# Regional and local controls on dissolved mercury and dissolved organic carbon in streams

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## Abstract

In streams, dissolved mercury ($Hg_D$) is often strongly associated with dissolved organic carbon (DOC), but due to spatial and temporal variability the ratio of $Hg_D$:DOC can vary between watersheds and even within an individual watershed. This thesis examines soil organic carbon (SOC) and stream pH as regional and local controls, respectively on $Hg_D$:DOC. A meta-analysis of published studies and geospatial datasets was conducted to test the regional importance of SOC, while stream pH was evaluated during a field-based study in a small, first-order stream.

At the regional scale, $Hg_D$:DOC from 19 watersheds across the U.S. was related to mean watershed SOC derived from a soil geospatial database. DOC quality measured by specific ultraviolet absorbance at 254nm and Hg wet deposition from the Mercury Deposition Network were also considered as possible controls. SOC was a strong primary control on $Hg_D$:DOC, while DOC quality and Hg wet deposition were secondary in comparison. Results from this study show that SOC data may be utilized to predict stream $Hg_D$:DOC ratios on a more geographically widespread basis. For streams with DOC data, $Hg_D$ could also be predicted without expensive, time consuming field work.

At the local scale, pH was lowered in a small, first-order stream to analyze the impacts on $Hg_D$ and DOC. Two stream acidification experiments revealed that at acidic pH levels $Hg_D$ and DOC concentrations are reduced in the water column. High-quality (i.e. aromatic) DOC was preferentially adsorbed, which caused the $Hg_D$:DOC ratio to decrease with decreasing pH. The likely mechanism is adsorption to stream sediments and suspended particulates which is enhanced by hyporheic mixing and exchange. Results from this study suggest that changes in stream and soil solution pH may influence the export of $Hg_D$ and DOC.

This work shows that regional and local watershed characteristics can help explain variance in the ratio of $Hg_D$:DOC. Identifying and understanding controls on the association of $Hg_D$ and DOC in streams can help better predict $Hg_D$ export to streams under changing environmental conditions. Future regulations on Hg emissions need to consider watershed processes that influence Hg and DOC concentrations to accurately predict water quality impacts.

## Table of Contents

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# Chapter 1: Introduction

## *1.1 Chemical properties of mercury and dissolved organic carbon*

Mercury is a heavy metal that primarily occurs in elemental ($Hg^0$) and divalent ($Hg^{2+}$) forms. $Hg^0$ is volatile and mostly resides in the atmosphere, while $Hg^{2+}$ is highly reactive and can be found in water, soil, plants, and animals (U.S. Environmental Protection Agency, 1997; Liu et al., 2012). As a soft metal, Hg prefers to bond covalently with $Cl^-$, $OH^-$, and organic matter (Schuster, 1991). The strongest Hg complexes occur with reduced sulfur functional groups within humic acids of organic matter (Xia et al., 1999; Skyllberg et al., 2000; Hesterberg et al., 2001). Because of the strong affinity of Hg for organic matter, its transport through terrestrial and aquatic ecosystems is often tightly associated with dissolved organic carbon. This association has been observed in precipitation (Åkerblom et al., 2015), soils (Skyllberg et al., 2000; Obrist et al., 2011; Burns et al., 2014; Yu et al., 2014; Navrátil et al., 2014), sediments (Marvin-Dipasquale et al., 2009; Flanders et al., 2010; Hinkle et al., 2014), and streams (Scherbatskoy et al., 1998; Grigal, 2002; Shanley et al., 2008; Schuster et al., 2008; Selvendiran et al., 2008; Brigham et al., 2009; Dittman et al., 2010; Riscassi and Scanlon, 2011; Schelker et al., 2011; Schuster et al., 2011; Journey et al., 2012; Demers et al., 2013; Burns et al., 2013; Oswald and Branfireun, 2014). Understanding how DOC interacts with Hg is essential to predicting how Hg moves through the environment.

Dissolved organic carbon (DOC) is a heterogeneous mixture of numerous compounds that has a highly variable composition based upon its source. DOC is generally comprised of humic and fulvic fractions with varying functional groups (Ravichandran, 2004). DOC can be aromatic; a chemical property that creates unusually stable bonds between DOC and other chemical species including Hg. Aromaticity of DOC is attributed to the hydrophobic organic acids (HPOA), which are typically associated with the humic fraction, though HPOA can occur in the fulvic fraction. HPOA has an elevated concentration of reduced sulfur sites that strongly bind Hg (Xia et al., 1999; Hesterberg et al., 2001; Ravichandran, 2004). Proxies of aromatic carbon content are often used as indicators of DOC composition and are referred to as DOC quality. Higher quality (i.e. aromatic) DOC has been shown to bind more mercury per unit DOC (Weishaar et al., 2003; Dittman et al., 2009; Burns et al., 2013). Chemical properties of DOC play an important role in the transport of Hg through the environment.

### *1.2 Mercury in the environment*

Since the industrial revolution, global environmental mercury concentrations have become significantly elevated by anthropogenic activities (Schuster et al., 2002; Mast et al., 2010). Geologic and volcanic sources also influence environmental mercury concentrations (Pirrone et al., 2010), but it has been estimated that human inputs to the global mercury cycle are approximately three times background levels (Selin, 2009). As a result of global atmospheric transport, even pristine remote ecosystems have become polluted by anthropogenic mercury (Fitzgerald et al., 1998). Hg is atmospherically deposited to terrestrial watersheds through dry and wet deposition (Schroeder and Munthe, 1998). In forested watersheds, the majority of deposited Hg is stored in soils, while a small percentage is lost from watersheds through volatilization or transport by streams and rivers (Aastrup et al., 1991; Krabbenhoft et al., 1995; Scherbatskoy et al., 1998; Hintelmann et al., 2002; Oswald et al., 2014). Soil reservoirs of legacy Hg represent a potentially large source of Hg to streams and rivers in years to come despite changing emissions scenarios (Pacyna et al., 2010). Within soils, stream sediments, and wetlands, Hg can be converted to methylmercury (MeHg). MeHg is a potent neurotoxin that has harmful effects on humans and wildlife. Because MeHg binds to proteins, it easily bioaccumulates and biomagnifies in food chains. This often leads to dangerous Hg concentrations in species of higher trophic status (Wolfe et al., 1998; Scheuhammer et al., 2007).

Recovery of watersheds from acidification by acid deposition may also exacerbate current Hg pollution as stream pH and watershed export of DOC increase in North America and Europe (Evans et al., 2005; Monteith et al., 2007; Futter and de Wit, 2008). But it is uncertain if stream Hg concentrations will exhibit a similar trend. Further research is needed to fully understand the mechanisms that drive the association of Hg and DOC in streams.

### *1.3 Thesis Organization*

This thesis is organized as two chapters of self-contained papers that examine the relationship between Hg and DOC in streams. Chapter 2 examines the role of watershed soil organic carbon (SOC) in mediating the association of dissolved mercury ($Hg_D$) and DOC in streams throughout the U.S. This study was designed to test the hypothesis put forth by *Riscassi and Scanlon* (2011) that SOC is a primary control on the ratio of $Hg_D$ to DOC across geographically-distinct watersheds. Atmospheric wet Hg deposition and DOC quality are also considered as additional factors that influence $Hg_D$:DOC. We find that watershed SOC is a strong predictor of stream $Hg_D$:DOC and show that large-scale geospatial datasets, such as SOC, may be useful in predicting stream Hg as an alternative to expensive, field-based measurements.

Chapter 3 focuses on pH impacts on $Hg_D$ and DOC in a small, first-order stream. Two acidification experiments were conducted to examine the influence of lowering stream pH on the association of $Hg_D$ and DOC. The first acid injection looked at differences over a pH range, while the second injection looked at spatial differences at a steady-state acidic pH. We find that $Hg_D$ and DOC concentrations are reduced with lower pH in the stream water column and that the quality of DOC decreases. Reductions in $Hg_D$ and DOC concentrations are enhanced by hyporheic mixing and exchange. These results suggest if pH and DOC quantity and quality continue to increase in streams and soils recovering from acidification, it is possible $Hg_D$ concentrations in these streams may remain the same or even increase despite stricter emissions standards.

Chapter 4 summarizes and draws conclusions from the work presented in each paper. Future research ideas and possibilities stemming from this work are also discussed. Elevated concentrations of Hg from anthropogenic sources are likely to persist in the environment for decades to come. As a result, continued research and monitoring will be needed to inform future regulations of this toxic contaminant.

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# Chapter 2: Association of dissolved mercury with dissolved organic carbon in U.S. rivers and streams: The role of watershed soil organic carbon

## Abstract

Streams and rivers are important pathways for the export of atmospherically deposited mercury (Hg) from watersheds. Dissolved Hg ($Hg_D$) is strongly associated with dissolved organic carbon (DOC) in stream water, but the ratio of $Hg_D$ to DOC is highly variable between watersheds. In this study, the $Hg_D$:DOC ratios from 19 watersheds were evaluated with respect to Hg wet deposition and watershed soil organic carbon (SOC) content. On a subset of sites where data were available, DOC quality measured by specific ultraviolet absorbance at 254 nm, was also taken into account. No significant relationship was found between Hg wet deposition and $Hg_D$:DOC, but SOC content (g $m^{-2}$) explained 81% of the variance in the $Hg_D$:DOC ratio (ng $mg^{-1}$) following the form: $Hg_D$:DOC=17.8*$SOC^{-0.41}$. The inclusion of DOC quality as a secondary predictor variable explained only an additional 1% of the variance. A mathematical framework to interpret the observed power-law relationship between $Hg_D$:DOC and SOC suggests a Hg supply limitation for adsorption to soils with relatively large carbon pools. With SOC as a primary factor controlling the association of $Hg_D$ with DOC, SOC data may be used to predict stream $Hg_D$:DOC ratios on a more geographically widespread basis. Future Hg emissions policies must consider soil-mediated processes that affect the transport of Hg and DOC from terrestrial watersheds to streams for accurate predictions of water quality impacts.

## 1. Introduction

Emissions of mercury (Hg) from anthropogenic sources have led to elevated levels in the environment as a result of atmospheric deposition (Schroeder and Munthe, 1998; Mast et al., 2010). Stream and river systems represent a major pathway for mercury export upon deposition in terrestrial watersheds (Grigal, 2002; Brigham et al., 2009). Within watershed soils (Matilainen et al., 2001) and especially within stream sediments and wetlands (Gilmour et al., 1992; Rudd, 1995; Driscoll et al., 1998), terrestrially deposited mercury may be converted to the more toxic form of methylmercury. Mercury in streams can be present in particulate or dissolved forms, but the dissolved form is thought to be more bioavailable (Aiken et al., 2000). Dissolved mercury ($Hg_D$) has a strong, positive correlation with dissolved organic carbon (DOC) in many watershed studies (Shanley et al., 2008; Brigham et al., 2009; Dittman et al., 2010; Demers et al., 2010; Riscassi and Scanlon, 2011), but the ratio of $Hg_D$ to DOC varies from site to site (Shanley et al., 2009; Riscassi and Scanlon, 2011). Mercury associates with DOC by binding to reduced sulfur sites within humic substances in DOC (Xia et al., 1999; Hesterberg et al., 2001). In most natural waters, reduced sulfur binding sites within DOC exceed the supply of mercury available for binding (Schuster, 1991; Haitzer et al., 2002; Ravichandran, 2004) thereby enhancing this association. An additional factor that affects the affinity of Hg for DOC is DOC quality (Shanley et al., 2008; Dittman et al., 2009). Hydrophobic organic acids (HPOA) are an aromatic component of DOC (Aiken et al., 1992) with elevated reduced sulfur content. Reduced sulfur in HPOA is responsible for binding the majority of the available Hg (Ravichandran, 2004), therefore the relative amount of DOC composed of HPOA will influence the $Hg_D$:DOC ratio (Schuster et al., 2008; Dittman et al., 2009; Riscassi and Scanlon, 2011; Burns et al., 2013). Aromatic carbon content, measured by specific ultraviolet absorbance at $\lambda = 254$ nm ($SUVA_{254}$), is commonly used as an indicator of DOC quality (Weishaar et al., 2003).

Both $Hg_D$ and DOC concentrations tend to be positively correlated with discharge in forested catchments, and the ratio of $Hg_D$:DOC remains fairly stable over a range of flow conditions (Shanley et al., 2005; Brigham et al., 2009; Dittman et al., 2010; Riscassi and Scanlon, 2011). This is typically true for watersheds with extensive wetland areas, which play a dominant role in governing coupled

DOC and $Hg_D$ dynamics (Brigham et al., 2009; Burns et al., 2012), although certain types of wetlands may have weaker correlations (Demers et al., 2013). In watersheds without wetlands, the more complex flow paths involved in runoff generation lead to greater variability in stream water $Hg_D$ and DOC. However, statistically significant relationships between $Hg_D$ and DOC in these watersheds are nonetheless observed (Riscassi and Scanlon, 2011; Schelker et al., 2011; Oswald and Branfireun, 2014).

In a review *Grigal* (2002) reported a mean Hg:DOC ratio for streams in the Northern Hemisphere of about 0.2 ng Hg per mg DOC based on six studies, although he noted the existence of regional and local differences. A large number of new studies since *Grigal's* (2002) review paper prompted *Riscassi and Scanlon* (2011) to compile all available Hg:DOC data (including both unfiltered and filtered Hg). They determined that for 22 sites in the Northern Hemisphere the range in Hg:DOC ratios spanned an order of magnitude, from a value of 0.12 ng Hg per mg DOC for the peatland-dominated Saint Mary's River in Florida (Brigham et al., 2008) to a value of 1.4 ng Hg per mg DOC at the talus-sloped Andrews Creek in Colorado (Shanley et al., 2008). Invoking the concept of biodilution put forth by *Meili* (1991), *Riscassi and Scanlon* (2011) made a preliminary attempt to determine if organic matter abundance could be driving the variability in Hg:DOC ratios. They assessed the correlation between the Hg:DOC ratio and the mean upper 10% of stream DOC, as a proxy for carbon content in watershed soils, and found a strong ($r^2$=0.67) power-law relationship. While a good first step, a more comprehensive assessment is necessary to properly investigate this hypothesis, using more direct (and functionally independent) measures of watershed carbon content. Furthermore, although total Hg deposition was reported not to be linked to Hg:DOC ratios in *Riscassi and Scanlon* (2011), only a small subset of sites (n=5) was evaluated. A more complete assessment of Hg deposition and Hg:DOC ratios would add confidence to this preliminary finding.

In this study, we use estimates of soil organic carbon (SOC) within individual watersheds to test the concept that SOC acts as a first-order control on $Hg_D$:DOC ratios. We also assess the importance of DOC quality and atmospheric Hg deposition as additional controls on $Hg_D$:DOC in streams. Because particulate and dissolved Hg fractions exhibit different transport dynamics (Riscassi and Scanlon, 2013), we focus on the dissolved phase. Specifically, our objectives were to (1) compile previously published and any newly available $Hg_D$, DOC, and Hg deposition data from the U.S. and calculate the associated SOC content for each of those watersheds, (2) evaluate the role of watershed Hg deposition, SOC content and DOC quality in determining stream $Hg_D$:DOC ratios, and (3) present a conceptual model for the inferred processes affecting the in-stream $Hg_D$:DOC ratio. Results from this investigation provide a means for making watershed-scale estimates of Hg transport in streams and rivers and for better constraining the fate of atmospherically deposited Hg in terrestrial systems.

## 2. Methods

### *2.1 Site Descriptions*

A total of 19 watersheds (Figure 1), ranging in size from 0.13 to 875,500 $km^2$, across the US were selected for this study based on availability of $Hg_D$, DOC, $SUVA_{254}$, and SOC data in previous publications and databases (Table 1). Each data set was collected over a range of seasons and for a variety of flow conditions. Watershed boundaries were delineated with the spatial analyst hydrology toolset on ArcMap 10.1 (ESRI, 2012) using the National Elevation Dataset digital elevation model (NED-DEM) (Gesch, 2007) and outlet coordinates provided in published papers.

**Table 1.** Site names, locations, data sources, watershed area, mean watershed SOC content, Hg$_D$:DOC ratio, number of samples (*n*), fraction of variance of Hg$_D$ explained by dissolved organic carbon (r$^2$), SUVA$_{254}$, NADP-MDN wet Hg deposition, NED-DEM resolution, and USDA-NRCS soil survey map scale for each watershed in study.

| Location | Data Source | Area (km$^2$) | Mean Watershed SOC (g m$^{-2}$) | Hg (ng L$^{-1}$) per unit DOC (mg L$^{-1}$) | n (Hg$_D$:DOC) | r$^2$ (Hg$_D$:DOC) | SUVA$_{254}$ (L mg C$^{-1}$ m$^{-1}$) | Wet Hg Deposition (µg m$^{-2}$) | DEM Resolution (m$^2$) | Soil Survey Map Scale |
|---|---|---|---|---|---|---|---|---|---|---|
| Santa Fe River, FL | *Brigham et al.*, 2008 | 2,630 | 20,210 | 0.25 ± 0.01 | 25 | 0.98 | 4.1 | 13.12 | 30 | 1:12,000; 1:15,840; 1:20,000; 1:24,000 |
| Saint Mary's River, FL | *Brigham et al.*, 2008 | 1,810 | 45,764 | 0.12 ± 0.06 | 27 | 0.42 | 4.7 | 13.08 | 30 | 1:15,840; 1:20,000; 1:24,000 |
| Evergreen River, WI | *Brigham et al.*, 2008 | 167 | 12,623 | 0.33 ± 0.03 | 29 | 0.94 | 3.1 | 7.28 | 30 | 1:12,000; 1:20,000 |
| Pike River, WI | *Brigham et al.*, 2008 | 660 | 17,088 | 0.31 ± 0.04 | 32 | 0.89 | 3.7 | 7.04 | 30 | 1:12,000; 1:20,000 |
| Lookout Creek, OR | *Brigham et al.*, 2008 | 62 | 16,243 | 0.47 ± 0.24 | 23 | 0.42 | 2.5 | 11.62 | 30 | 1:20,000 |
| Fishing Brook, NY | *Burns et al.*, 2013 | 66 | 23,434 | 0.17 ± 0.08 | 43 | 0.31 | 3.8 | 7.07 | 30 | 1:62,500 |
| Hudson River, NY | *Burns et al.*, 2013 | 493 | 27,209 | 0.17 ± 0.16 | 12 | 0.28 | 3.4 | 8.61 | 30 | 1:62,500 |
| Lake Inlet, Archer Creek, NY | *Dittman et al.*, 2009, 2010 | 1.35 | 23,756 | 0.37 ± 0.05 | 27 | 0.91 | 2.8 | 6.92 | 10 | 1:62,500 |
| Beaver Meadow, Archer Creek, NY | *Dittman et al.*, 2009, 2010 | 0.65 | 23,375 | 0.47 ± 0.09 | 25 | 0.83 | 3.3 | 6.92 | 10 | 1:62,500 |
| Watershed 6, Hubbard Brook, NH | *Dittman et al.*, 2009, 2010 | 0.13 | 8,284 | 0.33 ± 0.09 | 32 | 0.61 | 2.8 | 8.80 | N/A | N/A |
| Edisto River, SC | *Journey et al.*, 2012 | 7,071 | 8,115 | 0.31 ± 0.12 | 22 | 0.57 | 3.8 | 9.47 | 30 | 1:15,840; 1:20,000 |
| Staunton River, VA | *Riscassi and Scanlon*, 2011 | 10.8 | 7,026 | 0.51 ± 0.04 | 131 | 0.8 | 3.9 | 8.58 | 10 | 1:15,840; 1:20,000 |
| Piney River, VA | *Riscassi and Scanlon*, 2011 | 12.6 | 4,499 | 0.60 ± 0.08 | 73 | 0.74 | 4.3 | 8.17 | 10 | 1:20,000 |
| Paine Run, VA | *Riscassi and Scanlon*, 2011 | 12.4 | 2,390 | 0.55 ± 0.04 | 98 | 0.89 | 2.9 | 9.21 | 10 | 1:15,840 |
| Yukon River, AK | *Schuster et al.*, 2011 | 853,500 | 14,318 | 0.22 ± 0.05 | 37 | 0.81 | 3.1 | N/A | 60 | 1:63,360 |
| Andrews Creek, Loch Vale, CO | *Shanley et al.*, 2008 | 1.79 | 488 | 1.40 ± 0.68 | 5 | 0.93 | 4.0 | 12.00 | 10 | 1:24,000 |
| Allequash Creek, Trout Lake, WI | *Shanley et al.*, 2008 | 13.95 | 16,244 | 0.29 ± 0.09 | 25 | 0.66 | N/A | 6.95 | 30 | 1:20,000 |
| Watershed 9, Sleepers River, VT | *Shanley et al.*, 2008;<br>*Dittman et al.*, 2009, 2010 | 0.41 | 16,322 | 0.31 ± 0.04 | 48 | 0.85 | 3.3 | 8.77 | 10 | 1:24,000 |
| Neversink River, NY | Unpublished data[1] | 173 | 8,218 | 0.74 ± 0.05 | 14 | 0.99 | 2.5 | 11.41 | 10 | 1:15,840 |

[1] D. Burns (pers. comm.)

### *2.2 Atmospheric Mercury Deposition*

Wet mercury deposition data were obtained from the Mercury Deposition Network (MDN, http://nadp.sws.uiuc.edu/MDN), part of the National Atmospheric Deposition Program (NADP). Within this network, precipitation samples were collected using automated samplers at MDN field sites, which are located throughout the contiguous US, to determine Hg concentrations in precipitation (µg $m^{-3}$) (Prestbo and Gay, 2009; Latysh and Wetherbee, 2012). From 2003-2010, the NADP used inverse distance weighting to interpolate field-based mercury measurements and precipitation data to determine Hg deposition (µg $m^{-2}$). In 2011, the NADP also included the PRISM (Parameter-elevation Regression on Independent Slopes Model) precipitation data to generate more accurate interpolation results, especially in mountainous terrain (Latysh and Wetherbee, 2012). We imported the gridded wet deposition data of the US from the MDN into ArcMap 10.1 where we used raster analysis to find average wet Hg deposition from 2003-2011 for each watershed. Methods to generate reliable estimates of dry Hg deposition are actively being researched (Zhang et al., 2009; Gay et al., 2013; Gustin et al., 2013; Huang and Gustin, 2015) and high resolution data are not readily available and therefore are not included in this study.

### *2.3 Soil Organic Carbon and $Hg_D$:DOC Ratios*

Watershed soil organic carbon (g $m^{-2}$) for most sites was determined using spatial data from the Soil Survey Geographic database (SSURGO) which is maintained by the U.S. Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS). The mapped SOC information was estimated from field-based measurements of SOC, spatially extrapolated to nearby regions using previously published soil survey maps (United States Department of Agriculture – Natural Resources Conservation Service, 1994). The SSURGO database is the most detailed and most accurate U.S. soil database available for estimating SOC pools at multiple spatial scales (Zhong and

Xu, 2011). We used the estimate of SOC content (g $m^{-2}$) through the entire soil profile, which includes all organic and mineral soil horizons above bedrock. Due to the high variability of the vertical extent of soil horizons between watersheds, it was not practical to choose a standard depth in the soil profile for this dataset. Three sites did not have SSURGO data available: Yukon River, AK, Lookout Creek, OR and Watershed 6, Hubbard Brook, NH. SOC values for the Yukon River watershed were determined using the Northern Circumpolar Soil Carbon Database (NCSCD), which included soil horizon data for SOC from 0-100 cm (Hugelius et al., 2013). SSURGO data for Lookout Creek, OR was unavailable so data from the similar nearby watershed of South Fork Gate Creek, OR was utilized as a representative replacement. *Fahey et al.* (2005) reported soil organic matter (SOM) for Watershed 6 in Hubbard Brook, NH to the bottom of the B horizon. We used a conversion factor of $SOM/SOC = 1.9$ (Pribyl, 2010) to estimate the SOC content at this site. For watersheds where SSURGO data were available, ArcMap 10.1 was used to determine mean SOC content for each watershed. Portions of the watershed that contained null values were not included in the watershed average. Reasons for null values included missing data or presence of a water body.

### *2.4 Statistical Analyses*

Statistical analyses were performed using MATLAB software (version 8.3, The MathWorks Inc., Natick, MA). The MATLAB Curve Fitting Toolbox was used to analyze single ($Hg_D$ vs DOC, $Hg_D$:DOC vs SOC, $Hg_D$:DOC vs Hg wet deposition, $Hg_D$:DOC vs $SUVA_{254nm}$) and multiple ($Hg_D$:DOC vs SOC + $SUVA_{254nm}$) regressions. Data used in regressions were not log transformed. $Hg_D$:DOC ratios for each watershed were calculated as the slope of the linear regression between stream water $Hg_D$ and DOC concentrations, which is preferable to taking the mean or median of the individual ratios (Atchley et al., 1976; Curran-Everett, 2013). The intercepts of individual watershed

$Hg_D$ and DOC regressions were analyzed for statistical difference from zero using Microsoft Excel (version 14.0, Microsoft Corporation, Redmond, WA).

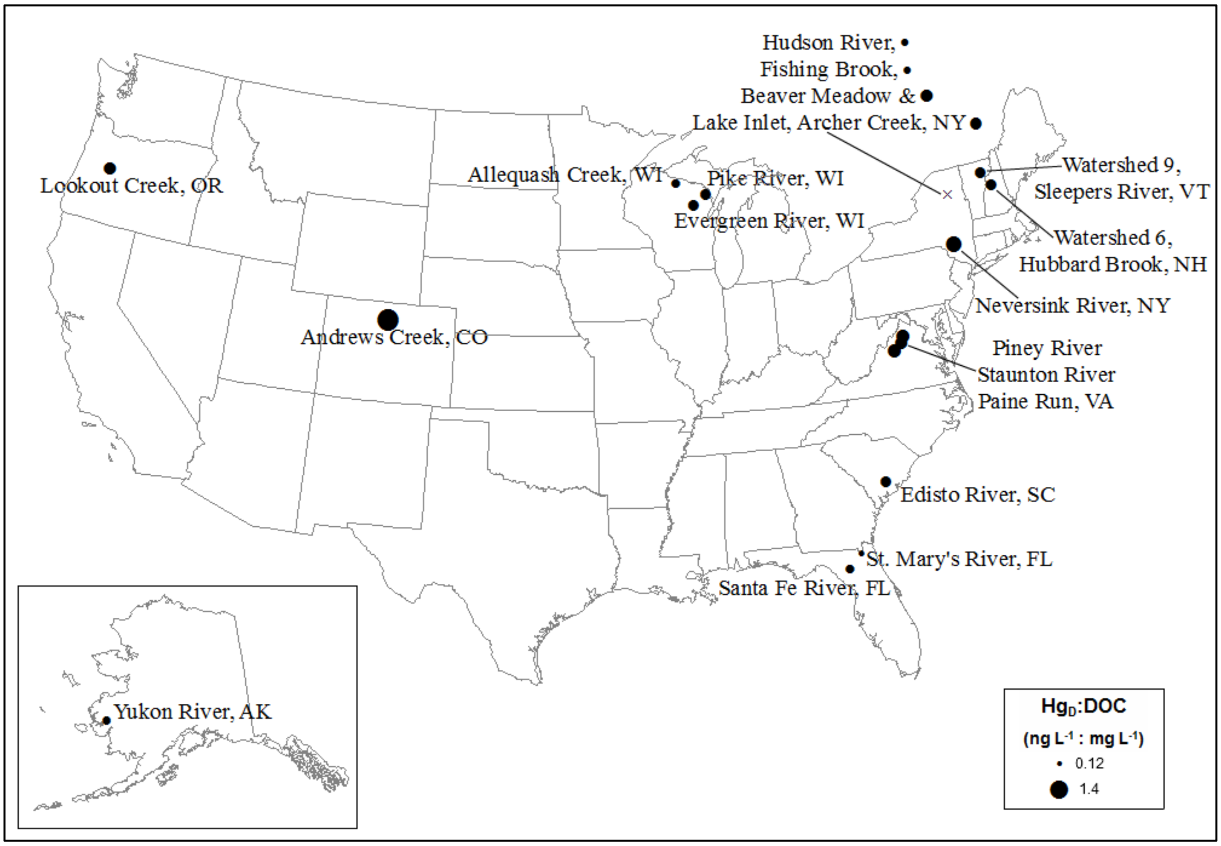

**Figure 1.** Map of study watersheds throughout the United States with circle areas proportional to the $Hg_D$:DOC ratio for each watershed.

## 3. Results

We found that SOC is able to explain about 81% of the variation in the $Hg_D$:DOC ratio, including sites with non-zero intercepts (adjusted $r^2 = 0.81$; Figure 2). This relationship is also statistically significant ($p < 0.01$) and conforms to a power law in the form of $Hg_D\text{:DOC} = 17.8*\text{SOC}^{-0.41}$ where $Hg_D$:DOC has units of ng $mg^{-1}$ and SOC has units of g $m^{-2}$. When non-zero intercept sites were excluded (n=15) the power-law relationship remained ($Hg_D\text{:DOC} = 15.6*\text{SOC}^{-}$

$^{0.40}$) and the correlation of the relationship decreased slightly ($r^2 = 0.78$; $p = 0.01$). For the subset of 18 sites where $SUVA_{254}$ data were available (Allequash Creek, WI had no associated $SUVA_{254}$ data), SOC and $SUVA_{254}$ combined explained an additional 1% of the variance in the $Hg_D$:DOC ratio.

There was no significant relationship found between atmospheric mercury wet deposition and the ratio of $Hg_D$:DOC ($r^2 = 0.08$; $p = 0.27$). Hg wet deposition values ranged from 6.92 μg $m^{-2}$ at Lake Inlet and Beaver Meadow, Archer Creek, NY to 13.12 μg $m^{-2}$ at Santa Fe River, FL. For 18 sites where data was available, DOC quality as measured by $SUVA_{254}$, had no significant relationship with the ratio of $Hg_D$:DOC ($r^2 = 0.001$; $p = 0.88$). Mean $SUVA_{254}$ ranged from 2.5 L mg $C^{-1}$ $m^{-1}$ at Neversink River, NY and Lookout Creek, OR to 4.7 L mg $C^{-1}$ $m^{-1}$ at St. Mary's River, FL. Mean watershed SOC spanned a much wider range with values from 488 g $m^{-2}$ at Andrews Creek, Loch Vale, CO to 45,764 g $m^{-2}$ at Saint Mary's River, FL. These same locations had the maximum ratio, 1.4 $Hg_D$ (ng $L^{-1}$) per unit DOC (mg $L^{-1}$) and minimum ratio, 0.12 $Hg_D$ (ng $L^{-1}$) per unit DOC (mg $L^{-1}$), respectively. For four sites, Neversink River, NY, Santa Fe River, FL, Evergreen River, WI, and Pike River, WI, the intercept of the watershed $Hg_D$ and DOC regression was statistically different from zero.

## 4. A Mathematical Framework for Interpretation of Results

The observed behavior of the stream water $Hg_D$:DOC ratio scaling with SOC content can be further explored by considering soil-level processes. For individual watersheds, models might account for spatial heterogeneity (both vertical and horizontal) in soil Hg and carbon pools (Demers et al., 2013; Burns et al., 2014) and/or depict transport along distinct flow pathways under variable hydrological conditions (Demers et al., 2010; Oswald and Branfireun, 2014; Haynes and Mitchell, 2015). Modeling the coupled transport of $Hg_D$ and DOC across a diverse array of watersheds necessarily requires simplifications, with a focus on first-order processes and bulk properties of the watersheds. Here, we take this approach while acknowledging the inherent limitations involved in the application of such a generalized mathematical framework.

The relationship between the Hg adsorbed to the soil ($Hg_{soil}$, ng kg$^{-1}$) and Hg in the soil solution ($[Hg_D]$, ng m$^{-3}$) can be approximated by a linear isotherm:

$$Hg_{soil} = k\,[Hg_D] \tag{1}$$

where $k$ is the isotherm coefficient (m$^3$ kg$^{-1}$), following *Skyllberg et al.* (2000). This coefficient is related to the density of organic carbon in the soils ($SOC_{dens}$, g kg$^{-1}$) and concentration of DOC in the soil solution ($[DOC]$, g m$^{-3}$ of water), both of which have binding sites that compete for Hg. Therefore, the coefficient can be expressed as:

$$k = a\frac{SOC_{dens}}{[DOC]} \tag{2}$$

where $a$ (unitless) is a constant. *Åkerblom et al.* (2008) noted the similarity between Hg:C ratios in the solid versus dissolved phases within the soils of two Swedish watersheds, which would imply that $a \approx 1$ (i.e. no fractionation as SOC decomposes and dissolves). However, since it is not known if this approximation can be universally applied, we do not prescribe a value to $a$. For sake of simplicity, we do not consider the effect of pH on the isotherm coefficient.

We adopt the general framework developed by *Cosby et al.* (1986) for sulfate dynamics, here applied to Hg within watershed soils. In its original form, the model by *Cosby et al*. (1986) assumed conservative transfer between deposition, soil storage, and stream export in evaluating lags between sulfate deposition and stream export. Since re-emission to the atmosphere accounts for a large portion of the watershed Hg budget (Hintelmann et al., 2002; Grigal, 2002; Oswald et al., 2014), we relax this assumption and constrain our analysis to the soil exchange processes depicted by Eq. 2, only applied at the watershed scale.

Considering the entire soil profile, the total amount of mercury in the subsurface ($Hg_{tot}$, ng m$^{-2}$) is the sum of the SOC-bound and aqueous components:

$$Hg_{tot} = D * B * Hg_{soil} + D * \theta * [Hg_D] \tag{3}$$

where $D$ is the soil depth (m), $B$ is the bulk density of the soil (kg m$^{-3}$), and $\theta$ is the volumetric soil moisture (unitless). Substituting (1) and (2) into (3) and rearranging yields:

$$D * B * a * \frac{SOC_{dens}}{[DOC]}[Hg_D] = Hg_{tot} - D * \theta * [Hg_D]. \tag{4}$$

The product $D*B*SOC_{dens}$ is equivalent to the measure of soil organic carbon content ($SOC$, g m$^{-2}$) expressed as mass per unit area (as earlier in this paper). We also note that the entire right side of (4) is equivalent to the quantity of Hg adsorbed to SOC in the soil profile ($Hg_{ads}$, ng m$^{-2}$), again as mass per unit area. This results in:

$$\frac{[Hg_D]}{[DOC]} = \frac{Hg_{ads}}{a*SOC} \quad . \tag{5}$$

The power-law relationship observed in Fig. 2 indicates that $[Hg_D]/[DOC]$ scales according to SOC$^{-\beta}$. By examining (5), if the ratio of $Hg_{ads}$ to $SOC$ remains constant (i.e. the amount of soil Hg per unit SOC was the same from watershed to watershed), $\beta$ would have a value of 0 (Fig. 3a). If the quantity $Hg_{ads}$ remained constant (i.e. the amount of soil Hg was the same from watershed to watershed), $\beta$ would have a value of 1 (Fig. 3c). In general terms, (5) implies that $Hg_{ads}$ α $SOC^{-\beta+1}$. The intermediate, empirically derived value of $\beta$ (0.41 ± 0.08, from Fig. 2) means that $Hg_{ads}$ roughly scales with the square root of $SOC$ (Fig. 3b). The inferred behavior that $Hg_{ads}$ does not appreciably increase at high levels of *SOC* points toward a Hg supply limitation relative to available binding sites, combined with the ability of soils with larger carbon pools to adsorb more Hg.

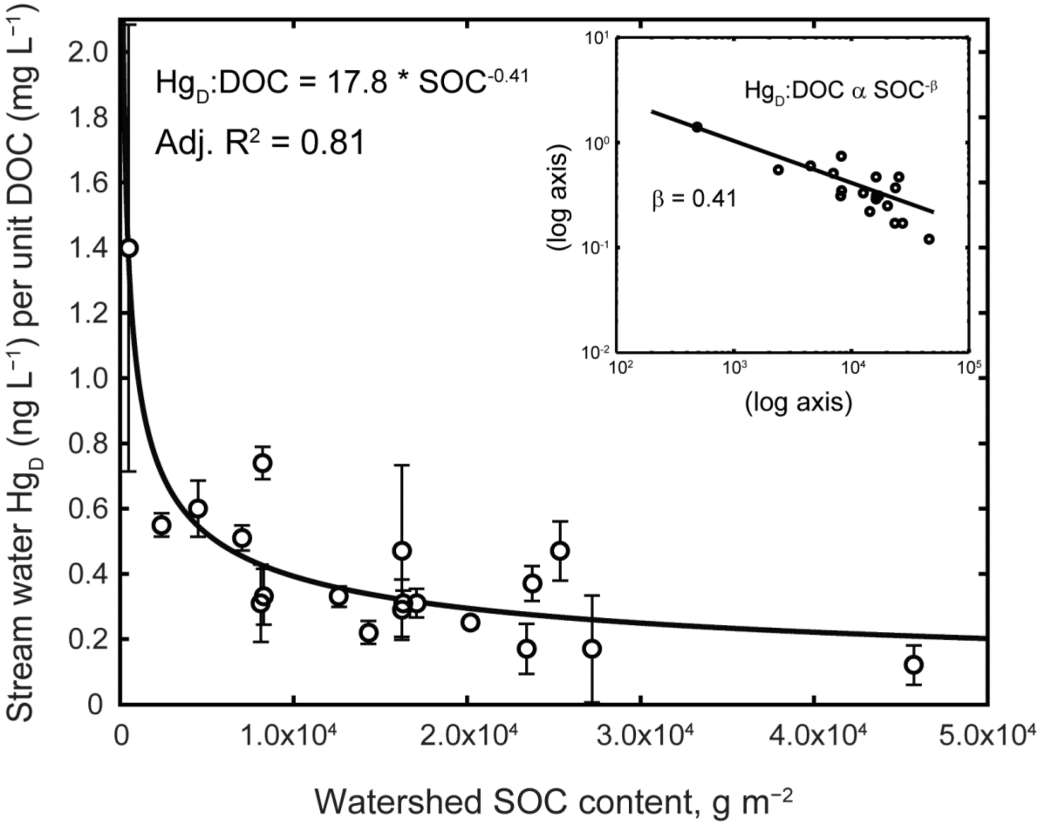

**Figure 2.** Hg$_D$ per unit DOC versus SOC with power-fit line and error bars (95% confidence intervals) of individual watershed Hg$_D$:DOC ratios. Inset shows data with log-transformed axes.

## 5. Discussion

The concentration of mercury in streams exhibits a high degree of spatial variability. Studies attempting to find landscape or hydrological metrics that predict this variability have had difficulties identifying a particular variable that works across a diversity of watershed types (Shanley et al., 2005; Brigham et al., 2009; Burns et al., 2012). The close coupling of Hg$_D$ with DOC improves predictive power but is not sufficient for accurate estimates of Hg$_D$ concentrations due to the variable ratio of $Hg_D$ to DOC. To address this, we explored potential factors that could influence the $Hg_D$:DOC ratio for watersheds throughout the United States and attempt to provide a mechanistic explanation for the observed variability.

Soil organic carbon content was highly variable across the watersheds examined in this study, spanning a range of two orders of magnitude. This landscape-level predictor exhibited a significant relationship with the $Hg_D$:DOC ratio and explained 81% of its spatial variability (Fig. 2). SOC data are widely available in national or global data sets (United States Department of Agriculture – Natural Resources Conservation Service, 1994; Hiederer and Köchy, 2011), which can be leveraged for spatial extrapolation of $Hg_D$ export from watersheds. Although the spatial resolution can be quite large, estimated SOC data sets can still compare favorably with direct estimates made at watershed scales. For example, *Burns et al.* (2014) reported soil organic matter for the Fishing Brook, NY watershed as 38,800 g $m^{-2}$ (median estimate areally-normalized, n = 163 soil cores). Converting this value using the *Pribyl* (2010) conversion factor of $SOM/SOC = 1.9$, SOC would be approximately 20,420 g $m^{-2}$. This compares with the SSURGO-derived SOC estimate of 23,430 g $m^{-2}$, resulting in a difference of only 14.7%. This difference lends some confidence to our analysis but additional data will be needed to accurately compare SSURGO derived SOC to direct estimates. We note that the relationship derived between $Hg_D$:DOC and SOC based on our meta-analysis may mask some potentially important factors that influence $Hg_D$:DOC at individual watersheds. Among other factors, disturbance history (Amirbahman et al., 2004), vertical variability of Hg:C within soil horizons (Demers et al., 2013), variable source area (Demers et al., 2010; Oswald and Branfireun, 2014), the spatial distribution of SOC within watersheds, and soil texture may play roles in governing stream $Hg_D$:DOC ratios. Another factor known to influence affinity of $Hg_D$ to DOC, the aromatic carbon content, could also account for some of the variability between watersheds.

$SUVA_{254}$ analysis from 18 of our sites explained less than 1% of the variation in the $Hg_D$:DOC ratio between sites and was not statistically significant. When both SOC and $SUVA_{254}$ were considered in a multivariate relationship, the variance of the $Hg_D$:DOC ratio explained increased by only 1%. These results indicate that when comparing across watersheds, DOC quality is clearly secondary to SOC content as a control on the $Hg_D$:DOC ratio.

We found no significant relationship between the $Hg_D$:DOC ratio and recent (2003-2011) wet deposition. Variability in wet deposition between sites was relatively low, with only a twofold range in means. Dry deposition was not included due to a lack of nationally available high-resolution data. Dry deposition may exceed wet deposition in some regions (Schroeder and Munthe, 1998; Sakata et al., 2006; Graydon et al., 2008; Risch et al., 2012; Yu et al., 2014) and could potentially be a significant factor affecting Hg availability in such settings. However, when modeled dry deposition was included for five of the sites, *Riscassi and Scanlon* (2011) found that the $Hg_D$:DOC ratio actually declined as total deposition increased. Further, there is generally a positive correlation between wet and dry Hg deposition (Wan et al., 2009; Risch et al., 2012) which would not increase the strength of the relationship between $Hg_D$:DOC and total Hg deposition. It does not appear that recent wet deposition controls the spatial variability of the stream $Hg_D$:DOC ratio between sites, but it is important to note that MDN data does not reflect historical atmospheric Hg loading to the soil. Previous studies have reported a disconnect between recent atmospheric Hg deposition and Hg in streams (Hintelmann et al., 2002; Brigham et al., 2009; Oswald et al., 2014), lakes (Harris et al., 2007), and soils (Obrist et al., 2011; Yu et al., 2014). This suggests a time lag between the deposition of Hg to terrestrial watersheds and its transport to streams or a possible loss of Hg during transport (e.g. volatilization). Both watershed Hg retention and loss of Hg could contribute to the lack of relationship between stream $Hg_D$:DOC ratios and current wet Hg deposition. Instead, soil properties appear to play a larger role in mediating the association of Hg and DOC within streams.

The endpoints of our data set, Andrew's Creek, CO and St. Mary's River, FL, have very different $Hg_D$:DOC ratios (1.4 and 0.12 ng $Hg_D$ $mg^{-1}$ DOC, respectively) when compared to the overall mean of 0.42 ng $Hg_D$ $mg^{-1}$ DOC. The ratios are likely driven by differences in SOC content which can be attributed to the disparate physical characteristics of these watersheds. Andrew's Creek is an alpine watershed dominated by talus slopes and steep bedrock. Poorly developed, immature soils cover only 5-15% of the basin (Campbell et al., 1995) in this very low SOC watershed. In contrast, St. Mary's River is a low relief watershed dominated by peatlands with headwaters and tributaries originating in swamps. Forests and wetlands cover 41% and 36% of the basin, respectively (Bell and Lutz, 2008), creating a very high SOC watershed. Because these watersheds serve as extremes in SOC content, Andrew's Creek and St. Mary's River may have a strong influence on the observed relationship between stream water $Hg_D$:DOC and SOC. To investigate the leverage of the individual points, we conducted additional regressions that excluded Andrew's Creek and St. Mary's River. When both sites were excluded from the analysis, power law fits to the remaining data still had lower root mean squared errors compared with linear fits. While having more uncertainty, the power law exponent for the relationship when Andrew's Creek was excluded ($-0.36 \pm 0.21$) was similar to the power law exponent obtained for the entire dataset ($-0.41 \pm 0.08$). Excluding St. Mary's River, which has the highest SOC content, resulted in no change in the power law exponent ($-0.41 \pm 0.08$). It is also important to note that despite the limited dataset for Andrew's Creek (n=5), the samples were collected over ranges in both discharge and DOC that spanned an order of magnitude. The non-linear relationship between SOC and $Hg_D$:DOC reported here does not appear to depend on particular sites.

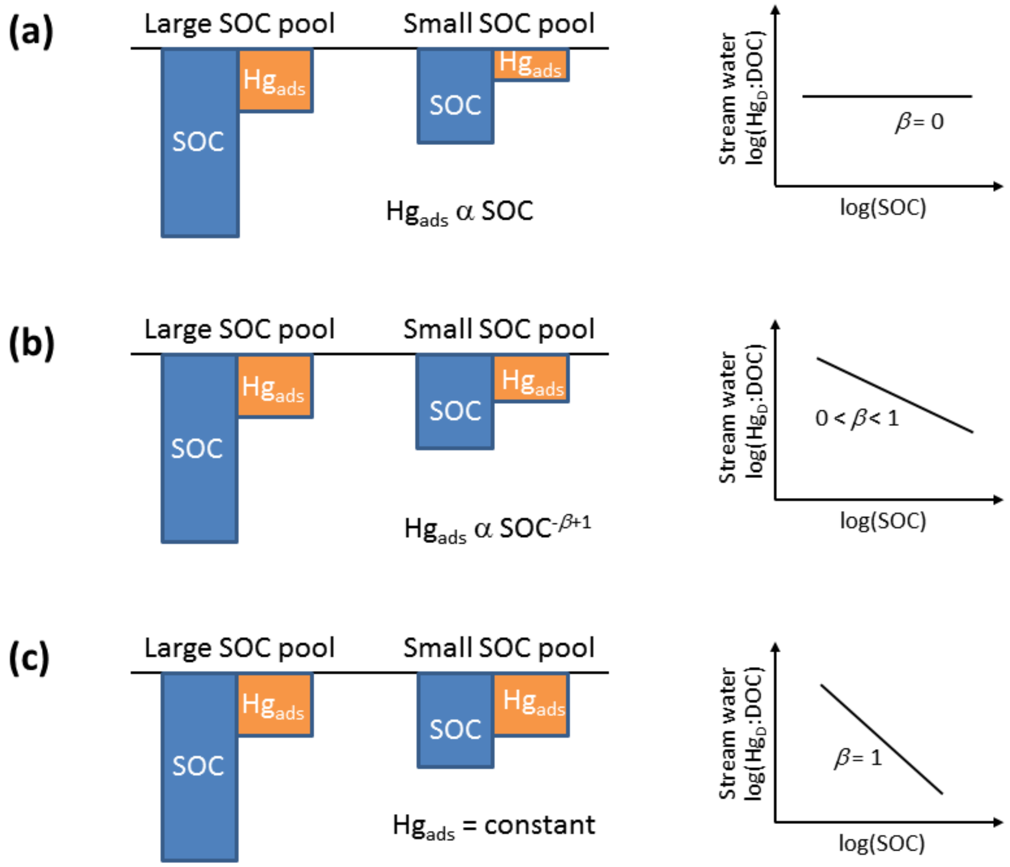

**Figure 3.** Scenarios by which the amount of SOC-bound Hg stored in watershed soils ($Hg_{ads}$) scales with watershed soil organic carbon (SOC). (a) $Hg_{ads}$ is proportional to SOC, leading to $Hg_D$:DOC scaling with SOC$^{-\beta}$, where $\beta = 0$, (b) $Hg_{ads}$ is proportional to SOC$^{-\beta+1}$, leading to $Hg_D$:DOC scaling with SOC$^{-\beta}$, where $0 < \beta < 1$, and (c) $Hg_{ads}$ is constant, leading to $Hg_D$:DOC scaling with SOC$^{-\beta}$, where $\beta = 1$.

It is clear from our empirical analysis that watersheds with higher SOC content have stream water that is less enriched in $Hg_D$ with respect to DOC (Fig. 2). The mathematical framework described in Section 4, along with the specifics of the power-law relationship relating $Hg_D$:DOC ratios to SOC, allow for inferences about how Hg accumulates in soils and associates with DOC as it is transported to streams. The most likely explanation for the negative correlation between $Hg_D$:DOC and SOC is a “dilution” effect, meaning that watersheds with larger SOC pools would release more DOC to streams, thereby overwhelming the amount of co-transported Hg and diluting the $Hg_D$:DOC ratio. If the amount of SOC-bound Hg available for transport to streams were roughly constant amongst locations, $Hg_D$:DOC would scale with $SOC^{-\beta}$, where $\beta = 1$ (Fig. 3c). An absence of a dilution effect would result from the amount of Hg stored in soils being roughly proportional to watershed SOC, leading to $\beta = 0$ (Fig. 3a). The observed value of $\beta = 0.41$ (Fig. 2) points toward an intermediate scenario, in which accumulated soil Hg is more abundant in watersheds with higher SOC, but dilution still occurs because the stored soil Hg does not scale with SOC in a proportional manner (Fig. 3b). Such inferences of soil Hg storage and release should be made while keeping in mind some of the model simplifications (e.g., the use of a “lumped” model with no vertical or horizontal variability in Hg and SOC pools within the watershed, and absence of a pH effect on the linear isotherm) made necessary by its application to a diverse array of watersheds.

The enhanced deposition of anthropogenically derived Hg is confined to the post-Industrial Revolution period, which places a constraint on the residence time of this pool of Hg in soils (Smith-Downey et al., 2010; Yu et al., 2014). Meanwhile, the residence time of SOC can exceed thousands of years, especially for soils with deep carbon pools and/or temperature limitations on biological activity (Schimel et al., 1994). It has previously been speculated that this disparity in residence timescales influences the ratio of Hg to SOC stored in soils and ultimately the ratio of $Hg_D$:DOC in lakes and streams (Meili, 1991). The emergent $Hg_D$:DOC ratios found in streams are the product of complex interactions associated with the cycling of carbon and Hg in soils, including decomposition, volatilization, and translocation. Previous research has characterized these specific processes through direct sampling of watershed soils (Hintelmann et al., 2002; Demers et al., 2007; Selvendiran et al., 2008; Obrist et al., 2011; Demers et al., 2013; Oswald et al., 2014; Yu et al., 2014), but a generalized, process-based theory that can be applied across a diverse range of watersheds remains a current research priority. While the present analysis may place some constraints on such a theory, process-based models that explicitly consider the timescales associated with carbon and Hg cycling in watershed soils are ultimately desired.

According to the mathematical framework presented in section 4, soil mercury pools, $Hg_{ads}$, would be expected to scale with $SOC^{-\beta+1}$, where $\beta$ has a value of 0.41 based on empirical data (Fig. 2). Observational datasets of how pools of soil Hg scale with SOC are relatively scarce in the literature. A recent study characterized soils pools throughout the northeastern United States (Yu et al., 2014) from measurements of Hg and SOC concentrations in the O and B horizons. Based on data from 122 soil pits (raw data from X. Yu, pers. comm.), soil Hg pools (ng $m^{-2}$) scale with SOC pools (mg $m^{-2}$) to the 0.57 (±0.16) power ($r^2 = 0.33$), which suggests non-linearity consistent with our theoretical expectations. However, a study in the Czech Republic (Navrátil et al., 2014) using a more limited survey of 15 soil pits to depths of 0.5-1.0 m resulted in scaling to the 1.53 (±0.81) power ($r^2 = 0.60$) (raw data from T. Navrátil, pers. comm.), heavily influenced by three samples from a watershed with particularly high SOC and Hg. Even more uncertainty is found in the relationship between soil Hg pools reported by *Obrist* (2012) and the corresponding SOC pools (raw data from D. Obrist, pers. comm.). Excluding a contaminated site (Oak Ridge, TN), soil Hg pools to depths of 0.40 m scaled with SOC pools to the 0.96 (±1.31) power ($r^2 = 0.18$) for 13 sites located throughout the U.S. It is likely that the history of Hg exposure relative to soil age (which is not necessarily proportional to the size of the SOC pool) could contribute to site-to-site variability in the association of $Hg_{ads}$ to SOC (Obrist et al., 2011). As a final point, the disparity in spatial scales associated with soil pits relative to watersheds, which integrate over much larger areas, could result in relatively poor relationships for the soil-based observations. At this point it is difficult to verify if the scaling indirectly implied by the stream water data combined with theoretical framework presented in Section 4 holds for Hg adsorption to organic carbon in soils.

Mercury concentrations have been successfully modeled for individual watersheds (Ambrose et al., 2005; Dai et al., 2005; Loux, 2005; Brown et al., 2007; Futter et al., 2012), but predictions of Hg in streams at the regional scale have proven to be challenging. The relationship between $Hg_D$:DOC and SOC may improve such estimates without the need for extensive field measurements or modeling, aided by the widespread availability of SOC databases throughout North America and Europe. SOC values and $Hg_D$:DOC ratios estimated from these databases used with predictions of stream DOC (Hope et al., 1997; Aitkenhead et al., 1999) may prove useful for indirect estimates of $Hg_D$ stream concentrations. The manner by which $Hg_D$ associates with DOC may provide insight about the future behavior of $Hg_D$ within freshwater systems. For example, long-term records have revealed an increase in DOC concentrations in lakes and streams throughout North America and Europe, most likely the result of decreased soil ionic strength due to reduced acid deposition (Evans et al., 2005; Monteith et al., 2007; Futter and de Wit, 2008). The observed differences in $Hg_D$:DOC ratios between watersheds would imply that Hg mobilization from soils would be more pronounced in some systems than in others if such trends continue. Furthermore, climate change may also lead to an increase in DOC and Hg released to streams (Tipping et al., 1999; Cole et al., 2002; Golden et al., 2013), but the importance of climate influences on DOC and Hg export will be strongly determined by the coupling of $Hg_D$ and DOC within individual watersheds. Our results suggest that watershed soils play an important role in the $Hg_D$ and DOC relationship found in streams. Therefore, proposed legislation to reduce Hg emissions must consider how soils mediate the movement of Hg to surface waters in order to more accurately predict water quality impacts.

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# Chapter 3: Impacts of pH on dissolved mercury and dissolved organic carbon in a small, first order stream

## Abstract

Elevated levels of mercury (Hg) emissions from anthropogenic sources have led to the global contamination of streams and rivers. Hg stored in soils of terrestrial ecosystems represents a potential long-term source of Hg to streams. Within streams, Hg is often strongly associated with dissolved organic carbon (DOC), but due to spatial and temporal variability the ratio of Hg:DOC can vary within an individual watershed. This study explores the effects of stream acidification on dissolved mercury ($Hg_D$) and DOC through two in-stream acid injection experiments. Lowering stream pH caused both $Hg_D$ and DOC to be removed from the water column. The likely mechanism is adsorption to stream sediments or particulates enhanced by hyporheic mixing and exchange. More aromatic DOC was preferentially adsorbed, thereby decreasing the ratio of $Hg_D$:DOC in the water column. A second acid injection experiment that created a spatially uniform low pH revealed losses of $Hg_D$ and DOC along the stream reach that was enhanced by hyporheic exchange. If this process is similar to what occurs in soil solution, watersheds recovering from acidification by declining acid deposition in North America and Europe may experience increased mobilization of $Hg_D$ and DOC to streams and rivers. Even with stricter emission standards, stream $Hg_D$ concentrations in these regions may not change or possibly increase.

## 1. Introduction

Mercury (Hg) is a toxic pollutant that has become a global environmental concern. Since the industrial revolution, anthropogenic activities have contributed to Hg concentrations elevated above natural background levels (Schuster et al., 2002; Selin, 2009; Mast et al., 2010). Atmospheric transport and deposition of Hg has resulted in the contamination of even pristine, remote ecosystems (Fitzgerald et al., 1998). Forested watersheds retain a large portion of atmospherically deposited Hg (Aastrup et al., 1991; Krabbenhoft et al., 1995; Scherbatskoy et al., 1998; Hintelmann et al., 2002; Oswald et al., 2014). Soil reservoirs of Hg could potentially serve as long-term sources of Hg to streams and rivers, which may obscure the intended benefits of stricter emission controls (Pacyna et al., 2010). Ultimately these terrestrial systems are the source of Hg to downstream aquatic systems where it can be converted to methylmercury, a potent neurotoxin to humans and wildlife (Wolfe et al., 1998; Scheuhammer et al., 2007). Understanding Hg biogeochemistry in these systems is necessary to predict stream export of Hg.

In streams and rivers, Hg is strongly associated with dissolved organic carbon (DOC) (Grigal, 2002; Schuster et al., 2008; Shanley et al., 2008; Brigham et al., 2009; Demers et al., 2010; Dittman et al., 2010; Riscassi and Scanlon, 2011; Schelker et al., 2011; Schuster et al., 2011; Demers et al., 2013; Oswald and Branfireun, 2014). Reduced sulfur ($S_{red}$) sites within aromatic portions of DOC, such as hydrophobic organic acids (HPOA), strongly bind Hg. In the environment, $S_{red}$ binding sites exceed the concentration of Hg available for binding. This causes most available Hg to be associated with DOC (Xia et al., 1999; Skyllberg et al., 2000; Haitzer et al., 2002). Ultraviolet absorbance at $\lambda = 254$ nm ($UV_{254}$) has been shown to be a good indicator of HPOA and DOC aromaticity (Dilling and Kaiser, 2002; Dittman et al., 2009). In some watersheds, $UV_{254}$ can have a stronger relationship with Hg than DOC (Shanley et al., 2008; Dittman et al., 2009; Riscassi and Scanlon, 2011; Burns et al., 2013) indicating that aromaticity of DOC influences the ability of DOC to bind Hg. The ratio of Hg bound per unit DOC (Hg:DOC) is known to vary between watersheds (Shanley et al., 2009; Riscassi and Scanlon, 2011; Stoken et al., in review.). Due to the spatial and temporal variability of Hg and DOC in streams, Hg:DOC can also vary within an individual watershed (Schelker et al., 2011; Demers et al., 2013). Several factors may influence the watershed-scale variability of Hg:DOC including DOC source and composition (Burns et al., 2013), hydrologic flow paths (Oswald and Branfireun, 2014), and pH (Haitzer et al., 2003).

In North America and Europe, mean stream pH and DOC concentrations have exhibited a positive trend as watersheds recover from acidification (Stoddard et al., 1999; Evans et al., 2001; Monteith et al., 2007). “Brownification” of stream water through increased export of DOC is expected to continue along with this recovery but it is uncertain if Hg concentrations will follow the same trend. Despite the potential environmental consequences of pH on the association of Hg and DOC, there has been a lack of studies that examine this interaction in streams. In lab studies at acidic pH, both Hg and DOC become less soluble in soil solution and tend to adsorb to soil surfaces (Yin et al., 1996; You et al., 1999). The likely mechanism for this reduced solubility is an increase in the concentration of hydrogen ions in solution. Protonation of DOC functional groups by hydrogen ions causes the net charge of DOC to become more positive. As the charge of DOC increases, it is able to bind to more negatively charged soil inorganic surfaces (Tipping and Hurley, 1988; Tipping and Woof, 1991; Kalbitz et al., 2000). Proton competition can also occur for Hg binding sites on DOC (Haitzer et al., 2003). Higher molecular weight humic substances tend to adsorb to soil surfaces more readily as pH decreases causing overall aromaticity in soil solution to also decrease (Donahue et al., 1998; You et al., 1999; Pédrot et al., 2009). *Ekström et al.* (2011) acidified soil plots in a Swedish forest to look at pH effects in soil water. Consistent with lab studies, they found a significant decrease in DOC concentration and aromaticity in soil solution in their highest acid treatments. While these findings lend insight, more field-based studies are needed to determine the influence of pH on DOC, and in particular how it affects association with Hg.

In this study, we investigate the influence of pH on stream Hg and DOC concentrations in a small forested watershed in Virginia. We focus only on the dissolved phase of mercury ($Hg_D$) because this form is more bioavailable (Aiken et al., 2000; Munthe et al., 2007). Specifically our objectives were to 1) explore how lowering stream pH affects $Hg_D$ and DOC concentrations in the water column in a controlled field-setting, and 2) investigate the process by which this occurs. Results from this work are intended to contribute to the understanding of $Hg_D$ and DOC co-transport in streams and to provide insight into the processes that may operate within watershed soils.

## 2. Methods

### *2.1 Site Description*

The study watershed is located in a mixed-hardwood forest owned by the University of Virginia in Fluvanna County, VA (Figure 1). This region is in the Piedmont Plateau physiographic province where silt loam Ultisols are the most prevalent forested soils. Mean annual temperature of this region is 13.1 °C, while mean annual precipitation is approximately 1040mm (Southeast Regional Climate Center). The 20 ha watershed is drained by a small headwater stream. Discharge was measured using a rating curve developed from a 90° v-notch polycarbonate weir and a pressure transducer (Level Troll 500, In-Situ, Inc.) placed inside a stilling well. An in-situ water quality sonde (EXO2, YSI, Inc.) was deployed just upstream of the weir to monitor stream temperature, conductivity, pH, turbidity, and fluorescent dissolved organic matter (fDOM) at 30 minute intervals. In-situ fDOM is a good proxy for DOC and $UV_{254}$ after corrected for temperature and turbidity interference (Saraceno et al., 2009; Downing et al., 2012; Pellerin et al., 2012).

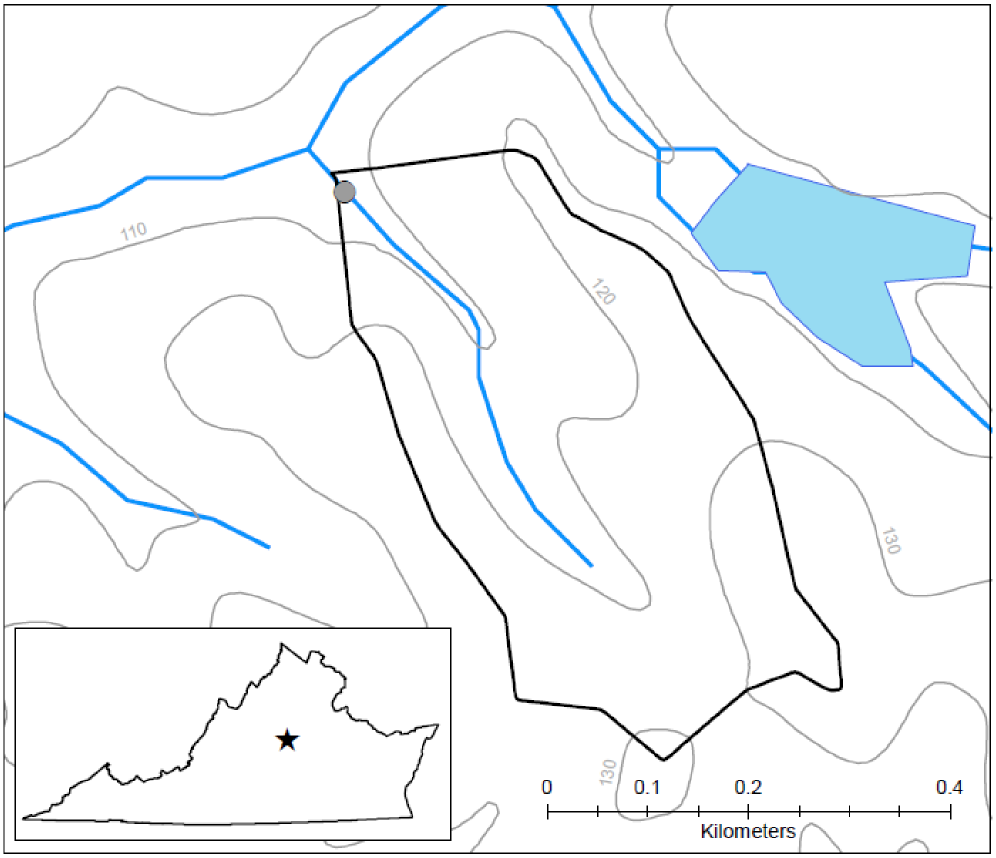

**Figure 1.** Map of study watershed. Circle denotes stream sampling site. Star denotes location of study watershed in Virginia. Elevation contours in meters.

### *2.2 Sample Collection*

Stream base flow was sampled manually approximately twice a month for 10 months (January – October 2015). Duplicate stream grab samples were taken every other sampling trip. All samples were collected using trace level clean techniques following the "clean hands, dirty hands" protocol found in *U.S. EPA* (1996). A stage-actuated automated sampler (Teledyne Isco 3700) retrofitted with Teflon parts was deployed to sample high flow during storm events. Automated sampling using this method has no significant difference from manual sampling of total Hg (Riscassi et al., 2010) and $Hg_D$ (Riscassi and Scanlon, 2011). Base flow pH was recorded in the field immediately after sampling using a field pH probe (Pro Plus, YSI, Inc.). Storm flow pH was taken from the closest logged measurement on the in-situ sonde. All samples were filtered and analyzed for $Hg_D$, DOC, and $UV_{254}$.

### *2.3 Stream Acidification Experiments*

Two stream acidification experiments were designed to explore pH effects during base flow on $Hg_D$ and DOC concentrations. The first experiment looked at the relationship between these variables as pH decreased in the stream. On March 30th, 2015, a 15-m stream reach below the weir was acidified with 3% trace metal grade nitric acid ($HNO_3$, Omni Trace Ultra, EMD Millipore) using a mariotte bottle retrofitted with a Teflon valve and fittings. Duplicate manual samples were taken prior to the acid injection to sample base flow $Hg_D$ and DOC. As the stream was acidified from pH 6.5 to pH 3.8, two samples were taken at approximately each 0.5 pH step. Additionally, duplicate samples were taken an hour post-injection after the stream pH recovered to pre-injection conditions. Over the entire experiment a total of 14 samples were collected from the same point near the end of the stream reach.

The second acidification experiment investigated the spatial changes in $Hg_D$, DOC, and DOC quality at a steady-state acidic pH during base flow. On August 21st, 2015, the experimental stream reach was shortened to 12-m with four sampling sites spaced at 2, 4, 7, and 12 meters below the weir. The stream was acidified using 6% trace metal grade $HNO_3$ until the pH stabilized around 3.3 along the stream reach. Three sampling sites were monitored for pH using separately calibrated handheld pH probes (YSI, Inc., Oakton Instruments, Hanna Instruments), while the fourth and final site was monitored using the in-situ sonde (YSI, Inc.). One grab sample was taken at each sampling site prior to beginning the experiment except the first site. Once a constant pH of approximately 3.3 was attained in the stream reach, two samples were taken at each site 20 minutes apart for a total of

14 samples. A nitrate ($NO_3^-$) probe was installed on the in-situ sonde to monitor for the possibility of UV interference (Weishaar et al., 2003). During both injection experiments, the sonde was placed in the stream at the end of the experimental reach and was set to log water quality measurements (temperature, conductivity, pH, fDOM, turbidity, and $NO_3^-$) every 30 seconds during the acid injection.

### *2.4 Chemical Analyses*

Mercury samples were filtered and preserved in the laboratory at the University of Virginia within 48 hours of sample retrieval. Storm samples were collected within one week after automated sampling was completed. Filtering was done under a Class 100 clean bench following *Lewis and Brigham* (2004). Samples were filtered through pre-baked quartz fiber filters (Whatman, QM-A grade) in a vacuum-desiccator chamber using an acid-leached Teflon filtering apparatus. Filtered samples were preserved within one hour of filtration with a 100% BrCl solution (0.5 mL BrCl / 100 mL of sample) and double-bagged in storage until analysis. $Hg_D$ in the samples was analyzed using cold-vapor atomic florescence spectrophotometry (2600 series, Tekran Instruments Corp.) following the methods in *U.S. EPA* (2002). The method detection limit (MDL) was determined to be 0.19 ng $L^{-1}$ (U.S. Environmental Protection Agency, 1986).

Hg instrumentation and measurements were subject to quality control and assurance methods outlined in *U.S. EPA* (2002). Instrument performance was evaluated using method and system blanks, ongoing precision and recovery (OPR) analysis, and matrix spikes. All system and method blanks (n=53) were less than the MDL except one (0.28 ng $L^{-1}$). OPR samples (n=28) and calibration standards (n=45) were within 15% of expected concentrations. All matrix spike pairs (n=15) had a relative percent difference (RPD) of less than or equal to 6% except one pair with a RPD of 17.4%. As an independent check of laboratory accuracy, a quality control sample (QCS), made from a source different than the one used to make the standards, was evaluated within each laboratory analysis run. Recoveries of the QCS standard (n=9) ranged from 91 to 100.5%. In June 2015, the lab participated in an interlaboratory proficiency test administered by Environment Canada to ensure accuracy of Hg measurements. The lab received the highest ranking with all sample recoveries within one standard deviation of each sample mean (n=5) for Hg concentrations ranging from 1.16 to 54.0 ng $L^{-1}$. All field (n=14) and filter (n=18) blanks were below the MDL except one (0.47 ng $L^{-1}$). The RPD between duplicate field samples (n=11) was within 7%.

Filtered sample water was decanted from the Teflon $Hg_D$ sample bottle into a 40 mL glass amber vial for DOC analysis. The DOC sample was preserved with 0.5 mL of $H_3PO_4$ and refrigerated until analysis. UV/persulfate digestion (U.S. Environmental Protection Agency, 2005) was used to analyze DOC (Teledyne/Tekmar Phoenix 8000 TOC analyzer). The MDL was determined to be 0.09 mg $L^{-1}$. All but two field blanks (n=14) and one filter blank (n=18) were below the MDL (0.12, 0.16, and 0.10 mg $L^{-1}$ respectively). The RPD for duplicate grab samples (n=11) was within 5%. Quality control standards were run every 10 samples to ensure laboratory accuracy. All QC standards (n=18) were within 10%, except one that was 30% above the standard concentration. It is possible carry over effects caused contamination as a relatively high concentration sample (19.06 mg $L^{-1}$) was run before the low standard (1.5 mg $L^{-1}$ DOC).

$UV_{254}$ was quantified on a UV-visible spectrophotometer (Shimadzu UV-Mini 1240) with a stated accuracy of ± 0.003 absorbance units. Samples were analyzed in a 1cm path length quartz-cell at room temperature within 24 hours of filtering. Instrument accuracy was verified by analyzing an outside check standard with each batch of samples (In-Spec UV Standard No. 3). Instrument stability was ensured by measuring deionized water blanks and sample duplicates after every 10 samples. Field and filter blanks were analyzed with each batch to check for contamination in sampling and filtering materials and methods. Field duplicates were used to evaluate reproducibility of UV measurements. Filtered water samples were analyzed for inorganic species that can cause UV interferences (Weishaar et al., 2003) to determine if corrections to measured data were required. Nitrate in stream water was determined using an ICS-3000 Ion Chromatography System (Dionex) following *U.S. EPA* (1997). The stream water nitrate concentration was well below the level of UV interference. Iron was analyzed on the same UV-visible spectrophotometer following *Gibbs* (1986). Stream water iron(III) concentrations were all above the 0.02 mg $L^{-1}$ limit for absorbance interference and ranged from 0.02 to 0.09 mg $L^{-1}$. pH of all samples, including the acid injection experiments, were in the range of non-interference for UV measurements (Weishaar et al., 2003). Specific ultraviolet absorbance at $\lambda = 254$ nm ($SUVA_{254}$) was calculated by dividing the UV absorbance by the concentration of DOC (mg $L^{-1}$). It is reported as liter per mg carbon per meter. UV absorbances were corrected for iron(III) prior to calculating $SUVA_{254}$ (Poulin et al., 2014).

### *2.5 Statistical Analyses*

All statistical calculations and analysis were performed using R software (version 3.2.1, The R Foundation). Linear regressions were performed to calculate $r^2$ and associated p-values.

## **3. Results**

### *3.1 $Hg_D$, DOC, UV, and SUVA*

A total of 43 samples were collected to determine ambient stream $Hg_D$, DOC, $UV_{254}$, and $SUVA_{254}$. Twenty four of these samples were collected at high flow during a storm event by the ISCO automated sampler. $Hg_D$ concentrations ranged from 0.98 ng $L^{-1}$ to 14.48 ng $L^{-1}$, while DOC concentrations ranged from 2.04 mg $L^{-1}$ to 27.21 mg $L^{-1}$. $Hg_D$ and DOC had a significant positive correlation ($r^2 = 0.98$, $p < 0.001$, Figure 2). Concentrations of both $Hg_D$ and DOC increased during high flow conditions.

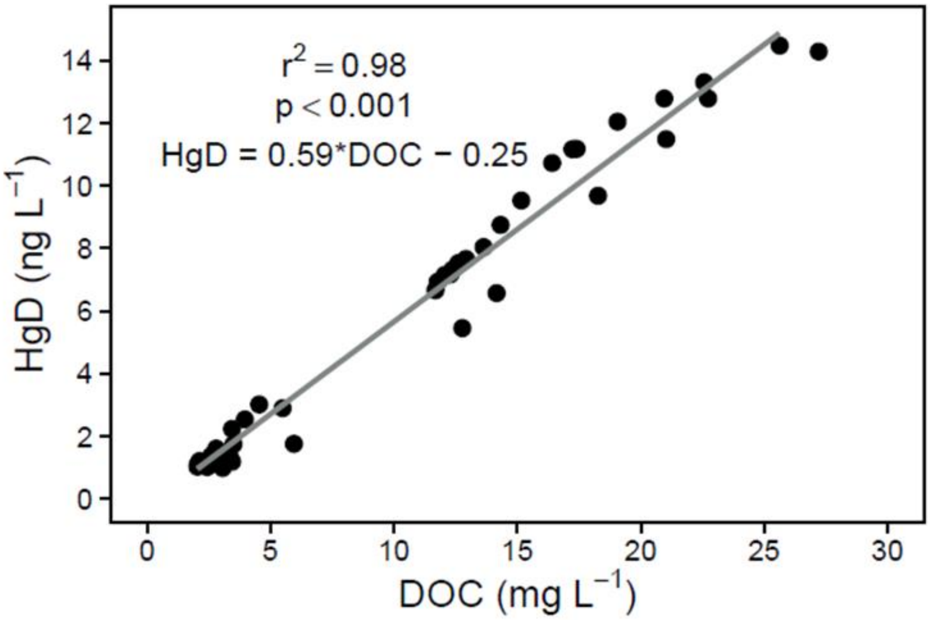

**Figure 2.** Dissolved Hg (ng L$^{-1}$) vs dissolved organic carbon (mg L$^{-1}$) with linear best fit line.

Based on the slope of the linear regression, the overall ratio in the stream was 0.59 ng L$^{-1}$ $Hg_D$ per mg L$^{-1}$ DOC. $UV_{254}$, a measure of both DOC quantity and quality, ranged from 0.068 cm$^{-1}$ to 0.950 cm$^{-1}$ after correction for iron interference. $Hg_D$ and $UV_{254}$ had a significant positive relationship ($r^2 = 0.97$, $p < 0.001$). $SUVA_{254}$, a measure of the average aromaticity of DOC, ranged from 2.58 m to 4.85 L mg C$^{-1}$ m$^{-1}$. There was no relationship between $Hg_D$ and $SUVA_{254}$ ($r^2 = 0.02$, $p = 0.33$). fDOM ranged from 23.52 to 243.28 ppb quinine sulfate units (QSU) after correction for temperature and turbidity. fDOM had a strong positive correlation with DOC ($r^2 = 0.96$, $p < 0.001$), $UV_{254}$ ($r^2 = 0.95$, $p < 0.001$), and $Hg_D$ ($r^2 = 0.97$, $p < 0.001$; $n = 39$). For the entire sampling season (January to October 2015), stream pH ranged from 5.48 to 7.12, while stream temperature ranged between 0.01 to 22.81 °C.

### *3.2 Stream Acidification Experiments*

The first stream acidification experiment had a pH range starting at the pre-injection pH of 6.52 down to 3.8 (Figure 3). $Hg_D$ decreased with decreasing pH from 2.53 ng $L^{-1}$ to 1.92 ng $L^{-1}$. The loss of $Hg_D$ from the stream water column had a strong linear relationship with pH ($r^2 = 0.89$, $p < 0.001$, Figure 4). DOC was also lost from the water column as pH decreased (4.04 mg $L^{-1}$ to 3.65 mg $L^{-1}$). This loss had a strong linear relationship with pH ($r^2 = 0.88$, $p < 0.001$, Figure 4). $SUVA_{254}$ ($r^2 = 0.92$, $p < 0.001$, Figure 4) also decreased linearly with pH indicating that average DOC aromaticity had a positive relationship with pH. $Hg_D$:DOC decreased with declining pH from 0.64 ng $L^{-1}$ per mg $L^{-1}$ to 0.51 ng $L^{-1}$ per mg $L^{-1}$. This relationship was also highly significant ($r^2 = 0.75$, $p < 0.001$, Figure 5). $Hg_D$:$UV_{254}$ remained consistent and had no relationship with pH during the experiment ($r^2 = 0.18$, $p = 0.17$). $Hg_D$ and DOC were strongly correlated throughout the experiment ($r^2 = 0.79$, $p < 0.001$). This relationship was improved when DOC quantity and quality were accounted for with $UV_{254}$ ($r^2 = 0.89$, $p < 0.001$).

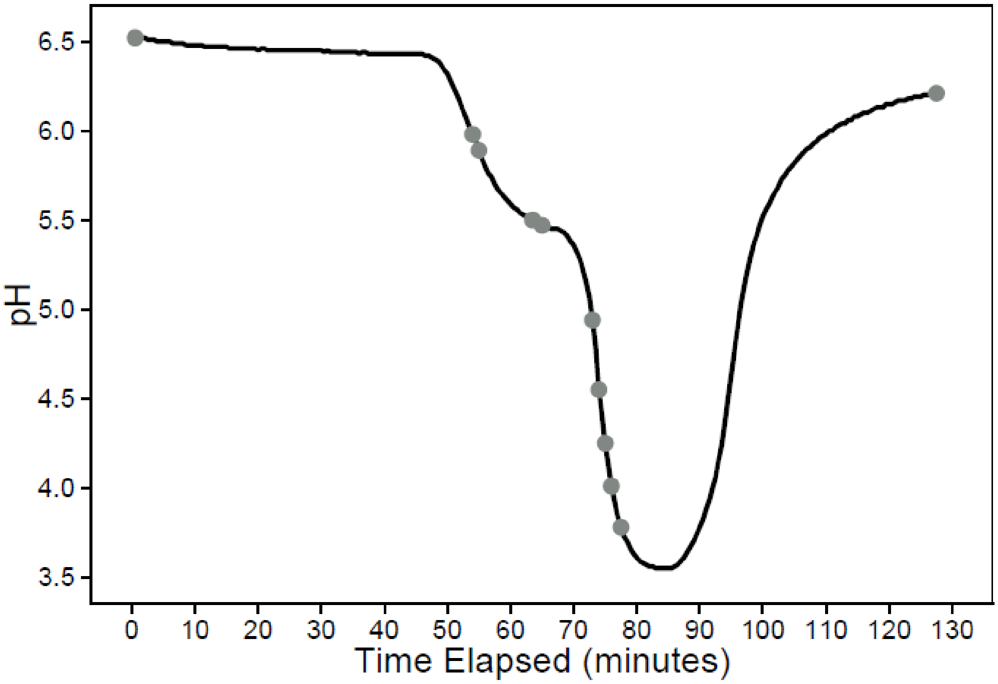

**Figure 3.** Time series of pH from first acid injection experiment. pH values (black line) were recorded every 30 seconds by the in-situ sonde. Gray circles denote time when $Hg_D$/DOC manual samples were collected.

The second stream acidification experiment had four sampling sites spaced longitudinally along the stream reach. Stream pH was similar between sampling sites before the acid injection (6.86 ± 0.21 pH units; Figure 6). Samples taken at each site before the injection had almost identical concentrations of $Hg_D$ (1.19 ± 0.02 ng $L^{-1}$, Figure 7A), DOC (3.42 ± 0.03 mg $L^{-1}$, Figure 7B), $SUVA_{254}$ (3.50 ± 0.14 L mg $C^{-1}$ $m^{-1}$, Figure 7C), and $Hg_D$:DOC ratios (0.35 ± 0.01 ng $L^{-1}$ per mg $L^{-1}$, Figure 7D). After the stream reach was lowered to a spatially uniform pH (3.31 ± 0.3 pH units; Figure 6), $Hg_D$, DOC, $Hg_D$:DOC, and $SUVA_{254}$ decreased at all sampling sites. The first three sites, spaced 2-7m downstream from the injection point, had similar decreases from background concentrations of $Hg_D$ (0.94± 0.03 ng $L^{-1}$), DOC (3.08 ± 0.05 mg $L^{-1}$), $Hg_D$:DOC (0.30 ± 0.02 ng $L^{-1}$ per mg $L^{-1}$) and $SUVA_{254}$ (2.83 ± 0.06 L mg $C^{-1}$ $m^{-1}$; Figure 7).

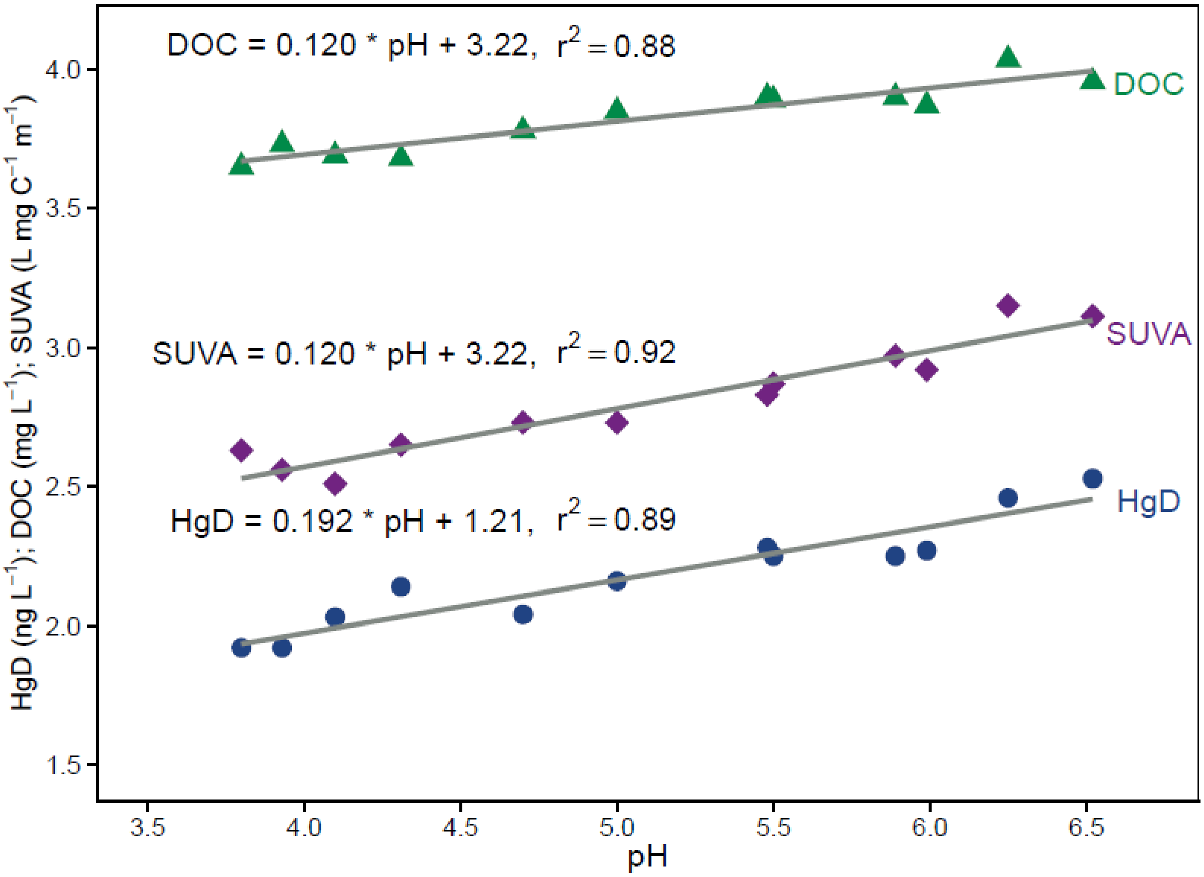

**Figure 4.** pH vs $Hg_D$, DOC, and $SUVA_{254}$ from the first acid injection experiment. All samples were taken at the same point in the stream reach.

The fourth sampling site, which was after a large riffle section in the stream, had larger losses of $Hg_D$ (0.47 ng $L^{-1}$), DOC (2.25 mg $L^{-1}$), $Hg_D$:DOC (0.21 ng $L^{-1}$ per mg $L^{-1}$), and $SUVA_{254}$ (1.91 L mg $C^{-1}$ $m^{-1}$). Replicate samples were taken at each site 20 minutes after reaching the steady-state pH of 3.3. Results of these samples were very similar to the first set of samples taken at each site during the acid injection (Figure 7). Acid blanks from both injection experiments were below the MDL for $Hg_D$.

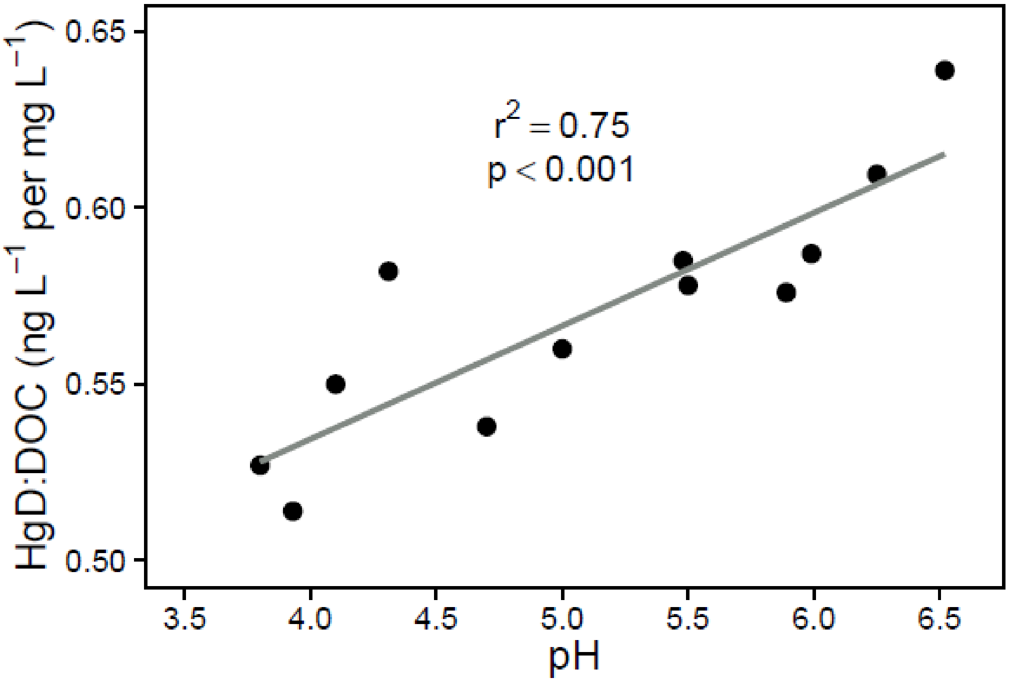

**Figure 5.** pH vs $Hg_D$:DOC from the first acid injection experiment with linear best fit line.

## 4. Discussion

### *4.1 Stream $Hg_D$, DOC, UV, and SUVA*

Ranges of $Hg_D$, DOC, $UV_{254}$, and $SUVA_{254}$ in our stream were similar to other studies in forested watersheds (Scherbatskoy et al., 1998; Shanley et al., 2008; Schuster et al., 2008; Dittman et al., 2010; Demers et al., 2010; Riscassi and Scanlon, 2011). The $Hg_D$:DOC ratio of 0.59 ng $L^{-1}$ $Hg_D$ per mg $L^{-1}$ DOC at our study watershed falls near the middle of the known range of the ratio of 0.12 to 1.4 ng $L^{-1}$ $Hg_D$ per mg $L^{-1}$ DOC (Riscassi and Scanlon, 2011; Stoken et al., in review.). Interestingly, the correlation of $Hg_D$ is slightly stronger with DOC than $UV_{254}$ unlike other studies that have found a stronger relationship between $Hg_D$ and $UV_{254}$ (Shanley et al., 2008; Dittman et al., 2009; Riscassi and Scanlon, 2011; Burns et al., 2013). A lack of relationship between $Hg_D$ and

$SUVA_{254}$ has been found at other small forested watersheds (Schuster et al., 2008; Riscassi and Scanlon, 2011), though $SUVA_{254}$ can have stronger explanatory power for $Hg_D$ in larger watersheds with variable contributing source areas (Burns et al., 2013). This lack of relationship was apparent at base flow, but became more skewed at high flow as $SUVA_{254}$ had little to no variation during storm events despite large increases in DOC concentration. Clearly, DOC quantity acts as the primary control on $Hg_D$ in this stream. This explains why fDOM is a good proxy for DOC and $Hg_D$ at the study site.

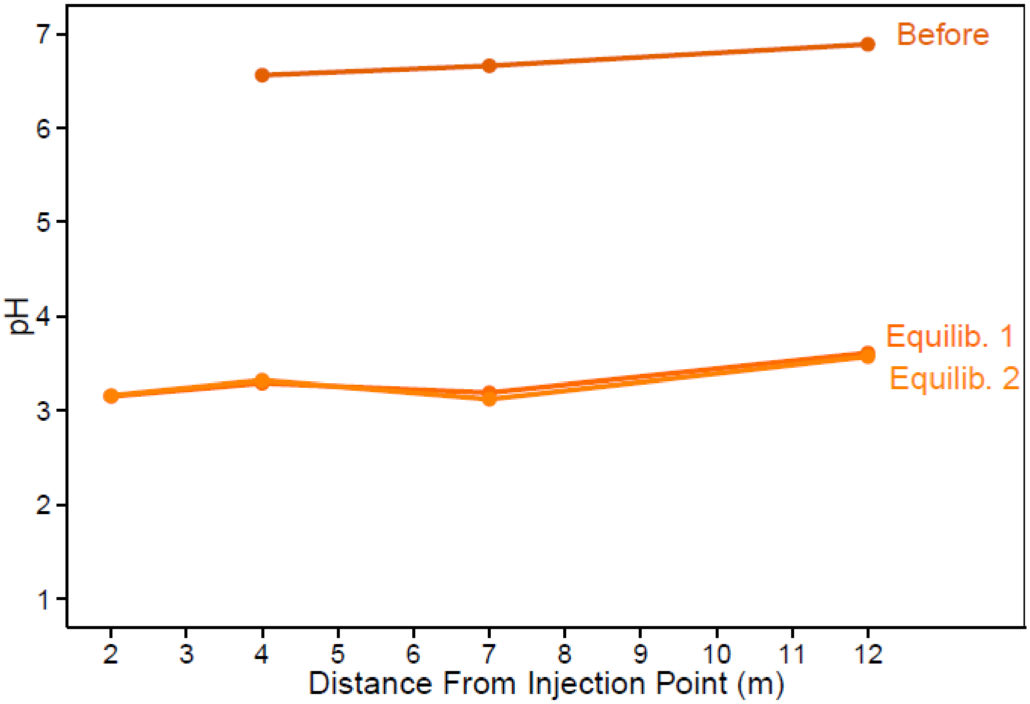

**Figure 6.** pH for all four sampling sites during the second acid injection experiment. “Before” in each figure represents stream concentrations at each site before the experiment.” Equilib. 1” denotes samples collected at each site upon reaching the steady-state pH. “Equilib. 2” denotes samples collected at each site 20 minutes after reaching steady-state pH.

### *4.2 Stream Acidification Experiments*

The first acid injection experiment isolated the effects of stream pH on $Hg_D$ and DOC in a "controlled" field-setting. Both $Hg_D$ and DOC concentrations were reduced in the stream water column as pH decreased, but the overall loss of $Hg_D$ was 19% greater than the loss of DOC. Differences in the rates of decrease can be explained by DOC quality data. While pH was lowered, $SUVA_{254}$ data shows that more aromatic carbon moved out of the water column while less aromatic carbon remained in solution in the stream. Because aromatic carbon binds $Hg_D$ more efficiently, the DOC removed from the water column was relatively enriched in $Hg_D$. The ratio of $Hg_D$:DOC that remains in the water column reflects this as it decreases with pH. $Hg_D$ and $UV_{254}$ had similar percent losses during the experiment (27.2 and 28.8% respectively). $UV_{254}$ is a metric of both DOC quantity and quality, so it seems that the change in the $Hg_D$:DOC ratio with pH is likely driven by changes in DOC quality.

We can further analyze pH effects on DOC quality and $Hg_D$ by calculating the ratio of $Hg_D$:DOC moving out of solution using the slopes of the linear regressions of $Hg_D$ and DOC with pH (Figure 4). These linear relationships imply that the $Hg_D$ and DOC masses that drop out of solution with lowering pH do so with a constant $Hg_D$:DOC ratio of 1.6 ng $mg^{-1}$ (= 0.192 ng $Hg_D$ / 0.120 mg DOC). Again, $SUVA_{254}$ evidence suggests that it is the more aromatic fraction of DOC that is removed from the water column leading to this much higher $Hg_D$:DOC ratio compared with that remaining in the water column which contains a more heterogeneous mixture of weakly aromatic and aliphatic organic compounds. Presumably as pH is lowered, $Hg_D$ and DOC are dropping out of the water column and adsorbing to stream sediments or particulates which is enhanced by hyporheic mixing and exchange.

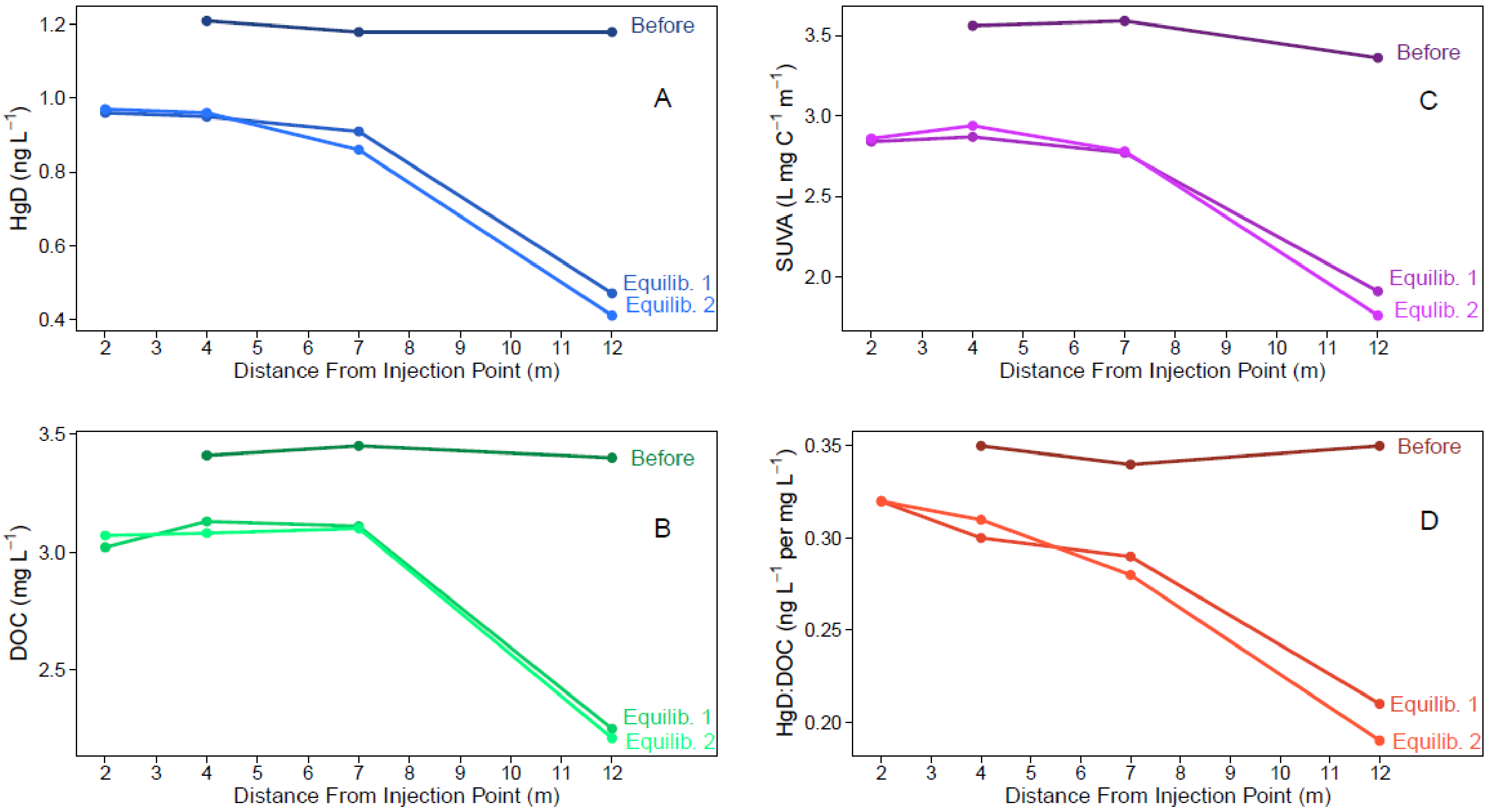

**Figure 7.** $Hg_D$, DOC, $SUVA_{254}$, and $Hg_D$:DOC for all four sampling sites from the second acid injection experiment. “Before” in each figure represents stream concentrations at each site before the experiment.” Equilib. 1” denotes samples collected at each site upon reaching the steady-state pH. “Equilib. 2” denotes samples collected at each site 20 minutes after reaching steady-state pH.

The second acid injection experiment lends support to our sediment adsorption hypothesis. During this experiment, the stream reach was acidified to a steady-state, spatially uniform pH and the stream was longitudinally sampled at four different sites. pH was constant at all sampling sites during the injection (Figure 6) meaning the acid was well-mixed along the stream reach. However, $Hg_D$ and DOC were both reduced in concentration along the reach, indicating that they are both falling out of solution over distance in this low-pH environment. The removal of $Hg_D$ and DOC from the water column does not happen instantaneously indicating that this loss may be limited by interaction with substrate onto which they adsorb. Because of the small size of the stream, the first three sampling sites were located in a low velocity pool section while the fourth sampling site occurred after a higher velocity riffle section. $Hg_D$ and DOC concentrations decreased significantly after the riffle section. It is possible their adsorption may be enhanced between the third and fourth sampling locations due to enhanced hyporheic exchange in the riffle section. Assuming that this process is similar to what occurs within soil solution (Yin et al., 1996; You et al., 1999; Haitzer et al., 2003; Ekström et al., 2011), soil water acidity could exert a significant control on $Hg_D$ and DOC transport.

### *4.3 Implications for long-term recovery*

It is clear from these acidification experiments that at base flow pH is a strong control on $Hg_D$ and DOC in streams. This is similar to findings from lab studies in soil solution (Yin et al., 1996; Haitzer et al., 2003). *Ekström et al.*, (2011) found pH also exerts a strong control on DOC in soil solution in a field setting. Our findings suggest that pH influences $Hg_D$ in addition to DOC in soil solution. If soil solution pH increases as watersheds recover from acidification, DOC and $Hg_D$ concentrations in soil solution will likely increase as well. $Hg_D$ concentrations may increase in a greater proportion as more aromatic DOC is released into solution, carrying with it a greater concentration of $Hg_D$. This could potentially increase the amount of $Hg_D$ and DOC available for mobilization from soils to streams. Atmospheric Hg emissions have declined as a result of increased regulation of point sources in North America and Europe, but pH and DOC export has increased in streams recovering from acidification in these same regions (Stoddard et al., 1999; Evans et al., 2001; Monteith et al., 2007). The increase of pH and DOC concentrations in these streams has been driven by increasing soil pH (Monteith et al., 2007; Ekström et al., 2011). As watersheds affected by acidification continue to recover, increases in soil solution pH are likely to cause increased mobilization of $Hg_D$ and DOC from soils to streams and rivers. Hg stored in watershed soils is more available for mobilization to streams than recently deposited Hg (Oswald et al., 2014) which suggests a dampening of any positive benefits that would occur from increased regulation of Hg emissions.

Overall, pH exerts a strong control on the association of $Hg_D$ and DOC in streams. Acidification of stream water causes $Hg_D$ and DOC to adsorb to sediments or particulates through hyporheic zone mixing and exchange. Aromatic DOC that binds more $Hg_D$ tends to be more readily lost causing a decrease in the $Hg_D$:DOC ratio in the water column at acidic pH levels. As systems affected by acid deposition recover from acidification, base flow $Hg_D$ concentrations may remain the same or even increase if soil solution and stream pH and DOC concentrations continue a positive trend despite decreases in Hg emissions from stricter regulation.

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# Chapter 4: Summary and prospects for future research

## 1. Summary and implications

### *1.1 Regional controls on $Hg_D$:DOC*

The ratio of $Hg_D$ to DOC in streams was analyzed with respect to watershed SOC, DOC quality, and Hg wet deposition for 19 watersheds across the U.S. SOC was a strong first-order control on $Hg_D$:DOC, while DOC quality and Hg wet deposition had no relationship. When DOC quality was considered in addition to SOC, the variance explained increased only slightly. DOC quality is clearly secondary relative to watershed SOC. A mathematical framework developed to interpret the observed power-law relationship implies that there is a Hg supply limitation for adsorption to soils with relatively large carbon pools. This points to a possible dilution effect, where there is an excess concentration of DOC relative to available Hg. Pools of Hg and DOC in soils may scale with $Hg_D$:DOC ratios in streams, but more field datasets are needed to fully test this idea. This work demonstrates that watershed SOC derived from large geospatial databases can be used to predict $Hg_D$:DOC in streams. If DOC data is also available, stream $Hg_D$ concentrations can be predicted without time consuming and expensive field work. Adding SOC and $Hg_D$:DOC data from the Pace Estate in Fluvanna County, VA improves the relationship by 1% (Figure 1). The robustness of this relationship is expected to increase as data from more watersheds becomes available.

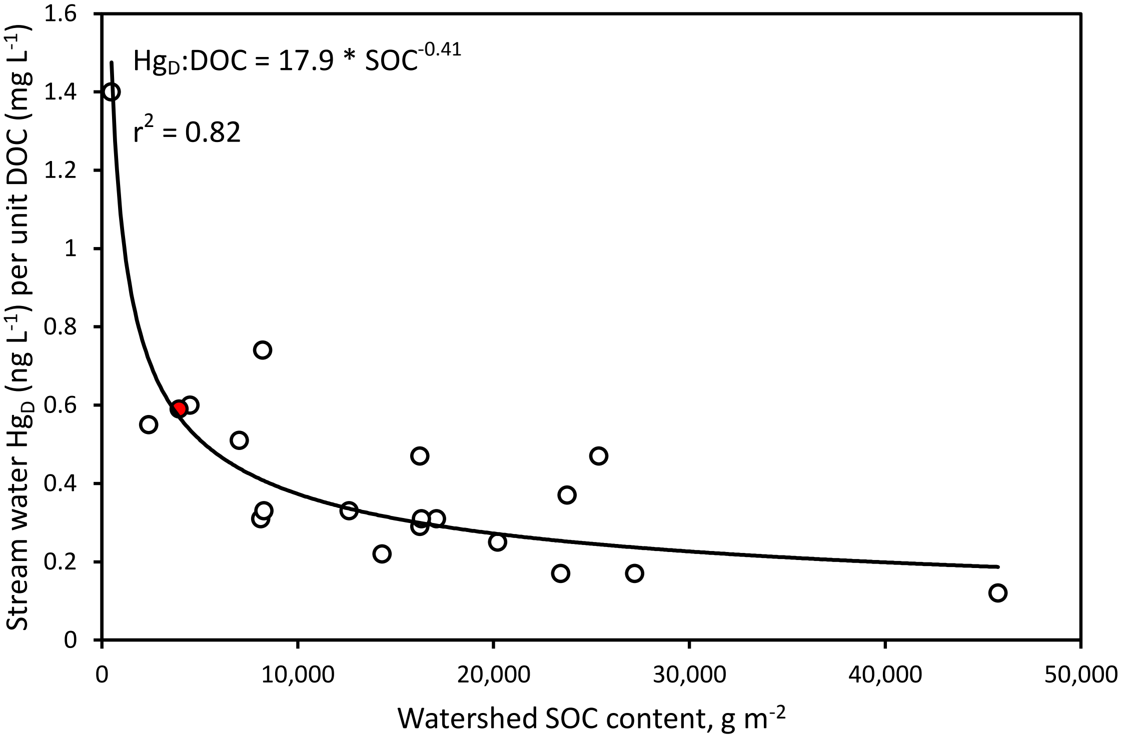

Figure 1. $Hg_D$ per unit DOC versus SOC with power-fit line from Chapter 2. Pace Estate point is colored red.

### *1.2 Local controls on $Hg_D$:DOC*

Two stream acidification experiments were conducted in a small, first-order Virginia stream to investigate the effects on $Hg_D$ and DOC concentrations. During the first acid injection experiment, samples were taken continuously at one point in the stream reach as the pH was lowered. $Hg_D$ and DOC were both removed from the stream water column as pH decreased, but the overall loss of $Hg_D$ was 19% greater than DOC. DOC quality changes were able to explain the differences in these losses. $SUVA_{254}$ data showed that more aromatic DOC was preferentially lost from the water column. The ratio of $Hg_D$:DOC decreased with pH because DOC with a higher aromaticity more efficiently binds $Hg_D$. The likely mechanism of these losses is adsorption to stream sediments or particulates enhanced by hyporheic mixing. The second acid injection experiment investigated spatial variability of $Hg_D$ and DOC along the stream reach at a steady-state acidic pH. $Hg_D$ and DOC concentrations decreased along the stream reach, but there was a significant reduction between sampling sites that occurred before and after a riffle section. It is possible enhanced hyporheic mixing in the riffle intensified the adsorption of $Hg_D$ and DOC to stream sediments. If this process is similar to what occurs in soil solution, it is possible that soil solution acidity could exert a significant control on the transport of $Hg_D$ and DOC to streams. Watersheds recovering from acidification by acid deposition in North America and Europe may have increases in stream $Hg_D$ concentrations despite stricter emissions regulations.

## 2. Avenues of future research

The biogeochemistry of Hg in soils and streams and the impacts on Hg transport have been a focus of many studies, yet there are still many questions to be answered. Hg pools in the soils of upland watersheds are potential long-term sources of Hg to streams and rivers. Identifying controls on the association $Hg_D$ and DOC is necessary to understand and predict stream export of Hg stored in watershed soils. This work has shown that at a regional scale watershed SOC can explain a large portion of the variance in $Hg_D$:DOC between watersheds. However, this study is limited to the United States and to watersheds that are relatively undisturbed. Collecting $Hg_D$, DOC, and SOC data from watersheds in other countries where watershed carbon sequestration and Hg deposition may be different and exploring different watershed land-use types (i.e. urban, agricultural) may provide greater insight into the strength of the SOC and $Hg_D$:DOC relationship. SOC in this study was derived from the SSURGO and NCSCD geospatial databases. As future databases are developed, comparisons of SOC estimates can be made between databases and to field data to provide estimates of uncertainty.

The stream acidification experiments demonstrate that pH exerts a strong control on $Hg_D$:DOC in streams and likely soil solution. Extending this work from the stream to watershed soils would provide valuable insight to the applicability of the study. This could be accomplished by acidifying soils and measuring $Hg_D$ in addition to DOC in soil solution in a natural field-setting, similarly to *Ekström et al.* (2011). Additional stream studies could also be done to gain a better understanding of the $Hg_D$ and DOC adsorption during stream acidification. First, while $SUVA_{254}$ is a good proxy, it only provides the average aromaticity for the entire pool of DOC. More detailed chemical analyses of the DOC pool, such as determining DOC fractionation (Leenheer and Croué, 2003), could provide a clearer picture of how the acid injection is affecting DOC and $Hg_D$ adsorption to sediments or particulates. The quantity and quality of DOC can vary seasonally in streams (Mulholland and Hill, 1997; Burns et al., 2013), thus acid injections conducted during different seasons may have different results for DOC fractionation. It would also be interesting to measure $Hg_D$ and DOC concentrations in the stream sediments before and during an acid injection to see if increases in sediment concentrations compare to decreases in water column concentrations. Finally, conducting similar acidification experiments in soils and streams where watershed soil properties differ may elucidate whether soil composition (i.e. clay, sand dominated) plays a role in pH effects similar to what has been found in lab studies (Yin et al., 1996).

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