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Estimating Watershed Mercury Contribution to Lake Fort Smith State Park, Arkansas, USA

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Estimating Watershed Mercury Contribution to Lake Fort Smith State Park, Arkansas, USA

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

by

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University of Arkansas
Bachelor of Science in Geology, 2013

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This thesis is approved for recommendation to the Graduate Council.

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Abstract

Mercury contamination associated with human activities poses global human health and environmental risks. A fish-consumption advisory has been in effect at Lake Fort Smith in central west Arkansas for more than a decade due to observed methylmercury concentrations in fish tissue. Lake Fort Smith is an important municipal drinking water supply and recreational resource. Water samples from the majority contributing tributary stream, Frog Bayou creek, were collected periodically, under differing hydrologic conditions in order to quantify the allochthonous mercury load delivered to the lake. Temperature, specific conductance, and turbidity data were collected and used to estimate dissolved organic carbon, methylmercury and mercury concentration in Frog Bayou creek. Dissolved organic carbon (DOC) concentration has been previously shown to have a strong correlation with total mercury (THg) and methylmercury (MeHg) presence and mobility in surface waters. Whereas a weak correlation was observed between DOC and THg concentrations ($r^2 = 0.47$), the relation between turbidity and THg was strong ($r^2 = 0.95$), enabling use of turbidity as a proxy for the estimation of influx of THg in Frog Bayou creek. Analysis of water samples collected from streamflow indicated very little methylmercury contribution from the watershed, suggesting methylation of mercury is occurring predominantly within the body of Lake Fort Smith itself. Turbidity proved an inexpensive, real-time proxy for quantitative determination of mercury and methylmercury load in streamflow. This methodology provided better understanding of variations in mercury concentrations under differing hydrologic regimes and provided a tool for long-term watershed mercury load approximation to Lake Fort Smith.

Acknowledgements

I would like to thank Dr. Phil Hays, Tim Kresse, and Dr. Ralph Davis for their guidance and support during the course of this project. Many thanks to Don Clover at Fort Smith Utilities Department for his input and help with conceptualizing the problem and sample analysis. Mercury analysis was conducted at the USGS Wisconsin District Mercury Research Lab, and I am very thankful for the work of Drs. Dave Krabbenhoft, John DeWild, and all the laboratory employees who provide the Nation with great mercury data. A special thanks to Ferrell Killion for his help with gage installation, it made a difficult job much easier. Thanks to Nick Barsotti for helping to design the water-quality monitor install and for your continued “critiques”. Thank you Joey Fleming, for sacrificing a Friday afternoon to help clean up water quality data with me. A special thank you to Dan Wagner for burning the midnight oil in order to walk me through some new statistical approaches, and to Anna Nottmeier for catching problems in my figures I never would have seen. I would also like to thank the USGS Lower Mississippi Gulf Water Science Center for the opportunity to serve as a Pathways Hydrologic Technician -Trainee during the course of this project, as it has only made me a better equipped scientist.

Dedication

This thesis is dedicated to my family.

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Introduction

In recent years, scientific and public concern about mercury in environmental systems has increased significantly. Mercury pollution due to natural abundance and human activity poses global human health and environmental risks (Selin, 2001). As of 2001, 41 states had at some time issued fish consumption advisories due to elevated levels of mercury in aquatic bodies and fish tissue (U.S. EPA, 2001a). By 2006, American Samoa and at least two Tribes also had issued fish-consumption advisories. These advisories represented 14,177,175 lake acres and 882,963 river miles, or 35 percent of the Nation's total lake acreage and about 25 percent of its river miles (U.S. EPA, 2007). At Lake Fort Smith (LFS) State Park, Arkansas, methylmercury (MeHg) has been found in concentrations sufficient to warrant fish consumption advisories. Local resource managers are concerned about mercury in LFS, as the lake is used as both a source of recreation and as a municipal drinking-water supply. By quantifying mercury entering LFS each year via its watershed, water managers and other stakeholders gain a foundational knowledge of mercury sources to the lake and can begin to take action to reduce mercury contamination to both wildlife and humans.

Mercury is naturally mobilized into earth's hydrologic systems from reservoirs in the earth, through processes including volcanic and geothermal output and surface exposure and weathering through plate tectonism (Fitzgerald, et al. 2005). Total mercury output from natural sources prior to human industrial activities has been estimated at up to 500 Mg year⁻¹. Recent work has suggested modern anthropogenic-sourced emissions of mercury to the environment range from 2200-4000 Mg year⁻¹ (Pacyna, et al, 2000). Anthropogenic contribution to the global mercury budget is primarily from industrial activities including burning of fossil fuels for energy

and transportation, cement production, gold mining and refining, as well as mining of cinnabar ore (HgS).

Mercury is present in the environment in multiple forms, including elemental mercury [Hg(0)], divalent mercury [Hg(II)], methylmercury [CH₃Hg⁺] and mercury in particulate material [Hg(P)]. The specific chemical forms are often associated with varying complexes and colloids. Natural sources of mercury in the environment include geothermal output through ocean vents and volcanoes, and weathering of mercury-bearing rock. Western North America, southern China, and central Europe contain tectonically active areas with high amounts of mercury-bearing rock known as the global mercuriferous belts (GMBs). In these GMBs, mining of cinnabar ore is a substantial source of mercury to the environment, along with natural weathering of rock (Varekamp, 1986). Natural sources of mercury primarily emit Hg(0). However, this Hg(0) can quickly change form in natural systems through geochemical and biochemical processes, including oxidation and reduction. Anthropogenic sources of mercury include combustion of fossil fuels, mining of metals, cement production and incineration of waste. Mercury from these sources can vary in form, with Hg(0) the most common form emitted from the combustion at coal-fired power plants (Selin, 2009). Hg(0) constitutes about 97% of total atmospheric mercury (Lindberg and Stratton, 1998).

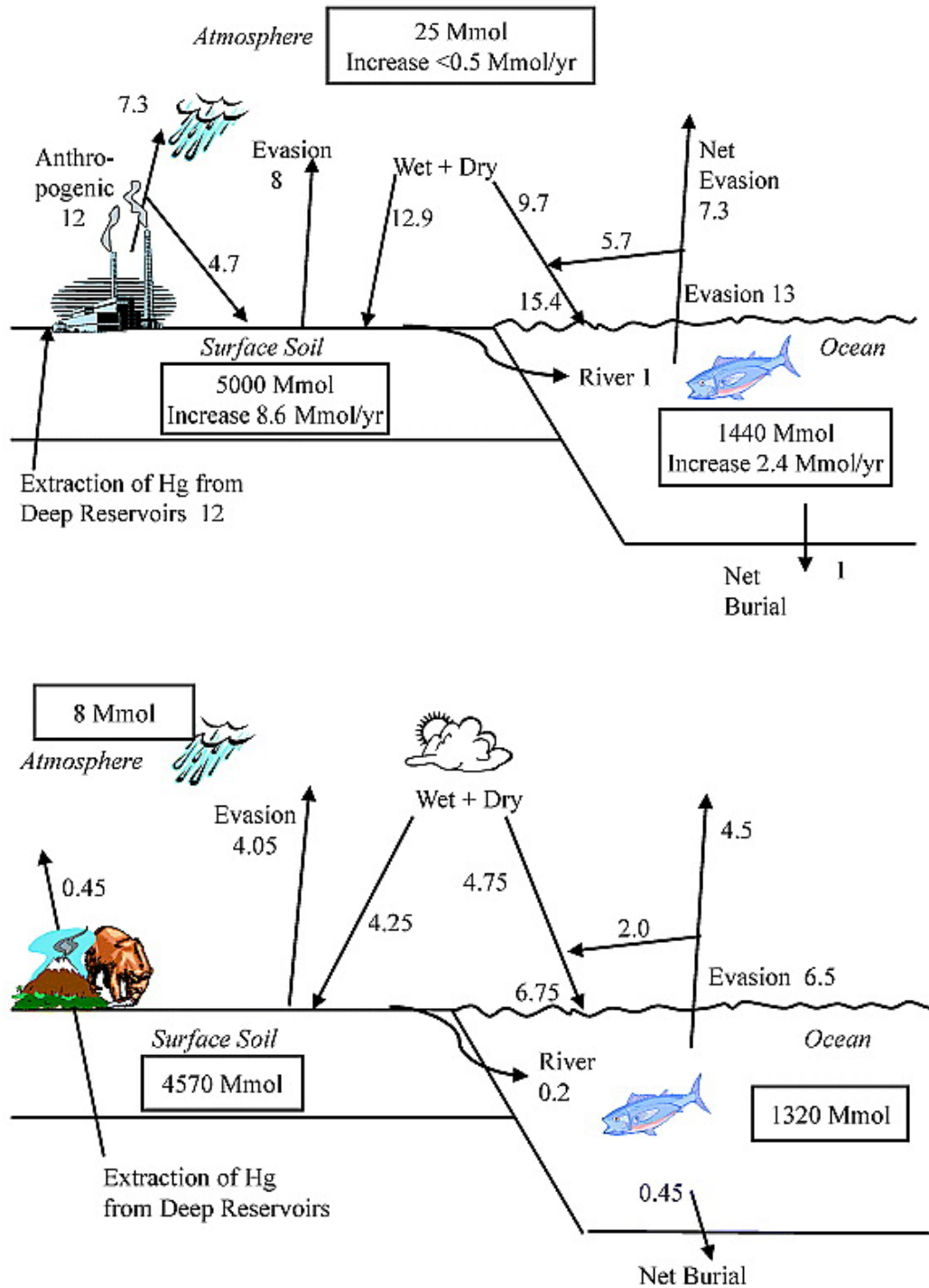


Figure 1. Schematic diagram of modern (top) and preindustrial (bottom) global mercury cycle. Flux values expressed in Mmol yr^{-1} (Mason and Sheu, 2002).

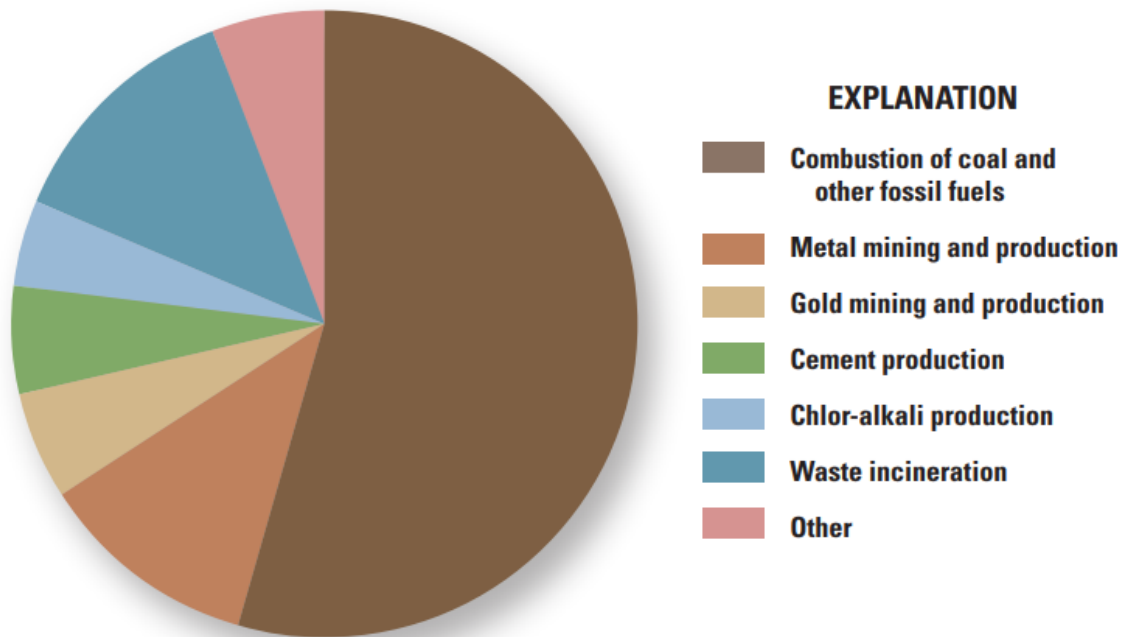


Figure 2. Sources of anthropogenic mercury to the environment in North America, for the year 2005. Burning coal for energy production was the single largest component of anthropogenic mercury emissions in the United States (Wentz, 2014).

The natural biogeochemical cycling of mercury involves atmospheric transport, deposition to terrestrial and aquatic environments, and mobilization and revolatilization (Figure 1). The ultimate fate of mercury is burial in deep-ocean sediments (Mason and Sheu, 2002). Prior to human industrial activities beginning in the mid-18th century, the global mercury budget was primarily controlled by the weathering of mercury-bearing rocks and natural geothermal output of mercury. Mercury from these natural sources may enter the soil pool, be transported by flowing water, or enter the atmosphere as volatile mercury. Some mercury may also be captured and stored in plants, later to be released during decomposition or burning (Turetsky, et al., 2006). Soil has been shown to be the largest reservoir of atmospherically deposited mercury in a

watershed (Krabbenhoft et al., 2005). Up to 90% of the mercury deposited to a watershed is thought to be retained in soils making this a potentially important source of mercury to downstream ecosystems (Krabbenhoft et al., 1995; Scherbatskoy et al., 1998; Kamman and Engstrom, 2002). This is primarily due to the elevated levels of natural organic material (NOM), a product of decomposition, that can bind mercury at time scales of hundreds to thousands of years. Riparian areas and wetlands contain large amounts of NOM and are located near the water table. These areas are likely zones where mercury/mercury-organic complexes form and are mobilized to stream water, particularly during high-flow events (Grigal, 2002).

Streamflow is a significant transporting agent for mercury, with streambed sediments acting as a sink for mercury as well as a zone of transformation between mercury species. Both dissolved organic carbon (DOC) and suspended particulate matter are important sources for facilitated transport of mercury in streams (Brigham et al., 2009). In streams where the watershed is experiencing high soil-erosion rates, suspended particulates in the water are usually the dominant mercury mover. In streams with elevated DOC, such as wetlands, the DOC will be the principal transporter of Hg. In streams with limited DOC and particulate availability, very little mercury will typically be transported (Brigham et al., 2009). Although streamflow can transport a significant amount of Hg through a watershed, removal rates of Hg from a given study area will typically be much less than accumulation rates from modern atmospheric deposition (Journey et al., 2012). This will generally result in a build-up of mercury through time in watershed soils.

Of major importance to this project is the fate of mercury that enters freshwater aquatic environments, principally streams and lakes (Figure 1). Mercury enters these systems through either dry deposition or wet deposition through precipitation. This mercury is primarily in the

form of Hg(II), with MeHg comprising only about 1 percent of total mercury in precipitation (Grigal, 2002). Most forested basins receive the majority of mercury through dry deposition, with rates 2-3 times greater than wet mercury deposition in forested watersheds of northwestern Ontario (Evers, 2005). Through redox reactions within the water, mercury can and commonly does change from Hg(II) to Hg(0). This process can be reversed, and this changing of form may take place many times through time. A substantial amount of mercury in the water can reenter the atmosphere through a process of revolatilization (Hartman et al., 2009). Hg(II) can be buried in lacustrine sediments, or remain suspended in the water column.

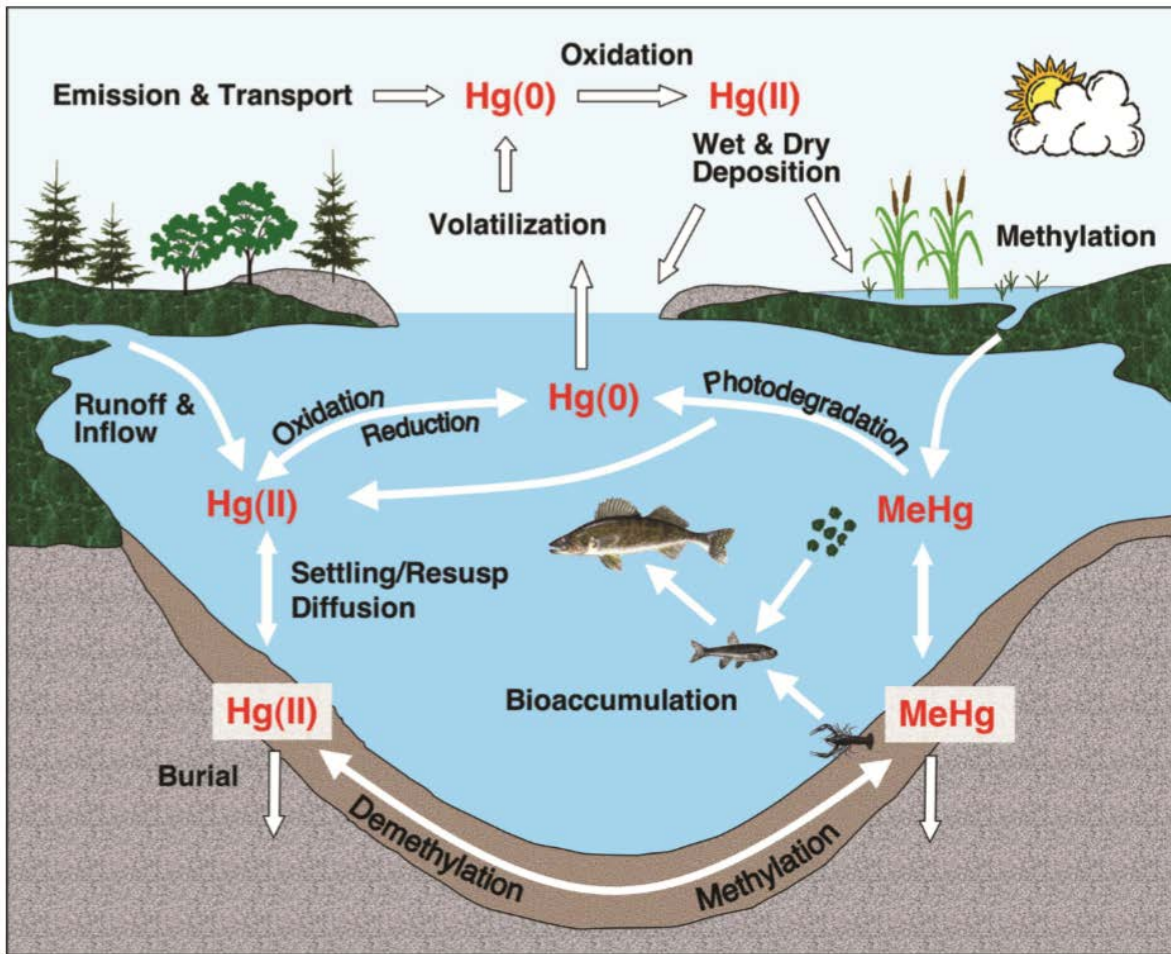


Figure 3. Mercury cycling in a lake and its watershed (Engstrom, 2007).

Formation of Methylmercury

In the shallow, near-shore littoral zones of lakes and at sufficient water depth, anaerobic water conditions can prevail. Within these anaerobic environments, the generation of methylmercury (MeHg), a mercury species of great scientific concern, takes place. Littoral zones are areas characterized by inundation and reexposure, a result of fluctuations in lake pool elevation, usually located along the shoreline of reservoirs. Repeated wetting and drying cycles have been shown to increase MeHg production and subsequent release to downstream ecosystems (Snodgrass et al., 2011, Brigham et. al, 2009). Deep lake depths in reservoirs are also areas of increased methylmercury production, due to anaerobic conditions, and high nutrient and organic carbon availability (Bonzogo et al., 2007). Methylation of mercury occurs in natural systems primarily due to the action of anaerobic bacteria. Sulfate-reducing bacteria are the most common biogeochemical agent responsible for methylation of mercury, although iron-reducing bacteria have been shown to play a role in some environmental settings, as well as other types of terminal electron acceptor process bacteria (Benoit, 2003). Higher concentrations of sulfate in aquatic ecosystems, both within water and sediments, increase rates of mercury methylation (Brigham et al., 2014). Anaerobic bacteria produce MeHg during metabolic processes. MeHg will either be released by these anaerobic bacteria into the water and sediments or remain within the organism. If MeHg is released into the water, it can transform through photodegradation into a less toxic form, Hg(II).

MeHg stored in anaerobic bacteria is of great importance to the biogeochemical cycling of mercury in aquatic ecosystems. Organisms feed on these bacteria, ingesting MeHg in the process. As predation continues, MeHg levels in each successive trophic layer increase, through a process of bioaccumulation. Ultimately, top predators including humans will consume aquatic

foods such as game fishes and shellfish, thereby becoming exposed to concentrated MeHg. Most mercury found in prey fishes is in the form of MeHg (Bloom, 1992).

MeHg can have significant health effects in both humans and other animals. MeHg acts as a potent neurotoxin, with global human exposure primarily due to consumption of top predator fish from affected aquatic ecosystems (Mergler, 2007). Laboratory studies have shown that the bioaccumulative potential for MeHg is a thousand-fold greater than that of inorganic mercury (Ribeyre and Boudou, 1994). Health effects resulting from consumption of high levels of MeHg include neurological damage in the form of sensory, auditory, and visual impairment. Other health effects in humans include problems with speech, cerebral palsy, deafness, and blindness (Comm. Toxicol, 2000). Studies have shown that wildlife exposed to increased MeHg exhibit toxic effects, including behavior, hormonal, and possibly reproductive changes (Scheuhammer, et al. 2007).

Dissolved Organic Carbon and Methylmercury Formation

Organic carbon is abundant in most environmental systems, and is a product of the breakdown of natural organic-matter sources, including plant and animal decomposition. Organic carbon often serves as a substrate for microbially mediated reactions. It can serve as a proton donor or acceptor, which can have a resulting strong influence on biogeochemical reactions in natural aquatic settings. Organic carbon can be in the form of DOC or particulate organic carbon (POC). DOC is defined as organic carbon dissolved in water that will pass through typical water quality filters (0.7 to 0.22 μm), whereas POC is too large to pass through and will be removed by filtering. Total organic carbon is the sum of DOC and POC in a given water-quality sample. Decomposition of terrestrial plant material including deciduous and coniferous leaves and other plant material in soil is likely a substantial source of DOC in the watershed of LFS. Along

natural streams, DOC is often generated and accumulates in low-energy backwater areas, principally wetlands (Brigham et al., 2009). In streams that include wetlands as part of their watershed, the concentration of DOC in runoff increases with increasing proportion of the wetlands in the watershed (Aitkenhead et al., 1999). Phytoplankton and algae secrete organic compounds which are often significant sources of organic carbon in streams (Kraus et. al, 2011). During methylation of mercury, organic carbon functions as a terminal electron acceptor. Higher organic-carbon concentrations allow greater and faster rates of methylation by anaerobic bacteria, and therefore a strong positive correlation exists between high availability and concentrations of DOC and MeHg presence (Brigham, 2009). Lakes and streams with high concentrations of DOC generally have high mercury concentrations (Wentz et al., 2014) (Figure 4). Previous work (Driscoll et al., 2007) has shown instantaneous concentrations of filtered Hg and MeHg to exhibit strong positive correlations with both DOC and streamflow for most streams.

Detecting the presence and concentration of DOC in-situ at real-time study sites is a relatively novel technique, and in recent years has commonly involved the use of specific ultraviolet absorbance (SUVA), specifically at 254 nm (Dittman, 2009). However, SUVA sensors are prohibitively expensive for many projects and require the gathering of discrete samples to verify the validity of real-time DOC concentration estimation data (Fichot et al., 2015). Along with the prohibitive cost associated with the use of SUVA sensors, high-turbidity conditions in a sample can cause significant fouling errors that must be corrected for the values to be considered valid. Due to the time and budgetary limitations of this project, the use of SUVA was not a viable option.

In order to approximate DOC concentration in streamflow, a proxy relation was desired. As previously discussed, streams with limited presence of wetlands in their watersheds will typically contain limited concentrations of DOC during base flow. During higher-flow conditions, DOC concentrations will typically be greatest, in tandem with maximum sediment transport. Suspended sediment concentrations in the water column have shown to be strongly correlated with DOC, MeHg and total mercury concentrations in many forested streams (Bringham et al., 2009). During times of high suspended sediment concentrations, turbidity values are at their highest, along with increased DOC concentration (Uhrich et al., 2010, Rasmussen et al., 2009). By measuring turbidity values with an in-situ sensor and constructing valid proxy relations, DOC, MeHg, and THg concentrations were theorized as being able to be approximated real-time with this routine water-quality parameter.

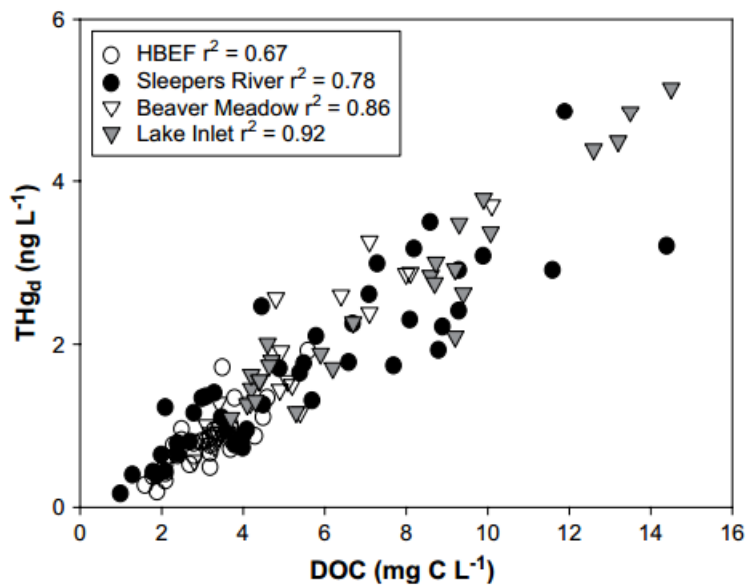


Figure 4. Stream water dissolved total mercury (FTHg) concentration (ng L^{-1}) as a function of dissolved organic carbon (DOC) concentration (mg C L^{-1}). An example of the correlation between the substances commonly observed in freshwater ecosystems. (Dittman, 2009)

Turbidity and Dissolved Organic Carbon

Turbidity is an optical property of water. It is an estimation of how “cloudy” a water sample is, or more directly, a water sample’s ability to transmit light. Many factors can influence turbidity, including the presence of clays, silts, inorganic and organic matter, microscopic organisms, algae, and other substances (Swanson, 1965). Turbidity is routinely collected as an indicator of water quality.

The relation between elevated organic carbon values and higher turbidity values in natural systems is well established (Carpenter, 2013, Smart et al., 1976). Moreover, the physical presence of organic carbon in stream sediments contributes to its correlation with higher turbidity values. In natural systems, organic carbon is often bound to stream sediments and soil due to slight electromagnetic attractive forces. When stream sediments are suspended during higher-discharge events, due to faster water velocities and turbulent flow, organic carbon is suspended as well, both of which contribute to elevated turbidity values (Meyer and Tate, 1983) (Figure 5). Significant increases in both DOC and turbidity during high-stage events are more noticeable in streams with low turbidity values at low-flow conditions. During base flow, tributary streams to LFS have turbidity values of around 10 FNU. However, precipitation within the watershed contributes sediments and organic material to the streamflow and increases turbidity values. Resuspension of by scouring of stream bottom and sides also contributes sediments to flow. During runoff events, a “flushing out” of wetland areas takes place, allowing DOC formed from the breakdown of organic matter to move into the stream channel and downstream. Water that has been trapped and stored by riparian zones also joins streamflow, and is often enriched in organic carbon due to the biological activity of flora and fauna (Moore, 1989). Soil eroded from the watershed, which can often function as a sink for DOC and mercury,

is eroded during high flow events and suspended in the water column. During precipitation events water often takes a shallower path through soil as it approaches saturation, and within the shallow soil the highest DOC concentrations are typically observed. Not only will precipitation in the watershed allow for erosion of soil into the stream, but shallow soil is often the most enriched in DOC (McDowell and Likens, 1988); therefore, total mercury, MeHg and DOC concentrations were hypothesized to be greatest in Frog Bayou creek during higher turbidity, higher-flow conditions.

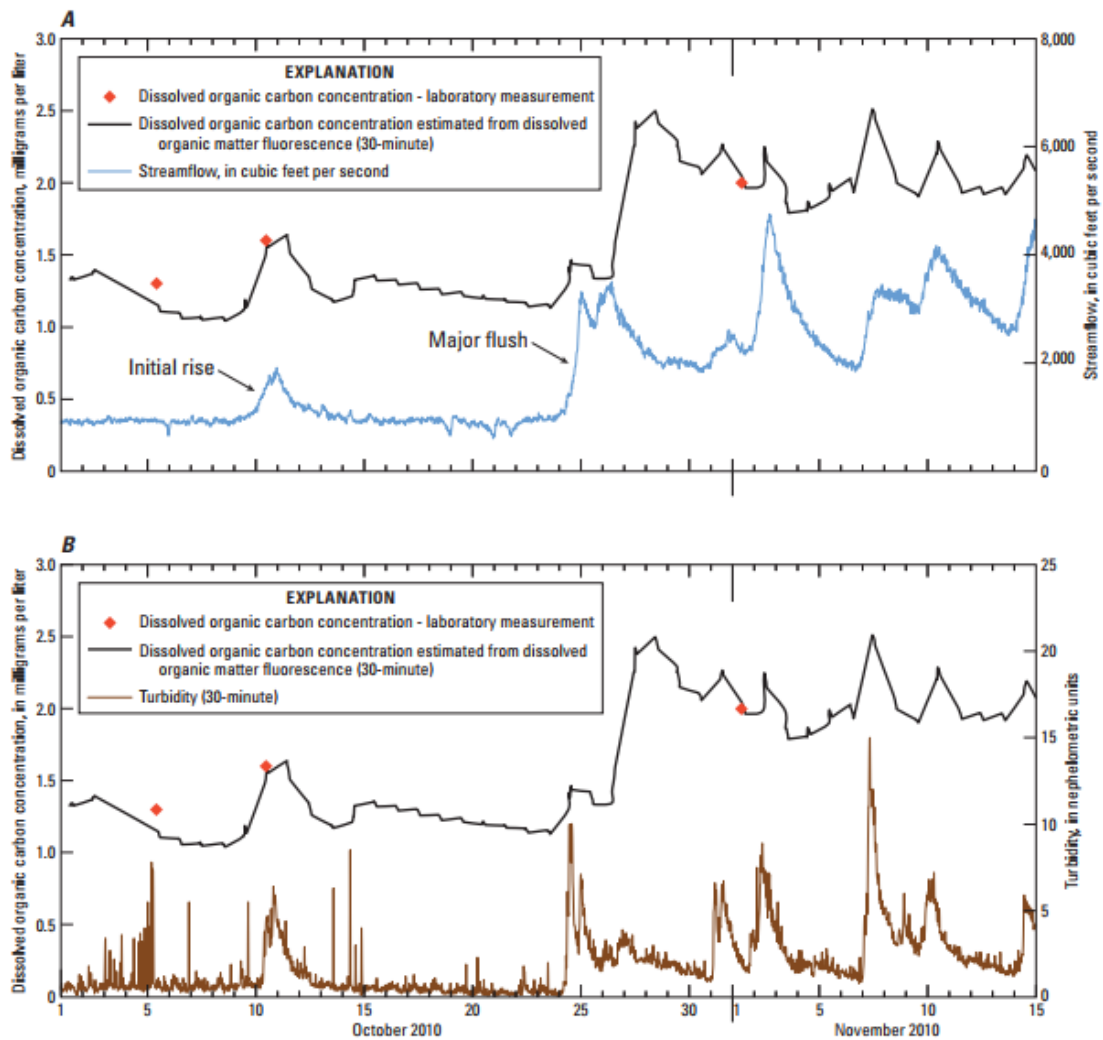


Figure 5. Stream chemistry responses to a series of floods on the Clackamas River, OR. Note similarities between discharge (floods), turbidity, and DOC concentrations estimated by UV254. (Carpenter et. al, 2013)

Study Area

Lake Fort Smith (LFS) is a manmade freshwater lake located in Crawford County, Arkansas. The lake was formed in 1956 by construction of an earthen dam across the valley of Frog Bayou creek. The area of the modern lake originally consisted of two separate lakes, with Lake Shepherd Springs upstream of the historical LFS. Lake Shepherd Springs functioned as a

sediment trap and regulatory pool for LFS. The modern lake was formed by the destruction of the original dam and construction of a larger dam, combining Lake Sheppard Springs and the historic LFS into one body covering approximately 1,400 surface acres. The new dam for the modern lake was finished in the summer of 2006. The lake and surrounding park is used for a variety of purposes, including boating, fishing, hiking, and as a municipal drinking-water supply. The land immediately bordering the lake is mostly forested, with a small portion of shoreline reserved for State Park buildings and boat launch. The lake is totally contained within the boundaries of Lake Fort Smith State Park.

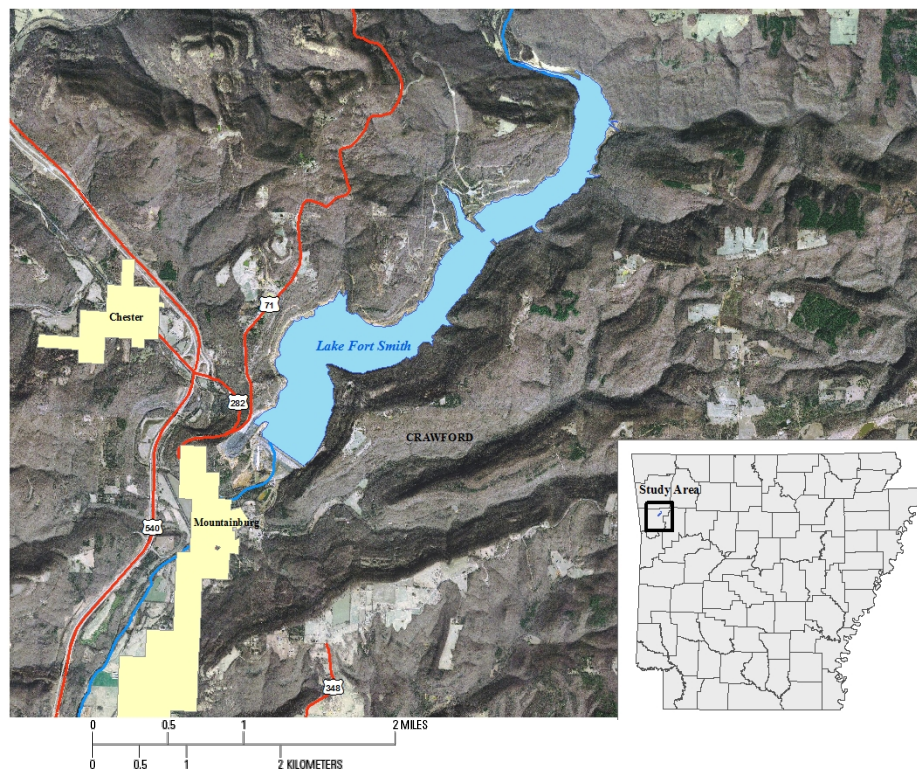


Figure 6. Location of Lake Fort Smith study area. (Hays, 2014)

LFS is located within the Boston Mountains of northern Arkansas Ozarks, a section of the Ozark Plateaus Province (Adamski et al., 1995). The lithology of the watershed is composed completely of the Pennsylvanian Upper Atoka Formation. The Upper Atoka is characterized by

marine, mostly tan to gray silty sandstones and grayish-black shales. Slopes within the watershed range from 3 percent along the floodplains of Frog Bayou to greater than 50 percent on steeper slopes (USDA Soil Survey). 90 percent of slopes within the watershed fall in the range of 15 to 30 degrees (Odhiambo, 2002). The watershed is primarily oak/hickory temperate deciduous forest, with thick understory vegetation. Limited agricultural development in the area is primarily concentrated along the valley floor and the creek just upstream of the confluence with LFS. Agricultural activity is mostly in the form of animal grazing, with no significant row-crop agriculture. Very few families live within the watershed, as most of the land is set aside as part of the Ozark National Forest or is owned and managed by the City of Ft. Smith in an effort to minimize negative human impacts on water quality through agriculture or other land development. Within the northwestern Arkansas Ozarks, the average temperature is 15.6°C. (Adamski et al., 2005). Annual total precipitation averages 118 cm (Davis and Shepherd, 2010). Precipitation tends to be slightly higher in the spring (averaging 11.6 cm/month), with another slight increase in fall precipitation (9.6 cm/month) (National Oceanic Atmospheric Administration, 2009).

Two streams function as significant tributaries to LFS. The smaller of the two, Jack Creek, contributed an estimated $2.886 \times 10^7 \text{ m}^3$ of flow during the period of January 2015 to December 2016 (USGS). The larger of the tributary streams, Frog Bayou, contributed an estimated $2.159 \times 10^8 \text{ m}^3$ of flow for the same period. Frog Bayou contributed approximately 7.5 times more flow than Jack Creek, and is considered the dominant tributary stream to LFS. Unit runoff for the watershed (total volume of recharge to lake [m^2] / drainage area [m]) of LFS for the given period was 1.54 m (USGS). Due to its dominance in contributing discharge, and the limitations of equipment and sampling procedures, Frog Bayou Creek was chosen as the

representative stream for understanding watershed contribution of mercury to LFS. Additionally, land use and forest cover were similar in both sub-watersheds so that conditions in Frog Bayou Creek would be similar and representative of those in Jack Creek.

Previous Studies at Lake Fort Smith

Determination of the presence and concentrations of mercury and its variable forms in Lake Ft. Smith was accomplished by a joint study between the United States Geological Survey and the Fort Smith Utilities Department in 2012 and 2013 (Hays et al., 2014). Samples were collected for total organic carbon and mercury concentrations in the anaerobic deep water, littoral zone water and soils. Samples were collected for major dissolved metals, along with water-quality measurements of temperature, dissolved oxygen (DO) concentration, specific conductance and pH. Analysis of MeHg concentrations in the tissue of top predator fishes (including spotted and largemouth bass) showed a range of 0.30 – 0.71 mg/kg. These concentrations are significant and represented mercury-impacted fish populations, as many countries have set maximum concentrations of MeHg in consumed fishes at 0.5 mg/kg (Nauen, 1983).

The sedimentation infill rate at LFS was calculated as 0.89 cm/yr via radiometric chronology using ^{210}Pb (Hays et al., 2014). This rate is relatively similar to previous estimates of 0.4 cm/yr. from dual-frequency echo sounder bathymetric surveys (Odhiambo and Boss, 2004). Mercury concentrations in soil cores were determined over time intervals established by radiometric dating, and an overall increase was observed, from around 44 $\mu\text{g}/\text{kg}$ in 1960 to 68 $\mu\text{g}/\text{kg}$ in 2010. This increase in concentration would be expected, as mercury deposition to land in North America through aerial fallout increased significantly over the last century (Bindler et al., 2001).

Mercury Deposition

Wet deposition rates of mercury, or deposition via precipitation at the earth's surface, is monitored by the U.S. Mercury Deposition Network. This nationwide network of monitoring stations records and archives wet deposition rates of mercury at monthly and weekly intervals, and daily at some sites. Although no data exist specifically for deposition rates at LFS, data demonstrating both short and moderate trends in mercury deposition through precipitation at a regional scale are useful and available. LFS is located within the area of greatest mercury deposition rates in the United States (Figure 7). As of 2015, total mercury deposition within the watershed of LFS is estimated at $12.3 \mu\text{g}/\text{m}^2$, approximated from the nearest monitoring station at Stillwell, OK, approximately 45 km to the west (NADP, 2018).

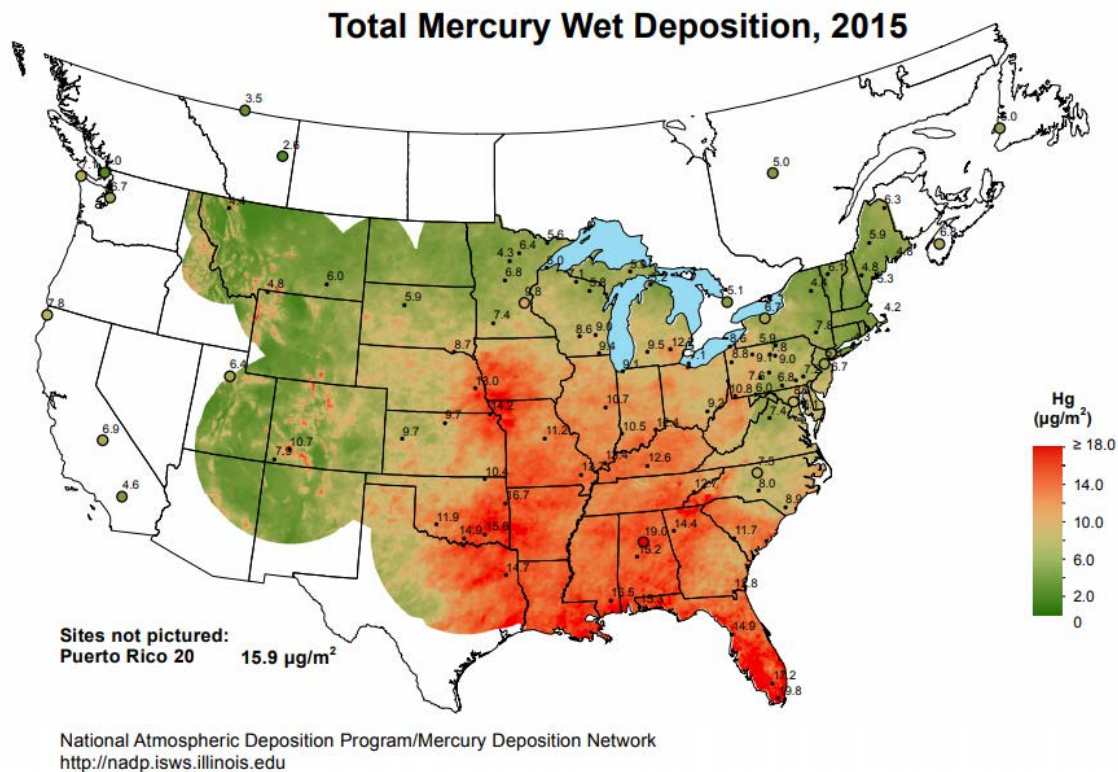


Figure 7. Total Mercury Wet Deposition, 2015 (NADP, 2018)

Methods

Field Methods

Field deployed water-quality monitor

The United States Geological Survey (USGS) maintains a continuous streamgaging station on Frog Bayou creek approximately 0.6 km upstream of the confluence with LFS. Routine stage and discharge measurements have allowed for the development of a stage-discharge relation (Buchanan and Somers, 1969). A field deployed OTT brand bubbler system provides a stage measurement every 15 minutes. These values are logged in a Satlink V2 Data logger/Transmitter. Once an hour the four stage measurements along with hourly precipitation data are transmitted via telemetry to the Geostationary Operational Environmental Satellite (GOES) array and received by the USGS. These values are then reviewed and validated under published USGS quality-control standards and made available for public and governmental uses. Beginning in October of 2017, a continuous water-quality monitor was installed at the site by USGS personnel. This water-quality monitor collected instantaneous values of temperature ($^{\circ}\text{C}$), specific conductance at 25°C (SpC, $\mu\text{S}/\text{cm}$) and turbidity, measured in Formazin Nephelometric Units (FNU). Routine field calibration of the water quality monitor was maintained according to USGS Water Quality Standards (Wagner et al., 2006, Wilde, 2006). Water-quality information gathered at the site was transmitted along with the stage and precipitation data to the GOES satellite array, and ultimately to the USGS internal archive for review.

Dissolved Organic Carbon Sampling

Field sampling for DOC in surface streams is relatively simple, but must be conducted in a manner as to limit interference from outside sources of contamination. The samples were

collected directly into a clean, inert glass bottle, previously acid-washed and rinsed with deionized water. The samples were then stored in a dark and chilled cooler until delivery to the USGS Water-Quality Laboratory at the Fayetteville Field Office of the Lower Mississippi Gulf Water Science Center in Fayetteville, AR. The samples were then filtered through a 0.45 μ m quartz filter to remove any particulates. After filtering, the samples were acidified with sulfuric acid (H₂SO₄) and shipped to American Interplex Labs in Little Rock, Arkansas for analysis.

Mercury and Methylmercury Sampling

Extreme care must be used when sampling for trace mercury, as subnanogram per liter results are attainable and possible extraneous interferences are abundant. Sampling for mercury in its variable forms including MeHg was accomplished using a proven mercury low-level sampling protocol (USGS, 2006). Frog Bayou creek is a wadeable, well-mixed stream, so samples were obtained by dipping a 1-liter media bottle (Nalgene polyethylene terephthalate copolyester, glycol-modified [PETG]) into the approximate centroid of flow. During high flow, sampling bottles were attached to the end of a 12-ft extension pole in order to sample from the centroid of flow. Sampling crews wore nitrile gloves during sample collection, and took care to sample upstream of themselves to reduce any potential sources of contamination. Due to the potential for low-concentration sample contamination, all sample preparation materials were prepared by and shipped from the USGS Wisconsin District Mercury Research Laboratory (USGS-WDML). After sampling, samples were placed in a chilled cooler and transported to the Water-Quality Lab at the Fayetteville Field Office of the Lower Mississippi Gulf Water Science Center in Fayetteville, AR. Once at the lab, samples were vacuum-filtered through prebaked (550°C) quartz-fiber filters. The filtering apparatus consisted of a filtration tower attached to a mercury-clean filtration vacuum chamber. The vacuum for the chamber was provided by a

Campbell Scientific electric air-pump, supplied by the USGS-WDML. The filtered samples were collected in mercury-clean sample bottles and acidified with 6N mercury-clean hydrochloric acid. Filtered samples were then refrigerated until shipment. Quartz filters were placed in mercury-clean petri dishes and wrapped in tape, then frozen until shipment on dry ice, so as to remain frozen until received by the USGS-WDML. All coolers were shipped priority-overnight to ensure the sample integrity. After sampling was completed and all sample preparation materials were returned, the USGS-WDML tested the equipment for potential mercury contamination, specifically on filter forceps, within the hydrochloric acid solution, and on filtration equipment. No items were found to be contaminated.

Laboratory Methods

Dissolved Organic Carbon

DOC concentrations in fresh-water samples were analyzed at American Interplex Laboratory in Little Rock, AR. Upon arrival, the samples were analyzed according to Standard Method SM5310C. DOC in the filtered sample was oxidized to CO₂ persulfate in the presence of ultraviolet light or heat. The CO₂ produced was purged from the sample, dried, and transformed with a carrier gas to a nondispersive infrared (NDIR) analyzer. Alternatively, the CO₂ was coulometrically titrated, or separated from the liquid stream by a membrane that allowed the specific passage of CO₂ to high-purity water, where a change in conductivity was measured, and related to the CO₂ passing the membrane (National Environmental Methods Index).

Filtered total mercury

Filtered samples were analyzed via EPA Method 1631 Rev. E, or Total Mercury in water by Oxidation, Purge and Trap and cold-vapor atomic fluorescence spectrometry (CVAFS) at the

USGS-WDML. Once the sample arrived at the lab, 0.2 N BrCl solution was added to oxidize all Hg compounds to Hg(II). This solution was allowed to sit for at least 5 days. After oxidation, the sample was sequentially prereduced with $\text{NH}_2\text{OH}\cdot\text{HCl}$ to destroy free halogens, and then reduced with SnCl_2 to convert Hg(II) to volatile Hg(0). The Hg(0) was separated from solution by purging with nitrogen gas onto a gold-coated sand trap. The trapped Hg was thermally desorbed from the gold trap into an inert gas stream that carried the released Hg(0) into the cell of a CVAFS for detection. Data quality was ensured through calibration and testing of the oxidation, purging, and detection systems.

Filtered methylmercury

Sample-analysis procedures for filtered MeHg followed those described by DeWild et al, (2001). Water samples were distilled to remove any matrix interferences. The pH of the distillate was adjusted to 4.9 using acetate buffer. The distillate was then ethylated using sodium tetraethyl borate (NaBEt_4) and allowed to react for 15 minutes. After reaction, the distillate was purged with nitrogen gas for 20 minutes and the ethylated mercury species were collected on a sample trap containing Carbotrap graphitized black carbon. These ethylated mercury species were desorbed thermally from the sample trap, separated using a gas chromatographic column, reduced using a pyrolytic column, and analyzed using CVAFS.

Particulate Total Mercury

Particulate Total Mercury concentration was determined via USGS Techniques and Methods Paper 5 A-8. An aliquot of solid material homogenized with a Teflon rod with flattened ends was digested and oxidized in a Teflon digestion vessel with aqua regia at room temperature overnight to convert all Hg to Hg^{2+} . The digested sample was then diluted to volume with 5

percent bromine monochloride (BrCl). After dilution, the sample was pre-reduced with hydroxylamine hydrochloride (NH₂OH·HCl) to remove any free halogens, then reduced with stannous chloride (SnCl₂) to convert Hg²⁺ to gaseous mercury (Hg⁰). The Hg⁰ was purged, captured on a gold trap, thermally desorbed, and then detected using CVAFS. This method can be used to determine total mercury concentrations in solid samples with a method detection limit of 0.3 ng in a digestion bomb.

Particulate Methylmercury

Filters containing suspended solids were placed in distillation bottles, reagents were added, and the samples were distilled. The distillation procedure extracted MeHg from the solid matter into the dissolved phase, converted MeHg into MeHg chloride, and removed potential interferences. Analysis of the distillate then followed the method described in “*Particulate Total Mercury*”.

Data Analysis Methods

Corrections and analyses of water-quality monitor data were accomplished through the USGS Aquarius database, Data Correction Toolbox. Sample statistical analyses were accomplished using RStudio, a free and open-source integrated development environment for R, a programming language for statistical computing and graphics. DOC values below detection limit were approximated using the *USGS-R/smwrQW: Tools for censored data analysis package*, also known as *censReg*, which allows for construction of a linear regression model for censored response data (Cohn, 1988, Helsel and Hirsch, 2002). Regression relations for turbidity, DOC concentration, and mercury/MeHg concentrations were determined via the USGS-R/smwrQW package.

Results

Temperature and Specific Conductance Values

Installation and maintenance of a continually monitoring water-quality sonde at the sampling location allowed for a much larger, denser data set than would be available through discrete sampling alone. Temperature data revealed daily fluctuations and a correlation to seasonality on a longer timescale, but also reacted quickly to precipitation within the watershed (Figure 8). The lowest temperature recorded at the site was 1.23°C (34.2°F) on 1/17/2018 at 9:15 AM. The highest temperature recorded was 24.32 °C (75.7 °F) on 10/14/2018 at 3:15 PM (Figure 8).

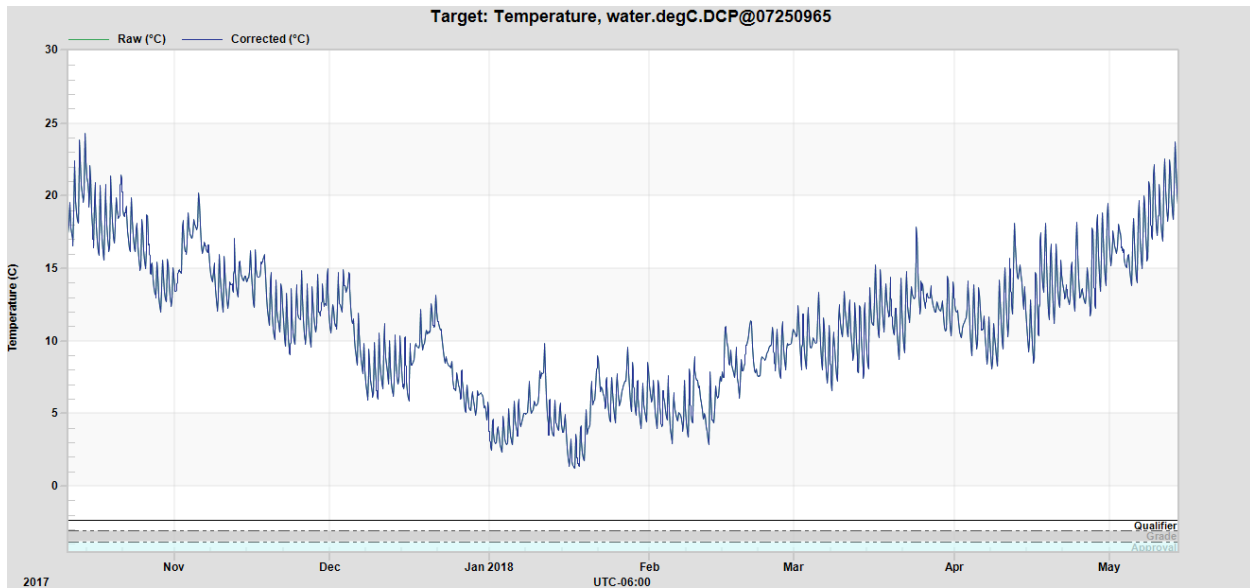


Figure 8. Water temperature (°C) through time at Frog Bayou Creek, Arkansas.

Specific conductance within the creek was substantially higher in late-October and early-November, likely a product of a greater proportion of streamflow originating as groundwater, as opposed to surface runoff (Figure 9). At the time of water-quality equipment installation,

October 2017, the region was experiencing drought conditions and had not received any major precipitation since mid-August 2017. As precipitation increased in the fall months, specific conductance decreased and began to strongly and inversely correlate with precipitation events-- in tandem with a greater proportion of streamflow originating as surface runoff (Figure 9). The highest specific conductance value recorded was 81.29 $\mu\text{S}/\text{cm}$ on 10/14/2018 at 9:45PM. The lowest value recorded was 26.33 $\mu\text{S}/\text{cm}$ on 3/27/2018 at 11:15AM.

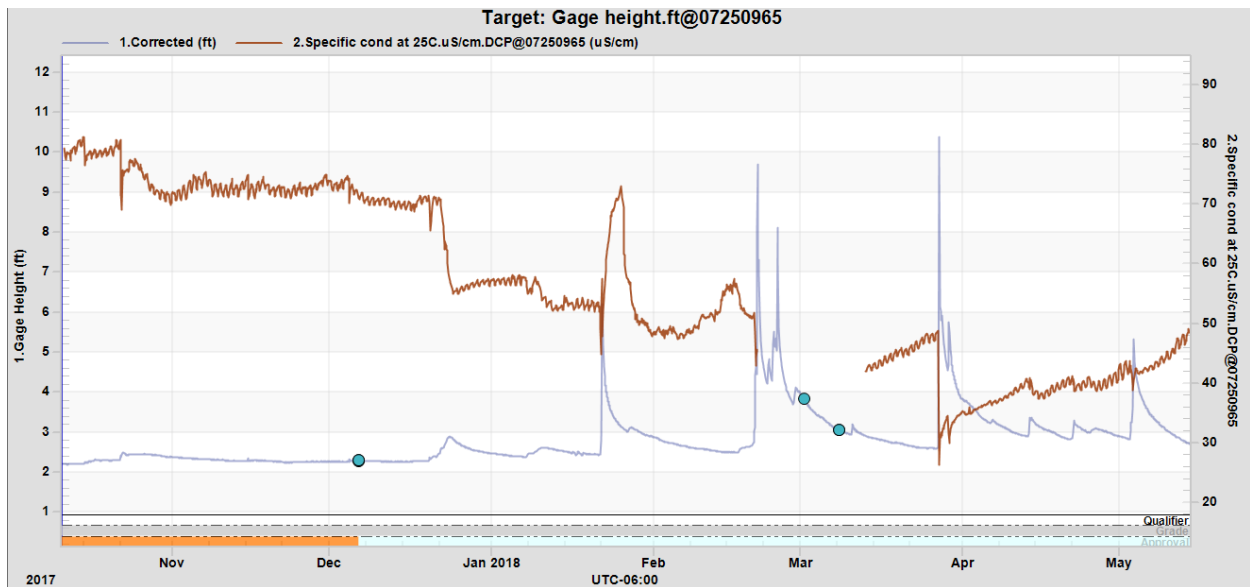


Figure 9. Specific conductance ($\mu\text{S}/\text{cm}$ at 25°C, brown line) as a function of gage height (in feet, blue line) at Frog Bayou Creek, AR.

Turbidity Values

Changes in turbidity correlated strongly with changes in gage height (Figure 10). The lowest turbidity value (0.15 FNU) was recorded at the lowest stream-gage height recorded (2.24 ft. gage datum on 11/24/17 at 09:00). This relation held true during very high stage as well, with the peak turbidity reading (1084.3 FNU) occurring at the same time as the peak gage height of the measured period (10.38 ft. gage datum, on 3/27/2018 at 11:45). The increase in turbidity

following precipitation events was an expected pattern, and is attributed to the relatively undeveloped nature of the Frog Bayou watershed. Low-flow turbidity values were likely due to very little soil erosion taking place within the watershed. Turbidity only increased substantially when greater streamflow allowed for entrainment of stream sediments and eroded soil, in tandem with higher gage height (Figure 10).

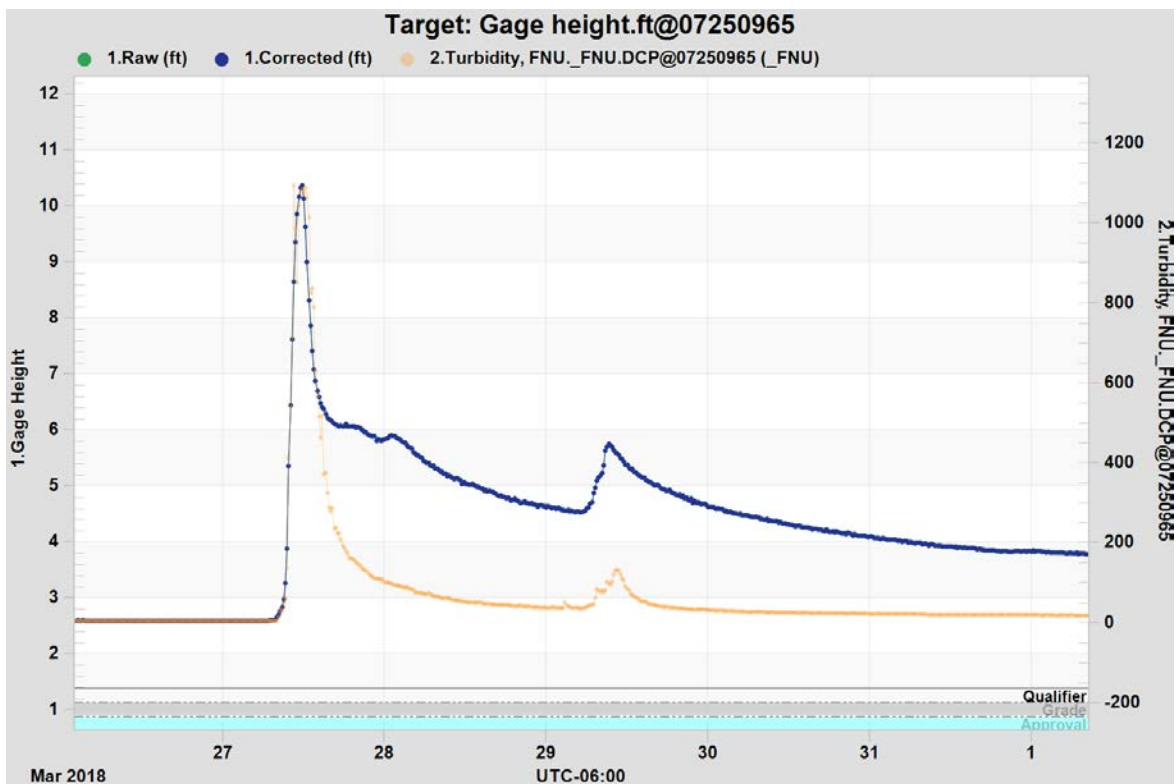


Figure 10. Gage height (blue) and turbidity (yellow) over several day precipitation event (March 27 – April 1, 2018).

Dissolved Organic Carbon

DOC concentration revealed a weak correlation with turbidity ($r^2 = 0.45$, Figure 11, Table 2). DOC concentrations were lowest during low-flow conditions, with several samples below the detection limit of 1.0 mg/L. Higher DOC concentrations were observed during periods of

higher stage and increased turbidity, with the highest DOC sample concentration (7.7 mg/L) occurring in tandem with the highest turbidity reading (1084.3 FNU). Although the ability of turbidity to predict DOC concentrations accurately was limited from the somewhat weak correlation, a general increase in DOC concentration was observed in tandem with increased turbidity values. This relation was expected, as DOC concentrations in natural fluvial systems are generally highest within riparian zones and wetlands surrounding streams, and at shallow soil depths. The Frog Bayou creek watershed does not contain any large wetland areas, but small backwater areas and healthy riparian zones are present along limited sections of the creek. During and immediately following rainfall events these areas were likely “purged” and the DOC-enriched water joined streamflow, contributing to both elevated DOC concentrations and increased turbidity in Frog Bayou creek (Table 2).

Methylmercury and Total Mercury

Concentrations of MeHg in Frog Bayou streamflow were very low (Table 1). Filtered methylmercury (FMHg) concentrations in all water samples were below detection limit of 0.04 ng/L. The only detection of MeHg occurred in the PMHg grab sample acquired during the highest flow regime recorded, when turbidity values were highest. Concentration of particulate methylmercury (PMHg) for the sample was 0.399 ng/L. Only during very high turbidity conditions were measurable concentrations of MeHg transported, with MeHg bound to particles in suspension. Soil has been shown to be a major sink of mercury in the environment, and MeHg appears to be present in such low amounts in the LFS watershed that it was detectable only when streamflow contained elevated amounts of flushed sediments.

Filtered total mercury (FTHg), representing total dissolved mercury, concentrations ranged from 0.97 ng/L to 7.84 ng/L, with a median concentration of 4.68 ng/L (Table 2). Despite a limited number of samples, a general correlation was observed FTHg and turbidity. The lowest concentration of FTHg corresponded to the lowest turbidity sample, while highest FTHg concentrations corresponded to the highest turbidity value sample (Appendix, Table 1). PTHg concentrations, or mercury attached to particles, ranged from 0.227 ng/L to 63.9 ng/L with a median concentration of 4.64 ng/L (Table 2). Similar to FTHg, the highest PTHg concentration was in the sample with the highest measured turbidity value, and the lowest PTHg concentration was in the sample with the lowest measured turbidity value.

Discussion

Methylmercury Contribution to Lake Fort Smith from the Watershed

One of the most significant results of this study is an increased understanding of the path of MeHg into LFS. Due to fish consumption advisories resulting from elevated MeHg concentrations in fish, local resource managers desired an estimation of how much allochthonous MeHg is delivered to the lake through the watershed, in contrast to MeHg formed within the lake. Results show very little MeHg is transported into the lake from the watershed, and therefore the majority of MeHg can be theorized to originate within the anaerobic environments of LFS itself, primarily littoral zones and anaerobic lake depths. This agrees with previous sampling (Hays et. al, 2014) that found total MeHg concentrations in littoral-zone water ranging from 0.05 to 1.12 ng/L. Median total MeHg concentrations in littoral-zone water samples (0.237 ng/L, n = 13) were nearly 6 times that of streamflow in Frog Bayou creek. Anaerobic lake depth samples contained total MeHg concentrations in the range of 0.058 ng/L to 0.322 ng/L, with a median concentration of 0.062 ng/L (n = 3). Although anaerobic lake depths contained

significantly lower total MeHg concentrations than littoral zones, the anaerobic deep water of LFS was still enriched in MeHg relative to streamflow in Frog Bayou creek. MeHg samples from Frog Bayou creek showed that only during exceptionally high turbidity conditions is MeHg transported to LFS in measurable concentrations, primarily bound to sediments in streamflow. It is theorized that the minute contribution of MeHg from the watershed is being delivered principally during floods. Future successful efforts to minimize the negative impacts of MeHg contamination at LFS will need to focus primarily on MeHg generated within the lake, and not MeHg transported from the watershed.

Water-quality proxy relations for Frog Bayou creek and Lake Fort Smith

Turbidity as a proxy for Dissolved Organic Carbon

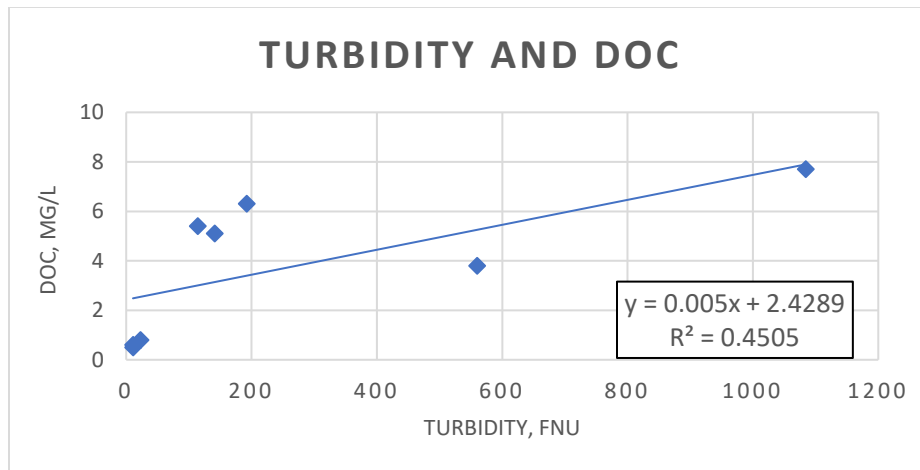


Figure 11. DOC concentration (mg/L) as a function of Turbidity (FNU) at Frog Bayou Creek, AR.

Turbidity was initially theorized to potentially function as a water quality proxy for DOC concentration, which in turn would function as a proxy for mercury and MeHg concentrations in Frog Bayou creek. However, turbidity proved to be weakly correlated with DOC concentrations over the range of measurements (Figure 11, $p = 0.068$). Many constituents can influence stream

turbidity, including entrained sediments, microscopic organisms, organic carbon, and presence of algae, among others. During low turbidity flow conditions, DOC concentrations were below 1.0 mg/L. As turbidity in Frog Bayou increased, DOC increased as well, but the relation was not statistically valid. An increase in stream sediment moving downstream, erosion of streambank soil, mobilizing of inorganic debris and other factors can increase turbidity values while having minimal impact on DOC concentration. As previously discussed, the watershed topography of Frog Bayou creek is quite steep, and during periods of rainfall, soil may be easily eroded with significant quantities transported downstream, increasing turbidity in the stream substantially but not necessarily increasing DOC concentration. In natural environments, DOC is generally concentrated in wetland or marshy areas bordering streams (Aitkenhead et al., 1999). Due to the high gradient of the topography surrounding Frog Bayou creek, very limited low-gradient backwater environments or wetlands exist, and DOC concentration from the watershed is naturally limited. Factors that are decoupled from DOC appear to influence turbidity in Frog Bayou creek; hence, no strong relation with DOC concentration exists. Additional DOC samples could allow for the relation with turbidity to be better defined, but due to the strong correlation observed between turbidity and mercury concentrations, further DOC concentration estimation is unnecessary.

Turbidity as a proxy for Total Mercury

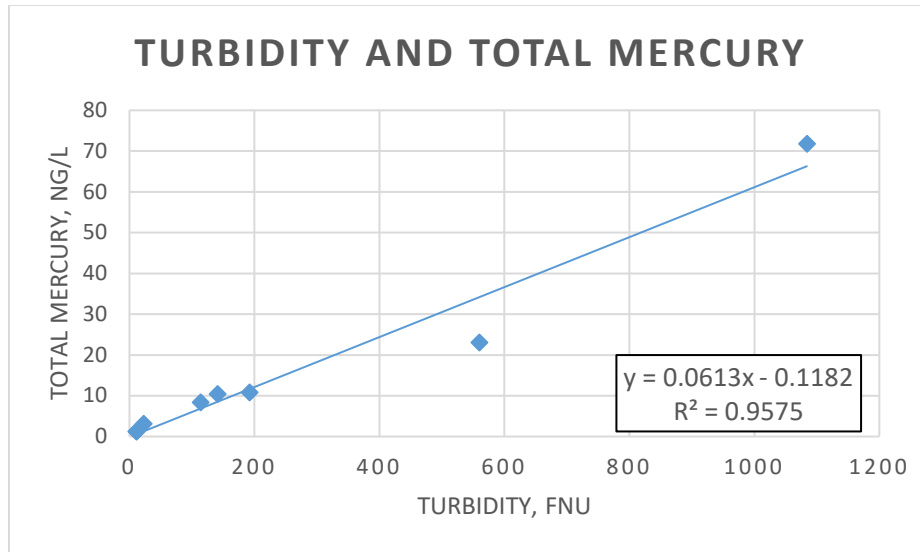


Figure 12. Total mercury (sum of PTHg and FTHg) concentration (ng/L) as a function of turbidity (FNU) for samples at Frog Bayou Creek, AR.

Turbidity proved to be strongly correlated to total-mercury concentrations (Figure 12, $p < 0.0001$). As turbidity within Frog Bayou creek increased, total-mercury concentrations increased. Many streamflow constituents are capable of influencing turbidity readings, but the signal of mercury concentration seemed to be valid across the full spectrum of turbidity conditions in Frog Bayou creek. Of the mercury transported during low-turbidity conditions, the majority was mercury dissolved in streamflow (FTHg), and not bound to sediments. The relation between turbidity and FTHg was well defined (Figure 14, $p < 0.0001$). For samples with low turbidity values, ranging from 10.8 to 114 FNU, FTHg was in higher concentrations than PTHg (Appendix, Table 1). This is an expected relation, as only very fine-grained sediments are capable of staying suspended in streamflow during low-flow conditions, principally clays and silt. However, as streamflow and turbidity increased, greater amounts of sediment were capable of moving downstream entrained in flow. As stream turbidity increased, the majority of mercury

transported in Frog Bayou creek changed from FTHg to PTHg, or mercury bound to stream sediments (Appendix, Table 1). At turbidity values greater than 114 FNU, PTHg concentrations surpassed those of FTHg. At the highest sample turbidity values of 560 and 1084 FNU, PTHg concentrations reached 16.6 and 63.9 ng/L, respectively (Figure 13). In the 1084 FNU turbidity sample taken during flood conditions, more than 8 times the concentration of total mercury was bound to stream sediments than was dissolved in streamflow. As was the case for MeHg, the majority of total mercury transported into LFS is attached to suspended particles and occurs during high-turbidity, high discharge flow conditions, a relation that has been observed in previous studies (Gray et al., 2002).

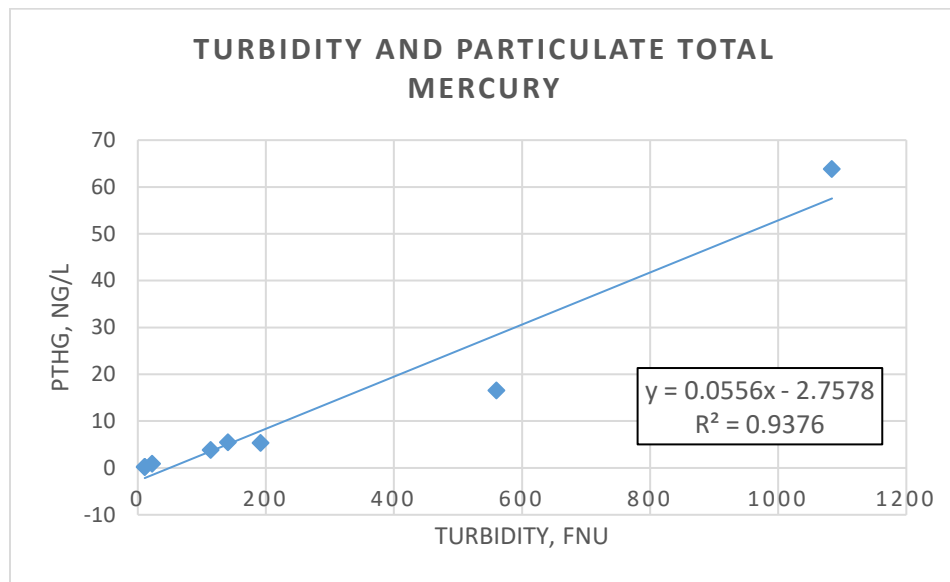


Figure 13. Particulate total mercury (PTHg) concentration (ng/L) as a function of turbidity (FNU) for samples at Frog Bayou Creek, AR.

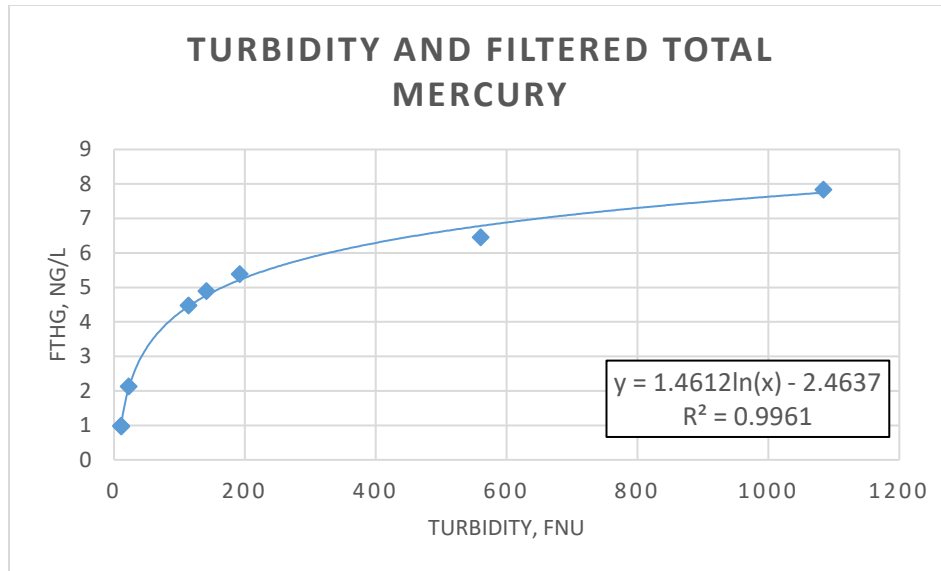


Figure 14. Filtered total mercury (FTHg) concentration (ng/L) as a function of turbidity (FNU) for samples at Frog Bayou Creek, AR.

Potential for long-term mercury load estimation

In order to mitigate public exposure to MeHg, understanding the transport pathways for mercury in all its forms moving into LFS is important. A fundamental understanding of the magnitude of mercury delivery to the lake on an annual basis, and under varying hydrologic regimes is very useful for those concerned about mercury contamination. This research revealed that the watershed is not a significant source of MeHg to LFS. However, the presence of MeHg in littoral zones and deep anaerobic lake depths suggests that methylation of mercury is occurring within LFS. Quantifying the total mercury delivery to LFS would allow for forecasting of MeHg formation and concentration trends in the future (Davies, 2008, Gray et. al, 2002, Howard et. al, 2010). The relation observed between turbidity and total mercury proves very useful to this end. Multiple turbidity measurements on an hourly basis allows for much more precise approximations of annual load than could be accomplished through discrete sampling alone.

Although a large part of the mercury delivered to LFS on an annual basis occurs during large precipitation events, Frog Bayou is at low flow, low-turbidity conditions for much of the year. The strong correlation of FTHg concentrations and turbidity ($r^2 = 0.996$, Figure 14) allows for a precise estimation of THg concentration during times of low flow. Although the correlation between turbidity and total mercury concentration is strong over a large spectrum of turbidity values, the precision provided by the FTHg-turbidity relation allows for fine tuning of mercury load estimations during low flow, which will greatly improve total mercury load estimations on an annual basis. Continuous field deployment of a turbidity sensor is relatively inexpensive, and site preparation and equipment installation is already completed. In order to maintain the validity and precision of this defined relation, future routine measurements of MeHg and total mercury will be necessary. However, an inexpensive proxy of mercury has been developed that if maintained will allow for responsible, long-term monitoring of an important natural resource.

Application to neighboring watersheds

Beyond its use at LFS, the relation between turbidity and total mercury concentrations has the potential to quantify total mercury loads to other lake bodies within neighboring watersheds. Although the authors know of no neighboring lakes or reservoirs where a turbidity-total mercury relation has been developed, the results of this study suggest that it is likely an exportable methodology. In order for this methodology to remain useful in other watersheds, drainage area characteristics must be similar to those at Frog Bayou creek. A local anthropogenic or rock source of mercury or MeHg in the watershed would likely reduce the accuracy of using turbidity as a proxy relation, including coal burning power plants or mercury bearing rock. Greater soil erosion rates would likely result in a stronger relationship between PTHg and turbidity. Watersheds containing greater proportion of wetland areas would likely transport more

FTHg during base flow conditions due to elevated presence of DOC, and would likely vary from the relation observed at Frog Bayou. Future research will hopefully evaluate this theoretical model in other watersheds, and may prove it a vital link in understanding the sources, movement and fate of mercury and MeHg in natural systems.

Summary

By constructing proxy relations at Frog Bayou creek, interested parties have a useful tool for understanding mercury and MeHg sources, formations and movement into Lake Fort Smith. This study has revealed the validity of turbidity as a useful water-quality parameter for the study of environmental pollutants. Long-term evaluation this technique will hopefully continue to provide insight into mercury and MeHg dynamics in other watersheds, within the Arkansas Ozarks and beyond.

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Appendix

Table 1. Water Analysis Mercury Data from USGS-WDML

Sample ID	Sampled Depth (m)	Particulate total mercury (ng/L)		Particulate methyl mercury (ng/L)		Filtered total mercury (ng/L)		Filtered methyl mercury (ng/L)		Turbidity (FNU)
		Results	DDL	Results	DDL	Results	DDL	Results	DDL	
FBRISE	0.1	3.89	0.0076	< 0.038	0.0038	4.48	0.0190	< 0.04	0.0070	114
FBPEAK	0.1	5.39	0.0110	< 0.036	0.0036	5.39	0.0190	< 0.04	0.0073	192
FBFALL	0.1	5.52	0.0113	<0.044	0.0044	4.89	0.0190	< 0.04	0.0074	141
FBAFTFL	0.1	0.961	0.0099	<0.029	0.0029	2.13	0.0190	< 0.04	0.0073	22.5
FRGBYUA	0.1	< 0.249	0.0108	<0.02	0.0020	0.99	0.0190	< 0.04	0.0074	10.8
FRGB55	0.1	0.227	0.0058	<0.02	0.0020	0.97	0.0190	< 0.04	0.0069	11.2
FRGHII	0.1	63.9	0.0778	0.399	0.0235	7.84	0.0190	< 0.04	0.013	1084
FRGHNL	0.1	16.6	0.0352	< 0.112	0.0112	6.45	0.0190	< 0.04	0.012	560

Table 2. Water Analysis Results for Samples at Frog Bayou Creek, AR.

Sample ID	Sample Date	Sampling Time (24 hr.)	Gage Height	Turbidity (FNU)	DOC (mg/L)
FBRISE	2/20/2018	09:30	4.39	114	5.4
FBPEAK	2/20/2018	10:30	4.40	192	6.3
FBFALL	2/20/2018	11:30	4.64	141	5.1
FBAFTFL	2/25/2018	12:05	4.60	22.5	0.8
FRGBYUA	3/8/2018	12:30	3.05	10.8	0.5
FRGBYUB*	3/8/2018	12:30	3.05	10.8	0.5
FRGB55	3/13/2018	11:50	2.92	11.2	0.6
FRGHII	3/27/2018	12:35	10.33	1084	7.7
FRGHNL	3/27/2018	16:05	6.18	560	3.8

* Denotes replicate sample

Summary Statistics for Turbidity and DOC Regression

Regression Statistics	
Multiple R	0.671162294
R Square	0.450458825
Adjusted R Square	0.358868629
Standard Error	2.261401906
Observations	8

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	25.15136851	25.15136851	4.918199	0.06841405
Residual	6	30.68363149	5.113938582		
Total	7	55.835			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	2.428921981	1.003820113	2.419678536	0.051886	-0.027337349	4.88518131	-0.02733735	4.885181311
Turb	0.005042671	0.002273828	2.217701327	0.068414	-0.000521185	0.01060653	-0.00052119	0.010606527

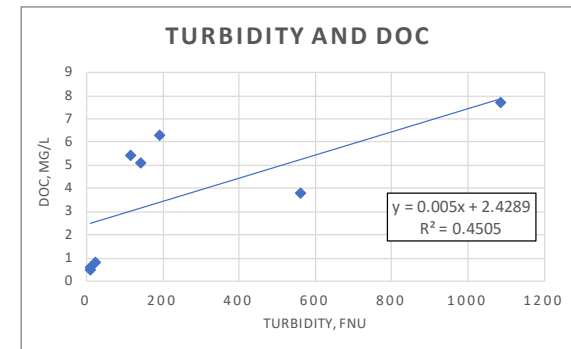
RESIDUAL OUTPUT

Observation	Predicted DOC	Residuals
1	3.003786487	2.396213513
2	3.397114834	2.902885166
3	3.139938607	1.960061393
4	2.542382081	-1.742382081
5	2.483382829	-1.983382829
6	2.485399897	-1.885399897
7	7.895177463	-0.195177463
8	5.252817802	-1.452817802

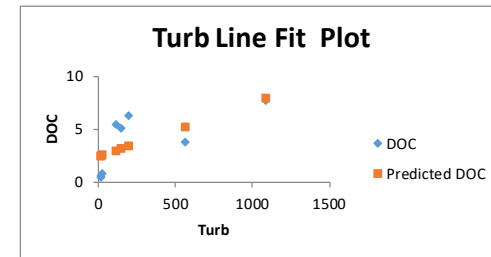
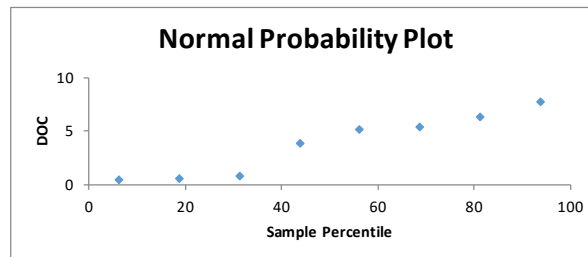
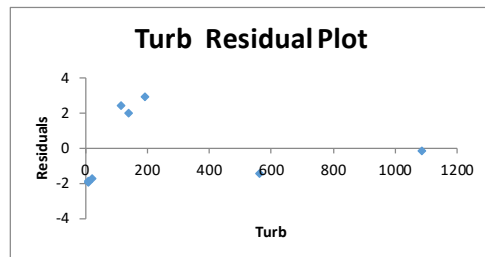
PROBABILITY OUTPUT

Percentile	DOC
6.25	0.5
18.75	0.6
31.25	0.8
43.75	3.8
56.25	5.1
68.75	5.4
81.25	6.3
93.75	7.7

REGRESSION



MODEL OUTPUT GRAPHS



Summary Statistics for DOC and Total Mercury Regression

Regression Statistics	
Multiple R	0.687205179
R Square	0.472250957
Adjusted R Square	0.384292784
Standard Error	18.4655629
Observations	8

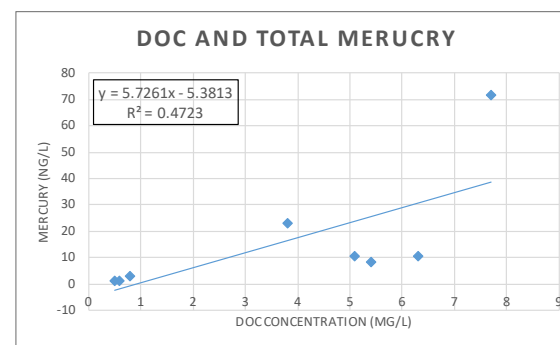
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	1830.71924	1830.71924	5.369040047	0.059683983
Residual	6	2045.86208	340.9770133		
Total	7	3876.58132			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-5.38133702	11.38634368	-0.472613261	0.653190217	-33.2427163	22.48004226	-33.2427163	22.48004226
DOC	5.726082654	2.471207942	2.317118911	0.059683983	-0.320745345	11.77291065	-0.320745345	11.77291065

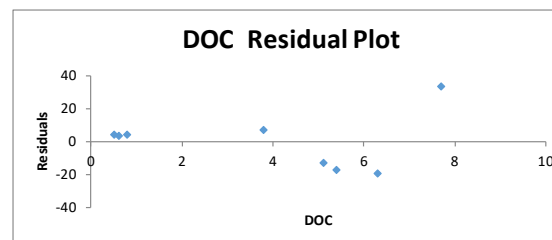
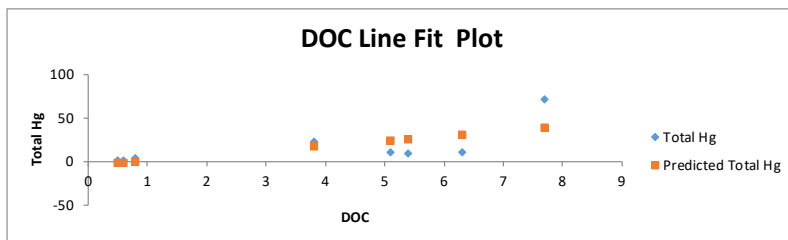
RESIDUAL OUTPUT

Observation	Predicted Total Hg	Residuals
1	25.53950931	-17.16950931
2	30.6929837	-19.9129837
3	23.82168452	-13.41168452
4	-0.800470896	3.891470896
5	-2.518295693	3.757295693
6	-1.945687427	3.142687427
7	38.70949942	33.03050058
8	16.37777707	6.67222934

REGRESSION



MODEL OUTPUT GRAPHS



Summary Statistics for Turbidity and Total Mercury Regression

Regression Statistics	
Multiple R	0.978541609
R Square	0.957543681
Adjusted R Square	0.950467628
Standard Error	5.237451244
Observations	8

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	3711.995947	3711.995947	135.321719	2.43061E-05
Residual	6	164.5853732	27.43089554		
Total	7	3876.58132			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.118214299	2.324867103	-0.05084777	0.96109734	-5.806959165	5.57053057	-5.806959165	5.570530568
Turbidity	0.061260929	0.00526623	11.6327864	2.4306E-05	0.048374929	0.07414693	0.048374929	0.07414693

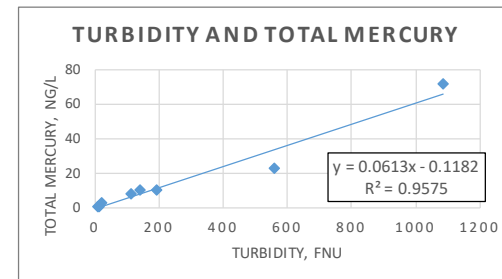
RESIDUAL OUTPUT

Observation	Predicted Total Hg	Residuals
1	6.865531634	1.504468366
2	11.64388412	-0.863884115
3	8.519576724	1.890423276
4	1.260156609	1.830843391
5	0.543403737	0.695596263
6	0.567908109	0.629091891
7	66.288633	5.451367003
8	34.18790608	-11.13790608

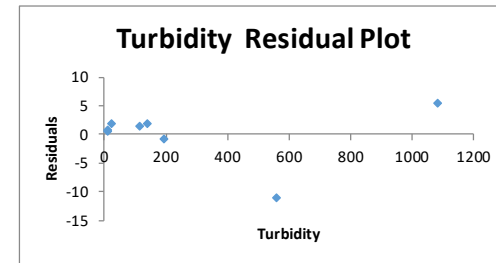
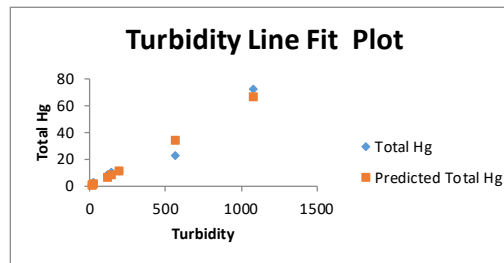
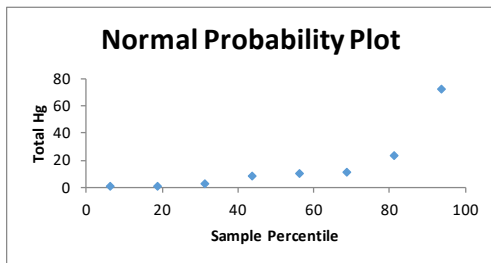
PROBABILITY OUTPUT

Percentile	Total Hg
6.25	1.197
18.75	1.239
31.25	3.091
43.75	8.37
56.25	10.41
68.75	10.78
81.25	23.05
93.75	71.74

REGRESSION



MODEL OUTPUT GRAPHS



Summary Statistics for Turbidity and Filtered Total Mercury, ln(Turbidity) and Filtered Total Mercury

Regression Statistics	
Multiple R	0.998055269
R Square	0.996114321
Adjusted R Square	0.995466708
Standard Error	0.171238799
Observations	8

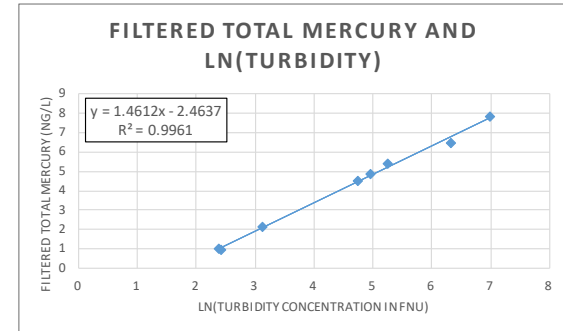
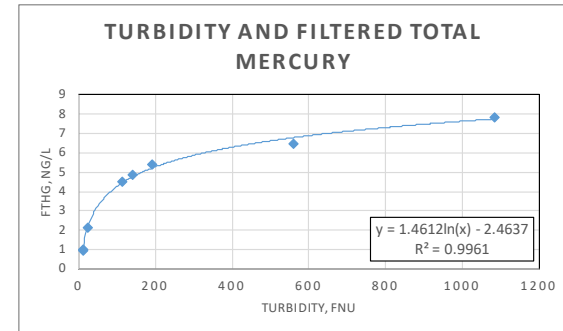
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	45.10221364	45.1022136	1538.13166	1.83605E-08
Residual	6	0.175936358	0.02932273		
Total	7	45.27815			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-2.463705387	0.178993553	-13.764213	9.1461E-06	-2.901686833	-2.025723942	-2.901686833	-2.025723942
ln(Turbidity)	1.461235517	0.037258337	39.2190216	1.8361E-08	1.370067651	1.552403383	1.370067651	1.552403383

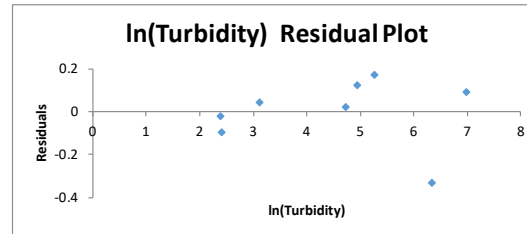
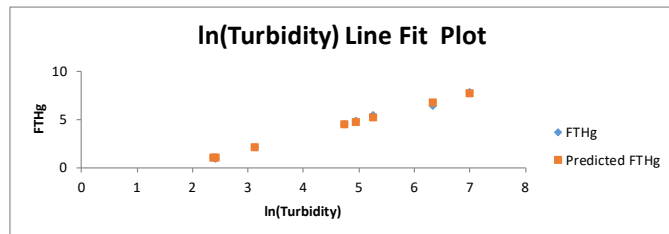
RESIDUAL OUTPUT

Observation	Predicted FTHg	Residuals
1	4.456996001	0.023003999
2	5.218733581	0.171266419
3	4.76759833	0.12240167
4	2.085873765	0.044126235
5	1.013371938	-0.023371938
6	1.066513632	-0.096513632
7	7.748012162	0.091987838
8	6.782900591	-0.332900591

REGRESSION



MODEL OUTPUT GRAPHS



Summary Statistics for Turbidity and Particulate Total Mercury Regression

Regression Statistics	
Multiple R	0.968306792
R Square	0.937618043
Adjusted R Square	0.92722105
Standard Error	5.826072641
Observations	8

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	3061.04702	3061.04702	90.1816569	7.77066E-05
Residual	6	203.6587345	33.9431224		
Total	7	3264.705755			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-2.757805553	2.586151926	-1.0663741	0.32727213	-9.08589135	3.570280243	-9.08589135	3.570280243
Turbidity	0.05563074	0.005858086	9.49640231	7.7707E-05	0.04129652	0.069964959	0.04129652	0.069964959

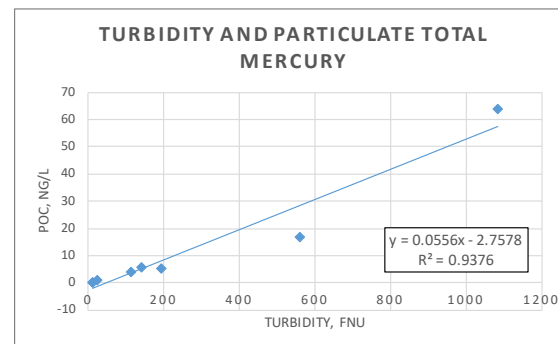
RESIDUAL OUTPUT

Observation	Predicted PTHg	Residuals
1	3.584098762	0.305901238
2	7.923296451	-2.533296451
3	5.086128731	0.433871269
4	-1.506113912	2.467113912
5	-2.156993565	2.405993565
6	-2.13474127	2.36174127
7	57.54591618	6.354083822
8	28.39540863	-11.79540863

PROBABILITY OUTPUT

Percentile	PTHg
6.25	0.227
18.75	0.249
31.25	0.961
43.75	3.89
56.25	5.39
68.75	5.52
81.25	16.6
93.75	63.9

REGRESSION



MODEL OUTPUT GRAPHS

