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Spatial and temporal variation in the isotopic composition of mercury in the South River, VA

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ABSTRACT

Historic point source mercury (Hg) inputs from industrial processes on the South River (Waynesboro, Virginia) ended many decades ago, but sediment and surface water Hg concentrations remain elevated relative to the regional background. To understand Hg sources, mobility, and fate in the South River, we analyzed total Hg concentrations and Hg stable isotope compositions of streambed sediments, bank soils, suspended particles, filtered surface waters, and channel margin hyporheic zone pore waters. Hg isotopes allow for the identification of three distinct Hg end-member inputs to the South River, consisting of a regional background source and two isotopically distinct contaminant sources. Hydrologic conditions are demonstrated to have an influence on within-channel Hg isotope fractionation and Hg partitioning, with no observed isotopic discrimination between suspended particulate Hg and filtered surface water Hg during elevated flow conditions. Channel margin hyporheic zone porewaters had significantly higher δ^{202}Hg values than surface waters (δ^{202}Hg = −0.52 ± 0.44‰ and δ^{202}Hg = −0.89 ± 0.20‰ respectively [mean ± 1SD]). A subset of porewaters exhibited mass independent fractionation signatures (Δ^{199}Hg = 0.33 ± 0.06‰; Δ^{200}Hg = 0.19 ± 0.03‰ [mean ± 1SD]) that are suggestive of a precipitation-derived origin for the dissolved Hg pool. Sediments from a floodplain profile were analyzed to explore the temporal variation in Hg isotopic composition within the South River, indicating brief excursions (up to δ^{202}Hg = +0.61‰) from the average composition observed in modern samples (δ^{202}Hg = −0.52 ± 0.09‰). By improving understanding of the spatial, temporal, and hydrologic conditions that contribute to variations in Hg isotopic composition, this study provides insights into the processes that control Hg isotopic end-member sources, Hg-loading to the channel during elevated flows, and Hg fate in the South River.

1. Introduction

As a toxic trace metal with an active biogeochemical cycle, mercury (Hg) has been the subject of extensive study (e.g., Selin, 2009). Anthropogenic activity has altered the cycling of Hg in the biosphere on a global scale (Driscoll et al., 2013), and locally at industrial sites where Hg discharges to surface waters and can lead to biomagnification in aquatic food webs (Kocman et al., 2013). Discharges of anthropogenic Hg to freshwater ecosystems are understudied compared to other components of the global Hg cycle (Kocman et al., 2017), yet humans often rely directly on these ecosystems for both sustenance and recreation.

The South River, VA is the site of extensive anthropogenic Hg contamination originating from a former DuPont textile manufacturing plant in Waynesboro, VA. Mercuric sulfate was used as a catalyst at the plant between 1929 and 1950 in the production of acetate fibers (Carter, 1977). The production of acetic anhydride produced a sludge that contained mercury, and this waste sludge was transported to a building that housed a retort furnace that was used to recover elemental mercury (URS, 2015). During this period of mercuric sulfate catalyst use at the former DuPont facility, a significant amount of Hg was lost and entered the South River channel. Hg-contaminated sediments have been identified throughout the channel, river banks, and over-bank deposits of the South River and the South Fork Shenandoah River (Turner and Southworth, 1999). Prior work has demonstrated the ongoing impacts that this Hg contamination has had on the downstream ecosystems, documenting elevated Hg levels within the biota of both the aquatic (Murphy et al., 2007; Neufeld, 2010; Bergeron et al., 2010; Brent and Kain, 2011) and associated terrestrial environments (Cristol et al., 2008; Jackson et al., 2011).

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The current conceptual model for Hg cycling within the South River postulates that erosion of Hg-laden bank soils is the dominant input of Hg into the South River channel environment (Flanders et al., 2010; URS, 2012). Thus, understanding the processes that control Hg mobility within the South River is critical to understanding the Hg-related ecosystem risks. Adaptive management models have demonstrated that uncertainties in current Hg loading to the South River contribute to the uncertainty in assessing the most effective remediation efforts (Foran et al., 2015). To this end, studies that add to the understanding of Hg loading dynamics within the South River are important for guiding informed remediation implementation.

Measurement of Hg stable isotope ratios in environmental samples is an excellent tool to probe biogeochemical cycling of Hg in fluvial systems (Blum et al., 2014; Yin et al., 2010). A number of recent studies have explicitly demonstrated the utility of Hg isotopes in aquatic freshwater systems, including contaminated rivers (Sonke et al., 2010; Perrot et al., 2010; Liu et al., 2011; Foucher et al., 2013; Bartov et al., 2013; Yin et al., 2013; Donovan et al., 2014; Smith et al., 2015; Donovan et al., 2016a; Donovan et al., 2016b; Demers et al., 2018; Marshall et al., 2018; Baptista-Salazar et al., 2018), relatively pristine rivers (Tsui et al., 2012; Tsui et al., 2013; Tsui et al., 2014; Jiskra et al., 2017; Woerndle et al., 2018), and lakes (Ma et al., 2013; Lepak et al., 2015; Gray et al., 2015; Wiederhold et al., 2015; Guedron et al., 2016; Chen et al., 2016; Xu et al., 2016; Yin et al., 2016b; Yin et al., 2016c). However, environmental systems are complex, and due to the time-intensive sampling and laboratory work necessary for high precision Hg isotope ratio measurements, many of these studies have been limited in either spatial or temporal scope, particularly with regards to changing discharge conditions or across hydrologic zones. Most studies that have explored temporal changes in Hg isotope signatures of sediments have focused their investigations on lake ecosystems (Ma et al., 2013; Guedron et al., 2016; Yin et al., 2016b, 2016c), with no long-term Hg isotope records from fluvial ecosystems, with the exception of an altered oxbow lake sediment core reported in Gray et al. (2015). At present, there is a limited understanding of how temporal variation in the isotopic composition of Hg delivered to fluvial systems is recorded in physical reservoirs.

In addition to temporal variability related to Hg sources, environments like the South River exhibit dynamic conditions (e.g. wide ranges in discharge, watershed land use, water column chemistry) that can affect Hg cycling over spatial regions and across hydrologic gradients (e.g. Shanley et al., 2005). For example, a previous study demonstrated that monomethyl-mercury (MMHg) concentrations were the highest in contaminated South River sediments in late May, while the potential methylation rates were highest in August (Yu et al., 2012). The study authors postulated that Hg methylation by sulfate- and iron-reducing bacteria in South River sediments fluctuates due to processes that vary in both space and time. Recent mesocosm experiments with periphyton in the South River demonstrated that Hg in the water column had a greater contribution to biological uptake of MeHg in periphyton than Hg associated with sediments (Brent and Berberich, 2014). Taken together, the results of these studies suggest that observations during only one time interval would likely fail to capture important aspects of the Hg dynamics of the ecosystem.

A study by Washburn et al. (2017), established the baseline Hg isotopic composition of the main physical reservoirs of Hg within the South River, although this study was conducted with limited spatial resolution and over a limited range of hydrologic conditions compared to those that are observed in the South River. To address knowledge gaps identified by Washburn et al., we conducted sampling and analysis of additional physical reservoirs of Hg within the South River, targeting increased spatial coverage and a wider range of hydrologic conditions. This study expands both spatial resolution in the reach adjacent to the former DuPont facility and downstream in impacted reaches and provides constraints on the Hg dynamics within the South River channel. In particular, we sampled the South River under an elevated hydrologic flow regime to assess the influence on the observed Hg isotopic compositions of the dissolved and particulate phase Hg within the channel system, and to explore the Hg isotopic composition of the hyporheic zone and its connection to Hg dynamics within the channel. In addition, sediments from a floodplain core were analyzed to improve understanding of the longer term temporal variations in the isotopic composition of Hg released to South River sediments and stored during sediment deposition. By improving understanding of the spatial and temporal variations in Hg isotopic composition this study provides insights into the processes that control Hg sources, mobility, and fate in the South River.

2. Materials and methods

2.1. Sample collection and processing

The South River is a fourth order, single-thread, gravel-bed river located in the Shenandoah Valley of Virginia, USA (Rhoades et al., 2009). The details of sample collection and processing for samples collected during 2014 are presented in Washburn et al. (2017). Additional samples presented in this study were collected during late May of 2016, and were focused on a 7 km reach of the river, from 4 km upstream of the former DuPont plant in Waynesboro, VA to 3 km downstream of the former industrial site. During this effort 6 different sample types were acquired: streambed sediments, bulk bank soils, filtered surface water (and associated suspended particulates), and filtered channel-margin hyporheic porewater (and associated suspended particulates). Following the convention of previous work on the South River system (Washburn et al., 2017; Flanders et al., 2010), sampling locations are labeled according to their distance, in relative river kilometers (RRKm), along the channel from a known historic point source of Hg at the former DuPont plant (e.g., RRKm 0.0). Bank soil and streambed sediment samples were also collected at downstream locations (RRKm 3.9, 7.8, 15.9, 26.4) to improve the spatial resolution of the longitudinal profile presented in Washburn et al. (2017).

Streambed sediment and bank soil samples were collected from fourteen locations along the South River channel in May 2016 (5/24/16 to 5/31/16). Bulk bank soil samples were collected from exposed banks, by compositing soils from the surface to a depth of 10 cm using a hand trowel. Streambed sediments were collected using a hand-operated plastic bilge pump to effectively sample fine-grained sediment distributed within the coarse streambed. Sediments and bank soils were collected into acid washed containers in the field. Sample containers were placed on ice in the field, frozen within 8 h of collection, shipped on ice to the University of Michigan, and then stored at −18 °C. Sediment and bank soil samples were subsampled, freeze-dried, and dry sieved through acid-cleaned nylon mesh to remove detritus > 2 mm. The < 2 mm size fraction was then homogenized in an alumina ball mill. The ball mill was cleaned between each sample by washing with water and ethanol and then grinding Hg-free quartz.

Filtered stream water and suspended sediment samples were collected at ten locations during May 2016 (5/25/16 to 5/31/16). Discharge at the USGS Waynesboro gage ranged between 7.08 and 3.26 $m^3 s^{-1}$ during the sampling period, with consistently decreasing total discharge rates (Table S3) (USGS, 2017). These discharge conditions represent flow elevated above baseflow for May, with return periods ranging from 7.69 to 2.63 years. Water samples were collected, filtered, and preserved in the field, using trace-metal clean sampling methods following a modification of EPA Method 1669 (USEPA, 1996). Water samples were collected from the middle of the channel using acid-cleaned HDPE bottles, in which samples remained for no > 15 min before being filtered into acid-cleaned 1 L borosilicate glass media bottles containing 5 mL of concentrated HCl (trace metal grade). Water samples were filtered using a hand operated vacuum-pump and disposable, pre-cleaned 0.45 μm pore-size cellulose nitrate vacuum filter housings (Thermo Scientific). Filters were removed from the vacuum