Assessment of Mercury Cycling in a Coupled Estuarine/Terrestrial Ecosystem and Development of a Long-term Ecosystem-level Mercury Monitoring Site at the Smithsonian Environmental Research Center

Report 1:
Early Results 2007-2008

Maryland Department of Natural Resources

Resource Assessment Service
Monitoring and Non-Tidal
Assessment Division

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Assessment of Mercury Cycling in a Coupled Estuarine/Terrestrial Ecosystem and Development of a Long-term Ecosystem-Level Mercury Monitoring Site at the Smithsonian Environmental Research Center

Report 1: Early Results 2007-2008

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Executive Summary

This study was initiated to characterize the links between mercury deposition on the Maryland Coastal Plain landscape and mercury bioaccumulation in terrestrial and estuarine biota. With controls of mercury emissions through the Clean Air Interstate (CAIR) and Clean Air Mercury Rules (CAMR) of 2005 coming on line in Maryland in 2010, there was an obvious need to assess the performance of these rules in reducing human and wildlife exposure to mercury, and to reduce uncertainty in cost/benefit assessment of these regulations. While it is expected that it may be relatively easy to track changes in atmospheric deposition response to mercury emissions reductions, largely through the Mercury Deposition Network (MDN), observing these changes on MeHg concentrations in the various environmental compartments of the ecosystem, including the biological receptors, is likely to be more difficult. We have developed a coherent monitoring and assessment framework as was proposed in Mason et al. (2005). At the Smithsonian Environmental Research Center we are building a holistic, multi-media, long-term approach to detecting change across a range of ecosystems of differing sensitivity to mercury. In this study we are monitoring Hg deposition, as part of the MDN network, and total mercury (T-Hg) and methylmercury (MeHg) fluxes from three watersheds of differing land use. We are also measuring concentrations in target organisms, starting with young of the year fish. This first report describes the results of scoping studies and the steps made in the implementation of the study from 2005 to 2006 and the first 2 years of data obtained between 2007 and 2008.

Deposition of Hg in precipitation was 5.98 and 8.2 ug m^{-2} in 2007 and 2008, respectively, and was greatest in the spring and summer as opposed to the fall and winter in both years. This distribution was largely driven by the amount of rainfall. The Hg deposited at SERC came from air masses arriving from the south west in both 2007 and 2008. The three watersheds produced relatively high yields of Hg (20 to 37%) in relation to deposition, exporting approximately 30 mg of Hg ha^{-1} in 2008. We found substantial production of MeHg in all 3 of the watersheds which resulted in fluxes ranging from 0.6 to 1.3 mg ha^{-1} in 2008. Studies within the watersheds suggest that a substantial fraction of MeHg is produced in stream banks/riparian zones. A small number of precipitation events had a large influence on the annual flux. Surprisingly in 2007 and 2008, these were summer storms, with the winter precipitation mostly recharging the groundwater. While others have observed the importance of bank water as a source of MeHg, such as Bishop et al. (1995) and Rool et al. (2006), the variations in productivity based on the seasonal distribution and amount of precipitation have only been hypothesized and not documented. We suggest Hg methylation in stream banks and subsequent flux are an undocumented yet potentially significant source of MeHg to the Chesapeake Bay.

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1. Study Rational

This study was initiated to characterize the links between atmospheric mercury deposition on the coastal plain landscape and mercury bioaccumulation in terrestrial and estuarine biota, and to begin a time-series of ecosystem-level long-term mercury monitoring, using the Rhode River and its watershed as a study site. This first report describes the results of scoping studies and the steps made in the implementation of the study from 2005 to 2006 and the first 2 years of data obtained between 2007 and 2008. During this time period the sampling design and methods were established and a time series of data long enough to assess the studies overall design was collected. Detailed discussion will follow in future publications.

There are four parts to the study, 1) Hg deposition, 2) Hg movement in the watershed, 3) Hg export from the watershed and 4) Hg accumulation in target biota, in this case young of the year fish *Morone americana* (White Perch). Each of these sections has been advanced to different degrees as each component has different levels of complexity and dependence on environmental conditions. The study is ambitious and each of the study components presents challenges that require both unique solutions and compromises. In this report, we will discuss the first three study parts, as the fish study has not advanced to a sufficient point from which we can draw any conclusions. We will then summarize our current holistic understanding of Hg cycling in the Rhode River watershed. Finally, we will discuss the challenges and future directions of the study.

1.1 Introduction

There is a key need to characterize and monitor mercury in coastal plain watersheds. Almost all of the existing ecosystem-level mercury study and monitoring programs are freshwater systems, in which the receptors are fish in lakes. This focus has resulted in a dearth of information regarding impacts if any on other aquatic ecosystems. The coastal zone plays an integral role in the global Hg cycle (Mason and Sheu 2002) not only as a sink for terrestrially-derived Hg but also as a potential source of methylated Hg to the ocean (Cossa et al. 1996; Benoit et al. 2003). Current estimates indicate that 50-80% of the riverine total Hg input to the ocean is trapped within the estuarine zone (Cossa et al. 1996; Benoit et al. 1998). Despite the importance of this region, both in terms of the global Hg cycle and as an economic resource, little process-oriented Hg research has been done in the coastal and shelf zone. Budgets for Hg and MeHg in the Chesapeake Bay (Mason et al. 2000), in the Patuxent River (Benoit et al. 1998; Riedel et al. 2000), and other coastal systems suffer from lack of information on key processes. These include the impacts of land use on Hg and MeHg transport, and the role of wetlands and coastal marshes in estuarine methylmercury production. Few studies of coastal systems have collected enough baseline data to assess how changing deposition rates may affect Hg transport, methylation and bioaccumulation through time.

With the promulgation of a number of regulations to control mercury emissions in the US, an evaluation of the effectiveness of those regulations is becoming a priority for federal and state agencies. The Clean Air Mercury Rule continues to evolve toward a late

2011 implementation. Existing control of mercury emissions through the Clean Air Interstate Rule (CAIR) and the pending CAMR heightens the need to assess the performance of these rules in reducing human and wildlife exposure to mercury, and to reduce uncertainty in cost/benefit assessment of these regulations. Supporting documents for the recent Clean Air Mercury Rule (EPA CAMR NODA, Feb, 2005) show that current models provide widely divergent assessments of both the effectiveness of emissions controls in the US on deposition within the US; and on the effectiveness of decreases in Hg deposition on Hg concentrations in biota.

The 1997 “Report on Mercury to Congress” listed long-term monitoring of mercury deposition and effects as a very high priority need. Efforts have been made since that time to define appropriate assessment and monitoring programs. The Mercury Deposition Network (MDN) has been developed to assess spatial and temporal changes in Hg wet deposition rates across the US. Although the records for most MDN sites are not long enough to evaluate temporal change, there are enough sites (88 as of 2005) to provide a rough spatial analysis of Hg deposition patterns across the US. However, the network was originally designed to monitor mercury wet deposition at “background” sites away from sources and urban areas. Recently, with increasing interest in deposition rates and patterns downstream from sources, the network has begun to add sites closer to those sources. There also remain gaps in regional coverage, including a lack of sites in the heavily populated mid-Atlantic urban corridor.

Some would argue that global Hg emissions are so large that any reduction in US emissions would yield no reduction in Hg deposition. However, local reductions in Eastern Europe had a profound impact on Hg deposition in Sweden and the Mercury Deposition Maps (MDN) (http://nadp.sws.uiuc.edu/maps/Default.aspx) show clear regional bias in Hg deposition in the eastern US where the majority of emissions originate.

While there is an expectation that it may be relatively easy to track changes in the response of atmospheric Hg deposition to Hg emissions reductions, any assessment of the measured response needs to be integrated into a risk framework. Apart from detecting differences in atmospheric inputs, the monitoring program needs to further examine the impact, if any, of these changes on MeHg concentrations in the various environmental compartments of the ecosystem, including the biological receptors. Sediment (e.g. Benoit et al. 1998) and glacier (e.g. Schuster et al. 2002) records in North America suggest that Hg accumulation rates in many areas probably peaked in the 1980’s or 1990’s and are continuing to decline. However, there are few data that can be used to assess the resultant changes in mercury exposure. The pathways of mercury from deposition, through methylation, to bioaccumulation are complex. As a result, linearity of response, either in space or time, to changing deposition cannot be assumed. The mercury research community has identified a need to document the changes in methylmercury production, transport and bioaccumulation in ecosystems in response to changes in contemporary mercury deposition.

In order to develop a coherent monitoring and assessment framework for mercury, EPA Office of Air, and the Society for Environmental Toxicology and Chemistry convened a group of 32 research scientists in fall 2003. The resultant strategy was outlined in a Feature Article in the Jan.1, 2005 issue of Environmental Science and Technology (Mason et al. 2005). The framework is further developed in the book "Ecosystem Responses to Mercury Contamination: Indicators of Change" from the SETAC Press (Harris et al. 2007). The workshop participants identified a set of suitable biological and chemical indicators of mercury and methylmercury in the environment, and developed a spatial network structure for documenting changes resulting from reduction of mercury emissions. The group advocated a holistic, multi-media, long-term approach to detecting change across a range of ecosystems of differing sensitivity to mercury. Further, the immediate data collection was advocated to establish current baselines before CAIR and CAMR begin to impact mercury emissions.

As the timescale of the response to change in deposition rate is not well known, the metrics used to evaluate change must necessarily include factors or biotic indicators that respond on different timescales. The overall group of metrics needs to be chosen to exclude the confounding impacts of short-term variability and be able to integrate the signal while not responding so slowly that no change can be ascertained on a "reasonable timescale." Clearly, as other factors besides changes in mercury deposition impact mercury methylation and MeHg fate and bioaccumulation, it is also necessary to identify ancillary data needs and possible confounding factors that should be considered and/or documented to ensure the defensible application and interpretation of the indicators. In the mid-Atlantic, changes in sulfate deposition that are occurring concomitantly with mercury reductions are potentially a large confounding factor (Gilmour et al. 1992; 1998). Fortunately, decreases in sulfate deposition are expected to slow the relative rate of methylmercury production in freshwater aquatic ecosystems. The ability to interpret trends in mercury concentrations in indicators will depend on knowledge of the influence of such concomitant factors on mercury biogeochemical cycling.

With a substantial portion of the study focusing on what is largely a stream ecosystem, a specific set of challenges is presented. The water to land surface area is small, thus any direct benefit of reduced Hg deposition to the water surface is lost. All reductions in Hg export will therefore stem from a decrease in the transfer of Hg to the stream via surface and groundwater pathways. The age of the water entering the streams in some ways becomes the time limiting step, and any response will not become evident until the average age of the stream water post dates the reduction in Hg deposition. Therefore, for such a study to be useful in detecting changes over time, headwater basins are required with a minimum of deep groundwater supply to the streams.

In studies conducted in the Boreal forest, two factors play an important role in the export of Hg. The rate of soil decomposition appears to limit the remobilization of recently deposited Hg and the hydrologic connectivity of compartments (subcatchments) within the watershed controls export of Hg to flow paths. Decomposition is important as Hg strongly binds to organic material, in most cases plant surfaces, following deposition. The later decomposition of plant material and release of Hg bound to dissolved organic matter in part control the Hg residence time. In the boreal forest the half-life of this processes is on the order of 40 years, thus transfer of recently deposited Hg is likely to be muted by at least this time period. In the mid-Atlantic, decomposition rates are faster, thus the half-life of Hg during the decomposition phase is likely to be much less. The term hydrologic connectivity refers to how well water flows from the compartments within the watershed to the watershed outlet. On the Canadian Shield, bedrock sills can block the easy transfer of water, requiring local water table rises to be achieved before water can move between watershed compartments, and thereby limiting the contributions of some areas of the watershed to water export. This is not an obvious problem in the Atlantic-Coastal plain watersheds, as the relatively steep slopes and lack of bedrock allow easy migration of water through near surface flow paths. However, a deep impervious clay layer inhibits the transfer of surface water to deep groundwater and deep groundwater to near surface sediments.

1.2 SERC Study Design

The parameters selected for assessment of Hg cycling in the SERC ecosystem are based on research experience in other ecosystems (c.f. Benoit et al. 2003; Cleckner et al. 1999; Gilmour et al. 1992, 1998; Krabbenhoft et al. 1998, 2000; Marvin-DiPasquale et al. 2000) and the set of indicators identified by the SETAC workgroup (Table 1.1). The current study has been implemented in stages, as funds allowed. The goals are:

- Characterize the flux of Hg and MeHg from the Rhode River watershed to the Rhode River
- Characterize the importance of land use on yield of Hg and MeHg
- Understand the transport of Hg through the watershed
- Understand the influence of tides on the flux of Hg and MeHg through coastal wetlands
- Begin a long-term data base of a small number of key mercury indicators in the system: wet deposition; Hg and MeHg flux from watersheds; MeHg bioaccumulation in yearling fish

Efforts to address these questions have been implemented in stages.

- 2005: baseline data on Hg and MeHg fluxes from Rhode River watersheds, and baseline information on concentrations along the Rhode River salinity gradient were collected.
- 2006: A Mercury Deposition Network collector at the existing SERC atmospheric deposition tower was established and weekly monitoring began in December.
- 2006: Three study watersheds were selected for detailed study after surveys in 2005. Instrumentation was installed late in 2006 and collection began in the spring 2007.

- 2006: Wells for water chemistry sampling and water level recording were installed in 2006. The wells were calibrated and data collection and sampling began in 2007.
- 2006/2007: Intensive study of Hg biogeochemistry and cycling in SERC tidal marshes (Mitchell and Gilmour 2008). Study of fluxes of Hg and MeHg from marshes to the Rhode River (not included in this report).
- 2006 - 2007: Collected and analyzed Hg levels in white perch from the Rhode River to establish a sampling protocol for the detection of inter-annual change in mercury levels in fish. Young of the year white perch were not found in the Rhode River in 2008.

Details of the initial phases of each study component are provided in the sections below.

Table 1.1 Current and future SERC watershed Hg study components

Indicator	**Current**	**Start date of routine monitoring**	**Future**
Air			
Wet Deposition (weekly total Hg)	X	Dec. 2006	
Atmospheric speciation			X
Watershed			
Stream fluxes/watershed yield	X	Spring 2007	
Shallow groundwater fluxes	X	Spring 2007	
Dry deposition			X
Hg^0 evasion			X
Soil concentrations and accumulation rate			X
Riparian zone cycling	X	Spring 2008	
Terrestrial and stream biotic indicators (birds, amphibians, stream invertebrates)			X
Estuary			
Water column concentrations	X	Spring 2007	
Marsh concentrations and net methylation rate		Spring 2007 – Fall 2008	
Sediment concentrations and net methylation rate			X
Yearling White Perch	X	Fall 2006	
Other biotic indicators (ie. zooplankton, benthic infauna; wetland birds)			X

2. Watersheds and Screening Studies

The Smithsonian Environmental Research Center (SERC) is located on the inner mid-Atlantic Coastal Plain (38° 51' N, 76° 32' W) approximately 20 km south of Annapolis, MD (Figure 2.1). With this location in the urban mid-Atlantic corridor, there is an expectation of future change in local and regional emissions and deposition of mercury, sulfate and nitrate to the SERC watershed. The protected, 2800 acre SERC property constitutes most of the watershed of the Rhode River, a sub-estuary on the western shore of Chesapeake Bay. The research site includes extensive forested and agricultural uplands, tidal and non-tidal wetlands, and estuarine habitats. Continuous records of sulfate and nitrate deposition data, meteorology, and stream flow and chemistry data for multiple watersheds and the Rhode River extend almost 35 years, including the longest record of acid deposition and its chemical impacts in the mid-Atlantic region. The SERC landscape is very well characterized, including detailed GIS information, LIDAR surveys of forest structure, and characterization of soil structure. Ecosystem ecology is also well understood, with a 26-year database on species composition and population dynamics, for plants and animals in both the Rhode River and its watershed. Subsurface hydrology is less well characterized, although it is clear that near surface groundwater is a major contributor to flow and element mass flux in SERC watersheds.

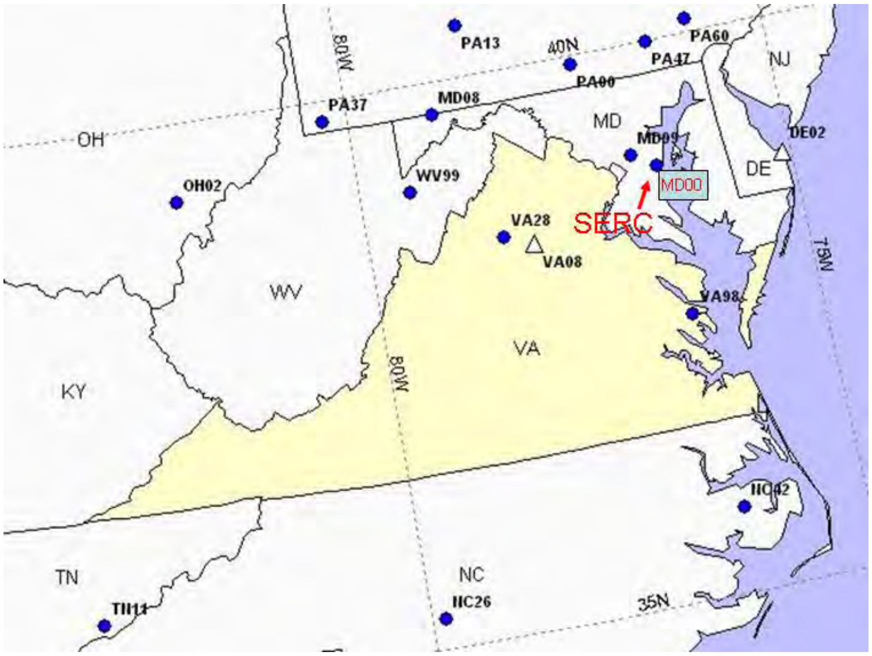


Figure 2.1. Location of the Smithsonian Environmental Research Center (SERC) and the Mercury Deposition Network Sites in the region.

2.1 Geology and Vegetation

The geology of the Rhode River watershed is described in Chirlin and Schaffer, (1977) and Chapelle and Drummond (1983). The soils are described as sandy loams, with Westphalia fine sandy loam formed from the Calvert formation and the Collington sandy loam formed form the Nanjemoy. These soils are intact upslope but at valley bottoms the soils have a mixture of parent material. The Calvert formation is the most recent unit and consists of fine grained sand and diatomaceous silt and forms an unconfined shallow aquifer. It lies above 14.5 to 14.7 meters above sea-level where it contacts the Nanjemoy formation, which is comprised of fine grained silt clay pale to deep green in color. The unit contains heavy mineral assemblages, significant gypsum and a mix of clay types; montmorillonite, illite and kaolinite. This unit can be coarse at the surface. The Marlboro Clay underlies the Nanjemoy, and acts as a barrier to vertical flow. This is an important attribute of these watersheds, as the barrier eliminates deep groundwater from entering the streams, thereby minimizing the age of stream water and any lag in response to changes in Hg loading caused by the watershed water residence time. The contact between the two units is near sea level and the unit can be up to 9 meters from the surface. The Nanjemoy formation contains oxidized and reduced zones. In the reduced zones, as much as 40% of the iron is Fe^{2+} and sulfide levels of 1290 ppm as sulfur have been measured. The extent and duration of the reducing zones will depend on the hydrologic conditions in the watershed.

2.2 Watershed Site Selection: Land Use and Watershed Size

Seventeen Rhode River watersheds on or around the SERC property have been monitored at some time during the past 35 years for flow, nutrient concentrations and other basic chemistry; eight are currently monitored. Some of the data sets stretch back more than three decades. The SERC watersheds were originally chosen for study to cover a range of size, land use, and soil type and were chosen to address questions about nutrient fluxes. Land use includes large areas of old growth forest, newer forest, controlled cultivation, and residential development in some of the upper watersheds outside of the SERC property. To select watersheds for long-term study, dissolved and particulate Hg and MeHg concentrations in runoff were obtained for seven of the watersheds of different size and land use during the summer of 2005. The characteristics of the watersheds are given in Table 2.1.

Objectives in choosing long-term watersheds for the Hg study included availability of flow and chemistry data, a range of Hg and MeHg fluxes and yields, a range of land use that is representative of the Rhode River watershed as a whole, and stability of those land use characteristics through time. To select watersheds for the long-term study, Hg, MeHg and particulate concentrations in runoff were obtained for seven of the SERC watersheds, of different sizes and land use, during summer 2005. Particulate and filterable (<0.7 um) Hg and MeHg were examined at the outflow of all the watersheds early in the summer. The samples were “grab samples” thus they represent only one small moment in time.

Clear patterns in Hg and MeHg flux from the watershed emerged from the summer 2005 stream survey. Total mercury concentrations in streams decreased with the size of the watershed (Figure 2.2 top panel). Estimated watershed yields (the flux of Hg from the watershed expressed on a per m^2 basis) also decreased with watershed size, as expected (Figure. 2.2 bottom panel). Estimated watershed yields were correlated with land use (Figure 2.3). Particulate Hg loads increased most significantly with development, and decreased with the fraction of wetlands in the watershed. Filterable Hg concentrations increased with the fraction of forest in the watershed. The relationship between agriculture and yield was not significant for this sampling date.

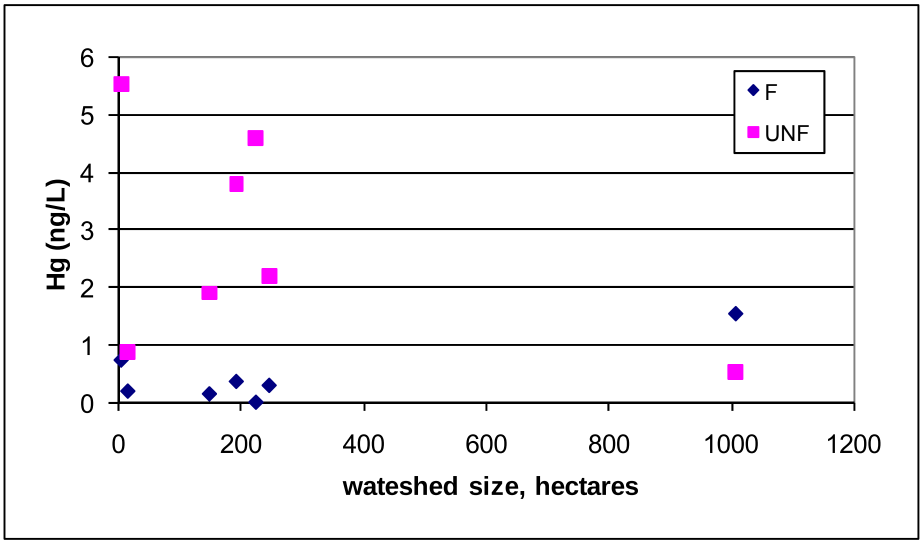
Based on the data, collected in the summer of 2005, three watersheds were selected for the long term study (Figure 2.4). Watersheds 110 and 109 are similarly sized small watersheds, with relatively low Hg concentrations in stream water and relatively high Hg yields. They have contrasting land use, with 109 mainly agricultural, and 110 entirely old-growth forest. Watershed 101 was also chosen. Amongst the SERC watersheds, 101 is relatively large; it is a mixed-use watershed with some residential development, and is representative of a substantial fraction of land use in the MD coastal plain.

Watershed 109 was studied heavily during the 1970's and 80's. This watershed has a riparian forest buffer downslope from agricultural fields and was used by Jordan, Correl and others to study the role of riparian buffers in nutrient fluxes from cultivated fields. Peterjohn and Correl (1986) describe the watershed as a 16.3 acre agricultural watershed located in the narrow mid-Atlantic Coastal Plain, with a shallow perched aquifer overlying a clay layer with low vertical hydraulic conductivity (Chirlin and Schaffner, 1977). They describe the soil above the clay aquiclude as a non-calcareous fine sandy loam. From Peterjohn and Correl:

"The average basin slope is 5.44% and the channel slope is 2.65%. A 10.4 ha area located at the higher elevations of the watershed was planted in row crops. The remaining 5.9 ha of the watershed is composed of hedgerows and a riparian forest which completely surrounds the stream draining the watershed. The dominant tree species in the riparian forest are sweetgum and red maple."

Table 2.1 Size and land use of the seven long-term SERC Rhode River watersheds sampled in the scoping study. Land use data is from National Land Cover Data Set (NLCD) 1990.

SERC Watershed	101	102	103	108	109	110	119
Area, hectares	226	194	247	150	17	6	1008
Land use %							
Wetland	2	0	2	0	0	0	7
Developed	4	5	3	0	0	0	2
Forest	50	55	71	43	17	100	52
Agriculture	43	40	24	56	83	0	39



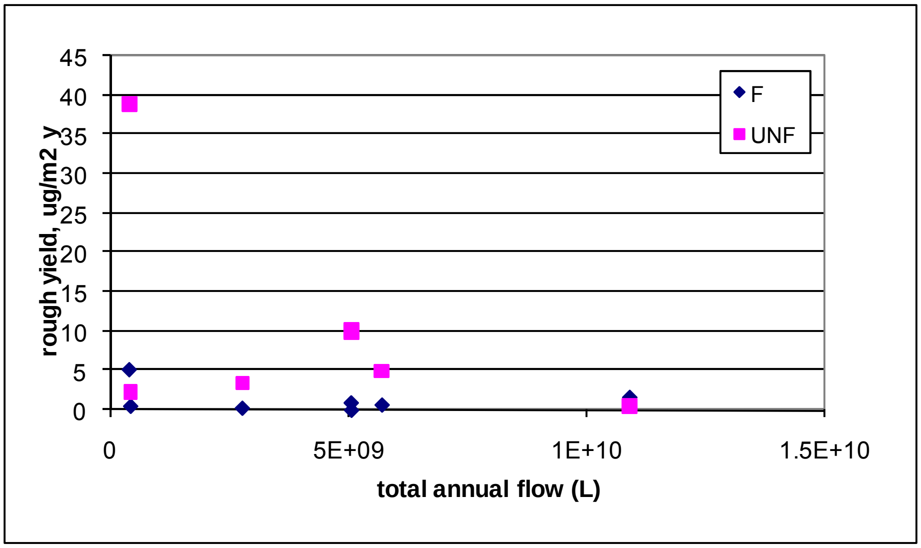


Figure 2.2 Total mercury concentrations (top) in grab samples from streams draining seven Rhode River watersheds, on May 31, 2005. Bottom, "roughly" estimated annual watershed yields. "Rough" because the flux is estimated from the May 31 samples, the average annual flow for each weir, and the size of each watershed. F = filtered and UNF is unfiltered sample.

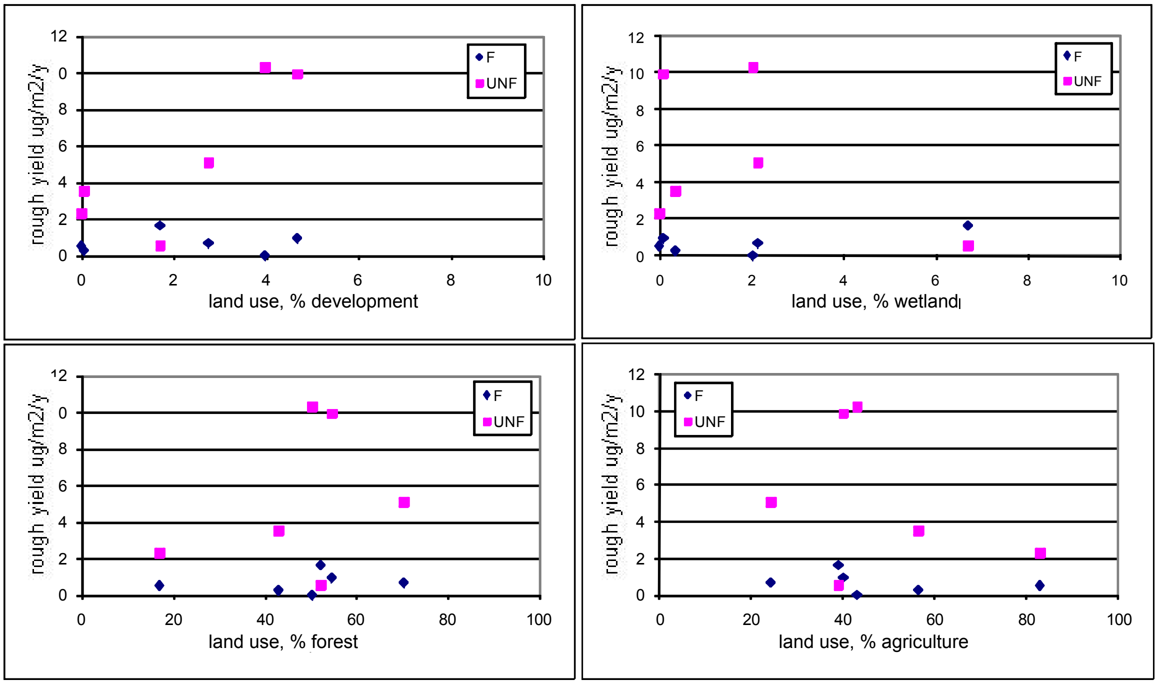


Figure 2.3 “Rough” estimate of Hg yield by land-use of the 7 Rhode River watersheds, based on the concentrations collected in the scoping study. Annual watershed yields were calculated using May 31, 2005 water concentrations, the average annual flow for each weir, and the size of each watershed.

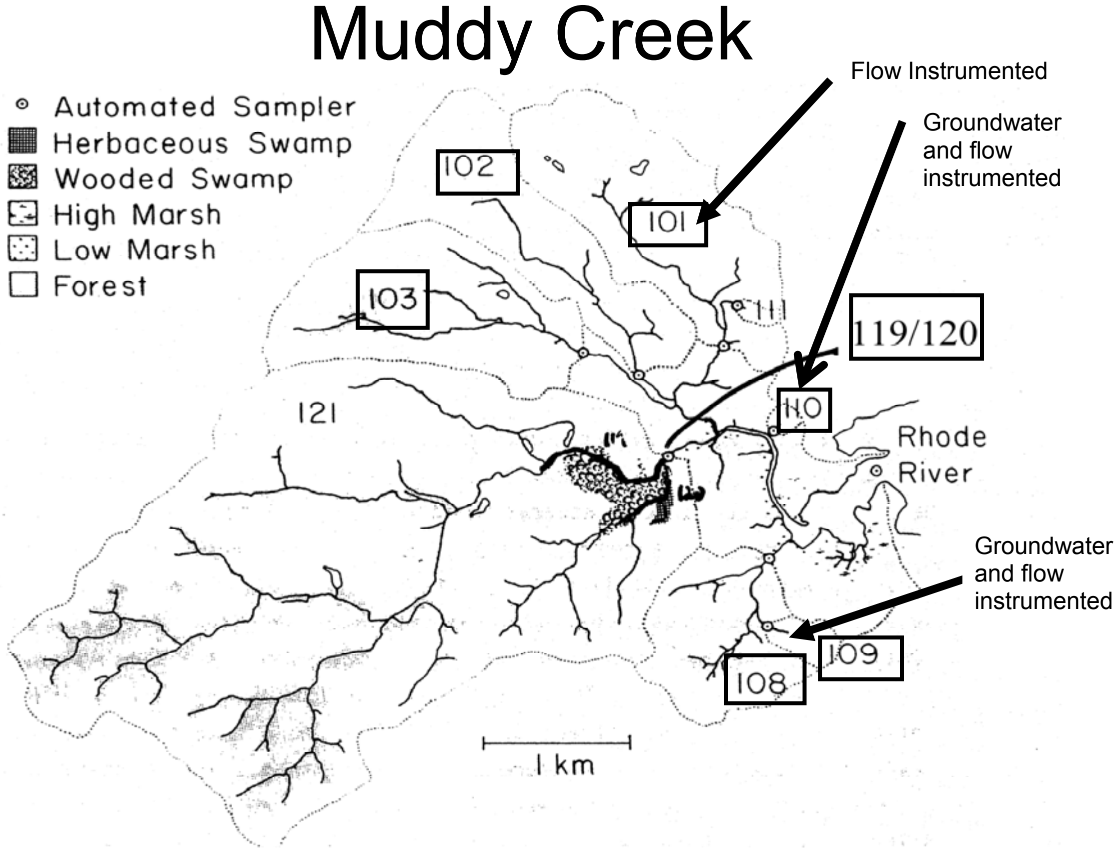


Figure 2.4 Watershed locations, boundaries and hierarchy for long-term Rhode River study watersheds at SERC. Watersheds 101, 109 and 110 were chosen for the long-term Hg study.

2.3 Watershed Sample Timing

Most of the mercury transported in Rhode River tributary streams during the 2005 scoping study was in the particulate form. Because particle flux is strongly tied to flow and flow events, we examined the response of particulate and filterable Hg concentrations to changes in flow during a storm event in summer 2005. Stream Hg concentrations were followed in two streams (101 and 108), over their hydrographs, following a rain event in July 2005. Particulate Hg flux responded strongly to increased flow in both streams (Figure 2.5).

While the concentration of Hg on particulates did not change, the flux of particulates did. Particulate concentrations were highest within 6 hours before the peak in the hydrograph (maximum flow rates). Filterable Hg concentrations increased in both streams with flow, with maxima at or after the time of maximum flow rate. Total particulate loads were much higher in watershed 108, and this watershed had the largest change in particulate Hg. Flow-related changes in filterable Hg were similar in both watersheds.

From the pattern of Hg flux across a hydrograph it is eveident that the particle flux is strongly tied to flow and that flow-weighted sampling of the study streams is critical to obtaining accurate long-term records of Hg flux in these watersheds. The relatively small SERC watersheds respond fairly quickly (hours) to most rain events. Therefore, the three Hg watersheds were instrumented with trace-metal clean flow-weighted samplers for the long-term study (see details below). A weekly sampling frequency was chosen to match ongoing flow and chemistry data collections for these watersheds.

To make sure that MeHg would not degrade over the week that samples remain in the field, we tested the stability of MeHg in the sample containers over 9 days (Figure 2.6). Freshly collected, unfiltered stream water from watershed 119 was held in the dark at 4 or 40 degrees C. More than 99% of the initial MeHg was recovered after 9 days at 4^0C. At 40^0C, 92% of the initial MeHg was recovered. The relative standard deviation for the analysis of 4 replicate samples was about 1%.

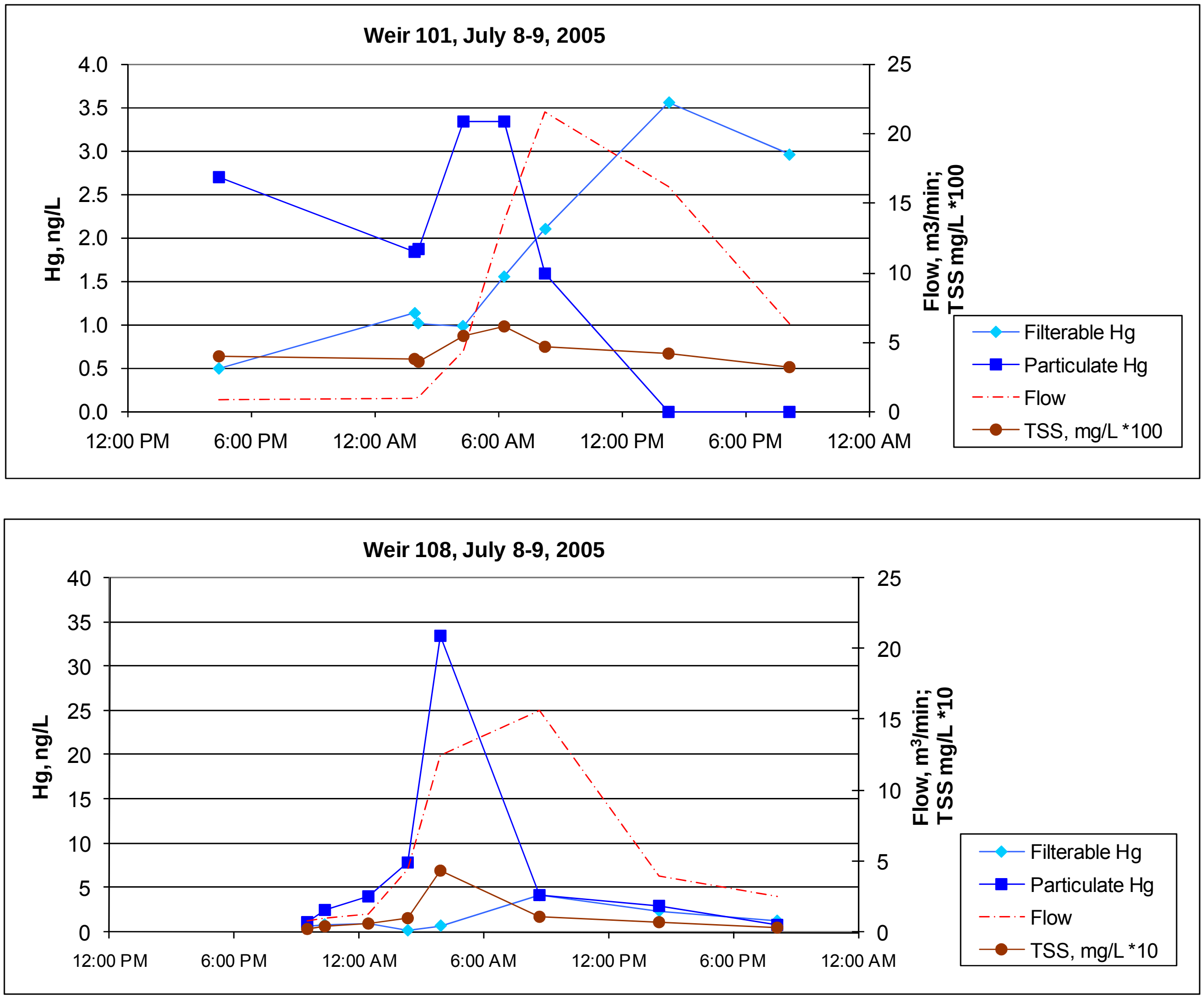


Figure 2.5 Mercury concentrations in streams at two SERC weirs over 24 hrs following a rain event on July 8, 2005. Watershed 101 (top) is a mixed land use watershed and watershed 108 (bottom) is mainly an agricultural watershed. TSS = total suspended solids. Note the differences in scale for Hg concentrations.

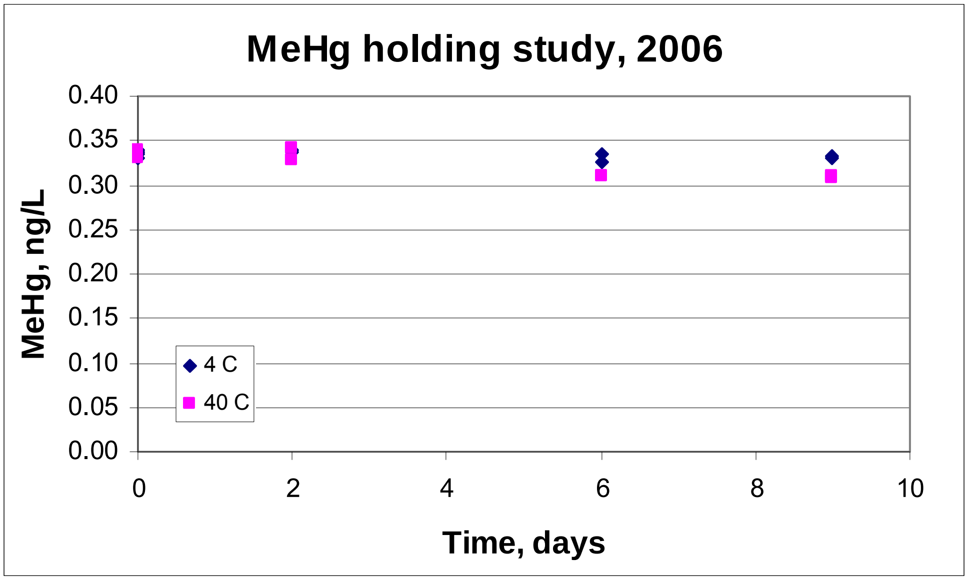


Figure 2.6 MeHg holding study, examining the change in MeHg concentration through time in unfiltered Watershed 119 stream samples held in PETG containers at two different temperatures over 9 days.

3. Precipitation and Wet Hg Deposition Measurements

3.1 MDN00 Site Description

Measurement of wet Hg deposition at SERC began in December 2006. The SERC site (designated MD00) is one of three operating Mercury Deposition Network (MDN) sites in Maryland (Figure 3.1). Sites have operated at other locations for short periods of time in the past. The MDN network is a national monitoring network coordinated through the National Atmospheric Deposition Program (NADP). Network membership provides a high level of quality assurance, comparability with over 80 other MDN sites in the US and some data analysis. More information on MDN, including data from over 85 sites in the US, can be found at http://nadp.sws.uiuc.edu/mdn/.

Data collected at MDN sites include weekly precipitation (rain and snow) and wet Hg deposition. Mercury samples are collected using a dedicated modified Aerochem Metrics model 301 collector (heated in winter). Samples are weekly composites. All precipitation samples are sent to Frontier Geosciences for total Hg analysis. Precipitation is measured using an ETI instrument systems NOAH IV total precipitation gage, with a wireless PDA to download precipitation data. Precipitation data are sent to MDN weekly.

The MDN00 site is located on the SERC meteorology tower, which is located above the tree canopy near SERC's main campus (120' height with stairway access). Other meteorological data collected on the SERC tower currently include temperature, wind speed and direction, light data (including UV), rainfall, and wet deposition for nutrient analyses, using a separate Aerochem collector.

3.2 MDN00 Site Data

During 2007 and 2008, the average wet Hg deposition to MD00 was 5.98 and 8.2 ug/m^2, respectively. This reflects a large difference in total precipitation in the last two years, 791 mm in 2007 and 1129 mm in 2008. Average precipitation at Reagan National Airport (1971 to 2000) is 999 mm (NOAA). Figure 3.2 shows the 2007 and 2008 precipitation and deposition data by week, and Figure 3.3 by month. On average across both years, about 40% of precipitation and of Hg wet deposition occurred in spring (Table 3.1). However, for the 30 year normal period (NOAA, Reagan National Airport), precipitation was roughly evenly spread across seasons (See top panel in Figure 3.3). The somewhat unusual precipitation pattern in the last 2 years was reflected in the stream flow patterns at SERC (see section 4), with highest flows in spring, and much lower flows, or no flow in summer, when precipitation slows and is exceeded by evapotranspiration. Weekly and seasonal Hg deposition patterns at MD00 closely followed precipitation patterns for 2007-2008. Precipitation accounted for more than two thirds of the variability in Hg deposition (Figure 3.4). However, the concentration of Hg in precipitation in any week is inversely related to the amount of precipitation. This is the commonly observed "wash out" phenomenon (Figure 3.5)

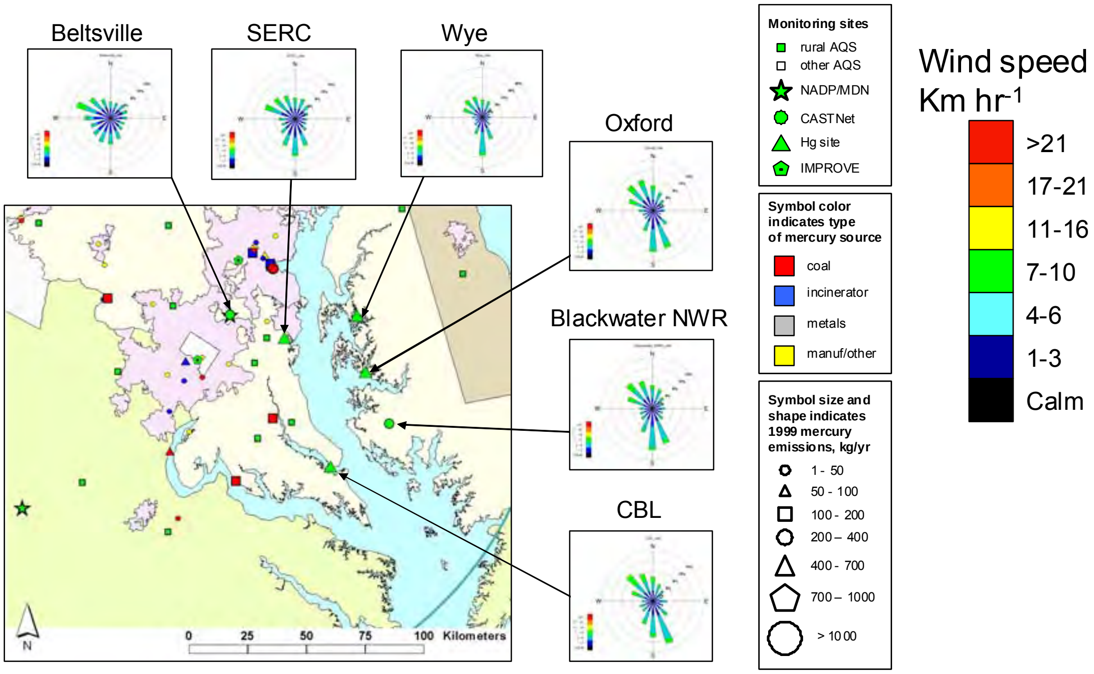
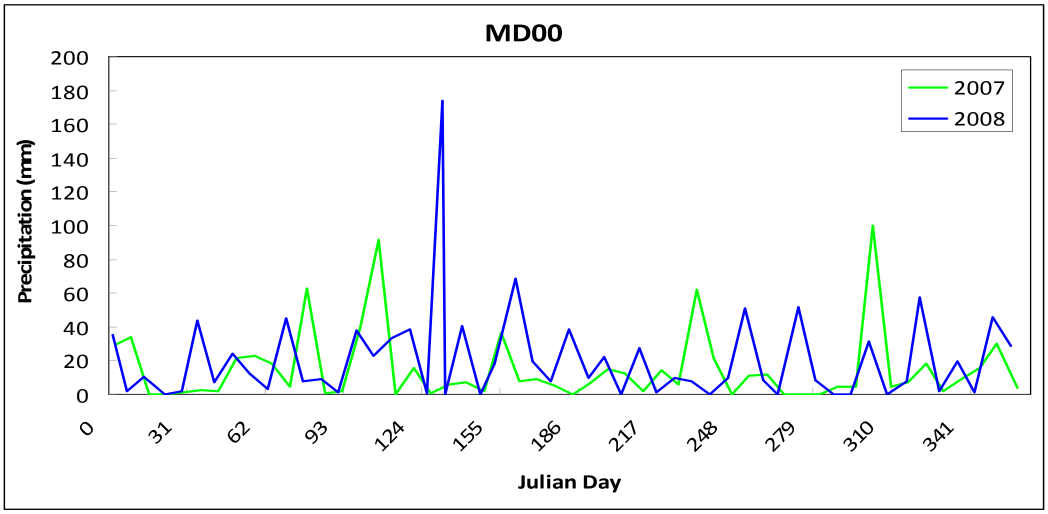


Figure 3.1 Wind trajectory rosettes for current and former MDN sites in Maryland, including sites that were run for a short time in the past on the eastern shore and in Solomons. Data compiled by the National Atmospheric Deposition Program. Sites at SERC, Beltsville and Piney Reservoir (not shown and is located in western MD) are currently active.

Table 3.1 Precipitation and Hg deposition by season for 2007 and 2008.

	Precipitation (mm)		Hg deposition (ng/m2)	
	2007	**2008**	**2007**	**2008**
Winter	22%	18%	18%	14%
Spring	28%	39%	35%	46%
Summer	21%	21%	23%	16%
Fall	30%	22%	24%	24%



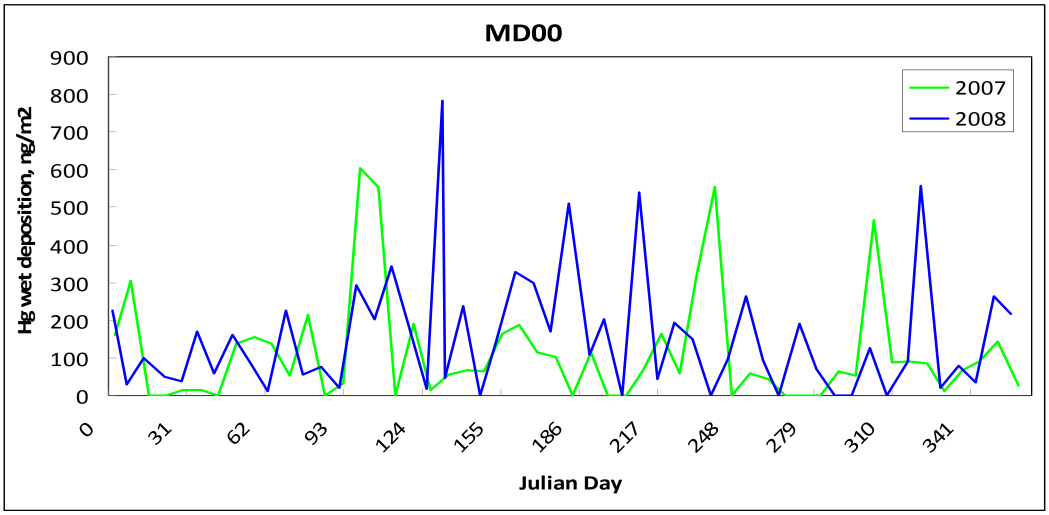


Figure 3.2 Weekly precipitation (top) and Hg deposition (bottom) for MD00 for 2007 and 2008.

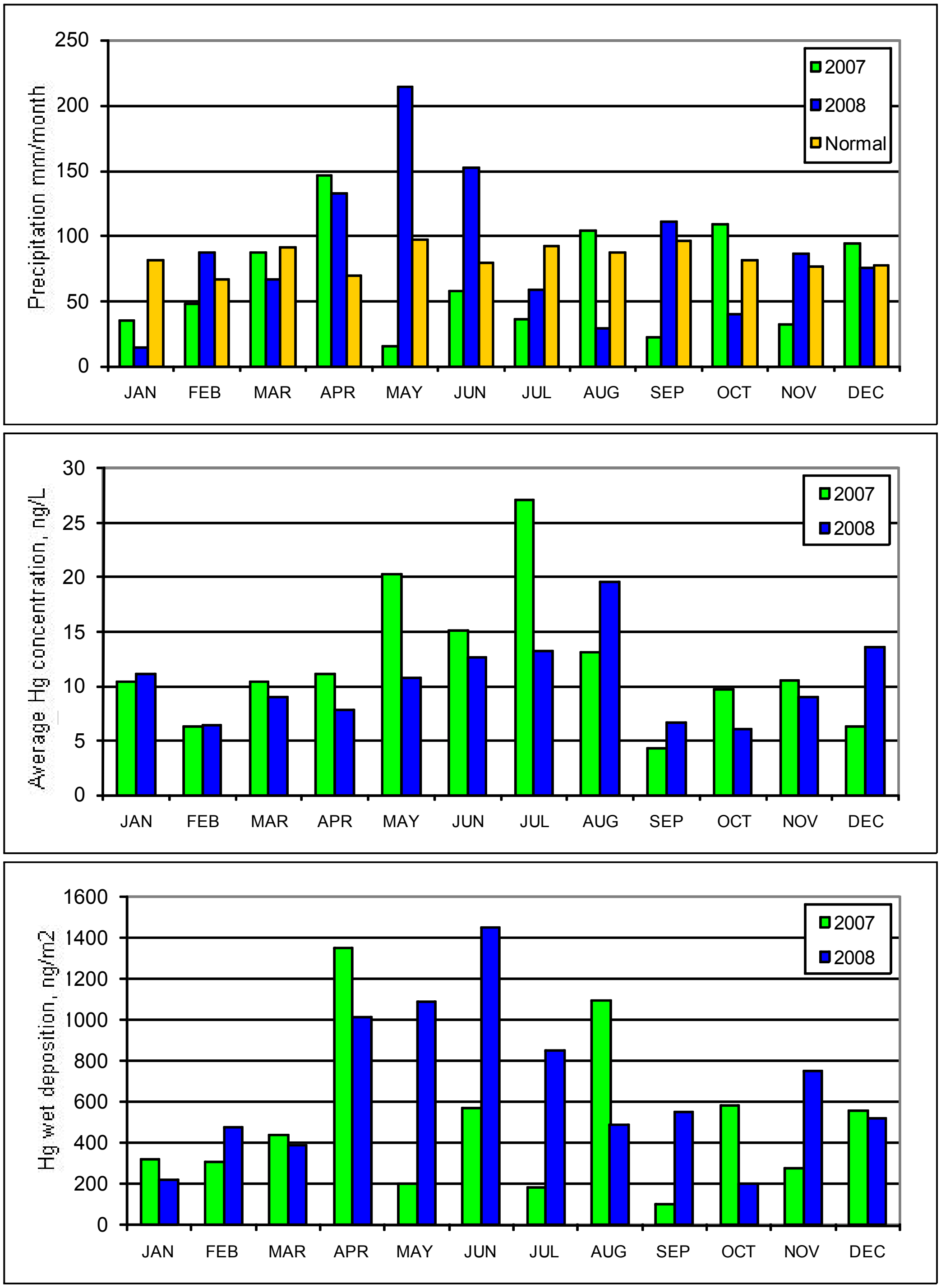


Figure 3.3 Monthly precipitation (top); average monthly Hg concentration in precipitation (middle) and monthly Hg wet deposition (bottom) for 2007 and 2008 at MD00. Normal precipitation is for Reagan National Airport (NOAA).

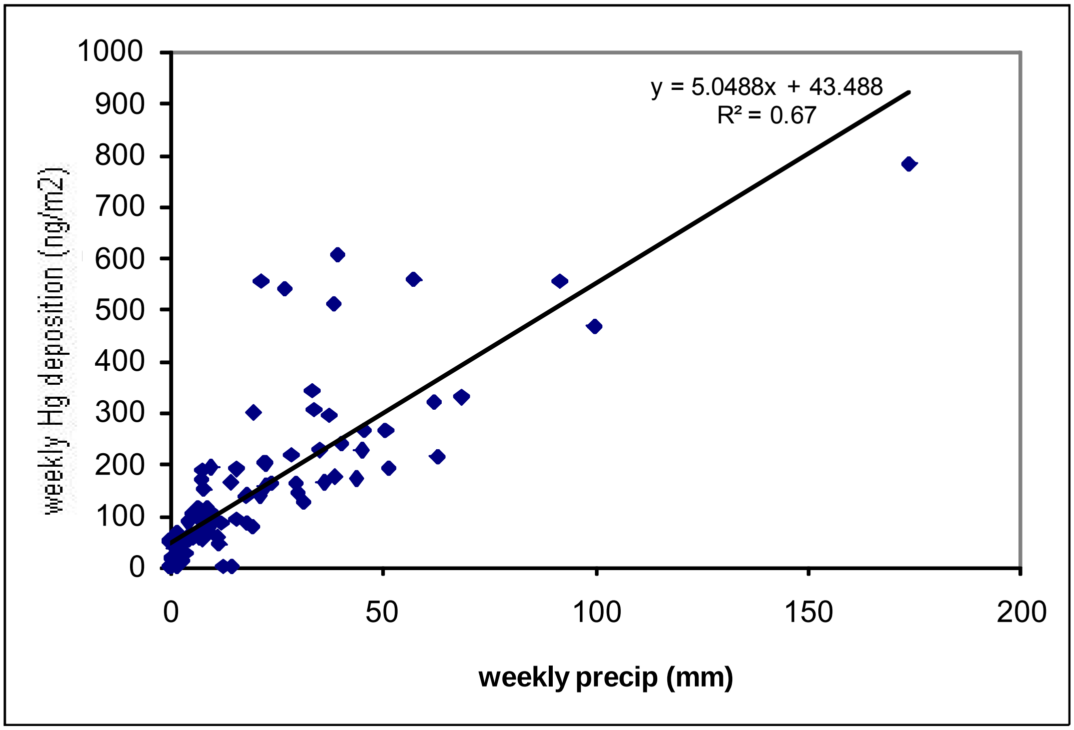


Figure 3.4 Correspondence between weekly precipitation and weekly Hg deposition at MD00 for 2007-2008.

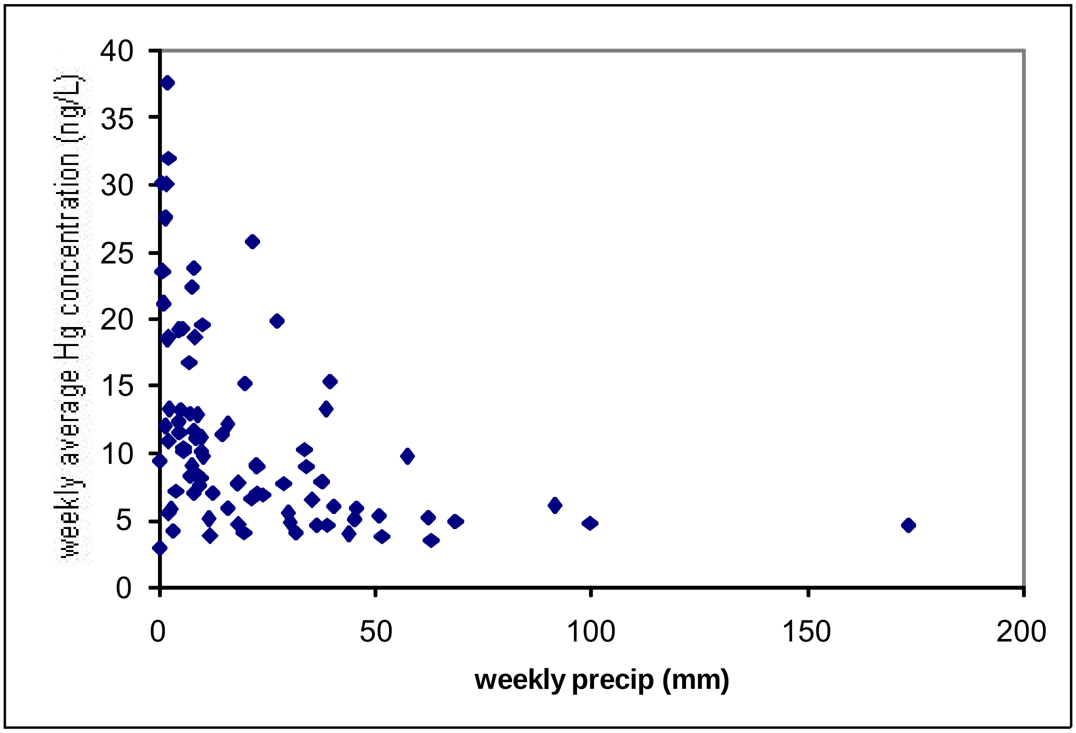


Figure 3.5 Inverse relationship between weekly precipitation amount and Hg concentration in rain at MD00 for 2007-2008.

Wind direction, and sources of Hg deposition. During 2007/2008 the predominant wind direction at SERC was SSW (Fig. 3.6). Precipitation and wet Hg deposition were also dominantly delivered from the SW quadrant, mainly between 180 and 230 degrees. This dominant wind direction differs somewhat from the nearby MDN site at Beltsville (Figure. 3.1) where the dominant wind direction is more to the north and west. SERC is often downwind from the two large coal-burning power plants in southern Maryland (Chalk Point and Morgantown), while Beltsville is more often downwind from the DC metro area, and large Hg point sources in Pennsylvania.

3.3 Comparison with Regional MDN Sites

Tables 3.2-3.4 show Hg deposition, precipitation, and average Hg concentration in rain from MDN sites in MD, VA, PA and WV. During 2007 and 2008, MD00 received the lowest amount of Hg in wet deposition of the three Maryland sites, and was among the lowest sites in the region. Beltsville and SERC had comparable amount of precipitation in both years, but SERC had lower average Hg concentrations in rain. Frostburg received more precipitation than SERC or Beltsville, but the average Hg concentration in rain were slightly lower at Frostburg than at SERC. However, caution should is warranted in drawing conclusions from only 2 years of data. The Beltsville site receives some of the highest average Hg concentrations in rain in the region. However, it is the only designated “urban” site in the set. The Valley Forge site, in suburban Philadelphia, also receives precipitation with relatively high concentrations of Hg.

An analysis of covariance showed no change in Hg deposition rates over time for the suite of sites listed in Table 3.2. A general linear model of annual Hg deposition rate using year, site, and precipitation showed significant differences among sites, and with precipitation amount, but no change through time. All data were normally distributed and were used without transformation. None of the sites showed significant changes in Hg deposition over time when examined individually, although all but one of the sites with more than 6 years of data showed downward trends. However, only a few of the sites in the region have more than a few years of data available. Further, large changes in precipitation across years confound the analysis.

To summarize, site MD00 receives what appears to be significantly lower levels of wet Hg deposition than site MD99 in Beltsville, only 10’s of miles away. Differences in the prevailing wind direction, and the point sources in those quadrants may account for differences in Hg deposition. Proximity to the urban DC area may also increase Hg deposition at Beltsville. None of the regional MDN sites, taken individually or together, show significant declines in Hg deposition during their short recording histories.

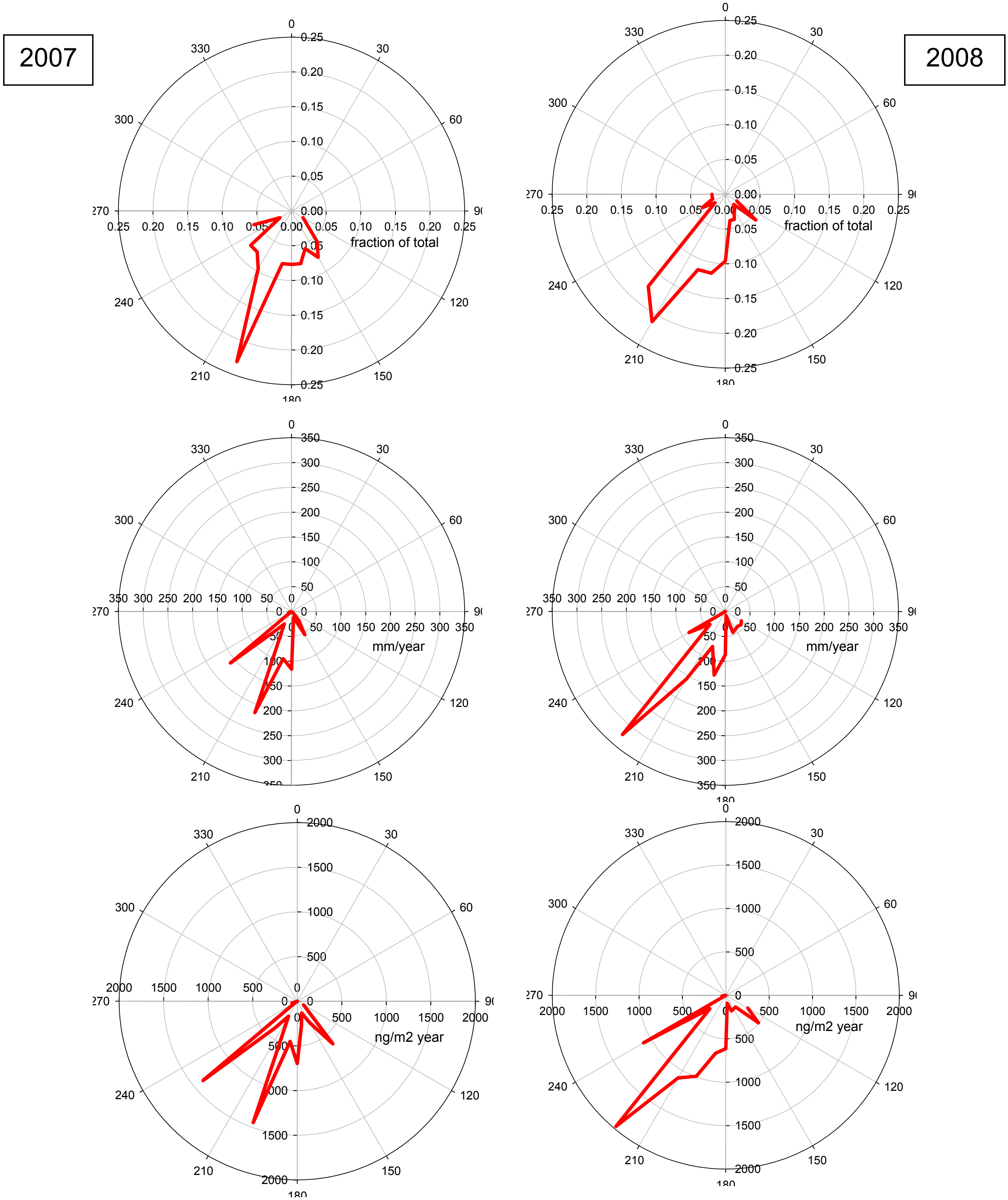


Figure 3.6. Directional roses for wind (top); rain (middle) and Hg wet deposition (bottom) for 2007 (left) and 2008 (right). All data were binned into 10 degree wind direction increments, based on weekly sums or averages, for these plots.

Table 3.2 Annual wet mercury deposition measured at regional Mercury Deposition Network sites (ng/m^2 year). Also included are Hg wet deposition rates measured at three Maryland sites by Mason in 1997/98 (Sheu et al. 2002).

Site	**Location**	**Start Date**	**End Date**	**1997/8 (Mason)**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**
MD08	Frostburg, MD	2004		15000						5808	7376	8093	11278
MD99	Beltsville, MD	2004								11843	10519	8338	9464
MD00	Edgewater, MD	2006										5975	8202
VA08	Culpepper, VA	2002	2006					12420	7698	8811	6445		
VA28	Shenandoah NP, VA	2002						11873	9727	7074	8986	8494	12411
VA98	Gloucester Co, VA	2004								8149	8029	5881	8982
PA00	Adams Co, PA	2000				6237	7881	9747	8930	8015	8033	9263	9642
PA37	Holbrook, PA	1999			9242	9407	9197	11469	9872	7218	8655	8882	
PA47	Millersville, PA	2002						10270	9296	7837	9868	7758	8385
PA60	Valley Forge, PA	1999			12555	7649	9065	11919	11559	8078	8509	8828	11076
OH02	Athens Super Site	2005								9770	10054	7549	
WV99	Canaan Valley	2007											11584
	Solomons, MD			14000									
	Baltimore			30000									
	Eastern Shore			14000									

Table 3.3 Annual total precipitation measured at regional Mercury Deposition Network Sites (mm/year).

Site	Location	Start Date	End Date	2000	2001	2002	2003	2004	2005	2006	2007	2008
MD08	Frostburg, MD	2004							868	892	994	1289
MD99	Beltsville, MD	2004							1138	1197	817	1102
MD00	Edgewater, MD	2006									791	1129
VA08	Culpepper, VA	2002	2006				1505	1148	1217	960		
VA28	Shenandoah NP, VA	2002					1997	1665	1422	1510	1060	1411
VA98	Gloucester Co, VA	2004							1226	1448	981	1173
PA00	Adams Co, PA	2000			598	1070	1133	1262	1039	1081	951	992
PA37	Holbrook, PA	1999		839	953	1145	1258	1254	976	1016	1120	
PA47	Millersville, PA	2002					1346	1181	1126	1237	941	1066
PA60	Valley Forge, PA	1999		1196	751	1189	1389	1438	1137	1343	1136	1200
OH02	Athens Super Site	2005							855	1095	948	
WV99	Canaan Valley	2007										1535

Table 3.4 Annual average total mercury concentration measured at regional Mercury Deposition Network Sites (ng/L**).**

Site	**Location**	**Start Date**	**End Date**		**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**
MD08	Frostburg, MD	2004								10.5	10.5	10.4	10.0
MD99	Beltsville, MD	2004								13.9	14.0	17.6	12.6
MD00	Edgewater, MD	2006										11.9	10.6
VA08	Culpepper, VA	2002	2006					7.9	6.9	4.8	5.6		
VA28	Shenandoah NP, VA	2002						9.9	8.5	7.6	9.0	9.8	8.6
VA98	Gloucester Co, VA	2004								8.2	10.2	12.6	9.7
PA00	Adams Co, PA	2000				18.3	9.4	10.7	9.5	10.0	11.5	13.2	15.1
PA37	Holbrook, PA	36307			10.0	9.8	6.3	8.0	7.3	3.8	6.8	6.2	
PA47	Millersville, PA	2002						8.9	11.5	10.2	13.1	11.9	10.2
PA60	Valley Forge, PA	1999			15.7	13.4	14.0	12.8	11.6	12.1	15.6	14.9	11.8
OH02	Athens Super Site	2005								10.4	10.4	11.5	
WV99	Canaan Valley	39259											8.4

4.0 Watershed Hg and MeHg Transport

4.1 Stream Sampling Approach and Development

Preparation for the weekly flow-weighted stream sampling program began in the summer of 2005. We made use of the existing stream discharge loggers at SERC, but added new sampling equipment for clean Hg/MeHg sampling. All three of the monitored streams had been fitted with a 120° sharp-crested V-notch weir and a stilling well in the 1970's. The base of the weirs rest on a clay layer that underlies the watersheds just above sea level and isolates shallow groundwater from deeper aquifers (Peterjohn and Correll, 1984; Chirlin and Schaffner, 1977). Discharge is calculated from water height in the stilling wells, using depth monitors and Campbell Scientific® data loggers. The data loggers are also used to trigger a water sampling event each time a known volume of discharge occurs (Correll and Weller 1989).

After choosing three watersheds for the study, sampling methods were tested in order to develop the lowest cost procedure that would yield adequate trace-metal blanks for stream sampling. We began by testing the existing stream sampling equipment at SERC, which was designed for nutrient and organic matter sampling. We found that the existing continuous-flow sampling systems - which use Tygon and rubber sampling lines, and acid-washed polypropylene carboys - gave Hg blanks that were unacceptably high (blanks were similar to stream Hg concentrations). Thus, dedicated sample trains, including trace-metal clean tubing and sealed sample containers, were required. In 2006, we obtained 3 flow- weighted samplers (ISCO®), modified them for Hg sample collection, and tested cleanliness. Blanks from the system were well below stream concentrations. Out installation include acid washed Teflon sampling lines and acid washed tubing in the pump head. Water samples are collected in large acid washed Polyethylene Terephthalate (PETG) bottles. Water samples are retrieved weekly and the sampling bottle and lines are exchanged as needed.

Routine stream monitoring using this system began in the 101, 109 and 110 watersheds in April 2007. During early 2008, we discovered that the weir in the 109 watershed had been compromised, and that water from one portion of the watershed had been routed around the weir. This was corrected in the summer of 2008. We estimated the excluded area in 1997 to be on the order of 4 hectares and present the flow and flux data from 109 with the 4 hectare correction. This corrected data will be further adjusted if required following data collections in 2009 and 2010.

4.2 Watershed Hydrologic Response and Export of Hg and MeHg

Precipitation and watershed flow from April 2007 to December 2008 are shown in Figure 4.1 and Table 4.1. The 226 ha watershed 101 exports the largest amounts of water, but yields a similar fraction of precipitation than the smaller 109 and 110 watersheds (Table 4.1). All three watersheds responded in the same general manor to individual precipitation events but the magnitude of the responses to individual events was dependent on the antecedent moisture conditions within the watershed. This is most evident when the responses to events are compared between seasons (Figure 4.1).

For 2007 and 2008, the seasonal water flow pattern in the watersheds can be divided into a wetting up period over the winter and spring and drying out period over the summer. In 2007 a long decline in flow occurred from April through June. The watersheds all experienced a period of zero flow during the summer and flow began again in December. In 2008, flow peaked in June after a large rain event, followed by a period of declining flow. The watersheds stopped flowing in August 2008 and flow did not return until December 2008. To account for the importance of evapotranspiration to the water balance of watershed, the hydrologic year has been segmented into growing (April 15 to Nov 1) and non growing periods (Nov 1 to April 15). The greatest flow and yield occurred in the summer period despite periods of no flow. The rain events were most intense during the summer months (Figure 4.1), which may have resulted in more overland flow with less water being transferred to storage. Understanding differences in hydrologic response is important to Hg cycling. For example soil retention likely decreases with increasing rain intensity and MeHg export likely increases with duration of saturation.

Table 4.1 Water export as percent of input and total volume from each watershed in 2008.

Precipitation	1537.6 mm/m2					
Watershed	101		109		110	
Catchment area	226 ha		13 ha (estimated)		6.3 ha	
	Water %	Water m3	Water %	Water m3	Water %	Water m3
Winter	7.0	158531	4.1	5273	4.3	2722
Summer	30.5	371007	18.1	12641	36.0	12224
Total	15.2	529538	9.0	17914	15.4	14946

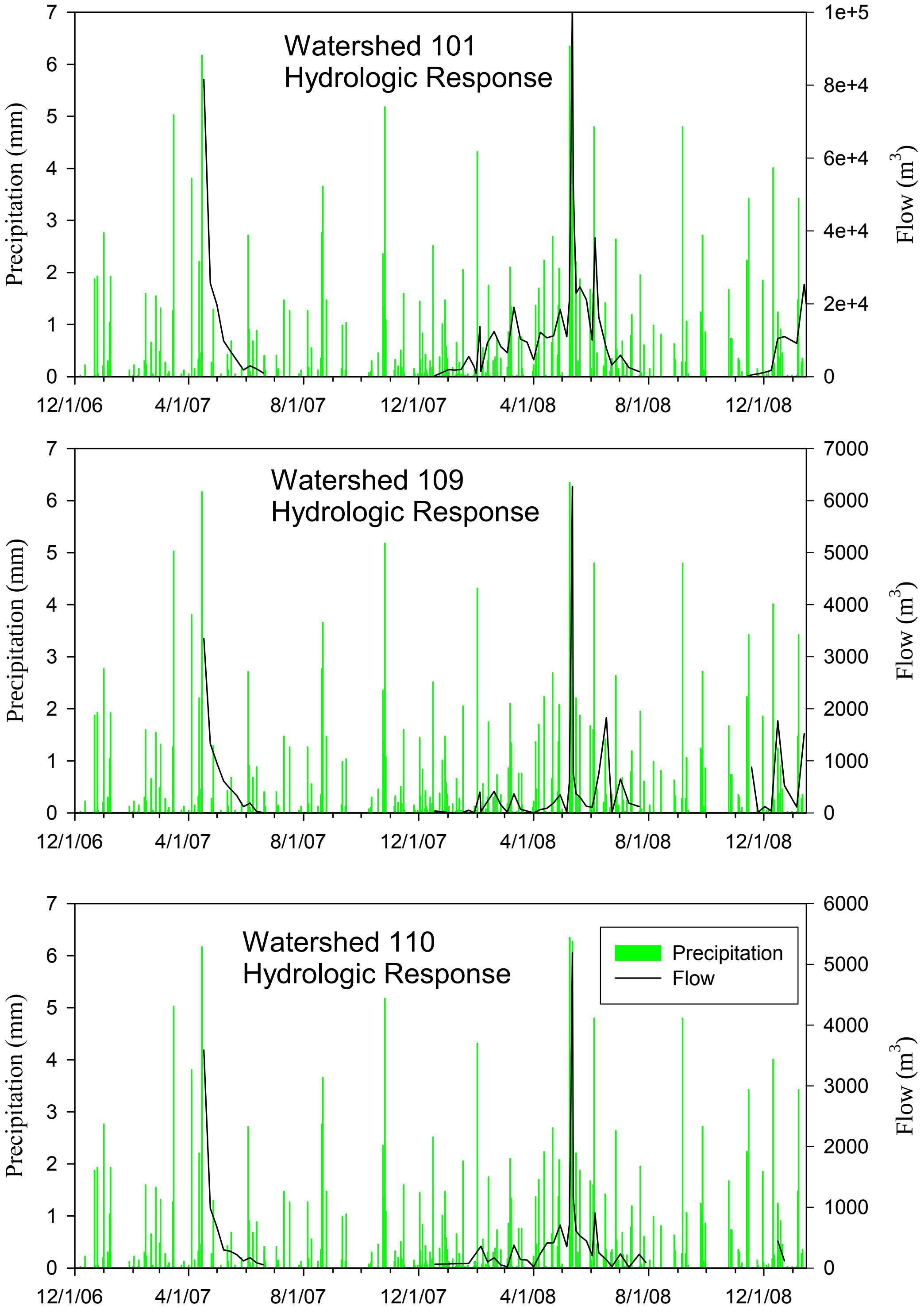


Figure 4.1 Precipitation from December 2006 to December 2008 for SERC. Event-based record taken from MDN NOAH-IV precipitation gage on the SERC meteorological tower.

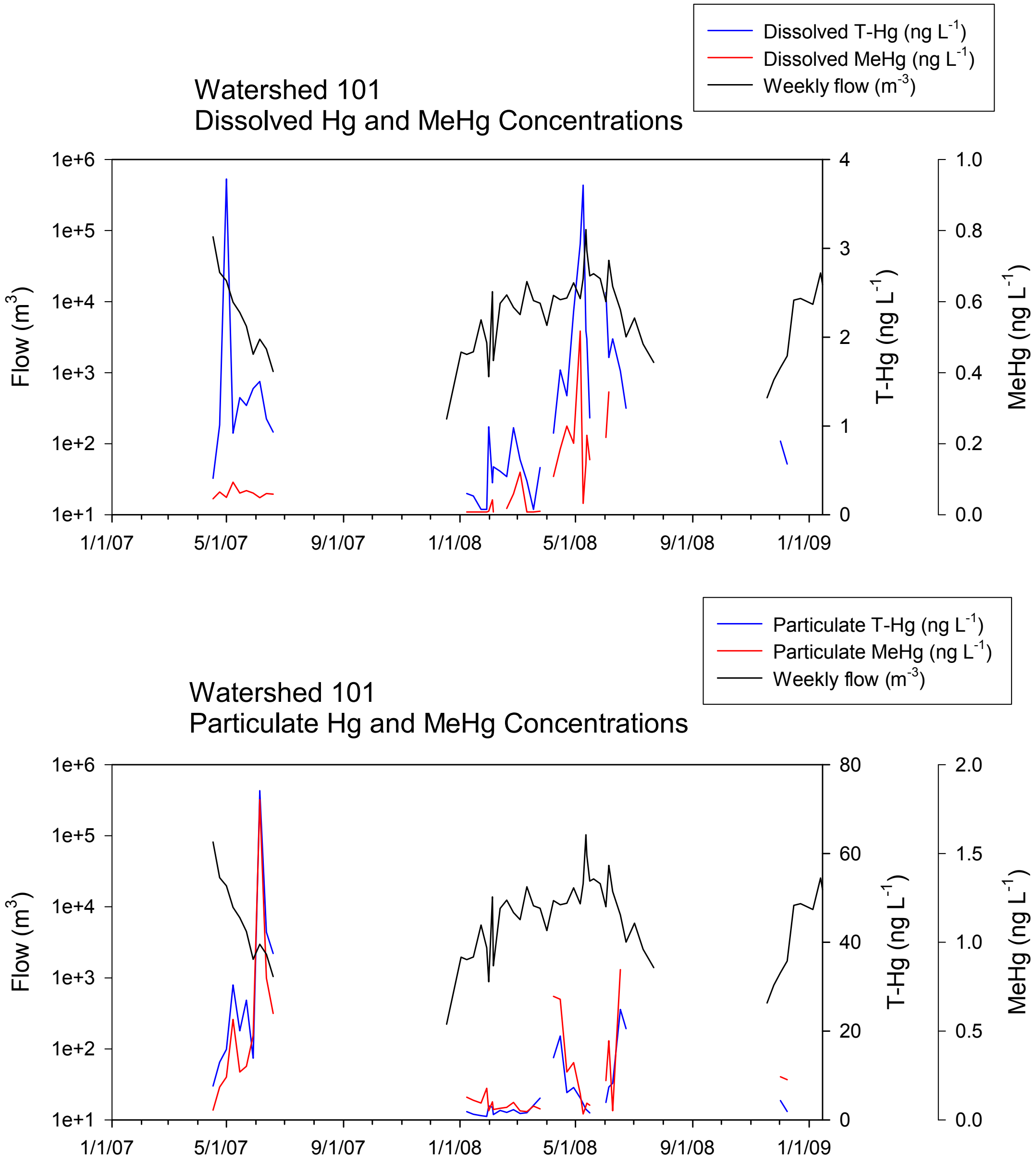


Figure 4.2 Flow weighted average dissolved and particulate concentrations of Hg and MeHg in the water passing through the weir of the 101 watershed. Note concentrations are on a linear scale whereas flow is on a log scale. Breaks in lines indicate missing data.

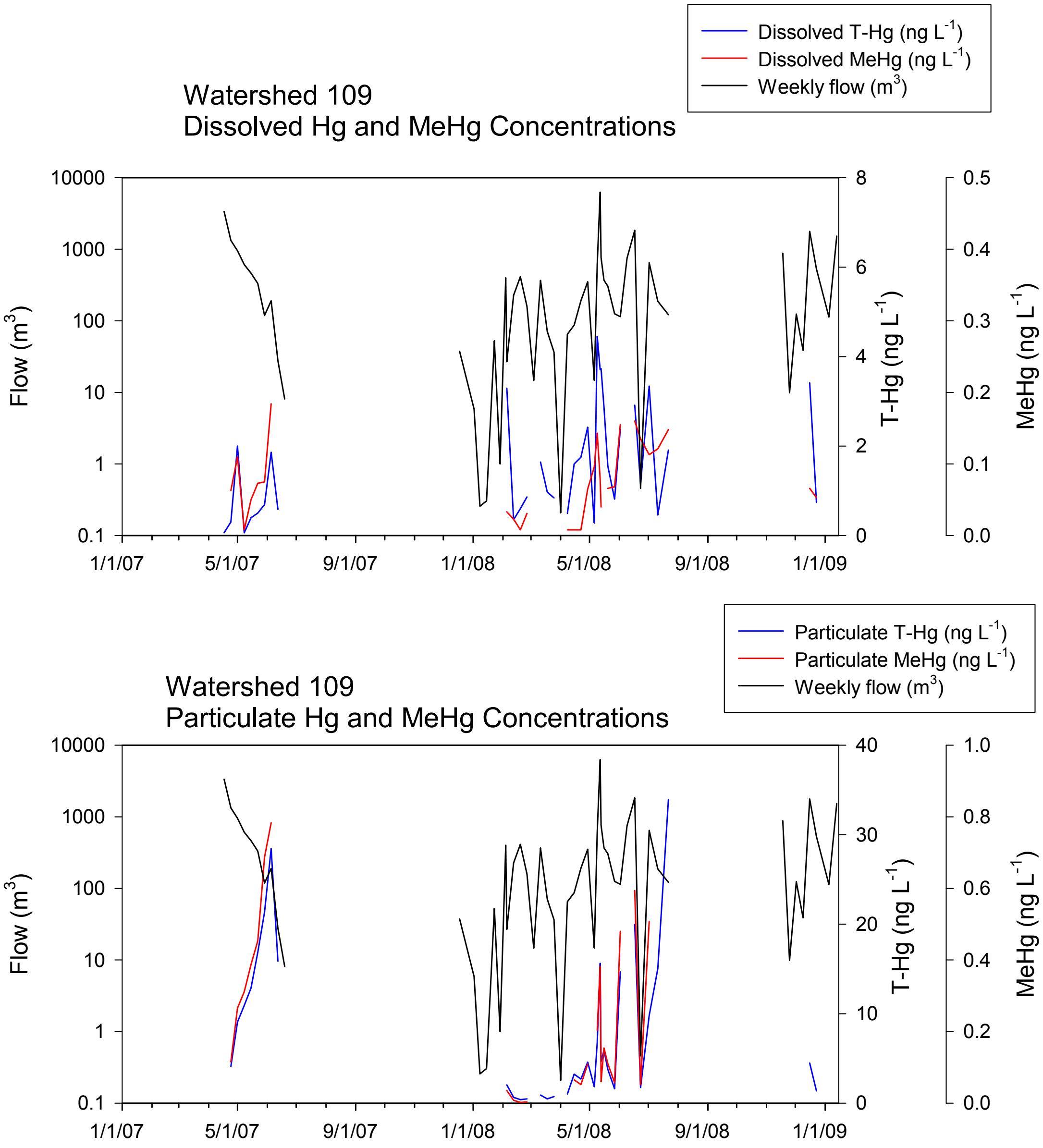
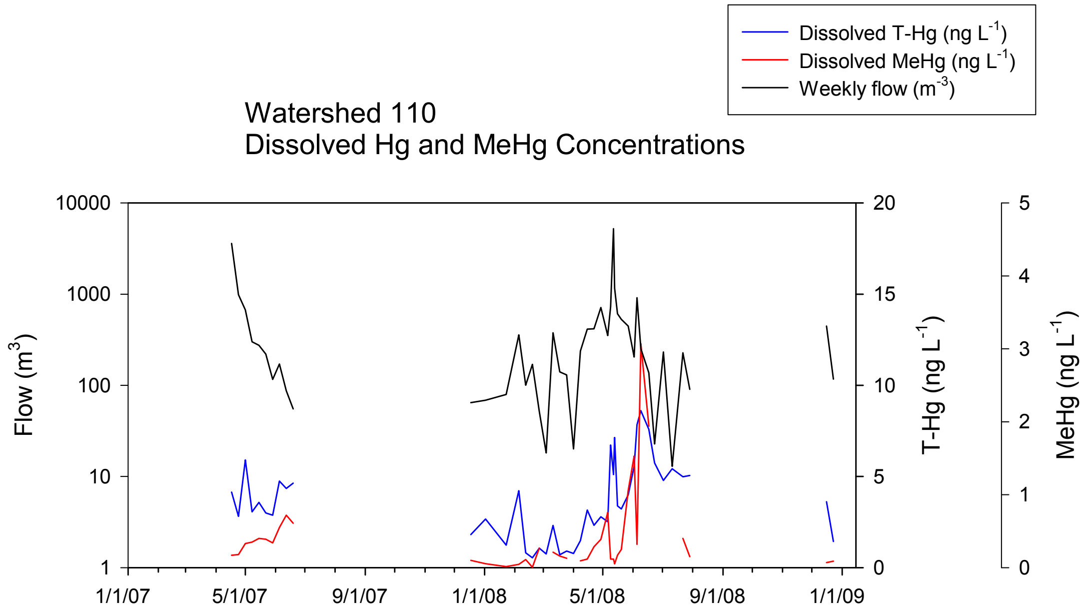


Figure 4.3 Flow weighted average dissolved and particulate concentrations of Hg and MeHg in the water passing through the weir of the 109 watershed. Note concentrations are on a linear scale whereas flow is on a log scale. Breaks in lines indicate missing data.



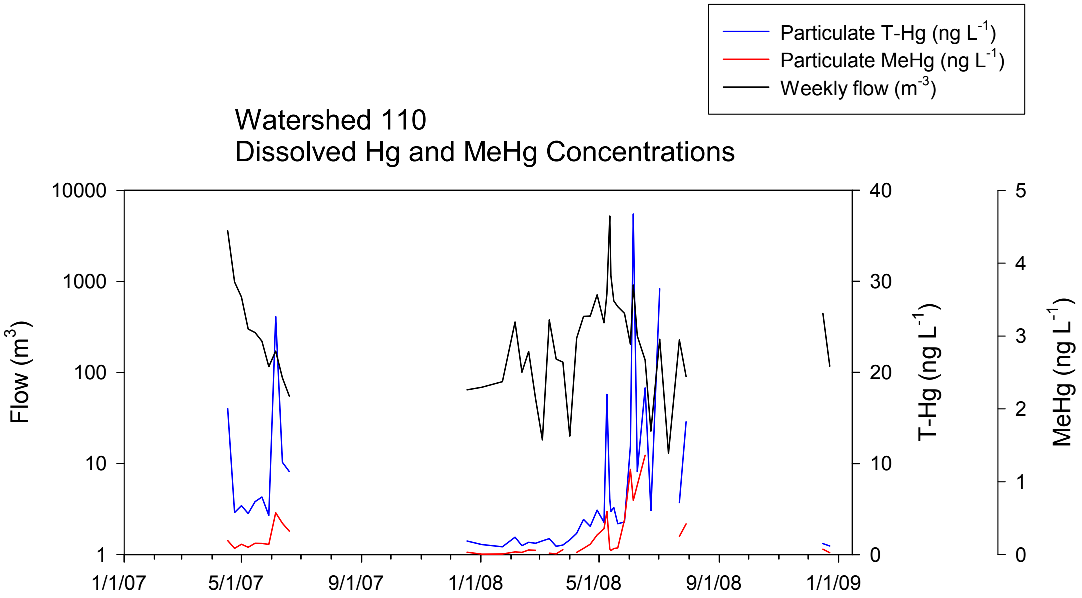


Figure 4.4 Flow weighted average dissolved and particulate concentrations of Hg and MeHg in the water passing through the weir of the 110 watershed. Note concentrations are on a linear scale whereas flow is on a log scale.

The flow weighted average weekly concentrations of Hg and MeHg for watersheds 101, 109, and 110 are shown in figures 4.2, 4.3 and 4.4. Dissolved concentrations of T-Hg in outflow water of watershed 101 ranged from 0.1 to 4 ng L^{-1} but particulate concentrations were much higher, and peaked at nearly 80 ng L^{-1} in the summer of 2007. Concentrations of dissolved and particulate Hg in the outflow from watershed 109 ranged from 0.1 to 4 ng L^{-1} and 0.2 to 35 ng L^{-1}, respectively. Dissolved T-Hg concentrations in water exported from watershed 110 ranged from 1 to 9 ng L^{-1} and particulate Hg ranged from 0.2 to 40 ng L^{-1}. In 2008, dissolved T-Hg concentrations corresponded with flow, but this was not the case in 2007. While a small increase in flow generated elevated Hg concentrations in June of 2007, prior to this period concentrations had been much lower under a much higher period of flow. Thus, no overriding relationship between flow and T-Hg concentration in either the dissolved or particulate phase is apparent (also see Fig. 4.10). Such variations have been recorded in other studies but most studies have not been conducted for a period long enough in time to elucidate the relationship (Allan and Heyes, 1998, Allan et al. 2001).

The large pond at the outflow of watershed 101 is a particle sink, thus under the highest flow conditions, dissolved Hg concentrations increase and particulate concentrations decrease. Interestingly, T-Hg concentrations associated with particles in water exported from watersheds 109 and 110 increased from the spring through the summer despite decreased discharge. The increase in particulate T-Hg lagged the increase in dissolved Hg concentration. We hypothesize this phase shift occurs because the particles are biotic and have accumulated Hg from the water. The particles exported from 101 are also almost entirely organic.

Concentrations of MeHg were low in stream water of all three watersheds during the winter, with concentrations at or below the method detection limit of 0.02 ng L^{-1} on some occasions. MeHg concentrations increased steadily through spring in both the dissolved and particulate phases, and the highest MeHg concentrations occurred during the summer. This is not surprising given MeHg is produced as a result of bacterial activity, which increases with temperature. We observed differences in MeHg concentrations among watersheds. Particulate and dissolved MeHg peaked at 2.0 and 0.5 ng L^{-1}, in watershed 101; 0.2 and 0.7 ng L^{-1} in watershed 109 and 3.0 ng L^{-1} and 1.0 ng L^{-1} in watershed 110. The high concentrations in watershed 110 are surprising given the watershed is dominated by forest. The reason for this likely is the result of the watershed structure and connectivity between runoff, the vadose zone and the weir. This will be discussed in detail in Section 4.3.

Using weekly flow-weighted concentrations and the weekly water flows, the weekly mass fluxes of Hg and MeHg were calculated for each watershed (Figure 4.5, 4.6 and 4.7). The 2008 Hg and MeHg fluxes are shown in Table 4.2. Fluxes could not be calculated for 2007 because of the April start.

Table 4.2 2008 fluxes of Hg and MeHg from the SERC watersheds.

Flux Table						
Site	101	101	109	109	110	110
Analyte unit	Hg mg	MeHg mg	Hg mg	MeHg mg	Hg mg	MeHg mg
Particulate						
Nov-April	482.8	19.1	20.6	0.4	5.0	0.1
April-Nov	2082.3	76.5	291.8	5.1	113.6	3.2
Total	2565.1	95.6	312.4	5.5	118.6	3.3
Dissolved						
Nov-April	93.5	4.6	13.5	0.3	6.6	0.3
April-Nov	911.0	97.0	48.3	1.7	63.3	4.1
Total	1004.5	101.6	61.8	2.0	69.9	4.4
2008 Total	3569.5	197.2	374.2	7.6	188.5	7.7

The greatest fluxes of Hg and MeHg from the watersheds occurred between January and August, largely because little water flowed from the watersheds between August and January. Furthermore, the majority of export occurred during a few large rain events. Approximately 70% of the T-Hg was released in the particulate phase (>0.2 um) but the MeHg was more evenly divided between the dissolved and particulate fractions. Not surprisingly, the largest watershed, watershed 101, exported the largest mass of Hg and MeHg. Both Hg and MeHg fluxes are far more dependent on flow than on concentration. In fact the flux of total Hg in all three watersheds is strongly related to flow (Figure. 4.8), as is MeHg flux, although the MeHg:flux relationship is not as strong (Figure. 4.9). Note the log:log scales in both figures. There is one interesting exception. The flux of MeHg from watershed 110 increased despite the water flow decreasing in the summer of 2008 (Figure 4.7). In this case, combined dissolve and particulate MeHg concentrations exceed 4 ng L^{-1} which we hypothesize is driven by increased MeHg production within the watershed. In the broader sense, the concentration of Hg and MeHg in stream water however, was unrelated (particulate Hg and MeHg) or inversely related (dissolved Hg and MeHg) to flow in the streams (Fig. 4.10).

Net retention of Hg by watersheds is a common finding in all watershed studies (Allan and Heyes, 1998; Harris et al. 2007). Retention simply means a loss of Hg occurs between input and export. The capacity for Hg storage or “retention time” is not well known because Hg deposition increased through the 20th century and has only recently been in decline and changes in output fluxes have not yet been documented. This is in part because long term studies of small watersheds are few in number. Other factors confound making accurate mass balances. Factors such as reemission of Hg to the atmosphere are commonly not taken into account in yield calculations. Dry deposition is difficult to measure and is also not often included in the input term. Because these measurements are also lacking in this study, for mass balance estimates deposition is limited to wet deposition and all Hg not released in export via the weir is classed as retained.

Table 4.3 Mercury yields from the SERC watershed calculated from wet deposition and weir export.

Hg Yield	Watershed 101 Hg % of precipitation	Watershed 109 Hg % of precipitation	Watershed 110 Hg % of precipitation
Winter	3.1	3.2	2.2
Summer	16.1	31.9	71.2
Total	19.3	35.1	36.5

Retention of Hg by the SERC watersheds appears to be correlated with size, with watershed 101 retaining 81% and the 109 and 110 watersheds retaining about 65% of the Hg deposited in precipitation (Table 4.3). There is a strong seasonal bias, with deposited Hg being almost entirely retained in the winter. Watershed 110 is the smallest of the studied watersheds but yields the largest amount of Hg and water. The steep nature of the watershed may promote the transfer of water via overland flow or through the near surface vadose zone during the larger storm events. Its stream channel is also the shortest. Thus one could conclude that Hg would have less chance of being absorbed. Results from the METAALICUS study of a boreal watershed (Harris et al. 2007, Hintelmann 2002), clearly indicate that Hg released from even soilless bedrock outcrops is not the same Hg that was deposited in precipitation. Rather surface and near surface flow results in the mobilization of Hg that, through decomposition, has become associated with DOM and can be exported (Hintelmann et al. 2002). It is unclear how long decomposition and remobilization of Hg takes in the mid-Atlantic region but it appears to be decades in the colder northern climates where METAALICUS is being conducted.

Table 4.4 Mercury yields per unit area from the SERC watersheds.

Yield Table						
Site	101	101	109	109	110	110
Analyte unit	Hg mg/ha	MeHg mg/ha	Hg mg/ha	MeHg mg/ha	Hg mg/ha	MeHg mg/ha
Particulate						
Nov-April	2.14	0.08	1.72	0.03	0.83	0.02
April-Nov	9.21	0.34	24.31	0.43	18.94	0.53
Total	11.35	0.42	26.03	0.46	19.77	0.55
Dissolved						
Nov-April	0.41	0.02	1.13	0.03	1.09	0.05
April-Nov	4.03	0.43	4.02	0.14	10.56	0.68
Total	4.44	0.45	5.15	0.17	11.65	0.73
2008 Total	15.79	0.87	31.18	0.63	31.42	1.28

One goal of the study was to investigate how land use and watershed size in the mid-Atlantic coastal plain influences Hg export. The lowest T-Hg fluxes came from the larger, mixed vegetation watershed 101, while the fluxes from watersheds 109 (agriculture) and 110 (forest) were about the same per unit area (Table 4.4). Despite watershed 109 and watershed 110 having different land use, the fluxes per unit area of Hg from the watersheds was almost identical. The area immediately around the streams in both watershed 109 and 110 are heavily forested which may explain this observation. Since the particulate flux is the largest portion of the overall Hg flux, the sedimentation of particulate Hg in the pond is probably part of the reason why watershed 101 has the lowest export per unit area.

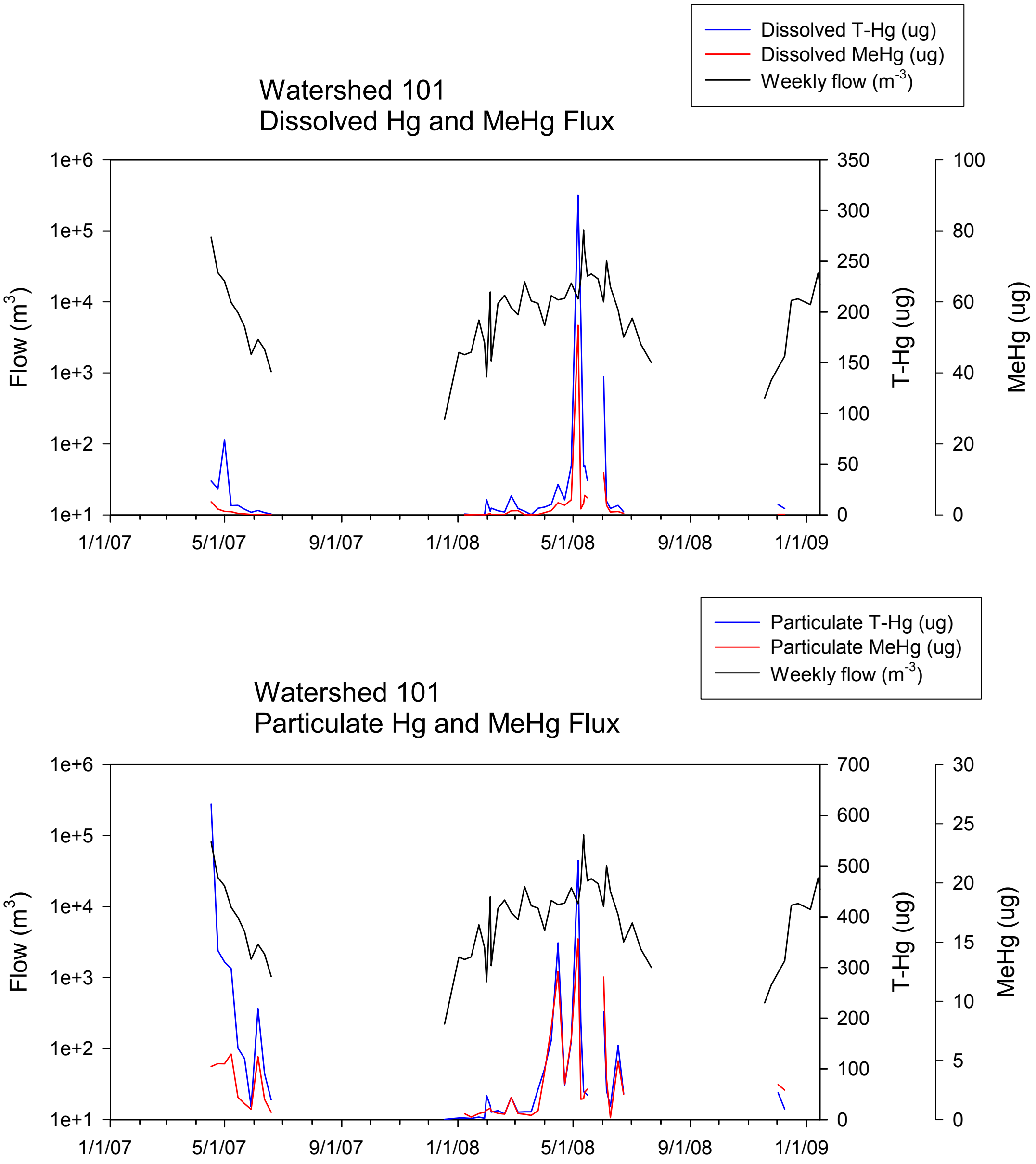


Figure 4.5 Flow weighted average dissolved and particulate fluxes of Hg and MeHg from watershed 101. Note concentrations are on a linear scale whereas flow is on a log scale.

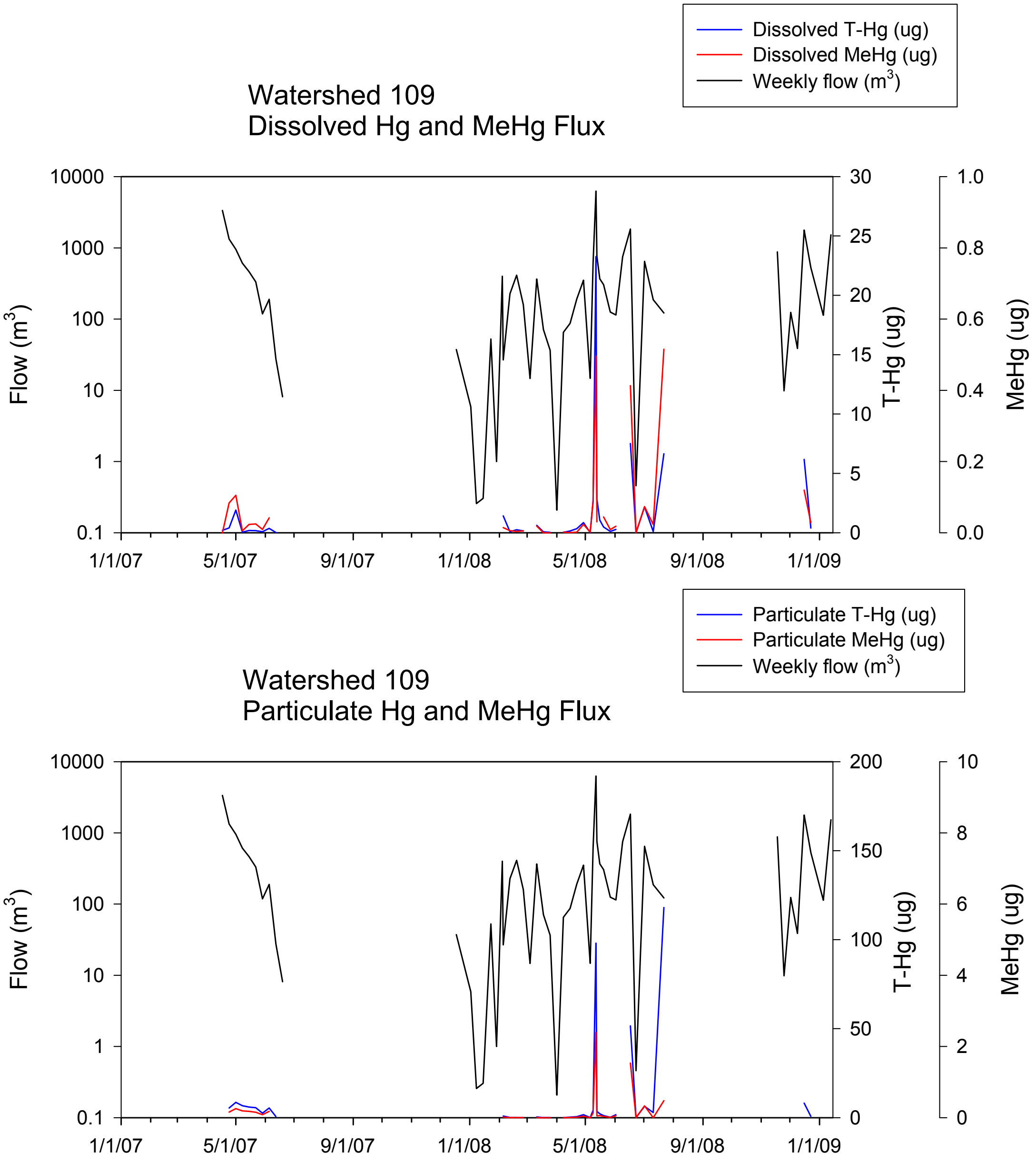
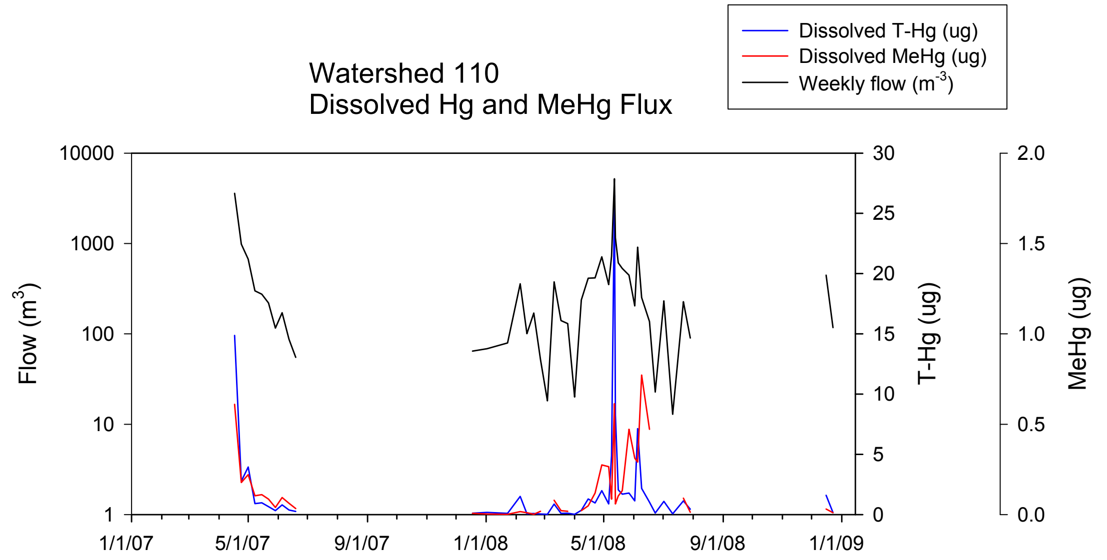


Figure 4.6 Flow weighted average dissolved and particulate fluxes of Hg and MeHg from the 109 watershed. Note concentrations are on a linear scale whereas flow is on a log scale



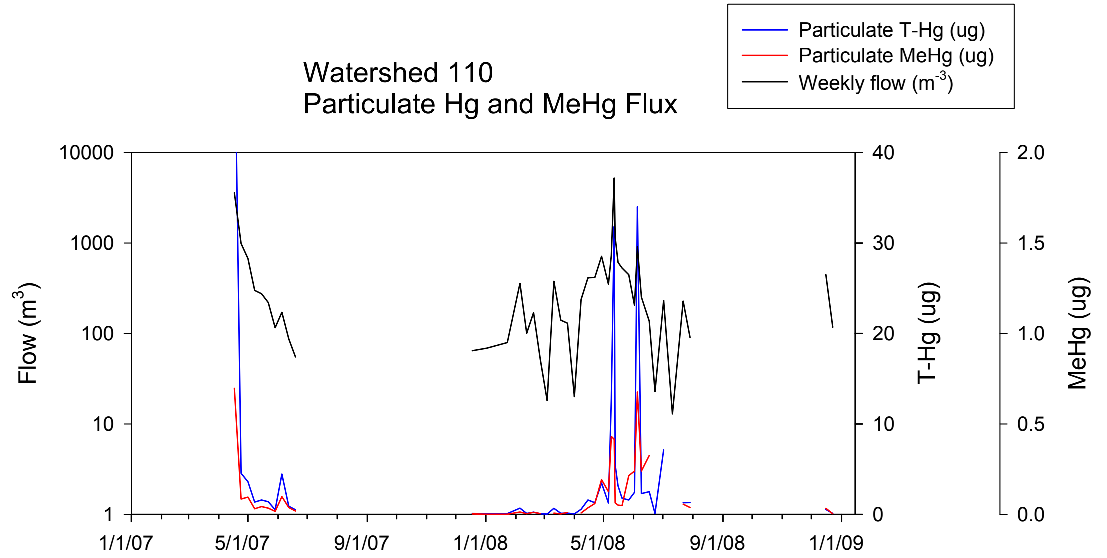


Figure 4.7 Flow weighted average dissolved and particulate fluxes of Hg and MeHg from the 110 watershed. Note concentrations are on a linear scale whereas flow is on a log scale.

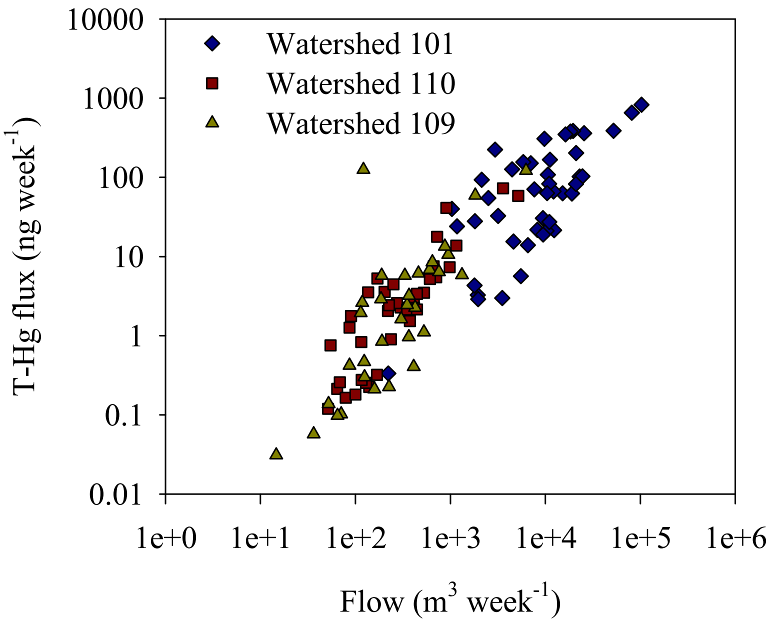


Figure 4.8 Total Hg flux (dissolved + particulate) vs flow for the three watersheds (2007-2008).

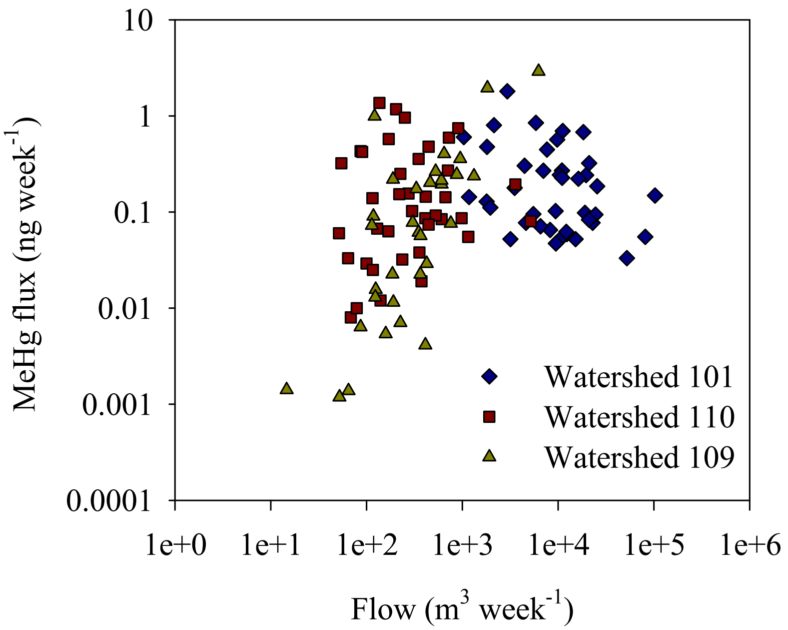


Figure 4.9 Total MeHg flux (dissolved + particulate) vs flow for the three watersheds (2007-2008).

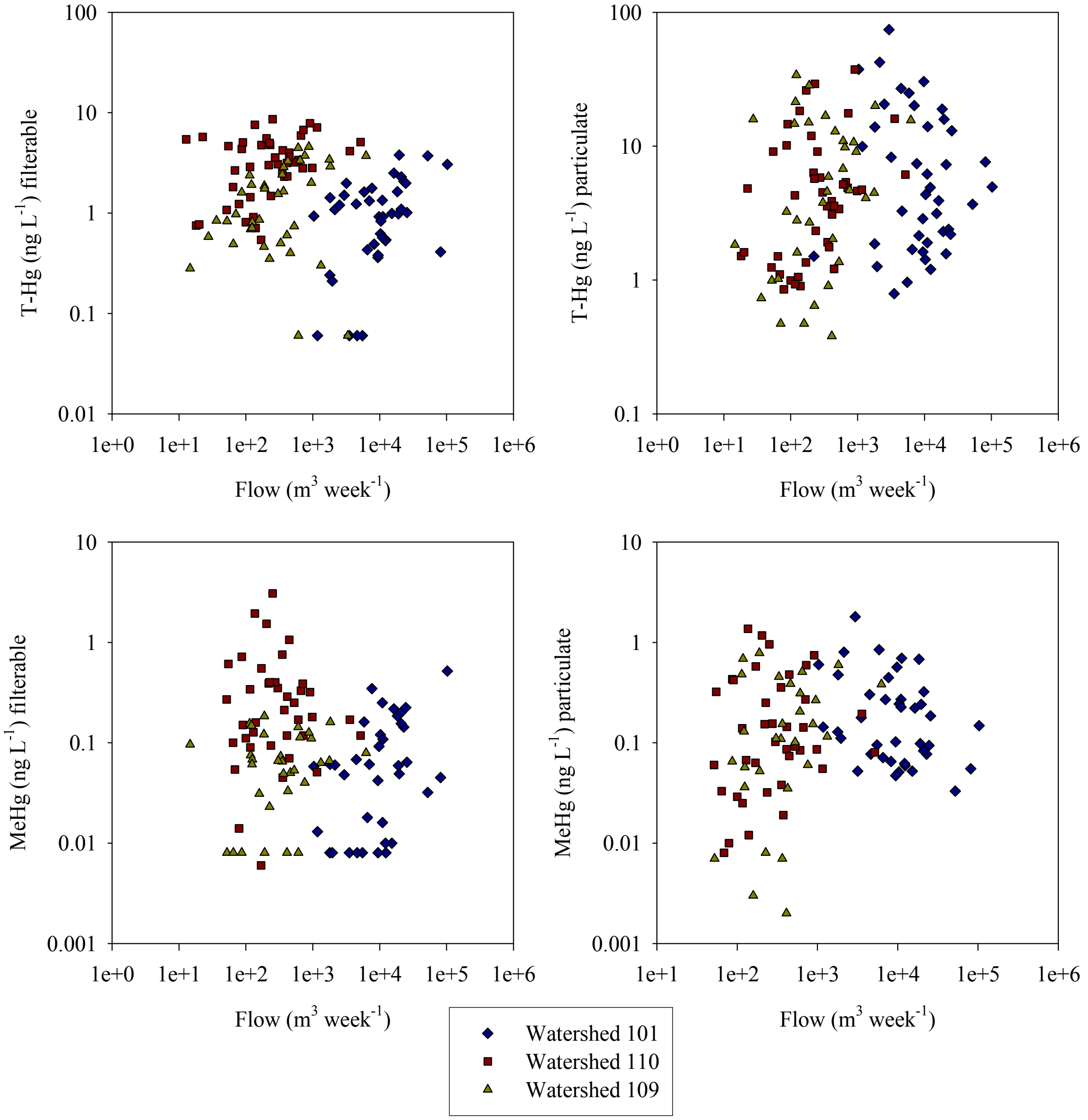


Figure 4.10 Relationships between Hg and MeHg concentrations in SERC streams and stream flow. Top left – filterable THg; top right – particulate THg; bottom left – filterable MeHg; bottom right – particulate MeHg.

4.3 Groundwater

Water entering the study streams can come from overland flow, through shallow groundwater and deeper groundwater seeps. Correll et al. (2001) indicated that while the streams were flashy, with large storms generating large amounts of overland flow, 65-70% of the stream flow is generated by groundwater. The streams in watershed 109 and 110 have deeply incised banks, near their headwaters, that yield shallow groundwater which maintains a base flow in the upper reaches of the streams for some time during dry periods. A cross section of watershed 109 is shown in Figure 4.11 and a 3d projection is shown in Figure 4.12, to illustrate the topography (From O'Connel 2000). Watershed 110 has a similar shape although smaller in terms of elevation and size. Unfortunately, no detailed topographic mapping or cross sections have been done in watershed 110.

O'Connell determined watershed 109 stream water to be between 1 and 8 years old with near bank water being generally less than 2 years old. Water ages have not been determined in the 110 watershed. However, being smaller and lower in elevation than 109, we suspect the stream water in watershed 110 to be younger than in watershed 109. Further investigation and confirmation of water ages is needed.

To establish the relative contributions of near surface groundwater to the streams, wells were installed in both watershed 109 and 110 (Figure 4.11 and 4.12). In watershed 109 wells were installed along a transect that extend from the field edge through the forest and across the stream channel. This was done to intercept the water as it neared and entered the stream. In watershed 110, three well transects were established bisecting the stream at different points along the channel. Wells were placed in the stream channel, adjacent the channel in the stream bank and at up slope locations. Two wells were installed side by side; one for sampling and a second with an Odyssey® water level recorder. Odessey® recorders use a capacitance approach to record water height along a cable. Changes in the charge to potential difference ratio are driven by the amount of water in contact with a length of wire. Thus, as water moves up and down in the well the capacitance changes in relation to the water level in the tube. The height was recorded every 10 minutes which allowed rapid changes in ground water to be recorded. In total there were 19 groundwater instillations in the two watersheds. This approach allows many locations to be measured as the units are "stand alone". We did experience some difficulties with the loggers. During the summer, high humidity disabled some loggers or caused sharp fluctuations in the measurements. Winter ice also caused erroneous readings. Thus, the loggers required more maintenance than anticipated and filtering of the data. In this report, the well heights are referred to an arbitrary datum (the top of the well) and are currently used to show changes in the local groundwater level. In the future, data will be used to calculate groundwater fluxes once the hydrologic conductivity of soil and sediment layers is determined.

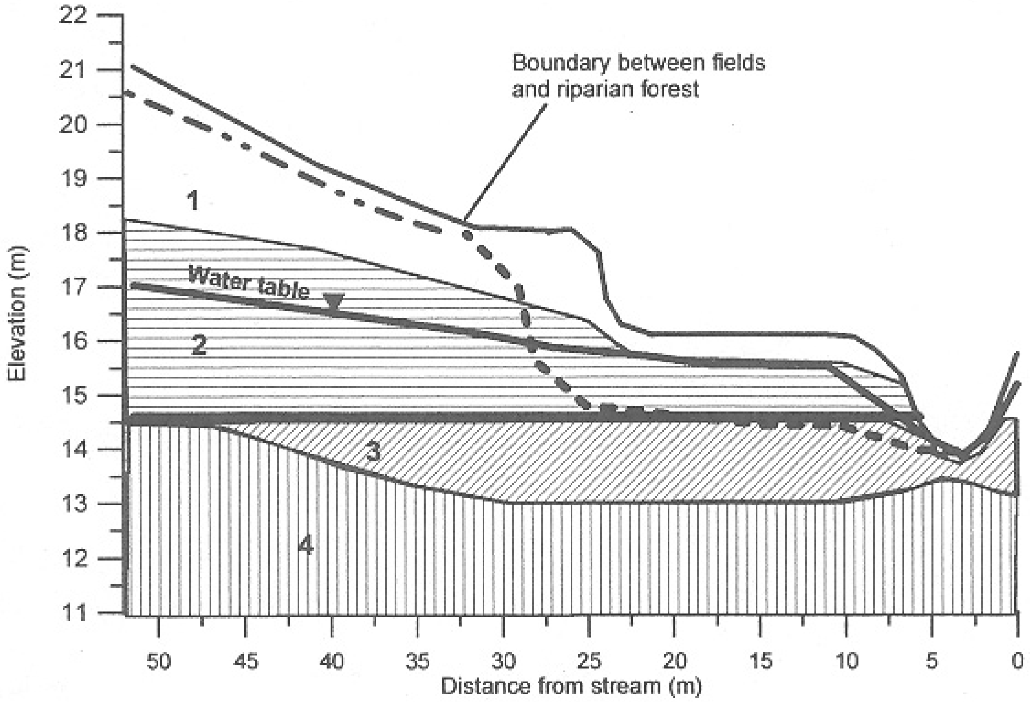


Figure 4.11. Cross section of sediments in the 109 watershed near the sampling transect in this study (modified from O'Connell (2000).

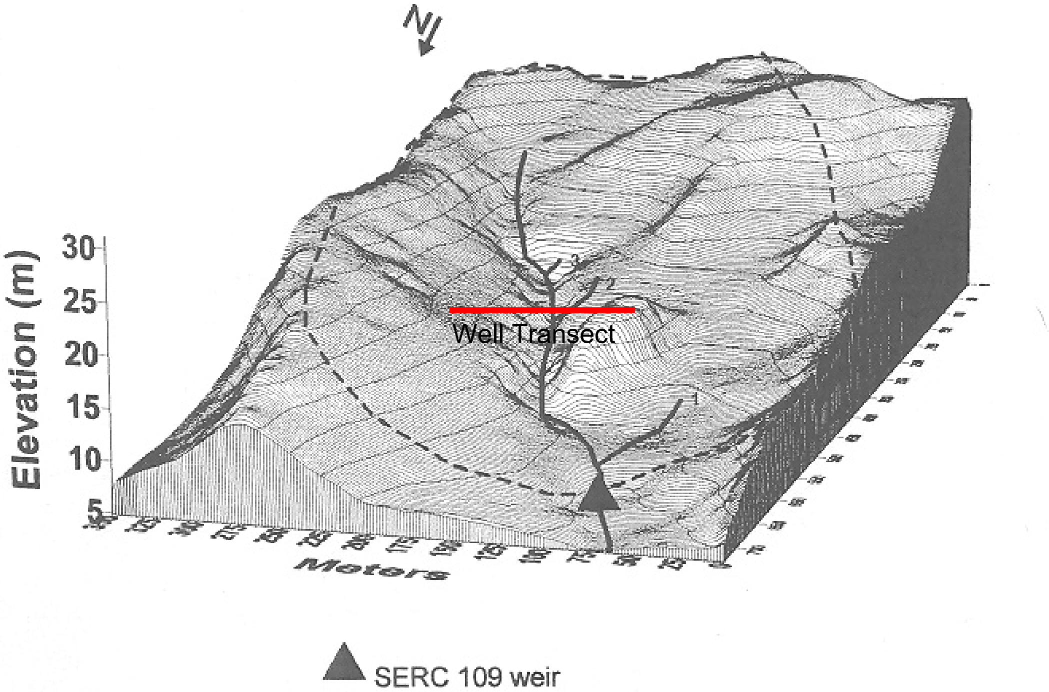


Figure 4.12. 3D rendering of the 109 watershed with location of the well transect (modified from O’Connell 2000).

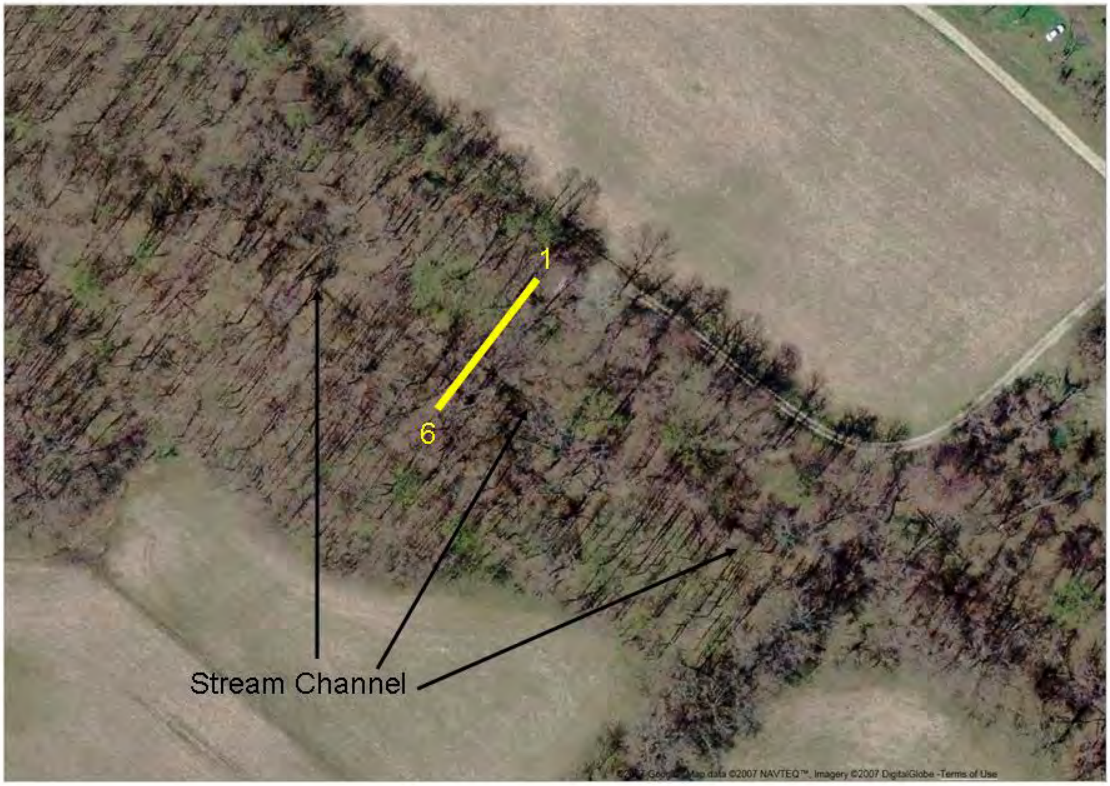


Figure 4.13 An aerial perspective of the well transect in the 109 watershed (picture from Google Earth).

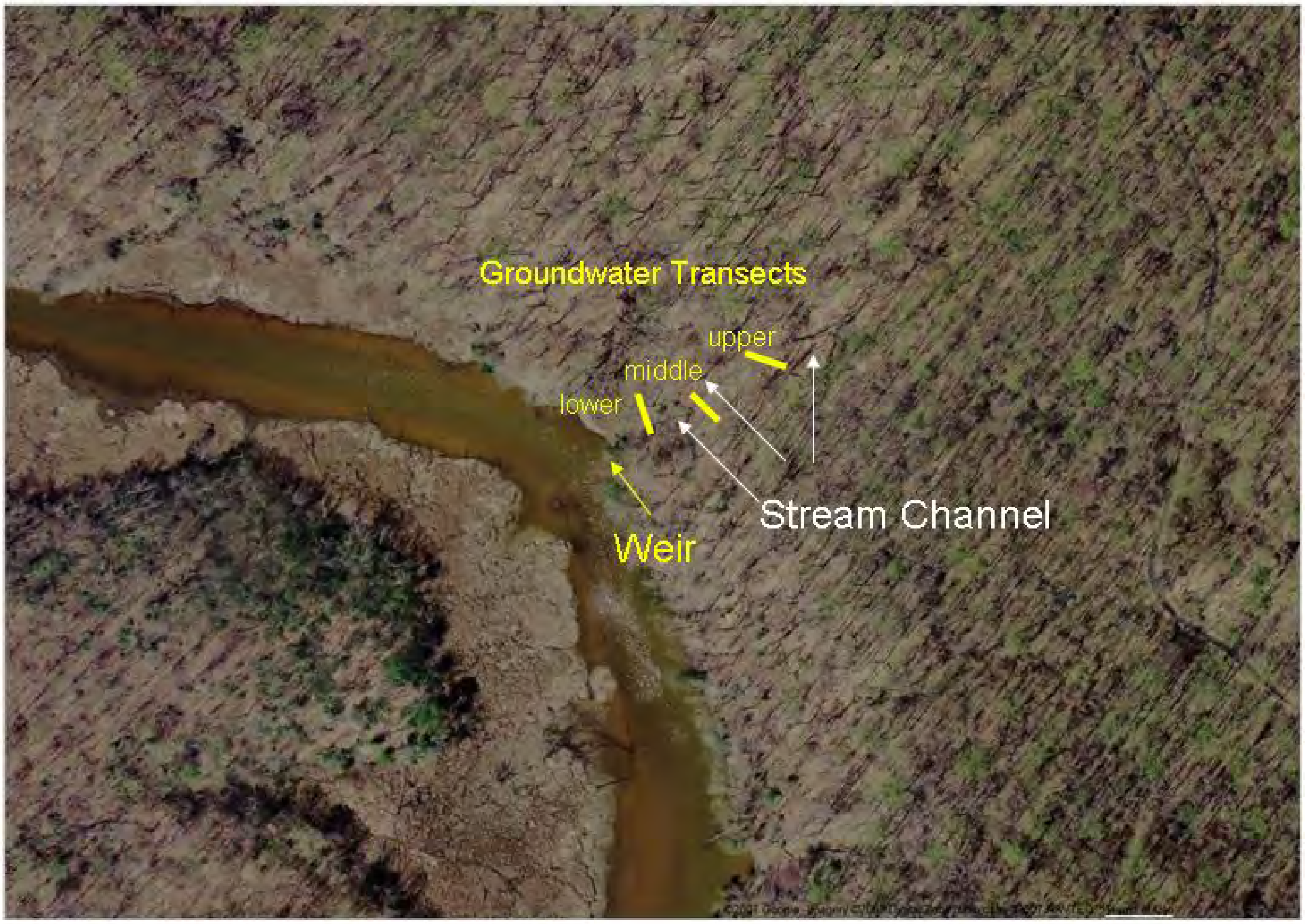


Figure 4.14. An aerial perspective of the groundwater instillations in watershed 110. Three transects indicated by the yellow lines have been established along different degrees of slope (picture from Google Earth).

4.3.1 Watershed 109

The well transect at 109 consists of a deep 4 m well (Well 1) located upslope at the edge of the forest and agricultural field, a deep 3 m well (Well 2) located mid way down the slope in the forest, a 1.5 meter well located in the stream bank (Well 3), a well in the stream bed (Well 4), a well located on the flood plain (Well 5), and a deep 3 m well located midway up the forested slope (Well 6) (Figure 4.11 and Figure 4.13). The goal was to intercept groundwater moving toward the creek from the large farm fields located up the slopes (Figure 4.11). The loggers in Well 1 and Well 4 were both problematic and failed multiple times during the study. The remaining wells functioned for the majority of the study period (Figure 4.15). Dry periods in figure 4.15 are denoted with circled areas and breaks in the lines indicate periods where data was lost. There is also a vertical drift in the base lines of water level plots probably caused by sedimentation in the wells.

The slope and bank wells responded differently to precipitation events than the stream well. Fluctuations of a few centimeters were recorded in the slope wells, with the largest responses coinciding with large precipitation events. However, some precipitation events generated little response, especially in the summer when the watershed was receiving less consistent rain. The most consistent water level responses to rain events occurred during the spring which can be seen in the proportional responses of the wells (Figure 4.15). Water levels fell below the bottoms of Wells 2, 3 and 5 during the late summer of 2007 and again in 2008. The water in the stream well fluctuated over a range of more than a meter and was unresponsive to small rain events. As suggested by O'Connell, the 109 watershed appears to store water up slope providing water to the stream between rain events but not for prolonged periods as the stream dried up in both 2007 and 2008. The watershed responds relatively quickly to rain events, with the flux dependent on antecedent moisture conditions.

The T- Hg concentrations in groundwater across all the wells ranged from 0.3 to 7.0 ng L^{-1} (Figure 4.16). The concentration of T-Hg groundwater from the deep wells, (1 and 6) was similar to the concentrations in Well 4, located in the stream bed. Groundwater from the shallow groundwater in the stream banks (wells 2,3,5) tended to be higher in T-Hg concentration. Dissolved T-Hg concentrations in the stream water averaged 1.6 ng L^{-1} at the weir over the 2007-2008 period and 1.9 ng L^{-1} during the shorter period that the wells were sampled. In a longitudinal transect along the stream channel in April 2008, dissolved T-Hg concentrations from 5 locations averaged 3.1 ng L^{-1} which was similar to the ground water at the time. Given the stream water Hg concentrations reflect the groundwater concentrations, we hypothesize the majority of water entering the stream comes via the bed sediments and little bank-water stream water mixing occurred in 2008.

Concentrations of MeHg in groundwater of watershed 109 ranged from undetectable to 4.5 ng L^{-1}(Figure 4.17). Concentrations of MeHg where highest in the stream banks (wells 2,3 5) indicating the banks are most likely the sites of MeHg production. Concentrations of MeHg in the stream water itself were extremely low, being 0.04 ng L^{-1} in the vicinity of the wells and 0.08 at the weir. The low concentration of MeHg in the stream water further supports the hypothesis of limited interaction between the bank water and stream water.

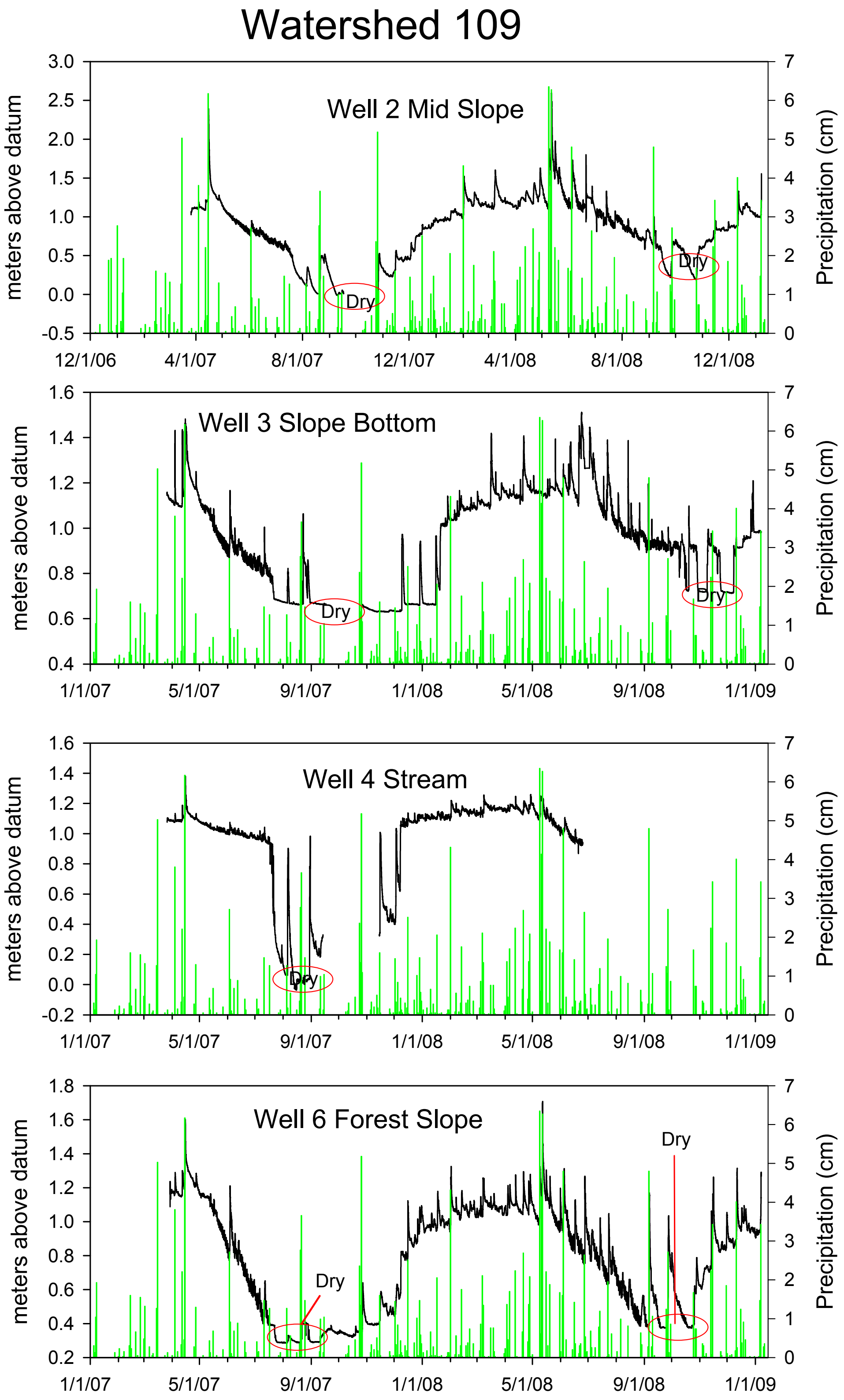


Figure 4.15 Response of water levels to precipitation events in the groundwater of watershed 109. The Datum is arbitrary for each site.

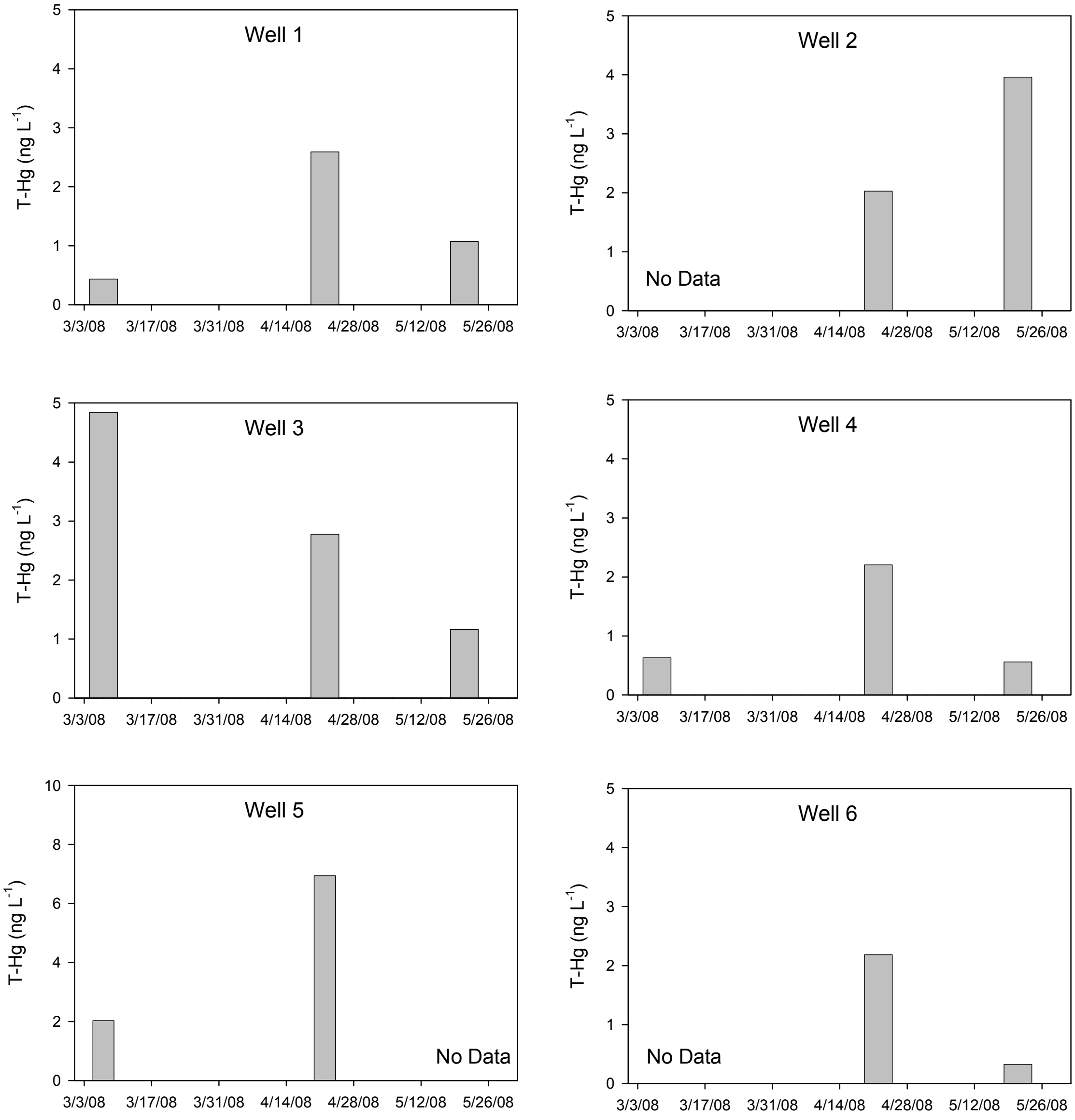


Figure 4.16 Concentrations of T-Hg in the groundwater of watershed 109.

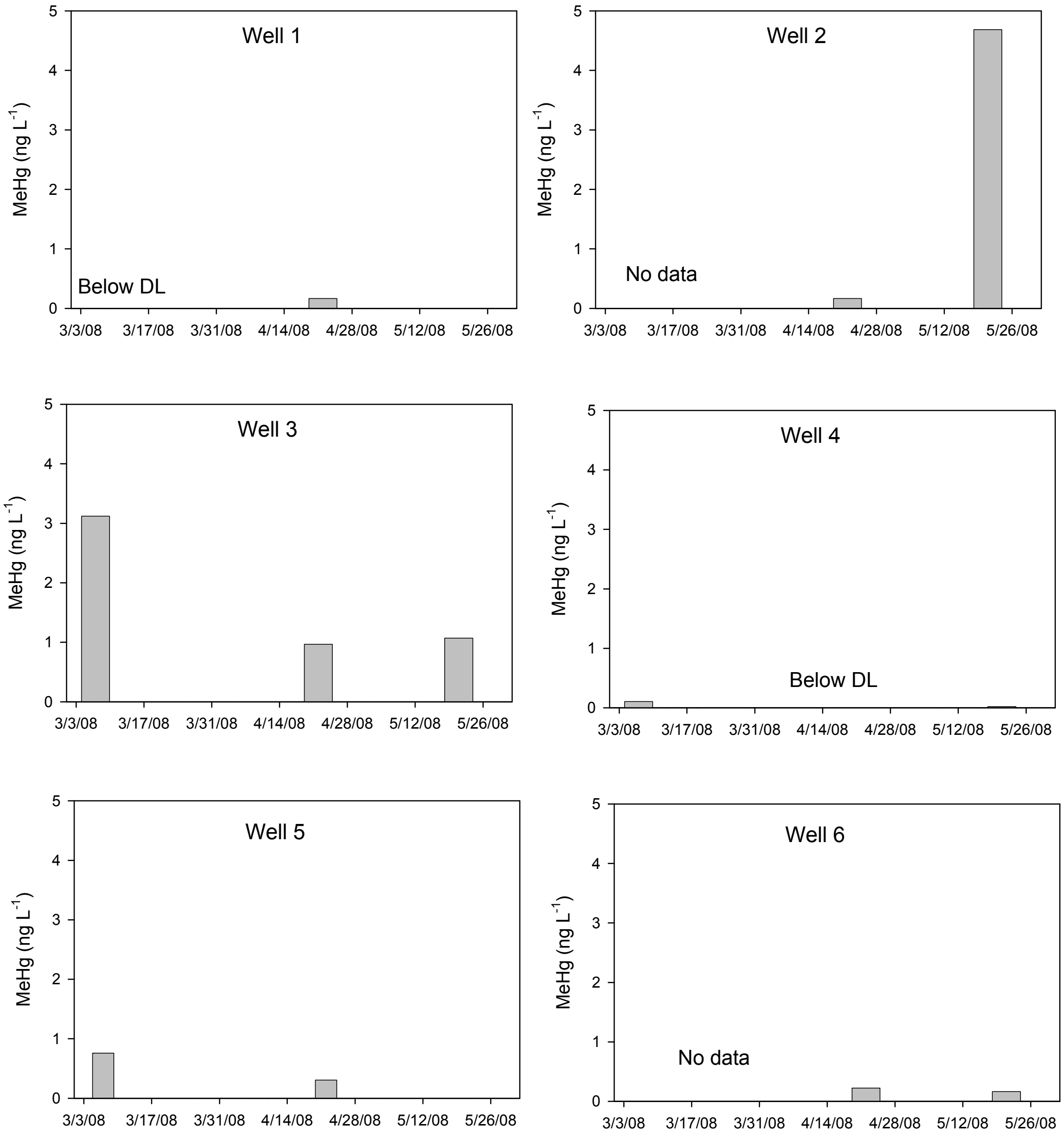


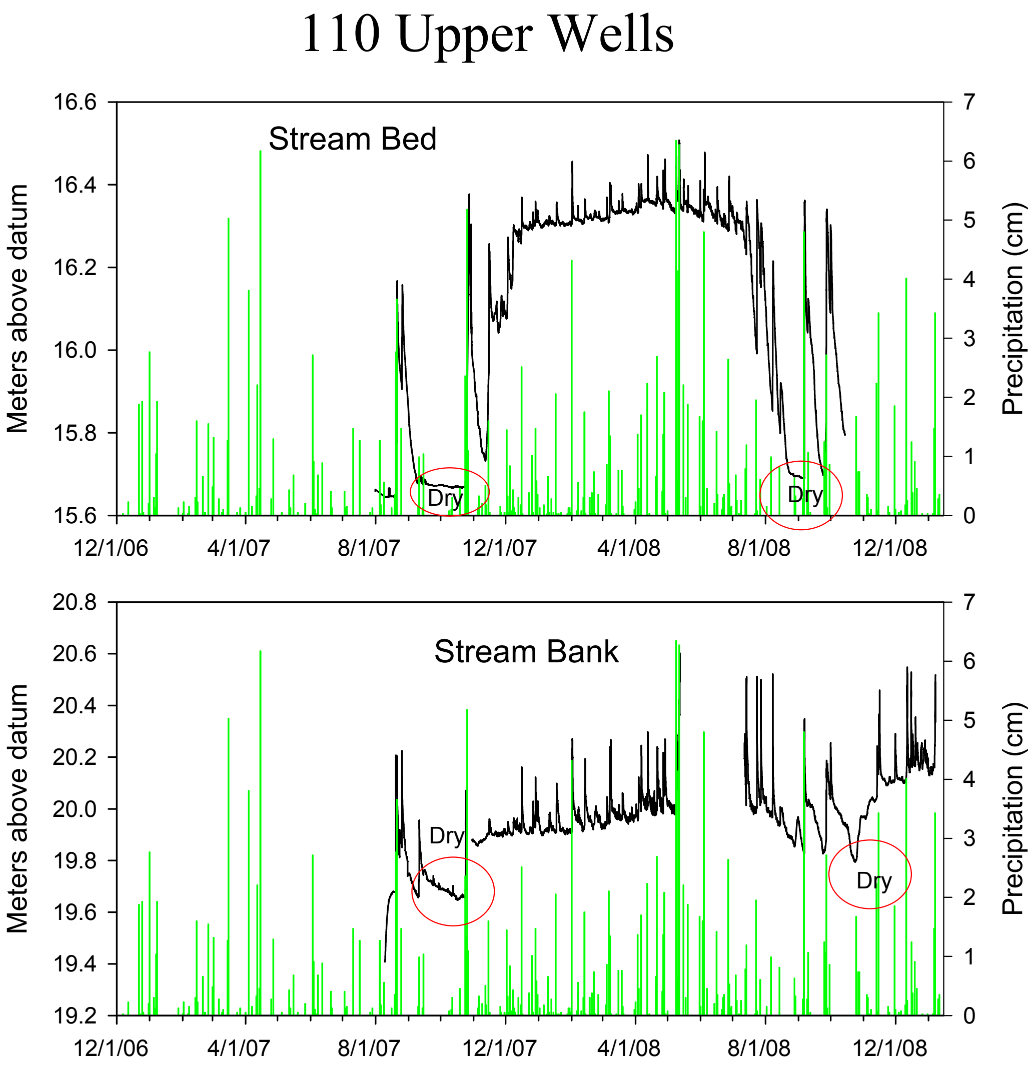
Figure 4.17 Concentrations of MeHg in groundwater of Watershed 109.

4.3.2 Watershed 110

The wells placed in watershed 110 were installed in three groups at different topographical positions along the length of main stream channel (Figure 4.14). An upper watershed site (Upper Wells) was established where steep slopes converged on a 50 cm wide 50 cm deep incised stream channel. At this location, wells were placed in the stream bed, stream bank and a small channel or rivulet, which funnels surface flow during large rain events. The water levels in the wells responded very quickly to rain events but the magnitude of the response was small, just a few centimeters and of short duration (Figure 4.18). The durations were so short that many events would not have been detectable using manual measurements. The data logger in the rivulet performed poorly over the period and is not shown. As discussed earlier, some data gaps occurred because of logger failure (gaps in lines) and the water table dropped below the level of the wells on occasion (indicated by red circle and dry) (Figure 4.18). At some sites the loggers were periodically plagued by humidity, which resulted in erroneous or noisy data. An example of this problem is shown in Figure 4.19 (Bank well) where the late summer decline in the water table (red box) in the stream bank is marred by interference.

A second site was established midway down the watershed, at a point where the watershed slope diminishes and the channel becomes less incised. A flood plain of sorts develops at this location. Wells were placed in the stream bed, the bank and on the flood plain. At the lower portion of the watershed, wells were placed in the stream channel and the stream bank. The data loggers at these sites recorded throughout the study period (Figures 4.19 and 4.20). While individual rain events are recorded in all the wells, the responses do not appear to be proportional to increases in storm size. This was particularly evident in the large summer (2.6) cm rain event on June 17, 2008. We interpret this to indicate either the vadose zone is highly porous and water can not accumulate in the zone or a large amount of water enters the stream via overland flow.

As in watershed 109, all the wells in watershed 110 showed a seasonal pattern of falling water tables in the summer and water table recharge in the winter. In fact, the water table fell below the bottom of the wells late in the summer and the watershed (flow at the weir) did not respond to rain events as the precipitation went entirely to recharge.



110 Upper Wells

Figure 4.18 Groundwater levels and response to precipitation in wells from watershed 110 upper site.

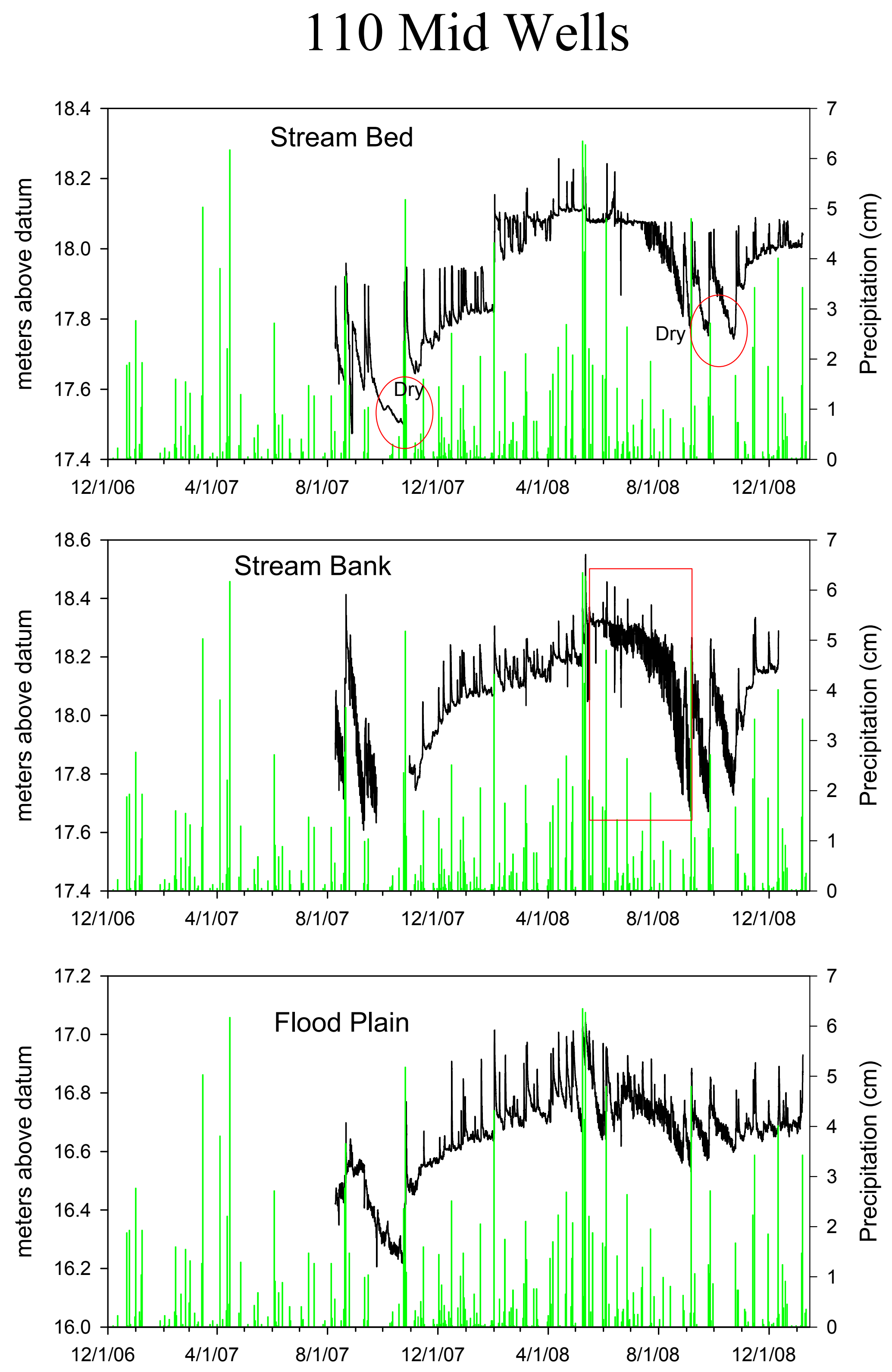


Figure 4.19. Groundwater levels and response to precipitation in wells from watershed 110 middle site.

Lower Wells

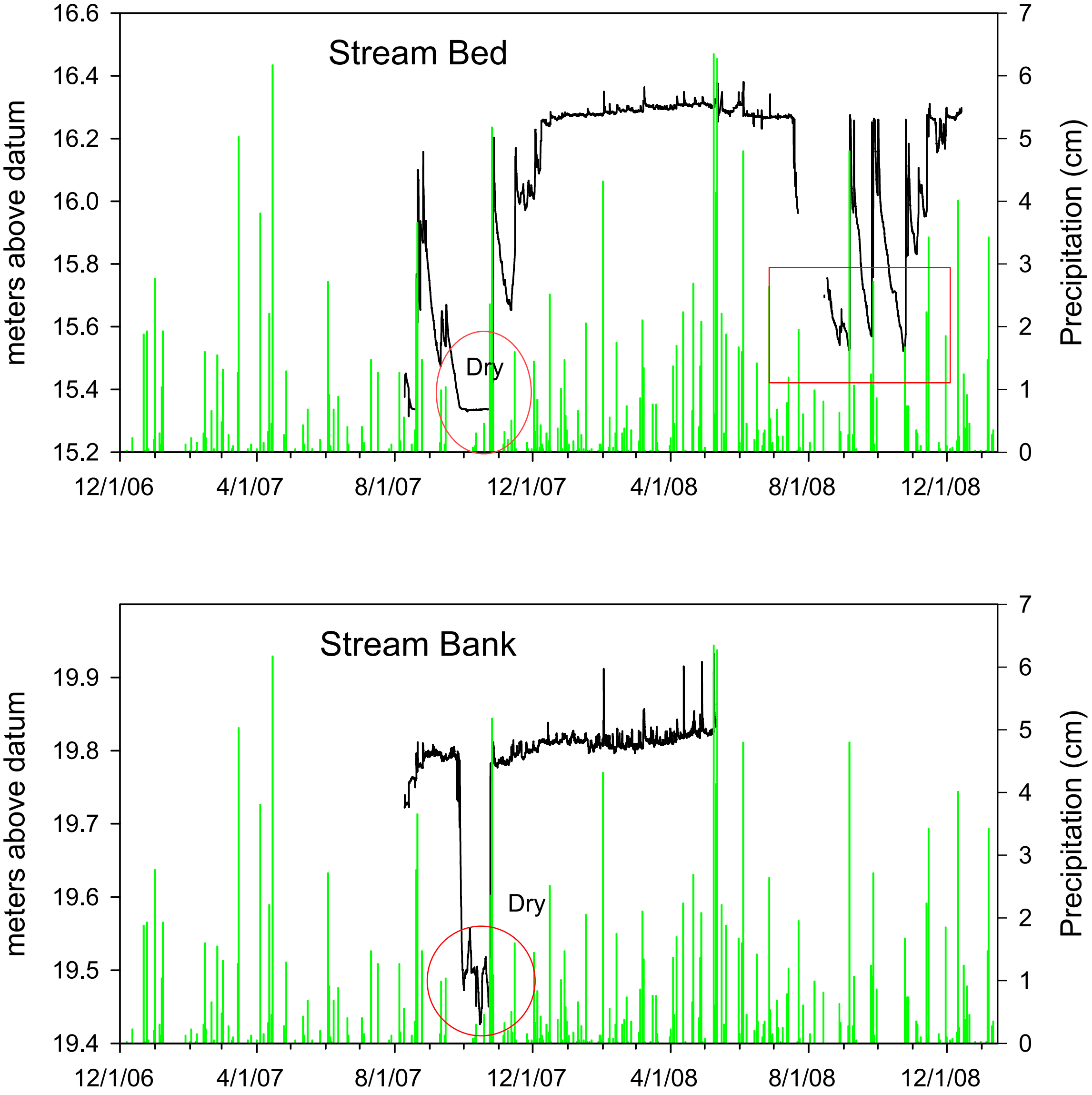


Figure 4.20 Groundwater levels and response to precipitation in wells from watershed 110 lower site.

The wells in watershed 110 were sampled for Hg and MeHg from March through May 2008. Water levels fell dramatically in the summer which made the broad scale collection of samples impossible. Over the March to May period both T-Hg and MeHg concentrations in the shallow groundwater demonstrated great variability in time and space. Concentrations of T-Hg ranged from 0.38 to 14.7 ng L^{-1} and MeHg ranged from undetectable to 12.9 ng L^{-1} (Table 4.5). While variation in MeHg concentration were expected because of biological influences on MeHg production, the large temporal variation in T-Hg concentration was more surprising. Both T-Hg and MeHg increased in concentration between March and May almost entirely regardless of location. For example, in the Upper Site bank well, T-Hg increased from 6.6 to 13.9 ng L^{-1} and MeHg increased from 0.1 to 7.7 ng L^{-1} (Figure 4.21). For this to have occurred, either new water entering the groundwater was elevated in both Hg and MeHg concentration and/or Hg and MeHg are released from the soil to the groundwater of which a very large portion (>50%) is MeHg. While the groundwater level increased through recharge over the winter, it did not increase dramatically. Therefore, the change in concentration was likely not related to a sudden change in water source. The *in situ* methylation of Hg bound to soil and release of the MeHg into groundwater could explain the increase in both MeHg and T-Hg, given the very high percent MeHg in the groundwater samples. While the partition coefficient of MeHg is generally an order of magnitude less for MeHg than inorganic Hg, we would expect a change in chemistry to influence both Hg and MeHg adsorption, which does not appear to be the case (Heyes et al 2006). The complexation of MeHg in porewater by Dissolved Organic Carbon (DOC) may further its ability to stay in the "dissolved" phase. We hypothesize the increase was in fact driven by enhanced methylation of Hg stored in the bank soils and released to the groundwater.

As was observed in watershed 109, concentrations of both dissolved T-Hg and MeHg were lower at the stream weir than in the ground water. In fact transects along the stream show a steady decrease in Hg from the headwater to the weir (Figure 4.22). Dissolved concentrations of MeHg were also high in the bank and rivulet sites in the upper watershed, but lower in the stream bed. Concentrations were also high in the bank and stream bed of the lower site and bed of the stream bed of the mid site. Lower MeHg concentrations were present in mid bank and flood plain sites. These waters tend to be less colored. We believe infiltration of deeper groundwater, such as observed in these wells, occurs along the stream channel diluting the Hg and MeHg concentrations released from microbial activity in the near stream zone. To truly investigate this phenomena, water aging and mixing studies are required.

Table 4.5 Concentrations of Hg and MeHg in groundwater collected from wells in the 110 Watershed.

Upper Site									
	Stream Bed			Stream Bank			Rivulet		
Date	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg
3/7/2008	0.4	0.0	0.0	6.6	0.1	1.8	0.4	0.2	39.5
4/22/2008	1.3	0.2	11.3	8.1	0.0	0.0	7.3	0.1	1.1
5/14/2008	4.4	1.1	25.1	5.9	4.8	81.6	13.1	10.4	79.2
5/21/2008	3.3	1.6	49.0	13.9	7.7	55.1	10.2	4.4	43.1
Middle Site									
	Stream Bed			Stream Bank			Flood Plain		
Date	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg
3/7/2008	0.5	0.0	0.0	0.3	0.0	0.0	1.4	0.0	0.0
4/22/2008	6.5	No data	No data	1.6	0.1	5.4	0.6	0.0	8.1
5/14/2008	14.6	12.9	88.3	0.6	0.4	69.9	1.3	0.3	22.7
5/21/2008	12.0	3.3	27.6	2.7	0.3	11.0	1.4	0.6	46.2
Lower Site									
	Stream Bed			Stream Bank					
Date	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg	T-Hg ng/L	MeHg ng/L	MeHg % T-Hg			
3/7/2008	2.4	1.0	41.8	4.4	1.9	42.2			
4/22/2008	3.4		0.0	10.0	0.2	2.3			
5/14/2008	8.3	6.9	83.3	5.7	4.7	83.3			
5/21/2008	10.2	7.0	68.6	14.7	8.7	59.1			

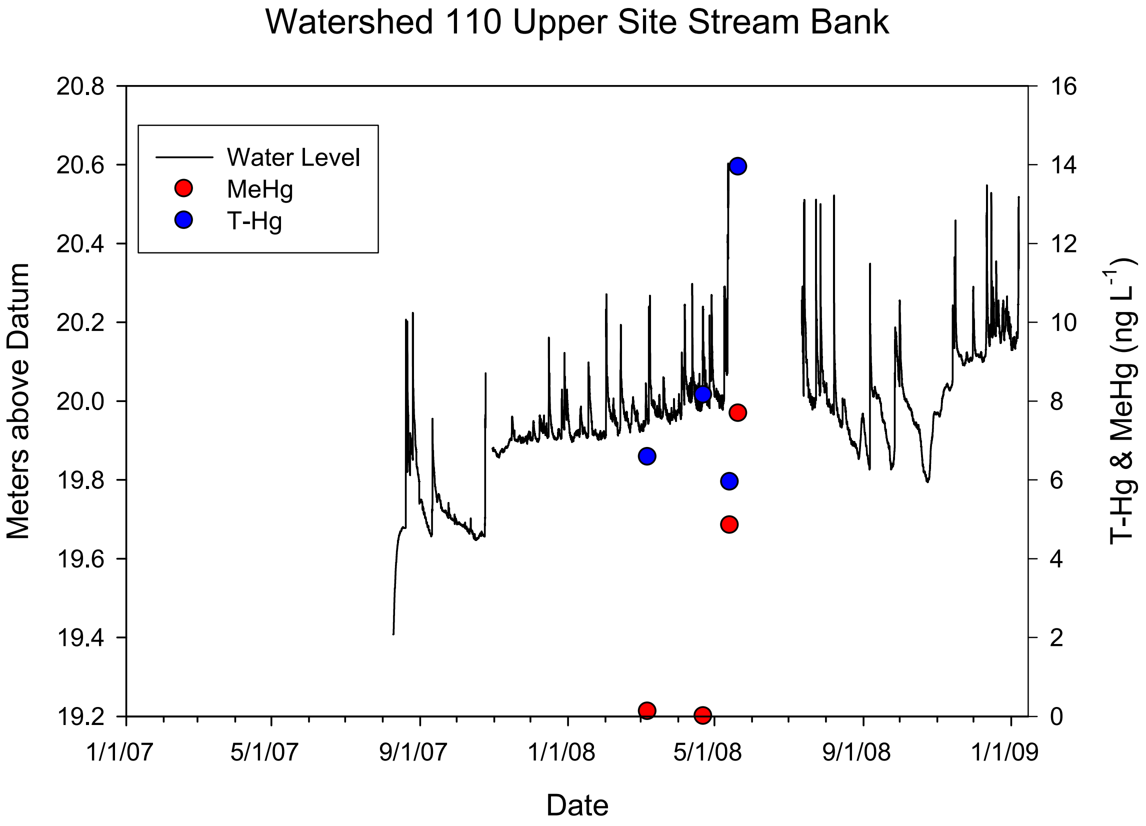


Figure 4.21 Water table elevation and concentrations of Hg in groundwater of the well located in the stream bank of the upper site. The break in the water level data is the result of instrument failure.

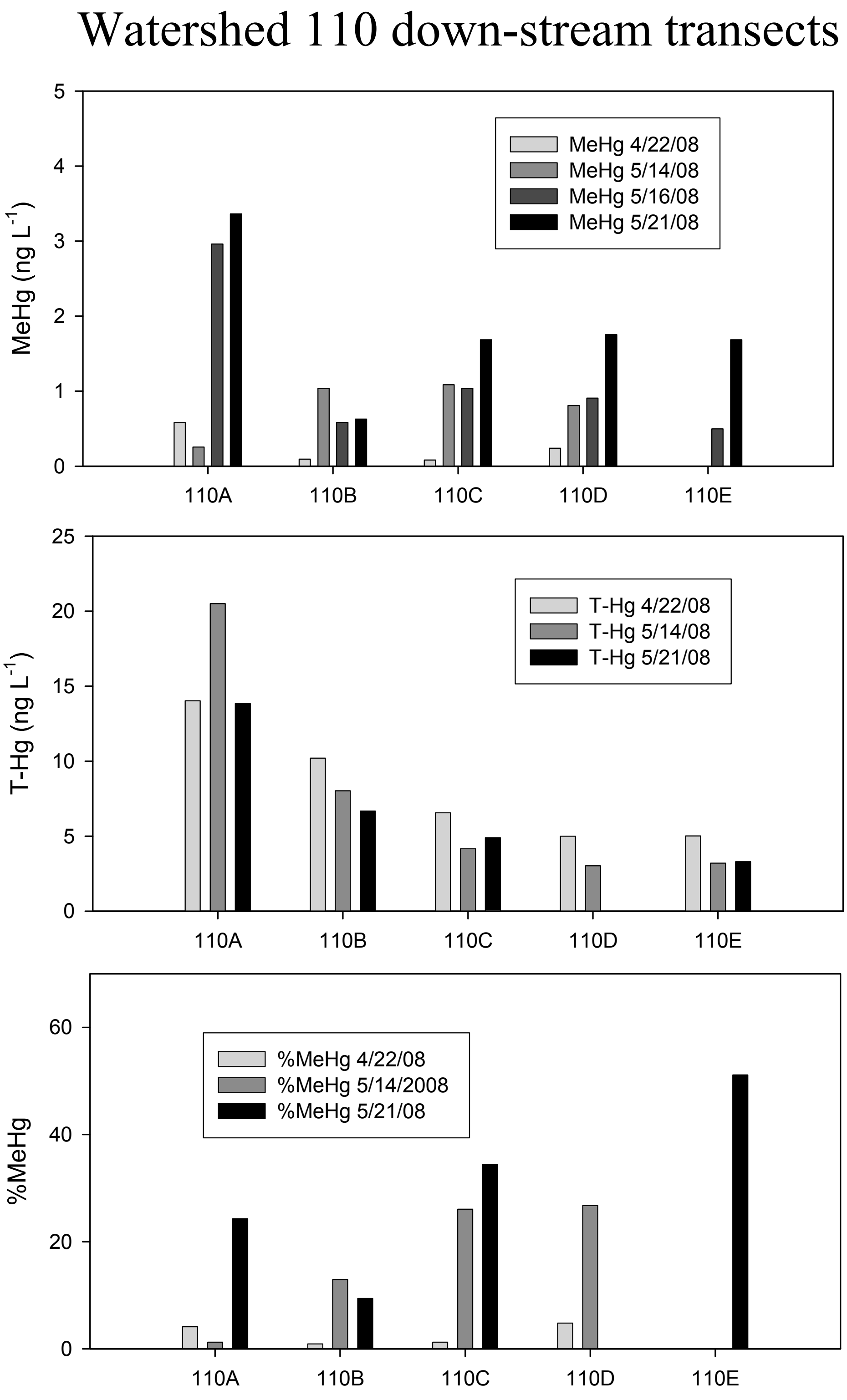


Figure 4.22 Concentrations of Hg and MeHg along the 110 stream channel in April and May of 2008.

5.0 Summary and Discussion

SERC watersheds The small to mid-sized mid-Atlantic watersheds studied produced relatively high yields of both water and Hg. We found substantial production and flux of MeHg in all three of the watersheds. Our well and stream transect studies suggest that a substantial fraction of MeHg is produced in stream banks/riparian zones.

There are a few documented examples of high %MeHg (the percentage of total Hg as MeHg) in riparian, streambank and hyporheic waters (Bishop et al. 1995; Skyllberg et al 2003; Stoor et al. 2006), but wetlands are generally thought of as the main zones of MeHg production in terrestrial watersheds (Munthe et al. 2007; Selvendiran et al. 2008). Stoor et al. (2006) showed that groundwater is an important source of MeHg to two streams that drain into Lake Superior. They suggested that MeHg is produced during periods when groundwater is anoxic, and pushed into streams during the next high flow period. That is consistent with what we are observing in Rhode River watersheds. Although a pulse flux of MeHg from the hyporheic zone is likely, the actual process and effect of shifting redox on the quantity and flux of MeHg remains to be demonstrated.

All three of the watersheds studied are subwatersheds of the Rhode River, a tidal tributary to the Chesapeake Bay in Maryland, U.S.A. Soils in this region are characteristically highly erodible. Precipitation often comes in frequent intense events in spring and summer and intense storms generate overland storm flows (Correll et al. 2001). Nevertheless, Correll et al. (2001) estimated that 65 to 75% of annual water discharge in these watersheds is via (generally shallow) groundwater. The nature of the watersheds is such that overland flow and groundwater discharges move into the stream bed draining each watershed.

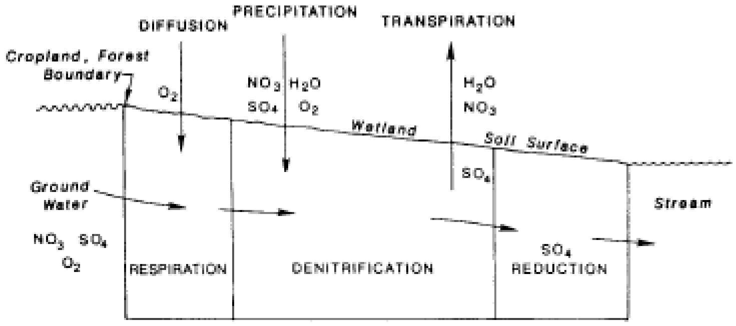


Figure 5.1 Conceptual model of belowground processes affecting groundwater composition in the riparian forest at Watershed 109 (from Correll and Weller 1989).

A small number of events have a great influence on the Hg flux. Surprisingly in 2007 and 2008, these were summer storms, with the winter acting mostly as a period of recharge. Observation of flow from these and other SERC watersheds have more varied patterns in discharge (Jordan et al. 1997). Since the water discharge pattern of 2007 and 2008 repeated, we must consider this the climate norm on which to base sampling in

2009 and 2010. This has important ramifications as the quantity of sampling that can be done is limited. The sampling regime will again be revisited in 2011.

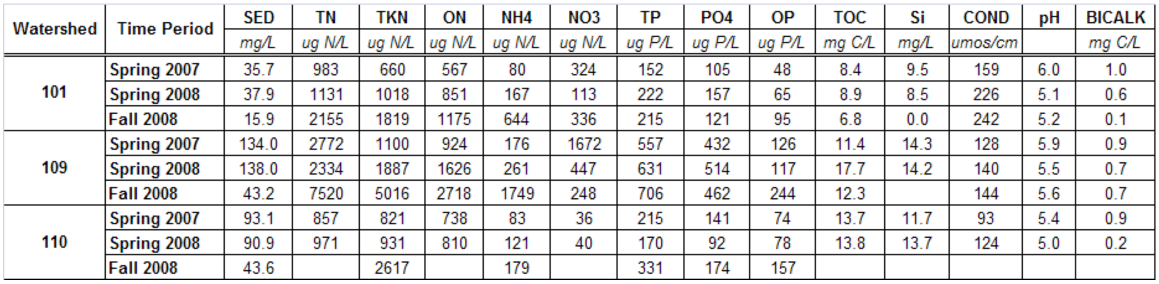
In general, fluxes of mercury and methylmercury from the watersheds are influenced by a number of factors. Watershed size is the dominant control on the total flux of both MeHg and T-Hg, but the organization of the streams and the specific catchment morphology play an important role. The large pond at the base of watershed 101 acts as a particle sink and we assumed the pond and its associated wetlands would result in the highest MeHg exports from this watershed. While this is true with regard to total mass of MeHg, watershed 110 released the most MeHg per unit area. Watershed 110 is dominated by forest and has not been used for agriculture. The steep stream banks and beds in watershed 110 were extremely effective in producing MeHg. While watershed 109 has a large area of forest around the stream (5 ha) and similar bank structure, MeHg yield was half that of watershed 110. The stream bed in 109 is made up largely of sand whereas the bed in 110 contains more organic matter indicating there are differences in local conditions that could influence Hg methylation. In both cases, but perhaps to different degrees, a significant amount of event water must move or interact with the bed and bank water prior to exiting the watershed.

Correll and Weller (1989) developed a conceptual model of belowground processes in Watershed 109, based on water chemistry in a series of well transects. By examining the concentration of terminal electron acceptors in space and time, they concluded that the riparian zone grades from a region that supports oxic respiratory process at the top of the slope near the agricultural fields, through a reduced zone where denitrification occurs, and finally, near the stream, a more reduced zone where sulfate reduction occurs (Figure 5.1). These zones vary seasonally and with flow. The reduced zone would be largest when the riparian zone is saturated, during warmer months that support more biological oxygen demand. The stream water chemistry measured at the weir supports such a hypothesis as the peak in MeHg concentration occurs following a depletion of nitrate and sulfate and coincides with an increase in ammonia (Figure 5.2, 5.3 and Table 5.1). High concentrations of dissolved organic matter in shallow groundwater support high rates of microbial activity. Nitrate and sulfate budgets for the riparian zone in this watershed show substantial nitrate removal in all seasons (presumably denitrification), but lower percentage of sulfate removal (presumably microbial sulfate reduction). Sulfate removal occurred most noticeably in spring and early summer. Nitrate and dissolved oxygen levels were also lowest in the riparian zone near the stream in spring. These findings are preliminary and based on only a small sample size and “watershed integrated” results obtained from the weir.

While others have observed the importance of bank water to MeHg fluxes from watersheds, such as Bishop et al. (1995) and Rool et al. (2006), the variations in MeHg productivity based on the seasonal distribution and amount of precipitation have only been hypothesized, not documented. For the Mid-Atlantic region, variations in precipitation amount and temporal distribution are likely significant, thus we must better understand the importance of these processes and how they relate to MeHg production and flux. If we assume the concentration of Hg in riparian porewater is controlled by Hg deposition, and not repartitioning of stored Hg to the groundwater, we would expect a large decrease in MeHg concentration in the banks as MeHg comprises such a high proportion of T-Hg in the groundwater. If the porewater Hg is controlled by partitioning of Hg from old stores, the flux of Hg may last for a substantial period post changes in Hg deposition. However, the total store of Hg is unlikely to be available for export, but rather some much smaller exchangeable pool, the size of which has not been determined.

To date, the greatest MeHg fluxes and concentrations occur during the spring and early summer where they might have the greatest influence on developing organisms. Laurier et al. (2007) implied that MeHg bioaccumulation in coastal mussels in France is related to coastal groundwater discharge zones. They found high Hg concentrations during times and periods of high discharge, but did not examine MeHg concentrations in discharge. Organisms that inhabit the SERC watersheds, such as amphibian larvae, would be exposed to high levels of MeHg during development. With such high variation in MeHg concentrations in spring less detailed sampling would not allow for accurate measurements of exposure. Accumulation of MeHg by amphibians provides a vector for the transfer of MeHg to the terrestrial ecosystem.

Table 5.1 Preliminary average stream water chemistry for the three study watersheds (2008). All analytes are total concentrations in unfiltered monthly flow-weighted composite samples, averaged across the time period, except pH, conductivity and alkalinity, which were measured from fresh grab samples.



Watershed	Time Period	SED	TN	TKN	ON	NH4	NO3	TP	PO4	OP	TOC	Si	COND	pH	BICALK
		mg/L	*ug N/L*	*ug N/L*	*ug N/L*	*ug N/L*	*ug N/L*	*ug P/L*	*ug P/L*	*ug P/L*	*mg C/L*	*mg/L*	*umos/cm*		*mg C/L*
101	**Spring 2007**	35.7	983	660	567	80	324	152	105	48	8.4	9.5	159	6.0	1.0
	Spring 2008	37.9	1131	1018	851	167	113	222	157	65	8.9	8.5	226	5.1	0.6
	Fall 2008	15.9	2155	1819	1175	644	336	215	121	95	6.8	0.0	242	5.2	0.1
109	**Spring 2007**	134.0	2772	1100	924	176	1672	557	432	126	11.4	14.3	128	5.9	0.9
	Spring 2008	138.0	2334	1887	1626	261	447	631	514	117	17.7	14.2	140	5.5	0.7
	Fall 2008	43.2	7520	5016	2718	1749	248	706	462	244	12.3		144	5.6	0.7
110	**Spring 2007**	93.1	857	821	738	83	36	215	141	74	13.7	11.7	93	5.4	0.9
	Spring 2008	90.9	971	931	810	121	40	170	92	78	13.8	13.7	124	5.0	0.2
	Fall 2008	43.6		2617		179		331	174	157					

The results to date set the foundation for future work in the SERC watersheds with a focus on Hg cycling in riparian zones and identifying the stores and mobility of the Hg in the watershed compartments.

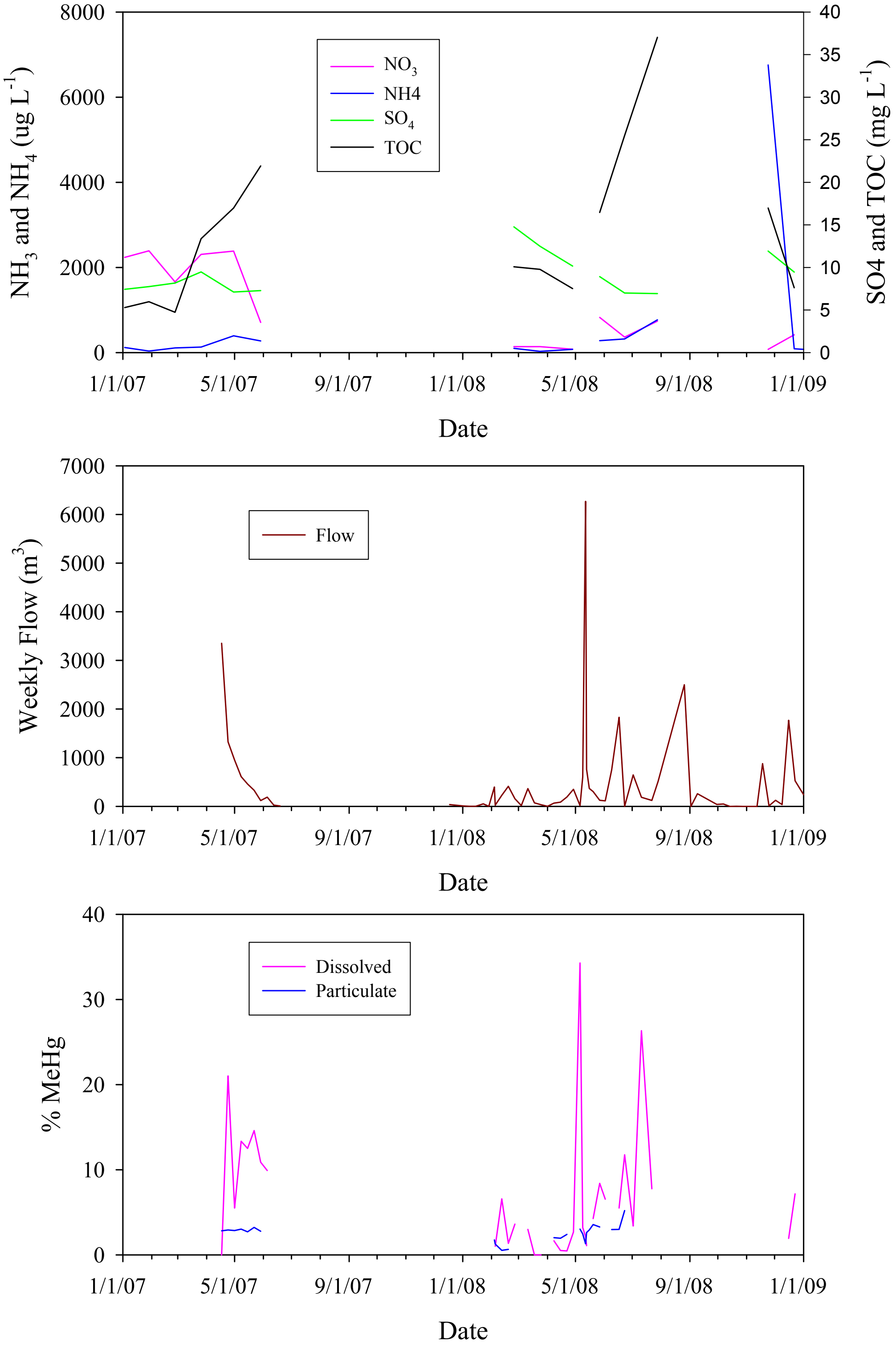


Figure 5.2 Stream chemistry (top), water discharge (center) and %MeHg (MeHg as a percentage of filterable and particulate Total-Hg (bottom) for Watershed 109. For the top graph NO$_3$ and NH$_4$ are on the left axis, SO$_4$ and TOC are on the right axis.

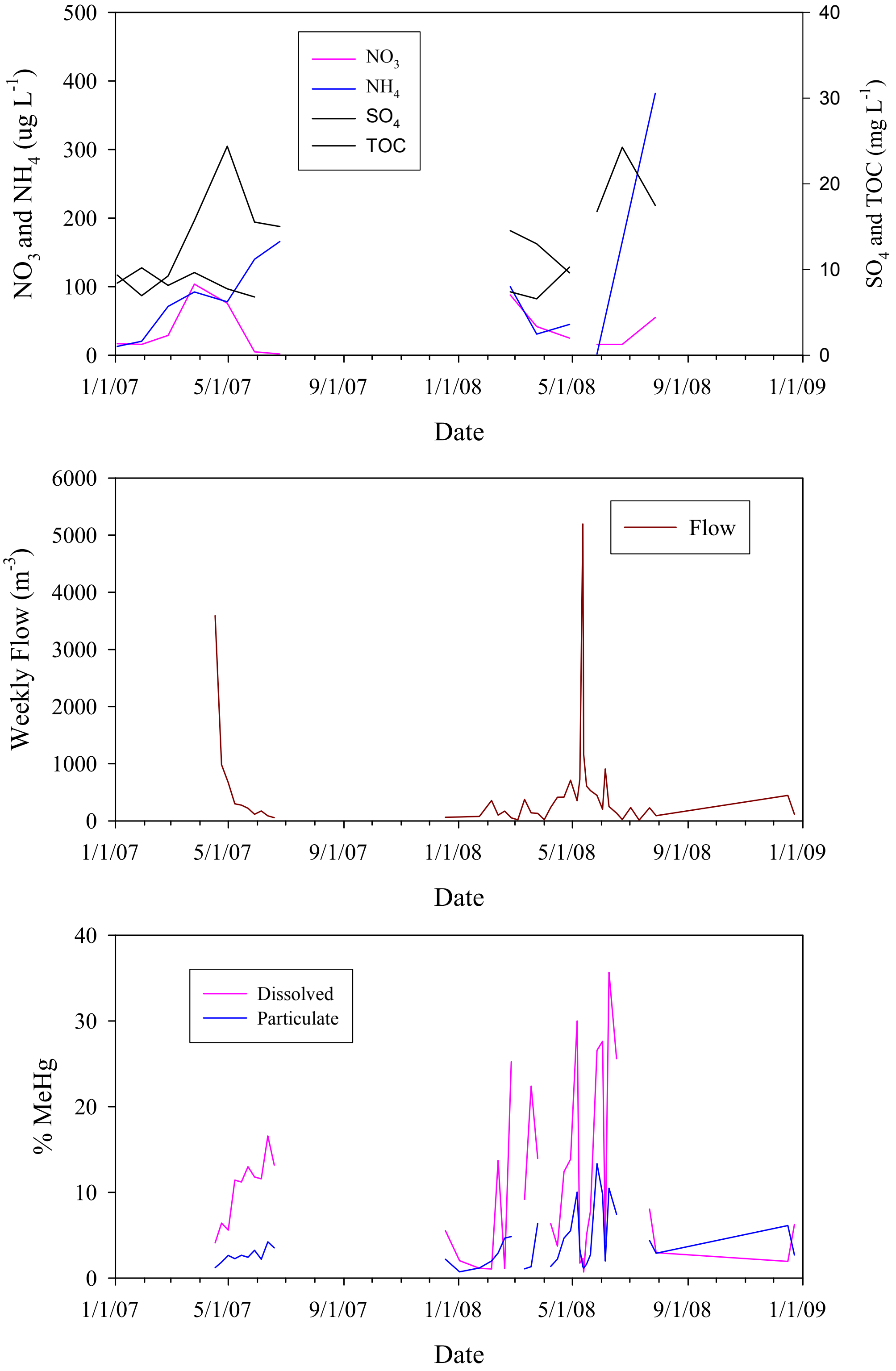


Figure 5.3 Stream chemistry (top), water discharge (center) and %MeHg (MeHg as a percentage of filterable and particulate Total-Hg (bottom) for Watershed 110. For the top graph NO_3 and NH_4 are on the left axis, SO_4 and TOC are on the right axis.

6.0 References

Allan, C.J. and A. Heyes. 1998. A preliminary assessment of wet deposition and episodic transport of total and methyl mercury from low order southern Blue Ridge watersheds S.E. USA. Water Air and Soil Pollut. 105:573-592.

Allan, C.J., A. Heyes, N.T. Roulet, V.L. St.Louis and J.W.M. Rudd. 2001. Spatial and temporal dynamics of mercury and organic carbon in Precambrian Shield runoff. Biogeochem. 52:13-40.

Benoit, J.M, C. Gilmour, A. Heyes, R.P. Mason, C. Miller. 2003. Geochemical and Biological Controls Over Methylmercury Production and Degradation in Aquatic Ecosystems. In: "Biogeochemistry of Environmentally Important Trace Elements", ACS Symposium Series #835, Y. Chai and O.C. Braids, Eds. American Chemical Society, Washington, DC. pp. 262-297.

Benoit, J.M., C.C. Gilmour, R.P. Mason, G.S. Riedel, and G.F. Riedel. 1998. Behavior of mercury in the Patuxent River estuary. Biogeochemistry 40:249-265.

Bishop, K., Lee, Y-H., Pettersson, C. and Allard. 1995. Terrestrial sources of methylmercury in surface waters: the importance of the riparian zone on the Svartberget catchment. Water air Soil Pollut. 80:435-444.

Chapelle, F.H. and Drummond, D.D. 1983. Hydrogeology, digital simulation, and geochemistry of the Aquia and Piney Point Nanjemoy aquifer system in southern Maryland, Report of Investigation. No. 38. 100pp.

Chirlin, G.R. and Schaffiner, R.W. 1977. Obesrvations on the water balance for seven subbasins of the Rhode River, Maryland. 277-306. In D.L. Correl. Watershed Research in Eastern North Amercica, Vol. 1. Smithsonian Press. Wash. DC.

Cleckner, L., Gilmour, C.C., J.P. Hurley and D.P. Krabbenhoft.1999. Mercury methylation in periphyton of the Florida Everglades. Limnol. Oceanogr. 44:1815-1825.

Correll, D.L. and Weller, D. 1989. Factors limiting processes in freshwater wetlands: an agricultural primary stream riparian forest. In Freshwater Wetlands and WildLife. Proceedings, Charleston SC 1986. Ed. R.R. Sharitz, and J.W. Gibbons. US Dept. Energy.

Correll, D.L., Jordan, T.E., Weller, D.E. 2001.Effects of precipitation,air temperature and land use on organic carbon discharges from Rhode River watersheds. Water Air Soil Pollut. 128:139-159.

Cossa, D., Coquery, M., Martin, J-M., and Gobell, C. 1996. Mercury fluxes at the ocean margins. In: Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances, W. Baeyens, R. Ebinghaus, and O. Vasiliev, Eds., Kluwer Academic Publishers, The Netherlands, pp. 292-248.

Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochem. 40:327-345.

Gilmour, C.C., E.A. Henry and R. Mitchell. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. Environ. Sci. Technol. 26:2281-2287.

Harris, R.C., Rudd., J.W.M., Amyot, M., Babiarz, C.L., Beaty, K.G., Blanchfield, P.J., Bodaly, R.A., Branfireun, B.A., Gilmour, C.C. Graydon, J.A., Heyes, A. Hintelmann, H., Hurley, J.P., Kelly, C.A., Krabbenhoft, D.P., Lindberg, S.E., Mason, R.P. Paterson, M.J. Podemski,C.L., Robinson, A., Sandilands, K.A., Southworth, G.R., St. Louis, V.L., Tate, M.T. Whole ecosystem study shows rapid fish mercury response to changes in mercury deposition. 2007. Proc. Nat. Acad. Sci. 104:16586-16591.

Heyes, A., R.P. Mason, E-H Kim and E. M. Sunderland. 2006. Mercury methylation in Estuaries: incites from measuring rates using mercury stable isotopes. Marine Chemistry 102:134-147.

Hintelmann, H. and Evans, R.D. 1997. Application of stable isotopes in environmental tracer studies - Measurement of monomethylmercury (CH3Hg+) by isotope dilution ICP-MS and detection of species transformation. Fresenius J. Anal. Chem., 358: 378-385.

Hintelmann, H., Harris, R., Heyes A., Hurley, J.P., Kelly, C. A., Krabbenhoft D. P., Lindberg, S., Rudd J.W.M., Scott, K.J., and St. Louis, V.L. 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. Environ. Sci. Technol. 36:5034-5040.

Krabbenhoft, D., J. Hurley, G. Aiken, C. Gilmour, M. Marvin-DiPasquale, W. Orem and R. Harris. 2000. Mercury cycling in the Florida Everglades: A mechanistic study. Verh. Internat. Verein. Limnol. 27:1657-1660.

Laurier, F.J.D, Cossa, D., Beucher, C. 2007. The impact of groundwater discharges on mercury partitioning, speciation and bioavailability to mussels in a coastal zone. Marine Chem. 104:143-135

Jordan, T.E., Correll, D.L. and Weller, D.E. 1997. Effects of agriculture on discharges of nutrients from coastal plane watersheds of Chesaoeake Bay. J. Environ. Qual. 26:836-848.

Krabbenhoft, D.P., C.C. Gilmour, J.M. Benoit, C.L. Babiarz, A.W. Andren and J.P. Hurley. 1998. Methylmercury dynamics in littoral sediments of a temperate seepage lake. Can. J. Fish. Aquat. Sci. 55:835-844.

Marvin-DiPasquale, J. Agee, C. McGowan, R.S. Oremland, M.. Thomas, D. Krabbenhoft and C.C. Gilmour. 2000. Methyl-mercury degradation pathways: A comparison among three mercury -impacted ecosystems. Environ. Sci. Technol. 34: 4908-4916.

Mason, R. P., Lawson, N. M., and Sheu, G.-R. 2002 The urban atmosphere: an important source of trace metals to nearby waters? R.L. Lipnick, R. P. Mason M. L. Phillips and C. U. Pittman Jr. eds. Chemicals in the Environment: Fate, Impacts, and Remediation. 203-222. American Chemical Society Publ. ACS Symposium Series No. 806.

Mason, R.P., N.M. Lawson, and G.-R. Sheu. 2000. Annual and seasonal trends in mercury deposition in Maryland. Atmos. Environ. 34: 1691-1701.

Mason, R. P., M. L. Abbott, R. A. Bodaly, Jr. O. R. Bullock, C. T. Driscoll, D. Evers, S. E. Lindberg , M. Murray, and E. B. Swain. 2005. Monitoring the Response to Changing Mercury. Environ. Sci. Tech. 39:14A-22A.

Munthe, J., Hellston, S , Zetterberg, T. 2007. Mobilization of methylmercury from forest soils after a severe storm-fell event. Ambio36:111-113.

Peterjohn, W.T. and Correll, D.L. 1986. The effect of riparian forest on the volume and chemical composition of the baseflow in an agricultural watershed. Watershed research perspectives. D.L. Correll Ed. Smithsonian Press Washington DC. Pp 244-262.

Riedel, G.F., S.A. Williams. G.S. Riedel, C.C. Gilmour and J.G. Sanders. 2000. Temporal and spatial patterns of trace elements in the Patuxent River Estuary: A whole watershed approach. Estuaries. 23:521-535.

Schuster, P. F., D.P. Krabbenhoft, D.L. Naftz, L.D. Cecil, M.L. Olson, J.F. Dewild, J. F. D.D. Susong, J.R. Green, and M.L. Abbott. 2002. Atmospheric mercury deposition during the last 270 Years: A glacial ice core record of natural and anthropogenic sources. Environ. Sci. Technol. 36:2303-2310.

Selvendiran, P., Driscoll, C.T., Bushey J.T. ,2008. Wetland influence on mercury fate and transport in a temperate forested watershed Environ. Pollut. 154:46-55.

Sheu, G-R., Mason, R.P. and Lawson, N.M. 2002. Speciation and distribution of atmospheric mercury over the Northern Chesapeake Bay. 223-242. In Chemicals in the Environment. Fate Impacts and Remediation. In ACS symposium Series 806. R.L. Lipnick and R.P. Mason Ed. 2002.

Skyllberg, U. Qian, J., French, W. Xia, K., Bleam, W.F. 2003. Distribution of mercury methyl mercury and organic sulphur species in soil, soil solution and stream of a boreal forest catchment. Biogeochem. 64:53-76.

Stoor, R.W., Hurley, J.P., Babiarz, C., Armstrong, D.E. 2006. Sunsrface sources of methyl mercury to Lake Superior from a wetland-forested watershed.Sci. Tot. Environ.368:99-110.