2010

Trace Metal Fluxes in Southwest Ohio Watersheds

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TRACE METAL FLUXES IN SOUTHWEST OHIO WATERSHEDS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

AVANI NAIK
B.S., University of Michigan, 2007

2010
Wright State University
September 14, 2010

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY AVANI NAIK ENTITLED TRACE METAL FLUXES IN SOUTHWEST OHIO WATERSHEDS BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Naik, Avani. M. S., Department of Earth and Environmental Sciences, Wright State University, 2010. Trace Metal Fluxes in Southwest Ohio Watersheds.

Land-use and watershed characteristics affect riverine trace metal cycling and transport. I investigated land use and water physicochemistry influence on loadings, partitioning, and speciation of Hg, Zn, Cr, Ni, V, Cd, Cu, and Pb in three contrasting watersheds near the Dayton, Ohio over a 13-month period; Wolf Creek (urban), Holes Creek (urban), and Little Miami River (agricultural). Metal concentrations were related positively to discharge in each stream. Dissolved organic ligands appear to influence trace-metal partitioning; however, particulate metals were dominant in each site. Total Hg was significantly greater in Wolf Creek, indicating a source of Hg in addition to atmospheric deposition. Unlike Hg, areal fluxes of most other trace metals showed little inter-site variability indicating a ubiquitous source such as atmospheric deposition or weathering processes. Trace metal fluxes were disproportionately increased during spring in the Wolf Creek watershed suggesting pronounced seasonal flushing effect and increased mobilization.
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I. INTRODUCTION

Metals are ubiquitous in natural waters and many are present in trace quantities. Some of these so-called trace metals include zinc (Zn), lead (Pb), mercury (Hg), nickel (Ni), chromium (Cr), cadmium (Cd), copper (Cu), and vanadium (V). Trace metals at concentrations well exceeding the water quality criteria have proven to be a human health and environmental concern globally. Greater than one-sixth of the world’s population lives in close proximity to impaired water bodies (WHO, 2008). A large fraction of these water bodies are impaired due to elevated levels of trace metals. In Japan, for example, new cases of mercury poisoning emerge regularly (Davidson et al., 1998), whereas in Bangladesh and India, millions of people have their drinking water contaminated with the metalloid arsenic (Smith et al., 2000).

Trace-metal pollution of surface water also is a major concern in the United States. About a dozen trace metals and their compounds are identified in the U.S. Environmental Protection Agency’s National Priority Pollutants List for the nation’s water supply (EPA, 2009). The EPA, in the 2006 Section 303(d), also lists over 6000 water bodies as “impaired” due to metals contamination with an equal number of water bodies listed for impairment due to Hg alone. In Ohio, more than 200 water bodies are listed as being impaired, with about 25% of them having the cause of their impairment attributed to metals including Hg. There are 33 sites in Ohio listed on the U.S. EPA’s
National Priorities List, several of which are located in the Dayton area associated with the Wright-Patterson Air Force Base and several city landfills (US EPA, 2009). Thus, trace-metal contamination is pervasive, and knowledge of trace-metal sources and cycling in the aquatic systems is an environmental research priority.

**Trace Metal Exposure and Toxicity**

Exposure to trace metals can occur through many pathways including inhalation, skin absorption, and ingestion of contaminated water or food (Foy and Chaney, 1978; Peraza et al., 1998). Retention of trace metals in the body is increased greatly in humans with inadequate dietary intake of micronutrients such as iron and calcium (Peraza et al., 1998). This results in the majority of the world’s population, particularly in developing countries, vulnerable to trace metal toxicity. Human age and dosage have a significant effect on toxicity as well. Most trace metals also have a long biological half life; for example, cadmium has a half life of 17 to 30 years in humans (Peraza et al., 1998). A long half life, combined with exposure throughout a lifetime, results in bioaccumulation and a potential health threat. Because trace metals are cations, they can react with most ligands (e.g. carboxyls, thiols) present in the body. As a result, exposure can lead to severe impairment and dysfunction of cardiovascular, endocrine, enzymatic, immune, nervous, reproductive, urinary, and gastrointestinal systems (Clarkson, 1987; Peraza et al., 1998; Sakurai, 1994).

Though naturally occurring, a major fraction of trace metals in the aquatic environment can be linked to anthropogenic sources. Many metals have industrial uses
and are thus often found to be prevalent in urbanized areas. Ni and Cd, for example, are used almost exclusively for the production of batteries (Burton and Pitt, 2002). Other trace metals such as Zn, Cu, Cr and Ni are common in automobile and machinery parts (Burton and Pitt, 2002). Owing to its long-range atmospheric distribution (Lamborg et al., 2002), Hg is the most ubiquitous heavy metal in the environment. It has been used for medicinal and industrial purposes for millennia and is derived largely from the burning of fossil fuels, particularly coal (Pacyna et al., 2006). Historically, Pb has been used in many household and industrial products, including paint, plumbing, and gasoline (Burton and Pitt, 2002). Each of these metals are eventually mobilized to surface waters.

Once in aquatic systems, trace metals are subject to many processes that can change their speciation, oxidation state, and phase association. They can become bound to organic or inorganic particulate matter or be taken up biologically. Biotransformation is especially important for Hg and Pb, which enter into aquatic environment in forms that are largely unavailable biologically, but can then be methylated by microbial processes to more bioavailable forms (Burton and Pitt, 2002). Monomethylmercury (CH$_3$Hg$^+$ or MMHg) is the highly toxic form of Hg that bioaccumulates readily and biomagnifies in food webs (Weiner et al., 2003). The bioavailability and associated toxicity of trace metals often depends on their speciation and phase association. For many trace metals, the free ion is believed to more bioavailable than complexed forms. Bioavailability also can depend on the specific oxidation state of the metal in both dissolved and particulate forms (Shafer et al., 1997),
and is important in determining toxicity. For example, the ambient water criterion for 
Cr$^{3+}$ through ingestion of water and contaminated aquatic organisms is 170,000 µg/L, 
whereas the criterion for Cr$^{6+}$ is recommended to be only 50 µg/L (Burton and Pitt, 
2002). Therefore, knowledge of the speciation of trace metals in the aquatic 
environment is important to understand their bioavailability and potential toxicity.

*Trace Metal Chemistry in the Aquatic Environment*

![Diagram](image.png)

Figure 1. Schematic representation of metal partitioning in the aquatic environment. Adapted from Tessier and Campbell, 1987.

In the aquatic environment, a portion of a trace metal is complexed with 
dissolved organic and inorganic ligands, some is free ion, and another fraction is
associated with particulate matter due to adsorption, precipitation or co-precipitation, or uptake by organisms (Figure 1). Within sediments, trace metals can be bound with various phases including organic material, carbonates, metal oxyhydroxides, and as congruous mineral precipitates (Tessier and Campbell, 1987). The distribution among these phases depends on variables such as the composition and concentration of ligands and reactive solid substrates. The nature of the dissolved and solid-phase organic and inorganic ligands is affected largely by water chemistry. Lowering of pH or acidification, for example, can lead to solubilization of sediment-bound trace metals (Tessier and Campbell, 1987). In the case of Hg, it can also lead to an increase in MMHg from the acid-hydrolysis of dimethylmercury (Wood, 1985) and changes in the rate of MMHg production by bacteria (Winfrey and Rudd, 1990). Changes in the reduction-oxidation potential can lead to release of trace metals bound to sediments (Simpson et al., 1998).

Many field and laboratory studies have been conducted to understand the partitioning of trace metals between water and particles; behavior that is described most commonly with-partitioning coefficients. The distribution coefficient ($K_D; \text{L kg}^{-1}$) is defined as the ratio of the particle-bound to “dissolved,” or filtered metal concentration. Thus, a greater $K_D$ represents a greater affinity of the metal for the solid phase. $K_D$ is a function of the properties of the individual metal and of the abundance and strength of dissolved and particulate ligands, and is useful in describing the biogeochemistry of trace metals (Pankow and McKenzie, 1991).

Trace metal association with organic matter, especially dissolved organic carbon (DOC), is an important factor influencing trace metal concentrations in the dissolved
phase as well as with suspended particles (Kerr et al., 2008). DOC also can influence the bioavailability and toxicity of metals (Cloran et al., 2010; Tessier and Campbell, 1987).

Trace metals, such as Hg and Pb for example, have high affinity for DOC, and therefore, greater concentrations of DOC can have implications for trace metal solubility, transport, and cycling (Shafer et al., 1999). Greater concentrations of DOC can result in relatively lower partitioning coefficients (Hammerschmidt et al., 2004; Kerr et al., 2008).

Recent Studies

Urban stormwater has been recognized since the 1980s as a major source of dissolved and particulate trace metals to aquatic systems (Ohio Department of Natural Resources, 1980). The dissolved portion, considered to be more bioavailable, is often considered for toxicity assessment (Morel and Hering, 1993). However, particle-associated metals accumulate in sediments, where they increase the risk of toxicity to benthic aquatic organisms (Allen and Hensen, 1996) and can be remobilized to overlying water (Simpson et al., 1998). Metals can be mobilized to neighboring water bodies from both point and non-point sources (Shafer et al., 1997; Li et al., 2009; Tiefenthaler et al., 2008; Balogh et al., 2005; Eckley and Branfireun 2008). In addition to studying the effects of various parameters such as DOC, nutrients, and suspended solids on metal availability, many studies have focused on seasonal as well as intra-storm variability of dissolved and particulate metal concentrations and fluxes (Shafer et al., 1997; Li et al., 2009; Tiefenthaler et al., 2008; Balogh et al., 2005; Eckley and Branfireun 2008).

One of the first studies contrasting trace-metal fluxes from different watersheds was conducted to understand the potential influence of DOC, suspended particulate
matter (SPM), and hydrology in forested and agricultural watersheds of Wisconsin (Shafer et al., 1997). Fluvial DOC was influenced by intensity of storm events and watershed type, with greatest concentrations from forested watersheds. Dissolved metals were correlated positively with DOC, indicating that DOC is an important transport vector for metals. SPM was greater in rivers draining agricultural watersheds and corresponded well with peak discharge during storm events.

Research by Li and colleagues (2009) examined trace metal mobility and bioavailability through varying hydraulic gradients in an urban watershed of British Columbia, Canada. Greatest levels of dissolved and sediment-bound trace metals (Cu, Fe, Mn, Pb, Zn) were found in low gradient reaches, which was attributed mainly to sediment deposition and remobilization from the benthos. Deposition of trace metals was influenced by land-use changes and hydrologic characteristics. Urbanization would decrease the infiltration capacity of sediment-bound trace metals and, thus, increase mobility.

One of the most recent studies involving the study of trace metal flux and concentration at urban and non-urban watersheds was performed at Southern California (Tiefenthaler et al., 2008). Heavily urbanized and industrial watersheds had the greatest mean concentrations and fluxes of trace metals (including Cd, Cr, Cu, Pn, Hg, Ni, Cd, Ag, Zn) and fluxes were largest during early spring.

Recent work on Hg mobilization in urban stormwater runoff, by Eckley and Branfireun (2008), investigated the relationship between total Hg (THg; sum of all Hg species) and total suspended solids (TSS) and the importance of surface-derived Hg in
runoff. THg was related strongly to TSS in surface runoff ($r^2=0.77$). During dry periods, Hg and other pollutants can accumulate on surfaces from dry atmospheric deposition and non-atmospheric sources. However, no significant relationship was found between the antecedent dry conditions and Hg in runoff. Surface-derived Hg inputs could have origins from both wet and dry atmospheric deposition, automobile exhaust, anthropogenic or vegetative litter and abrasion of surface materials.

HgT and MMHg yields were contrasted between two Minnesota watersheds by Balogh and colleagues (2005). HgT fluxes increased in proportion to water discharge and decreased with increasing watershed area. MMHg fluxes also increase during periods of greater discharge. This is attributed mainly to the flushing of adjacent wetlands where MMHg is hypothesized to be produced (Balogh et al., 2005).
II. HYPOTHESES AND STUDY SITES

The purpose of this study is to understand the concentrations and fluxes of Hg, MMHg, and other trace metals (Cd, Cu, Cr, Pb, Ni, V, and Zn) in agricultural and (sub)urban watersheds of southwest Ohio. My principal hypothesis is that aqueous concentrations and fluvial fluxes of metals are greater in urbanized compared to agricultural watersheds. While there is a substantial and growing knowledge of how land use can affect riverine nutrient concentrations and fluxes, comparatively little is known for trace metals, including Hg (Balogh et al., 2005), particularly in the Midwestern United States. This study increases knowledge of trace-metal dynamics in fluvial systems by investigating particle-water partitioning and loadings as they relate to nitrate, TSS, DOC, conductivity, and pH. Seasonal variations also are expected in the fluvial fluxes and levels of trace metals. Greater fluxes and concentrations are hypothesized to occur during periods of increased discharge in spring and fall.

These hypotheses will be tested in three contrasting watersheds in the greater Dayton, Ohio, metropolitan region (Figure 2). Wolf and Holes Creeks, both in Montgomery County, were chosen to represent urban/residential watersheds (EPA, 1997). Both Wolf (Site #03217000) and Holes (Site #03217300) Creeks have gauging stations maintained by the U.S. Geological Survey (USGS, 2010) and they were the locations from which I sampled water. The watershed areas of Wolf and Holes Creeks upstream of my sampling locations are 92 and 25 km², respectively. These two streams drain into the Great Miami River, which has a total drainage area of 13,496 km² (ODNR,
The third watershed was the Little Miami River, which is representative of other agricultural catchments (about 5% urban land use) in southwest Ohio. The total drainage area of the Little Miami River is 4,545 km² and the watershed area upstream of my sampling location, at USGS gauging station (# 03242050) in Spring Valley, OH, is 492 km² (ODNR, 2002). The Waynesville, OH, waste water treatment facility (WWTF) is about eight km downstream of my sampling location on the Little Miami River. I also sampled water from the Little Miami River at a location about 2 km downstream of the facility to investigate the potential influence of waste water discharge on trace metal loadings and biogeochemistry. All three watersheds are located in the Till Plains region of the Central Lowland Province of Ohio, with the geology comprised mainly of glacial moraine deposits and Ordovician-Silurian age calcareous shales and limestones (ODNR, 2002).
III. METHODS

Water Sampling and Sample Preparation

River water was sampled from each of the watersheds over a 13-month period (April 2009–May 2010). Conductivity, pH, and temperature were measured in situ with electrochemical probes and a thermocouple. Water was sampled with clean techniques (Gill and Fitzgerald, 1985) into acid-cleaned, 2-L FEP Teflon bottles and transported promptly to Wright State University for processing and chemical analysis. Particulate and filtered (<0.2 µm) phases of metals in water were separated by vacuum filtration through polycarbonate membranes with an acid-cleaned filtration funnel. Filtrate for total metals analysis was preserved by acidification to 0.2% with HNO₃ (J.T. Baker Instra-Analyzed) and for MMHg determination by acidification to 0.2% with H₂SO₄ (J.T. Baker Instra-Analyzed) in acid-cleaned glass bottles. A separate aliquot was preserved frozen (no acid) in LDPE bottles for determination of nitrate. Membrane filters were stored frozen in acid-cleaned, 15-mL centrifuge tubes until analysis of particulate trace metals and MMHg. Samples for TSS analysis were prepared by vacuum filtration through pre-cleaned, 0.47-µm glass fiber filters with a glass filtration funnel (APHA et al., 1995). The filtrate was preserved for DOC analysis by acidification to 1% with HCl and stored refrigerated in glass vials.
Metals Analysis

Total Hg in filtered water and particles was determined by cold-vapor atomic fluorescence spectrometry (CVAFS). Particles were digested with 4 N HNO₃ in a 60 °C water bath prior to analysis (Hammerschmidt and Fitzgerald, 2006). Filtered water and particle digestates for analysis of total Hg were oxidized with BrCl for > 12 h and pre-reduced with NH₂OH prior to an aliquot being reduced with SnCl₂ and Hg determination by dual-Au amalgamation CVAFS (Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988). Total Hg determinations were calibrated versus Hg⁰ taken from the headspace over pure liquid (Gill and Fitzgerald, 1987) and verified by comparison to analyses of aqueous Hg²⁺ standards traceable to the U.S. National Institute of Standards and Technology (NIST). Recovery of aqueous Hg²⁺ averaged 106 ± 12% (n = 40) for filtered water and 102 ± 12% (n = 24) for particle digestates. The precision of determinations was quantified by analysis of replicate subsamples. The precision of duplicate measurements averaged 8.7 RPD (range, 0.06–30; n = 25) for filtered water and 10.2 RPD (range, 0.06–18, n = 48) for particles. Detection limits for total Hg analyses were 0.01 ng/L for both filtered and particle digestates. Recovery of known Hg additions from river water averaged 95 ± 4% (n = 3).

MMHg was measured in particle digestates and filtered water by flow-injection, gas-chromatographic CVAFS (Bloom, 1989; Tseng et al., 2004). Filtered water was
reacted with 1% H$_2$SO$_4$ for 12 h prior to direct ethylation derivatization with sodium tetraethylborate (Bowman and Hammerschmidt, submitted), whereas aliquots of the digestates were reacted directly with the derivatizing agent after pH adjustment with acetate buffer. Determinations of sample MMHg were calibrated with an aqueous solution of CH$_3$HgCl that was standardized versus Hg$^0$ and a NIST-traceable Hg$^{2+}$ standard. Accuracy of MMHg measurements was assessed by analysis of procedural standards, blanks, known additions, and replicate subsamples. Precision of MMHg determinations averaged 20.1 RPD (range, 1.5–41, $n = 27$). Recovery of known MMHg additions from river water averaged 90 ± 7% ($n = 6$).

Particle and filtered Cd, Cu, Cr, Pb, Ni, V, and Zn were determined by inductively coupled plasma mass spectrometry (ICPMS) with a PerkinElmer ELAN 9000 (U.S. EPA, 2007). Metals in filtered water were measured directly, and particle samples were digested with 4 N HNO$_3$ in a 60$^\circ$C water bath prior to analysis (Hammerschmidt and Fitzgerald, 2006). All metals analyses were calibrated with procedural standards traceable to the U.S. NIST. Quality assurance analyses included procedural and filtration blanks, replicate samples, and sample aliquots with known additions of metals. ICPMS measurements were recalibrated 15 samples to minimize potential bias associated with changing instrument sensitivity. The recovery and precision of measurement varied among metals, with higher precision and recoveries for metals with greater concentrations. The average RPD for filtered and particulate metals determinations were 20 ($n = 32$) and 6 ($n = 35$), respectively. Spike recoveries for aqueous samples were 87 ± 16 % ($n = 7$).
Metal concentrations on particles were normalized to the mass of TSS to estimate a particle-specific concentration:

\[
\text{Solid-phase metal (µg kg}^{-1}\) = \frac{\text{conc. of metal from digested filter (µg L}^{-1}\)}{\text{TSS (kg L}^{-1}\)} \tag{Equation 1}
\]

Distribution coefficients were calculated from particle-specific concentrations according to the following equation:

\[
K_D (\text{L kg}^{-1}) = \frac{\text{solid-phase metal (µg kg}^{-1}\)}{\text{filtered metal (µg L}^{-1}\)} \tag{Equation 2}
\]

**Ancillary Physicochemistry**

DOC was measured by an infrared combustion method with Apollo 9000 TOC/TN Combustion Analyzer (Sharp et al., 1995). Filtered nitrate (ion chromatography) and TSS (gravimetric) were determined with standard methods (APHA et al., 1995).

Precision of duplicate nitrate and DOC measurements averaged 9.7 RPD (range, 0.1–20, \(n = 14\)) and 4.3 RPD (range, 0.2–20, \(n = 20\)).
IV. RESULTS AND DISCUSSION

**Stream physicochemistry.** Water physicochemistry varied among the three streams over the 13-month sampling period (Table S1). Statistical tests were used to compare pH, temperature, conductivity, TSS, DOC, and NO$_3^-$ among streams to understand their potential influence on trace metal concentrations and partitioning. ANOVA tests showed that temperature ($p$-value = 0.35), pH ($p$-value = 0.07), and TSS ($p$-value = 0.96) were similar among all three streams, with each having an annual temperature range of about 1–24 °C, a mean annual pH of about 8.3, and an average suspended sediment load of about 30 mg/L (Table S1). Similarities of temperature and pH were expected because the watersheds have the same base geology, replete with calcareous shales and limestones that buffer the water (ODNR, 2002), and are subject to the same climate and weather variations. In contrast, Holes Creek had greater levels of DOC than Little Miami River (TUKEY, $p$-value = 0.02) and greater conductivity than either of the other two streams (TUKEY, $p$-value < 0.001). Nitrate was significantly different among each watershed (TUKEY, $p$-values < 0.05), with the Little Miami River (mean annual NO$_3^-$, 11.2 ± 4.0 mg L$^{-1}$), the agricultural/residential watershed, having greater concentrations than Wolf (8.0 ± 7.2 mg L$^{-1}$) and Holes (4.6 ± 2.7 mg L$^{-1}$) Creeks.

Differences in water physicochemistry also were evident seasonally and corresponded with hydrography. Each stream had four distinct hydraulic periods; greatest discharge occurred during wet seasons identified, for the purpose of this study, as spring (March 1 to June 30; Julian days: 60–181) and fall (September 1 to
November 30; Julian days: 244–334) interspersed by drier periods in the summer and winter (Figure S1). Significant differences in either stage height (Little Miami River, TUKEY; p-value < 0.05) or volumetric discharge (Holes and Wolf Creeks, TUKEY: p-values < 0.001) were observed among all seasons except between spring and fall, which had similarly high discharge. In each stream, pH was greater in winter and spring compared to summer and fall (TUKEY, p-values < 0.05), presumably as a result of differences in biological respiration. Conductivity was greatest during winter (TUKEY, p-value < 0.001) whereas DOC was significantly greater during spring and fall, seasons of high discharge, than in winter and summer in each stream (TUKEY, p-values < 0.05). Increased conductivity in winter, especially in Holes Creek, is attributed to runoff to road salt and is evidenced by increased levels of chloride. DOC and TSS were related positively with either volumetric discharge or stage height in each river (Figures S2 and S3), which is typical of other rivers (e.g., Brigham et al., 2009). Seasonal variation was not significant for nitrate (ANOVA, p-value = 0.051).

**Total Hg.** Levels of total Hg also differed among the three streams (Table 1). Total Hg in filtered water (< 0.2 µm) was greater in Wolf Creek than in Holes Creek or the Little Miami River (TUKEY, p-values < 0.05). Increased total Hg in the Wolf Creek watershed also was evident when filtered and particle concentrations were added to estimate an “unfiltered” concentration (i.e., Hg_U = Hg_F + Hg_P). Unfiltered total Hg also was greater in Wolf Creek than either of the other two watersheds (TUKEY, p-values < 0.05), which were not statistically different from each other. Levels of total Hg in
southwest Ohio streams are comparable to those at other locations in North America (Table 2). On average, about 70% of Hg in the three streams was associated with particles (Table 1). Atmospheric deposition is a principal source of Hg to most locations (Fitzgerald et al., 1998), and it is presumed that atmospheric fluxes of Hg are comparable among each of these nearby watersheds (MDN, 2010). Accordingly, increased levels of total Hg in Wolf Creek must be related to either point sources in the watershed or watershed characteristics that enhance the delivery of Hg to the stream (Li et al., 2009).

Total Hg varied seasonally in each stream (Figure 3). Total Hg was generally lowest during periods of low stream discharge in summer and winter and increased during the spring and fall. Indeed, levels of filtered Hg were significantly greater in fall and spring than in winter, and unfiltered Hg was enhanced in fall compared to winter (TUKEY, p-values < 0.05). In each stream, unfiltered total Hg was related positively to instantaneous discharge ($r^2 = 0.23–0.76$; p-values < 0.05, Figure S4). The correlation between unfiltered Hg and water discharge can be dissected into two components that affect the transport of Hg —DOC and TSS, both of which also were correlated positively with instantaneous discharge (Figures S2 and S3).

Filtered total Hg was related to DOC in southwest Ohio streams (Figure 4). A similar relationship was observed in the Scioto River, Ohio (Lyons et al., 2006). DOC is a transport vector for dissolved metals (Shafer et al., 1997) and such a relationship between filtered Hg and DOC might be expected given the high affinity of Hg$^{2+}$ dissolved organic ligands (Lamborg et al., 2003). However, the ratio of Hg:DOC is much less than
expected if all of the Hg-binding organic ligands ($L$) were saturated with Hg. Measured $L$:DOC ratios in river water range from about 10–80 × 10^{-6} (Lamborg et al., 2004). Accordingly, for river water that contains from 2 to 20 mg L^{-1} DOC (Figure 4), one would predict a dissolved $L$ concentration of 2 to 130 nM, which is substantially greater than measured Hg in the filtered fraction (0.003–0.01 nM). This suggests that Hg-binding organic ligands associated with DOC are not fully saturated with Hg. This may result from competition by other metals for the same binding sites.

Additionally, particulate total Hg was related strongly to TSS (Figure 5). Similar relationships have been observed in the Hudson River estuary (Balcom et al., 2008) and rivers draining into Chesapeake Bay (Lawson and Mason, 2001). Hg species are associated largely with the organic phase of particulate material (Hammerschmidt et al., 2004). It was surprising to find such similarity in the particle Hg versus TSS relationship among streams, given that the organic content of suspended particles can vary independently of TSS and that particulate organic matter has been thought to be a better proxy than TSS for HgT (Hydroqual, 2006; Mason and Sullivan, 1998; Mason et al., 1999). This suggests that the composition of particles is fairly consistent among all three streams, and this is supported by similarities of the particle-water partitioning of Hg.

Distribution coefficients of total Hg were comparable among the three study streams (Table 1). Partitioning coefficients of total Hg in southwest Ohio streams are within the range of those determined in other fluvial systems, including the Hudson River estuary (log $K_D = 5.3$–6.5 L kg^{-1}; Balcom et al., 2008), Maryland rivers (log $K_D =$
5.1–5.5 L kg$^{-1}$; Lawson et al., 2000), and Wisconsin, Florida, and Oregon rivers (log $K_D =$ 2.8–6.6 L kg$^{-1}$; Brigham et al., 2009), although they are modestly greater than those measured in the Scioto River in central Ohio (log $K_D =$ 4.4–4.9 L kg$^{-1}$; Lyons et al., 2006).

Distribution coefficients of total Hg were related inversely to DOC (Figure 6; $r^2 = 0.22$, p-value<0.001). This suggests that proportionately more of the Hg is in the filter-passing phase of water as DOC increases. This can be explained by DOC competing with particle-phase ligands for Hg. That is, proportionately more Hg complexes with dissolved organic ligands when DOC is increased. An alternative hypothesis is that the affinity of Hg for particles decreases under conditions that correspond with greater DOC levels. I have observed that both DOC and TSS are correlated positively with instantaneous discharge. One might expect that greater stream discharge would suspend particles that have a lower affinity of Hg (e.g., sand, clay) than organic material (Hammerschmidt et al., 2004) and thereby lower the $K_D$. Indeed, the distribution coefficient of total Hg also was related inversely to TSS ($r^2 = 0.56$; p-value < 0.001; Figure 7), which would seem to support a “particle-dilution” hypothesis. However, particulate Hg concentration is related strongly to TSS concentration and, by extension, instantaneous discharge (Figure 5). Such a relationship would not be expected if particle dilution were operative: Particle dilution would result in Hg$_P$ not increasing with TSS. Together, these results imply that differences in the particle-water partitioning of Hg are influenced by variations of dissolved organic ligands in my study streams.

Particle-specific concentrations of Hg were highly variable in suspended solids within and among the three study streams (Table 1). Suspended solids in Holes Creek
and the Little Miami River contained between about 10 and 400 ng g\(^{-1}\) Hg. These concentrations are within the range of those measured in surface soils of Greene and Montgomery counties (range, 0.7–373 ng Hg g\(^{-1}\) dry weight; Tabatchnick, 2010). In contrast, suspended material in Wolf Creek contained from about 20 to 1700 ng Hg g\(^{-1}\). Concentrations at the upper end of this range are much greater than can be explained from atmospheric deposition alone and suggest that Wolf Creek watershed has current or historic point sources of Hg, which is consistent with differences of Hg in filtered water among streams.

**MMHg.** In contrast to total Hg, filtered MMHg was measured during spring, summer, and fall only. Mean levels of filtered MMHg were comparable among each of the three streams and averaged about 0.04 ng L\(^{-1}\) (Table 1). For the April–December sampling period, filtered MMHg averaged 5.6% (range, 0.11–35%) of filtered total Hg which is comparable to rivers in Connecticut (2–5%, Balcom et al., 2004), Wisconsin (0.2 – 11%, Hurley et al., 1995), and Maryland (0.8 – 3%, Lawson and Mason, 2001). Mean MMHg levels in southwest Ohio streams are considerably less than those in agricultural watersheds of Minnesota (0.20–0.35 ng/L; Balogh et al., 2005) but within the range of those in Wisconsin (0.03–0.09 ng/L; Hurley et al., 1995) and Connecticut (0.04–0.40 ng/L; Balcom et al., 2004). Filtered MMHg was significantly less in summer than during spring or fall (TUKEY, \(p\)-values \(\leq 0.004\)), which did not differ. Similar seasonal differences of MMHg have been observed in Minnesota and Wisconsin rivers (Hurley et al., 1995; Balogh et al., 2005), streams in the Chesapeake Bay watershed (Lawson et al.,
Seasonal variations of MMHg have been attributed to production in watershed soils and subsequent mobilization through high discharge events during spring. However, no significant relationship between filtered MMHg and discharge was found for this study ($p$-value = 0.76).

**Other trace metals.** Unlike total Hg, levels of Cd, Cu, Cr, Pb, Ni, V, Zn were not different among streams (Table 2). The only exceptions to this generalization were filtered Ni being less in Wolf Creek than the other two streams (TUKEY, $p$-value < 0.001), filtered Cu being greater in Holes Creek (TUKEY, $p$-value < 0.001), and particulate Cd being greater in Wolf Creek. Additionally, and also in contrast to total Hg and MMHg, there was no seasonal variation of trace metal concentrations, with the exception of Pb being reduced in summer (TUKEY, $p$-value < 0.001) and Cr being greater in spring than in any other season (TUKEY, $p$-value < 0.05). Sources of these metals include atmospheric deposition, weathering processes, and local anthropogenic inputs. The relative similarity of trace metal concentrations among streams suggests that the dominant source is ubiquitous, which is consistent with inputs from either weathering or atmospheric deposition. Indeed, Pb levels in rivers have been found to correspond well with Pb in wet atmospheric deposition (Lawson and Mason, 2001).

Similar to Hg, each of the seven trace metals exhibited a high affinity for suspended solids. Particulate metal concentrations were related significantly and positively with TSS ($Cd, r^2 = 0.35; Cu, r^2 = 0.36; Cr, r^2 = 0.55; Pb, r^2 = 0.61; Ni, r^2 = 0.59; V,$
With the exception of Pb and V, the affinity of each metal for suspended particles was less than that of Hg (Table 3). For metals with \( \log K_D \approx 4 \), a suspended solid concentration of about 100 mg L\(^{-1} \) is required for the particle phase to dominate speciation (Lawson et al., 2000), TSS levels that were rarely observed in this study. In contrast, particles dominate trace metal speciation at much lower TSS levels when the \( K_D \) is greater (Lawson et al., 2000). This phenomenon likely explains why coefficients of determination for particulate metal versus TSS concentrations are typically greater for Hg and Pb than the other metals. Distribution coefficients of trace metals in the study streams are within the range of those reported for rivers in Wisconsin (Shafer et al., 1998) and Maryland (Lawson et al., 2000).

**Impact of wastewater treatment plant.** The Little Miami River, unlike Wolf and Holes Creeks, is the receiving water for several wastewater treatment facilities upstream of the gauging station and my sampling location. To investigate to the potential of these facilities on water quality and metals loadings, I also sampled water from the river at a location 8 km downstream, about 2 km below the outfall of the Waynesville, OH, facility. Samples were collected at the downstream site about 30 minutes after sampling the upstream location, on each of the sampling days. None of the measured physicochemical variables or trace metal concentrations differed significantly between the upstream and downstream sampling locations (paired \( t \)-test, \( p \)-values > 0.3). While I did not sample effluent from the waste water treatment facility,
these results indicate that it was not a significant source of metals to the river. By extension, I infer that upstream facilities also do not influence substantially levels of trace metals in the Little Miami River.

**Hg fluxes.** The areal flux of total Hg can be estimated for Wolf and Holes Creeks watersheds. Unfiltered total Hg concentrations were a function of discharge in each creek (Figure S4). Accordingly, a discharge-weighted mean Hg concentration was estimated for each stream at the mean instantaneous volumetric discharge during the study period (Holes Creek = 0.94 m$^3$s$^{-1}$; Wolf Creek = 2.48 m$^3$s$^{-1}$). Watershed fluxes were estimated as the product of discharge-weighted mean concentrations (Holes Creek = 2.31 ± 1.12 ng L$^{-1}$; Wolf Creek = 4.97 ± 0.68 ng L$^{-1}$) and measured annual water discharge (Holes Creek = 0.022 km$^3$ y$^{-1}$; Wolf Creek = 0.070 km$^3$ y$^{-1}$). Uncertainty of the discharge-weighted mean is the 95% confidence interval of the linear regression of unfiltered total Hg versus discharge. Discharge-weighted mean concentrations were similar to the arithmetic mean in each stream (Holes = 2.33 ng L$^{-1}$; Wolf = 5.05 ng L$^{-1}$). Mass fluxes of Hg were normalized for upstream watershed area (Holes Creek = 25 km$^2$; Wolf Creek = 92 km$^2$) to estimate an areal flux. Estimated watershed fluxes of Hg were 2.0 ± 0.2 µg m$^{-2}$ y$^{-1}$ for Holes Creek and 3.8 ± 1.0 µg m$^{-2}$ y$^{-1}$ for Wolf Creek.

The same approach was used to estimate total Hg fluxes from Wolf and Holes Creeks watersheds during the period of high discharge in spring, when the mean instantaneous volumetric discharge (Holes Creek = 1.3 m$^3$s$^{-1}$; Wolf Creek = 3.5 m$^3$s$^{-1}$) and volume-weighted Hg concentrations (Holes Creek = 2.61 ± 0.27 ng L$^{-1}$; Wolf Creek =
6.36 ± 1.30 ng/L) were increased. Estimated watershed fluxes of Hg during this 122-d period account for 51% of the annual flux from Holes Creek watershed and 74% of the annual flux from Wolf Creek. Given that 45% and 58% of the volumetric discharge occurs during this period, it appears that a disproportionate amount of Hg is mobilized during the spring from Wolf Creek.

Instantaneous discharge was not measured at my sampling location on the Little Miami River; however, the mean volumetric discharge at Spring Valley was measured to be 0.38 ± 0.12 km$^3$ y$^{-1}$ during a 15-y period from 1968 to 1983 (USGS, 2010). Additionally, I can estimate the annual water discharge of the Little Miami River at Spring Valley from the upstream watershed area and assuming precipitation runoff in the Little Miami watershed is similar to that in Wolf (0.76 m y$^{-1}$) and Holes (0.86 m y$^{-1}$) Creeks. These values were estimated by dividing measured volumetric discharge by watershed area. The product of watershed area (492 km$^2$) and estimated runoff velocity (0.8 m y$^{-1}$) for the Little Miami River yields an estimated volumetric flux for the study period of 0.39 km$^3$ y$^{-1}$, which is in good agreement with the 15-y mean (0.38 ± 0.12 km$^3$ y$^{-1}$).

The areal flux of Hg from the Little Miami River watershed was estimated as the product of arithmetic mean (± SD) concentration of unfiltered Hg (3.17 ± 3.02 ng L$^{-1}$) and annual volumetric flux normalized for watershed area. A discharge-weighted mean could not be determined for the Little Miami River, but I found it is similar to the arithmetic mean in Wolf and Holes Creeks. The estimated watershed flux of Hg from the Little Miami watershed is 2.4 ± 2.3 µg m$^{-2}$ y$^{-1}$. Areal Hg fluxes from the three study
watersheds are within the range of those at other locations; 1.4–22.2 µg m\(^{-2}\) y\(^{-1}\) in Chesapeake Bay watersheds (Lawson and Mason, 2001; Lawson et al., 2000), 2.4 µg m\(^{-2}\) y\(^{-1}\) in the Connecticut River watershed (Balcom et al., 2004), 0.16–20 µg m\(^{-2}\) y\(^{-1}\) in Wisconsin rivers (Hurley et al., 1995), 0.26–6.4 µg m\(^{-2}\)y\(^{-1}\) in Minnesota watersheds (Balogh et al., 2005), and 0.87–1.36 µg m\(^{-2}\)y\(^{-1}\) for catchments in Oregon, Wisconsin and Florida (Brigham et al., 2009).

Estimated wet atmospheric deposition of Hg in southwest Ohio is about 10 µg m\(^{-2}\) y\(^{-1}\) (MDN, 2010). Prior studies have found that about 25% of Hg deposited atmospherically to terrestrial catchments is exported to receiving waters (Swain et al., 1992; Lawson and Mason, 2001; Engstrom et al., 1994). Accordingly, I would predict that runoff of atmospherically deposited Hg would be about 2.5 µg m\(^{-2}\) y\(^{-1}\) in my three watersheds. This is consistent with measured fluxes in Holes Creek (2.0 ± 0.2 µg m\(^{-2}\) y\(^{-1}\) ) and the Little Miami River (2.4 ± 2.3 µg m\(^{-2}\) y\(^{-1}\) ) and suggests that atmospheric deposition is the principal source of Hg to these catchments. The flux of Hg from the Wolf Creek watershed (3.8 ± 1.0 µg m\(^{-2}\) y\(^{-1}\) ) is considerably greater than that predicted from atmospheric deposition alone. The greater export of Hg from Wolf Creek suggests that either atmospherically deposited Hg is more mobile in this watershed or that there are sources of Hg in addition to atmospheric deposition. While neither hypothesis can be tested unequivocally in this study, the unusually high levels of particle-specific Hg in Wolf Creek strongly suggest that there are point sources of Hg in the watershed.
Trace metal fluxes. Watershed fluxes were calculated similarly for the other trace metals, both on an annual and seasonal basis (Table 4). The only exception being Cr in Wolf and Holes Creeks, where arithmetic mean concentrations were used because Cr levels were unrelated to discharge. Fluxes of Cd, Cu, Cr, Pb, Ni, V, and Zn were orders of magnitude greater than those of Hg in each of the three streams (Table 4), however, they compare well with those the Potomac and Susquehanna River watersheds (Lawson et al., 2000). As observed for Hg, almost 50% or more of the trace metal flux occurred during spring. The similarities of trace metal fluxes among the three watersheds suggest common sources, including, for example, atmospheric deposition and weathering. However, the Wolf Creek watershed appears to have a disproportionately high efflux of many metals, particularly Cu, Pb, V, Zn, and Hg, during spring compared to the rest of the year. This indicates that metals may be more mobile in Wolf Creek watershed compared to Holes Creek, where annual proportion of metals flux during the spring (39–55%) is comparable to the fraction of volumetric discharge that occurs during this period (45%). Greater mobility in the Wolf Creek watershed could be attributed to a greater extent of paved surfaces (Eckley and Branfireun, 2008).
VI. IMPLICATIONS

The results of this study suggest that, with the exception of Hg, metals loadings to streams in southwest Ohio are relatively homogeneous and independent of land use. This suggests that factors that affect the source strength of metal delivery to the watersheds will subsequently influence trace metal loadings in rivers. An obvious factor would be point source discharges of trace metals. However, a less obvious factor could be climate change. I have hypothesized that either atmospheric deposition or weathering reactions are the source of most metals to my study streams. Accordingly, a warmer and wetter climate would be expected to cause greater metal loadings to streams. Increased precipitation will result in greater atmospheric fluxes, and increased precipitation and temperature will enhance weathering reactions. The effect of greater metal loadings on aquatic biota is less certain and may be mitigated by suspended solids and DOC attenuating bioavailability.
VII. LITERATURE CITED


Table 1. Annual mean (± 1 SD) concentrations and distribution coefficients ($K_D$) of Hg species in the three study streams ($n = 61$ for each). MMHg was sampled from April – December 2009.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Filtered Hg (ng L$^{-1}$)</th>
<th>Particulate Hg (ng L$^{-1}$)</th>
<th>Particulate Hg (ng g$^{-1}$)</th>
<th>log $K_D$ Hg (L Kg$^{-1}$)</th>
<th>Filtered MMHg (ng L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wolf Creek</td>
<td>1.50 ± 2.12</td>
<td>3.43 ± 6.04</td>
<td>302 ± 304</td>
<td>5.35 ± 0.60</td>
<td>0.036 ± 0.026</td>
</tr>
<tr>
<td>Holes Creek</td>
<td>0.87 ± 0.78</td>
<td>1.44 ± 1.66</td>
<td>133 ± 83</td>
<td>5.18 ± 0.50</td>
<td>0.040 ± 0.032</td>
</tr>
<tr>
<td>Little Miami R.</td>
<td>0.75 ± 0.52</td>
<td>2.48 ± 2.86</td>
<td>107 ± 57</td>
<td>5.17 ± 0.38</td>
<td>0.043 ± 0.027</td>
</tr>
</tbody>
</table>
Table 2. Annual mean (± 1 SD) concentrations of trace metals in filtered (<0.2 µm) and particulate phases of water from Wolf Creek, Holes Creek, and Little Miami River (LMR).

<table>
<thead>
<tr>
<th>Stream</th>
<th>Metals in filtered water (µg L⁻¹)</th>
<th>Particulate metals (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Cr</td>
</tr>
<tr>
<td>Wolf Creek</td>
<td>4.06 ± 8.53</td>
<td>2.53 ± 5.27</td>
</tr>
<tr>
<td>Holes Creek</td>
<td>3.22 ± 3.76</td>
<td>2.77 ± 2.24</td>
</tr>
<tr>
<td>LMR</td>
<td>3.98 ± 2.91</td>
<td>3.29 ± 3.33</td>
</tr>
<tr>
<td>Wolf Creek</td>
<td>4.86 ± 7.40</td>
<td>0.51 ± 0.79</td>
</tr>
<tr>
<td>Holes Creek</td>
<td>3.78 ± 5.73</td>
<td>0.64 ± 0.71</td>
</tr>
<tr>
<td>LMR</td>
<td>4.17 ± 3.63</td>
<td>0.87 ± 0.74</td>
</tr>
</tbody>
</table>
Table 3. Mean (± 1 SD) distribution coefficients ($K_D$) of trace metals in the three study streams ($n = 37–61$).

<table>
<thead>
<tr>
<th>Stream</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wolf Creek</td>
<td>4.85 ± 0.61</td>
<td>4.43 ± 0.58</td>
<td>4.62 ± 0.48</td>
<td>4.06 ± 0.24</td>
<td>6.39 ± 0.46</td>
<td>4.52 ± 0.35</td>
<td>5.16 ± 0.47</td>
</tr>
<tr>
<td>Holes Creek</td>
<td>4.46 ± 0.62</td>
<td>4.33 ± 0.42</td>
<td>4.26 ± 0.36</td>
<td>3.94 ± 0.43</td>
<td>6.03 ± 0.49</td>
<td>4.38 ± 0.42</td>
<td>4.99 ± 0.51</td>
</tr>
<tr>
<td>LMR</td>
<td>4.55 ± 0.52</td>
<td>4.13 ± 0.50</td>
<td>4.39 ± 0.48</td>
<td>3.75 ± 0.26</td>
<td>5.9 ± 0.39</td>
<td>4.18 ± 0.30</td>
<td>4.64 ± 0.38</td>
</tr>
</tbody>
</table>
Table 4. Annual areal trace metal fluxes for Wolf Creek, Holes Creek and Little Miami River (LMR) with percent (%) of annual flux during spring period.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wolf Creek</td>
<td>0.040±0.010</td>
<td>2.3±1.9</td>
<td>1.6±0.2</td>
<td>2.5±0.1</td>
<td>0.8±0.2</td>
<td>1.0±0.20</td>
<td>6.0±1.3</td>
</tr>
<tr>
<td>% in Spring</td>
<td>69</td>
<td>46</td>
<td>73</td>
<td>63</td>
<td>89</td>
<td>73</td>
<td>70</td>
</tr>
<tr>
<td>Holes Creek</td>
<td>0.033±0.005</td>
<td>2.9±1.9</td>
<td>2.7±0.4</td>
<td>3.4±0.1</td>
<td>0.5±0.1</td>
<td>1.8±0.4</td>
<td>5.7±1.1</td>
</tr>
<tr>
<td>% in Spring</td>
<td>48</td>
<td>39</td>
<td>48</td>
<td>47</td>
<td>55</td>
<td>48</td>
<td>50</td>
</tr>
<tr>
<td>LMR</td>
<td>0.027±0.010</td>
<td>3.1±1.3</td>
<td>1.8±1.0</td>
<td>3.0±0.5</td>
<td>0.7±0.5</td>
<td>1.4±0.7</td>
<td>6.4±2.2</td>
</tr>
</tbody>
</table>
Figure 3. Temporal variation of unfiltered total Hg (HgT) and either instantaneous discharge at Wolf (a) and Holes (b) Creeks or instantaneous stage height at Little Miami River (c) over the 13-month sampling period.
Figure 4. Combined linear regression of filtered total mercury (Hg_F) versus dissolved organic carbon (DOC) in Wolf and Holes Creeks and Little Miami River (LMR).

$H_{g_{F}} = 0.06 \text{(DOC)} - 0.46$

$r^2 = 0.27$

$p < 0.001$
Figure 5. Correlation between particulate total mercury (Hg$_P$) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).

$Hg_P = 0.58 \cdot \text{TSS} - 0.45$

$r^2 = 0.64$

$p < 0.001$
Figure 6. Variation of the distribution coefficient ($K_D$) of total Hg with dissolved organic carbon (DOC) in the three study sites.

$\log K_D = -7.5 \text{ (DOC)} + 0.76$

$r^2 = 0.22$

$p < 0.001$
Figure 7. Variation of the distribution coefficient ($K_D$) of total Hg with total suspended solids (TSS) in the three study streams.

$\log K_D = -0.06 (\log \text{TSS}) + 0.77$

$r^2 = 0.56$

$p < 0.001$
## VIII. APPENDIX

Table S1. Mean annual (range) physicochemical characteristics of water in Wolf Creek, Holes Creek, and Little Miami River (LMR).

<table>
<thead>
<tr>
<th>Stream</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Conductivity (µS m⁻¹)</th>
<th>DOC (mg L⁻¹)</th>
<th>NO₃ (mg L⁻¹)</th>
<th>TSS (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wolf Creek</td>
<td>8.39</td>
<td>13.1</td>
<td>735</td>
<td>5.5</td>
<td>8.0</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>(8.01-8.97)</td>
<td>(0.10-22.1)</td>
<td>(235-1280)</td>
<td>(1.8-16.1)</td>
<td>(0.0-54.9)</td>
<td>(1-471)</td>
</tr>
<tr>
<td>Holes Creek</td>
<td>8.30</td>
<td>13.4</td>
<td>959</td>
<td>6.2</td>
<td>4.6</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>(7.39-8.85)</td>
<td>(0.9-23.9)</td>
<td>(331-2338)</td>
<td>(2.1-16.6)</td>
<td>(1.0-18.0)</td>
<td>(1-299)</td>
</tr>
<tr>
<td>LMR</td>
<td>8.30</td>
<td>14.3</td>
<td>775</td>
<td>5</td>
<td>11.2</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>(7.90-8.80)</td>
<td>(0.4-25.2)</td>
<td>(248-1154)</td>
<td>(2.2-14.1)</td>
<td>(5.6-27.8)</td>
<td>(3-225)</td>
</tr>
</tbody>
</table>
Table S2. Comparison of total Hg concentrations in southwest Ohio streams with other locations.

<table>
<thead>
<tr>
<th>Streams</th>
<th>Hg Concentration (ng L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Filtered</td>
</tr>
<tr>
<td>SW Ohio streams (This study)</td>
<td>0.52 – 2.12</td>
</tr>
<tr>
<td>Minnesota rivers (Balogh et al., 2005)</td>
<td>--</td>
</tr>
<tr>
<td>Wisconsin rivers (Hurley et al., 2005)</td>
<td>0.28 – 24.2</td>
</tr>
<tr>
<td>Connecticut rivers (Balcom et al., 2004)</td>
<td>0.24 – 3.40</td>
</tr>
<tr>
<td>Maryland rivers (Lawson et al., 2000)</td>
<td>--</td>
</tr>
<tr>
<td>Scioto R., central Ohio (Lyons et al., 2006)</td>
<td>0.52 – 2.6</td>
</tr>
</tbody>
</table>
Figure S1. Hydrologic variability of mean daily discharge at Wolf (a) and Holes (b) Creeks and mean weekly stage height at Little Miami River (c) over the 13-month sampling period.
Figure S2. Dissolved organic carbon (DOC) versus either instantaneous discharge for Wolf and Holes Creeks, or instantaneous stage height for Little Miami River (LMR). (Wolf Creek: \( y = 0.35x + 0.62 \), \( r^2 = 0.41 \); Holes Creek: \( y = 0.13x + 0.82 \), \( r^2 = 0.15 \); LMR: \( y = 0.65x + 0.66 \), \( r^2 = 0.18 \); p-values < 0.05).
Figure S3. Total suspended solids (TSS) versus either instantaneous discharge for Wolf and Holes Creeks or instantaneous stage height for Little Miami River (LMR). (Wolf Creek: $y = 1.31 \times + 0.65$, $r^2 = 0.66$; Holes Creek: $y = 0.88 \times + 1.38$, $r^2 = 0.59$; LMR: $y = 2.67 \times + 1.22$, $r^2 = 0.48$; p-values < 0.05).
Figure S4. Unfiltered Total Hg versus either instantaneous discharge for Wolf and Holes Creeks or instantaneous stage height for Little Miami River (LMR). (Wolf Creek: $y = 1.3 x + 1.7$, $r^2 = 0.48$; Holes Creek: $y = 0.8 x + 1.5$, $r^2 = 0.77$; LMR: $y = 6.47 x - 3.83$, $r^2 = 0.44$; p-values < 0.001).
Figure S5. Correlation between particulate zinc (Zn\textsubscript{p}) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).
Figure S6. Correlation between particulate chromium ($\text{Cr}_p$) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).
Figure S7. Correlation between particulate nickel ($\text{Ni}_p$) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).

$\text{Ni}_p = 0.81 \text{ (TSS)} - 1.39$

$r^2 = 0.59$

$p < 0.001$
Figure S8. Correlation between particulate vanadium (V<sub>P</sub>) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).
Figure S9. Correlation between particulate cadmium ($\text{Cd}_p$) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).
Figure S10. Correlation between particulate copper (Cu\textsubscript{p}) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).

Cu\textsubscript{p} = 0.75 (TSS) – 1.14

r\textsuperscript{2} = 0.35

p < 0.001
Figure S11. Correlation between particulate lead (Pbₚ) and total suspended solids (TSS) in Wolf and Holes Creeks and Little Miami River (LMR).

\[ \text{Pb}_p = 0.80 \times \text{TSS} - 1.29 \]

\[ r^2 = 0.61 \]

\[ p < 0.001 \]
Figure S12. Relationship between the metal partitioning coefficients ($K_D$) and atomic mass of metals in this study.
Figure S13. Relationship between partitioning coefficient ($K_D$) and the percentage of trace-metal flux during the spring period for Wolf Creek.