al reported several events during which RGM levels increased without concomitant increases in Hg(0) (Lindberg). They were able to present coincident data on SO_2, NO_x and ozone to strengthen their argument that these changes were caused by a plume fumigation event resulting from coal-fired utility boiler emissions. They also presented data suggesting that RGM levels conform to a diel cycle, with highest readings during late morning and afternoon hours. The absence of data on additional pollutants limits our ability to distinguish between natural variability and source influences on RGM levels, however several lines of evidence support the argument for natural variability. Most importantly, these events were almost completely confined to daytime hours - consistent with the diel cycle described above and contrasted with the continuous operating schedules of local mercury emission sources. Secondly, winds during these events were primarily northerly and westerly and likely comprised of cool, dry air - favorable conditions for the existence of RGM. Finally, Hg(0) levels remained at baseline suggesting the absence of plume impacts from ground-level sources in the immediate vicinity of Riegelwood. At present there is no known diel pattern for Hg(0), although some have speculated that such a pattern might exist (Schroeder 1999).

The possible association with northerly winds could provide an argument for long-range regional transport of RGM from emission sources to the north and west of Riegelwood. Major emission sources exist in this direction including coal-fired utility boilers that serve the Charlotte, Fayetteville, Winston-Salem and Raleigh-Durham areas. The closest unit is positioned 95 km to the west-northwest near Lumberton, NC (1998 reported mercury emissions: 90 lbs.). Given these distances and the necessary convergence of emissions and meteorological conditions favoring downward mixing of the plume aloft, it seems improbable that upwind sources are the cause of all short-term fluctuations in RGM. Further study, including co-monitoring of additional pollutants such as SO_2 or trace metals would be needed to determine the extent of source impacts.

The relative impact of natural vs. man-made effects on atmospheric RGM deserves further attention. Many of our highest readings for RGM were obtained under conditions that are most likely to reflect natural variation. These increases were also far more common than events suspected to be due to local source impacts and exhibited

considerable variability in magnitude and duration. Measurements at ground-level only tell a small part of the picture since sources with tall stacks are also likely to affect atmospheric mercury levels at much higher elevations. Additional critical measurements would include short-term wet deposition samples or cloud water analysis. We believe our study provides very strong evidence for point source contributions of RGM. However, at this point it would be premature to attempt to use the data from this study to quantitatively define natural vs. man-made impacts. Both are clearly important phenomena and should be factored into the design of future studies.

REGIONAL ANTHROPOGENIC EMISSIONS

The preceding data support a possible relationship between man-made mercury emissions and regional levels of mercury in ambient air and precipitation. To further investigate this possibility, we collected information on emission sources proximal to Lake Waccamaw and Pettigrew State Park. We utilized all available information on reported emissions and the most recent estimates on the physicochemical speciation of mercury pollution. In addition, we explored several major changes in regional industrial activities that may have had a significant impact on mercury emissions. The improvements made at several of these sources ultimately may result in reduced quantities of atmospheric mercury reaching the sensitive waterways of eastern North Carolina.

Table 1-10 includes summary information on the most significant sources of anthropogenic mercury emissions surrounding Lake Waccamaw and Pettigrew State Park (Figure 1-3). The data shows that several significant changes occurred between 1998 and 1999. The reported 1999 process emissions from the chlor-alkali facility are provided. The facility experienced frequent power disruptions during the first few months of 1999 then ceased mercury-cell operations in favor of an alternate non-mercury chlorine production process in April. Reported emissions are most likely related to normal mercury cell chlor-alkali production activity occurring during early 1999. A reduction in mercury emissions between 1998 and 1999 at the adjacent pulp and paper mill may be due in part to the discontinued use of mercury-contaminated products from the adjacent mercury cell chlor-alkali plant. Apparent reductions from the coal-fired electric utility boilers likely resulted from improved emission estimates[14]. Additional reductions in regional mercury emissions are also likely. For example, a carbon injection system was added to the largest stack at the municipal waste incinerator in New Hanover County during late 2000. This modification could reduce mercury emissions from that stack by as much as 90% and facility-wide mercury emissions by 40% (40 CFR Part 60). Mercury emissions from other large sources have remained relatively stable. These emissions generally arise from the combustion of coal in large industrial boilers and may fluctuate depending on facility energy consumption.

All sources reported emissions prior to 1999 as "mercury vapor" or "mercury and compounds," consistent with guidance for applicable emissions inventories. Mercury

emissions were not distinguished by chemical or physical characteristics largely because information on these parameters was lacking. However, this information is critical in determining the atmospheric fate of mercury emissions. Emissions of Hg(0) vapor would be prone to long-range transport and could be carried hundreds or even thousands of miles before undergoing processes that would lead to removal from the atmosphere. RGM and particulate mercury could undergo rapid removal from the atmosphere and could thus contribute to local or regional deposition patterns following release to the air.

Table 1-10: *Mercury emissions near Waccamaw and Pettigrew S.P. Includes estimates of mercury speciation based on 1999 emissions. Refer also to Figure 2.*

	Reported Hg emissions (lbs)[1]		1999 Speciated emissions (est.) [2]		
Source (category)	1998	1999	Hg(0) (lbs, est.)	RGM (lbs, est.)	Hg(p) (lbs, est.)
Holtrachem Manufacturing	1276	328	230	98	0
New Hanover Waste-to-Energy	362	337	67	202	67
CP&L Sutton Plant	354	153	45	105	3
PCS Phosphate	266	236	118	71	47
International Paper Riegelwood	93	39	20	12	8
CP&L Weatherspoon	90	33	24	9	< 1
Weyerhaeuser	64	68	34	20	14
E. I. DuPont Co.	60	53	27	16	11
Occidental Chemical Co.	29	26	13	8	5
Weyerhaeuser	12[3]	12	6	4	2

[1]Reported emissions from state air quality permit database, self-reported values or TRI.
[2]Estimates of speciation from EPA Mercury Study Report to Congress.
[3]Reported emissions from 1996 state air quality permit database.

In its 1997 Mercury Study Report to Congress, the USEPA provided estimates of physicochemical speciation of mercury emissions from a variety of anthropogenic sources including industrial boilers, waste incineration units and coal-fired electric utility boilers. The authors based these estimates on limited stack tests and conceded "considerable uncertainty as to the actual speciation." Improved information was collected by the USEPA and major coal-fired electric utility boilers throughout 1999 as part of the ICR program. Advanced methods were used to speciate mercury in exiting stack gases from a handful of large (>25 MW) coal-fired electric utility boilers. Facilities were categorized based on plant configuration and emission control devices. Data from representative utilities were then used to estimate speciated mercury emissions from other similarly configured plants. For this report we utilized ICR data to estimate 1999 speciated mercury emissions from the coal-fired electric utility boilers. For all other sources we relied on the EPA's 1997 report. Our estimates of speciated mercury emissions are provided in Table 1-10, based on 1999 reported emissions.

Plume dispersion factors also play a large role in affecting the environmental fate of mercury emissions. Ground-level releases would be more likely to result in measurable changes at nearby monitoring sites. Pollution released from an elevated source is more likely to undergo significant dispersion before impacting ambient air at ground level. This effect would broaden the area of impact but would also result in more modest increases in ground level air pollution. Plume rise and dispersion are also enhanced by higher stack gas exit velocities and temperatures, such as those encountered in many high-temperature combustion processes. Meteorological conditions including wind turbulence, temperature, boundary layer mixing and humidity can dramatically enhance or impede plume dispersion. Calm conditions will often result in the formation of an atmospheric inversion, thus trapping mercury emissions near ground level. Finally, surface features such as elevation changes, vegetation, buildings, traffic patterns and waterways will all affect plume dispersion to varying extents.

The variables above will all affect regional fate and transport of atmospheric mercury emissions and influence the likelihood that emissions will lead to measurable changes in ground-level atmospheric mercury. Local ground level emission sources releasing large quantities of Hg(0) at ambient temperatures would be most likely to impact nearby surface measurements of atmospheric TGM. In contrast, distant releases of predominantly particulate mercury or RGM under conditions favorable for plume dispersion would be less likely to result in measurable increases in ground-level TGM. Instead, these emissions would contribute more substantially to regional wet and dry deposition patterns.

The point sources described above possess a wide array of emissions characteristics. The coal-fired electric utility boilers have tall stacks and release Hg(0) and RGM at high temperatures and velocities. These factors would enhance dispersion and possibly give rise to a modest increase in mercury deposition rates over a relatively wide area. The same considerations might affect gaseous mercury released by large coal-fired industrial boilers, such as those found at many of the local chemical manufacturing facilities and pulp and paper mills. Mercury emitted by the New Hanover County municipal waste incinerator is primarily in the form of RGM or particulate mercury. This factor would contribute more directly to localized deposition rather than medium or long-range changes in atmospheric TGM.

The most significant regional source of mercury emissions is the mercury cell chlor-alkali operation in Riegelwood, NC. Mercury cell chlorine production facilities use thousands of pounds of mercury, housed in electrochemical cells. These cells act to provide an electrical charge that forms the products chlorine gas, sodium hydroxide and hydrogen gas from brine. Mercury may be released in the hydrogen gas stream, in cell end box ventilation air or in cell room ventilation air. Spills and maintenance activities involving the opening of cells may add large amounts of mercury vapor to cell room air. Generally, cell rooms are vented directly to the outside air. It is believed that the predominant form of mercury emitted from chlor-alkali facilities is Hg(0) vapor, however the presence of large quantities of chlorine could act to produce smaller quantities of RGM species such as $HgCl_2$ (USEPA, 1997a). Recent ambient monitoring studies

conducted in the vicinity of active mercury cell chlor-alkali plants have shown fluctuations in RGM and Hg(0), both independently and in tandem (Stevens, personal communication).

Chlor-alkali mercury emissions fit many of those characteristics that would increase ground level TGM. Releases of Hg(0) would likely disperse outward from the source, carried by prevailing winds over long distances. The areas surrounding Riegelwood and Lake Waccamaw contain very few terrain features that would significantly disrupt ground-level plume dispersion. Outward migration of RGM might be hindered by adherence to vegetation or ground surfaces or atmospheric scrubbing during precipitation or high humidity events. These factors would decrease atmospheric levels but add to the depositional load in the immediate vicinity of the source.

Ambient monitoring data from Lake Waccamaw seems to bolster the link between chlor-alkali plant activities and regional atmospheric mercury levels. Elevated TGM readings were frequently encountered during 1998, when the facility was in normal operating mode. However, in 1999, when the plant began experiencing manufacturing interruptions and then ceased using the mercury-cell process, measured levels of TGM in ambient air at Lake Waccamaw dropped off and the peaks that were associated with easterly winds disappeared. No other regional emission sources to the east of Lake Waccamaw underwent such dramatic changes in their mercury emissions during this same time frame.

Although several of the mercury emission sources in the vicinity of Wilmington, NC, contribute significant quantities of mercury to the air, they are less likely to contribute to detectable changes in ground-level TGM because they 1) do not release substantially large amounts of mercury, 2) release predominantly RGM, or 3) release their emissions from tall stacks at high temperatures, thereby diluting local ground-level plume impacts. However, the Lake Waccamaw data cannot be used to rule those sources out as potential contributing factors. Fortunately, the positioning of the Riegelwood Flynn site to the east of the chlor-alkali industrial complex allowed us to determine that a continued influence from the east was not present. As evidenced in Figure 8, elevated mercury values were not affiliated with easterly winds. Instead, events were linked to winds arriving from the N and NW, in the direction of the chlor-alkali/pulp and paper mill industrial complex. At the Riegelwood Ballpark site, events were correlated to northeasterly winds – again, consistent with an impact from the nearby industrial complex.

The most obvious remaining question concerns the cause of ongoing fluctuations of TGM in Riegelwood. The patterns observed at these sites were reminiscent of earlier results from Lake Waccamaw and strongly suggestive of nearby emissions of both Hg(0) and RGM. Although mercury cell chlor-alkali production was terminated in April 1999, several potential sources of mercury emissions remain on site including chlor-alkali plant deconstruction, site cleanup activities, gross site contamination and mercury-laden waste ponds. In addition, combustion of coal and other organic materials at the pulp and paper

mill will give rise to mercury emissions that could lead to detectable changes in nearby ground-level atmospheric mercury.

Dismantling of the cell rooms commenced almost immediately following the termination of mercury cell operations in April of 1999. Many of the associated activities could result in significant releases of mercury to the air. For example, the opening of covered mercury cells for product removal exposes a large quantity of mercury to the atmosphere that could lead to significant loss by volatilization. Subsequent transfer of mercury to large shipping containers could lead to spillage and further loss through volatilization. Building washing and other decontamination activities could involve the exposure of mercury contaminated surfaces, further facilitating loss of mercury to the atmosphere.

Between May 26 and June 8, 1999 over 57 tons of mercury was removed from covered cells and shipped offsite. By July 12 another 38 tons of mercury was recovered during continued cell draining and washing activities. Subsequent activities focused on cleaning work areas and removing process components such as scrap aluminum and copper. Disassembly of cell covers began in November 1999 and continued into the first half of 2000. It was reported that residual mercury was contained within the cells. Thus the opening of these cells may have facilitated mercury volatilization. Several interruptions of normal deconstruction activities were documented including a prolonged period during August and September of 1999 when Hurricanes Dennis and Floyd made landfall. Only limited reports are available after August 2000 but it is likely that cleanup efforts continued during the remainder of 2000.

It is difficult to ascertain whether specific mercury removal activities were directly related to increases in atmospheric mercury at either Riegelwood monitoring site. For example, during the May 26 - June 8, 1999 timeframe when over 57 tons of mercury was drained and recovered, several large peaks for TGM were detected at the Flynn site; however, the majority of these were associated with light and variable winds, making a source-receptor relationship difficult to pinpoint. At the Ballpark site the few events that occurred were both associated with winds arriving from the plant as well as winds arriving from other directions. During subsequent weeks, when additional mercury cells were drained and another 27 tons of mercury was recovered, very few large peaks of TGM were seen at the Flynn site. At Ballpark a series of peaks between June 4 and 6 appeared to arrive from the chlor-alkali plant but another series between June 15 and 20 showed only a weak relationship to wind direction. It is also worth noting that inconsistent monitoring results were obtained during "down times" when little or no mercury cell room activity was taking place. For example, between July 3 and 8, 1999 no cell room activities were reported and no peaks of atmospheric mercury were observed at either Riegelwood site. In contrast, a similar downtime between July 17 and 22, 1999 saw several short-term peaks in atmospheric mercury appear at both sites on July 21 and 22. Further in-depth analysis of ambient monitoring data, a more detailed accounting of decommissioning events and on-site monitoring data would be necessary to fully explore the relationship between specific site activities and off-site mercury measurements.

The chlor-alkali operation also maintained mercury-contaminated waste ponds that could act as a source of mercury emissions. Lindberg and Turner identified residual waste deposits at former mercury cell chlor-alkali facilities as important atmospheric mercury emission sources (Lindberg and Turner). In their study they estimated that approximately 160 pounds of mercury per year (predominantly Hg(0)) would be released to the air from the mercury-containing waste ponds they studied. Although they point out that a well-mixed atmosphere would substantially dilute mercury levels at distances outside of 1.5 kilometers from the source, they were able to measure an increase in mercury levels at distances exceeding 1 kilometer from the source. The authors highlighted a positive relationship between waste pond surface temperature and mercury emission rate with dramatically increased emissions above 20^{o}C. A similar relationship was seen for air temperature.

The mercury contaminated soils and waste ponds at this facility undoubtedly act as a source of mercury emissions. Tremendous variability in emissions would be expected due to water temperature, air temperature, pH or the chemical composition of the pond water and ongoing addition of wastes. As with surface waters, photochemical reactions might enhance volatilization of mercury thus sunlight could also impact emissions from the waste ponds. Our data do not exhibit a relationship between air temperature and mercury levels. However, other site deconstruction activities most likely would confound this relationship.

Although total emissions are relatively insignificant compared to many of the sources discussed above, the pulp and paper mill is less than a mile from monitoring stations in Riegelwood and thus cannot be ruled out as a potential local influence on atmospheric mercury levels. In addition to the pulp and paper mill and chlor-alkali plant, Wright Chemical Corporation, a chemical manufacturer was also active in the Riegelwood area. This facility is located approximately 1 kilometer to the south of Riegelwood Flynn and 2 kilometers to the east-southeast of Riegelwood Ballpark. The primary emissions from this facility include ammonia, formaldehyde and hydrogen chloride resulting from the synthesis of organic chemicals. In 1999, 1.13 pounds of mercury emissions were reported, primarily a result of industrial boiler activity. This represents less than 0.1% of the level of reported annual emissions from the chlor-alkali facility.

Note: Recently (February, 2002), a site investigation performed by the USEPA and the DENR Division of Waste Management turned up abnormally high readings for atmospheric mercury on Holtrachem plant property. Measurable readings taken with a Jerome mercury vapor analyzer recorded levels in the air between 0.03 and 0.077 mg/m^3 near the mercury cell building and retort pad. Visible contamination of plant structures with liquid mercury was reported during the visit. If this level of site contamination can be confirmed, then it may explain in large part the fluctuations in atmospheric mercury observed at our Riegelwood monitoring sites.

THE CHARLOTTE MERCURY STUDY

Background

Charlotte is the largest urban city in North Carolina. It is surrounded by several significant point sources of mercury emissions including coal-fired electric utility boilers, medical and municipal waste incinerators, and large industrial boilers. Since mercury emitted to the atmosphere is capable of undergoing both short and long-range transport it is probable that emissions from the Charlotte area affect downwind locations, including local aquatic systems and sensitive waterways of eastern North Carolina. Continuous atmospheric monitoring for mercury will help to identify the magnitude and nature of these influences.

Sufficient information is not currently available to determine long-term trends for atmospheric mercury in the Charlotte area. This information is required to better understand relevant trends for atmospheric pollutants in the urban areas, especially in rapidly growing population centers. Monitoring data during this study will help provide a picture of atmospheric mercury trends in and around the Charlotte area. A mobile monitoring unit is providing DAQ information to assess geographical variability in the atmospheric levels.

Project Description

This study proposed to define temporal and geographic trends in atmospheric mercury in the vicinity of Charlotte, North Carolina. To achieve this, two sampling sites are being operated continuously for length of the study, beginning March 2002. The fixed location site is near the center of downtown Charlotte. Continuous data on total gaseous mercury (TGM) and meteorological conditions is generated at this site. This site also houses a variety of other instruments providing data for other DAQ atmospheric monitoring initiatives. It is anticipated that this data will create a snapshot of "urban" air quality conditions for this area. A mobile monitoring trailer will also be positioned at three other locations on the perimeter of Charlotte over the course of the study. This station will be equipped to monitor for TGM/RGM/Hg(0) with the capability to also monitor for VOCs and carbonyls. This site is designed to capture air quality conditions on the rapidly changing periphery of Charlotte. Sites will be chosen to capture a variety of influences including seasonal upwind/downwind patterns, local major point sources and/or heavy traffic areas.

Meteorological data will be collected at each sampling site. Parameters to be measured include temperature, relative humidity and wind speed and direction.

Sampling Sites

Three mobile sites located around the periphery of Charlotte have been selected. These sites are located to the N, SW and SE of the city center. The first site is located at

Smithville Park; approximately 30.5 kilometers north of Charlotte and 0.5 kilometers east of Interstate 77 at the corner of Catawba Avenue and South Ferry St in Cornelius, NC. The park includes a picnic shelter, playground, large soccer field, lighted ball field and another unlighted ball field. The park is surrounded by residential neighborhoods and some small businesses to the northeast.

The second site, referred to as the Matthews site, is located approximately 1 kilometer to the northwest of the Mecklenburg County line and 3 kilometers southeast of Matthews, NC. The closest major thoroughfares are NC Highway 74, 2 kilometers to the east, and I-485, two kilometers to the north and west of the site. The area around the site is hilly, rural and sparsely populated. The site itself is located on a slightly elevated area in the middle of an open field with waist-high natural vegetation. The clearing extends for at least 300 feet in all directions. A small portion of the clearing is maintained for power lines, which traverse the middle of the site. A satellite campus of the Central Piedmont Community College is located approximately ½ mile to the north of the site, across a two lane local road that is 200 feet from the site. A medical waste incinerator is present, approximately 2 kilometers to the west of the site. Although the incinerator operation is not visible from the monitoring site due to a buffer of trees, a steam plume can be seen when the incinerator is operational.

The third site is located at Kennedy Middle School (KMS) in rural southwest Mecklenburg County, near the intersection of Sandy Porter Road and Brown Grier Road. The site is approximately 12 kilometers to the southwest of downtown Charlotte. The nearest significant source of mercury emissions is the Duke Power Allen Steam Plant, located approximately 6 kilometers to the northwest of KMS. Other significant local features include Charlotte-Douglas International Airport (6 kilometers N) and I-485 (1 kilometer E). Areas to the immediate north, west and south are predominantly rural or sparsely populated. To the east, considerable residential and commercial development exists along the I-485/I-77 corridor.

By providing continuous, multi-site monitoring coverage, we hope to be able to characterize differences between urban and "suburban" Charlotte air and determine the relative influence of major point sources versus mobile or area sources clustered around Charlotte. It is assumed that our chosen monitoring sites will be representative of air typical of this environment. If highly unusual data are retrieved or local point sources completely swamp out other potentially relevant influences on local air quality, repositioning of the mobile sampling site may be considered.

Fluctuations in total gaseous mercury can be indicative of point source influences but lack the specific information to determine the potential for transfer between the air and the earth's surface. By characterizing multiple species of atmospheric mercury, e.g. elemental and RGM, we hope to gain an understanding of the potential for regional movement of those species predisposed to atmospheric deposition and the relationship between fluctuations in TGM and RGM in this urban/suburban environment.

MERCURY IN WATER

Waters affected by fish advisories by the Department of Health and Human Services (DHHS) are considered to be impaired by the DWQ. Therefore, DWQ is required to perform Total Maximum Daily Load (TMDL) studies. The TMDL is the amount of a given pollutant that a waterbody can assimilate while maintaining its designated uses. This allowable pollutant load must be allocated to the various point and area sources within the watershed. To establish a TMDL, the current level of contamination must be determined.

In the past, water samples collected by the DWQ were analyzed according to EPA Method 245.1, which has a method detection limit of 0.2 ug/L. All sample results were reported as being below the method detection limit. The most recent sampling effort by the DWQ, known as the *NC Eastern Regional Mercury Study*, utilizes EPA Method 1631. This method has a detection limit three orders of magnitude lower than EPA Method 245.1 and is also below the current water quality standard for mercury of 0.12 ug/L.

The DWQ has identified 4 major goals for this study. They are:

1. To determine levels of ambient mercury in the surface water system.

2. To estimate site-specific total mercury methylmercury translators to evaluate water quality criteria.

3. To develop site-specific water to fish bioaccumulation factors (BAFs).

4. To determine levels of mercury in treatment plant effluent.

Study plans call for quarterly sampling from twelve sites in selected waterbody systems in the eastern portion of the state where the majority of fish advisories have been issued or are anticipated (Table 1-11).

Table 1-11
Water Study For Mercury Contamination

Mercury study sites		

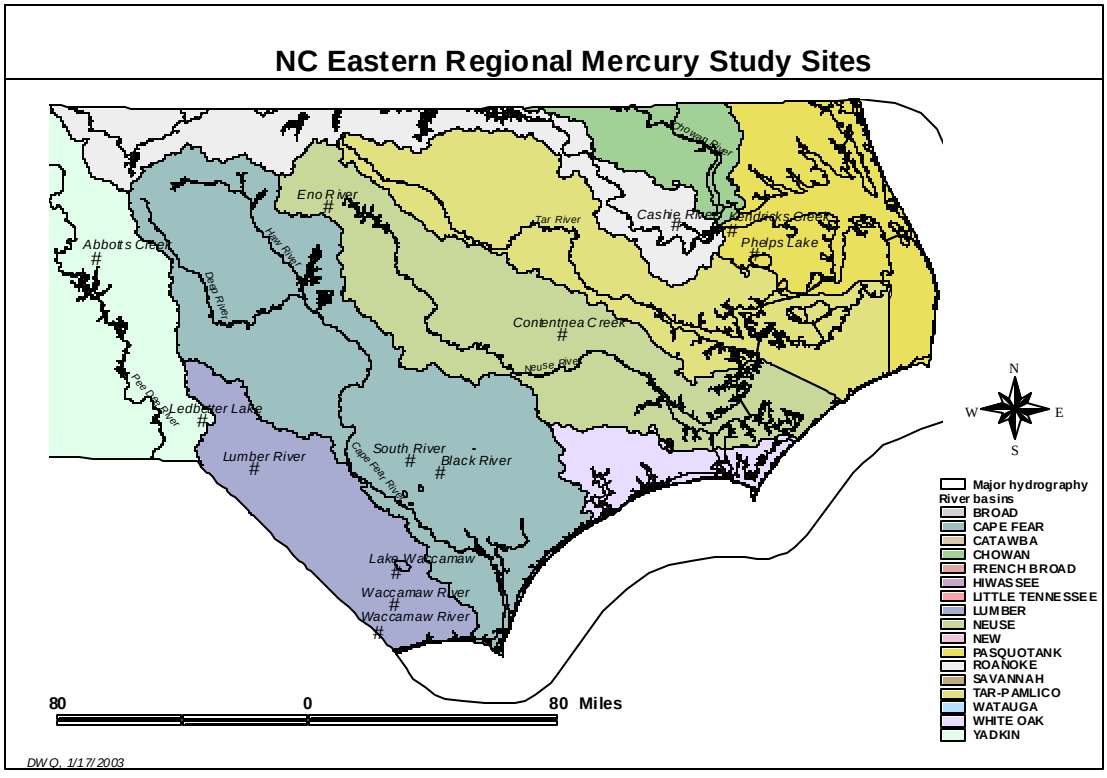
Intensive monitoring at each system on a quarterly basis should reveal seasonal variations in mercury levels and methylmercury percentages, as well as time-variable data for potential model construction.

Surface water will be collected each quarter and analyzed for total mercury (THg), total methylmercury (MeHg), dissolved organic carbon (DOC), and acid volatile sulfides (AVS). Sediment will be collected during the summer and winter quarters and analyzed for THg and MeHg. A comprehensive synoptic look at levels in wastewater treatment plant (WWTP) effluent is also being conducted as part of this project. Effluent from approximately 40 facilities in eastern North Carolina will be sampled and analyzed for total mercury using EPA Method 1631. Figure 1-29 shows the water study area.

Interim Results

The first two quarters of ambient monitoring are complete. This includes two quarters of data for surface water, and winter data for sediment. The monitoring of WWTP effluent is underway. Ambient monitoring results are plotted against United State Geological Survey (USGS) 2000 data collected in *National Ambient Water Quality Assessment* river basins. The Santee River Basin includes the Catawba and Broad River Basins in North and South Carolina.

Figure 1-29
Location of Water Study Areas



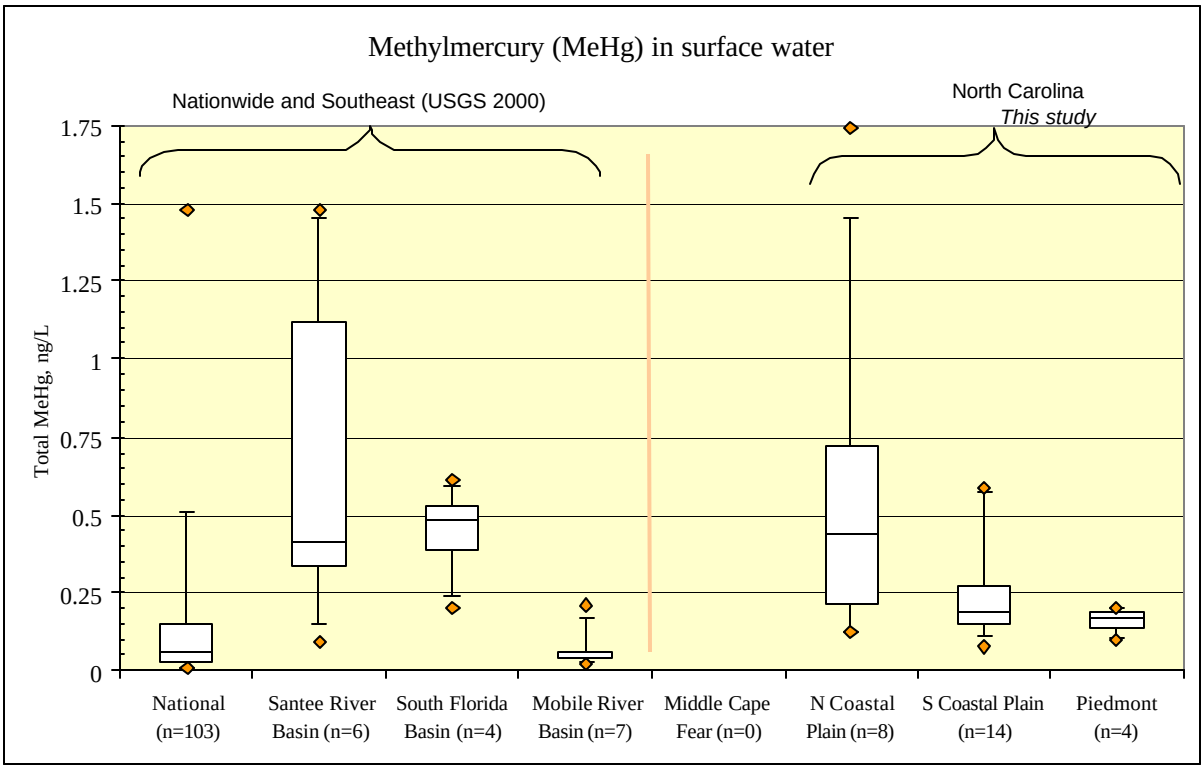
It is difficult to compare actual results with the USGS data with only two quarters of non-summer data collected. However, using the USGS data as a base, total mercury and methylmercury concentrations in North Carolina waters do not appear to be significantly different than those observed in other areas of EPA Region IV. The total mercury chart includes data the Middle Cape Fear River Basin Association collected in 1999 and 2000.

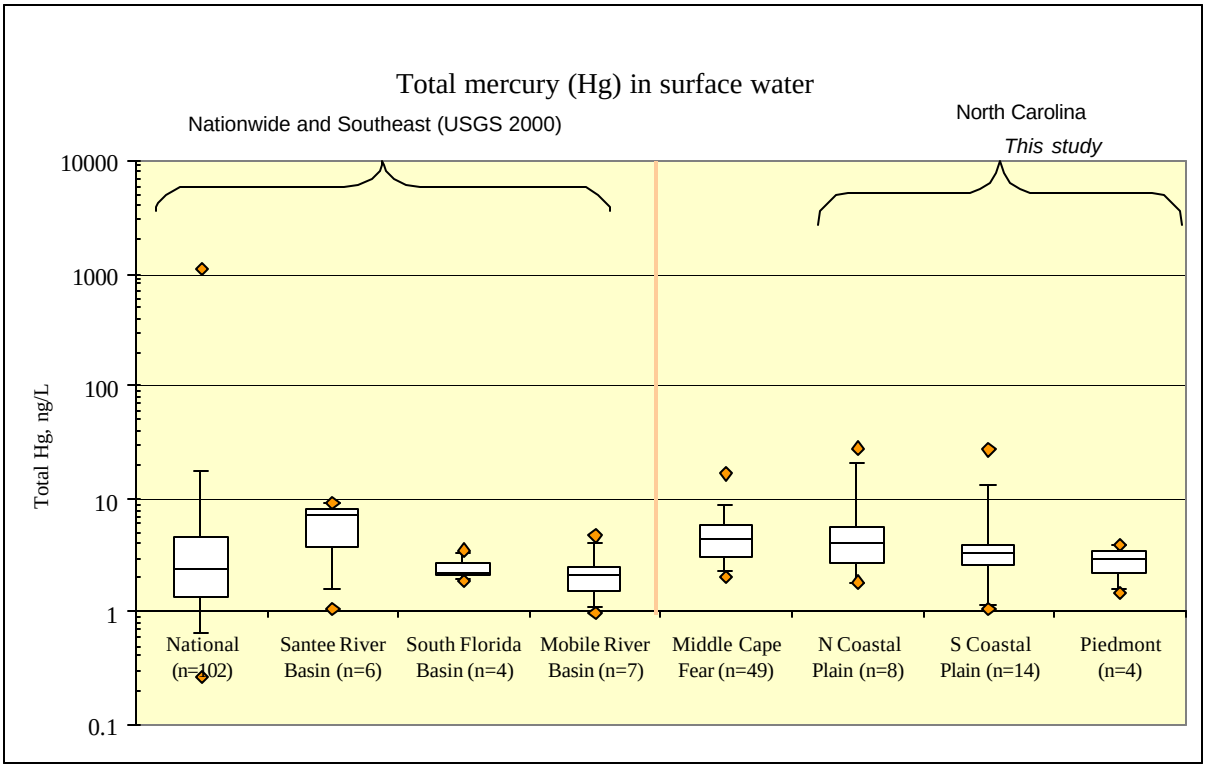
CURRENT AND FUTURE MERCURY MONITORING EFFORTS

The MDN sites at Lake Waccamaw and Pettigrew State Park continue to collect data. If improvements in source emissions and total gaseous mercury at Lake Waccamaw in fact are related to declining mercury levels in regional precipitation, then rainwater data from this site should be comparable to results from Pettigrew State Park in future years. Atmospheric total gaseous mercury remained stable at baseline conditions during 2000 at Lake Waccamaw. Mercury levels in rainwater during this period rose slightly relative to the previous year but remained lower than results from 1996 to 1998. This could be partly a reflection of lower precipitation rates, which declined by approximately 40 percent between 1999 and 2000. Mercury levels in rainwater at Lake Waccamaw were slightly higher than levels at Pettigrew State Park during the same period, but they were comparable to historical data from that site. Mercury levels in rainwater levels rose again at Lake Waccamaw between 2000 and 2001. Again this rise could reflect lower precipitation rates, which fell an additional 30 percent between 2000 and 2001. Or the increase could be due to cleanup efforts at the defunct chlor-alkali facility. More data, collected over several years is needed to determine whether trends seen over the past two to three years support evidence for a relationship between regional anthropogenic activities and total gaseous mercury levels, or instead represent normal year-to-year variability in mercury wet deposition.

The DWQ will continue to monitor mercury in fish across North Carolina and has several studies in the works:

- Continue low-level waterborne mercury study in eastern NC.
- Monitor tissue analysis in marine species after removal of known atmospheric source.
- Operate six stations around the defunct Riegelwood chlor-alkali plant (begun in 2001 and will continue as resources allow for the foreseeable future).
- Monitor 12 sites for low-level ambient mercury.
- Determine ambient levels of mercury in surface water.
- Develop site specific BAF's with fish.
- Continue methylmercury analysis of marine species (Spot, Croaker, Speckled Trout, and Bluefish, with more species as resources allow) jointly with the DWQ, DHHS, and DMF.


Methylmercury (MeHg) in surface water
Nationwide and Southeast (USGS 2000)
North Carolina
This study
Total MeHg, ng/L
1.75
1.5
1.25
1
0.75
0.5
0.25
0
National (n=103)
Santee River Basin (n=6)
South Florida Basin (n=4)
Mobile River Basin (n=7)
Middle Cape Fear (n=0)
N Coastal Plain (n=8)
S Coastal Plain (n=14)
Piedmont (n=4)


Total mercury (Hg) in surface water
Nationwide and Southeast (USGS 2000)
North Carolina
This study
Total Hg, ng/L
10000
1000
100
10
1
0.1
National (n=102)
Santee River Basin (n=6)
South Florida Basin (n=4)
Mobile River Basin (n=7)
Middle Cape Fear (n=49)
N Coastal Plain (n=8)
S Coastal Plain (n=14)
Piedmont (n=4)

DATA MANAGEMENT

Mercury Vapor Analyzers

Analytical data from the Tekran 2537A unit was stored in ASCII text files and saved on a computer hard drive located at the sampling sites. Information stored included identification of sampling date and time, sample type, channel, peak status, units factor, adsorption time, sample volume, baseline voltage, baseline deviation voltage, maximum voltage, peak area, and average mercury vapor concentration. TGM concentration was calculated and presented based on area values and total sample volume. Periodic calibration outputs (conducted every 25 hours) performed on zero air and permeation source air also appeared on data outputs (Fig 2-1).

Data files were copied onto floppy diskette and labeled with time, date and sampling site by the field operator and returned to the laboratory. Here, the weekly data were converted to worksheet form using Microsoft Excel and transferred to a master file containing data from previous weeks' sampling during that quarter. Data were color-coded to delineate calibration data from actual sampling data. Data preceding or following an unsuccessful calibration exercise were coded as rejected data and were not considered valid.

Validated, quality-coded meteorological and analytical data were posted by the Data Manager on the DAQ network drive weekly. The original data files were not manipulated by anyone other than the Data Manager. A second study participant reviewed the converted data to assure proper data handling. Weekly analytical data was kept in its raw unconverted form, in addition to the final color-coded form. This allowed the data manager to back-check data to confirm integrity through the conversion process.

Data in this report are presented using outputs from Microsoft Excel and Harvard Graphics. All statistical evaluations were carried out using Microsoft Excel.

Mercury Speciation Unit

Data are stored at the site on a computer hard drive and handled as described above for the mercury vapor analyzers. The same data evaluation procedures were used to verify or reject data based on QA/QC parameters. However, in addition to 5-minute continuous data on Hg(0) levels the instrument outputs data on clean and analysis cycles for RGM. Data on the zero air (flush) runs were inspected closely to assure that sufficient cleaning of the sample lines was taking place prior to the

Date	Time	Type	h	tat	dTim	ol	l	lDev	axV	rea	g^{0} (ng/m^3)	g^{2+} (pg/m^3)	g^{2+} (pg/m^3)
0 9/08/2000	1 6:20:00	ONT		K	00	.00	.200	.152	.219	7659	.657		
0 9/08/2000	1 6:25:00	ONT		K	00	.00	.200	.209	.218	1781	.580		
0 9/08/2000	1 6:30:00	ONT		K	00	.00	.199	.132	.217	2944	.556		
0 9/08/2000	1 6:35:00	ONT		2	00	.00	.200	.219	.217	6310	.459		
0 9/08/2000	1 6:40:00	ONT		K	00	.00	.199	.138	.218	3622	.570		
0 9/08/2000	1 6:45:00	ONT		K	00	.00	.200	.207	.218	2991	.606		
0 9/08/2000	1 6:50:00	ONT		K	00	.00	.200	.157	.218	4503	.589		
0 9/08/2000	1 6:55:00	ONT		K	00	.00	.199	.118	.216	6370	.461		
0 9/08/2000	1 7:00:00	ONT		K	00	.00	.200	.108	.218	3332	.564		
0 9/08/2000	1 7:05:00	ONT		K	00	.00	.199	.114	.218	3392	.615		
0 9/08/2000	1 7:10:00	ONT		2	00	.00	.200	.137	.220	1701	.742		
0 9/08/2000	1 7:15:00	ONT		K	00	.00	.199	.129	.217	3538	.618		
0 9/08/2000	1 7:20:00	ONT		K	00	.00	.200	.143	.218	1773	.531		
0 9/08/2000	1 7:25:00	ONT		K	00	.00	.199	.141	.216	7088	.476		
0 9/08/2000	1 7:30:00	ONT		K	00	.00	.200	.197	.218	2734	.551		
0 9/08/2000	1 7:35:00	ONT		K	00	.00	.199	.174	.216	1503	.573		
0 9/08/2000	1 7:40:00	ONT		K	00	.00	.200	.171	.218	4882	.597		
0 9/08/2000	1 7:45:00	ONT		K	00	.00	.199	.153	.217	9695	.534		
0 9/08/2000	1 7:50:00	ONT		K	00	.00	.201	.137	.218	0776	.509		
0 9/08/2000	1 7:55:00	ONT		K	00	.00	.200	.142	.217	1144	.566		
0 9/08/2000	1 8:00:00	ONT		K	00	.00	.200	.148	.219	7876	.661		
0 9/08/2000	1 8:05:00	ONT		K	00	.00	.199	.154	.218	7338	.702		
0 9/08/2000	1 8:10:00	ONT		K	00	.00	.200	.162	.219	4281	.584		
0 9/08/2000	1 8:15:00	ONT		K	00	.00	.199	.191	.217	8970	.518		
0 9/08/2000	*1 8:20:00*	*ONT*		*KF*	*00*	*.01*	*.200*	*.182*	*.203*	*825*		*.695*	
0 9/08/2000	*1 8:25:00*	*ONT*		*KF*	*00*	*.00*	*.199*	*.104*	*.201*	*090*		*.192*	
0 9/08/2000	*1 8:30:00*	*ONT*		*KF*	*00*	*.00*	*.199*	*.177*	*.200*	*471*		*.397*	
0 9/08/2000	***1 8:35:00***	***ONT***		***KF***	***00***	***.00***	***.199***	***.179***	***.220***	***3317***			***.640***
0 9/08/2000	***1 8:40:00***	***ONT***		***PF***	***00***	***.00***	***.200***	***.128***	***.000***				***.000***
0 9/08/2000	***1 8:45:00***	***ONT***		***PF***	***00***	***.00***	***.199***	***.213***	***.000***				***.000***
0 9/08/2000	*1 8:50:00*	*ONT*		*KF*	*00*	*.00*	*.200*	*.155*	*.201*	*70*		*.086*	

0		*1*								
9/08/2000	*8:55:00*	*ONT*	*PF*	*00*	*.00*	*.200*	*.138*	*.000*		*.000*

desorption and analysis cycle for RGM. Ideally the final zero air run should read 0.000 ng/m^3. In addition, readings for RGM were scrutinized to assure that sequential values declined over each of the three readings. This ensures that proper displacement of RGM from the denuder surface is taking place during the desorption and analysis cycle. In theory, almost all captured RGM should arrive at the gold traps within the first 5-minute sampling period. Suspect samples were flagged and removed from all subsequent analyses of the RGM data.

Generally data for both reactive gaseous and Hg(0) are presented as simultaneous 2-hour averages. RGM values are calculated by summing the first two analysis values and subtracting two times the final system flush reading.[15] A limit of detection of 0.4 pg/m^3 was calculated for RGM based on the reported 0.1 ng/m^3 limit of detection for TGM (see calculation, below). All RGM readings less than 0.4 pg/m^3 have been reported as non-detect.

Average[16] Span value (AUC) per ng/m^3 Hg(0) = 44268.4

Area at 0.1 ng/m^3 Hg(0), reported minimum level of detection = 4426.8

Average AUC value per pg/m^3 Hg(2+) = 10494.9

Level of Hg(2+) at 4426.8 AUC minimum level of detection = **0.4 pg/m^3**

Meteorology

All data from meteorological stations were stored electronically and downloaded weekly from Climatronics CR-10 and CR-10x data loggers onto laptop computer hard drives. At the laboratory, data was converted from its raw text form to tabular form in Microsoft Excel and was reviewed closely by the data manager to ensure reasonable values had been recorded. Meteorological data included sampling interval, average wind speed, average and standard deviation of wind direction, and temperature. Additionally, information on relative humidity was available from the Riegelwood Ballpark site during mercury speciation studies. A copy of the raw meteorological data was kept on floppy diskette to allow the data manager to confirm the integrity of the data.

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HEALTH EFFECTS

Consumption of fish can be beneficial for both pregnant and breastfeeding women, and their developing children. The developing retina and nervous system of an unborn child may benefit from maternal consumption of fish during pregnancy. Additionally, fish consumption has been associated with a decreased risk of heart attack and coronary artery disease in adults (Neuringer, M., S. Reisbick, and J. Janowsky, 1994. The role of n-3 fatty acids in visual and cognitive development: current evidence and methods of assessment. J. Pediatr. 125:S39-47. Toxicology Excellence for Risk Assessment TERA, 1999. Comparative Dietary Risks: Balancing the Risks and Benefits of Fish Consumption. Results of a Cooperative Agreement between US. Environmental Protection Agency and Toxicology Excellence for Risk Assessment Final). However, a form of methylmercury known as methylmercury can accumulate to harmful concentrations in predatory fish (Environmental Protection Agency EPA, 1997. Summary. Vol. 1. In: Environmental Protection Agency (US). Methylmercury Study Report to Congress. Washington: EPA. Pub. No.EPA-452/R-97-001). Consumption of these fish by pregnant and/or nursing women and by children poses a health risk to children and fetuses.

The developing human nervous system is particularly sensitive to methylmercury. Several studies have reported increasing effects on the developing nervous system of an unborn child with increasing maternal methylmercury exposure from routine fish and whale consumption. Neurological processes in the areas of language, attention, and memory were most affected. According to the National Academy of Sciences, studies conducted in the New Zealand and Faroe Islands show that the deficits observed can be considered predictive of problems in cognitive and academic performance associated with methylmercury exposure, or can affect the way the children may think, learn, and problem solve. These studies have shown the developing fetus to be at least three times more sensitive than adults (NRC National Research Council 2000. Toxicological Effects of Methylmercury. Committee on the Toxicological Effects of Methylmercury, Board on environmental Studies and Toxicology, Commission on Life Sciences, National Research Council. Washington, DC: National Academy Press).

Routine consumption of fish containing concentrations of 0.4 mg/kg or greater of methylmercury poses an increased risk of neurodevelopmental effects for the developing fetus and children under 15 years of age (US EPA Water Quality Criterion for the Protection of Human Health: Methylmercury, Final. Office of Science and Technology, Office of Water, Washington, DC. EPA-823-R-01-001. January 2001). The US EPA reference dose for methylmercury is 0.1 ug/kg-day (corresponds to maternal hair level of 1 mg/kg and blood level of 5.8 ug/L). This is the dose that is not likely to be associated with health effects for the developing fetus and child. Routine consumption of fish containing 0.4 mg/kg of methylmercury can result in exceedance of the US EPA reference dose for methylmercury. To derive the reference dose of 0.1 ug/kg-day, EPA calculated benchmark doses (BMD) or doses associated with a 5% incremental risk above background (background associated with 5% risk) of having abnormal

neuropsychological test scores for children from the Faroe Islands located in the North Sea between Scotland and Iceland. These test scores provide a measure of the way children learn, think, and problem solve. The mothers of these children consumed three fish meals per week and less than one pilot whale meal per month. The benchmark dose chosen based on EPA and National Academy of Science review was 85 ppb in cord blood which corresponds to 15 mg/kg in hair. At these blood and hair levels, there is an estimated 5% incremental risk above background of having abnormal neuropsychological test scores. EPA determined the 95% confidence interval or the range of doses that would be expected to be associated with a total 10% risk of having abnormal scores or 5% incremental risk above background. The lowest dose of this interval was 58 ppb in cord blood or 10 mg/kg in maternal hair and is designated as the Benchmark Dose Limit (BMDL). This corresponds to an intake of 1.081 ug/kg-day. An uncertainty factor of 10 was applied to the 1.081 ug/kg-day to account for variability in susceptibility within the study cohort, variability in pharmacokinetic parameters for methylmercury, and lack of data on long term sequelae of in utero exposure. The resulting reference dose is 0.1 ug/kg-day or 0.0001 mg/kg-day corresponding to hair level of 1.0 mg/kg. (Reference dose of 0.0001 mg/kg-day supported by the National Academy of Sciences as referenced in the Toxicological Effects of Methylmercury, National Research Council, National Academy Press, Washington, DC 2000.)

The Centers for Disease Control and Prevention's 1999 National Health and Nutrition Examination Survey (NHANES) reported blood and hair methylmercury sample results for women ages 16 to 49. Approximately 10 percent of the women surveyed had hair methylmercury levels above the EPA-recommended hair level of 1 mg/kg to protect developing fetuses (corresponds to reference dose of 0.1 ug/kg-day). According to the Centers for Disease Control and Prevention, this indicates a narrow margin of safety for some fetuses (Blood and Hair Methylmercury Levels in Young Children and Women of Childbearing Age–United States, 1999. 1999 National Health and Nutrition Examination Survey, *MMWR* March 02, 2001 /50 (08);140-3). EPA estimates that at or below the reference dose of 0.1 ug/kg-day or maternal hair level of 1 mg/kg, chronic noncancer health effects are not likely to occur. But as the exposure dose increases above the EPA reference dose, the probability of adverse health effects also increases.

FISH TISSUE SAMPLING LED TO STATE ADVICE

In January 2001, the United States Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) issued national advisories for fish due to the presence of methylmercury in fish. Some fish like shark, swordfish, king mackerel, and tilefish contain high levels of methylmercury. EPA and FDA are concerned that maternal or child consumption of these fish could cause harm, particularly to the developing brain of the fetus and child. The federal advisories recommend that women of childbearing age and children not eat shark, swordfish, king mackerel, and tilefish. However, federal officials recognize the health benefits of eating fish and are recommending that women of childbearing age and children eat up to two meals a week of other fish including fish sold in stores and restaurants as well as those caught in freshwater and the ocean. The NC Department of Health and Human Services has developed fish consumption advice that supplements the EPA and FDA advisories for sensitive populations which can be found at http://www.epi.state.nc.us/epi/fish/.

This new advice was based on the toxicological review completed by the National Academy of Sciences and the 1990-1999 methylmercury freshwater fish tissue data collected across the state (Toxicological Effects of Methylmercury, National Research Council, National Academy Press, Washington, DC 2000; Booker, J. memo to Williams, L. 2001. Center for Health Informatics and Statistics statistical analyses of North Carolina methylmercury fish tissue data).

The mean and/or median levels for all the basins sampled are compared to the level of concern of 0.4 mg/kg. Based on the statewide basin-by-basin review, the median methylmercury levels for largemouth bass, bowfin, and chain pickerel are equal to or greater than the 0.4 mg/kg in a majority of the basins located south and east of Interstate 85. For largemouth bass, the median methylmercury levels for 10 out of 16 basins sampled were equal to or greater than 0.4 mg/kg. For bowfin, the median methylmercury levels for 11 out of 12 basins sampled were equal to or greater than 0.4 mg/kg. For chain pickerel, the median methylmercury levels for 9 out of 10 basins sampled were equal to or greater than 0.4 mg/kg. In addition, the statewide mean and median methylmercury levels for largemouth bass, bowfin, and chain pickerel are all greater than 0.4 mg/kg. The number of largemouth bass, bowfin, and chain pickerel sampled across the state was 820, 475, and 103, respectively.

Approximately 26 states have issued methylmercury fish consumption advisories for largemouth bass, bowfin, and chain pickerel (http://www.epa.gov/ost/fish).

Based on NC DHHS review of the fish tissue data and risk assessment, three freshwater species have been added to the federal list of fish recommended for no consumption for sensitive populations. NC DHHS is advising that women of childbearing age – including women who are likely to get pregnant, nursing women, and pregnant women – and children under 15 years of age follow FDA advice and not eat shark, swordfish, king mackerel, and tilefish. According to FDA, the average methylmercury levels for tilefish, swordfish, shark, and king mackerel are 1.45 mg/kg,

1.00 mg/kg, 0.96 mg/kg, and 0.73 mg/kg, respectively. Also, these individuals should not eat bowfin (blackfish), chain pickerel (jack fish) or largemouth bass collected from North Carolina waters south and east of Interstate 85 (areas of concern for these species).

NC DHHS is advising that women of childbearing age and children eat two meals per week of fish low in methylmercury like farm-raised fish, canned tuna and other canned fish, fish sticks, shrimp, crab, lobster, clams, oysters, scallops, salmon, trout, cod, whitefish, pollock, mahi-mahi, ocean perch, halibut, haddock, flounder, croaker, herring, crappie, sunfish, white perch, yellow perch, and bream.

HUMAN METHYLMERCURY BURDEN

Methylmercury is a metal and never degrades or breaks down in the environment to a less toxic form. In fact, methylmercury is often converted in the aquatic environment to a much more toxic form, methylmercury. This is the form of methylmercury that is incorporated into the food chain so efficiently that fish at the top of the aquatic food chain can have concentrations of methylmercury in their muscle tissue that can be one million times higher than the methylmercury concentration in the water. Fish consumption is the primary way that both humans and wildlife are exposed to methylmercury. Methylmercury can accumulate to harmful concentrations in predatory fish. In North Carolina, high levels of methylmercury (levels at 0.4 mg/kg or greater) have been found in ocean fish like shark, swordfish, king mackerel, and tilefish, and in freshwater fish like largemouth bass, bowfin, and chain pickerel south and east of Interstate 85. Women of childbearing age and children have been notified through advisories to not eat the four ocean fish and the three freshwater fish south and east of Interstate 85 (primarily located in the south eastern portion of the state) but have been given recommendations to eat other low methylmercury fish. See attached maps. These advisories have been issued to protect the most sensitive population, the developing child. The developing human nervous system is particularly sensitive to methylmercury. Several studies have reported increasing effects on the developing nervous system of an unborn child with increasing maternal methylmercury exposure from routine fish and whale consumption. Neurological processes in the areas of language, attention, and memory have been most affected.

The NC DHHS is seeking funding from the Centers for Disease Control and Prevention to conduct biomonitoring in seven counties including Columbus (Co), Brunswick (Br), Bladen (Bl), Moore (Mo), Scotland (Sc), Duplin (Du), and Martin (Ma) Counties. The largemouth bass and bowfin in these counties have some of the highest methylmercury fish tissue concentrations in the state. Based on consultation with local residents from these counties and with the North Carolina Fish and Wildlife, there are recreational and subsistence fishermen in these counties. The potential for exposure to high levels of methylmercury exists for individuals living in these counties. Even though there are advisories in these areas, the people may not be aware of the advisories or may choose to ignore them. An epidemiological study consisting of blood and hair methylmercury analysis was completed in 1990 after discovering elevated fish tissue levels in largemouth bass and bowfin for Columbus and Brunswick Counties. Some of

the highest levels of methylmercury in human hair and blood ever recorded in the United States have been identified among residents living in Columbus and Brunswick Counties. The purpose of this study was to determine if the subsistence fishermen in these counties had elevated methylmercury blood or hair levels. A total of 64 blood samples and 77 hair samples were collected for 81 residents living in these two counties. There was a positive correlation between residents with high rates of fish consumption from the waters under advisory and elevated methylmercury hair and blood levels. The blood levels ranged from non detect to 141 ug/L (well above 5 % effect level of 58 ug/L associated with abnormal neurodevelopmental scores above background). The hair levels ranged from non detect to 33.5 mg/kg (well above 5% effect level of 10 mg/kg associated with abnormal neurodevelopmental scores above background).

Additional biomonitoring is needed to prevent illness and improve public health through the following:

- To determine awareness of the fish advisories pertaining to methylmercury and to also communicate the fish advisories.
- To modify and/or expand approach for communicating fish advisories if decreased awareness or individuals are not following advice.
- To determine methylmercury body burden levels among women of childbearing age and children within the counties that have some of the highest methylmercury fish tissue levels in the state and to recommend low methylmercury fish choices.

The results of the study will benefit women of childbearing age and their offspring. The program will obtain information about the proportion of women who are aware of the advisory and how to successfully distribute advisory information to women who are not getting the message. By increasing the proportion of women who are aware of the advisory, the program will decrease methylmercury exposure to the women and their offspring. In addition, the intervention design will be shared with other states so that their advisory information will be distributed successfully to this subpopulation. The end result is to ensure that women of childbearing age are getting the advisory information so that they will limit their exposure to methylmercury and other contaminants through consumption of fish.

ESTIMATED RISK TO NEWBORNS IN NORTH CAROLINA

The potential number of newborns in North Carolina at risk from maternal exposure to methylmercury is calculated using data from the 1999 National Health and Nutrition Examination Survey (NHANES). This survey reported blood and hair methylmercury sample results for women ages 16 to 49. Approximately 10 percent of the women surveyed had hair methylmercury levels above the EPA-recommended hair level of 1 mg/kg to protect developing fetuses (corresponds to reference dose of 0.1 ug/kg-day). According to the Centers for Disease Control and Prevention, this indicates a narrow margin of safety for some fetuses (Blood and Hair Methylmercury Levels in Young Children and Women of Childbearing Age–United States, 1999. 1999 National Health and Nutrition Examination Survey, *MMWR* March 02, 2001 /50 (08);140-3). EPA

estimates that at or below the reference dose of 0.1 ug/kg-day or maternal hair level of 1 mg/kg, chronic noncancer health effects are not likely to occur. But as the exposure dose increases above the EPA reference dose, the probability of adverse health effects also increases.

Using this information, one may extrapolate to find the number of newborn infants in North Carolina that may potentially be at risk. This extrapolation assumes that the NHANES population surveyed is representative of a cross section of North Carolina and that women in North Carolina have methylmercury levels similar to levels found in the NHANES survey.

Based on the 1995 national fecundity rates for women ages 15 to 44 and the population data for North Carolina, it is estimated that there are 1,105,045 fertile women in North Carolina (National Center for Health Statistics, http://www.cdc.gov/nchs/data/series/sr_23/sr23_19.pdf). Using the North Carolina fertility rate of live births of 67.5 per 1,000 fertile women for 1999, one can expect 74,590 live births (Center for Health Informatics and Statistics, http://sdc.state.nc.us). If one assumes that 10 percent of the maternal hair levels for the 74,590 births are greater than 1 mg/kg as reported in the national survey, then 7,459 North Carolina fetuses may be at a dose higher than that recommended by EPA. EPA estimates that chronic noncancer health effects are not likely to occur at or below the reference dose. But as the exposure dose increases above the EPA reference dose, the probability of adverse health effects also increases.

NEED FOR MERCURY BIOMONITORING IN NORTH CAROLINA

Mercury is a metal and never degrades or breaks down in the environment to a less toxic form. In fact, mercury is often converted in the aquatic environment to a much more toxic form, methylmercury. This is the form of mercury that is incorporated into the food chain so efficiently that fish at the top of the aquatic food chain can have concentrations of methylmercury in their muscle tissue that can be one million times higher than the mercury concentration in the water. Fish consumption is the primary way that both humans and wildlife are exposed to mercury. Methylmercury can accumulate to harmful concentrations in predatory fish. In North Carolina, high levels of methylmercury (levels at 0.4 mg/kg or greater) have been found in ocean fish like shark, swordfish, king mackerel, and tilefish, and in freshwater fish in the south eastern portion of North Carolina like largemouth bass, bowfin, and chain pickerel. Women of childbearing age and children have been advised through advisories to not eat the four ocean fish and the three freshwater fish south and east of Interstate 85 (primarily located in the south eastern portion of the state) but have been given recommendations to eat other low mercury fish. These advisories have been issued to protect the most sensitive population, the developing child. The developing human nervous system is particularly sensitive to mercury. Several studies have reported increasing effects on the developing nervous system of an unborn child with increasing maternal mercury exposure from routine fish and whale consumption. Neurological processes in the areas of language, attention, and memory have been most affected.

As shown in the attached maps, the seven counties considered in the mercury biomonitoring study include Columbus (Co), Brunswick (Br), Bladen (Bl), Moore (Mo), Scotland (Sc), Duplin (Du), and Martin (Ma) Counties which have some of the highest mean methylmercury concentrations reported in the state for largemouth bass and bowfin. Based on consultation with local residents from these counties and with the North Carolina Fish and Wildlife, there are recreational and subsistence fishermen in these counties. The potential for exposure to high levels of methylmercury exists for individuals living these counties. Even though there are advisories in these areas, the people may not be aware of the advisories or may choose to ignore them. Some of the highest levels of mercury in human hair and blood ever recorded in the United States have been identified among residents living Columbus and Brunswick Counties (two counties being considered in the study and have some of the highest methylmercury levels in largemouth bass and bowfin in the state). After finding elevated methylmercury levels in largemouth bass and bowfin, an epidemiological study in 1990 was conducted where 64 blood samples and 77 hair samples were collected for 81 residents living in these two counties. There was a positive correlation between residents with high rates of fish consumption from the waters under advisory and elevated mercury hair and blood levels. The blood levels ranged from non detect to 141 ug/L (well above 5 % effect level of 58 ug/L associated with abnormal neurodevelopmental scores above background). The hair levels ranged from non detect to 33.5 mg/kg (well above 5% effect level of 10 mg/kg associated with abnormal neurodevelopmental scores above background).

Additional biomonitoring is needed to prevent illness and improve public health through the following:

- To determine awareness of the fish advisories pertaining to mercury and to also communicate the fish advisories.
- To modify and/or expand approach for communicating fish advisories if decreased awareness or individuals are not following advice.
- To determine mercury body burden level among women of childbearing age and children within the counties that have some of the highest methylmercury fish tissue levels in the state and to recommend low mercury fish choices.

The results of the study will benefit women of childbearing age and their offspring. The program will obtain information about the proportion of women who are aware of the advisory and how to successfully distribute advisory information to women who are not getting the message. By increasing the proportion of women who are aware of the advisory, the program will decrease mercury exposure to the women and their offspring. In addition, the intervention design will be shared with other states so that their advisory information will be distributed successfully to this subpopulation. The end result is to ensure that women of childbearing age are getting the advisory information so that they will limit their exposure to mercury and other contaminants through consumption of sport fish.

References

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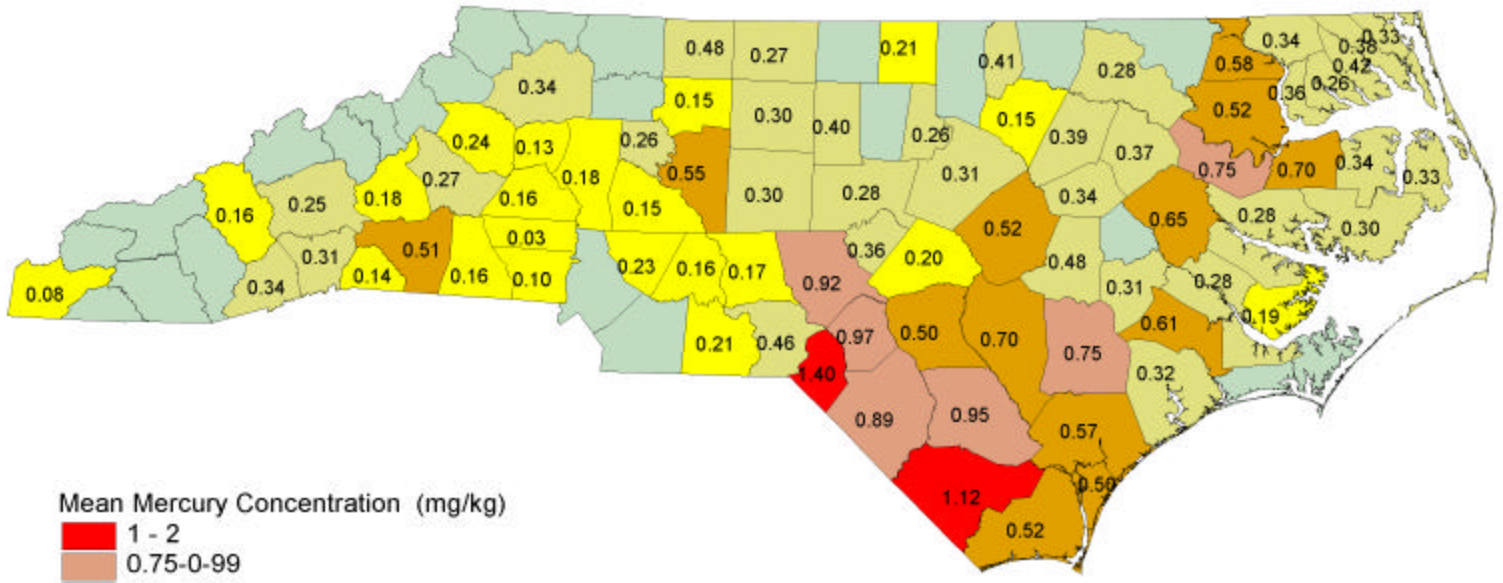
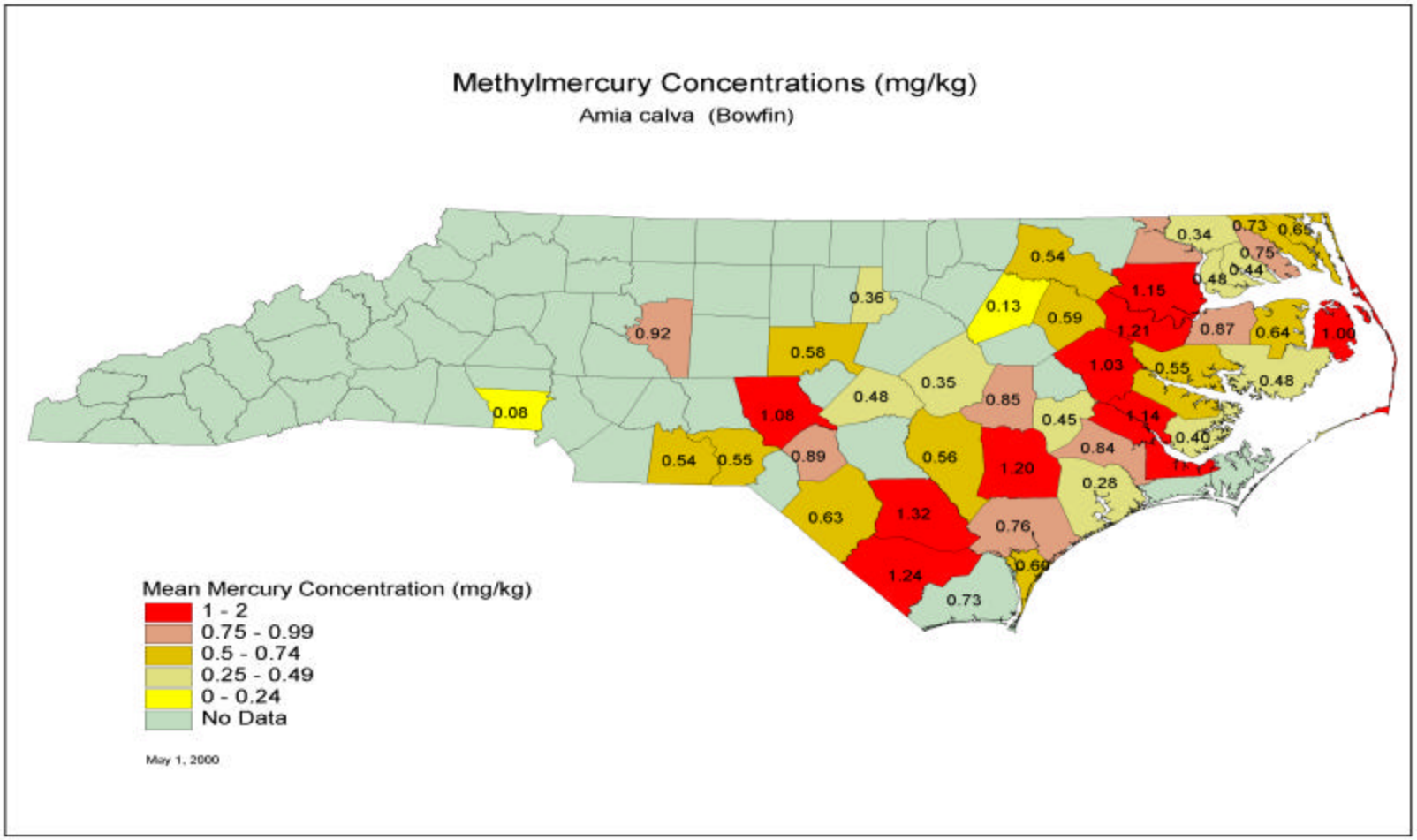
4. NRC (National Research Council). 2000. Toxicological effects of methylmercury. Committee on the Toxicological Effects of Methylmercury, Board on environmental Studies and Toxicology, Commission on Life Sciences, National Research Council. Washington, DC: National Academy Press.
5. Booker, J. memo to Williams, L. 2001. Center for Health Informatics and Statistics statistical analyses of North Carolina mercury fish tissue data.

Methylmercury Concentrations (mg/kg)

Micropterus salmoides (Largemouth Bass)




Methylmercury Concentrations (mg/kg)
Amia calva (Bowfin)
0.08
0.92
0.36
0.58
0.54
0.55
1.08
0.48
0.89
0.63
1.32
1.24
0.73
0.35
0.56
0.13
0.54
0.59
0.85
1.20
0.76
0.69
0.45
0.84
0.28
1.03
1.21
1.15
1.14
0.34
0.73
0.65
0.75
0.44
0.48
0.87
0.64
1.00
0.55
0.48
0.40
Mean Mercury Concentration (mg/kg)
1 - 2
0.75 - 0.99
0.5 - 0.74
0.25 - 0.49
0 - 0.24
No Data
May 1, 2000

NC SAFE FISH EATING GUIDELINES

Prepared by the
Medical Evaluation and Risk Assessment Unit (MERAU)

August 29, 2001

Women of Childbearing Age (15-44 years), Pregnant Women, Nursing Women, and Children Under 15 Years

- **Eat two meals per week of fish low in methylmercury** like farm-raised fish, canned tuna and other canned fish, fish sticks, shrimp, crab, lobster, clams, oysters, scallops, salmon, trout, cod, whitefish, pollock, mahi-mahi, ocean perch, halibut, haddock, flounder, croaker, herring, crappie, sunfish, white perch, yellow perch, and bream.*

- **Do not eat** shark, swordfish, tilefish, or king mackerel.** Also, **do not eat** bowfin (blackfish), chain pickerel (jack fish) or largemouth bass caught in North Carolina waters south and east of Interstate 85.

Other Women, Men, and Children over 15 Years

- **Eat four meals per week of fish low in methylmercury** like farm-raised fish, canned tuna and other canned fish, fish sticks, shrimp, crab, lobster, clams, oysters, scallops, salmon, trout, cod, whitefish, pollock, mahi-mahi, ocean perch, halibut, haddock, flounder, croaker, herring, crappie, sunfish, white perch, yellow perch, and bream.*

- **Eat no more than one meal per week** of shark, swordfish, tilefish, or king mackerel. Also**, eat no more than one meal per week** of bowfin (blackfish), chain pickerel (jack fish), or largemouth bass caught in North Carolina waters south and east of Interstate 85.

*All fish and shellfish should be properly prepared and cooked.

**On January 12, 2001 EPA and FDA issued national fish consumption advisories due to high levels of mercury in some marine fish. These advisories recommend that women of childbearing age and children should not eat shark, swordfish, king mackerel or tilefish. The advisories also recommend that these individuals eat one to two meals a week of other (low-mercury) fish.

DISCUSSION OF NORTH CAROLINA SAFE FISH EATING GUIDELINES
DUE TO METHYLMERCURY IN FISH

August 29, 2001

Medical Evaluation and Risk Assessment Unit (MERAU)

Risk Assessment

Maternal consumption of fish containing methylmercury is associated with adverse fetal neurodevelopmental effects. Fetal exposure to methylmercury may affect the way a child thinks, learns, and problem solves later in life. Children under age 15 are considered to be potentially at risk from consumption of methylmercury in fish, since the neurological systems of children are more likely to be affected by methylmercury exposure than the neurological systems of adults. The risk assessment for methylmercury in fish is in Attachment A. Fish meals per month and week are calculated for women of childbearing age (15 to 44 years), children (under 15 years), and general public (males 15 years and older and women older than 44 years). The reference dose for methylmercury used for women of childbearing age and children is 0.1 ug/kg-day (corresponds to maternal hair level of 1 ppm and cord blood level of 5.8 ppb). The reference dose for methylmercury used for the general public is 0.3 ug/kg-day. Based on the risk assessment and EPA guidance, fish tissue concentrations of 0.4 ppm or greater pose an increased risk of neurodevelopmental effects for the developing fetus and children under 15 years of age (US EPA Water Quality Criterion for the Protection of Human Health: Methylmercury, Final. Office of Science and Technology, Office of Water, Washington, DC. EPA-823-R-01-001. January 2001).

Estimated Risk

The potential number of newborns in North Carolina at risk from maternal exposure to methylmercury is calculated using data from the 1999 National Health and Nutrition Examination Survey (NHANES). This survey reported blood and hair methylmercury sample results for women ages 16 to 49. Approximately 10 percent of the women surveyed had hair methylmercury levels above the EPA-recommended hair level of 1 ppm to protect developing fetuses (corresponds to reference dose of 0.1 ug/kg-day). According to the Centers for Disease Control and Prevention, this indicates a narrow margin of safety for some fetuses (Blood and Hair Methylmercury Levels in Young Children and Women of Childbearing Age–United States, 1999. 1999 National Health and Nutrition Examination Survey, *MMWR* March 02, 2001 /50 (08);140-3). EPA estimates that at or below the reference dose of 0.1 ug/kg-day or maternal hair level of 1 ppm, chronic noncancer health effects are not likely to occur. But as the exposure dose increases above the EPA reference dose, the probability of adverse health effects also increases.

There were no mercury levels greater than the 5 percent effect level of 10 ppm hair and 58 ppb blood, both of which are associated with a 5 percent risk of abnormal neurodevelopmental scores above background. Therefore, the potential risk to the developing fetuses of the women surveyed was reported to be less than 5 percent.

Using this information, one may extrapolate to find the number of newborn infants in North Carolina that may potentially be at risk. This extrapolation assumes that the NHANES population surveyed is representative of a cross section of North Carolina and that women in North Carolina have methylmercury levels similar to levels found in the NHANES survey.

Based on the 1995 national fecundity rates for women ages 15 to 44 and the population data for North Carolina, it is estimated that there are 1,105,045 fertile women in North Carolina (National Center for Health Statistics, http://www.cdc.gov/nchs/data/series/sr_23/sr23_19.pdf). Using the North Carolina fertility rate of live births of 67.5 per 1,000 fertile women for 1999, one can expect 74,590 live births (Center for Health Informatics and Statistics, http://sdc.state.nc.us). If one assumes that 10 percent of the maternal hair levels for the 74,590 births are greater than 1 ppm as reported in the national survey, then 7,459 North Carolina fetuses may be at a dose higher than that recommended by EPA but still be at less than a 5 percent risk of developing abnormal neuropyschological test scores. EPA estimates that chronic noncancer health effects are not likely to occur at or below the reference dose. But as the exposure dose increases above the EPA reference dose, the probability of adverse health effects also increases.

General Comments

MERAU requested that the North Carolina Department of Health and Human Services Center for Health Informatics and Statistics do a statistical analysis of the 1990 to 1999 total mercury fish tissue data collected by the North Carolina Department of Environment and Natural Resources Water Quality Section (see Attachments B and C). The mean and/or median levels for all the basins sampled are compared to the level of concern of 0.4 ppm. Based on the statewide basin-by-basin review, the median methylmercury levels for largemouth bass, bowfin, and chain pickerel are equal to or greater than the 0.4 ppm level of concern south and east of Interstate 85. For largemouth bass, the median methylmercury levels for 10 out of 16 basins sampled were equal to or greater than 0.4 ppm. For bowfin, the median methylmercury levels for 11 out of 12 basins sampled were equal to or greater than 0.4 ppm. For chain pickerel, the median methylmercury levels for 9 out of 10 basins sampled were equal to or greater than 0.4 ppm. In addition, the statewide mean and median mercury levels for largemouth bass, bowfin, and chain pickerel are all greater than 0.4 ppm. The number of largemouth bass, bowfin, and chain pickerel sampled across the state was 820, 475, and 103, respectively.

Fish tissue data are not available for some basins and counties as identified in Attachments B and C. In addition, the sample size per county is small. Because of the limited sample size per county, the mean and/or median for each basin is compared to the action level of 0.4 ppm. Recommendations will be made to the Water Quality Section to continue fish tissue sampling and total mercury fish tissue analysis, particularly in areas not previously sampled.

The majority of the basins sampled across the state had median (50^{th} percentile) methylmercury levels of 0.4 ppm or greater for largemouth bass, bowfin, and chain pickerel (63%, 92%, and 90%) as identified in Attachment C. In other words, 50 percent of the

largemouth bass, bowfin, and chain pickerel within the majority of basins sampled are at levels of concern. Approximately 26 states have issued mercury fish consumption advisories for largemouth bass, bowfin, and chain pickerel (http://www.epa.gov/ost/fish).

Based on MERAU review of the fish tissue data and risk assessment, MERAU is advising that women of childbearing age – including women who are likely to get pregnant, nursing women, and pregnant women – and children under 15 years of age follow FDA advice and not eat shark, swordfish, king mackerel, and tilefish. According to FDA, the average methylmercury levels for tilefish, swordfish, shark, and king mackerel are 1.45 pm, 1.00 ppm, 0.96 ppm, and 0.73 ppm, respectively. Also, these individuals should not eat bowfin (blackfish), chain pickerel (jack fish) or largemouth bass collected from North Carolina waters south and east of Interstate 85 (areas of most concern for these species).

MERAU is advising that women of childbearing age and children eat two meals per week of fish low in methylmercury like farm-raised fish, canned tuna and other canned fish, fish sticks, shrimp, crab, lobster, clams, oysters, scallops, salmon, trout, cod, whitefish, pollock, mahi-mahi, ocean perch, halibut, haddock, flounder, croaker, herring, crappie, sunfish, white perch, yellow perch, and bream.

MERAU is advising that the general public – all other women, men, and children over 15 years – eat no more than one meal per week of fish that may be high in methylmercury such as shark, swordfish, tilefish, and king mackerel. These individuals should eat only one meal per week of bowfin, chain pickerel, or largemouth bass collected in North Carolina waters south and east of Interstate 85. In addition, the general public should eat 4 meals per week of fish low in methylmercury, like farm-raised fish, canned tuna and other canned fish, fish sticks, shrimp, crab, lobster, clams, oysters, scallops, salmon, trout, cod, whitefish, pollock, mahi-mahi, ocean perch, halibut, haddock, flounder, croaker, herring, crappie, sunfish, white perch, yellow perch, and bream.

MERAU further recommends that all fish and shellfish be properly prepared and cooked.