Controls on streamwater dissolved and particulate mercury within three mid-Appalachian forested headwater catchments

Ami Louise Riscassi
West Hartford, CT

B.S., Wake Forest University, 1996
M.S., University of Virginia, 1999

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Department of Environmental Sciences

University of Virginia
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Todd Scanl

George M. Hornberger

Janet S Herman

ABSTRACT

This dissertation examines streamwater dissolved and particulate mercury dynamics (Hg_D and $Hg_{P,}$ respectively) to gain an improved understanding of factors that control Hg transport from the terrestrial to stream environment. The three study sites, Piney River, Staunton River, and Paine Run, are each forested, headwater systems situated within Shenandoah National Park, VA, and are distinguished by chemical (acidic to neutral pH) and physical soil (sands to clays) characteristics. At each of the three sites, streamwater Hg_D, Hg_P, dissolved organic carbon (DOC) concentrations, turbidity, as well as suspended sediment at one location, were evaluated over a range of discharge conditions within an 18-month period with a focus on frequent sampling during high-flow periods. Total Hg streamwater export ranged from 1.26-3.71 µg m^{-2} yr^{-1}, representing 4-19% of the Hg deposited through atmospheric deposition. Hg fluxes were dominated by the particulate fraction at each site. Brief high-flow rainfall/snowmelt events, corresponding to approximately 1% of the time, were found to export the majority (80%) of the annual Hg flux.

Hg_D was strongly coupled with DOC at all sites confirming the known association with organic carbon. Both soil solution chemistry as well as soil particle size distribution were found to be controlling factors on the mobilization of $Hg_{D.}$ More acidic systems mobilize less aromatic DOC, which relates to less Hg per unit DOC. Soil composition was also found to influence Hg_D export, with coarse sandy soils having a lesser capacity to retain Hg and keep it out of solution resulting in more Hg per unit DOC. Soil organic matter content appears to be a first-order determinant of the amount of Hg per unit organic carbon based on all available stream data, which include locations throughout the U.S. and Sweden.

Hg_P was strongly positively correlated with the organic fraction of suspended sediment, and due to a consistent organic fraction of the suspended solids, was also well correlated with total suspended sediment (TSS). Stream turbidity measured with an *in situ* sonde also had a strong correlation with TSS, enabling commutative association with Hg_P. Turbidity-Hg_P relationships established for each site allowed for improved quantification of Hg_P mass fluxes.

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CHAPTER 1

Introduction

Mercury chemistry

Mercury principally exists as elemental (Hg^0) and in the oxidized state (Hg^{+2}). Both forms of mercury are released to the environment through anthropogenic and natural processes. Due to its solubility in water, Hg^{+2} tends to become deposited with rainfall having a residence time on the order of hours to weeks (Poissant et al., 2005). Due to its volatility, Hg^0 tends to remain in the atmosphere for up to 1 year (Schroeder and Munthe, 1998). Once deposited, Hg^{+2} may be reduced to Hg^0 and returned to the atmosphere; alternatively it may be retained in soil or sediment, remain in aqueous solution, or be converted to methylmercury. In anoxic waters and sediments, sulfate and/or iron reducing bacteria methylate mercury through metabolic processes (Krabbenhoft and Rickert, 1995). Methylmercury is stable in aqueous solution and may enter the food chain via phytoplankton or bacteria.

As a soft (class B) metal ion, mercury favors ligands containing less electronegative donor atoms such as sulfur-containing functional groups, frequently found in organic molecules (Schuster, 1991, Yin et al, 1996; 1997; Zhang and Lindberg, 1999; Xia et al., 1999). Although Hg_T may be adsorbed to inorganics (Fe or Mn oxides and clay minerals) in soil, those complexes are not quantitatively important relative to organic carbon (Skyllberg et al., 2000). The exception to this may occur in soil horizons that are very low in organic carbon or in neutral/alkaline soils (Schuster, 1991). Hg_T can bind to both particulate and dissolved organic carbon (Schuster, 1991). As a consequence the physical partitioning of organic carbon (between aqueous and solid phases) determines the behavior and distribution of mercury within the terrestrial environment and its mobilization to downstream aquatic systems.

Mercury in the environment

Levels of mercury have more than doubled in the terrestrial environment in the last 150 years (Lorey and Driscoll, 1999; Schuster et. al, 2002). Increases have been attributed to atmospheric transport and deposition from anthropogenically derived point sources, with over 85% originating from coal-fired utilities and industrial boilers (U.S. EPA, 1997). Inorganic Hg deposited or transported to the terrestrial or aqueous environment may be converted to methylmercury (CH_3Hg^+) through microbial mediated processes. CH_3Hg^+ is a known neurotoxin which bioaccumulates, resulting in harmful concentrations in higher-trophic level organisms including humans (Wolfe et al., 1998). As of 2008, all fifty U.S. states have issued Hg fish consumption advisories in streams, rivers, and lakes (U.S. Environmental Protection Agency, 2009).

Mercury built up in soils from historic deposition represents a long-term source of mercury to aquatic systems, even when atmospheric loading rates are reduced (Krabbenhoft and Babiarz, 1992). Upland forests are particularly important reservoirs of Hg as they represent a large part of the landscape, combined with the fact that Hg deposition is enhanced at high elevations and in forested systems (St. Louis et al., 2001; Miller et al., 2005), and these undisturbed systems have been shown to retain most of the Hg deposited (Krabbenhoft et al., 1995; Allan and Heyes, 1998; Scherbatskoy et al., 1998; Shanley et al., 2008). Further research is needed to understand the watershed-scale factors that result in the mobilization of Hg from soil to stream. Such information is necessary to assess and separate the impacts of regulations and other environmental forcings, identify areas of concern for Hg contamination, and develop appropriate monitoring and remediation strategies. The work presented here investigates physical and chemical factors that control the transport of dissolved and particulate Hg from the terrestrial to the aqueous environment in forested mountain landscapes.

Dissertation organization

This dissertation is organized as four self-contained papers, all related to streamwater Hg transport in headwater systems subject to Hg inputs via atmospheric deposition within Shenandoah National Park. Chapter 2 examines the viability of using an automated device to sample streamwater during high-flow events for low-level Hg analysis. Automated sampling of streamwater during high-flow events was necessary to carry out the objectives of the research presented hereafter, as the majority of Hg is transported during these periods (Balogh et al., 1997, 2005; Allen and Heyes, 1998; Scherbatskoy et al., 1998; Shanley et al., 2002, 2008; Mast et al., 2005; Schuster et al., 2008). This manuscript is the first published account of a systematic evaluation of the potential errors associated with using an automated streamwater sampling technique for Hg analysis.

In Chapter 3, particulate Hg (Hg_P) and suspended sediment dynamics are evaluated to gain a better understanding of the factors that mobilize Hg_P downstream. An approach to estimate Hg_P with turbidity, measured at high frequency with the use of an *in situ* sonde, is also presented. High-frequency concentration data are needed to improve our understanding of particulate Hg dynamics, specifically during high-flow events when concentrations change substantially over short time intervals. Such high resolution data can also be used to improve flux estimates of Hg export. This manuscript is the first published account of using a turbidity sonde to approximate Hg_P concentrations in a system contaminated solely through atmospheric deposition.

Chapter 4 investigates the controls on dissolved Hg (Hg_D) concentrations at three sites which are distinguished by their streamwater chemistry and soil characteristics, factors that have been shown to affect Hg_D transport in laboratory studies. The quality and quantity of dissolved organic carbon (DOC) within and between sites was evaluated in conjunction with Hg_D, as organic carbon is known to be associated with Hg in most systems. In order to put Hg_D-DOC ratios in Shenandoah within the context of other watersheds, we compiled ratios from all available streamwater systems. A preliminary evaluation of the primary factors that likely drive large-scale differences in that ratio were evaluated. This is the first large-scale aggregation of Hg-DOC ratios and the first published attempt to evaluate factors which drive large-scale variability in that ratio.

Chapter 5 presents annual Hg_P and Hg_D fluxes computed at each site for the 2010 water year. The relative fraction of particulate and dissolved Hg exported from these three watersheds are evaluated in the context of all other watershed studies and storm contributions to the overall flux are quantified. The Hg_P- turbidity relationships at all three sites are presented and used to calculate Hg_P fluxes. This work represents the first use of high-frequency sonde data to estimate any component of long-term Hg fluxes.

A summary of the entirely of this work and likely implications from the results are presented in Chapter 6. Potential avenues of future research, to improve and expand upon the findings of this dissertation, are also included. Due to the increased presence of Hg in the environment as a result of anthropogenic actions in concert with its potentially toxic nature, Hg is an environmental contaminant that will continue to be a focus of research, monitoring and regulation efforts for years to come.

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CHAPTER 2

Evaluation of an automated sampling technique to measure total mercury in streamwater during storm events

Abstract

Understanding the processes by which mercury is mobilized from soil to stream is currently limited by a lack of observations during high-flow events, when the majority of this transport occurs. An automated technique to collect streamwater for unfiltered total mercury (Hg_T) analysis was systematically evaluated in a series of laboratory experiments. Potential sources of error investigated were 1) carry-over effects associated with sequential sampling, 2) deposition of Hg_T into empty bottles prior to sampling, and 3) deposition to or evasion from samples prior to retrieval. Contamination from carry-over effects was minimal (<2%) and Hg_T deposition to open bottles was negligible. Potentially greater errors are associated with evasive losses of Hg_T from uncapped samples, with higher temperatures leading to greater evasion. These evasive losses were found to take place primarily within the first eight hours. Hg_T associated with particulate material is much less prone to evasion than Hg_T in dissolved form. A field test conducted during a high-flow event confirmed unfiltered Hg_T concentrations sampled with an automated system were comparable to those taken manually, as the mean absolute difference between automated and manual samples (10%) was similar to the mean difference between duplicate grab samples (9%). Results from this study have demonstrated that a standard automated sampler, retrofitted with appropriately cleaned

fluoropolymer tubing and glass bottles, can effectively be used for collection of streamwater during high-flow events for low-level mercury analysis.

1. Introduction

Terrestrial systems are significant reservoirs of mercury (Hg) accumulated from decades of elevated anthropogenic deposition (Grigal, 2003). Hg retained within the landscape can be transported to downstream methylation sites, bioaccumulate, and pose a human health hazard. Concentrations of Hg in streamwater exhibit both seasonal (Hurley et al., 1995; Balogh and Meyer, 1998; Mast et al., 2005) and short-term (Hurley et al., 1998; Shanley et al., 2008) variability, which necessitates regular and event-based sampling to accurately determine the amount of Hg exported from a watershed. Paired with analyses of other water-quality parameters, frequent event sampling can also be used to assess Hg source areas (Bushey et al., 2008) and biogeochemical controls on Hg movement (Shanley et al., 2002) from soil to stream. Monitoring during periodic high-flow events such as snowmelt and storms, however, has been limited due to a lack of practical sampling techniques. Here we assess the viability of using automated streamwater sampling during high-flow events for measuring Hg concentrations.

Many studies have employed fixed-interval (*i.e.* weekly or monthly) sampling schedules to measure total Hg (Hg_T, comprised of particulate and dissolved fractions) over a range of discharge conditions (Balogh and Meyer, 1998; Hurley et al., 1998a, b; Babiarz et al., 1998; Scherbatskoy et al., 1998; Balogh et al., 2005; Brigham et al., 2009) while others have specifically targeted snow-melt periods (Shanley et al., 2002; Mast et al., 2005; Mitchell et al., 2008; Schuster et al., 2008). Results from this work have established that high-flow events dominate the transport of Hg_T. A few studies have included intensive sampling during storm events (Allan and Heyes, 1998; Bushey et al., 2008) and have found that Hg_T concentrations were variable both within and between storms and were not necessarily correlated with discharge. It is therefore problematic to infer Hg_T transport dynamics by extrapolating from a handful of storms or from only a few samples collected during many storms.

Consistent, high-frequency event sampling of streams for Hg_T has not been broadly implemented due to difficulties involved in manual sample collection. The timing of storm events can be unpredictable, and the EPA recommended ultra-clean sampling procedures (U.S. EPA., 1996) require two field personnel for the duration of the storm hydrograph (*i.e.* days to weeks). While automated sampling is routinely implemented for basic water-quality analyses, this method has generally not been used for Hg_T because samples are susceptible to both equipment contamination and losses due to evasion. Hg is present in solution in both the oxidized and elemental forms, Hg^{2+} and Hg^0 respectively. The dominant form in water, Hg^{2+}, is 'sticky' and therefore likely to adhere to sample tubing walls, while Hg^0 is volatile and can readily be lost from solution (Stumm and Morgan, 1996). If the magnitude of such errors are minimal or predictable, however, automated sampling could be viable.

Automated high-frequency sampling with a programmable Teledyne Isco has previously been demonstrated in several studies for trace metals (Isaac et al., 1997; Church et al., 1998; Bedsworth and Sedlak, 1999) and two studies in which a series of discrete samples were analyzed for Hg_T (Lawson and Mason, 2001; Nelson et al., 2007). For broad implementation of this sampling approach, it is essential to be aware of potential inaccuracies associated with various aspects of this technique. Errors encountered throughout the course of sampling for a range of Hg_T concentrations and temperature regimes have yet to be systematically evaluated.

Our overall objective is to determine the efficacy of automated samplers for use in streamwater Hg_T studies. In particular, we consider the following factors that could contribute to inaccuracies: (1) carry-over effects from sequential sampling using the same intake strainer and tubing during a single storm-event, (2) deposition of Hg_T into uncapped, empty bottles and (3) evasion and/or deposition of Hg_T from uncapped, aqueous samples prior to retrieval. With regard to this final objective, we also examine the effects of length of time between sample collection and retrieval, ambient air temperature, and Hg physical fractionation (dissolved or particulate).

2. Materials and Methods

Three sets of laboratory experiments were conducted to estimate errors incurred from sampling streamwater for Hg_T using an automated technique. An additional field test was used to corroborate the laboratory results. All experiments were conducted with commercially available Teledyne Isco 2900 automated samplers. Sample bottles were either 250-mL Teflon® (used for manual samples) or 375-mL glass with removable Teflon® lined caps (used for automated samples). All other sampling equipment (tubing, strainer, and connectors) was made from fluoropolymer materials (not available from the manufacturer), to minimize contamination except for a 1.0-m section of C-flex tubing used in the peristaltic pump. These were cleaned once prior to all tests by soaking in a heated (70 °C) 4N HCl vat for a minimum of 12-hrs, rinsed three times with de-ionized (DI) water, dried under a clean bench, and double bagged until use. Sample bottles were cleaned prior to each test and went through additional rinses of dilute (1%)

HCl, then were filled with the 1% HCl solution, capped and double bagged and warmed to 65 °C overnight in a clean oven. After cooling, bottles were rinsed three more times with DI water, filled with a 0.04% HCl solution, dried under a clean bench, and placed in a set of 2 plastic bags prior to storage (U.S. EPA, 2002).

Streamwater used in all experiments was collected during baseflow conditions from the Rapidan River in central Virginia. The site was selected due to its close proximity (~1 km downstream) to a regularly monitored streamwater site (Staunton River, referred to later in this paper) and due to its accessibility for ease of transport of the large volumes of water needed for all experiments. The watershed is a forested headwater ecosystem, underlain by metamorphosed bedrock, and characterized by second- to third-growth mixed hardwoods (Ryan et al., 1989; Young et al., 2006). The range of native Hg_T concentrations of streamwater used in the experiments was 0.29 – 0.40 ng L^{-1}. Particulate-bound Hg accounted for approximately 18% of Hg_T based on baseflow samples taken during the same period at Staunton River. Basic water quality parameters of the water used in the experiments are as follows: 6.8 pH, 21.1 µS conductivity, 122.4 µeq L^{-1} alkalinity, 40.9 µeq L^{-1} $SO_4{}^{2-}$, 22.8 µeq L^{-1} chloride, and 0.5 mg L^{-1} dissolved organic carbon. To simulate a range of Hg_T concentrations typically measured during storm event sampling, the baseflow streamwater was spiked with dissolved Hg_T from a standard solution of $HgCl_2$ except where noted. Laboratory experiments were conducted outdoors in Charlottesville, VA. Typical ambient atmospheric Hg concentrations are approximately 1.8 ng m^{-3} within the range typically encountered in an uncontaminated environment (Valente et al., 2007). All sample collection and handling procedures followed ‘clean’ techniques for trace metals established by the U.S. EPA (1996). After retrieval all samples were preserved in the sample bottle within an hour with a 100% bromium monochloride (BrCl) solution (5 mL BrCl per 1 L sample). The BrCl oxidizes all of the Hg which keeps it in solution (prevents volatilization) and also disaggregates organic matter to eliminate wall losses (Parker and Bloom, 2005).

2.1 Experiment 1: Carry-over effects

When using an automated system to sample streamwater, Hg_T within the sample could adhere to the interior sample tubing wall, leading to an underestimate of the true concentration and possible contamination of subsequent samples. To address this we sequentially collected streamwater over a range of Hg_T concentrations using two different methods (automated and manual) to determine the magnitude of carry-over effects from one sample to the next. As a rigorous test of the automated sampler, non-spiked streamwater was collected between each spiked sample, resulting in a sample sequence of streamwater, 0.5 ng L^{-1} spike, streamwater, 5.0 ng L^{-1} spike, streamwater, 25.0 ng L^{-1} spike, streamwater, 50.0 ng L^{-1} spike, and streamwater. The spike concentrations encompass the range typically measured during high-flow events (2, 5-7, 9-13, 17, 23).

The Isco was placed at the top of a gently sloping hillside with roughly 6 m of sample tubing connected to a strainer at the base of the hill. Two liters of either streamwater or a Hg-spiked streamwater solution was poured into a pre-cleaned plastic vat. Approximately 250 mL of the streamwater was first poured directly from the vat into a Teflon bottle, representing a manual sample (*i.e.* no contact with automated equipment). The intake strainer was then completely submerged in the remaining water and the sampler was activated. The Isco was programmed to rinse the tubing three times, in which the rinse water was successively purged back into the vat, before depositing the sample water into the bottle. Immediately after each sample was collected it was retrieved from the Isco, capped, and double bagged until preservation. The strainer and exterior tubing that came in contact with elevated Hg concentrations were rinsed with 50 mL of streamwater before the next sample to minimize any contamination from the outside tubing. In the stream environment this would not be a concern due to continuous flow-through conditions.

2.2 Experiment 2: Deposition to bottles

Atmospheric deposition to the interior of empty uncapped bottles in an Isco is another potential source of contamination. Two situations may result in varying amounts of contamination. First, when all bottles are empty, ambient atmospheric Hg can directly deposit onto interior bottle surfaces. Second, after the Isco has taken some samples, Hg may evade from the water and deposit into remaining empty bottles. These two situations were addressed in separate experiments.

To simulate conditions prior to sampling, duplicate empty bottles were placed in an empty Isco. To simulate conditions during/after event sampling, duplicate empty bottles were placed in a second Isco alongside streamwater and spiked streamwater samples ranging in concentration from approximately 0.2 – 50 ng L^{-1} Hg_T. Bottles were left in an Isco for 3 and 7 days, a typical amount of time that bottles may be left exposed to the atmosphere in a field setting. Separate Iscos were used for the 3-day time period so as not to disturb the 7-day experiment (4 Iscos total). At the appropriate time, bottles were retrieved, filled with streamwater, capped and double bagged until preservation. At the time of sampler deployment, streamwater was also poured into a clean (neveropened) bottle and immediately preserved to serve as the control. This experiment was performed twice, in cold (typical of VA winter) and relatively warm (typical of VA summer) conditions. Temperature ranges are defined in section 2.3.2.

2.3 Experiment 3: Deposition and/or evasion from samples

Once streamwater samples are collected by the Isco, they are left open to the atmosphere and are subject to Hg_T deposition and/or evasion before retrieval. Factors that may affect the amount of contamination from atmospheric deposition and/or evasion include the length of time bottles are left open, the ambient temperature during that period, and the physical fractionation (dissolved and particulate) of Hg_T in samples. Three separate experiments were conducted to evaluate each of these potential problems. Net atmospheric deposition/evasion was quantified for (1) time: streamwater spiked with 25-ng L^{-1} dissolved Hg_T and left open for periods ranging from 1 hour to 7 days, (2) temperature: streamwater and streamwater spiked with concentrations ranging from 0.5 to 50.0 ng L^{-1} dissolved Hg_T under four different temperature regimes and (3) physical fractionation: streamwater and streamwater spiked with concentrations of 0.5 to 35 ng L^{-1} Hg_T comprised of both dissolved and particulate forms. Details of the individual experiments are described in the following three sections.

2.3.1 Holding time

The length of time that samples are left open to the atmosphere prior to capping and preservation could affect the amount of Hg_T deposition/evasion. Samples collected over the course of a storm will inevitably have unequal holding times. In addition, samples will not be retrieved by field personnel at consistent lag times following automated sampling. To characterize the temporal effects, thirteen bottles containing streamwater spiked with 25 ng L^{-1} Hg_T were placed in an Isco and left uncapped for varying amounts of time. Samples were retrieved, capped and double bagged until preservation at hourly intervals for the first six hours, bi-hourly intervals for the following six hours., then at 1, 3 and 7 days (a total of 13 samples). A control sample was taken at hour zero. To avoid effects of variable temperatures, we used an Isco (model 6712, Avalanche®) that maintains a temperature of 3°C.

2.3.2 Temperature

Temperature has an effect on deposition/evasion from uncapped samples. In field studies, sampling is likely to span a range of seasons and therefore a variety of temperatures. We conducted deposition/evasion experiments under four different temperature regimes. Streamwater and streamwater spiked with concentrations of 0.5, 5.0, 25.0, and 50.0 ng L^{-1} Hg_T were poured into two sets of bottles. The first set served as the control and bottles were immediately capped and preserved. The second set was left uncapped in an Isco. After 3-days, bottles in the Isco were retrieved, capped and double bagged until preservation. This experiment was performed under ambient winter and spring conditions for Virginia, with daily mean temperatures of 3 (-3 to 10 °C) and 9 °C (3 to 14°C), respectively. To simulate summertime conditions, the experiment was repeated inside a heated storage box, diurnal variability was still present with a daily mean of 13 °C (5 to 22°C). Finally, the experiment was conducted within a refrigerated Avalanche® which maintains a temperature of 3 °C.

2.3.3 Physical Partitioning

Hg_T in solution is typically comprised of both dissolved and particulate fractions. All of the previously described experiments were conducted with streamwater spiked with dissolved Hg_T. We believe that these results represent the maximum errors incurred with regard to evasion, because particulate bound Hg is likely less available for reduction and subsequent evasion from solution. To confirm this, we made a slurry from a certified reference sediment standard (MESS-3 CRM marine sediment NRC Canada) so as to contain a combination of dissolved and particulate Hg. We conducted an additional deposition/evasion experiment with streamwater samples spiked with concentrations ranging from 0 to 35 ng L^{-1} Hg_T of the slurry. To avoid effects of variable temperatures, we used the refrigerated Isco to conduct the experiment. Duplicate samples were left in the Isco for 3-days, then capped and double bagged until preservation. Control samples were capped and preserved immediately.

2.4 Field implementation

Individual laboratory experiments may not capture all of the possible error sources associated with automated sampling in a stream environment. In the field, the strainer and tubing sit in the streamwater prior to sampling and the intake sits at a fixed position close to the streambed where bottom materials may be more likely to contaminate samples. To test whether the cumulative errors measured in the controlled experiments are similar to those incurred in a field setting, we took manual grab samples concurrently with those collected by an automated sampler over the course of a storm event. Hourly automated and manual sampling was conducted at Staunton River during a September 26-27, 2009 storm. Ambient atmospheric Hg concentrations were measured at a nearby site within Shenandoah National Park in the fall of 2008 and levels were approximately 1.3 ng m^{-3} (Converse et al., 2010). Rainfall totals for the entire storm duration were approximately 38 mm and generated a corresponding increase in stream discharge, normalized to the catchment area, from 0.02 to 0.18 mm hr^{-1} (85 to 566 L s^{-1}). The non-refrigerated automated sampler rinsed the tubing three times prior to sampling. The grab sample bottle was rinsed with streamwater slightly downstream (within 0.25 m) of the intake strainer three times prior to sampling. Every effort was made to take grab samples at the same depth as the strainer, although offsets of 0-10 cm were likely. A field blank, trip blank, and two grab sample duplicates were also collected. Manually-collected samples were preserved in the lab within 12 hours after the completion of sampling. Samples collected by the Isco were left at the site for 3 days to simulate typical field circumstances before being capped, double bagged and returned to the lab for preservation. The mean daily air temperature during the 3-day period was 17ºC with a mean daily range of 11 to 23ºC which most closely corresponds to the 'summertime' heated conditions in our lab experiment (mean 13ºC). An empty bottle, left open in the Isco during the experiment was collected with the samples to determine any bottle contamination prior to sample collection.

2.5 Analytical procedures and quality control

Analysis for unfiltered Hg_T was completed within a week of preservation under a Class 100 clean bench with a dual amalgamation cold vapor atomic fluorescence spectrometer (Tekran 2600; Tekran Toronto, ON) at the University of Virginia following U.S. EPA method 1631 Revision E (2002).The method detection limit (MDL) of 0.19 ng L^{-1} (U.S. EPA, 1986) was determined from the standard deviation (0.06) of seven aliquots of a 0.65 ng L^{-1} solution. The relative percent difference for field duplicates (1 for every 10 samples) was <15%. Overall laboratory accuracy was determined by participation in an inter-laboratory proficiency test administered by Environment Canada. The proficiency sample concentrations ranged from 6.6 to 47.8 ng L^{-1} and recoveries for our lab ranged from 97 to 102% (n=5). Laboratory accuracy was verified by ongoing analysis of a certified reference material (ORMS-4, Mercury in River Water) with each batch of samples. The concentration of the reference material was 22.0 +/- 1.6 ng L^{-1} and recoveries ranged from 93% to 117% (n=5). Matrix spikes, ongoing precision and recovery (OPR) analysis, method and system blanks were used to evaluate instrument performance. The accuracy and precision of the matrix spikes (1 in every 10 samples) and standards were maintained within 10% and the OPR samples were maintained within 15%. System and method blanks (n=35) were below MDL with the exception of two system blanks of 0.22 and 0.28 ng L^{-1}. Reported quality-control metrics are all within U.S. EPA (2002) guidelines.

3. Results and Discussion

3.1 Carry-over effects

Hg_T carry-over effects in Isco samples ranged from BDL to 0.84 ng L^{-1} Hg_T (Figure 1). Dilution effects from any residual water in the line influencing subsequent samples appears to be a minor concern. None of the four Isco samples collected subsequent to a non-spiked streamwater sample had a lower concentration than the corresponding grab sample, indicating no dilution from mixing with residual water from the previous sample as well as no adsorption of Hg onto the interior tubing wall from a spiked sample.

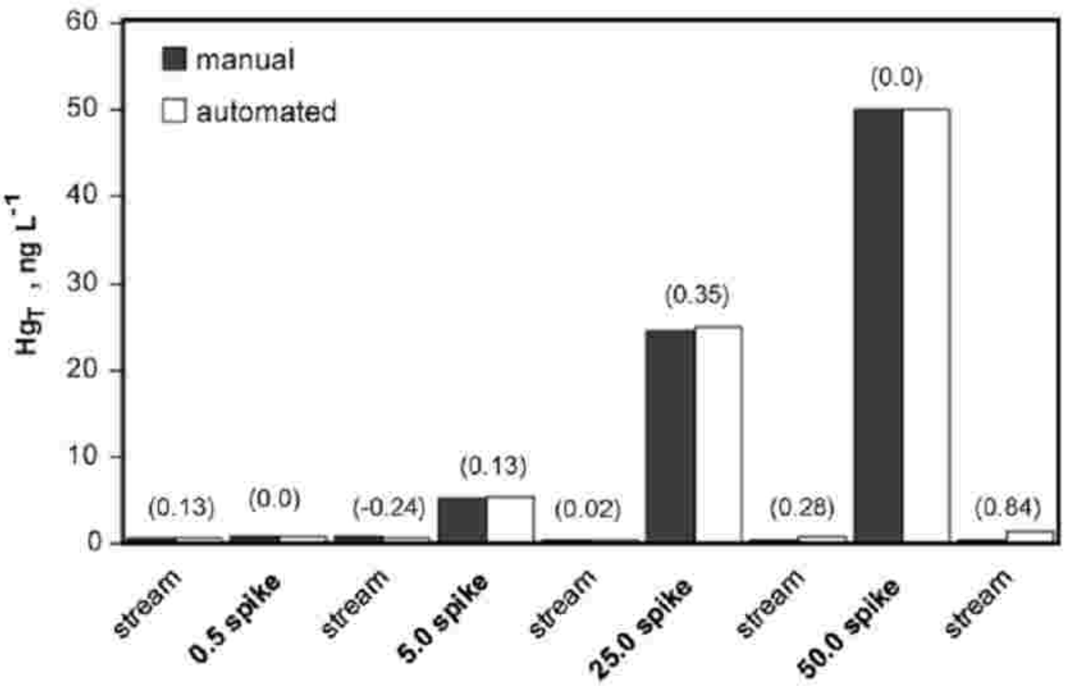

Figure 1. Results from the carry over test showing unfiltered total Hg (Hg_T) concentrations of streamwater and Hg-spiked streamwater collected by manual and automated techniques. The sequence of sampling progressed from left to right. Concentration differences (ng L^{-1}) between manual and automated samples are documented in parentheses above their respective bars. The carry over from higher concentration samples of 0.5, 5.0, 25.0 and 50.0 Hg_T ng L^{-1} was 0.0, 0.5, 1.1, and 1.7 percent, respectively.

Carry-over contamination from streamwater with high Hg_T concentrations to subsequent samples was greater in magnitude. In non-spiked samples collected subsequent to those spiked with 0.5 and 5.0 ng L^{-1} Hg_T, carry-over contamination was not present or minimal (0.02 ng L^{-1}). In non-spiked samples collected subsequent to those spiked with 25.0 and 50.0 ng L^{-1} Hg_T, concentrations were elevated by 0.28 and 0.84 ng L^{-1} Hg_T, respectively; percentage of carry-over from the previous sample was therefore 1.1% and 1.7%. As previously noted, no adsorption to the tubing from a high-concentration sample was detected; therefore any contamination of a non-spiked sample was due to mixing of residual water in the tubing from the previous spiked sample (*i.e.* not from Hg desorption from tubing). In a flow-through stream system, residual water in the line from a previous sample would be flushed downstream during the rinsing procedure and not influence the subsequent sample. Regardless, these carry-over effects are insignificant relative to the current analytical accuracy unless a high-concentration sample (*i.e.* 25-50 ng L^{-1}) is immediately followed by a low-concentration sample (i.e 0.0-5.0 ng L^{-1}), which is atypical behavior for Hg_T within a storm (Bushey et al., 2008; Shanley et al., 2008; Lawson and Mason, 2001).

3.2 Deposition to bottles

The amount of Hg deposited to an open empty bottle is minimal with respect to the volume collected (375 mL) with a mean increase in concentration of 0.16 ng L^{-1} in both heated and cool environments, over 3 and 7 day periods (Table 1). Amounts of contamination were similar between the warm and cold environments tested. No increasing trend in contamination was found in relation to the amount of time bottles were left open; in fact on average there was more contamination in the 3- than 7-day experiment (0.21, vs 0.10 ng L^{-1}). On average contamination was higher (0.19 vs 0.13 ng L^{-1}) in bottles that were located next to filled sample bottles, however the most individual contamination (0.26 ng L^{-1}) was found in a bottle without samples present. Because of the inconsistency of results, it is likely that the minimal contamination arose from a combination of atmospheric deposition and sample handling. Furthermore, contamination at the low levels measured would not be significant at the higher Hg_T concentrations (2-100 ng L^{-1} Hg_T) typically measured during storm events (Babiarz et al., 1998; Balogh, et al., 1997; Balogh and Meyer, 1998; Hurley et al., 1998a,b; Scherbatskoy et al., 1998; Lawson and Mason, 2001; Balogh et al., 2005; Shanley et al., 2008; Bushey et al., 2008).

Table 1. Hg_T deposition to empty uncapped bottles

air temperature regime	**time bottles left open (days)**	**sample environment (ng L^{-1})**	**Increase in Hg_T**
warm-heated	3	empty	0.26
warm-heated	3	with other samples	0.20
warm-heated	7	empty	0.03
warm-heated	7	with other samples	0.17
cold-ambient	3	empty	0.14
cold-ambient	3	with other samples	0.25
cold-ambient	7	empty	0.07
cold-ambient	7	with other samples	0.17
Mean			0.16

3.3 Deposition/evasion from samples

Net evasion or no difference was observed in the majority (83%) of samples for all three of the deposition/evasion experiments. Measured decreases in Hg_T were variable, ranging from BDL to 14.1 ng L^{-1} and were related to sample concentration as well as time left open, ambient temperature, and physical fractioning. Net deposition was observed in six of the thirty-seven samples. All measured increases in Hg_T were minimal (mean of 0.10 ng L^{-1}) and occurred in low concentration samples (streamwater and 0.5 ng L^{-1} spiked samples). There is likely a small amount of atmospheric Hg deposition to all samples, however evasive losses from solution dominate the net flux at concentrations greater than those typically found during baseflow conditions (<1 ng L^{-1}).

3.3.1 Holding time

Under constant cool (3 ºC) temperatures, Hg_T concentrations declined approximately exponentially from 26.0 to 24.0 ng L^{-1} during the first 8 hours (Figure 2). Concentrations remained fairly constant, with a standard deviation of 0.17 ng L^{-1} Hg_T, for the next 7 days. Based on these results, samples retrieved less than 8-hrs after the last sample was collected could be subject to a small amount of differential evasion caused by unequal holding times. It would not be necessary to consistently retrieve samples at a predefined time after a storm because longer timescale variability in Hg_T concentration (10 hrs. to 7 days) was found to be minimal.

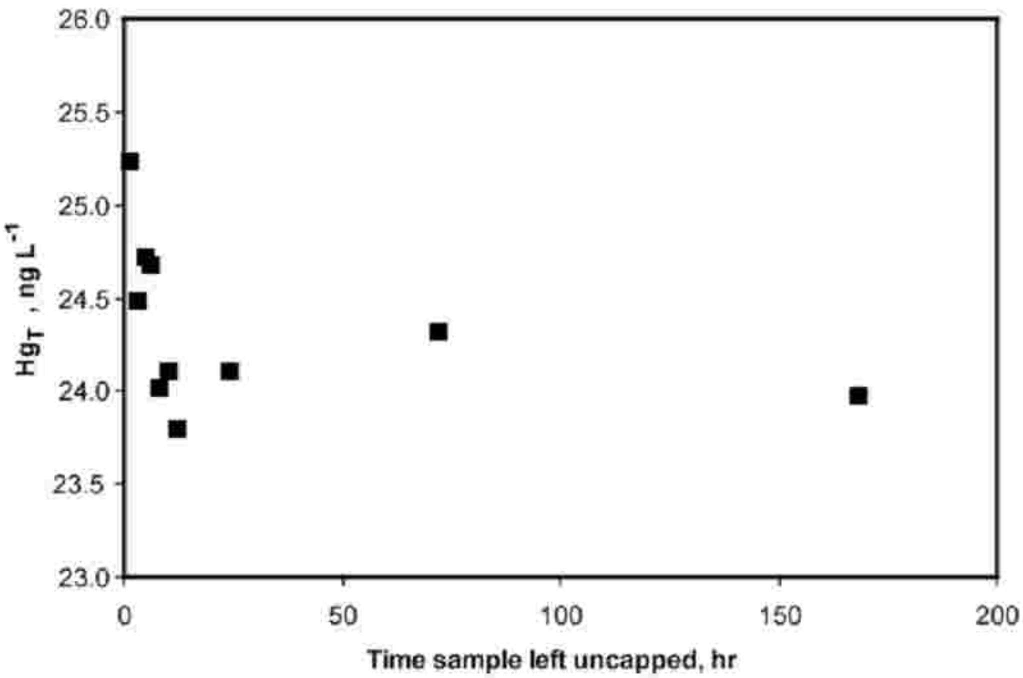

Figure 2. Results from the evasion test showing unfiltered total Hg (Hg_T) concentration of streamwater spiked with 25 ng L^{-1} Hg and left uncapped at 3°C for a periods ranging from 1 hour to 7 days. Note the y-axis range is 23 to 26 ng L^{-1}.

3.3.2 Temperature

Streamwater samples consistently remained constant or lost Hg_T over the duration of the 3-day experiments. Linear best fit lines for each temperature regime relating the control to the Isco Hg_T concentration illustrate that the fraction of Hg_T retained is related to the ambient temperature (Figure 3). The greatest retention (90%) is associated with the coolest temperatures, and the least retention (74%) is associated with the warmest conditions.

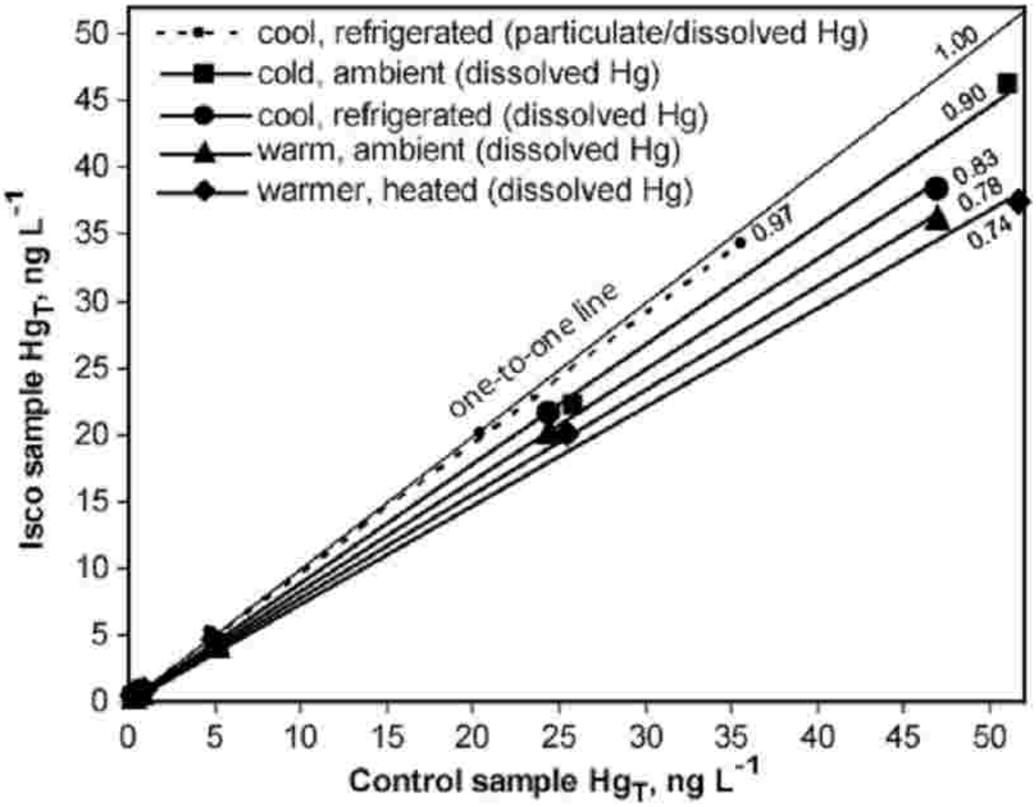

Figure 3. Results from the evasion test showing unfiltered total Hg (Hg_T) concentrations of samples left open in an Isco for 3 days versus concentrations in a control sample. Four different temperature regimes were used with samples spiked with dissolved Hg. One temperature regime (cool-refrigerated) was used for samples spiked with a particulate/dissolved Hg solution (dashed line). The slope of the linear best fit line is labeled next to the respective samples.

Since evasion appears to increase with increasing ambient temperature, it would be beneficial to maintain a constant cold temperature (as is available with the Avalanche®) to minimize losses and keep the magnitude of errors similar for between-site comparisons. It is worth noting that the Avalanche® is designed with the refrigeration vent directly blowing air onto the open water surface of samples. To assess if the Hg_T evasion is enhanced by this blowing air, tests were conducted using the Avalanche® with and without a cover designed to direct the air downward, away from the sample surface. For two of the samples, this measure significantly reduced the Hg_T loss: from 12.2 to 8.5 ng L^{-1} for the 50.0 ng L^{-1} Hg spiked sample and from 1.7 to 0.7 for the 5.0 ng L^{-1} Hg spiked sample. No significant improvements were found in any of the other samples, which may be attributed the positioning of the bottles relative to the air flow during the original experiment; bottles are in a circular configuration resulting in only a few positioned directly in front of the vent. The data presented in this paper are with the modified blower.

3.3.3 Physical partitioning

The streamwater sample comprised of both dissolved and particulate Hg fractions (within the 'cool' temperature regime) retained more Hg_T (97% vs 83%) than the corresponding samples of completely dissolved Hg based on the linear best fit lines (Figure 3). These results indicate that evasion from samples varies depending on the physical fractioning of the Hg_T in solution: a higher proportion of particulate-bound Hg results in less evasion. Experiments reported here that use only dissolved Hg_T spiked solutions likely reflect the upper limit of errors from evasion.

3.4 Field implementation

Concurrent grab and Isco samples were taken on the rising, peak, and falling limb of the storm hydrograph encompassing Hg_T concentrations from 2.5 to 7.5 ng L^{-1}. Hg_T concentrations in both grab and Isco samples followed similar patterns, peaking during the maximum discharge followed by a steady decline in concentration (Figure 4). An Isco sample taken at 5:00 a.m. did not fall in line with the pattern of decreasing concentration and was nearly twice the concentration of its corresponding grab sample (shaded triangle in Figure 4). The cause of this contamination is unknown. However, this outlier with respect to the rest of the Isco samples might have been considered suspect independent of any comparison with a concurrent grab sample.

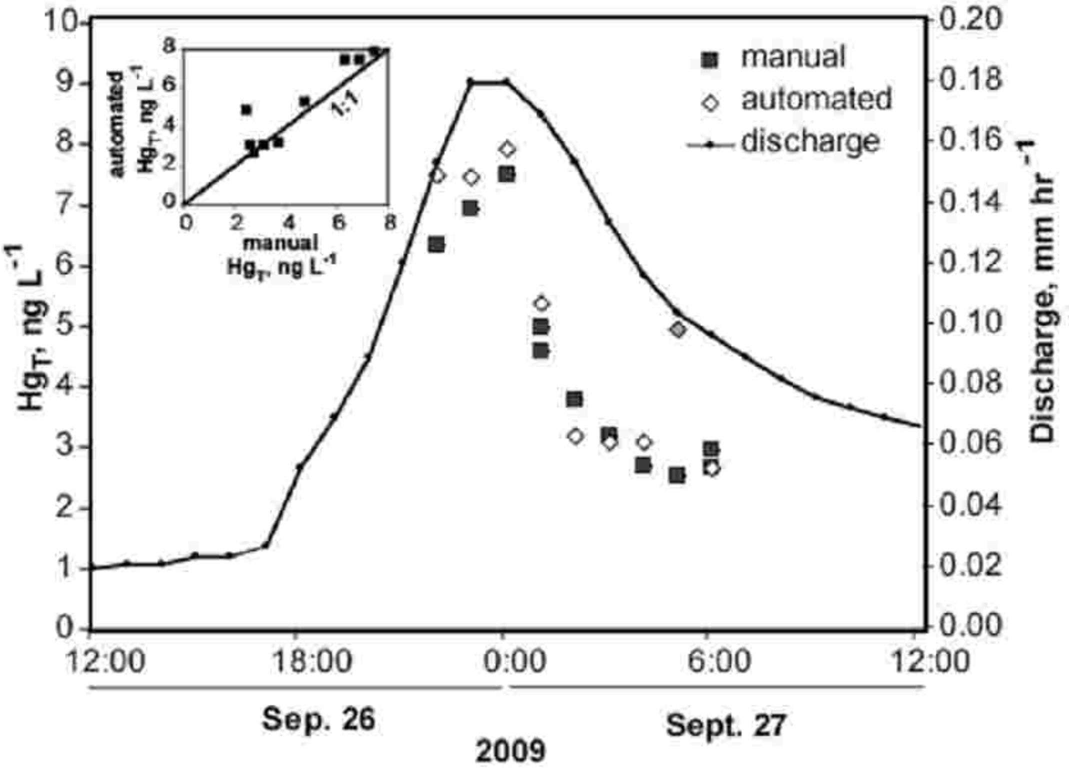

Figure 4. Unfiltered total Hg (Hg_T) concentrations taken by manual and automated techniques during a storm event at Staunton River in Shenandoah National Park, VA. The grey shaded diamond indicates the outlier automated sample. Inset is the same data presented as manual vs automated Hg concentrations against a 1-to-1 line.

Hg_T concentrations in all other Isco samples ranged from 17% greater to 17% less than their corresponding grab sample with a mean absolute difference of 10%. The duplicate grab samples taken side-by-side concurrently at 1:00 and 6:00 a.m. had absolute differences of 8 and 10 % different, respectively. No contamination was found in the field or trip blanks. The open empty bottle in the Isco, after being filled with DI water, had a concentration below our detection limit (0.11 ng L^{-1} Hg_T).

Differences in Hg_T concentrations between samples taken with manual and automated techniques in the field were of the same magnitude (0-20%) as those in our laboratory experiments for similar concentrations. However, the field test indicated that Isco samples were typically biased high, while laboratory tests generally showed automated samples to be lower than their corresponding grab sample. The apparent contradiction may be explained by the difference in the physical fractioning of Hg in the spiked water used for laboratory tests, which was 100% dissolved, and natural streamwater during the storm event. Particulate and dissolved Hg fractions were analyzed separately in samples taken during two previous storms (May 10-11, June 17-18, 2009) at Staunton River (data not shown) and the particulate fraction accounted for approximately 75% of the Hg_T concentration for samples taken throughout the duration of each storm. As previously demonstrated in this study, particulate Hg is less likely to evade from the sample, so losses from these particulate-dominated samples could be minimal. Alternatively, the higher concentrations of Hg in the field samples collected by the Isco may be attributed to non-uniform mixing of the particulates in the water column combined with the differences in sample location of the strainer relative to the grab sample bottle.

Our field and laboratory experiments have site- and streamwater-specific qualities that may affect the contamination/evasion of Hg from samples, so the specific findings should be applied to other sites with caution. Variability in atmospheric Hg concentrations may impact deposition to both empty bottles and samples. This was a minor concern in our setting since we observed insignificant contributions to bottle and sample contamination. In remote, relatively unpolluted sites where atmospheric Hg concentrations are between 1.5-1.8 ng m^{-3} (Valente et al., 2007) this would generally be the case. At polluted sites, when levels can reach >20 ng m^{-3} (*e.g.* Liu et al., 2002), contamination from atmospheric deposition may be a greater concern. Leaving one open Isco bottle empty for the duration of the sampling event for subsequent analysis of Hg contamination can verify the amount of bottle contamination from atmospheric sources. Differences in streamwater biogeochemistry may result in distinctions in Hg evasion rates from samples. The conversion of soluble Hg^{2+} to volatile Hg^0 can occur through biological as well as photochemical reduction. Biological reduction is governed by factors such as the nature of the microorganisms present (Mason et al., 1995) and reducing conditions, although this is thought to be the predominant mechanism only in polluted waters (Morel et al., 1998). Independent site-specific field experiments could verify the impact of differences in streamwater biogeochemistry on evasion rates.

4. Conclusion

Iscos retrofitted with the appropriate and thoroughly cleaned sampling materials can be useful to sample streams for Hg_T analysis during high-flow events when concentrations are typically elevated above background levels (>2 ng L^{-1}). Carry-over from sample tubing and deposition to bottles are not significant sources of contamination. Hg_T losses from evasion ranging from 0-25% can be expected from samples comprised mainly of the dissolved fraction. If particulate Hg accounts for a larger fraction of the sample, Hg_T losses could be significantly less. Losses are related to both Hg concentration and ambient temperature, with higher concentrations and higher temperature both having larger relative losses of Hg from the sample. Maintaining a cool, uniform temperature where samples are held until retrieval could help to minimize evasion and keep relative losses similar in magnitude. Like all constituents that have particulate-bound components, careful placement of the intake strainer of the automated sampler is essential to avoid over-estimation of Hg concentrations. Results from this study demonstrate that automated sampling to measure Hg_T in streamwater during high-flow events is possible with careful assessment of potential sources of error.

5. Acknowledgements

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CHAPTER 3

Streamwater particulate mercury and suspended sediment dynamics in a mid-Appalachian forested headwater catchment

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Abstract

Due to the inherent differences in bioavailability and transport properties of particulate and dissolved mercury (Hg_P and Hg_D), it is important to understand the processes by which each is mobilized from soil to stream. Currently there is a paucity of Hg_P data in the literature, despite the fact that it can be the dominant fraction in some systems. We analyzed Hg_P in conjunction with volatile solids (VS, an estimate of organic content) and total suspended solids (TSS) and investigated the viability of using turbidity as a site-specific surrogate measure of Hg_P. Samples were collected for flow conditions ranging from 72 to 8223 L s^{-1} during October 2009 through March 2010 in a 10.5 km^2 forested headwater catchment. Total Hg concentrations ranged from 0.28 to 49.60 ng L^{-1}, with the relative amount of Hg_P increasing with discharge from approximately 40 to 97%. Storm dynamics of Hg_P and Hg_D were not consistent, indicating unique controls on the export of each fraction. During high-flow events Hg_P was consistently higher on the rising limb of the hydrograph compared with the receding limb for a range of discharge events, with this hysteresis contributing to a degraded relationship between Hg_P and streamflow. Overall, Hg_P was strongly positively correlated with VS (r^2 = 0.97), confirming the known association with organic carbon. Due to a consistent organic fraction of the suspended solids (34 +/-6%), Hg_P was also well correlated with TSS (r^2 = 0.95) with an average of 0.10 ng of Hg_P per mg of TSS in this system. Stream turbidity measured with an *in situ* sonde also had a strong correlation

with TSS (r^2=0.91), enabling commutative association with VS (r^2=0.86) and Hg_P (r^2= 0.76). Turbidity can explain more than twice the temporal variance in Hg_P concentrations (n=50) compared with discharge (r^2 = 0.76 versus 0.36), which leads to improved monitoring of Hg_P dynamics and quantification of mass fluxes.

1. Introduction

Mercury (Hg) in the aqueous environment is a resource management concern because, given an appropriate mix of environmental conditions, it can be converted into the neurotoxin methylmercury, which can bioaccumulate and pose a health risk to both humans and wildlife. Due to anthropogenic activities over the last 150 years, there has been a significant increase in the global atmospheric pool of mercury (Fitzgerald et al., 1998) and the amount deposited and incorporated into the terrestrial environment (Lorey and Driscoll, 1999; Schuster et al., 2002). Greater than 90% of the Hg deposited to the land surface is likely retained annually (Krabbenhoft et al., 1995; Allan and Heyes, 1998; Scherbatskoy et al., 1998; Shanley et al., 2008), making it a potential long-term source to downstream ecosystems. A growing body of literature evaluating streamwater Hg dynamics has firmly established that the majority of Hg is mobilized from soil to stream during high-flow snow-melt or storm events (Balogh et al., 1997, 2005; Allen and Heyes, 1998; Scherbatskoy et al., 1998; Shanley et al., 2002, 2008; Mast et al., 2005; Schuster et al., 2008). A majority of these studies have examined the dynamics and controlling factors of total Hg (Hg_T; composed of both particulate and dissolved fractions) and/or dissolved Hg (Hg_D; alternatively referred to as ‘filtered’). Few studies have directly measured the particulate fraction (Hg_P), which can be the dominant form of streamwater Hg in some systems (Hurley et al., 1998a; 1998b; Schuster et al., 2008). Furthermore, no studies have measured Hg_P in conjunction with sediment quantity and quality at the high temporal resolution necessary to determine the factors influencing Hg_P mobilization. Due to the inherent differences in bioavailability for methylation (Aiken et al., 2000) and transport properties of the particulate versus dissolved fractions of Hg, an understanding of controlling factors for each component is essential to assess the potential vulnerability of downstream ecosystems.

1.1 Hg dynamics and association with organic carbon

The relative abundance of streamwater Hg_P and Hg_D can vary spatially due to watershed heterogeneity and temporally due to shifts in organic matter cycling and mobilization of Hg from different locations (*e.g.* upper versus lower soil horizon, stream bottom sediment) associated with changes in discharge. Within the same watershed, Hg_P can comprise varying amounts of the total Hg concentration. For instance in six different streams within Sleepers River research watershed, Vermont, flow-weighted Hg_P ranged from 42% to 78% (Schuster et al., 2008) of Hg_T. Furthermore, within a single stream, the temporal dynamics of Hg_P and Hg_D vary with discharge but can be uncoupled, with the relative amounts changing between summer storms and snowmelt events (Schuster et al., 2008). Variability in Hg_P and Hg_D dynamics occurs on even shorter timescales such as within a single storm, where brief periods of elevated Hg_P concentrations can dominate the overall Hg_T flux (Shanley et al., 2002).

It is well established that organic matter plays a significant role in the fate and transport of Hg. In the soil, Hg associates with reduced sulfur sites within organic matter (Schuster, 1991, Yin et al., 1996; Xia et al., 1999) and is then mobilized to downstreamwater bodies during high flow events. Consistent positive relationships between Hg_T and/or Hg_D and dissolved organic carbon (DOC) have been observed over a range of discharge conditions and physical watershed characteristics (Mierle and Ingram, 1991; Joslin, 1994; Bishop et al., 1995; Driscoll et al., 1995; Hurley et al., 1995; Allen and Heyes, 1998; Barbiarz et al., 1998; Kolka et al., 1999; Grigal, 2002; Shanley et al., 2002; 2008; Galloway and Branfireun, 2004; Ravichandran, 2004; Nelson et al., 2007; Schuster et al., 2008; Dittman et al., 2009; Brigham et al., 2009; Demers et al., 2010). Under turbid high flow conditions the relationship between Hg_T and DOC may degrade (Hurley et al., 1995), believed to be caused by an increase in the fraction of Hg_P (Grigal, 2002).

Relative to Hg_T and Hg_D, relationships between Hg_P and organic carbon are not as well documented and are typically based on indirect evidence. A positive relationship between Hg_T and POC measured in streamwater has been documented in Vermont, Puerto Rico, and Colorado (Shanley et al., 2008) and northern Minnesota (Kolka et al., 2001) as well as in two branches of the Anacostia River in Maryland (Mason and Sullivan, 1998). Sherbatskoy et al. (1998) found a strong relationship between calculated Hg_P (computed as the difference between Hg_T and Hg_D) and volatile solids (VS; alternatively referred to as loss on ignition or organic sediment in the literature) at one site in the Lake Champlain Basin, Vermont. A relationship between directly measured Hg_P and POC has only been examined in three studies, one in an industrially-impacted river in Wisconsin which demonstrated a positive but weak relationship (Hurley et al., 1998b) and two located in Vermont headwater catchments (Shanley et al., 2002; Schuster et al., 2008) which revealed a strong positive correlation over a range of discharge conditions. Evaluating the relationship between Hg_P and the organic fraction of suspended sediment in a variety of systems could be of significance because it may be associated with the majority of Hg_T (50-80%) even in streams where it accounts for a small fraction of all organic carbon (Kolka et al., 1999).

1.2 Potential Hg_P surrogates

During elevated discharge, Hg concentrations can be highly variable over short time intervals. Such periods are critical because a majority of the annual export can occur during a single day of spring snowmelt or one storm event (Sherbatskoy et al., 1998; Babiarz et al., 1998). As a result, high-resolution data are needed during these periods to gain insight into controls on Hg transport as well as to accurately estimate export from a catchment. However, sampling programs are often limited by the cost and labor required to collect samples and analyze Hg. One alternative to high-frequency sampling during events is the use of a proxy variable which can be measured more readily. In particular we are interested in identifying a surrogate for Hg_P, the dominant form of Hg transported from the forested headwater catchment described in the present study.

One option to estimate Hg_P at a high frequency is to use a discharge rating curve, because discharge is routinely measured at existing water-quality monitoring stations. However, Hg dynamics during storm events are characterized by hysteresis (*e.g.* Bushey et al., 2008), making a rating curve unreliable during these most important time periods. For example, fluxes of suspended sediment (which similarly exhibit hysteretic behavior) estimated with discharge relationships have been shown to be less than 50% of measured fluxes (Christiansen et al., 2002). Reasons why simple sediment (and Hg_P) discharge rating curves are likely to be inaccurate include variability in source area supply (e.g. land surface, streambanks or bed) which can change during a single storm event, seasonal changes (*e.g.* frozen conditions in winter limit erosion), and variability in tributary inputs for larger rivers (Colby, 1956).

In systems where there is a strong correlation between TSS and Hg_P, TSS could be used as a site-specific proxy variable for Hg_P. Although TSS is much cheaper and easier to analyze than Hg_P, sampling during storm events at a high enough resolution to capture the short-lived peaks in particulates may still be difficult to achieve on a routine basis in some environments. TSS concentrations are often approximated with turbidity, an optical measurement of the water clarity, which is reduced due to the presence of suspended particles and colloids. Turbidity can be measured at a high frequency using *in situ* sondes at remote locations for long-term deployments (Lewis, 1996; Christensen et al., 2002; Rasmussen et al., 2003). If suspended particles have a consistent size distribution then TSS will have a strong linear relationship with turbidity. Sediment fluxes estimated in this manner have been shown to be within 4-6% of measured fluxes (Christensen et al., 2002). If a relationship can be established between Hg_P and TSS, and in turn TSS and turbidity, Hg_P concentration could be accurately estimated at a high temporal resolution.

It is important to understand how hydrologic and sediment dynamics affect mobilization of Hg_P in concert with Hg_D in order to accurately estimate total Hg fluxes, with these respective forms affecting the downstream fate of this contaminant. For a headwater catchment within Shenandoah National Park our objectives are: (1) to characterize the dynamics of Hg_P and Hg_D at a high frequency during storm events, (2) to evaluate the relationship between Hg_P, TSS and VS, and (3) to evaluate the efficacy of using *in situ* turbidity measurements as a proxy for Hg_P concentrations to improve flux calculations for individual Hg fractions at this site-. For each of these objectives we incorporate data collected over multiple seasons and a wide range of discharge conditions.

2. Study Site Description

Staunton River is located within Shenandoah National Park (SNP), in the Blue Ridge province of central Virginia. The 10.5 km^2 forested headwater catchment drained by Staunton River is underlain by granitic bedrock (Gathright, 1976), is undeveloped, and is covered by second- to third-growth mixed hardwoods interspersed with <5% coniferous trees (Young et al., 2005). Streamwater has a circumneutral pH and low DOC concentrations (below 1 mg L^{-1} during baseflow, maximum of ~5 mg L^{-1} during storms). Measurements of Hg_P and Hg_D were made at Staunton River during baseflow and high flow conditions from March 2009 through March 2010. Discharge has been gaged at the catchment outlet since 1992.

3. Materials and Methods

3.1 Field Methods

From October 2009 through March 2010 a total of 5 baseflow and 15 stormflow samples were collected and analyzed for Hg_P, Hg_D, TSS and VS. All baseflow samples were collected manually and high flow samples were collected either manually or with automated samplers as described in Riscassi et al. (2010). High flow samples were collected on the falling limb of the hydrograph during two separate storm events (November 19, 2009 and January 25, 2010) and on the rising and falling limb of another storm (March 13, 2010). Samples were collected over a wide range of discharge conditions, from 72 to 8223 L s^{-1} representing the 75% to 0.05% exceedence for the seventeen-year period of record at this site. Turbidity measurements were recorded on an hourly basis from the start of TSS/VS sample collection through December 2009, and every 30 minutes for the remainder of the study. A power failure from January 10-29, which represented the only major gap in the turbidity measurements, resulted in this parameter not being recorded during the January storm event. Occasionally grab and/or automated samples were not taken exactly on the hour or half-hour increment requiring linear interpolation to estimate the associated turbidity values.

In addition to these samples for which all parameters were measured, concurrent measurements of Hg_P, Hg_D and turbidity (without TSS and VS) were available for 31 high flow samples. An additional 6 measurements of Hg_P and Hg_D (without turbidity, TSS and VS) were available for the rising limb of the January 25 storm. Concurrent measurements of TSS, VS and turbidity (without Hg_P) were available for an additional 6 high-flow samples on the rising and falling limb of the March 13 storm.

All Hg samples were taken with glass bottles with Teflon® cap liners or Teflon® bottles. Glass or fluoropolymer materials such as Teflon® are used to minimize adsorption of Hg onto the bottle walls, which could result in Hg losses from the sample or contamination of future samples (Parker and Bloom, 2005). Sample bottles were cleaned by soaking in a 75°C 4N HCl bath for 48 hours, rinsed three times with deionized water, stored, placed in two nested resealable bags and filled with 0.4% HCl until needed. All sample collection and handling procedures followed ‘clean’ techniques for trace metals established by the U.S. EPA (1996). The automated sampler was retrofitted with glass bottles and Teflon® tubing to minimize contamination (Riscassi et al., 2010). All Hg grab samples were taken within 0.5 meters of the sampler inlet. All TSS/VS grab samples were collected using Nalgene® plastic bottles at the same location. Samples were transported from the field to the laboratory in a cooler and refrigerated at 4°C until subsequent filtering and/or analysis.

A turbidity sensor (YSI 6136) was used in conjunction with a multiparameter water quality sonde (YSI 6020V2) to measure and record turbidity in nephelometric turbidity units (NTU). This sensor is an *in situ*, active, 90° nephelometer, which conforms to the ISO-7027 standard (Downing, 2005). By actively producing light and detecting its scatter in the water, the sensor can measure turbidity. This sensor is self wiping to prevent bio-fouling of the lens and self logging and built for long-term deployment. Prior to initial deployment, the sensor was calibrated with two turbidity solutions (0 and 123 NTU). Every two weeks after the initial deployment, data were downloaded from the sonde and a quality control solution was used to evaluate the accuracy of the sensor. The turbidity sensor passed all quality assurance criteria established by Wagner et al. (2006). The sonde was housed in a perforated PVC tube coated in a copper based anti-biofouling paint to discourage algal growth that could possibly affect turbidity measurements. The PVC tube and sonde were positioned parallel to the main channel flow direction. The sonde was located within 1 meter of the inlet used for automated sampling of streamwater for Hg analysis.

Stream stage was measured by a float and pulley within a stilling well slightly downstream (~5 m) of the sampling location. Routine manual discharge measurements were made to establish a rating curve which was used to calculate discharge at hourly intervals.

3.2 Laboratory Methods

Samples for Hg analysis were filtered and preserved in the Hg laboratory at the University of Virginia typically within one week of sample retrieval. Samples collected with the automated sampler during storm events were retrieved within a week after storm sampling completed; a recent evaluation of effects from the delay in retrieval times of automated samples showed minimal differences in Hg concentrations, specifically for particulate Hg (Riscassi et al., 2010). The filtering process was carried out under a Class 100 clean bench. Samples were filtered through a pre-baked quartz fiber filter (Whatman QM-A grade, 2.2 µm 98% efficiency particle retention in liquid) in a vacuum-desiccator chamber with an acid leached Teflon® filter apparatus according to procedures documented in Lewis and Brigham (2004). The filter with captured filtrate was placed in a Teflon® bottle and 100 mL of a 5% bromium monochloride (BrCl) solution was added, submerging the filter. The bottle was tightly capped, double bagged and placed in a 50°C oven for 5 days to leach all Hg on the filter into solution. The remaining filtered sample water was preserved within an hour of filtration with a 100% BrCl solution (5 mL BrCl per 1 L sample) and stored until analysis. Samples were analyzed for Hg_P and Hg_D using a Tekran® cold-vapor atomic florescence spectrophotometer according to U.S. EPA method 1631, Revision E (2002). The method detection limit (MDL) for Hg_P was determined to be 0.08 ng of Hg_P per filter based on procedures defined in Olund et al. (2004). The volume of water filtered was approximately 0.375 L (automated samples) or 1 L (grab samples), and this provides a minimum sample reporting limit of either 0.21 or 0.08 ng L^{-1}. Hg_P is operationally defined for this study to be Hg adsorbed to particles not passing through the quartz fiber filter (QFF). The MDL for Hg_D was determined to be

0.19 ng L^{-1} from the standard deviation (0.06) of seven aliquots of a 0.65 ng L^{-1} solution (U.S. EPA, 1986).

TSS sample water was filtered through a QFF, dried and weighed to obtain TSS concentration according to U.S. EPA method 160.2 (1971). The filtrate was then heated at 500°C for 2 hours to burn off any organic matter and weighed again to obtain the non-volatile solids (also referred to as inorganic or mineral solids) according to U.S EPA method 160.4 (1971). The difference between TSS and non-volatile solids concentrations is the volatile solids (VS), also referred to as the loss on ignition (LOI). LOI is often used as a surrogate for POC as well as soil organic carbon (SOC) and has been shown to maintain a unique linear relationship (r^2>0.94) with SOC for a particular location (Konen et al., 2002). The MDL for TSS and VS was determined to be 0.30, and 0.27 mg L^{-1}, respectively. TSS is operationally defined as particles not passing through the 2.2 μm QFF to be consistent with the Hg_P methods.

3.3 Quality Assurance and Quality Control

Overall Hg laboratory accuracy was determined by participation in an inter-laboratory proficiency test administered by Environment Canada in January 2010. The proficiency sample concentrations ranged from 6.6 to 47.8 ng L^{-1} and recoveries for our lab ranged from 97 to 102% (n=5). Laboratory accuracy was verified by ongoing analysis of a certified reference material and recoveries were within 90 to 110%. Matrix spikes, ongoing precision and recovery (OPR) analysis, method and system blanks were used to evaluate instrument performance. The accuracy and precision of the matrix spikes and standards were maintained within 10% and the OPR samples were maintained within 15%. System and method blanks (n=41) were below MDL with the exception of three system blanks, each in different analytical runs, of 0.21, 0.27 and 0.23 ng L^{-1}. Reported quality control metrics are all within U.S. EPA (2002) guidelines. During three filtering sessions, the 5% BrCl solution (analyzed separately in duplicate) had a concentration above detection limit (0.25, 0.78, 0.42 ngL^{-1}); the respective value was subtracted from all filter concentrations using that solution. All Hg_P and Hg_D laboratory blanks (n=13) were below MDL. The relative percent difference for field duplicates (n=4) was <6% for both Hg_P and Hg_D. All field blanks (n=5), which include de-ionized (DI) water collected during grab sampling and a bottle left open and empty in the automated sampler and subsequently filled with DI water in the lab, were all below the MDL. The relative percent difference for the TSS/VS field duplicate was less than 5% for both parameters.

4. Results

4.1 Hg_T concentrations and physical fractions

Hg_T concentrations at all sites ranged from 0.28 to 49.60 ng L^{-1} for all samples collected during the study, with the particulate fraction accounting for an average of 62% of Hg_T during baseflow and 86% during high flow. During baseflow conditions, Hg_T was consistently low, typically below 1 ng L^{-1}. Relative to baseflow conditions, both fractions of Hg_T increased during high flow, with Hg_P concentrations increasing dramatically (maximum of 48.3 ng L^{-1}) compared to Hg_D (maximum of 2.12 ng L^{-1}). Hg_T and Hg_P are each positively correlated with discharge, although the fraction of variance explained is low (r^2=0.35 and 0.36, respectively).

4.2 Hg_p and Hg_D storm dynamics

Hg_P and Hg_D concentrations were measured on both the rising and falling hydrograph limb of four storms of varying magnitude, with maximum discharges of approximately 350, 750, 7400, and 8200 L s^{-1}. During each storm, Hg_P concentrations were higher on the rising limb of the hydrograph compared with the receding limb and peaked around maximum discharge. An example of this typical behavior is shown in Figure 1. Peak concentrations of Hg_P were variable for each storm, ranging from about 3 to 48 ng L^{-1} with higher concentrations corresponding with higher peak discharge.

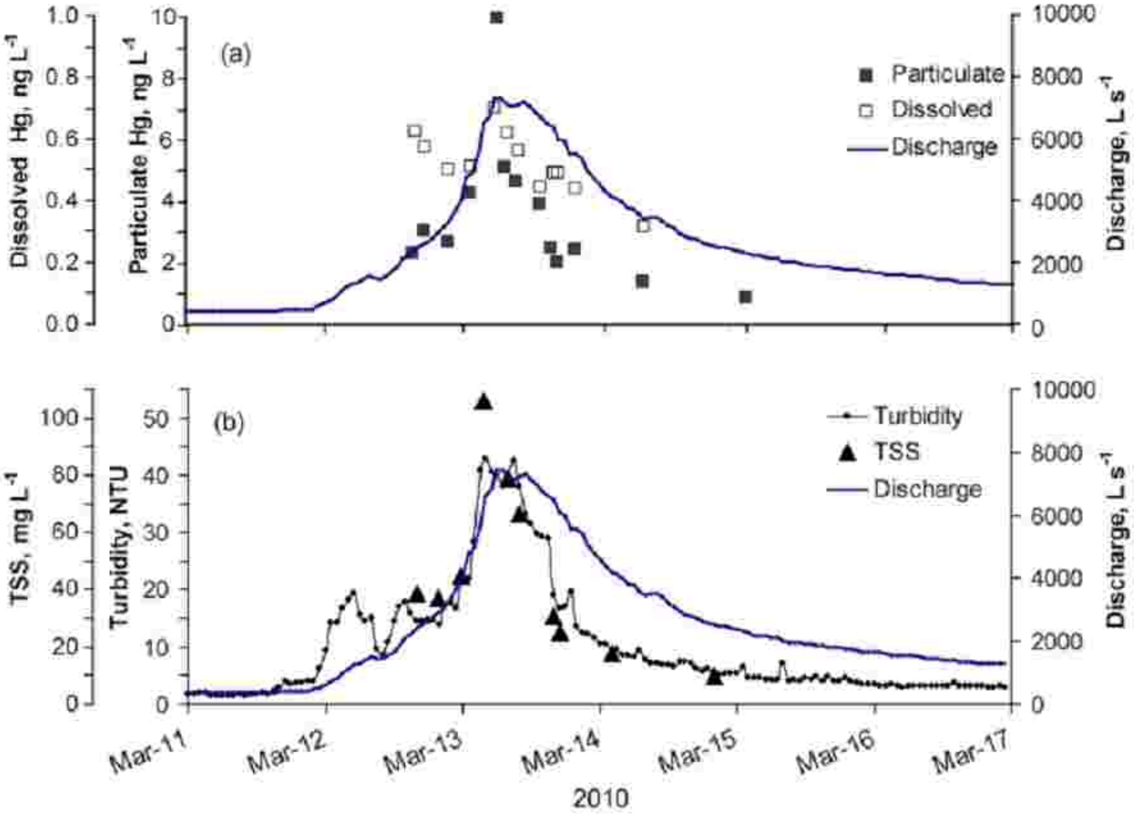

Figure 1. March 12-13, 2010 storm hydrograph illustrating (a) particulate and dissolved Hg dynamics and (b) turbidity and total suspended solids (TSS) dynamics. Note the differences in scale between each pair of y-axes.

Although Hg_D concentrations increased with discharge, the temporal dynamics were unique for each storm with peak concentrations occurring prior to, during and after peak discharge. Peak Hg_D had a relatively narrow concentration range, from 0.7 to 1.3 ng L^{-1}, and unlike Hg_P, the highest concentration was not associated with the highest peak discharges. As a result of the differences in dynamics within storms, the overall correlation between Hg_P and Hg_D is low ($r^2 = 0.26$).

4.3 Suspended Sediment Quantity/Composition and Hg_P

Hg_P is highly correlated with VS ($r^2 = 0.97$, Figure 2a) which is expected based on the known association of Hg with organic matter. The relationship is only slightly weaker between Hg_P and TSS ($r^2 = 0.95$, Figure 2b). The strength of the relationship between Hg_P and TSS is maintained because the relative fraction of VS remains constant (indicating a consistent source of the suspended sediment), comprising on average 34.8% ± 6.5% (Figure 3) over a wide range of discharge conditions and suspended sediment concentrations. While both relationships are robust for the study period, we acknowledge there are no samples during the growing season, a period in which the source of suspended sediment and associated amounts of VS and Hg_P may differ. For example, brief, intense summer thunderstorms with likely greater erosive power may mobilize larger amounts of near surface soils which could be more enriched in VS and Hg from recent decomposition and throughfall, respectively. As a result of these and other uncertainties, the predictive relationships should only be applied to the time period over which they have been calibrated.

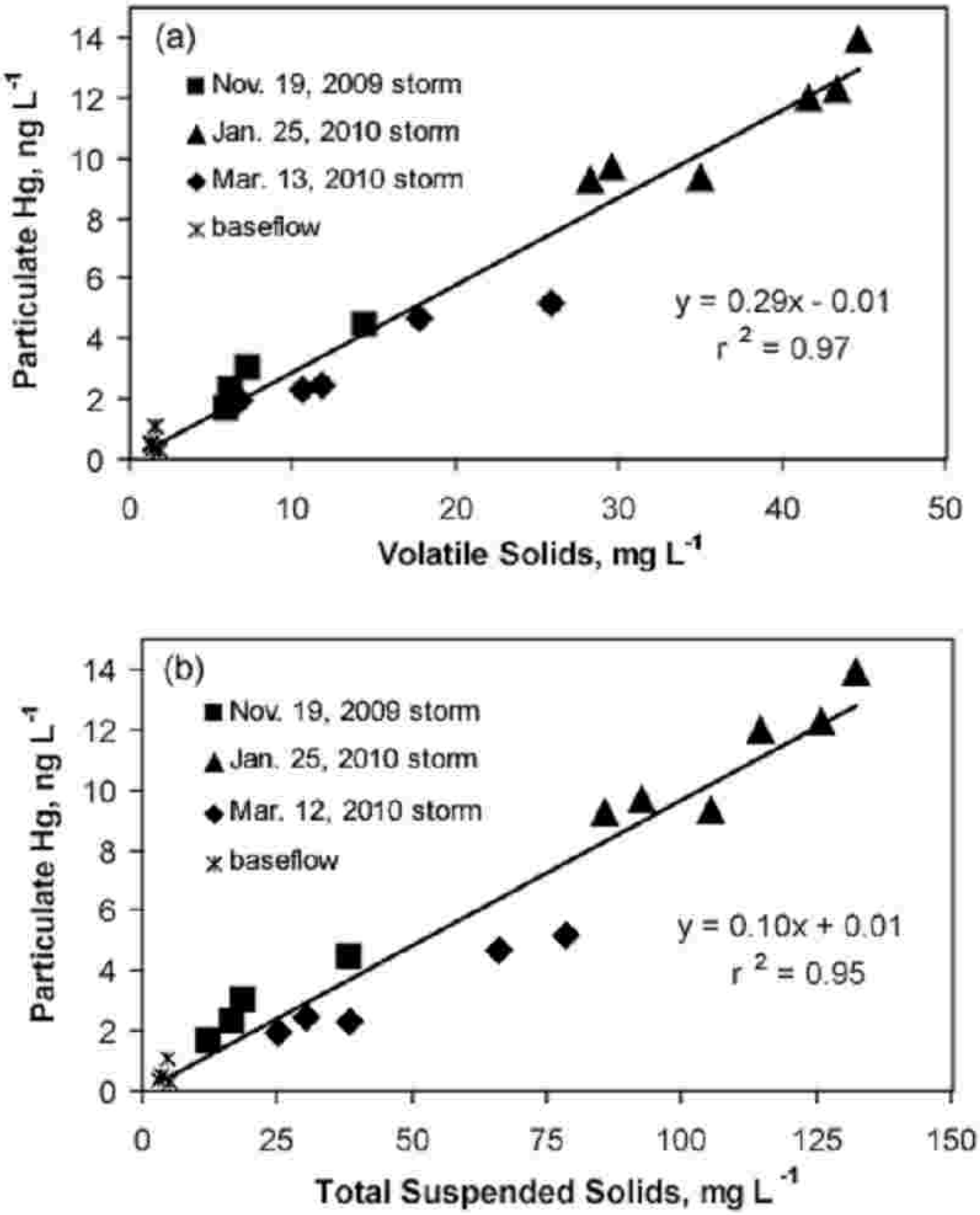

Figure 2. (a) Volatile solids and (b) total suspended solids versus particulate Hg for discharge ranging two orders of magnitude at Staunton River measured from October 2009 through March 2010. The linear best fit line shown is determined from baseflow and stormflow data.

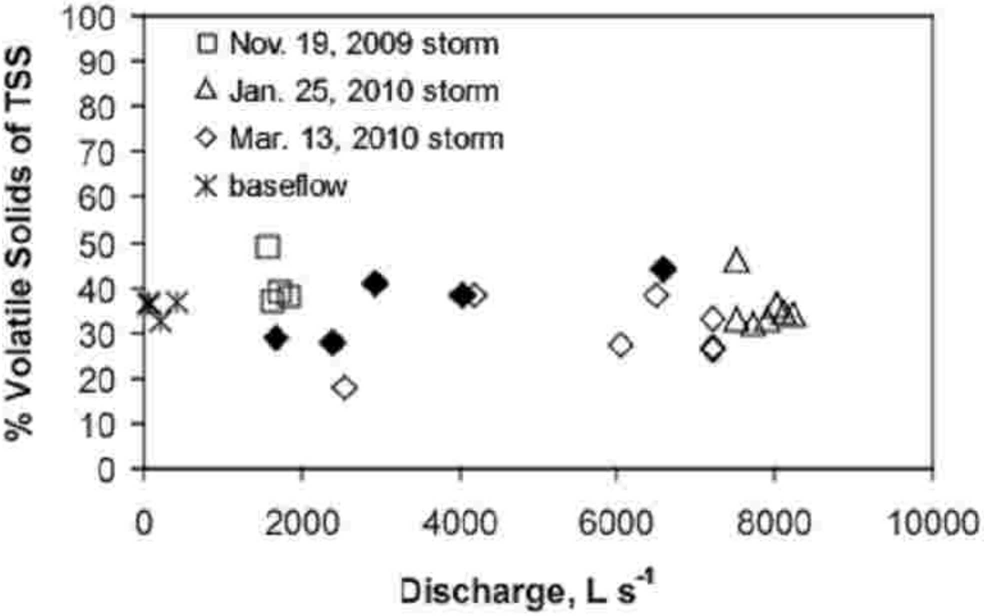

Figure 3. Percent volatile solids (VS) of total suspended solids (TSS) measured at Staunton River from October 2009 through March 2010. The percent VS is consistent for a variety of discharge conditions which includes both rising (closed symbol) and falling (open symbol) hydrograph limbs as well as baseflow periods.

4.4 Turbidity relationships to TSS/VS/Hg_P

At our study site, turbidity maintains a strong relationship with TSS (r^2=0.91) and VS (r^2=0.86) for the range of flow conditions measured (Figure 4). Because TSS can be used as a predictor for Hg_P and turbidity is a strong proxy for TSS in our system, turbidity can be used as a high-frequency surrogate for Hg_P as evident by its strong linear relationship with Hg_P for the seasons evaluated and range of discharge conditions measured (r^2=0.76) (Figure 5). Similar to Hg, turbidity has a positive but relatively weak relationship with discharge (r^2 = 0.50, Figure 6) due to both the variability between storms as well as the difference between the rising and falling hydrograph limbs for a single storm as illustrated in Figure 1b.

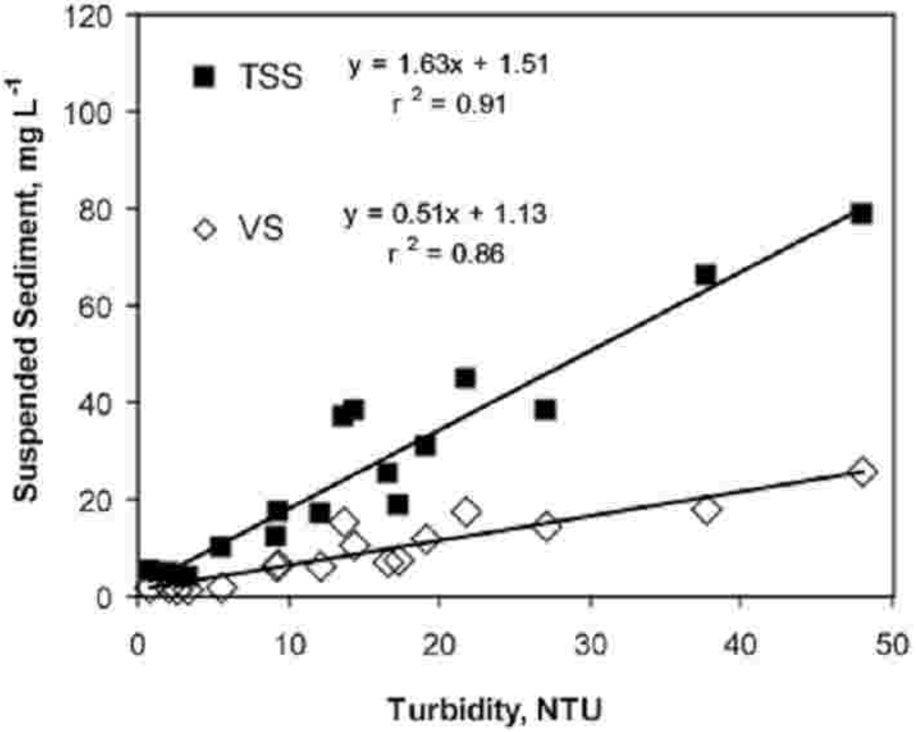

Figure 4. Turbidity versus total suspended solids (TSS) and volatile solids (VS) at Staunton River measured from October 2009 through March 2010.

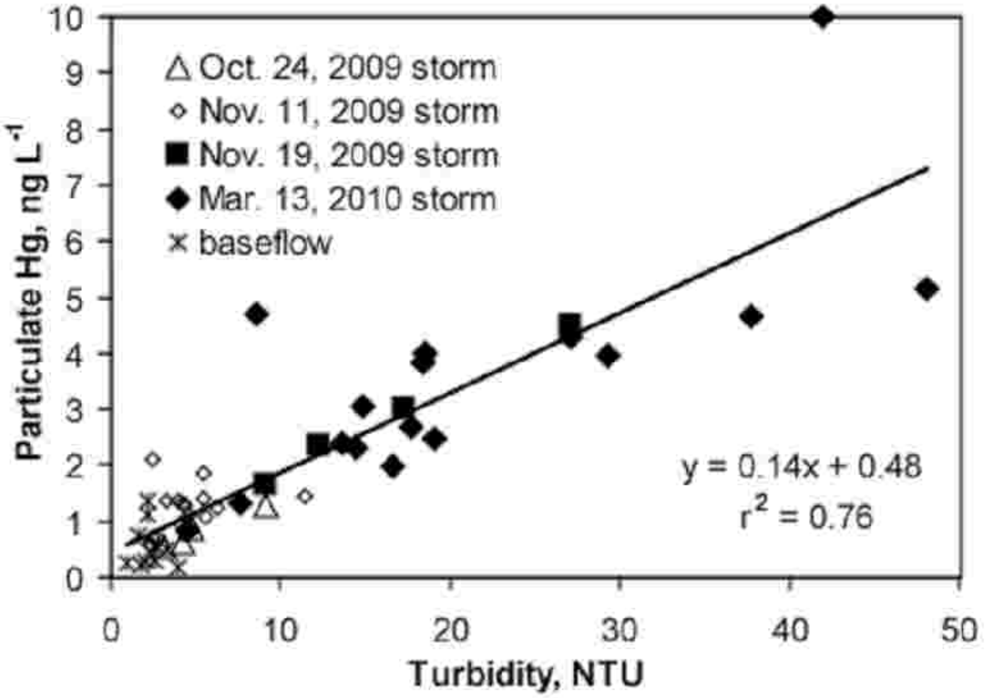

Figure 5. Turbidity versus particulate Hg at Staunton River recorded from October 2009 through March 2010. The linear best fit line is determined from both baseflow and stormflow data.

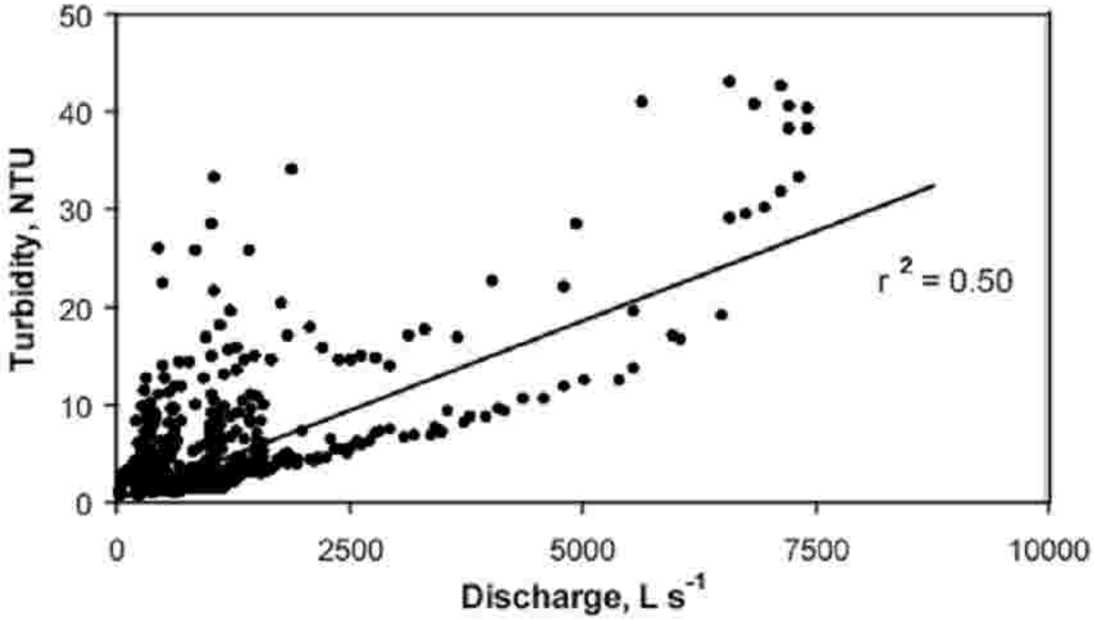

Figure 6. Discharge versus turbidity at Staunton River measured from October 2009 through March 2010.

5. Discussion

5.1 Hg_T and Hg_P

The range of Hg_T and Hg_P concentrations measured in Staunton River during the study period were similar to those found in other unpolluted streamwater studies (Westling, 1991; Balogh et. al, 1997; Kolka, et al., 1999; Babiarz et al., 1998; Sherbatskoy et al., 1998; Shanley et al., 2002, 2008; Porvari and Verta, 2003). Staunton River is typically dominated by Hg_P during both baseflow and high flow conditions. A few other watersheds have been shown to be similarly dominated by Hg_P annual export, but due to large amounts of export during brief periods within high flow events (Sherbatskoy et al., 1998; Shanley et al., 2002; 2008). Other forested watersheds (Hurley et al., 1995; 1998a; Schuster et al., 2008) have been shown to be dominated by Hg_D during all flow conditions. Differences in physical partitioning of Hg_T are typically explained by factors that account for differences in mobilization of the streamwater ‘carriers’, particulate and/or dissolved organic matter (Yin and Balogh, 2002). For example, watersheds with highly erodible soils and/or those that are subjected to physical disturbance in riparian areas will have larger amounts of particulate organic material, and likely Hg_P, in streamwater. Watersheds dominated by wetlands and peatlands have lower amounts of particulates due to reduced flow velocities and are likely to be dominated by dissolved Hg (Babiarz et al., 1998). Although our study system is an upland undisturbed watershed, it has relatively steep slopes and erodible soils which tend to increase particulate mobilization to streams. Furthermore our watershed contains no wetland or peatland habitat and is a low DOC system (< 3 mg L^{-1}, data not shown), so the dissolved carrier for Hg is minimal.

Differences in within-storm dynamics between Hg_P and Hg_D indicate that each is mobilized by distinct factors. The concentrations of particulates and associated Hg_P is related to the magnitude of the discharge event, with higher flow rates able to mobilize water in the more erodible upper soil horizons and also impart greater sheer stress to erode near-stream soils and mobilize in-stream sediment. Although Hg_D concentrations also increase from baseflow levels during storm events, the relative magnitude and timing are not influenced by discharge alone. An analysis of Hg_D in conjunction with the quality and quantity of DOC during the storm events is necessary to investigate the factors that control Hg_D dynamics, but that is beyond the scope of this paper. Studies that have evaluated Hg_D and DOC dynamics (Schuster et al., 2008; Dittman et al., 2010) have found that Hg_D export is correlated to both the quantity and quality of DOC. Shifts in flow paths associated with changes in stream discharge can mobilize organics from different source areas which may differ in both concentration and composition. Seasonal differences in decomposition rates will also affect DOC quantity and quality in streamwater and associated Hg_D export.

5.2 TSS and Hg

Studies that have evaluated both Hg_T and TSS have found relationships of considerably different strength with coefficients of determination ranging from 0.13 to 0.99 (Table 1). Several reasons may account for the large amount of variability in the strength of this relationship. Hg_T is comprised of both dissolved and particulate fractions and therefore significant Hg_D concentrations that vary independently from Hg_P can degrade the Hg_T-TSS relationship. Even if Hg_P is the dominant fraction of Hg, TSS may not always be able to account for the variability in Hg_T. Hg_P is known to associate with the organic fraction of TSS, but in order to use TSS as a simple linear estimator for Hg_P, the organic fraction must be relatively consistent. If the organic fraction varies, TSS will not have as strong a linear relationship with Hg_T. However, if the ratio changes with regularity which can be modeled (*i.e.* seasonally and/or with discharge) then the predictive power could be maintained. At Staunton River, Hg_P is the dominant form of Hg and the organic fraction of TSS is consistent over a range of discharge conditions, resulting in a strong linear relationship between TSS and Hg_T (r^2=0.91).

Table 1. Summary of r^2 values between total and particulate Hg (Hg_T and Hg_P, respectively) and total suspended solids (TSS), volatile solids (VS)/organic solids (OS) and particulate organic carbon (POC) for a variety of studies reported in the literature.

Study	Hg_T			Hg_P		
	TSS	VS/OS	POC	TSS	VS/OS	POC
Balogh et. al, 1997	0.96	-	-	-	-	-
Balogh et al., 1998	0.98	-	-	-	-	-
Hurley et al., 1998b	0.41	-	0.38	0.36	-	0.37
Mason and Sullivan, 1998	0.13	-	0.29	-	-	-
Sherbatskoy et al., 1998	0.41	-	-	-	0.85	-
Kolka et al., 1999	-	-	0.6	-	-	-
Whyte and Kirchner, 2000	0.96	-	-	-	-	-
Kolka, 2001	-	-	0.76	-	-	-
Lawson and Mason, 2001	0.41*	-	-	-	-	-
Shanley et al., 2002	-	-	-	-	-	0.84
Balogh et al., 2003	0.99*	-	-	-	-	-
Wall, 2005	0.91*	-	-	-	-	-
Shanley et al., 2008	-	-	0.82*	-	-	-
Schuster et al., 2008	-	-	-	-	-	0.72*
Present study	**0.91**	**0.94**	-	**0.95**	**0.97**	-

* average of multiple values

On average there was 0.10 ng of Hg_T per mg of TSS at our site, within the range found in other studies showing a strong correlation between Hg_T and TSS (excluding sites downstream of Hg point sources such as mine discharge). Our site has less Hg_T per mg of TSS than reported by Wall et al. (2005; 0.13 ng mg^{-1}) but higher than reported in Balogh et al. (1997, 1998, 2003) (0.044, 0.045, and 0.046-0.052 ng mg^{-1}, respectively). In contrast to our study, the others were conducted in large metropolitan rivers with 2 to 4 times the concentration range for TSS, although reported Hg_T concentrations were similar. Variability in the amount of Hg_T per mg TSS could be affected by differences in organic content and size distribution of TSS. The amount of Hg_D will also affect this ratio. There is insufficient information from existing studies to systematically explain the wide degree of variation observed in Hg_T-TSS relationships among sites.

For our study site, the relationship between Hg_T and VS (r^2=0.94) was stronger than other studies that compared Hg_T to POC concentration (Table 1). We attribute the weaker relationships in other systems to several factors: Hg_D may have had more influence on Hg_T concentrations, and the other catchments studied vary in hydrologic complexity (*e.g.* influenced by wetlands, peatlands and long spring thaw/snowmelt periods) mobilizing water from different source areas with different Hg_P to POC ratios.

VS is approximately 34% of TSS over the course of three storm events and during baseflow conditions. Because of this consistent fractioning, TSS is almost as good as VS in explaining variability in Hg_P concentrations (r^2 = 0.95 for TSS versus 0.97 for VS), despite the fact that Hg_P is known to predominantly associate with the organic fraction of the suspended sediment (Shanley et al., 2002; Schuster et al., 2008). Our results show that Hg_P at Staunton River has approximately 0.29 ng Hg_P per mg VS. Sherbatskoy et al. (1998) compared Hg_P to VS at a forested catchment in Vermont and found a weaker relationship (r^2=0.85), and the particulates transported approximately 0.55 ng Hg_P per mg VS, almost twice the amount at our site. The range of Hg_P and VS concentrations were similar between sites during their respective measurement periods and both are small forested watersheds receiving similar amounts of wet Hg deposition. However a smaller filter size was used in the earlier study (0.22 µm versus 2.2 µm in our study) and smaller particles may be relatively enriched in Hg owing to their larger ratio of surface area to mass. Future research efforts are needed to determine which factors contribute to the differences in the relative amount of Hg_P per unit VS. A few studies have compared Hg_P with POC. For example, Hurley et al. (1998b) investigated a large industrially impacted river in Wisconsin, while Shanley et al. (2002) and Schuster et al. (2008) examined several smaller forested/agricultural watersheds in Vermont. All sites reported a positive Hg_P-POC relationship but as expected the larger impacted river had a much weaker relationship (r^2=0.37 versus 0.84) and significantly more Hg_P per mg POC (~7 versus ~1.5 ng).

5.3 Turbidity, TSS and Hg

Stream turbidity measured with an *in situ* sonde had a strong correlation with concurrent measurements of TSS, VS, Hg_T and Hg_P concentrations for the measurement period, encompassing a variety of discharge conditions at Staunton River. Only one other published study is known to have compared turbidity and Hg. Whyte and Kirchner (2000) monitored Hg_T export from an abandoned mercury mine site in northern California where 99.97% of the Hg_T export was in the particulate form. Although our system is very different from the California site in both stream Hg concentrations (4 orders of magnitude greater at the mine site) and TSS concentration (an order of magnitude greater at the mine site) there are key similarities that result in turbidity being a good surrogate for Hg_P in both systems. There was a stable relationship between turbidity and TSS (r^2=0.90 at the mine site; r^2=0.91 at our site) for a range of conditions and the amount of Hg_P per unit of TSS was not affected by changes in discharge, TSS, or Hg concentration. We believe that this is due to two factors acting in concert in our system: the VS fraction of TSS which transports the Hg_P is temporally invariable, and the Hg-to-VS ratio is spatially consistent. This may not be true for all systems, especially in rivers with variable source areas with unique Hg and OC concentrations such as described in Bushey et al. (2008) in which Hg_T was not strongly related to TSS.

The motivation to use turbidity rather than simply using a discharge rating curve is also apparent at both sites. The relationship between Hg_T and discharge (r^2=0.56 at the mine site; r^2= 0.35 at our site) is significantly weaker than the relationship between Hg_T and turbidity (r^2=0.96 at the mine site; r^2=0.85 at our site). In both systems the release of Hg downstream is highly episodic and as a result, routine sampling programs are likely to miss the brief periods of elevated Hg_P and underestimate export. Conversely, storm-focused sampling programs such as the one in this study would likely overestimate downstream export if discharge were used as the sole predictor of Hg_P. As a consequence of all these factors, turbidity is a better surrogate to reliably estimate Hg_P at a high frequency for long term flux calculations at each of these unique sites.

5.4 Methods for computing Hg_P fluxes

When an ample data set has been acquired over a variety of hydrologic conditions, fluxes are typically computed by using some variation of a concentration model built on stream discharge to construct a continuous Hg record, with each measurement then multiplied by the associated discharge over the period of interest (Driscoll et al., 1998; Sherbatskoy et al., 1998; Krabbenhoft et al., 1995, Johansson et al., 1991; Lee et al., 1995; Mierle and Ingram, 1991; St. Louis et al., 1994; Shanley et al., 2008). As demonstrated in our system, the relationship between Hg and discharge can be relatively weak. Using the turbidity relationship to estimate continuous Hg_P and the corresponding Hg flux is a more appropriate method and can significantly improve the overall concentration and flux estimations. Overall, the mean absolute error in Hg_P concentrations (n=50) for the discharge estimation method was nearly three times greater (1.60 versus 0.54 ng L^{-1}) than for the turbidity rating (Figure 7). For the 5 month study period, the calculated Hg_P flux was 72% greater using the discharge compared to the turbidity rating (1.15 vs 0.67 µg m^{-2}) which is a large disparity when computing watershed Hg budgets. For perspective, the annual Hg wet deposition is approximately 9-12 µg m^{-2} (based on MDN values for nearby Big Meadows, Shenandoah National Park, VA). For our system, using a discharge rating to estimate Hg_P would lead to gross overestimations of export and underestimation of retention.

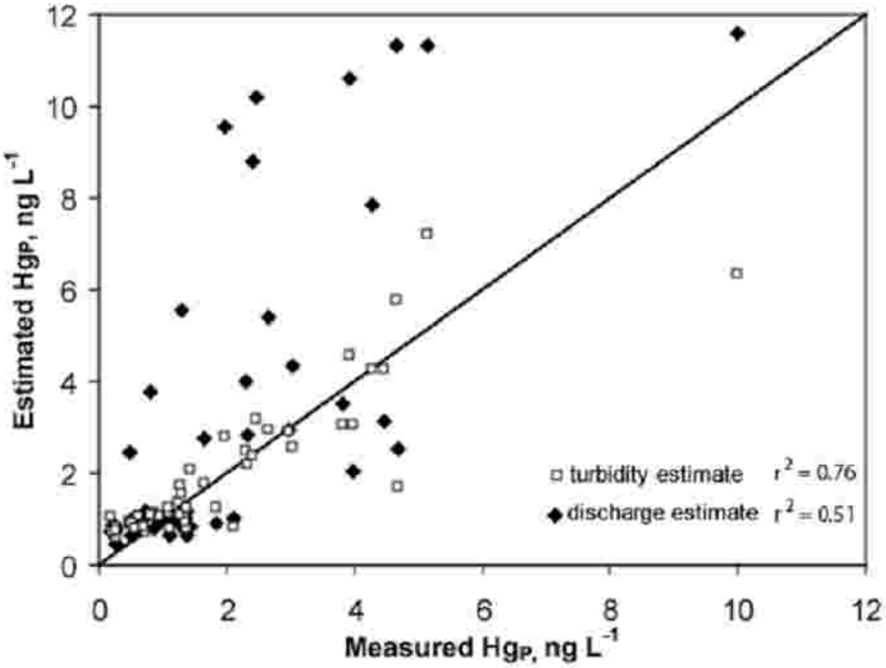

Figure 7. Measured and estimated particulate Hg (Hg_P) concentrations using the turbidity and discharge ratings. Both methods under and overpredict measured concentrations, but the magnitude of error is greater for the discharge rating. Both estimation methods consistently overpredict Hg_P when concentrations are below 0.8 ng L^{-1}.

It is worth noting that during baseflow conditions both methods consistently overestimate the Hg_P concentration. Analyzing baseflow data separately reveals that neither turbidity nor discharge has a significant relationship with Hg_P ($p<0.05$, $r^2<0.02$). Since turbidity values at baseflow are typically less than 3 NTU and Hg_P is less than 1 ng L^{-1}, this approaches the limit of our analytical detection limits making the relationship unreliable. Even though baseflow concentrations and discharge are both low relative to storm flow conditions, they typically represent a majority of the data period, so overestimation could influence the long term flux calculations. In this case, linear interpolation of concentrations between measurements would be more appropriate for baseflow periods.

6. Implications

Our research has demonstrated that a reliable predictive relationship can exist between turbidity and Hg_P concentrations during high flow conditions such that Hg_P can be estimated at a high frequency during storm events when the majority of Hg is transported downstream. Continuous Hg concentrations, in conjunction with discharge measurements, can then be used to calculate fluxes and evaluate short-term dynamics of Hg_P. Flux calculations are necessary inputs to mass balance and bioaccumulation models, used to understand and predict how and where Hg is stored and moves within an ecosystem. Accurate calculations of Hg fluxes are needed to establish baseline conditions necessary to evaluate the recovery of these systems resulting from the Hg regulations set forth in the U.S. EPA Clean Air Mercury Rule, which is scheduled to be finalized by November 16, 2011 (U.S. EPA, 2010).

The relationship between Hg_D and DOC has been established in the literature for some time and recently UV absorbance measurements at 254 nm (UV_{254}) have been shown to be reliable proxies for Hg_D concentrations (Dittman et al., 2009). Similar to the turbidity sondes, *in situ* optical measurement sondes are available to provide high-resolution time series data which can be used to calculate Hg_D fluxes after establishing an empirical relationship for a particular site (Dittman et al., 2009). Concurrent deployment of a turbidity and an optical sonde could be used to estimate the high resolution Hg_P and Hg_D concentrations necessary to make the most accurate Hg_T flux calculations possible. The relatively low costs associated with sonde deployment and maintenance are appealing in comparison to the labor intensive, high-cost regular Hg_T sampling programs currently in place. As a result, researchers will be more likely to maintain enduring Hg monitoring programs. These long-term data sets are necessary to evaluate the relatively slow response of aquatic environments to future changes in atmospheric Hg deposition.

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CHAPTER 4

Controls on streamwater dissolved mercury concentrations in three mid-Appalachian forested headwater catchments

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Abstract

Determining the controls on dissolved mercury (Hg_D) transport is necessary to improve estimations of export from unmonitored watersheds and to forecast responses to changes in deposition and other environmental forcings. Streamwater Hg_D and dissolved organic carbon (DOC) were evaluated over a range of discharge conditions in three streams within Shenandoah National Park, VA. Watersheds are distinguished by streamwater pH (ranging from neutral to acidic) and soil particle size distribution (ranging from clays to sands). At all sites, discharge was a significant but poor predictor of Hg_D concentrations (r^2 from 0.13–0.52). Hg_D was strongly coupled with DOC at all sites (r^2 from 0.74–0.89). UV absorbance at 254 nm (UV_{254}), a proxy for DOC quantity and quality, slightly improved predictions of Hg_D. Mean DOC quality differed between streams, with less aromatic DOC mobilized from the more acidic watershed. The site with less aromatic DOC and sandy soils mobilized more Hg to the stream for the same quantity and quality of DOC, likely due to the reduced capacity of the larger-grained soils to retain Hg, leaving a greater fraction associated with the organic matter. A similar amount of 0.54 ng Hg_D per mg DOC is transported at all sites, suggesting the less aromatic DOC transports less Hg per unit DOC, offsetting the effects of soil type. This research demonstrates that soil composition and DOC quality influence Hg_D export. We

also provide evidence that soil organic carbon is a primary control on Hg-DOC ratios (0.12–1.4 ng mg^{-1}) observed across the U.S. and Sweden.

1. Introduction

Increases in mercury (Hg) emissions to the atmosphere from anthropogenic sources have contributed to elevated concentrations in the environment since the industrial revolution (Lorey and Driscoll, 1999; Kamman and Engstrom, 2002; Schuster et al., 2008). Mercury deposited from the atmosphere to the terrestrial or aquatic environment can ultimately be converted into the bioavailable methylmercury (MeHg) which accumulates up the food chain and can have toxic effects on fish (Dillon et al., 2010), wildlife (Wolfe et al., 1998; Scheuhammer et al., 2007), and ultimately humans (Mergler et al., 2007). As of 2008, a fish consumption advisory for Hg has been issued in every U.S. state, encompassing 1.3 million river miles (U.S EPA, 2009). The U.S. Environmental Protection Agency is currently in the process of defining limits on Hg emissions from coal fired power plants, the largest single unregulated anthropogenic source remaining in the U.S. (Pacyna et al., 2006; 2010). While controlling emissions is an important step at reducing Hg in the environment, a large reservoir of mercury stored in soils from historic deposition will likely be a long-term source of Hg to streams (Krabbenhoft et al., 1995; Allan and Heyes, 1998; Scherbatskoy et al., 1998; Hintelmann et al., 2002; Shanley et al., 2008). Although total Hg (Hg_T) in streamwater is comprised of both particulate (Hg_P) and dissolved forms (Hg_D), concern is typically focused on Hg_D as it is likely more bioavailable (Aiken et al., 2000). A better understanding of the physical and chemical influences that govern Hg_D transport is needed to predict the fate of Hg in the environment under scenarios of changing Hg deposition and altered environmental forcing.

Wetlands, lakes and reservoirs have been the primary focus of aquatic Hg cycling studies over the past two decades, while more recent attention has turned to understanding the factors governing Hg transport and bioaccumulation in stream and river systems (Shanley et al., 2002, 2008; Bushey et al., 2008; Schuster et al., 2008; Brigham et al., 2009; Marvin-Dipasquale et al., 2009; Chasar et al., 2009; Tsui et al., 2009; Demers et al., 2010; Dittman et al., 2009, 2010; Schelker et al., 2011) where contamination is also widespread. Individual watershed studies have consistently found that total and/or dissolved Hg concentrations increase with discharge and are typically positively correlated with dissolved organic carbon (Mierle and Ingram, 1991; Joslin, 1994; Bishop et al., 1995; Driscoll et al., 1995; Hurley et al., 1995; Allen and Heyes, 1998; Barbiarz et al., 1998; Kolka et al., 1999; Grigal, 2002; Shanley et al., 2002; 2008; Galloway and Branfireun, 2004; Ravichandran, 2004; Mast et al., 2005; Nelson et al., 2007; Schuster et al., 2008; Dittman et al., 2009; Brigham et al., 2009; Demers et al., 2010). The basic conceptual model is that with increasing discharge, flow paths shift from the mineral soil horizon to the upper organic rich soil horizon where Hg has become bound to reduced sulfur sites within organic matter (Schuster, 1991; Xia et al., 1999; Skyllberg et al., 2000; Hesterberg et al., 2001; Haitzer et al., 2002; Ravichandran, 2004; Skyllberg et al., 2006). With this shift in flow paths, greater concentrations of solutes, including dissolved organic carbon (DOC), are mobilized to the stream (Boyer et al., 1997) along with the associated Hg_D. Similarly, higher water levels can connect DOC-rich wetland and/or peatland areas within a watershed, thereby mobilizing elevated levels of DOC and Hg to the stream (Selvendiran et al., 2008; Schelker et al., 2011).

While DOC and Hg transport are consistently linked, it is the hydrophobic organic acid fraction (HPOA) of DOC in particular that appears to be most important to Hg transport due to its significantly higher reduced sulfur content (Ravichandran, 2004). HPOA also contains almost all of the aromatic compounds in DOC (Dilling and Kaiser, 2002) as a result of lignin degradation (Malcom, 1990). Because humic aromatic compounds absorb light proportionally to their concentration, UV absorbance at 254 nm is a good surrogate for HPOA (Dilling and Kaiser, 2002; Dittman et al., 2009) and both parameters have been shown to explain more variability in Hg streamwater concentrations than DOC alone (Shanley et al., 2008; Dittman et al., 2009). With the principal factors of discharge, organic carbon quantity, and organic carbon quality governing Hg mobilization already generally established, our attention turns to deciphering the local environmental controls on Hg_D export from soils to streams.

Both soil solution pH and soil particle size distribution have been shown to influence the partitioning between Hg adsorbed to the soil matrix and Hg in soil solution, which may be mobilized in dissolved form to the stream. A comprehensive laboratory study by Yin et al., (1996) evaluated Hg adsorption for 15 different soils of varying organic matter and clay/silt/sand composition over a range of pH conditions. They found that Hg tended to exhibit greater retention (*i.e.* adsorption to soil particles) at low pH in the range 3-5. Significant desorption occurred at progressively higher pH. This general trend is caused by the association of Hg with organic matter, which is more soluble at high pH with the DOC in solution dominated by the more aromatic fraction (with more

Hg binding sites). The likely mechanism for increased desorption at higher pH is more negative charges on both organic matter and soil inorganic solid surfaces causing increased desorption (You et al., 1999; Pedrot et al., 2009; Donahue et al., 1998). At a fixed pH, however, there was also considerable variability (10-30 % difference) in the amount of Hg adsorbed to the soil (Figure 1). These differences were found to be dependent on soil properties, with soil surface area the most important factor (Yin et al., 1996). Clay soils retained more Hg due to a greater amount of adsorption sites. While there is precedence in laboratory literature, no watershed-scale studies have sought to determine the effects of soil particle size distribution and pH on Hg transport. It is essential to understand the relative importance of these processes at the field scale in order to, for example, predict where streamwater Hg transport is likely to be elevated or to separate the effects of reductions in Hg deposition from other factors such as decreases in acid deposition.

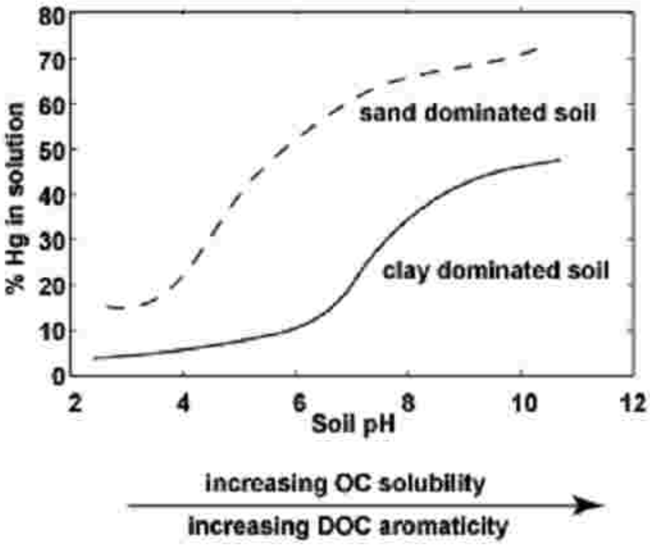

Figure 1. Schematic of percent Hg in solution as a function of pH for a sand and a clay dominated soil based on findings from Yin et al. (1996).

Only a few studies have attempted to identify controlling factors on Hg mobilization across a diverse set of streamwatersheds (*e.g.* Shanley et al., 2005; Brigham et al., 2009) with the results being inconclusive. In a regional assessment of physical controls on Hg_T concentration in streams, Shanley et al. (2005) found that excluding stream discharge, watershed factors such as percent forest or agriculture, soil permeability, annual precipitation and annual runoff could only explain 19% of variability and no one factor could explain more than 10%. Similarly, Brigham et al. (2009) assessed stream Hg concentrations in basins throughout the U.S. spanning large gradients in environmental conditions and found annual export to be highly variable and not correlated with atmospheric deposition. They put forth the conceptual model that Hg deposition sets the baseline for Hg concentrations and that specific basin properties govern stream export, although no basin properties stood out as clearly governing mean Hg concentrations with the exception of wetland density. Not surprisingly, wetland density is often the most significant predictor of mean Hg_D and or/Hg_T concentrations (Driscoll et al., 1994; Babiarz et al., 1998; Kolka et al., 1999; Hurley et al., 1995; Grigal, 2002; Brigham et al., 2009; Bushey et al., 2008), as wetlands are a dominant downstream source of organic carbon.

Difficulties encountered with identifying watershed-scale factors influencing Hg export are two-fold. First, stream Hg concentrations vary dramatically (1-2 orders of magnitude) with discharge and brief periods of high flow often transport the majority of the annual flux (Shanley et al., 2002; Scherbatskoy et al., 1998). Even if sampling programs target both low- and high-flow periods, using any form of mean overall concentration is likely not a good metric to compare between sites without a rigorous evaluation of the sampling distribution along the annual hydrograph. Assuming the sampling was representative of all discharge conditions at each site, and the distribution of low- and high-flow samples was consistent between sites, there are numerous spatial watershed characteristics that may influence export of Hg and organic carbon. These include climate, land use/land cover, soil properties, and acid/base status. The overlapping influence of each factor on Hg mobility would likely confound any attempt to discern the effect of a single characteristic. Determining the effect that individual watershed properties have on Hg concentrations and transport therefore requires a detailed understanding of temporal dynamics, while intentionally isolating the effects of these particular properties though careful site selection. We employ these governing principles to evaluate Hg transport at the watershed scale as it is controlled by soil composition and pH, two factors shown to influence both OC and Hg behavior at the laboratory scale.

In undertaking this study, we sampled at a high frequency and chose sites with similar spatial watershed characteristics. By sampling streamwater consistently throughout the year and frequently during high flow events we aim to determine the range of variability in Hg_D, DOC quality and quantity within an individual site due to variables that change temporally. These factors include discharge, seasonality, and storm characteristics. We monitored three watersheds of similar size with comparable climate, seasonal temperature, land use/land cover (no wetlands in any of the sites), soil organic carbon content, watershed slope, mean discharge, and Hg deposition, but with different underlying bedrock geology. Differences in bedrock weathering rates result in a gradient in soil composition (clays to sands) as well as acid neutralizing capacity (ANC) in streamwater, resulting in a range in streamwater pH (circumneutral to acidic) at the sites. A better understanding of how watershed descriptors such as soil composition and basic water chemistry affect the mobilization of Hg_D-DOC will improve models of Hg transport and our assessment of ecosystem responses. The focus of this paper is on dissolved components, although Hg_P was measured concurrently at all sites and will be assessed in a future publication.

The objectives of this study were to 1) quantify Hg_D and DOC concentrations at three southern Appalachian forested headwater streams throughout the year routinely at baseflow and at high frequency during storm events, 2) evaluate the effect of discharge on Hg_D and DOC quantity and quality dynamics at each site and 3) compare the Hg_D and DOC concentrations and relationships between sites differing in pH and bedrock/soil composition to determine if and to what extent these factors control Hg mobility. In addition, we determine if there are significant regional differences in the overall Hg_D-DOC relationships between sites monitored throughout the U.S. to gain insight into factors that may contribute to regional patterns of Hg export.

2. Methods

2.1 Study Watersheds

The three study watersheds, which are denoted by the steams that drain them (Piney River, Staunton River, and Paine Run, hereon referred to as Piney, Staunton, and Paine) are located within the boundaries of Shenandoah National Park (SHEN) in central Virginia within the Appalachian Highlands physiographic region (Figure 2). The three study watersheds are similar in size and have similar stream gradients. Each is a forested headwater ecosystem, characterized by second- to third-growth mixed hardwoods (Ryan et al., 1989; Young et al., 2006). A soil survey of the uppermost 20 cm and lower 80-100 cm of soil for each of the three bedrock types indicated that organic carbon content was similar for each of the bedrock types, with upper soil horizons comprised of approximately 8% carbon, and the deeper soil zone of approximately 2% carbon by dry weight (Welsch et al., 2000).

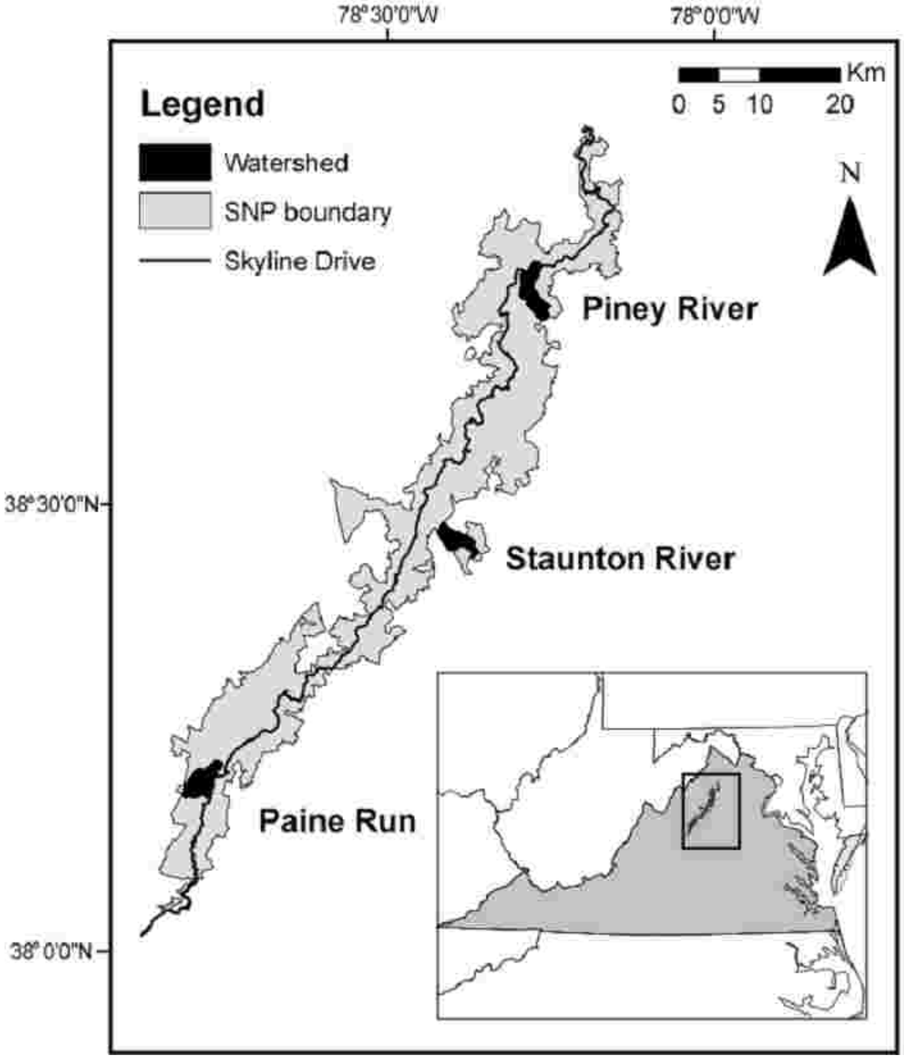

Figure 2. Map of study catchments within Shenandoah National Park, VA.

While similar in many basic physical characteristics, bedrock type differs between watersheds, with metabasaltic, granitic, and siliciclastic underlying Piney, Staunton, and Paine, respectively (Gathright, 1976). Each bedrock type has different weathering rates, rendering soils with different physical and chemical properties, ranging from clay rich soils with a high cation-exchange capacity (CEC) at Piney to sandy soils with a low CEC at Paine (Welsch et al., 2000). Soil chemistry manifests in distinctions in streamwater alkalinity. Short-term episodic acidification has been shown to occur in streams underlain by all three bedrock types, with siliciclastic being the most sensitive to acid inputs (Hyer et al., 1995). Selected characteristics for the three watersheds are presented in Table 1.

The mid-Atlantic Appalachian region is distinctly different in climate and geologic history from the northern and northeastern U.S. where the majority of prior Hg streamwater studies have been conducted. It has a warmer climate leading to reduced organic carbon content in soils (Brady and Weil, 2002). This region also lies south of the furthest reach of the Pleistocene glaciation, therefore catchments contain older and more deeply weathered soils and are also more efficient sulfate absorbers (Johnson et al., 1979; Galloway et al., 1983; Rochelle and Church, 1987; Rochelle et al., 1987). Differences in sulfate absorption capacities contribute to differences in the response of these systems to reductions in acid deposition. Sulfate retained in these unglaciated soils from a legacy of atmospheric sulfate deposition are a long-term source to surface waters in this region which contribute to acidification. Briefly, an increase in the sulfate in streamwater will be balanced by an equivalent increase in base cations. These cations can be acidic or basic and the export of acidic ions (primarily hydrogen) may contribute to surface water acidification.

Table 1. Selected characteristics of study watersheds in Shenandoah National Park.

Watershed Characteristic	**Piney River**	**Staunton River**	**Paine Run**
Area, km ^{2}	12.6	10.5	12.4
Stream gradient, %	9	10	9
Primary litology	basaltic	granitic	siliclastic
Soils description	silt loam with a silty clay loam to clay subsoil [a]	thin firm, sandy clay loam [b]	deep, well drained, fine sandy loam [c]
Soil hydraulic conductivity, mm hr $^{-1}$	15.2-50.8 [a]	50.8-152 [b]	50.8-508 [c]
Percent organic carbon in upper soil [d]	7.7	7.6	7.9
Percent organic carbon in lower soil [d]	2.0	2.3	1.6
Mean soil pH [e]	5.3	4.6	4.2
Mean soil SO_4^{2-}, µeq L^{-1} [e]	189.6	147.9	142.0
Mean stream pH [f]	7.1	6.7	5.8
Mean stream ANC, µeq L^{-1} [f]	229	86	7
Mean stream SO_4^{2-}, µeq L^{-1} [f]	64	44	110
Mean stream conductivity, microsiemens [f]	35	18	20
Mean stream ionic strength [f]	3.93×10^{-4}	1.88×10^{-4}	2.44×10^{-4}

[a] U.S. Department of Agriculture (USDA)(1961)

[b] USDA (1979)

[c] USDA (1975)

[d] Welsch et al., (2001)

[e] Rice et al., (2001)

[f] Water years 1993–2004

2.2 Sample Collection

At each of the three sites, from March 2008 through October 2010, baseflow samples were collected approximately every two weeks throughout the first full year, then every month subsequently. Duplicate grab samples were collected at one of the three sites on a rotating basis each month. Stormflow samples were typically collected at bi-hourly intervals with stage-actuated automated samplers as described in Riscassi et al. (2010). Additionally, concurrent grab and automated samples were collected on three different occasions during high flow. All materials, cleaning procedures, sample collection and handling procedures are described in detail in Riscassi et al. (2011). All samples were filtered and analyzed for Hg_D, DOC, UV absorbance at 254 nm, and pH.

2.3 Chemical Analysis

Samples for Hg analysis were typically filtered and preserved in the laboratory at the University of Virginia within one week of sample retrieval. Samples collected with the automated sampler during storm events were retrieved within a week after storm sampling completed; a recent evaluation of effects from the delay in retrieval times of automated samples showed minimal differences in Hg concentrations (Riscassi et al., 2010).

The filtering process was carried out under a Class 100 clean bench. Samples were filtered through a pre-baked quartz fiber filter (Whatman QM-A grade, 2.2 µm 98% efficiency particle retention in liquid) in a vacuum-desiccator chamber with an acid leached Teflon® filter apparatus according to procedures documented in *Lewis and Brigham* (2004). The filtered sample water was preserved within an hour of filtration with a 100% BrCl solution (5 mL BrCl per 1 L sample) and stored until analysis.

Samples were analyzed for Hg_D using a Tekran® cold-vapor atomic florescence spectrophotometer according to *U.S. EPA* method 1631, Revision E (2002). The method detection limit (MDL) for Hg_D was determined to be 0.19 ng L^{-1} from the standard deviation (0.06) of seven aliquots of a 0.65 ng L^{-1} solution (U.S. EPA, 1986).

Overall Hg laboratory accuracy was determined by participation in an inter-laboratory proficiency test administered by Environment Canada in January 2010. Our lab recoveries ranged from 97 to 102% for sample concentrations (n=5) ranging from 6.6 to 47.8 ng L^{-1}. Laboratory accuracy was verified by ongoing analysis of a certified reference material and recoveries were within 94 to 114%. Matrix spikes, ongoing precision and recovery (OPR) analysis, method and system blanks were used to evaluate instrument performance. The relative percent difference (RPD) for all pairs of matrix spikes (n=38) was equal to or less than 8%. OPR samples and standards were maintained within 15%. The majority (90%) of method and system blanks (n=131) were below the MDL, and the remaining 10% were < 0.5 ng L^{-1}. All quality control metrics are within U.S. EPA (2002) guidelines. All but two (0.26 and 0.29 ng L^{-1}) laboratory filter blanks (n=32) were below MDL. All field blanks (n=20), which include de-ionized (DI) water collected during grab sampling and a bottle left open and empty in the automated sampler and subsequently filled with DI water in the lab, were below the MDL. The mean absolute difference between duplicate field samples (n=27) was 0.03 +-0.06 ng L^{-1} Hg_D. Note that three of the field duplicate pairs were comprised of grab and automated samples, confirming Hg_D (not just Hg_T as examined in Riscassi et al., (2010)) measurements obtained with either method are comparable.

Filtered sample water for DOC analysis was decanted from the Teflon® Hg_D sample bottle into a 40 mL glass amber vial and preserved with 0.5 mL of H_3PO_4 and refrigerated until analysis. Samples were analyzed for DOC by UV/persulfate digestion (U.S. EPA Method 415.3 Revision 1.1, 2005) with a Teledyne-Tekmar Phoenix 8000 TOC analyzer. The MDL was determined to be 0.11 mg L^{-1}. Laboratory accuracy was evaluated with standards run every 10 samples; all were maintained within 3%. Field blanks and laboratory filter blanks were all below the MDL. The mean absolute difference for duplicate grab samples (n=26) was 0.03 +/- 0.10 mg L^{-1} DOC.

UV absorbance measurements at 254 nm were made in a UV-visible spectrophotometer (Hewlet-Packard Model 8453) with a stated accuracy of +/-0.005 absorbance units (AU). Sample water was analyzed at room temperature within 24 hrs of filtering within a quartz cell with a 1 cm path length. Measurements of the deionized water as a filter blank and duplicates were made at least every 10 samples to ensure instrument stability. An outside check standard (In-Spec® UV Standard #8) was analyzed with each batch of samples to verify instrument accuracy. Field blanks and filter blanks were used to ensure that sampling and filtering materials and methods were free from contamination and field duplicates were used to evaluate reproducibility. Inorganic species such as iron and nitrate that absorb light in the near UV and extreme pH values have been shown to influence UV measurements (Weishaar et al., 2003; Dilling and Kaiser, 2002), however all three of our streams are well within the ranges identified for non-interference for pH and nitrate. Iron has not been measured at our sites but, concentrations measured at other headwater streams in the Appalachian region indicate levels below concern (Margolis et al., 2001).

Specific ultraviolet absorbance ($SUVA_{254}$) was calculated by dividing the UV absorbance at ? = 254 nm (cm^{-1}) by the concentration of DOC (mg L^{-1}) and is reported as liter per mg carbon per centimeter. $SUVA_{254}$ is an 'average' molar absorbtivity and has been used as an indicator of DOC aromaticity (Chin et al., 1994; Weishaar et al., 2003). UV_{254} absorbance, which reflects both quantity and 'quality' or aromaticity of DOC, and has been shown to be an excellent proxy for Hg_D in some streams (Dittman et al., 2009).

2.4 Statistical Analysis

All descriptive statistical calculations and analysis were performed using Matlab® software (version 7.2.0.232, The MathWorks Inc., Natick, MA). During this study, a large number of additional high-flow samples were collected at Staunton River because at that site 1) the automated sampler deployed could collect more samples (23 vs 11) than the other two sites and 2) an additional concurrent study was conducted in which samples were collected at more frequent time intervals (half-hourly instead of every 2 hours) during high flow events. In order to statistically evaluate sample means between sites, data sets need to be collected with the same methodology. Therefore, we used a modified data set at Staunton River for the analysis of means between sites. All storm samples greater than 11 in sequence and those collected at intervals more frequent than 2 hours (total of 26 samples, 16% of entire data set) were removed for the analysis. With the modified data set, discharge at time of sample collection was not significantly different between sites, therefore no analysis of covariance was necessary to evaluate parameters that have a significant linear relationship with discharge (*e.g.* Hg_D, DOC, and UV_{254}).

Data sets were evaluated for the assumptions of homoscedasticity and normality with Cochran's test for equality of variances (Trujillo-Ortiz and Hernandez-Walls, 2003) and the Jarque-Bera test for goodness of fit to a normal distribution. The assumption of homoscedasticity was always met for log transformed data. For several variables the normality assumption was not met for log transformed data, in which case the Kruskal-Wallis test, a nonparametric version of one-way analysis of variance (ANOVA) was implemented. The assumption behind this test is that the measurements come from a continuous distribution, but not necessarily a normal distribution. When both assumptions were met, a traditional ANOVA was performed to determine if differences were statistically significant ($p=0.01$). The Tukey-Kramer post-hoc test was used to determine if significant differences existed between sites.

Matlab® was also used to compute linear regressions and calculate associated r^2 and p values. Regressions were performed on raw data and log transformed data. For all variables regressed against discharge, a logarithmic transformation for both variables improved the relationship slightly and are reported herein. For all other regressions, no transformations were necessary. Residuals were evaluated for the assumptions of normality and homoscedasticity. Differences in the slope and intercept of regression lines between sites were also determined.

3. Results

3.1 Hydrology

The range of flow conditions during the 2009-2010 water years (Oct. 1, 2008-September 30, 2010) was representative of the previous 18-year period of record at each site. The three sites have similar flow distributions for high discharge periods, but Paine Run has lower flow conditions throughout the year, with the most pronounced differences in the lower 20% of the flow distribution (Figure 3). Stream samples collected at each of the sites captured the full range of discharge conditions representing a flow exceedence range of at least 96.0 to 0.04%. It is worth noting that the most extreme high flows (~0.03% exceedence) were sampled at Staunton and Paine, but not at Piney. Overall the mean specific discharge for the study period (hourly data for 2 years) at Piney, Staunton and Paine was 0.08, 0.10 and 0.05 mm hr^{-1}, respectively.

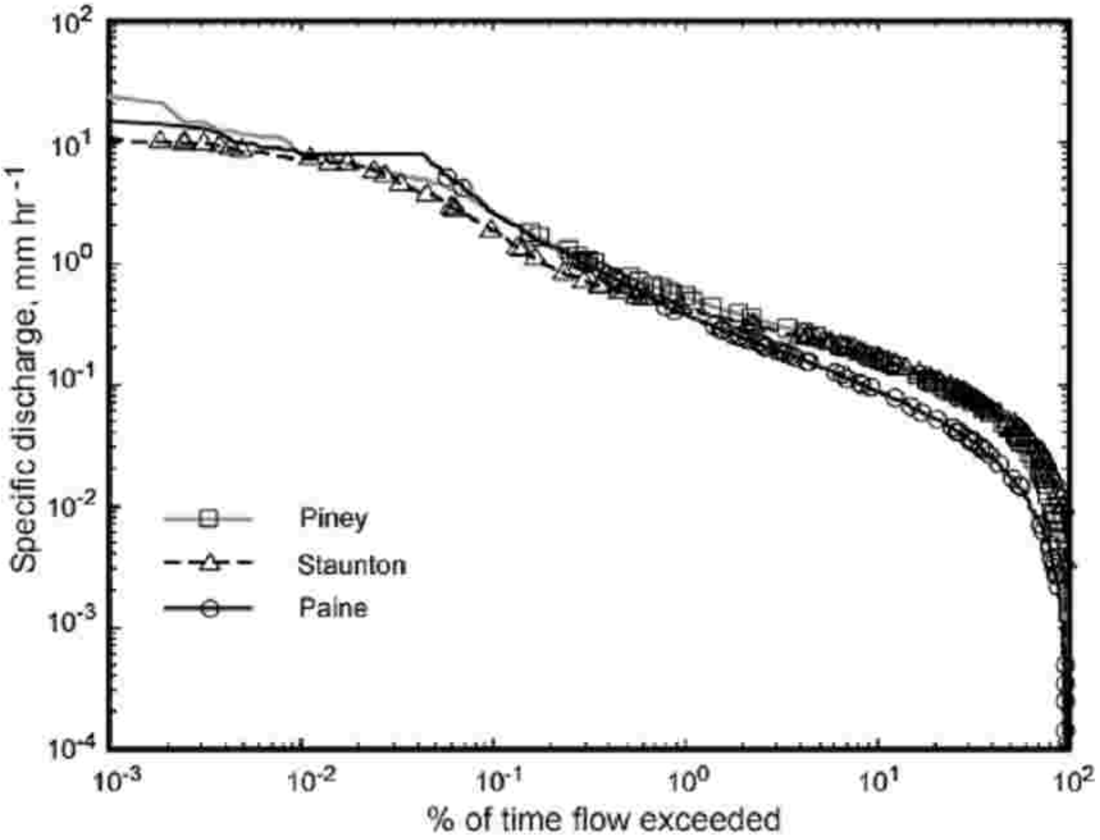

Figure 3. Flow exceedence curves for 18 year period of record (1992-2010) at Piney River, Staunton River, and Paine Run. Symbols on the line represent discharges when samples were collected.

3.2 Hg_D, DOC, SUVA and UV ranges and means

A total of 74, 105 (paired down from 131 total as described in Section 2.4), and 98 samples collected at Piney, Staunton, and Paine, respectively, were used to compare mean concentrations between sites. Between 41-45% of those samples were taken during baseflow periods. The mean specific discharge when samples were taken was 0.09, 0.15, 0.10 mm hr^{-1} for Piney, Staunton, and Paine, respectively, with the distributions being statistically similar ($p<0.01$). The associated flow exceedence probabilities for mean discharge are 18, 15, and 9%, respectively, illustrating the intentional bias towards high-flow sampling. Box plots illustrating ranges for all streamwater parameters discussed subsequently are illustrated in Figure 4.

Hg_D concentrations ranged from <0.19 (below detection limit) to 3.27 ng L^{-1} at all sites, with similar mean concentrations at Piney and Staunton, (0.43 and 0.47 ng L^{-1}, respectively). Concentrations at Paine were significantly higher (mean = 0.73 ng L^{-1}, $p<0.01$) than for the other two sites. DOC concentrations ranged from 0.35 to 5.38 mg L^{-1} at all sites. Similar to Hg_D, mean concentrations of DOC at Piney and Staunton were similar (0.89 and 1.04 mg L^{-1}, respectively), while concentrations at Paine were significantly higher (mean = 1.52, $p<0.01$). Hg_D and DOC are relatively elevated during baseflow at Paine, remaining above a minimum concentration of 0.21 ng L^{-1} and 0.60 mg L^{-1}, respectively, higher than the other two sites. Analyzing the stormflow samples separately (excluding baseflow samples) results in a statistically similar mean concentration to the other sites for both constituents. Therefore, Paine has higher mean Hg_D and DOC concentrations due to elevated baseflow concentrations. Analyzing a longer period of record available for DOC data (1995-2009, n=170, note: a 0.40 micron

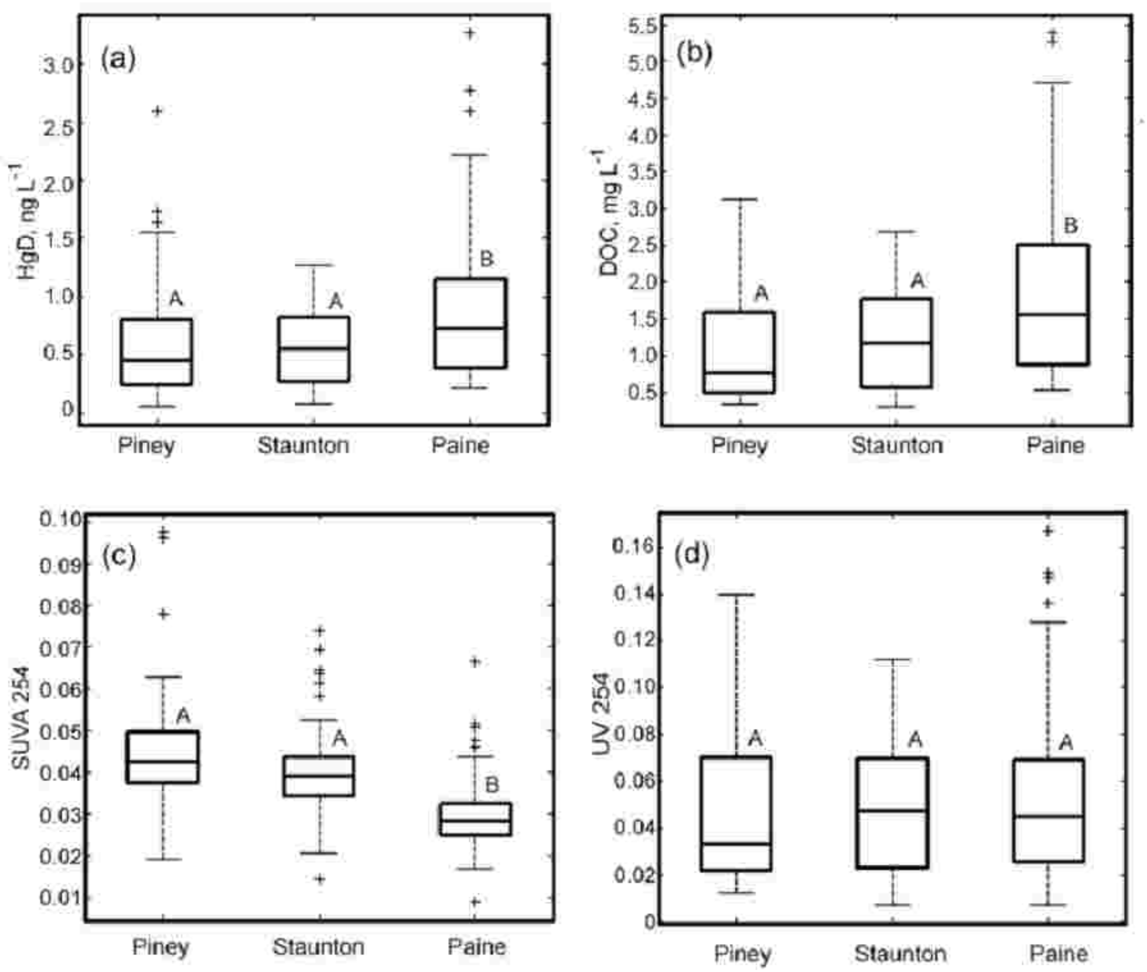

Figure 4. Box plots showing ranges for (a) dissolved Hg (Hg_D), (b) dissolved organic carbon (DOC), (c) specific UV absorbance ($SUVA_{254}$) and (d) UV absorbance (UV_{254}) at each of the three study sites. The horizontal bars within the boxes are median values; bottom and top are 25th and 75th percentile values and vertical lines are 10th and 90th percentiles. Capital letters denote which means are similar between which sites.

filter was used for these earlier measurements) at all three sites illustrates that for low flow periods, the minimum DOC concentration at Paine is higher (0.41 mg L^{-1}) than Piney and Staunton (0.10 and 0.13 mg L^{-1}) indicating this is a consistent long-term trend. $SUVA_{254}$ ranged from 0.013 to 0.098 at all sites and mean values were similar between Piney and Staunton (0.043 and 0.039, respectively) but were significantly lower at Paine (0.029, $p<0.01$).

UV_{254} is a measure of both the quantity and quality of dissolved organic matter. Because concentrations of DOC and $SUVA_{254}$ are statistically similar between Piney and Staunton, it follows that UV_{254} is also similar between those sites (mean = 0.039 and 0.042, respectively). Mean DOC concentration for Paine was significantly higher and mean $SUVA_{254}$ significantly lower than the other two sites, and these two factors combine to offset one another, resulting in a statistically similar mean UV_{254} value at Paine (0.044, $p=0.22$).

It is worth noting that the final storm sampled at Paine followed an extended dry period and some aspects of the storm dynamics, discussed subsequently in this paper, were found to be unique. To confirm that the samples from the single storm, not sampled at Piney and Staunton, did not bias the statistics on the cumulative data sets, an identical statistical analysis excluding the last storm from Paine Run was performed. Results showed that excluding those samples, discharge means were statistically similar and the significance of all mean comparisons did not change. Therefore, no statistical bias was caused by the single storm.

3.3 Storm dynamics and overall discharge relationships with stream chemistry

The correlation between discharge and both Hg_D and DOC is weak at Staunton (r^2=0.13 and 0.09 for Hg_D and DOC, respectively) and improves at Paine (r^2= 0.42 and 0.45 for Hg_D and DOC, respectively) and Piney (r^2= 0.52 and r^2=0.46 for Hg_D and DOC, respectively) as illustrated in Figures 5 and 6, respectively. The highest flows measured at Staunton during winter snowmelt events contribute substantially to the degraded relationships at that site as the extremely high flows do not correspond to high concentrations of Hg_D and DOC. At all sites, hysteresis in the concentration-discharge relationships during storm events contributed to the degraded relationships between Hg_D and DOC with discharge.

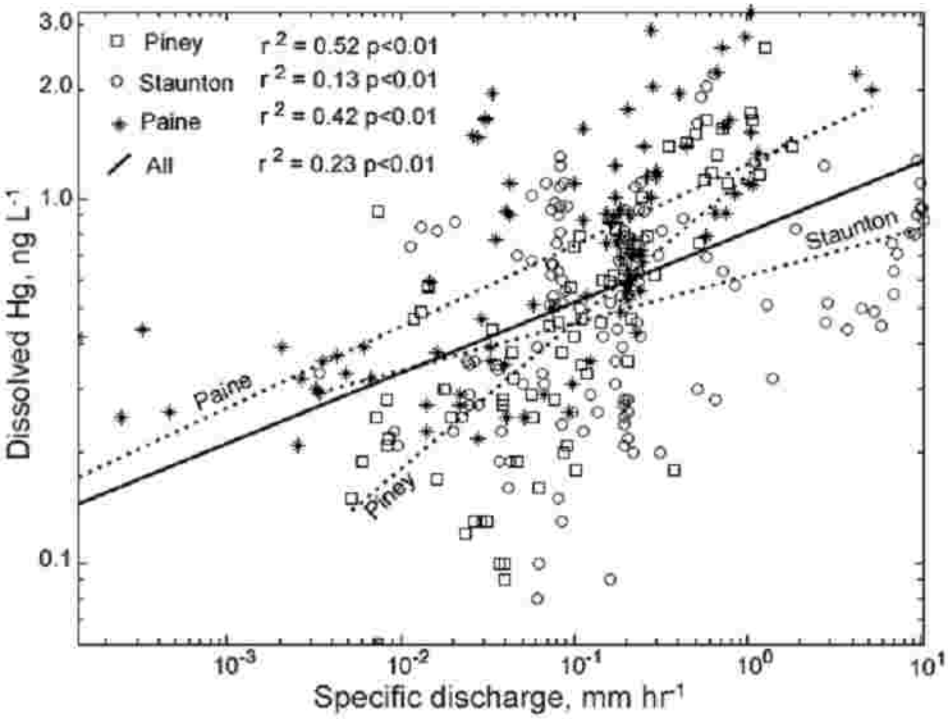

Figure 5. Specific discharge versus dissolved Hg (Hg_D) with best fit lines shown for individual sites and all sites combined. Note that Hg_D concentrations never fall below 0.21 ng L^{-1} for Paine, even at the lowest flows.

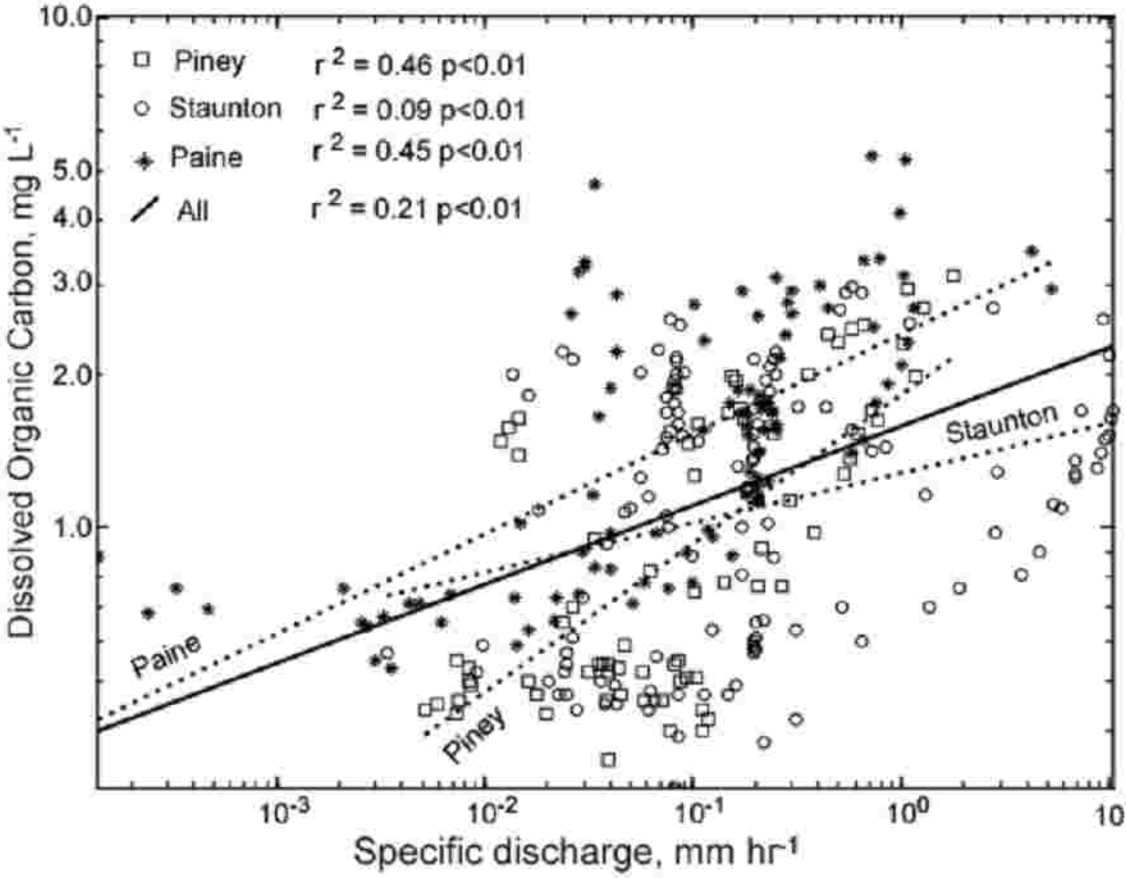

Figure 6. Specific discharge versus dissolved organic carbon (DOC), with best fit lines for individual sites and all sites combined. Note that DOC concentrations never fall below 0.60 mg L^{-1} for Paine, even at the lowest flows.

For individual sites and for all sites combined, no significant relationship exists between $SUVA_{254}$ and discharge. After excluding baseflow $SUVA_{254}$ values, for which any measurement errors are amplified when the term in the UV_{254}/DOC ratio are low, however, we found weak (r^2=0.16 and 0.23) but significant positive relationships at Piney and Paine, while the relationship at Staunton remained insignificant. UV_{254} has a significant positive relationship to discharge for individual sites (r^2= 0.51, 0.06, 0.31 at Piney, Staunton and Paine, respectively), as well as all sites together (r^2=0.20). These correlation coefficients are similar to those for DOC at each site.

3.3 Relationships between chemical constituents

Across all sites there was a significant positive correlation between Hg_D and DOC (all sites $p<0.01$, r^2= 0.74, 0.80, and 0.89 at Piney, Staunton, and Paine, respectively; Figure 7). The linear best fit lines for each of the three sites were coincident (statistically similar slope and intercept). For all data combined 0.54 +/-0.02 ng of Hg per mg DOC

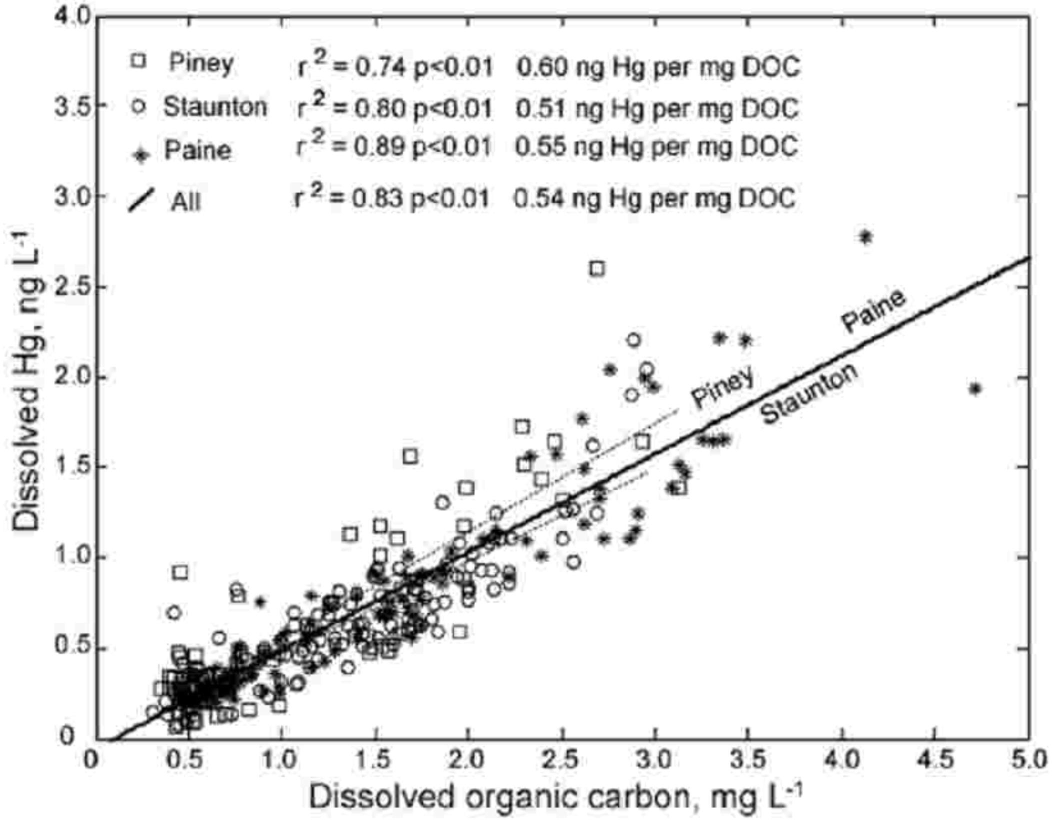

Figure 7. Dissolved Hg versus dissolved organic carbon for individual sites and all sites combined. Linear best fit lines have statistically similar slopes and intercepts.

was transported with an intercept of -0.05 +/- 0.03 ng L^{-1} ($p<0.01$, $r^2= 0.83$). Site specific Hg_D-DOC relationships were evaluated to determine if there were any distinctions based on the growing/dormant season (defined as April through September and October through March, respectively) or with snowmelt events as well as the rising and falling hydrograph limbs. No differences were apparent for the storms sampled at Piney and Staunton. However, at Paine three samples taken during the rising limb of a January 2010 snowmelt-rainfall event and seven taken on the rising limb of a Sept. 30, 2010 storm that followed an extended period with no rainfall had elevated Hg_D concentrations relative to the other samples for a similar DOC concentration. Possibilities for why this may have occurred are discussed in Section 4.1.2.

The mean pH of samples at Piney, Staunton and Paine are significantly different between all sites with means of 7.26, 6.83 and 5.64, respectively. The mean pH values have a rank order relationship with mean $SUVA_{254}$, with corresponding values of 0.043, 0.039, and 0.029, respectively. However, only Paine $SUVA_{254}$ is statistically different than the other two sites. For individual pH values and corresponding $SUVA_{254}$ at a particular site, there is no significant relationship for Piney and Staunton ($p=0.69$, 0.12, respectively), however this relationship is significant at Paine ($p<0.01$, $r^2=0.12$). For all data combined, the relationship is also significant ($p<0.01$, $r^2= 0.26$) with an increase in one pH unit corresponding to a 0.01 increase in $SUVA_{254}$ (Figure 8).

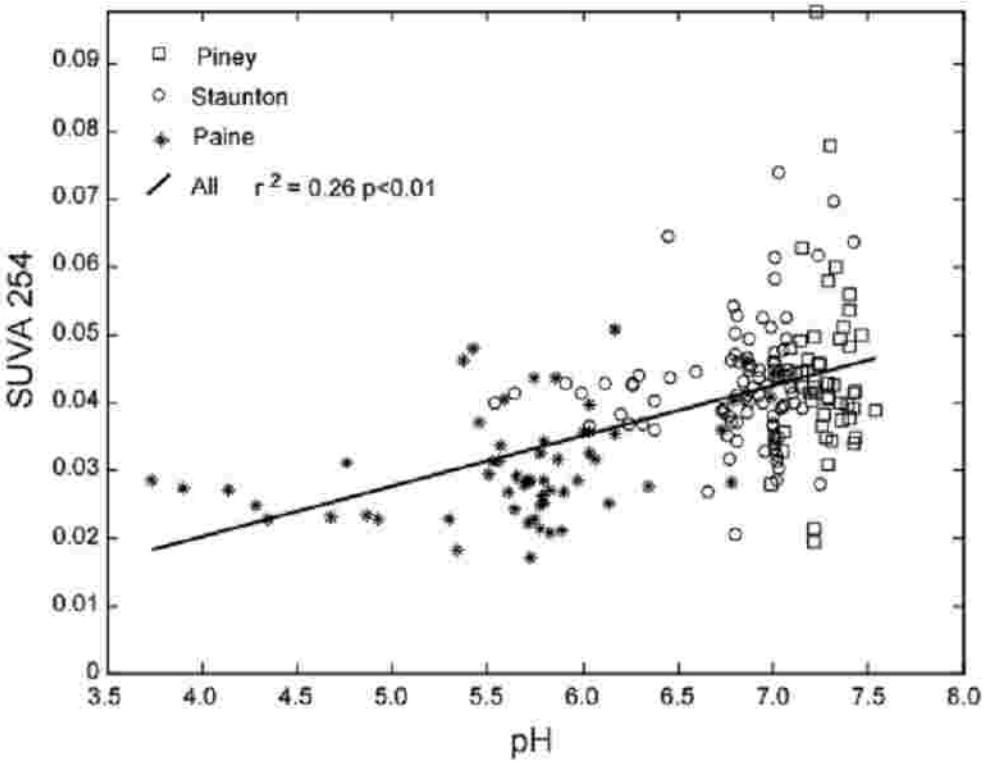

Figure 8. pH versus specific UV absorbance at 254 nm ($SUVA_{254}$). The linear best fit line for all data combined is significant.

There was a significant positive correlation between Hg_D and UV_{254} at each site (all sites $p<0.01$, r^2= 0.79, 0.81, and 0.79 at Piney, Staunton, and Paine, respectively; Figure 9). The strength of the individual site relationships between Hg_D and the quality and quantity of DOC as measured by UV_{254} improved slightly compared to DOC quantity alone at Piney and Staunton (r^2=0.74 improved to 0.79 and r^2=80 improved to 0.81, respectively). At Paine the relationship degraded slightly (r^2=0.89 decreased to 0.79), but this decrease can be attributed to the September 2010 storm; excluding those nine samples, the correlation improves slightly from 0.89 to 0.90. The linear best fit lines between Hg_D and UV_{254} for Piney and Staunton were coincident (Figure 9). However, the slope for Paine was significantly steeper indicating that ~4 ng L^{-1} more Hg_D per unit UV_{254}, is transported at that site.

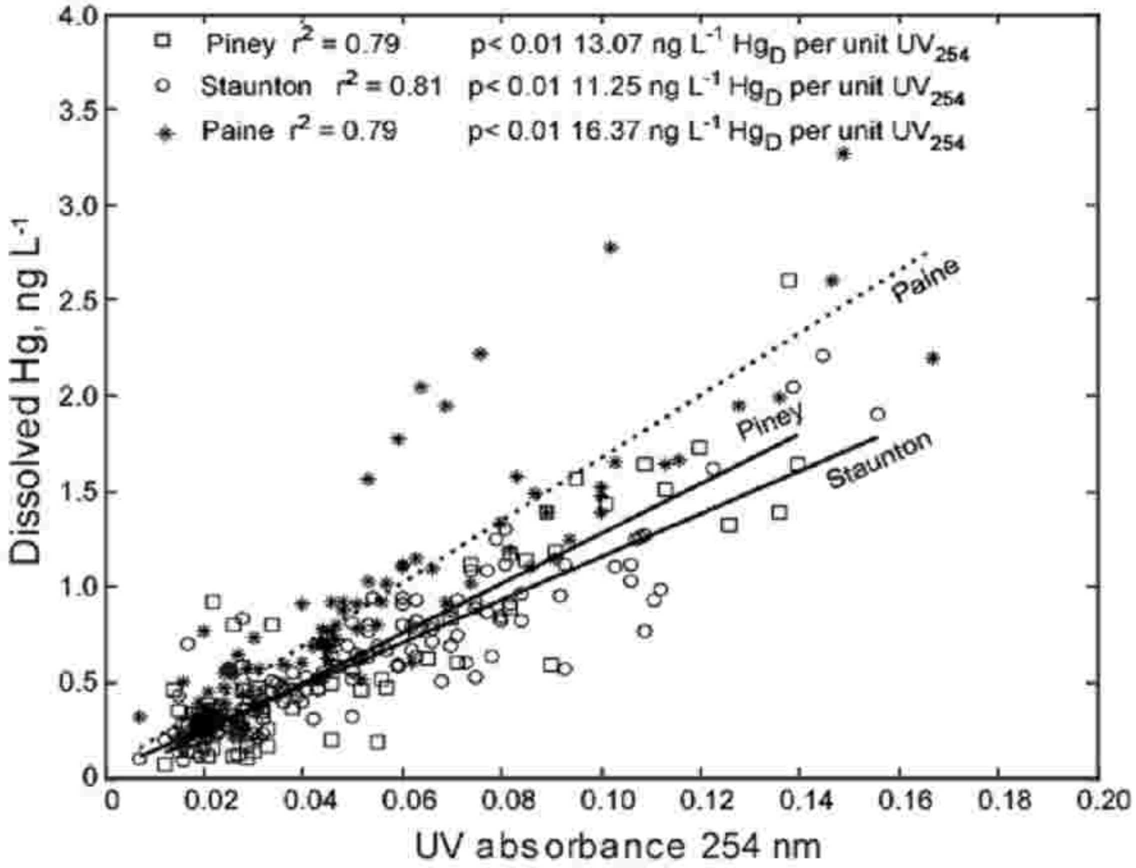

Figure 9. Dissolved Hg versus UV absorbance at 254 nm with best fit lines shown for individual sites. Linear best fit lines for Piney and Staunton have statistically similar slopes and intercepts and Paine has a significantly greater slope.

4. Discussion

4.1 Factors affecting mobilization of HgD

4.1.1 Discharge

Discharge can be an important mobilization factor for Hg_D as rainfall/snowmelt and the corresponding rising water table mobilize different source pools (*e.g.* surface soils or upstream wetlands) having typically higher organic carbon and Hg content. In agreement with findings from the majority of streamwater studies in forested catchments, discharge at all three sites had a significant positive relationship with Hg_D, explaining between 13 and 52% of the variability. Brigham et al. (2009) reported stronger correlations between discharge and Hg_D (r^2 ranging from 0.54 to 0.83) in four forested sites across the U.S.. However, these sites had significant wetland land cover as reflected by the relatively high DOC concentrations (mean of 3.3- 40 mg L^{-1} for individual sites). As concentrations in wetland areas are significantly elevated relative to other landscape units, mobilization from the wetland regions can dominate the overall catchment response. The single forested site without wetlands in their survey (Lookout Creek, OR) had lower DOC (mean 0.9 mg L^{-1}) and Hg_D concentrations (mean 0.49 ng L^{-1}) and a relatively poor Hg_D-discharge correlation (r^2=0.10) similar to our study sites. These results indicate that in the absence of wetlands, spatial and temporal complexities of Hg_D export from soil water to stream during high flow events confound any simple relationships with discharge.

4.1.2 DOC quantity

Hg_D closely tracked DOC at each site, irrespective of season, rising or falling hydrograph limb, storm characteristics, baseflow or storm flow conditions, over a range of antecedent conditions. The relative strengths of the Hg_D-DOC relationships (r^2=0.74, 0.80, and 0.89) are similar to those found in other forested watersheds (Allen and Heyes, 1998; Schuster et al., 2008; Shanley et al., 2008; Brigham et al., 2009; Dittman et al., 2009; 2010). However, our results encompass a considerably wider range of conditions than all other studies and therefore provide new evidence as to the possible robustness of that relationship. While strong relationships have been documented in many systems, Hg_D patterns do not always parallel those of DOC. For instance, Schelker et al., (2011) found that Hg_T (Hg_P was demonstrated to be a minor component) and DOC were not well correlated during a 17 month period, likely caused by varying spatial connectivity of heterogeneous source areas such as ponds and wetlands, each with unique Hg_T-to-DOC ratios. Similarly, Bushey et al., (2008) found that Hg_D and DOC were not correlated during storm events in a forested watershed in NY and similarly suggested contributions from different source areas caused the divergence in Hg_D versus DOC chemographs, including initial rapid delivery of throughfall Hg via overland flow or preferential flowpaths. Unlike the two studies that found poor Hg_D-DOC relationships, each of the three watersheds in SHEN are homogeneous forested sites without wetlands or ponds and overland flow is not typical; sources of water to the stream are dominated by groundwater, riparian and hillslope contributions. The timing of these source contributions have shown to be first-order controls on DOC concentrations (McGlynn and McDonnell, 2003) and for our sites the Hg_D-to-DOC ratios in each of these source areas must therefore be similar.

While the amount of Hg_D per unit DOC was similar for each site, average Hg_D concentrations were statistically higher at Paine, attributable to higher baseflow DOC concentrations. Differences in baseflow DOC concentrations are due to factors that influence the mobilization of organic material from the soil surface to the deeper mineral horizon within the groundwater zone. DOC adsorption to mineral soils has been found to increase with the Fe and Al oxides/hydroxides (Moore et al., 1992) and clay content (Nelson et al., 1993). Both of these factors may contribute to increasing soil surface area (Mayer and Xing, 2001) a key factor influencing adsorption capacity (Gu et al., 1994). While Al and Fe oxide/hydroxide content of soils has not been evaluated at our sites, underlying bedrock composition suggests the clay-rich soils derived from the basaltic and granitic bedrock would be enriched relative to the sandy soils derived from silicilastic bedrock. As a result of the lower clay content in soils at Paine it follows that the organic carbon would be less likely to be bound to soil particles at baseflow and therefore DOC would be elevated relative to the other sites as observed.

While not significantly affecting organic carbon adsorption in mineral soils, soil solution chemistry, including pH and ionic strength, has been shown to affect the mobility of DOC from the upper organic rich soil layers and the forest floor. Almost all laboratory studies have shown DOC release from organic soil horizons is positively correlated to pH, although field studies have reported contrasting results (Kalbitz et al., 2000). Decreases in ionic strength have been found to result in increased DOC mobilization (Fotovat and Naidu, 1998) as the diffuse double layer expands when ionic strength of the solution decreases leading to increased tendency to desorb from the surface to which they are attached (Stumm and Morgan, 1996). There were no differences in the concentration of DOC exported during high-flow conditions between sites when source waters are likely to originate from the more organic rich upper soil and riparian areas. Therefore, our results indicate that the effects of differences in pH and ionic strength on DOC mobilization are either not significant between sites or the contrasting effects of a relatively high pH and high ionic strength (*e.g.* Piney) vs low pH and low ionic strength (*e.g.* Paine) offset each other. As a result, DOC and Hg concentrations are similar during these high flow periods.

Antecedent conditions affect the amount of organic carbon and other decomposition products that accumulate in the subsurface before being transported to the stream during high flow events (Soulsby, 1995; Inamdar and Mitchell, 2006; Inamdar et al., 2009). Analyzed separately, the seven samples taken on the rising limb of the storm which occurred after an extended dry period (no perceptible hydrograph increase over 6 months) on September 30, 2010, had more Hg_D per unit DOC than all other samples. The $SUVA_{254}$ of the DOC transported during that event was consistent with all previous events, so differences in DOC quality could not account for the divergence in pattern. It is likely that the six months of dry deposition accumulated on leaves contributed to relatively high concentrations of Hg in throughfall, and with small amounts of overland flow possible during a large high flow event, resulted in increased amounts of Hg_D per unit DOC in streamflow. This ‘excess’ Hg_D was rapidly (*i.e.* within hours) flushed to the stream as samples taken on the falling hydrograph limb realigned with those taken during the previous year and a half of sampling.

4.1.3 DOC quality

The relationship between Hg_D and DOC improves slightly at each site when the quality of organic carbon is considered, similar to findings by Dittman et al., (2009) and Shanley et al., (2008). The UV_{254} measurement accounts for the increased mobilization of

Hg by the more aromatic carbon, likely due to additional reduced sulfur sites and/or more binding sites in general (Ravichandran, 2004; Schuster et al., 2008). The majority of $SUVA_{254}$ values at our sites are within 0.02 to 0.06 L mg C^{-1} cm^{-1}, similar to the range found in a variety of other systems from small Vermont streams (Schuster et al., 2008) to large Alaskan rivers (O'Donnel et al., 2010; Spencer et al., 2008).

Mean $SUVA_{254}$ is different between sites, with the least aromatic DOC at the site with the lowest pH (Paine) and statistically similar $SUVA_{254}$ at the more alkaline sites (Piney and Staunton). This difference in $SUVA_{254}$ is an expected result because lower pH solutions mobilize less aromatic organic carbon due to charge suppression (Tipping and Woof, 1991; You et al., 1999; Pedrot et al., 2009). Mobilization of the more hydrophobic humic substances requires the development of a large negative charge, which does not occur with excess H^+ in low pH solutions. An expected result of the overall lower $SUVA_{254}$ at Paine would be less Hg_D per unit DOC at that site, but we have shown that for all sites the Hg_D-DOC ratio is identical. Soil composition is believed to offset the organic carbon quality affects at these sites and is discussed subsequently in Section 4.1.4.

Variability in pH also occurs within a site during storm events due to a combination of factors including base-cation dilution, release of organic acids from soils, and contributions of sulfuric acid from atmospheric deposition. There was no relationship between pH and $SUVA_{254}$ for the two more alkaline sites; however pH changes at those sites are relatively small (< 0.5 pH units) due to the larger base-cation availability in the soils. Conversely, due to the low acid neutralizing capacity at Paine, there is more variability in pH during storm events (up to almost 2 pH units) and therefore a significant but weak (r^2=0.12) relationship between pH and $SUVA_{254}$ is apparent at that site.

The quality of organic carbon mobilized from various locations within the soil profile (*i.e.* for different discharge conditions) is a function of 1) the quality of organic carbon present at that location, which changes based on microbial degradation and 2) physical adsorption to soil particles, which ultimately determines what fraction is mobilized as DOC to the stream. Surficial soil water has been shown to contain DOC that is freshly leached, less degraded and therefore higher in aromatic humic compounds, while deeper in the soil horizon organic carbon is comprised of more degraded, less aromatic fulvic acids (Cronan and Aiken, 1985; Spencer et al., 2008). In line with this conceptual model, Schuster et al. (2008) found a significant relationship between $SUVA_{254}$ and discharge at the Sleepers River watershed. No significant relationship between discharge and $SUVA_{254}$ was found at our site, however, partially owing to the fact that baseflow $SUVA_{254}$ measurements are susceptible to relatively large amounts of error when the components of this ratio (UV_{254}/DOC) are low. Re-analysis of the site-specific relationships excluding baseflow samples revealed a significant but weak relationship (r^2=0.19 and 0.23) at Piney and Paine, respectively, and no statistically significant relationship at Staunton. These results indicate that while there is variability in DOC composition exported within a site, discharge is not a strong predictor of this variability.

4.1.4 Soil mineral composition

An unexpected finding was that more Hg_D per unit UV_{254} was mobilized at Paine than at the other two locations, which suggests another factor may be important in governing Hg mobilization. A plausible explanation is soil composition; Paine soils likely have a lower surface area compared to the other more clay-rich sites, so there is less competition for Hg at that site. This concept was put forth by Marvin-Dipasquale et al. (2009), who found that as the relative amount of pore water DOC increased or as the bed sediment percent fines (*i.e.* clays) decreased, more Hg_T partitions into the water, reflecting "the competition between the solid-phase binding of Hg species and the capacity of DOC to pull Hg into solution." Although we are investigating streamwater in the context of soil type (instead of pore water in the context of sediment type) the principle is the same. Mineral soils with low surface area will have a decreased capacity to retain Hg in comparison to clay rich soils, and as a result there is a greater opportunity for Hg to bind to DOC. Several laboratory studies evaluating the effect of soil type on the binding of Hg support this conceptual model. Yin et al. (1996) demonstrated that soils low in organic matter with larger portions of clay adsorbed more Hg than those without clays (see Figure 1). Semu et al. (1986) showed that adsorption of Hg was positively correlated with organic carbon and cation exchange capacity (reflecting both clay and organic carbon content).

As previously noted, the amount of Hg_D per unit DOC at the site with less aromatic carbon (lower mean $SUVA_{254}$) was expected to be lower, however all three ratios were similar. As the site with less aromatic carbon is also the site with sandy soils (Paine), it is likely that less Hg per unit DOC due to carbon quality differences is offset by more Hg per unit DOC attributed to the sandy soils resulting in similar Hg-DOC slopes at all sites (Figure 7). In low DOC systems, soil composition as well as the quality of organic matter mobilized to the stream is important in controlling the transport of Hg_D from the terrestrial to stream environment.

4.1.5 Soil organic carbon content

DOC quantity can explain much of the Hg variability in our three southern Appalachian sites, as well as in streams evaluated throughout the Northern Hemisphere. Despite the consistency in the relationship however, there is a wide range in the amount of Hg exported per unit DOC across watersheds as first noted by Shanley et al. (2009). To determine the distribution and range of Hg-DOC ratios, we compiled Hg and organic carbon data from an additional 19 stream locations representing a wide range of land-cover types (*e.g.* alpine tundra, forest, wetland), water chemistry (e.g high to low DOC) and locations/climates. Most data sets were collected for a range of flow conditions at a single stream site, however, a few were compilations of streams within a region. Information about the 19 sites, as well as the three in this study (total of 22 sites) is provided in Table 2. The number of measurements for each site (or group of sites) ranged from 4 to 1048 and each had a positive Hg-DOC relationship (a few sites measured total Hg and total organic carbon, as noted Table 2) with coefficients of variation ranging from 0.35 to 0.98. An order of magnitude range in the amount of Hg per unit DOC was observed (0.12 to 1.4 ng of Hg per mg DOC) with a mean of 0.46 +/- 0.26, illustrating a broad distribution of ratios as compared to the consistent 0.2 ng of Hg per mg DOC first reported din the review by Grigal (2002).

Table 2. Site names, locations, data sources, number of samples (n), and the fraction of the variance of Hg explained by organic carbon (r^2) for cross-site comparison data presented in Figure 10. Symbol and abbreviation for each site, or group of sites, as it appears in Figure 10 is also listed. All data used are the dissolved species except where noted.

symbol and abbreviation	site name, watershed	data source	n	r^2
□ Andrews Creek, CO	Andrews Creek, Lock Vale, CO	Shanley et al., 2008	5	0.93
+ HB, ME	Hadlock Brook, ME	Nelson et al., 2007[1]	242	0.74
■ RI, PR	Rio Icacos, Luquillo Forest, Puerto Rico	Shanley et al., 2008	4	0.90
✛ CB, ME	Cadillac Brook, ME	Nelson et al., 2007[1]	230	0.65
◇ PINE	Piney River, VA	this study	73	0.74
▲ LV, CO	The Lock Outlet, Lock Vale, CO	Mast et al., 2005 and unpublished data[1]	142	0.59
◈ PAIN	Paine Run, VA	this study	98	0.89
△ Coweeta, NC	Watershed 18 and Watershed 27, Coweeta Hydrologic Laboratory, NC	Allen and Heyes, 1998[1]	21	0.52
◆ STAN	Staunton River, VA	this study	131	0.80
▬ AC-BM, NY	Beaver Meadow, Archer Creek, NY	Dittman et al., 2009, 2010	25	0.83
● Lookout Creek, OR	Lookout Creek, OR	Brigham et al., 2008	23	0.42
– AC-LI, NY	Lake Inlet, Archer Creek, NY	Dittman et al., 2009, 2010	27	0.91
▪ AC, NY	Archer Creek Watershed (11 sites)	Selvendiran et al., 2008[1,2]	182	0.77
⊘ ER, WI	Evergreen River, WI	Brigham et al., 2008	29	0.94
◉ Pike, WI	Pike River, WI	Brigham et al., 2008	32	0.89
× Sleepers, VT	Watershed 9, Sleepers River, VT	Shanley et al., 2008 and Dittman et al., 2009, 2010	48	0.85
▣ Allaquash, WI	Allequash Creek, Trout Lake, WI	Shanley et al., 2008	25	0.66
╳ throughout Sweden	throughout Sweden (19 rivers)	Eklöf, K., in press[1,2]	1048	0.61
● Sante Fe, FL	Santa Fe River, FL	Brigham et al., 2008	25	0.98
⊠ Hubbard Brook, NH	Watershed 6, Hubbard Brook, NH	Dittman et al., 2009, 2010	32	0.61
⚹ throughout WI	throughout WI (7 rivers)	Babiarz et al., 1998[1,3]	62	0.35
○ St. Marys, FL	St. Marys River, FL	Brigham et al., 2008	27	0.42

[1] total Hg
[2] total organic carbon
[3] in Grigal [2002]

A leading candidate for driving the observed variability in the range in the Hg-DOC ratios is the amount of Hg deposited to the particular watersheds. However, estimates of annual wet and dry Hg deposition for five sites across the U.S. (Brigham et al., 2009) were negatively correlated with Hg_D-DOC ratios (data not shown), suggesting that deposition is not a dominant factor in explaining large scale differences in export ratios. As a result, we turn to soil organic carbon (SOC) to explain the large scale variability in ratios. Applying the concept of 'biodilution', defined as a decrease in concentration of an element *(e.g.* Hg) with an increase in biomass (*e.g* organic carbon), Meili (1991) was able to accurately predict Hg-DOC ratios in streamwater in northern and southern Sweden.

While soil organic carbon data were not readily available for the majority of the sites, soil carbon pools have been shown to be related to mean streamwater DOC concentrations and annual fluxes for a wide range of catchment sizes (Hope et al., 1997; Aitkenhead et al., 1999). As sampling strategies varied for the study sites, the mean of the upper ten percent of all DOC concentrations was used as a surrogate variable for the SOC pool in this initial evaluation. The relationship between the Hg_D-DOC ratio and mean of the upper 10% of DOC measurements at the 22 locations is described by a power law, with surprisingly high predictive power (r^2=0.67) considering no other factors were taken into account (Figure 10). In general, wetland-dominated, high-DOC sites fall at the low end of the ratios (0.13-0.3 ng Hg per mg DOC), while sites without wetlands, or relatively lower amounts of SOC due to warmer temperatures accelerating

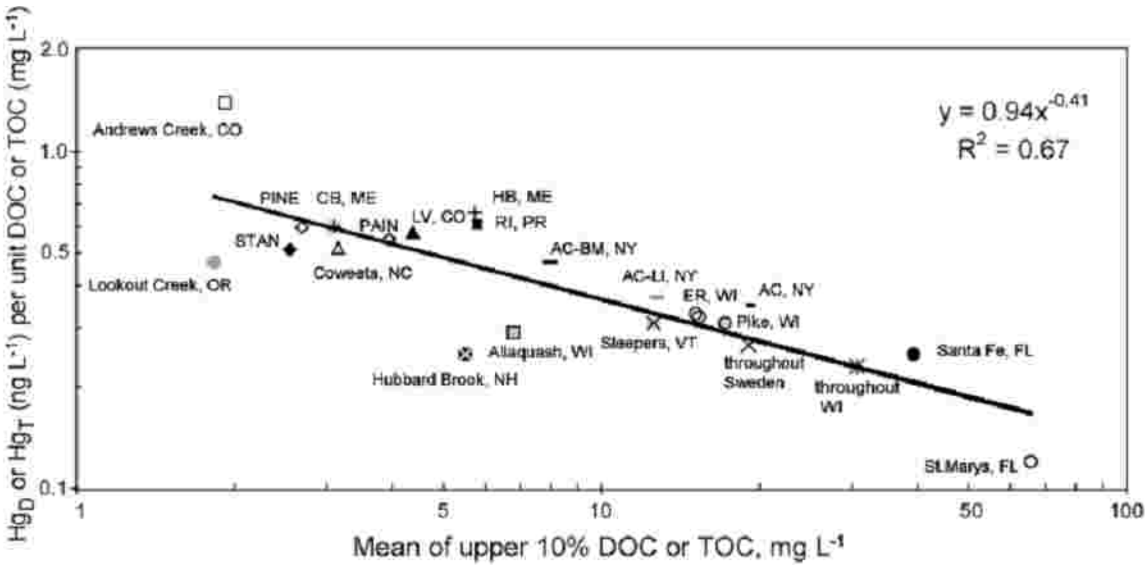

Figure 10. The y-axis represents the dissolved or total Hg (Hg_D or Hg_T, respectively) (ng L^{-1}) per unit dissolved or total organic carbon (DOC or TOC, respectively) (mg L^{-1}) derived from the linear best fit line for all available data at locations within the U.S. and Sweden. The x-axis corresponds to the mean of the top 10 percent of the OC concentrations for each site, a surrogate indicator of soil organic carbon content. Table 2 lists the complete site names, data sources, and number of samples for each site or group of sites. All data are the dissolved species except where noted in Table 2.

decomposition, such as our southern Appalachian sites, are relatively higher (0.5-0.6 ng Hg per mg DOC). The one site with tallus slopes, thin soils and likely lowest SOC had the highest ratio (1.4 ng Hg per mg DOC). These results demonstrate that SOC is likely a first-order control on the Hg-OC ratios found across a wide range of catchment systems. Differences in Hg deposition, organic carbon quality, soil mineral composition and water chemistry are also likely to affect this ratio, however their impacts appear to be secondary.

4.2 Implications for long-term recovery

With declines in atmospheric Hg concentrations over the past ten years due to the regulation of some point source emissions (*e.g.* chlor-alkalai plants and medical waste incineration) and future declines potentially enhanced by regulation of emissions from coal-burning power-plants, questions arise about expected trends in streamwater Hg concentrations. Evaluating changes in Hg_D export mediated by the terrestrial watershed is complicated by the time lag that exists between deposition and export (Harris et al., 2007) as well as ongoing simultaneous changes in soil solution chemistry due to declines in sulfur emission and deposition.

Increases in surface-water DOC concentrations have been observed since the late 1980's across Europe and North America, thought to be a result of decreased soilwater acidity and ionic strength from declining sulfur deposition (Evans et al., 2006; Monteith et al., 2007; Futter and Wit, 2008). In the Adirondack region of New York, Driscoll et al. (2003) documented increasing trends of about 0.8 mg L^{-1} DOC and 0.1 pH units over a ten year period. Using those trends as a guide, we would expect an increase ranging from 0.20 – 0.30 ng Hg_D L^{-1} over the same period based on Hg_D-DOC ratios (0.25-0.37 ng Hg per mg DOC) in that region. Demers et al. (2010) also noted that increases in DOC concentrations may have, and will continue to, exacerbated mercury mobilization. Our results indicate that in addition to increases in DOC quantity, there may also be concomitant increases in the aromaticity of that DOC with increasing pH. As a result of DOC increases due to continued declines in sulfur deposition, no change or possibly an increase in streamwater Hg_D could occur along with reductions in Hg emissions. Harris et al. (2007) have shown that recently-deposited Hg is more likely to be methylated and as a result, increases in the mobilization of ‘old’ Hg_D may not necessarily result in increases in MeHg.

5. Conclusions

In watersheds that do not contain a significant amount of wetlands or peatlands, there is a positive but consistently weak correlation between Hg_D and discharge. Meanwhile, the relationship between Hg_D and DOC is consistently strong. Furthermore, the relationship between Hg_D and $UV_{254,}$ which includes both the quality and quantity of DOC, is slightly improved making *in situ* optical sondes a good option for long term monitoring of these systems (Dittman et al., 2009; Saraceno et al., 2009). When collecting the necessary stream Hg_D data to develop an empirical rating curve to predict high resolution Hg data from UV absorbance measurements, caution should be used when evaluating concentrations after an extended dry period as there may be more Hg per unit absorbance than is typical for all other time periods.

Both soil solution chemistry as well as soil particle size distribution are controlling factors on the mobilization of Hg_D in the field environment. More acidic systems mobilize less aromatic DOC, which relates to less Hg per unit DOC. Systems with sandy soils have a diminished capacity to ‘hold’ Hg and keep it out of solution resulting in more Hg per unit DOC. While these two factors are important in understanding local watershed differences in Hg export, they cannot explain the order of magnitude range in the amount of Hg transported per unit DOC across sites throughout the U.S. and Sweden. Soil organic matter content (as approximated here by the upper 10% of DOC concentrations for the complete data set) appears to be a suitable first-order determinant of the amount of Hg per unit organic carbon, with locations higher in organic matter content having lower Hg-DOC ratios, most likely due to biodilution. Future attempts to model Hg-DOC ratios with increased accuracy should be based on the actual watershed SOC content as well as account for variability due to differences in soil type, organic carbon quality, and wet and dry Hg deposition.

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CHAPTER 5

Dissolved and particulate mercury export from three mid-Appalachian forested headwater catchments

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Abstract

Accurate estimates of dissolved and particulate mercury (Hg_D and $Hg_{P,}$ respectively) streamwater fluxes are needed to track the movement and storage of Hg within an ecosystem and evaluate the watershed response to environmental forcings. Streamwater Hg_D and Hg_P fluxes were computed for the 2010 water year at three forested watersheds in the mid-Appalachian region. Hg_P concentrations were determined from measured data and turbidity using a turbidity-Hg_P relationship established for each site (r^2 ranged from 0.78-0.98). Total Hg (Hg_T) export ranged from 1.26-3.71 ug m^{-2} yr^{-1}, within the range documented for other uncontaminated systems. Approximately 80% of the annual Hg_T flux was exported during the two largest discharge events at each site, corresponding to approximately 1% of the time in these flashy headwater systems. Hg_P accounted for them majority of annual Hg_T fluxes all three sites (58-85%) due to the exponential increase of Hg_P concentrations during peak flow, Hg_D also increased with discharge but more moderately. Relative to atmospheric inputs, approximately 4 to 19% of Hg was exported via streamwater from these undisturbed forested systems illustrating their role as reservoirs of Hg from atmospheric deposition.

1. Introduction

Concentrations of mercury (Hg) in the atmosphere have increased significantly since the onset of the industrial revolution, resulting in enhanced deposition and incorporation into the natural environment (Lorey and Driscoll, 1999; Schuster et al., 2002). Forested uplands are particularly important storage areas of atmospheric Hg because deposition is enhanced due to orographic effects and by the presence of the forest canopy (St. Louis et al., 2001; Miller et al., 2005). The majority of this Hg is likely retained in the terrestrial environment (Krabbenhoft et al., 1995; Allan and Heyes, 1998; Scherbatskoy et al., 1998; Shanley et al., 2008). The fraction of Hg that 'leaks' from these upland areas provides a potential long-term source of Hg to down-gradient landscapes. Downstream locations may contain wetland environments which are typically anoxic and rich in organic carbon and may provide a suitable setting for the conversion of Hg from inorganic to the organic form, methylmercury. Methylmercury is the potentially toxic form of Hg that bioaccumulates and poses a health risk to humans, typically through fish consumption. Accurate estimates of total Hg ($Hg_{T,}$ which is comprised of dissolved and particulate fractions, Hg_D and Hg_P, respectively) export from these terrestrial reservoirs to stream systems are needed to quantify the movement of Hg within an ecosystem and to evaluate the response of these systems to changes in atmospheric deposition and other environmental forcings.

Streamwater Hg_T fluxes have been computed for a variety of forested headwater systems, including sites in Vermont, Puerto Rico, Colorado, and Wisconsin (Shanley et al., 2008), Oregon (Brigham et al., 2009), Sweden, (Munthe and Hultberg, 2004; Lee et al., 1998), Ontario (St. Louis et al., 1996), Minnesota (Kolka et al., 1999), Maine (Nelson et al., 2007) and New Hampshire (Dittman et al., 2010). Large amounts of uncertainty surround those estimates due to a combination of factors: (1) Hg concentrations can vary up to two orders of magnitude during a short-lived high-flow event (Scherbatskoy et al., 1998; Munthe and Hultberg, 2004; Shanley et al., 2008), (2) high-frequency samples are difficult to obtain during these brief storm conditions in headwater systems (Shanley et al., 2008; Riscassi et al., 2010) and (3) Hg concentrations in forested systems (without wetlands) are typically not well correlated with discharge (r^2 range from 0.1 to 0.5) (Scherbatskoy et al., 1998; Brigham et al., 2009; this dissertation Chapter 4), yet are commonly used to calculate continuous concentrations for flux computations. Our research uses recently evaluated automated sampling methods to increase sample frequency during storm events (Riscassi et al., 2010) for Hg_D and Hg_P and makes use of turbidity sondes as continuous surrogate measures for Hg_P concentrations to compute and evaluate Hg fluxes at three sites within forested headwater streams.

Watershed studies that have calculated and compared both Hg_D and Hg_P contributions to total Hg export (based on flow-weighted concentrations, seasonal or baseflow/spring flow/event flow fluxes) have generally found that Hg_P dominates in disturbed and/or agricultural watersheds, while wetland/forested systems are dominated by Hg_D (Schuster et al., 2008; Babiarz et al., 1998; Hurley et al., 1998; Hurley et al., 1995). Earlier studies hypothesized that disturbed environments are more susceptible to erosion and therefore greater amounts of particulates and associated Hg transported downstream during high-flow periods. None of those studies collected samples throughout the duration of a storm hydrograph. Some non-disturbed forested systems have been found to be dominated by Hg_P including Nettle Brook, VT (Scherbatoskoy et al., 1998) and Sleepers River (W9), VT (Shanley et al., 2008; Dittman et al., 2010). Each of these studies focused on high frequency sampling during peak flow events (storms and snowmelt). Scherbatoskoy et al. (1998) noted that the steep mountainous slopes of the Nettle Brook watershed that contribute to the brief high-flow events with greater erosive power likely account for the dominance of Hg_P fluxes at that site.

Few studies have attempted to quantify the contributions of Hg_T during high-flow periods in the context of the annual flux which is probably due to a lack of consistent high-flow sampling during these periods. Schebatoskoy et al. (1998) estimated that 50% of the annual Hg_T flux occurred on one day of peak snow melt, but the relatively infrequent monthly sampling during the non-snowmelt period, including brief storm events, reduces the certainty of this estimation. Schuster et al. (2008) found that a single summer storm transported more Hg_T than an equivalent period of peak snowmelt, but annual and event Hg_T fluxes were not reported. Shanley et al., (2008) noted that the higher Hg_T export at Sleepers River compared to what is considered ‘typical’ for most watersheds may be due to the focus of event sampling which captured a component often overlooked. Consistent streamwater sampling at a fine temporal scale during brief high-flow periods is essential to accurately quantify the contributions of storm-specific Hg_T fluxes to overall Hg_T export.

Our research focuses on three watersheds within the southern Appalachians, that are characterized as undisturbed, forested, mountainous headwater systems, with little to no wetlands. The annual streamwater export at these sites is dominated by brief high-flow storm events throughout the year. For each of these three streams our objectives were (1) to evaluate the relationship of Hg_P to turbidity for use in the evaluation of short-term dynamics and computation of annual Hg_P fluxes (2) to determine if Hg fluxes are dominated by the particulate or dissolved fraction in these undisturbed, mountainous systems and (3) to evaluate the contributions of periodic high-flow events to overall Hg_T transport downstream. This information will improve our understanding of Hg dynamics in remote mountain systems and allow for more accurate quantification of downstream Hg fluxes.

2. Methods

2.1 Field Methods

This study was conducted at three watersheds within the central Appalachian Mountain region of Virginia. The Piney River, Staunton River, and Paine Run (hereafter referred to as Piney, Staunton, and Paine) watersheds are located in Shenandoah National Park (SHEN) within 100 km of each other. Each watershed is similar in size (~10-12km^2) and stream gradient (7-9%) and is characterized by second-to third-growth mixed hardwoods [Ryan et al., 1989; Young et al., 2006]. Mean annual rainfall measured at Big Meadows National Atmospheric Deposition Monitoring station (VA28), located on the mountain ridge in central SHEN, was 1357 mm for the 1981-2010 water years on record. Piney and Staunton are located on the east side of the Blue Ridge while Paine is located to the west, which has significance for rainfall patterns. Annual rainfall totals on the west side (Paine) are on average about 30% less than totals on the east side (Piney and Staunton) (Rice et al., 2004).

While similar in many qualities, sites are distinguished by underlying bedrock composition, with metabasaltic, granitic, and siliciclastic underlying Piney, Staunton, and Paine, respectively (Gathright, 1976). Bedrock differences result in distinctions in soil type and water chemistry. Piney is dominated by clays and streamwater with a circumneutral pH, while Paine is dominated by sands and streamwater is more acidic. Organic carbon content of soil is similar between sites and DOC concentrations are similarly low (typically 1-5 mg L^{-1}).

Streamwater samples were collected at each site from March 2008 through October 2010. Grab samples were collected approximately every two weeks throughout the first full year, then subsequently every month. Grab samples were collected for Hg_D and Hg_P analysis following 'clean' techniques for trace metals established by the U.S. EPA (1996). Automated samplers were typically used to collect high-flow samples at bi-hourly intervals as described in Riscassi et al. (2010). All Hg samples were taken with glass bottles with Teflon® cap liners or Teflon® bottles. Sample bottles were cleaned by soaking in a 75°C 4N HCl bath for 48 hours, rinsed three times with deionized water, stored, placed in two nested resealable bags and filled with 0.4% HCl until needed. All sample collection and handling procedures followed 'clean' techniques for trace metals established by the U.S. EPA (1996). All Hg grab samples were taken within 0.5 meters of the automated sampler inlet. Samples were transported from the field to the laboratory in a cooler and refrigerated at 4°C until subsequent filtering and/or analysis.

Stream stage was measured by a float and pulley within a stilling well slightly downstream (~5 m) of the sampling location. Routine manual discharge measurements were made to establish a rating curve which was used to calculate discharge at hourly intervals.

Identical turbidity sensors (YSI, model 6136) were used in conjunction with multiparameter water quality sondes (YSI, model 6020V2) to measure and record turbidity in nephelometric turbidity units (NTU) at each of the three sites. A more detailed description of the sensor specifications and field deployment methods are described in Riscassi et al. (2011). Sondes were deployed on October 22, 2009 at Staunton, on November 3, 2009 at Piney, and on November 15, 2009 at Paine. All sondes initially recorded turbidity at hourly intervals and were switched to half-hour intervals around January 1, 2010. The sondes at Piney and Staunton were located within 1 meter of the inlet used for automated sampling of streamwater for Hg analysis. The sonde at Paine was installed slightly further upstream of the sampling inlet (~10 m) to be less visible from a highly trafficked area. All sondes were removed by the first week in January, 2011.

2.2 Laboratory Methods

Samples were filtered through a pre-baked quartz fiber filter (QFF) at the University of Virginia according to procedures documented in Lewis and Brigham (2004). The filtered sample water and filter with captured filtrate for each sample were preserved and stored until analysis according to procedures defined in Riscassi et al. (2011) and in Chapter 4 of this dissertation. Samples were analyzed for Hg_D and Hg_P using a Tekran® cold-vapor atomic florescence spectrophotometer according to U.S. EPA method 1631, Revision E (2002). The method detection limit (MDL) for Hg_D was determined to be 0.19 ng L^{-1} and the MDL for Hg_P was determined to be either 0.21 or 0.08 ng L^{-1} depending if the volume of water filtered was 0.375 L (automated samples) or 1 L (grab samples).

2.3 Quality Assurance and Quality Control

Quality assurance (QA) for sample collection and transport was maintained in the field through blanks and duplicates. All field blanks (n=20) were below the MDL for Hg_D, and all but one (0.23 ng L^{-1} Hg_P) were below the MDL for Hg_P. The mean absolute difference for field duplicates (n=27) was 0.03 +/-0.06 ng L^{-1} for Hg_D and 0.04+/-0.37 ng L^{-1} for Hg_P. The higher standard deviation for Hg_P is largely due to duplicates taken during high flow periods when concentrations were elevated (10-15 ng L^{-1} relative to baseflow concentrations <5 ng L^{-1} Hg_P); the percent differences between duplicates of the higher concentration samples were all <10%.

QA was maintained in the laboratory through blanks (method, system, and filter) and matrix spikes with every batch of 10 samples. The majority (90%) of method and system blanks (n=131) were below the MDL, and the remaining 10% were < 0.5 ng L^{-1}. All but two (0.26 and 0.29 ng L^{-1}) laboratory filter blanks (n=32) were below MDL for Hg_D and all were below MDL for Hg_P. The accuracy of all standards, spikes, and OPR samples were maintained within 15%. Reported quality control metrics are all within U.S. EPA (2002) guidelines. Instrument performance within an analytical run was evaluated with ongoing precision and recovery (OPR) samples and verification of an independent standard. Overall laboratory accuracy was determined by participation in the January 2010 inter-laboratory proficiency test administered by Environment Canada. For sample concentrations (n=5) ranging from 6.6 to 47.8 ng L^{-1}, our sample recoveries ranged from 97 to 102%.

The turbidity sensor was evaluated before stream installation and maintained throughout the deployment period. Prior to initial deployment, the sensor was calibrated with two turbidity solutions (0 and 123 NTU). The accuracy of the sensor was maintained by evaluating the sensor's ability to accurately measure a quality control solution every two weeks at which time the sensor was downloaded, cleaned, and redeployed. The turbidity sensor passed all quality assurance criteria established by Wagner et al. (2006).

2.4 Flux calculations

Hg_P and Hg_D fluxes were computed for the 2010 water year using a combined period-weighted and regression-model approach herafter referred to as simply the "combined method". During baseflow periods, linear interpolation between measured Hg_D and Hg_P concentrations were used to estimate Hg concentrations. When samples were taken during high-flow events, linear interpolation between measurements (typically at 2-hr intervals) was similarly employed. When measurements were not available during high-flow events (when concentrations are known to increase) the Hg_D-discharge relationship established for each site was used to estimate Hg_D concentrations. Hg_P concentrations were similarly calculated, only with a turbidity rating (rather than discharge rating) at each site when available. There were periods when no samples were taken and turbidity data was not available. For these periods the discharge rating was used to estimate Hg_P concentrations. Hg_T concentrations for the 2010 water year were computed by adding together the Hg_P and Hg_D fluxes. Hg_D and Hg_P concentrations and fluxes were also estimated from the discharge rating for each site (Table 1). Estimated concentrations were then multiplied by the corresponding discharge values to obtain a flux.

4. Results

4.1 Relative fractions of Hg_P and Hg_D

The range of flow conditions during the 2009-2010 water years (Oct. 1, 2008-September 30, 2010) was representative of the previous 18-year period of record at each site. For high discharge periods the three sites have similar flow distributions, but Paine Run has lower flow conditions throughout the year. Overall the mean specific discharge for the study period (hourly data for 2 years) at Piney, Staunton and Paine was 0.08, 0.10 and 0.05 mm hr^{-1}, respectively. A total of 74, 131, and 98 samples were collected at Piney, Staunton, and Paine, respectively which included four to five storms periods at each site in which samples were taken frequently on both the rising and falling hydrograph limbs. As a result, samples were collected for a wide range of discharge conditions representing a flow exceedence range of at least 96.0 to 0.04% (Chapter 4 of this dissertation, see Figure 3).

Total Hg concentrations, calculated as Hg_D + Hg_P, ranged from a minimum of approximately 0.20 ng L^{-1} at all sites to a maximum of 46, 50, and 24 ng L^{-1} at Piney, Staunton and Paine, respectively. Hg_P accounted for 58, 69, and 37% of Hg_T concentrations measured at Piney, Staunton, and Paine, respectively (Figure 1). In term of flow-weighted concentrations, the %Hg_P was 58, 88 and 57% at Piney, Staunton and Paine, respectively. The considerably higher percentage at Staunton and Paine reflecting the increase in %Hg_P with increasing discharge. This general trend of increasing %Hg_P with increasing discharge is not apparent for the majority of flow conditions (Figure 2) as the trend is driven by the few samples taken at the highest discharge at each site (>2 mm hr^{-1}) that are consistently >80% Hg_P. No samples were taken during similar high flow periods at Piney and as a result, no change in the %Hg_P was found when weighted by flow.

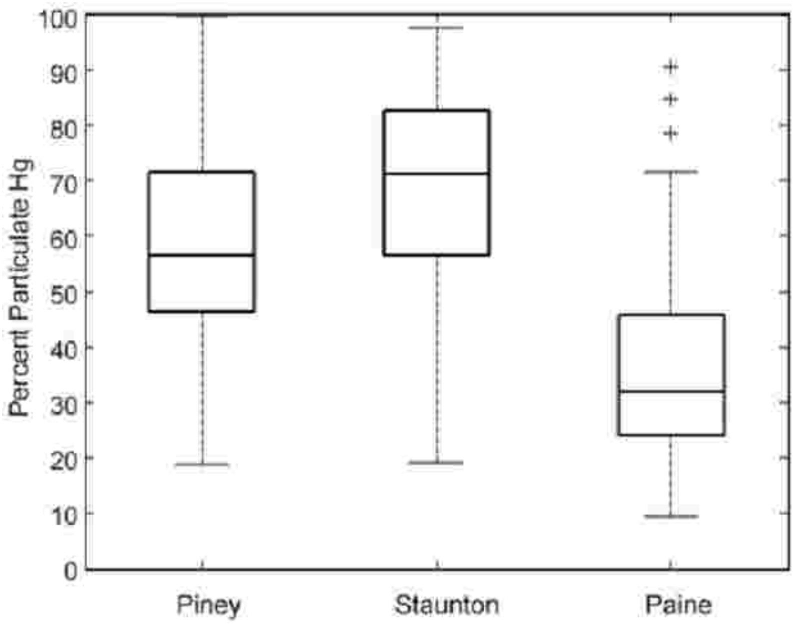

Figure 1. Box plots of the percent particulate Hg (of total Hg) for all measurements at the three study sites. The horizontal bars within the boxes are median values; bottom and top are 25th and 75th percentile values and vertical lines are 10th and 90th percentiles. Outliers are represented by crosses.

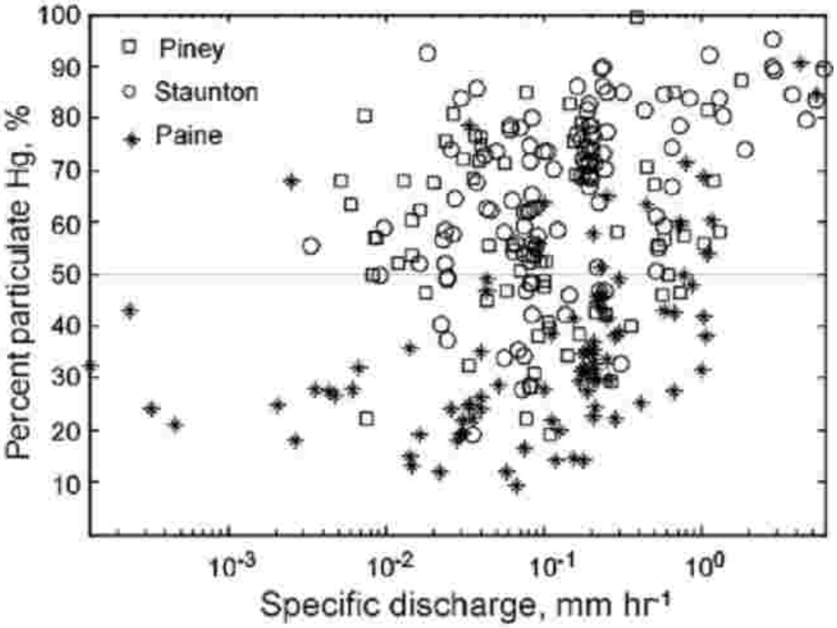

Figure 2. Percent particulate Hg versus specific discharge for each study site. The relative fraction of particulate Hg increased significantly ($p<0.001$) with discharge at Staunton and Paine, but the relationship was not significant for Piney ($p=0.44$). Note that for the highest specific discharge (>2 mm hr-1) the percent particulate Hg is consistently > 80% of Hg_T.

4.2 Turbidity and Hg_P

Turbidity measurements were available concurrently with 29, 61, and 40 Hg_P samples at Piney, Staunton, and Paine, respectively. Periods of concurrent Hg_P and turbidity measurements covered a wide range of discharge conditions based on the 18-year period of record at Staunton and Paine, representing the 0.01 to 95.95 and 0.06 to 99.43 percent exceedence, respectively. Samples at Piney represented a narrower range of flows along the distribution, ranging from 0.28 to 87.58 percent exceedence. At each site, turbidity was able to explain 81, 78 and 98 percent of the variability in Hg_P concentrations at Piney, Staunton, and Paine, respectively (Figure 3). The slope for the linear best fit line at Piney and Staunton were statistically similar (0.15 ng L^{-1} Hg_P per unit turbidity, NTU) and Paine had a significantly steeper slope (0.25 ng L^{-1} Hg_P per unit turbidity) than the other two sites. Intercepts were 0.07, 0.38, and -0.05 at Piney, Staunton, and Paine, respectively (Table 1).

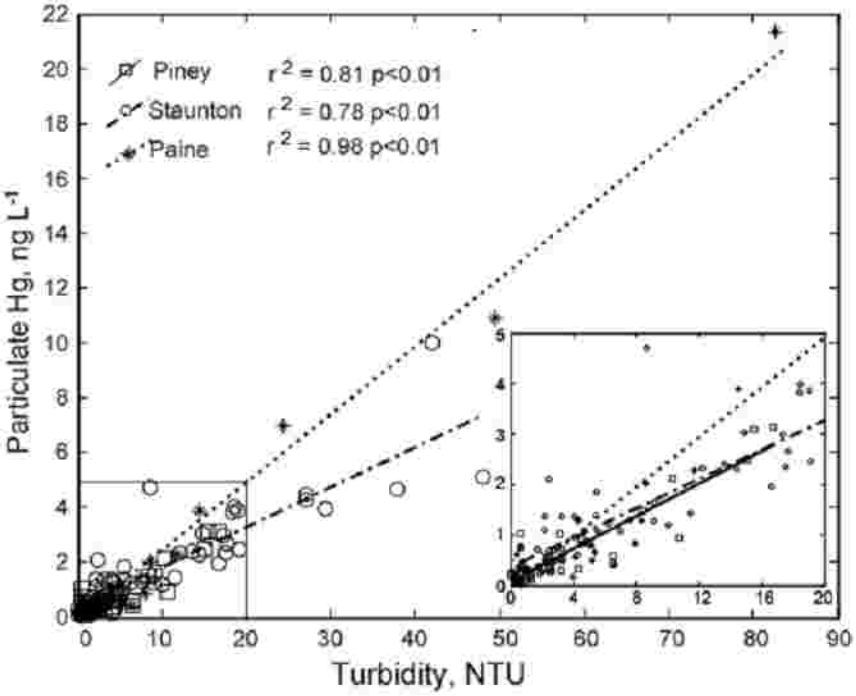

Figure 3. Particulate Hg versus turbidity versus with best fit lines shown for individual sites. Inset is the same data presented in the larger figure illustrating the details of a range of lower concentrations. Note the best fit line for Piney is not visible in the full size image, only in the inset.

Table 1. Values for the least squares linear regression of turbidity and Hg_P and for log_{10}-transformed specific discharge (q) and dissolved, particulate, and total mercury (Hg_D, Hg_P, and Hg_T) at the three study sites.

	Y		X		Y= bX + a		
Site	**variable**	**unit**	**variable**	**unit**	**b**	**a**	**r^2**
Piney	Hg_P	ng L^{-1}	turbidity	NTU	0.16	0.07	0.81
Staunton					0.15	0.38	0.78
Paine					0.25	-0.05	0.98
Piney	log [Hg_D]	ng L^{-1}	log [q]	mm hr^{-1}	0.40	1.07	0.52
Staunton					0.13	0.81	0.13
Paine					0.22	1.10	0.43
Piney	log [Hg_P]	ng L^{-1}	log [q]	mm hr^{-1}	0.47	1.39	0.36
Staunton					0.49	1.56	0.55
Paine					0.39	1.00	0.39

Gaps in turbidity data include periods of battery failure and periods when the sonde was known to have moved from the established sample location (*e.g.* natural dislodgement and vandalism) and when data were deemed invalid. Invalid data are defined as turbidity values that increase without a concurrent increase in discharge, likely due to a local disturbance not characteristic of the entire stream. Turbidity data were available for approximately 79%, 88%, and 78% of the 2010 water year at Piney, Staunton, and Paine, respectively. It is worth noting that turbidity data were not recorded during the largest storm event in late January 2011 at Piney and Staunton, but were recorded at Paine.

4.3 Hg concentrations and discharge

Correlations between discharge and Hg_P as well as Hg_D are significant at all sites with r^2 values ranging from 0.36 to 0.55 and 0.13 to 0.52, respectively (Figure 4). Slopes for the linear regressions of log-transformed discharge versus log-transformed Hg_P are statistically similar between the three sites. For all sites, slopes are steeper for discharge versus Hg_P as compared to Hg_D (Table 1). In terms of correlations between the forms of Hg, Hg_D had a weak positive relationship with Hg_P (data not shown) at Staunton and Paine ($r^2=0.14$ and 0.13, respectively, $p<0.001$) and were not significantly related at Piney ($p=0.44$).

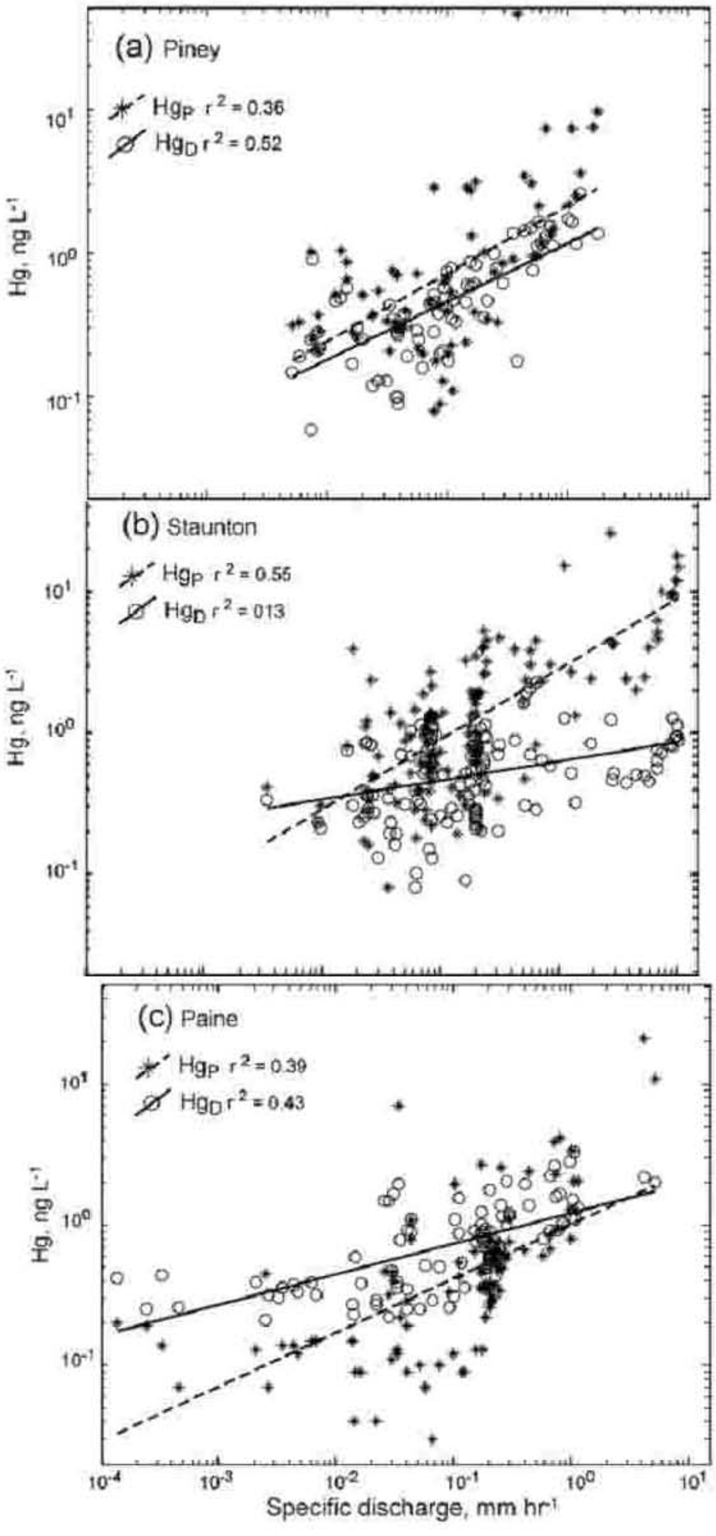

Figure 4. Particulate Hg (Hg_P) and dissolved Hg (Hg_D) versus specific discharge and the corresponding regression lines at (a) Piney, (b) Staunton, and (c) Paine. All relationships are statistically significant ($p<0.001$).

4.4 Streamwater Hg fluxes

Discharge for the 2010 water year was similar at 883 and 978 mm yr^{-1} at Piney and Staunton, respectively, and 533 mm yr^{-1} at Paine, possibly reflecting the lower rainfall totals likely experienced on the west side of the mountain range (as noted in Section 2.1). Hg_P fluxes estimated with the combined method were 1.02, 3.16, and 0.79 µg m^{-2} yr^{-1} at Piney, Staunton and Paine, respectively. Hg_D fluxes were 0.74, 0.55, and 0.47 µg m^{-2} yr^{-1}, resulting in a Hg_T flux of 1.76, 3.71, and 1.26 µg m^{-2} yr^{-1} at Piney, Staunton and Paine, respectively (Table 2). The annual Hg_T flux was dominated (58 - 85%) by the particulate fraction at all three sites.

Table 2. Streamwater and mercury input and output fluxes for the 2010 water year at the three study sites. The 'combined method' of calculating stream export is defined in Section 2.4.

Site	**Streamwater (mm yr^{-1})**	**Hg (µg m^{-2} yr^{-1})**					**%**
		Atmospheric input		**Stream output**			**Percent fluvial export**
		Wet [a]	**Dry low/high estimate** [b]	**Combined method**			
		Hg_T	**Hg_T**	**Hg_D**	**Hg_P**	**Hg_D+Hg_P**	**Hg_T**
Piney	883	9.97	10/20	0.74	1.02	1.76	5.9 - 8.8
Staunton	978	9.97	10/20	0.55	3.16	3.71	12.4 - 18.5
Paine	533	9.97	10/20	0.47	0.79	1.26	4.2 - 6.3

[a] Determined as the average of all available (2003-2009) annual Hg_T wet deposition measurements at Big Meadows Mercury Deposition Network Site, VA.

[b] Calculated as equal to wet deposition for the low estimate, and two times the wet deposition for the high estimate.

Atmospheric Hg input fluxes to the watersheds were estimated to calculate a percent retention. Input fluxes were calculated as a combination of wet and dry Hg deposition. Wet deposition was calculated as the average of all available total annual Hg wet deposition measurements (2003-2009) at Big Meadows, a Mercury Deposition Network site located within 50-km of the study sites, centrally located within Shenandoah National Park. To estimate the contributions from dry deposition, a low estimate equal to wet deposition and a high estimate of two times wet deposition were used (St. Louis et al., 2001). This method was also used to approximate dry deposition for forested sites in Shanley et al., (2008). Considering the ranges, the percent of atmospherically-deposited Hg that is exported through streamwater ranges from 6-9% at Piney, 12-19% at Staunton, and 4-6% at Paine.

5. Discussion

5.1 Turbidity and Hg_P

Turbidity measured with an *in situ* sonde had a strong linear correlation with concurrent measurements of Hg_P at each of the three sites. At one of those sites, Staunton, a previous study (Riscassi et al., 2011) analyzed the total suspended solids (TSS) and volatile solids (VS, a proxy for the organic sediment) content on a subset of those samples and demonstrated that (1) Hg_P was strongly correlated with VS, confirming the known association of Hg with organics, (2) Hg_P was also strongly correlated to TSS (due to the consistent VS fraction of TSS) and (3) stream turbidity had a strong correlation with TSS. These three factors allowed for a commutative association of Hg_P and turbidity (Riscassi et al., 2011) and we assume these same factors hold for the other two sites resulting in the strong turbidity - Hg_P relationships.

The slope of the best fit line relating turbidity to Hg_P is similar at two of the sites, but at Paine the concentration of Hg_P per unit turbidity is substantially greater. The relationship at Paine is driven by four or five high values (Figure 4) which could point to a storm-specific deviation not representative of the entire study period. However, those values are derived from two distinct periods (a snowmelt-rainfall event in mid-winter and a large summer storm event) making it likely that the relationship will hold for all high-flow periods.

There are several reasons why more Hg_P could be transported per unit turbidity at a particular site. First, the TSS-turbidity ratio could be elevated relative to the other sites as particle size variation can cause the turbidity to vary by a factor of four for the same concentration of TSS (Gippel, 1995). Variability in the Hg_P-turbidity relationship could also be caused by differences in the relative fraction of VS. Baseflow VS and TSS measurements at all three sites measured previous to this study indicate the fraction of VS was substantially higher at Paine (77% versus 44% and 30% at Piney and Staunton, respectively), although these samples were typically taken during baseflow conditions. Finally, the amount of Hg_P per unit VS may be elevated at Paine relative to the other two sites. Concurrent measurements of Hg_D and dissolved organic carbon (DOC) at all three sites demonstrated that for a variety of seasons and storm conditions, the amount of Hg_D per unit UV absorbance (a proxy for DOC quantity and quality) was higher at Paine, providing evidence that more Hg partitioned into organic matter versus mineral soils at that site (Chapter 4 of this dissertation). If this hypothesis is correct, it would follow that there would be more Hg_P per unit particulate organic carbon. Additional measurements of TSS and VS concurrent with Hg_P and turbidity during a variety of flow conditions at the other two sites would be needed to assess why the Hg_P-turbidity ratio at Paine is elevated in relation to other sites.

5.2 Hg_D and Hg_P fluxes

Hg_D fluxes ranged from 0.47 to 0.74 µg m^{-2} yr^{-1} at our three sites, similar to other forested systems in Wisconsin, Vermont (Brigham et al., 2009; Scherbatskoy et al., 1998) and slightly lower than others in Vermont, New York, and Oregon where fluxes ranged from 1.19 to 1.70 µg m^{-2} yr^{-1} (Shanley et al., 2008; Brigham et al., 2009; Dittman et al., 2010). These relatively small-scale variations are likely due to a combination of factors including differences in the hydrologic flux, variability in methods used to estimate Hg_D from discharge, as well as differences in dissolved organic carbon export (DOC) concentrations and Hg_D-DOC ratios. Our Hg_D fluxes were considerably smaller than the fluxes reported at the St. Marys River and Santa Fe River in Florida (annual Hg_D fluxes were 3.75 and 3.14 µg m^{-2} yr^{-1}, respectively) likely due to the order-of-magnitude greater concentrations of DOC and associated Hg_D export. DOC concentrations range from 1 to 77 mg L^{-1}at the Florida sites (which have significant amounts of wetlands with high organic carbon content) as compared to our three sites which typically range from 0.5-5 mg L^{-1} (Brigham et al., 2009). Although the amount of Hg_D per unit DOC was higher at our three sites than each of the FL sites (Chapter 4 of this dissertation) those sites export more Hg_D because the quantity of the DOC (and associated Hg_D) exported overwhelms the comparably subtle differences in the Hg_D/DOC ratios.

Hg_P fluxes were 3.16, 1.02 and 0.79 µg m^{-2} yr^{-1} at Paine, Piney, and Staunton, respectively, exhibiting more variability than the Hg_D fluxes. The disparity in Hg_P fluxes between Staunton and the other two sites are due largely to differences accrued during the largest storm event (in peak magnitude) on January 25, 2010. For the duration of the storm hydrograph (~ 24hr), the streamwater flux was higher at Staunton (200 mm versus 120 mm at both Piney and Paine). Concentrations of Hg_P were also higher at Staunton, likely due to the higher discharge having an enhanced ability to mobilizing particulates from the watershed (peak of 48.3 ng L^{-1} versus 21.3 ng L^{-1} at Paine) resulting in greater Hg_P mass export at that site. Studies conducted at Hubbard Brook, New Hampshire suggest that as discharge increases and the stream gets wider, backwater areas and channels become exposed to currents and particulates generated or deposited since the last storm are entrained (Fisher and Likens, 1973; Bilby and Likens, 1979, Meyer and Likens, 1979). The considerably lower concentrations of Hg_P at Piney (max 3.6 ng L^{-1}) are likely an artifact of using a discharge rating during the January event (no turbidity was recorded and or samples were taken during this event at Piney). The rating likely underestimated the Hg_P concentrations (and fluxes) based on the differences apparent between Hg_P computed with the discharge rating and measured at Staunton during the January event (Figure 5). It is likely that the Hg_P flux at Piney would be more similar to that reported for Staunton if turbidity data were recorded during that event, highlighting the need for consistent high-flow sampling in these headwater systems.

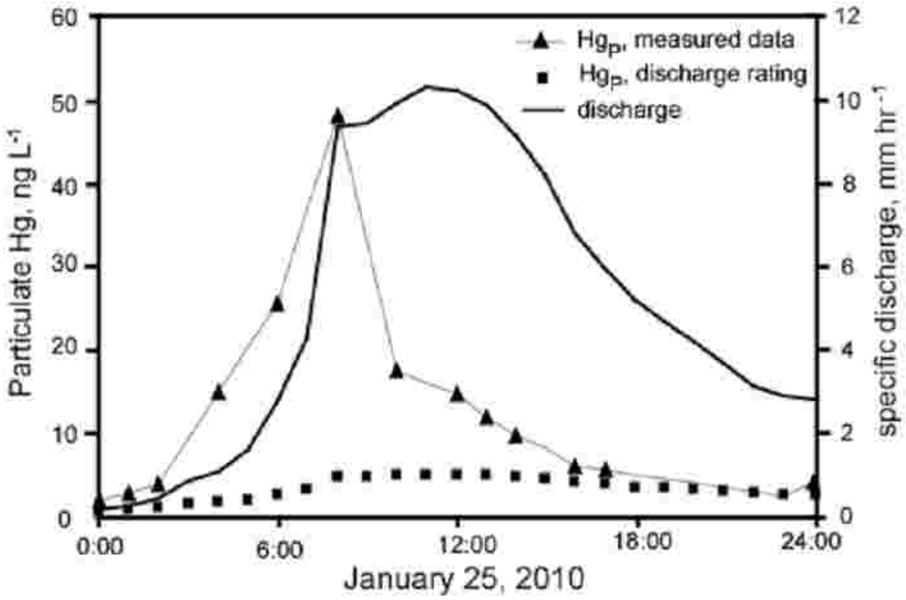

Figure 5. Particulate Hg concentrations measured and estimated with a discharge rating at Staunton during the January 25, 2010 storm.

5.3 Relative fluxes of Hg_P and Hg_D

Hg_P fluxes account for the majority of the overall Hg_T flux at each of the three sites (58-85%), similar to the fractioning for flow-weighted concentrations (57-88%). This fraction is higher than for the non flow-weighted concentrations (37-69%) due to the large increase in Hg_P during the highest flow periods as compared to Hg_D (Figure 4). Note that the relationship between Hg_D and Hg_P concentrations versus discharge are different for each site with lower (Paine), similar (Piney) and higher (Staunton) Hg_P (compared to Hg_D) during the majority of flow conditions (10^{-4} – 10^{0} mm hr^{-1}). Ultimately the relationship between Hg_P and Hg_D concentrations during peak flow conditions is responsible for the fractioning of the overall flux, with a clear increase in the Hg_P flux relative to the Hg_D flux occurring quickly during the two largest high-flow events (Figure 6). The greater increase in Hg_P concentrations relative to Hg_D during peak flows is likely a function of material availability. The source of particulates (and associated Hg_P) available for transport include the streambank, riparian areas and in-stream sediments with mobilization mostly limited by the ability of the streamwater to erode and entrain the particles (largely a function of discharge magnitude and rate of increase). In contrast, the supply of DOC and associated Hg_D is limited by the amount of labile material in the upper soil horizon which has shown to become depleted or 'flushed' during high flow events (Boyer et al., 1996; 2000).

Only two other sites, Sleepers River, VT, and Nettle Brook, VT, have reported similarly high Hg_P contributions as compared to our three study sites, approximately 70% at each (Shanley et al., 2008; Scherbatskoy et al., 1998). Total Hg_P fluxes were comparable to our sites, ranging between 1.85 – 4.80 $\mu g\ m^{-2}\ yr^{-1}$ (Table 3). Similar to our sites, both Sleepers River and Nettle Brook are forested mountainous watersheds with little or no wetland cover and sampling for those studies was focused on capturing Hg dynamics frequently during high-flow periods. The majority of other studies dominated by Hg_D typically have one of two key characteristics: 1) they contain significant wetland cover or 2) are lower gradient systems. Systems with wetlands typically export greater dissolved organic carbon and associated $Hg_{D.}$ Wetlands also serve to reduced peak discharge which promotes settling and retention of particulates and associated Hg_P while also retarding peak flows downstream, reducing erosion of streambank particulates and associated Hg_P. Similarly, low gradient systems are likely to have less flashy hydrographs, compared to mountain systems, with relatively diminished erosive power,

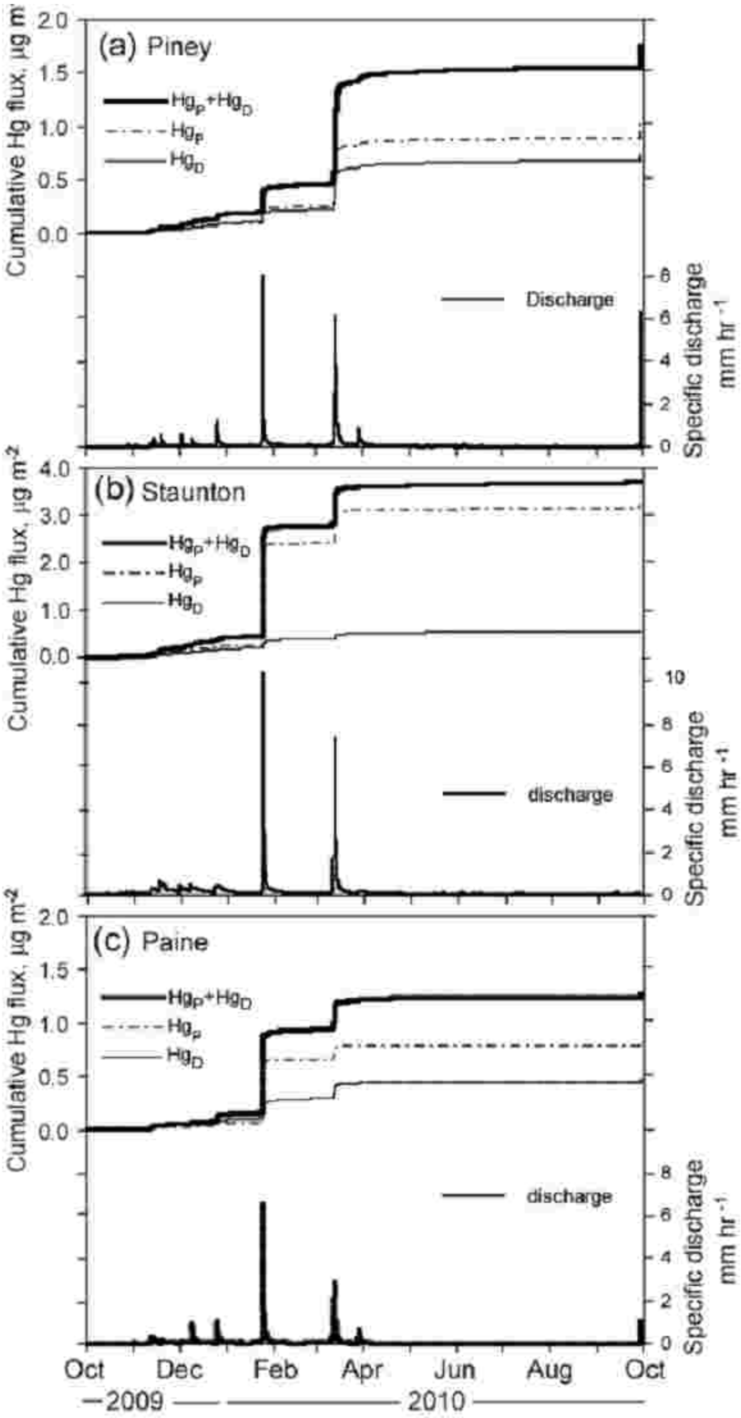

Figure 6. Cumulative streamwater Hg fluxes for individual physical fractions (particulate - Hg_P and dissolved - Hg_D) and combined ($Hg_P + Hg_D$) at (a) Piney, (b) Staunton, and (c) Paine for the 2010 water year. Hourly specific discharge is shown on the lower half of each graph for the respective site. Note that the Hg flux axis is expanded 2-fold at Staunton compared to Piney and Paine.

Table 3. Annual Hg_T fluxes as well as Hg_P and Hg_D when available, computed by various methods in undisturbed watersheds throughout the U.S. and Scandinavia. Sites evaluated in this study are in bold.

Watershed location	**Flux (μg m^{-2} yr^{-1})**				**Source**
	Hg_T	**Hg_P**	**Hg_D**	**% Hg_P [a]**	
Allequash Creek, WI	0.3	-	0.2	32	Shanley et al., 2008
Cadillac Brook, ME	0.4	-	-	-	Nelson et al., 2007
5 watersheds in MN	0.7-2.8	-	-	-	Kolka et al., 1999
Evergreen River, WI	0.9	0.4	0.4	51	Brigham et al., 2009 [b]
Pike River, WI	0.9	0.3	0.6	36	Brigham et al., 2009 [b]
3 watersheds in Ontario	1.0-2.0	-	-	-	St. Louis et al., 1996
Paine Run, VA	**1.3**	**0.8**	**0.5**	**63**	**this study**
Hadlock Brook, ME	1.3	-	-	-	Nelson et al., 2007
Svartberget, Sweden	1.3	-	-	-	Lee et al., 1998
Andrews Creek, CO	1.6	-	-	-	Shanley et al., 2008
Archer Creek, NY	1.6	0.3	1.2	25	Dittman et al, 2010
Lookout Creek, OR	1.7	0.3	1.4	18	Brigham et al., 2009 [b]
Piney River, VA	**1.8**	**1.0**	**0.7**	**58**	**this study**
Hubbard Brook, NH (W9)	1.8	0.9	1.0	44	Dittman et al, 2010
Gardsjon, Sweden	2.3	-	-	-	Munthe and Hultberg, 2004
Nettle Brook, VT	2.7	1.9	0.8	69	Scherbatskoy et al., 1998
Archer Creek, NY	3.0	0.6	2.3	23	Dittman et al, 2010
Paroninkorpi, Finland	3.2	-	-	-	Lee et al., 1998
Sleepers River, VT (2002-2005)	3.3	-	1.2	63	Shanley et al., 2008
Santa Fe River, FL	3.7	0.6	3.1	15	Brigham et al., 2009 [b]
Staunton River, VA	**3.7**	**3.2**	**0.6**	**85**	**this study**
St. Marys River, FL	4.4	0.6	3.8	14	Brigham et al., 2009 [b]
Sleepers River, VT (2005-2007)	6.5	4.8	1.7	74	Dittman et al, 2010
Icacos, Puerto Rico	54.4	-	3.5	-	Shanley et al., 2008

[a] %Hg_P is calculated for sites with Hg_D, but no Hg_P data as 100 minus %Hg_D.

[b] Data extracted from Supporting Information Table S3 and converted to appropriate units.

lower particulate loads and therefore less Hg_P transported. A more comprehensive evaluation of watershed characteristics including stream gradient, land cover composition and peak discharge is needed to determine if these theories hold. It is worth noting that although many of the studies that found Hg_D to dominate did sample over a range of flow conditions, they did not focus on frequent high-flow sampling. As the results from this work demonstrate that Hg_P is more flow activated than Hg_D, this fraction was likely to be underestimated in these previous studies if peak flows were not captured.

5.4 Importance of storm events

Annual fluxes at the three Shenandoah National Park sites were dominated by two individual events, the January 25th and the March 10-12th rainfall/snowmelt events (Figure 6). Combined, these two events accounted for approximately 81, 95, and 79% of the Hg_T annual flux at Piney, Staunton and Paine, respectively indicating the importance of individual storms events to the overall Hg flux. For another perspective, 80% of total Hg_T flux occurs in approximately 1% of the time at all three sites (Figure 7). This contrast with the streamwater flux which exports only 30% during the same time period (Figure 7). These results highlight 1) the significance of very brief periods of high discharge to overall flux and 2) the simultaneous increase in Hg_T concentrations along with the increase in discharge. Considering Hg_P and Hg_D fluxes separately, high-flow periods are more important to the Hg_P flux as compared to the Hg_D flux. The upper thirty percent of steamwater export contributes to approximately 90% of the Hg_P flux (excluding Piney data due to the likely underestimation during the Jan. 2010 storm as previously described) as compared to ~ 50% of the Hg_D flux (Figure 8).

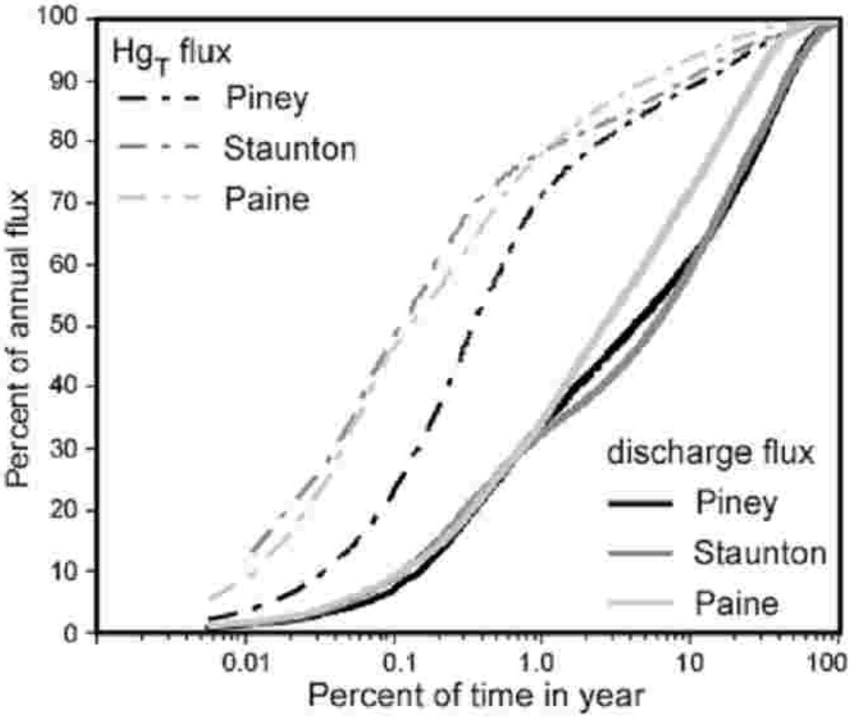

Figure 7. Percent of total Hg (Hg_T) flux and percent of total discharge flux versus percent of time in the 2010 water year for each site.

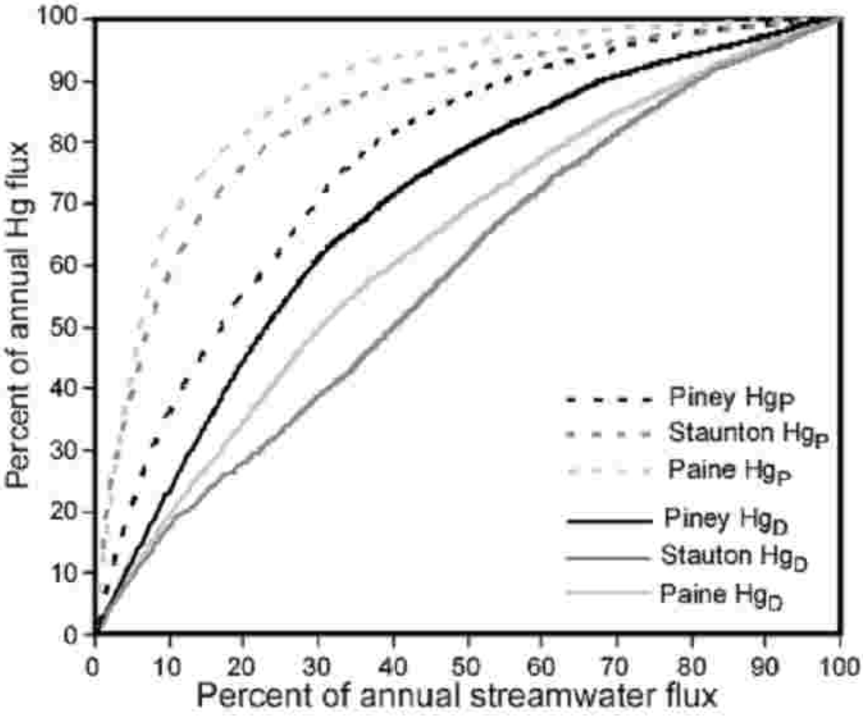

Figure 8. Percent of particulate and dissolved Hg flux (Hg_P and Hg_D, respectively) versus percent streamwater flux at each site for the 2010 water year.

5.5 Hg_T flux and watershed export

Hg_T fluxes ranged from 1.26-3.71 µg m^{-2} yr^{-1}at our three sites, similar to other studies in relatively undisturbed forested systems. Annual Hg_T fluxes computed at 15 other locations in the U.S. and Scandinavia generally ranged from 0.25 to 6.5 µg m^{-2} yr^{-1}, with one extremely high outlier (54.4 µg m^{-2} yr^{-1} in Puerto Rico) listed in Table 3. Possible explanations for the unusually high export in Puerto Rico include a geologic source or contamination from Hg used in gold mining in the area (Shanley et al., 2008). The amount of Hg exported in each of the three study watersheds ranges from 4-19% of the wet and dry Hg deposited. This export percentage is fairly typical with values reported ranging from about 5-30% of inputs in other undisturbed watersheds (Scherbatskoy et al., 1998; Allan and Heyes, 1998; Mast et al., 2005; Nelson et al., 2007; Shanley et al., 2008; Brigham et al., 2009). These results demonstrate that high-gradient, headwater systems export similar amounts, and retain as similar fraction, of Hg as compared to a variety of other systems in the U.S. and Scandanavia.

6. Summary and Implications

The majority of atmospherically deposited Hg is retained in three undisturbed forested headwater systems in the mid-Appalachians, similar to many other non-urban watersheds. Although these southeastern mountain systems have relatively low streamwater DOC (and associated Hg_D) concentrations, they export similar amounts of Hg_T as compared to other sites with high DOC export due to the contribution of Hg_P during brief intense storm events. The majority of the annual streamwater Hg_T export in the 2010 water year occurred during two high-flow rainfall/snowmelt events at each site. Despite differences in the physical fractioning of Hg within individual samples, annual fluxes at all sites are dominated by the particulate fraction due to the order of magnitude increases of Hg_P during the highest flows while Hg_D concentrations increase, but more moderately. While the particulate fraction has been hypothesized to be less bioavailable for methylation (Aiken et al., 2000) and therefore less relevant to the health of downstreamwaters, it may become available if desorbed or upon decomposition of the binding organic matter (Hurley et al., 1998).

Accurate flux measurements are necessary to evaluate the impact of atmospheric emission regulations and environmental changes on Hg mobilization downstream. Our study reinforces the importance of high-frequency monitoring during brief high-flow events to correctly account for the majority of fluxes and illustrates the potential errors associated with using a discharge rating to estimate Hg_P fluxes in the absence of measurements. Ideally, a turbidity sonde to estimate Hg_P in conjunction with an *in situ* optical sonde to estimate Hg_D to obtain high-frequency measurements of both particulate and dissolved Hg would be used to calculate long-term fluxes. Due to the considerably larger increase in Hg_P concentrations relative to Hg_D at high discharge, flux calculations using a discharge rating are subject to greater underestimation for Hg_P despite the similar explanatory power of discharge to predict Hg_P and Hg_D. As a result, there may be greater value in using *in situ* turbidity measurements to estimate Hg_P at high frequency (if a reliable relationship can be established) as compared to using an *in situ* optical sonde to estimate if the objective is to compute accurate Hg_T fluxes.

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CHAPTER 6

Summary and avenues of future research

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1. Summary and implications

1.1 Sampling and measurement techniques

Two approaches that would allow increased frequency of monitoring Hg in streamwater were evaluated with laboratory experiments and field measurements. A standard automated sampler, retrofitted with appropriately cleaned tubing and bottles, was found to be a viable technique for the collection of streamwater samples for low-level Hg (< 50 ng L^{-1}) analysis. Turbidity data, generated from *in situ* water quality sondes, was strongly positively correlated with Hg_P at each of the three study sites making it a useful high-frequency surrogate measure during high-flow periods when particulate Hg dynamics are prone to substantial error from the more commonly used discharge rating. Note that the turbidity to Hg_P relationship needs to be evaluated for individual sites as it is derived from a series of strong associations, Hg_P to volatile solids (VS, the organic fraction of solids), VS to total suspended solids (TSS), and between TSS and turbidity. As a result, using turbidity to approximate Hg_P may only be a practical monitoring technique in smaller more homogenous systems where all three of the aforementioned relationships hold. This research has added two important tools which can potentially be used by scientists and regulators to increase the frequency of streamwater Hg monitoring to facilitate an improved understanding of Hg dynamics.

1.2 Controls on dissolved and particulate streamwater Hg

Hg_D and Hg_P concentrations were monitored over an 18-month period for a wide range in flow conditions in three streams within Shenandoah National Park and exhibited significant within and between site variability. While discharge was a significant predictor of Hg_D concentrations, dissolved organic carbon (DOC) was more strongly coupled with Hg_D at all three sites confirming the known association of Hg with organic matter. UV absorbance at 254 nm (UV_{254}), a proxy for DOC quality as well as quantity, was a slightly better predictor of Hg_D, confirming laboratory and field studies demonstrating the quality, or aromatic content of DOC influences the amount of associated Hg. For the first time in the field environment our work provided evidence that physical soil characteristics affect Hg export, with sandy soils having a reduced capacity to retain Hg relative to clay rich soils, resulting in more Hg partitioned onto organic matter (evident in the Hg_D to UV_{254} ratio). Evidence for soil organic carbon content as a first order control on the Hg to DOC ratio, and therefore on Hg export, was also presented with the first aggregation of all Hg-DOC ratios in streamwater across the U.S. and Sweden. Similar to Hg_D, Hg_P concentrations were found to be significantly related to discharge, but much more strongly correlated to the organic fraction of suspended sediment. Both Hg_P and Hg_D increasing during the rising limb of storm hydrographs, however peak Hg_P concentrations were typically an order of magnitude greater than Hg_D.

This work has determined several watershed factors that affect Hg export from the terrestrial to the aqueous environment including 1) pH, as it affects organic matter quality, 2) soil type, as it affects the partitioning of Hg into the organic or mineral soil components, and 3) soil organic carbon content, as it affects the Hg-DOC ratio. This information can be used to inform biogeochemical models, decipher the causes of variability in Hg export between watersheds and, in the future, separate affects of reductions in atmospheric deposition from environmental forcings.

1.3 Export of Hg from forested headwater catchments

Hg_T export in three forested headwater catchments ranged from 1.26 to 3.71 µg m^{-2} yr^{-1}, within the range reported for other undisturbed watersheds throughout the U.S. and Scandinavia. At the three headwater sites the particulate fraction of Hg accounts for the majority of the annual total Hg flux (58-85%). Export of Hg from other stream systems have been shown to be dominated by Hg_P as well as Hg_D, with Hg_D typically more important in systems with considerable wetland composition. This work has demonstrated that undisturbed, forested, low-DOC systems (typically <5 mg L^{-1}) can export a significant amount of Hg downstream due to large contribution of Hg_P during brief intense storm events, with 80% of the Hg_P flux occurs during 1% of the streamwater flux. Export of atmospherically deposited Hg ranges from 4-19% at the three sites, confirming the role of watersheds as long-term reservoirs of historic Hg deposition.

2. Avenues of future research

2.1 Particulate Hg-OC ratios

This research demonstrated that soil type likely affects the partitioning of Hg onto organic versus mineral components of the soil using evidence from the variation in Hg_D to UV_{254} (metric of the quality and quantity of DOC) ratios between sites with a gradient in soil composition. To add more support to this theory at the field scale, a simple measure of the volatile solids (VS) in conjunction with Hg_P at the three sites would allow for a comparison of the Hg-OC ratio for the particulate fraction; we would expect more particulate Hg to partition onto a unit of VS at the site with a higher Hg_D to UV_{254} ratio. However, note that the VS metric does not account for quality differences like the UV_{254} metric. A more comprehensive analysis would involve measuring the percent aromaticity of the organic fraction of the particulate organic carbon by ^{13}C-NMR (nuclear magnetic resonance) as described by Weishaar et al. (2003).

2.2 High-frequency surrogate measure of Hg_D concentrations

A reliable relationship between Hg_D and UV_{254} was present at each of our three sites, indicating the potential to use an *in situ* optical sensor for intensive monitoring of Hg_D. Dissolved organic matter fluorescence (FDOM) measured by in an *in situ* sensor was found to be strongly correlated to UV_{254} (Saraceno et al., 2009). Similar to the use of the turbidity sensor as a surrogate for Hg_P concentrations at all three sites, a FDOM sensor would lead to an improved monitoring of Hg_D dynamics and quantification of mass fluxes of the arguably, more bioavailable dissolved Hg fraction. One potential limitation for the use of a FDOM sensor in a stream system is the interference caused by particulate organic matter, which as we have shown typically increases during high-flow periods. Saraceno et al. (2009) evaluated the differences between *in situ* FDOM measurements from unfiltered and filtered streamwater and found that at TSS concentrations of approximately 200 mg L^{-1} the FDOM signal was reduced by ~30%, while a 50 mg L^{-1} concentration reduced the signal by about 10%. TSS concentrations at Staunton were above 50 mg L^{-1} about 0.4% of the year, making the more simple, unfiltered system a promising approach. The maximum TSS at that site reached 200 mg

L^{-1} during one storm even, however by concurrently monitoring turbidity (and having a TSS-turbidity rating) a correction may be applied to the account for the interference.

2.3. Long-term monitoring

The U.S. Environmental Protection Agency has agreed to set standards to reduce Hg emissions from coal fired power plants by late 2011, with implementation likely to occur 2-3 years thereafter. As a result, there will be a need to assess baseline conditions and monitor the response of ecosystems in the near future. Located downwind of the Ohio Valley power plants, the mid-Appalachian landscape has elevated Hg wet deposition compared to most of the U.S. (excluding the Gulf Coast) and likely some of the highest dry deposition due to orographic effects and scavenging of Hg in these mountain forest systems. As a result, with respect to deposition, these locations are likely to be the most sensitive to changes in U.S. power plant emissions. Furthermore, because these watersheds are relatively low in soil organic carbon (SOC), changes in Hg deposition will be more apparent in the Hg-OC ratio in soils and in streamwater, making them excellent candidates for detecting the immediate effects of emission reductions.

The watersheds within Shenandoah National Park are also good candidates for the establishment of a monitoring program to assess the long-term recovery of these systems from decades of Hg deposition and retention in soils. Relatively inexpensive turbidity sondes, in conjunction with a turbidity-Hg_P rating curve, can be used to obtain accurate measurements of Hg_P. Similarly, FDOM sondes can likely be used to evaluate Hg_D at high temporal resolution. Furthermore these systems are already part of a long-term monitoring program so scientists are poised to be able to separate affects of environmental forcings to more easily identify the impact of Hg emission reductions on export. For example, with continued decreases in sulfate emission and deposition in the southern Appalachians, we may expect to observe stream systems respond with an increase in pH as noted in other systems in the north east and with them an increase in DOC (Driscoll et al., 2003). Our southern Appalachians sites have lagged behind other regions in recovery from acid deposition; however a recent analysis by *Miller* (2011) has shown that sites in this region are now showing signs of recovery. It follows that an increase in pH and an associated increase in DOC will occur in the future and as a result, we could expect an increase in Hg_D export. Conversely, with expected decrease in Hg emission and deposition we expect decreases in Hg_D export via lower Hg_D-DOC ratios. Having both long-term pH and DOC quantity and quality data as well as baseline Hg_D-DOC ratios in each of these three systems will allow for an improved understanding of the reasons behind changes in Hg export needed to address future regulations.

2.4. Regional Hg-DOC ratios

Our work demonstrated that soil organic carbon (SOC) is likely a first-order control on Hg-OC ratios found across a variety of watersheds. This initial investigation, however, used a surrogate variable for SOC. A more direct measure of SOC would likely improve the predictive relationship. As many of the sites used to generate the Hg-OC ratio were long-term research watersheds, there may be soils data from previous studies that could be used to determine an estimate of soil organic carbon content for the watershed. If no field data is available, regional soil organic carbon estimates from the State Soil Geographic (STATSGO) database could be used as an alternative independent source of watershed SOC data (Sundquist et al., 2009). By using a more direct estimate of SOC, variations from the best fit Hg-OC ratios may be investigated to determine if deviations are due to other factors such as variability in organic matter quality, soil type, and/or Hg deposition.

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