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Particulate and dissolved mercury export in streamwater within three mid-Appalachian forested watersheds in the US

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SUMMARY

Forested uplands retain Hg in soils from atmospheric deposition and are a potential long-term source of Hg to downstream waters. 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 in these ecosystems. It is well established that frequent sampling during high-flow events, when Hg concentrations can vary by orders of magnitude, is necessary to quantify Hg export in these systems. However, in part due to the difficulties of consistently sampling during these short-duration periods, and lack of alternative surrogate measures, no studies have quantified Hg_D and Hg_P export during storm flow relative to the total annual flux. At three mid-Appalachian forested watersheds, we sampled streamwater bi-weekly and hourly during storm events using both manual and automated techniques for 18 months and investigated the feasibility of using turbidity measured with an in situ sonde as a surrogate measure for Hg_P. We determined turbidity had a much stronger correlation to Hg_P (r^2 = 0.78–0.98) as compared to specific discharge (r^2 = 0.36–0.55), making it an effective high-frequency surrogate at each site. For the year-long study, we found that approximately 80% of the total Hg (Hg_T) flux was exported during the high-flow periods corresponding to approximately 1% of the time. Particulate Hg accounted for the majority of annual Hg_T fluxes at all three sites (58–85%) as a consequence of being more strongly flow-activated relative to the dissolved form. Despite being associated with relatively low dissolved organic carbon (DOC) concentrations, the Hg_T fluxes from these forested Appalachian watersheds, which ranged from 1.26 to 3.71 μg m^{-2} yr^{-1}, were comparable to fluxes reported in other regions of the world

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 slowly mobilizes 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 toxic form of Hg that bioaccumulates and poses a health risk to humans (Weiner et al., 2003), typically through fish consumption. Accurate estimates of total Hg (Hg_T, which includes both 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 obtained manually are difficult to obtain during these brief storm conditions in

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headwater systems (Shanley et al., 2008; Riscassi et al., 2010) and (3) Hg_D 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; Riscassi and Scanlon, 2011), yet are commonly used to calculate continuous concentrations for flux computations (Scherbatskoy et al., 1998; Shanley et al., 2008; Brigham et al., 2009; Dittman et al., 2010).

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/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); however in these studies, samples were not collected throughout the duration of a storm hydrograph. Some non-disturbed forested systems have been found to be dominated by Hg_P including Nettle Brook, Vermont (Scherbatskoy et al., 1998) and Sleepers River (W9), Vermont (Shanley et al., 2008; Dittman et al., 2010). Each of these studies focused on high frequency sampling during peak flow events (storms and snowmelt). Scherbatskoy 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, likely due to a lack of consistent high-flow sampling during these periods. Scherbatskoy et al. (1998) estimated that 50% of the annual Hg_T flux occurred on 1 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 focused on three watersheds within the central Appalachians, which are characterized as undisturbed, forested, mountainous headwater systems, with little to no wetlands. The annual export of stream water at these sites is dominated by brief high-flow storm events throughout the year. For each of these three streams we hypothesize (1) turbidity is well correlated with Hg_P in each watershed and can be used as a surrogate for Hg_P concentrations during high-flow periods, (2) annual Hg_T fluxes are dominated by the particulate fraction in these undisturbed, mountainous systems; and (3) periodic high-flow events transport the vast majority of Hg_T downstream on an annual basis. Improving our understanding of Hg_P and Hg_D dynamics in remote mountain systems will allow for a more accurate determination of the fate of atmospherically deposited Hg. In addition, this research adds to the body of Hg literature by evaluating fluxes within the unrepresented watersheds of the mid Appalachian region and applies newly evaluated technology (Riscassi et al., 2010) for high-frequency streamwater sampling and in situ instrumentation for Hg_P estimation.

2. Methods

2.1. Field methods

This study was conducted at three watersheds within the central Appalachian Mountain region of Virginia. Lower elevation areas of the region experience modified continental climate, with mild winters and warm, humid summers. The mean annual temperature in the lowland area at Luray, Virginia averages 12 °C (Sullivan et al., 2003). Higher elevations in this region experience winters that are moderately cold and summers that are relatively cool. The mean annual temperature at the National Atmospheric Deposition Program (http://nadp.sws.uiuc.edu) monitoring station at Big Meadows (VA28), located on the mountain ridge in central Shenandoah National Park (SHEN), averages about 9 °C (Sullivan et al., 2003). Precipitation is well distributed throughout the year. Snow and ice are common in winter, but they usually melt quickly, leaving the ground bare.

The Piney River, Staunton River, and Paine Run (hereafter referred to as Piney, Staunton, and Paine) watersheds are located in Shenandoah National Park within 100 km of each other. The watersheds are similar in size (~10–12 km^2) and stream gradient (7–9%), and characterized by second-to third-growth mixed hardwoods (Ryan et al., 1989; Young et al., 2006). Mean annual rainfall measured at the Big Meadows NADP station 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 rocks underlying Piney, Staunton, and Paine, respectively (Gathright, 1976). Bedrock geology differences result in distinctions in soil type and water chemistry. The soils in Piney are dominated by clays and the streamwater has a circumneutral pH, while soils in Paine are dominated by sands and the streamwater is more acidic. The soils at Staunton are a mixture of sand and clays. Organic carbon content of soil is similar between sites and dissolved organic carbon (DOC) concentrations in steamwaters are low, typically 1–5 mg L^{-1} (Riscassi and Scanlon, 2011).

Streamwater samples were collected at each site from March 2008 through October 2010. Grab samples were collected approximately every 2 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). Duplicate grab samples were taken on a rotating basis each week at one of the three sites. Automated samplers were typically used to collect high-flow samples at bi-hourly intervals. Concurrent sampling using both grab and automated techniques was conducted on three different high-flow occasions. Errors associated with using automated techniques, such as extended holding times prior to filtration and preservation, were evaluated in a series of laboratory experiments and verified with a field test (Riscassi et al., 2010); differences in concentration were found to be within the range of field duplicates (~10%). All materials, cleaning procedures, sample collections, and handling procedures are described in detail within Riscassi et al. (2011). All grab samples were taken within 0.5 m 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, preservation and 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