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Application of Diffusive Gradient in Thin-Film Passive Samplers to Assess Mercury Availability and Mobility in a Fresh Water River System

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by

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Dedication

To my parents and family, for the years of love and encouragement

To my wife, for support and love through this work and moving all over

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Application of Diffusive Gradient in Thin-Film Passive Samplers to Assess Mercury Availability and Mobility in a Fresh Water River System

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The accurate measurement of mercury in sediment porewater is a challenge using conventional sampling techniques which commonly require removal of sediment, transportation, and processing. Passive sampling is an alternative technique that measures sediment porewater concentrations in-situ and without significant sample disturbance. One passive sampling technique for mercury in sediment porewater is Diffusive Gradient in Thin-Films (DGT) samplers; a technique that has been employed since the 1990's but is relatively new for mercury and has been primarily utilized in the laboratory. The approach estimates porewater concentrations of mercury species in-situ based upon the rate at which the species diffuses through a thin film of controlled thickness. The modification of this technique for field applications could significantly improve measurement of mercury porewater concentrations;

however the technique lacks examples established quality assurance and control protocols, commercial availability, and examples of its successful implementation in a field setting.

Sediment systems are important to mercury fate in aquatic systems due to their role as both a sink for inorganic mercury and source for methylmercury. Within the sediment, porewater chemistry is important to understanding mercury speciation and reactivity. The interaction between the solid and dissolved mercury species ranges greatly between systems and controls availability of mercury for methylation, direct exposure, and transport.

This research uses DGT samplers in field applications to assess mercury speciation and mobility in sediment porewater. A representative site, the South River (Virginia, USA) was selected for evaluation of DGT sampling, development of sampling protocols and utilization of the technique for improving our ability to identify sources of mercury flux and evaluate of the biogeochemistry of a site. Through the use of DGT samplers, the river banks were identified as a potential source of mercury into the channel during flood events and the subsequent bank drainage. This behavior had not been identified using traditional sampling techniques and was not taken into account in the site conceptual model for mercury sources into the river. Using the DGT sampler data, a mercury flux budget was performed for a bank drainage event and it was determined that the river bank contributes significantly more mercury during large flood events than during baseline flow conditions. Laboratory studies were performed using South River bank sediment to better understand the biogeochemical behavior observed in the field.

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Chapter 1 – Introduction

Mercury is a global contaminant that comes from both natural and anthropogenic sources. Over 20,000 tons of mercury is released annually from anthropogenic sources annually, mostly from burning of coal. An additional 10,000 tons is released naturally from the earth's crust (Morel, Kraepiel, and Amyot 1998). Mercury and methylmercury has been associated with Alzheimer's, Parkinson's, sensory disturbances, decreases in motor function and muscular strength, multiple sclerosis, atopic eczema, a decrease in fertility, and a diminished immune system. The mercury can cycle through all phases of the environment once released. In the environment, mercury exists in two redox states, elemental (Hg^0) and inorganic (Hg^{2+}). Elemental mercury is more common in the atmosphere while inorganic mercury is more common in aquatic systems. Both redox forms of mercury can complex strongly with organic and inorganic ligands. Mercury can be converted to methylmercury in these conditions as a byproduct of biological reactions. Methylmercury is a more toxic form of mercury and is more easily bioaccumulated due to being lipid soluble.

Aquatic systems are an especially important environment since they can act as both a sink for mercury and produce methylmercury (Fitzgerald, Lamborg, and Hammerschmidt 2007). In aquatic systems, elemental, inorganic, and organic mercury species undergo a variety of biological and chemical processes which impact their speciation and mobility. Inorganic mercury species interact strongly with solids in aquatic systems. The interaction between the dissolved and solid-associated mercury is defined by the sediment-water partition coefficient (K_d). The K_d coefficient is defined as the ratio of mercury solid loading (e.g. mg/kg) and dissolved concentration (e.g. mg/L). In field measurements, the K_d for inorganic mercury can range from 10^3 to 10^7 L/kg (Fitzgerald, Lamborg, and Hammerschmidt 2007; Kocman et al.

2011). These coefficients show that inorganic mercury associates strongly with solids in aquatic systems. These solids then settle in the water body and the mercury accumulates in sediments. In general, the mercury associated with the solid phase is less mobile and less bioavailable than mercury suspended or dissolved in the porewater. As a result it is believed that porewater mercury such as that measured by passive samplers may be a better indication of mobility and risk than bulk solid concentrations of mercury.

Inorganic mercury undergoes speciation reactions in sediment porewater. Mercury can complex with a variety of ligands including organic matter, thiols, chloride, hydroxide, sulfide. In sediment systems, the interaction between these ligands and mercury is in addition to the interaction between the dissolved and solid phases. The balance between the ligands and solid phase are further complicated by redox changes which occur over depth in a sediment system. Dissolved oxygen is depleted in the upper layers of sediment porewater by microbial activity. After dissolved oxygen is depleted, less favorable electron receptors are utilized and reduced. These alternate electron receptors can include nitrate, manganese, iron, sulfate, and methanogens. As redox changes occur over depth into the sediment, the speciation of metals can change drastically (Guo, DeLaune, and Patrick Jr 1997). In reducing conditions, where sulfide is present, sulfide will dominate the speciation (Benoit et al. 1999). In oxic environments, with no sulfide present, the mercury speciation is controlled by other ligands such as chloride, hydroxide, thiols, and organic matter. Changes in the redox conditions of the system can also change the mercury speciation and mercury availability and mobility indirectly through changes in other parameters such as pH (Cappuyns and Swennen 2005). Dissolved organic matter (DOM) binds strongly with mercury and can outcompete even strong ligands, such as sulfide (Ravichandran

2004). DOM is known to enhance the solubility and mobility of mercury in river systems (Mierle and Ingram 1991).

Methylmercury is formed under reducing conditions, primarily by sulfate-reducing bacteria (Compeau and Bartha 1985). In order for methylmercury to be produced, sulfate-reducing bacteria must be active, which require sulfate and a carbon source, and there must be mercury available for methylation (Gilmour, Henry, and Mitchell 1992). Dissolved mercury in sediment porewater is expected to be more available for methylation than solid-associated mercury. The bioavailability of mercury and methylmercury has been shown to be strongly related to the sediment porewater concentration of these species (Ankley et al. 1994). DOM has also been shown to be capable of both enhancing (Weber 1993) and inhibiting (Miskimmin 1991) mercury methylation. Redox changes can impact both the biological and chemical processes which control mercury methylation (Himmelheber et al. 2008; Johnson, Reible, and Katz 2010). As solid-bound mercury is not readily available for methylation, accurate measurement of porewater concentrations is important to properly assessing methylation potential in a sediment system. Sediment systems can promote mercury methylation as they can be a sink for mercury and sulfate-reducing conditions often occur at depth. Methylmercury is more readily taken up by biota (Mason, Reinfelder, and Morel 1996), making the control of methylmercury production important for risk reduction.

Accurate measurement of mercury in sediment porewater is a challenge using conventional sampling techniques. Conventional sampling techniques rely on active processing of sediment samples to separate porewater for analysis. Commonly used active sampling techniques include centrifugation and displacement, both coupled with filtration. These techniques are complicated and can be tedious for collecting large volumes of porewater. They

require specialized equipment and training and have many steps which increase the opportunity for error and bias. The sediment must be removed and transported to a laboratory for processing. The removal and transportation of the sediment sample can change the redox conditions of the sample and disrupt porewater chemistry. Oxidation of the sediment sample changes porewater speciation of mercury and other metals. For example, oxidation of reduced iron species can cause precipitation and scavenging of mercury from the porewater (Bufflap and Allen 1995b). Transportation and processing of sediment samples can cause re-suspension of particles which disrupt porewater chemistry (Chapman et al. 1998). These particles are then removed from the sample through filtration, which can then remove mercury which was dissolved in-situ. The potential for these active sampling technologies to underestimate mercury porewater concentrations is high. Underestimating the mercury porewater concentration can lead to underestimating potential for bioaccumulation, toxicity, and mercury methylation.

Passive samplers are an alternative to sediment porewater active sampling techniques. Passive sampling techniques such as diffusion gradient in thin films (DGTs) are designed to measure porewater concentrations in-situ, lowering the potential for sample disturbance. DGTs rely on the diffusion of mercury into the sampler to measure porewater concentrations and thus are directly related to the mobile (i.e. capable of diffusing) phase. The DGT samplers were invented in the 1990's to measure cations in seawater. The DGT sampling method is well developed for other analytes and as a laboratory and surface water sampling technique, but it is relatively new as a tool for mercury in sediment porewater. The DGT samplers are used extensively to sample sediment porewater for mercury in this work to better understand their advantages and limitations.

The South River is a mercury contaminated site located in central Virginia that is a good example of a rock and cobble stream with relatively oxic conditions leading to inefficient methylation. Despite this, a variety of organisms including fish in the river and terrestrial organisms in the floodplain have accumulated mercury and methylmercury (Trice 2006), (Tom, Newman, and Schmerfeld 2010). Mercury was introduced into the river from a DuPont manufacturing facility between the 1930's and 1950. It was not until the 1970's, however, that the contamination was discovered and research has been done to characterize mercury behavior in the river ever since.

1.1 Research Objective

The objective of this work is to develop and apply a protocol for the field use of DGT samplers to measure mercury and methylmercury in sediment porewater. The DGT method is well developed for laboratory use and sampler materials have been optimized for measurement of mercury and methylmercury but field use of these samplers is the next step in their more widespread use. Field use presents new challenges such as new QA/QC protocols, deploying samplers in a variety of media, logistics of sampler transportation and storage and interpretation of the results in the complex porewater matrix in field systems. Practical methods for applying DGTs in the field are developed. DGT samplers are also compared to a variety of conventional porewater sampling techniques to identify differences and test the hypothesis that conventional approaches disrupt porewater chemistry leading to misleading estimates of concentrations. The DGTs are applied to assess the mercury availability and mobility in the South River (Virginia, USA), and to identify potential sources of mercury release and that might lead to mercury

movement and methylmercury formation. When a new source of mercury into the river was identified using the DGT samplers, laboratory experiments were conducted to explore the field observed processes in a more controlled environment and identify the causes of the observed behavior.

1.2 Research Outline

In order to address these issues, three separate tasks were undertaken with each building upon the previous to further understanding of DGT use for mercury in sediment porewater.

The first task is to compare results obtained using DGT samplers with other porewater sampling techniques to see how DGT samplers differ. DGT samplers were deployed in both field and laboratory experiments alongside other commonly used porewater sampling techniques. The DGT protocol was also enhanced by testing QA/QC procedures such as mercury contamination, sample stability in storage, and detection limits.

The second task is to use the DGT samplers extensively in a field setting to apply the technique to a real system to assess mercury sources and movement. The DGT samplers were used in the South River, Virginia over the course of 3 years in order to better characterize mercury behavior in the river channel and banks. DGT samplers allow more direct measurements of porewater mercury concentrations in the river banks and led to discovery of elevated mercury concentrations were measured during bank drainage events following high river flow.

The final task is to run experiments with the South River bank sediment in the laboratory to replicate and understand the mercury behavior seen in the field. Experiments were run using samples collected from the South River and a variety of sampling approaches were employed, including those used in the field and ones only available in the laboratory.

The combination of these tasks will show the applicability of DGT samplers in a real-world system and help us to better understand mercury behavior in that system. In addition, the application of the approaches will help indicate the applicability and the limitations of the approach to assess mercury behavior in field systems.

1.3 Document Structure

The work is divided into six chapters. A literature review of related work and concepts is shown in Chapter 2. The method of DGT samplers and their comparison to other techniques is shown in Chapter 3. The field work using DGT samplers in the South River and the mercury behavior during bank drainage found using DGT samplers are described in Chapter 4. Chapter 5 contains the results from laboratory experiments done with South River bank sediment to better understand the release of mercury from the banks during bank drainage events.

Chapter 2 – Literature Review

2.1 Mercury in the Environment

Mercury is a pollutant of global concern that enters the environment from both natural and anthropogenic sources. Mercury is naturally released from the earth's crust at a rate of 10,000 tons per year. Over 20,000 additional tons of mercury is released annually from anthropogenic sources, with the largest source burning of coal (Morel, Kraepiel, and Amyot 1998). In the environment, mercury predominantly exists in two redox states, elemental (Hg^0) and inorganic (Hg^{2+}) and can cycle through all phases of the environment in various forms. Elemental mercury makes up over 95% of mercury in the atmosphere while inorganic mercury is more common in aquatic systems. The third form of mercury in the environment is methylmercury, which is found predominantly in aqueous environments as it is unstable in its gaseous form. Methylmercury is a more toxic form of mercury and is more easily bioaccumulated due to being lipid soluble. Mercury and methylmercury have been associated with Alzheimer's, Parkinson's, sensory disturbances, decreases in motor function and muscular strength, multiple sclerosis, atopic eczema, a decrease in fertility, and a diminished immune system.

When mercury enters aquatic systems, it undergoes a variety of chemical and biological transformations which impact its speciation. All forms of mercury complex strongly with ligands, but inorganic mercury, in particular, strongly associates with solid phases. This strong association causes sediment systems to be a strong sink for mercury in aquatic environments. Approximately one sixth of all sites on the Environmental Protection Agency's National Priority List are metals impacted sediment sites (EPA NPL 2008) and many of these are associated with

mercury. Once in the sediment system, mercury speciation can change significantly from that in surface waters as there are different ligands present in sediment porewater, and there is the additional interaction between mercury and the sediment solid phase. The degree of interaction between the dissolved and solid-associated mercury is often characterized using by the sediment-water partition coefficient (K_d). The K_d coefficient is defined as the ratio of mercury solid loading (e.g. mg/kg) and dissolved concentration (e.g. mg/L). In field measurements, the K_d for inorganic mercury can range from 10^3 to 10^7 L/kg (Fitzgerald, Lamborg, and Hammerschmidt 2007; Kocman et al. 2011). As the partitioning coefficient ranges over several orders of magnitude depending on the composition of the sediment and background water, bulk mercury measurements do not give a complete picture of mercury behavior in sediment systems. High mercury loadings in a sediment system could have relatively low dissolved mercury concentrations and vice-versa. The dissolved mercury is more readily available for chemical complexation, physical transport, and biological transformation than the solid-bound mercury (Benoit et al. 1999). Sediment systems undergo changes in redox over depth as terminal electron acceptors are depleted. These redox changes can occur over depth changes of only a few centimeters. The active zone for these redox changes occur over a relatively small depth into sediment systems. In many systems, the active zone may occur in only the top 15 cm (Sunderland et al. 2004). Bulk mercury loadings may not change over depth but mercury speciation can change dramatically.

2.2 Mercury Porewater Chemistry

Mercury fate and transport in aquatic environments can be influenced by the speciation of the dissolved mercury. All forms of mercury will complex with a variety of ligands (organic matter, thiols, chloride, hydroxide, sulfide) and how it is complexed will influence its behavior. The interaction between aqueous and solid species becomes more important in sediment systems because of the high concentration of both mercury and complexing ligands. Dissolved organic matter (DOM) is found in higher concentrations in sediment porewater than surface water, binds strongly with mercury and can outcompete even strong ligands, such as sulfide (Ravichandran 2004). Dissolved organic matter complexation can affect solid-phase partitioning by lowering the freely-dissolved mercury concentrations to below the solubility limit of mercury-solids (Benoit et al. 1999). DOM is also known to enhance the solubility and mobility of mercury in river systems (Mierle and Ingram 1991). The solid-liquid partitioning coefficient has been shown to correlate with DOM concentrations (Bloom et al. 1999). The chemical dynamics between mercury and these ligands are not uniform within the sediment system due to the potential for the development of redox gradients and redox-driven chemical transformation and speciation. In reducing conditions, where sulfide is present, sulfide will dominate the speciation (Benoit et al. 1999). In oxic or less strongly reduced environments, with no sulfide present, the mercury speciation is controlled by other ligands such as chloride, hydroxide, thiols, and organic matter. The speciation of mercury is complicated in systems which have non-steady state redox conditions. Changes in the redox conditions of the system can also change the mercury speciation and mercury availability and mobility through changes in other parameters such as pH. (Cappuyns and Swennen 2005).

Dissolved mercury speciation and the sediment redox environment greatly influence the potential for mercury methylation. Aquatic systems are an especially important environment since they can act as both a sink for mercury and provide environmental conditions conducive to production and decomposition of methylmercury (Fitzgerald, Lamborg, and Hammerschmidt 2007). Mercury methylation has been shown to be a by-product of sulfate reduction by bacteria (Compeau and Bartha 1985; Gilmour, Henry, and Mitchell 1992). In order for mercury methylation to occur, freely available mercury, redox conditions conducive for sulfate reduction, and an organic carbon source for microbial communities are all needed. In sediment systems, steady-state methylmercury concentrations occur due a balance between methylation and demethylation processes (Drott et al. 2008). Methylation processes are strongly dependent on biological activity while demethylation is a function of both chemical and biological processes (Warner, Roden, and Bonzongo 2003). DOM has also been shown to be capable of both enhancing (Weber 1993) and inhibiting (Miskimmin 1991) mercury methylation. Enhancement of methylation is likely the result of an increase in readily exchangeable mercury in the water column due to the presence of both uncomplexed and DOM complexed mercury and/or the increase in microbial reduction resulting from the increase in available organic matter from DOM. However, high concentrations of DOM may reduce the most bioavailable forms of mercury.

The percent methylmercury (i.e. the ratio of methylmercury to total mercury) in either porewater or solids is indicative of the balance between methylation and demethylation. High methylation rates relative to demethylation will lead to relatively high methylmercury percentages. Low methylation rates relative to demethylation will lead to correspondingly lower methylmercury percentages. For sediment systems, the absolute methylmercury concentrations

are important for risk and biota exposure, but the percent methylmercury in porewater, i.e. the percentage of dissolved porewater mercury that is methylmercury, is more indicative of methylmercury productivity in the system. The solid-bound mercury is not thought to be available for methylation and so the ratio of methylmercury to total mercury in the porewater is likely a more direct indicator of methylation productivity. Methylmercury also does not interact as strongly with the solid phase as inorganic mercury species. This difference in partitioning strength between inorganic and organic mercury has a large effect on the relative composition of mercury in the aqueous and solid phases. In productive systems, methylmercury comprises between 10 and 80% of the total mercury in porewater as opposed to less than 5% in the solid phase. As a result, solid-phase sampling may not provide accurate estimates of the amount of methylmercury present in a sediment system especially since these percentages vary greatly between systems depending on porewater biology and chemistry (Kannan et al. 1998).

2.3 Sediment Porewater Sampling

The ability to accurately measure porewater geochemistry is important to understanding mercury mobility and availability for methylation in sediment systems. Accurately sampling sediment porewater can be extremely difficult. Many of the important dissolved species are redox sensitive, making it even more difficult to measure them accurately. There are a variety of sampling techniques available and the results from different techniques can vary greatly. The porewater sampling technique can functionally change the porewater chemistry and so it is important to understand how porewater is sampled (Chapman et al. 2002). The strong interaction between mercury and solid-phases present in sediment systems further complicate

porewater sampling techniques. Traditional porewater sampling techniques put a variety of stresses onto the sediment sample which can generate suspended particles in the porewater. These particles can then alter the mercury speciation in the porewater. Partitioning to suspended particulate matter is 10-100 times greater than partitioning in sediments (Fitzgerald et al. 2007) because suspended particles are typically enriched in high surface area clays and organic matter than settled solids. Thus, the generated suspended particles will not interact with dissolved mercury species in the same way that sediment solids did when the sample was in-situ. Suspended solids also typically interact much more strongly with inorganic mercury species than with methylmercury. In short, any sampling approach that modifies the distribution of solids between the porewater and the settled solids will change the mercury distribution.

2.3.1 Traditional Sampling Techniques

Most sediment porewater sampling techniques are active methods, including direct sampling, centrifugation and filtration, and displacement. These techniques generally require the removal of a sediment sample which may disturb the sample. The disturbance is especially problematic for metals since it may lead to disturbance of fine grained particles and resuspension of particulate matter. These particles can either release additional metals to the dissolved phase or scavenge metals from the dissolved phase (Chapman et al. 1998). The mercury that is associated with these particles is not available for methylation and transport in-situ and so measurements which include this phase may overestimate mercury transport and methylation potential. Filtration of samples gives a functionally defined dissolved phase, based solely on particle size. What filter size gives the most representative dissolved concentration? Is this consistent from site to site and chemical to chemical? Mason et al. 1998 observed total mercury concentrations that were 82% lower when filtered through at 0.1µm when compared to 5µm.

Iron losses were 94%, while manganese losses were negligible. The filter size and material chosen can have huge effects on the measured porewater and may not be representative of in-situ porewater. Sampling of redox sensitive species is even more complicated. Removal of the sample may expose it to oxygen which will oxidize the reduced constituents, such as sulfide and Fe^{2+}.

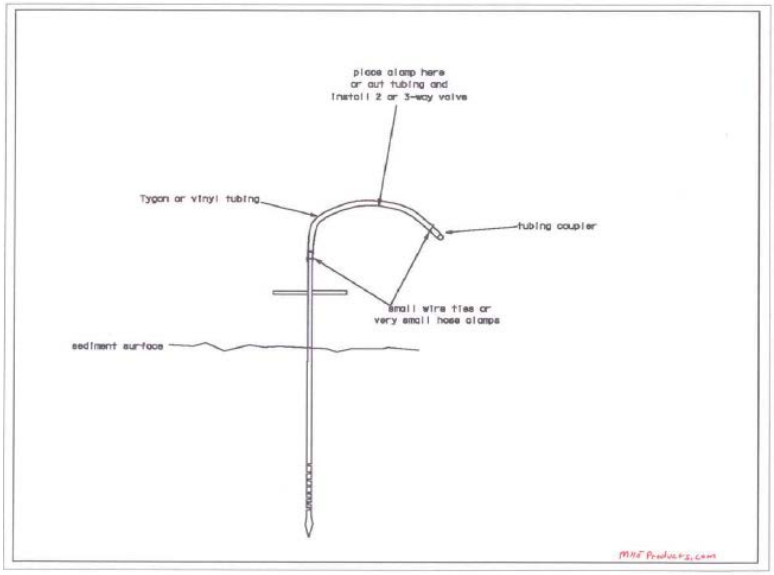

Figure 1 – Henry's Sampler "Pushpoint" Sediment Porewater Sampling System (M.H.E. Products)

One commonly used sediment porewater sampling technique is the direct withdrawal of porewater using a Henry's Sampler. A Henry's Sampler is a narrow probe which is inserted into the sediment to allow porewater extraction. A sample schematic of a Henry's Sampler probe is shown in Figure 1. The sampler used in this technique is a stainless steel tube, ranging in length from 14" to 72", with perforations on one end and a sampling port on the other. The tube diameter is either ¼" or 1/8". The perforated end is inserted approximately 2" into the sediment and then water samples are taken from the sampling port at the other end of the tube. Samples can be collected using either a syringe or peristaltic pump (MHE Products 2003). This method is

approved as an EPA sampling procedure and is described in EPA Operating Procedure SESDPROC-512-R2 last updated in February 2013. The major advantage of this technique is that is does not require collection of any sediment. This cuts down significantly on sampling and transportation costs as large amounts of sediment are required to produce useable porewater volumes for laboratory analysis. It has been used by a variety of state and federal agencies (EPA Operating Procedure SESDPROC-512-R2, 2013; State of Washington, Department of Ecology, April 2009). It is relatively simple to use and porewater can be collected quickly. However, there are some major drawbacks to this technique as well. Different sediment systems will have widely varying permeability and porosity, which strongly influence the performance of these samplers. It is impossible to tell what depth the sample is being collected from, a fine-scale vertical profile cannot be obtained. Collecting samples requires pumping of the porewater which can disturb solids. These disturbed solids can change the porewater chemistry significantly. Particles can either release contaminants into the porewater, or more likely in the case of metals, scavenge contaminants from the porewater. Since porewater is filtered after collection, the contaminants scavenged by these particles are then removed from the sample. This can lead to extremely high filter losses in porewater samples. Surface water can also be collected while pumping which dilutes the porewater samples. The likelihood of collecting water that is inconsistent with the in-situ porewater chemistry is increased as large amounts of water are collected, for example, to meet volume requirements for trace mercury analysis.

An alternative is to collect a sediment sample and collect a porewater sample in the laboratory. The most commonly used laboratory technique for sampling porewater is centrifugation (Mason et al. 1998). Sediment samples are collected, usually in cores, and sent to a laboratory for processing. The sediment is segmented and centrifuged under an inert

atmosphere to separate the porewater from the solids. The collected porewater is then filtered, usually through a 0.45 µm filter. The major advantage for centrifugation is the ability to generate relatively large volumes of porewater. In order for this technique to be effective, samples must be processed quickly and under precise conditions. Sediment samples have to be shipped to the laboratory as quickly as possible and be kept cold to prevent oxidation and sample loss. The centrifugation and filtration must be performed in an inert atmosphere. It is recommended that all processing be performed at 4^{o}C to slow losses. The long series of processing steps and sample storage conditions can lead to significant errors as they are not easily followed. Centrifugation also has a high likelihood of introducing suspended and colloidal particles into the porewater. These particles can increase total mercury into the unfiltered porewater and scavenge additional dissolved mercury which is then removed during filtration. Losses of mercury after centrifugation and filtration have been shown to range from 35% to 63% (Bufflap and Allen 1995b).

Another commonly used laboratory based porewater sampling technique is displacement. The displacement technique obtains porewater by displacing it within the pore spaces with another fluid or gas. A similar technique is core squeezing instead of replacing the porewater in the pore space, the pore space is reduced by mechanical squeezing and the displaced porewater is collected (Bufflap and Allen 1995a). Large volumes of porewater can also be extracted using this method, depending on sediment characteristics. Using low flowrates, the sample is not disturbed as greatly as in centrifugation, generating fewer suspended particles. This technique can require specialized equipment to displace the porewater using nitrogen to avoid dilution of the porewater with the displacement water. Porewater can also be displaced using a fluid, but low flowrates need to be used and small volumes collected to minimize mixing of the

displacement fluid and porewater. Filtration is also typically employed to process samples from this technique which still leaves the same questions regarding filter size and type and how that impacts the measured porewater.

2.3.2 Passive Sampling Techniques

Passive sampling is an alternative to these conventional sampling techniques. Passive sampling is any sampling technique which obtains a measurement without active media transport (pumping, extraction, purging). This greatly reduces disturbance of samples and can give a more representative measure of in-situ conditions. Passive sampling also does not require removal and transport of water or sediment samples which can reduce time and cost and increase safety of sampling. The majority of passive sampling devices rely on diffusion of analytes into a sorbing media in order to collect and concentrate the analyte. The sampling device and matrix that is used can affect which analytes can be measured, detection limits, and the physical parameters of sampling. Passive sampling devices for organics often attempt to achieve equilibrium between the sampling device and media. In order to achieve equilibrium, and low detection limits, long sampling times are required. This can be restrictive if you are trying to sample dynamic environments. Alternatives to equilibrium assumptions include addition of performance-reference compounds, non-equilibrium modeling, assumed linear uptake, or flux-measurement samplers. Performance-reference compounds are marked compounds which are spiked onto the sampler prior to deployment which have similar diffusion characteristics to the analytes. The performance reference compounds diffuse off the sampler at the same rate that the analytes diffuse into the sampler and so by measuring the remaining performance reference compound after deployment, the proximity to equilibrium can be measured (Thomas et al. 2014). For certain passive samplers, such as solid-phase microextraction, samplers of varying geometry can

be deployed and the proximity to equilibrium can be modeled by comparing the uptake rates of the varying samplers. The most common correction for non-equilibrium conditions is an assumed linear uptake rate (Alvarez 2008). The linear uptake rate is estimated in laboratory experiments which do not take into account field sampling conditions and is not quantitative. This method is most commonly used for organic compound passive samplers such as semi-permeable membrane devices (SPMD) and polar organic chemical integrative samplers (POCIS) (ITRC 2006). Dialysis membrane sampling devices, also known as peepers, are another sampling technique. Dialysis samplers have been used for sediment porewater sampling since the 1970's (Hesslein 1976). Peeper samplers have rigid cells which are filled with water free of the analyte to be measured in the porewater. The cells are separated from the sediment with a membrane and the analyte diffuses into the cell. The peeper can either be deployed until equilibrium is reached or a tracer can be utilized to measure the relative extent of equilibrium achieved. Dialysis samplers have the advantage of retaining vertical resolution in the sediment, minimizing disturbance of the sample, both physically and chemically, and being a direct chemical measurement of the porewater. One of the major disadvantages is that the volume of sample collected is limited by the size of the peeper sampler. Larger samplers allow for larger sample volume collection, but larger samplers are more difficult to deploy and increase potential sediment disturbance. Another disadvantage is that the time to equilibrium can vary greatly depending on the diffusion rate of the analyte being measured, site conditions such as temperature, and the physical design of the sampler. Without use of a tracer, either a very long deployment time, up to a month, needs to be used or uncertainty in the extent of equilibrium achieved will exist.

Employing an equilibrium sampler for mercury is problematic since the partition coefficient between a sorbing material and porewater is strongly matrix dependent. As an alternative, a flux sampler which measures the rate of mercury species uptake in a controlled manner is a better tool to measure mercury concentrations in porewater. Utilizing flux samplers is advantageous because they have no assumption of equilibrium and measure the analyte based on how much of the analyte entered the sampler over a given time under actual field conditions. One widely used flux based sampler is the diffusive gradient in gel thin-film (DGT) sampler.

2.4 Diffusive Gradient in Gel Thin-Film (DGT) Technique

Diffusive gradient in gel thin-film (DGT) was originally developed by Davison and Zhang (Davison, 1994) in order to measure cation concentrations in bulk seawater. Figure 2 shows the conceptual model used in DGT samplers.

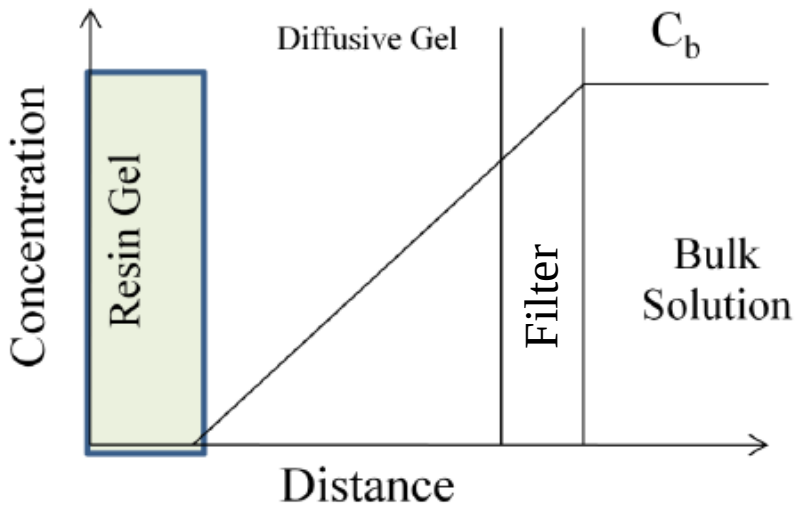

Figure 2 – Conceptual model of DGT sampler

DGTs measure porewater concentrations using Fick's first law of diffusion. The mercury and methylmercury diffusion rate is controlled by the diffusion gel. The equation describing the mass uptake is:

$$J = \frac{M}{At} = -D\frac{\delta\varphi}{\delta x} = \frac{DC_b}{\Delta g} \rightarrow C_b = \frac{M\Delta g}{DtA}$$

C_b = Porewater Concentration D = Mercury/Methylmercury diffusion coefficient

M = Mass accumulated in resin t = Time exposed

Δg = Diffuse layer thickness A = Sampler area exposed

The resin gel can hold a much larger amount of mercury then is contained in the surrounding porewater. Over a deployment time of several days, the concentration in the resin gel is effectively zero, which simplifies the porewater concentration calculation. The primary goal is to ensure that the dominant mass transfer resistance to uptake is the diffusion gel which provides a simple relationship between concentration in porewater and mass of mercury taken up. The porewater concentration can be calculated from the mass accumulated, the diffusion length, the diffusion coefficient, the area exposed, and the time exposed. The diffusion length and area exposed are physical parameters of the samplers. The diffusion coefficient is a chemical parameter of dissolved mercury and methylmercury. The diffusion coefficient through water can be used as an approximation or the site specific diffusion coefficient can be found experimentally (Chess 2010). The diffusion rate changes as the temperature changes and so the

diffusion coefficient used in the concentration calculation needs to be corrected for temperature. Davison and Zhang 1995 proposed the temperature correction for the diffusion coefficient shown below;

$$\log D_t = \frac{1.37023(t-25) + 8.36\ x\ 10^{-4}(t-25)^2}{109+t} + \log\frac{D_{25}(273+t)}{298}$$

D_t = diffusion coefficient at temperature t (cm^2/sec),

D_{25} = diffusion coefficient of ions in water at 25 °C (cm^2/sec),

t = temperature (°C).

DGT samplers rely on several assumptions to calculate the bulk concentration of the analyte being measured. The main assumptions are; 1) the geometric values of exposure area and diffuse thickness are well known, 2) analyte interaction with the diffuse layer and filter are negligible, 3) analyte binds to the resin layer at the surface instantaneously, 4) time to steady-state diffusion is negligible relative to deployment time, and 5) colloid-associated analyte species contribute negligibly to DGT uptake (Davison and Zhang 2012). Research testing these assumptions is an active area of work. The effective exposure area of DGT samplers has been shown to be effectively larger by up to 20% than the geometric area due to diffusion occurring laterally as well as perpendicularly into the samplers (Warnken, Zhang, and Davison 2006), leading to the potential to overestimate concentrations. The effective diffusion thickness can be greater than just the diffusion gel and filter thickness with the added impact of the diffuse boundary layer. A diffusive gradient forms outside of the sampler due to the analyte diffusion into the sampler, even in a relatively well-mixed system. This diffuse boundary layer was

estimated at 0.2 mm. The effectively larger exposure area and longer diffuse thickness counteract each other. The net effect has been shown to be an error of less than 10% (Davison and Zhang 2012). The second assumption of negligible diffuse layer interaction with analytes has also been studied. Diffuse layer gels can have a net negative charge due to an excess of reagents which can increase the interaction between the gel and analyte. This negative charge can be removed by thorough washing of the gel prior to construction of the sampler (Warnken, Zhang, and Davison 2005). Low ionic strength of the diffusion gel has also been shown to increase this interaction. At ionic strengths of higher than 1 mM, there has been shown to be no effect on the uptake kinetics (Zhang and Davison 1999). The kinetics of analyte binding with the resin layer is relatively fast, on the order of minutes, and is negligible for deployment times greater than two hours. The kinetics of binding has been shown to be even faster in systems where the analyte is present at high concentrations, such as a contaminated environmental site (Davison and Zhang 2012). The time to 95% of steady state is approximated by $\Delta g^2/2D$ and time to 99% of steady-state by $\Delta g^2/D$. For typical DGT samplers, these times would be approximately 13 and 27 minutes, respectively and would be insignificant relative to deployment times of several hours or more. The relative error in these approximations is low, with an error of 3.3% after 4 hours and only 0.56% after 24 hours (Garmo, Davison, and Zhang 2008). The assumption of the negligible impact of colloid-bound species, and the related issue of the effect of solution speciation, is not as clearly answered. If complexes readily disassociate or have the same diffusion coefficient as the freely dissolved species, they will be taken up by the DGT samplers and included in the measured concentration. These complexes are considered labile. Metal complexes with inorganics such as carbonates, hydroxides, sulfates, and chlorides all follow this behavior (Davison and Zhang 2012). The interaction between DGT samplers and

metals complexed with organic ligands is more complicated. In certain situations, the organic ligands can be taken up by the diffusion gel which increases the interaction between the gel and metals (Garmo, Davison, and Zhang 2008). Organic complexes can also directly diffuse into the samplers, but they will have diffusion rates which will vary widely. The total analyte uptake will be the sum of all diffusive fluxes (Zhang and Davison 2000). However, not all complexes are either fully labile or non-labile. These semi-labile complexes will partially disassociate and contribute to the diffusive uptake into the sampler, but not all of the complex will be available. The partial disassociation can be modeled, but requires a complete analysis of complexing ligands for an accurate calculation. Semi-labile complexes tend to disassociate more within the diffusion gel than they do in solution which could lead to overestimation of solution concentrations (Mongin et al. 2011). For nanoparticulates, based on the Stokes-Einstein equation, particles of approximately 5nm would diffuse at a rate roughly one tenth of that of freely dissolved particles (Lead et al. 1994). However, in testing the diffusion of particles of these size and smaller, the diffusion in DGT gels has been shown to be up to ten times slower than the theoretical value (Scally, Davison, and Zhang 2006). This is likely due to pore size restrictions of the diffusion gel. Agarose gels have been found to have a mean pore diameter of 74 nm (Fatin-Rouge, Starchev, and Buffle 2004), but detailed pore size characterization of these gels is not available. An exact size cutoff for particles that will be excluded by gels is unknown, but particles larger than 100 nanometers are likely excluded for all samplers. In studies with lead nanoparticles, it does not appear that the nanoparticles are directly being taken up by DGT sampler,s but they may be indirectly increasing uptake (Van Der Veeken, Pinheiro, and Van Leeuwen 2008). The total impact of nanoparticles on DGT samplers is still not fully understood and is an area of current research. Despite these uncertainties, DGTs are clearly less sensitive to

colloidal and suspended particulates than crude filters that invoke relatively large pore sized filters (e.g. 0.45 um) to separate “dissolved” species from particulate bound. The DGT appears to respond only to mercury associated with particulate and colloidal matter well below 100 nm in size.

DGT samplers have been recently developed for use with mercury and methylmercury (Fernández-Gómez et al. 2011). A new thiol resin; 3-mercaptopropyl functionalized silica gel (3MFSG), has a very high affinity for mercury and methylmercury (Clarisse and Hintelmann 2006). DGT resin gels using the 3MFSG beads absorb 91.6% of available mercury from solution and 96.5% of that mercury is able to be eluted back off the gels (Chess 2010). The high uptake and elution efficiency make this resin material ideal for use in DGT samplers and binding kinetics are sufficiently rapid. The diffuse layer is made from an agarose gel, which does not interact strongly with mercury, allowing linear diffusion through it. The impact of mercury association, including dissolved-speciation, nano-particulates, and colloidal-bound, is not well understood.

2.5 Mercury Mobility in the Environment

Mercury is often present in precipitated solids such as sulfides under reducing conditions. Thus, mercury can be mobilized by dissolution of these solids, especially sulfide solids, as a result of dynamic changes in oxidizing conditions. Mercury can complex directly with sulfides and precipitate or can sorb to the surface of other metal-sulfide precipitates. If these solid species are present, oxidation of the system could lead to large increases in mobile mercury. There has been a large amount of research on mercury-sulfide speciation and solubility

constants. However, much of this work was done at higher sulfide concentrations (>50mM) (Paquette and Helz 1995), which would only be found in strongly reducing systems.

There has also been research conducted on the release of metals due to oxidation of reduced sediments, however most of this research has focused on resuspension of sediments and little of it looked at mercury (Simpson 1998; Atkinson 2007). There are still parallels which can be drawn between these experiments and mercury in a river system. Resuspension of anoxic sediments does not mean that there will definitely be release of metals. In studies in which anoxic sediments were artificially resuspended in oxic waters, not all the sediments were oxidized over the course of 12 hours and the sediments that did oxidize did not all release metals (Burgess and Kester 2002). It is important to understand how the river system will react to redox changes and to see if there is significant heterogeneity which will affect its behavior. Redox changes can impact other geochemical parameters which influence metal speciation and availability. Research has also examined other metals in groundwater. The release of arsenic has been shown to vary with DOC and iron concentrations (Reza et al. 2010). Similar relationships should be valid for mercury as well. These relationships vary site to site, depending on site biology and geochemistry. One of the controlling factors for metal speciation is pH. For the release of freely dissolved metals, pH has been shown to be the one of most important chemical factors controlling aqueous concentrations (Hong, Kinney, and Reible 2011).

The kinetics of the dissolution of metals from redox changes can be fast, depending on the mineral. A comparison between dissolution of a variety of metal sulfides shows that some minerals (manganese sulfide, iron sulfide, nickel sulfide, and copper sulfide) dissolved in less than an hour. Other minerals (zinc sulfide, cadmium sulfide, and lead sulfide) did not fully dissolve within 8 hours (Simpson, Apte, and Batley 1998). Depending on what mineral form the

mercury is in, and what other minerals it's associated with, the mercury may or may not solubilize. There have been studies that examine geochemical changes caused by dynamic hydrologic systems, but many of these studies examined much longer timescales, on the orders of months to years (Vangriethuysen et al. 2005). The release of metals from oxidized sediments has been shown to spike within the first few days and stabilize within weeks (Hong, Kinney, and Reible 2011). This can be important in systems in which water chemistry changes suddenly, such as tidal areas or flooding rivers. Even if it takes weeks for the system to re-establish equilibrium, metals can be released in the short-term and the cycle can be repeated.

The river bank environment is influenced by both the channel flow and the groundwater flow in the area around the river. Studies have examined the impact of large precipitation events on mercury transport in river watersheds (Curtis et al. 2013) but have focused on precipitation driven erosion of Hg contaminated sediment. Studies have shown that groundwater can be a major source of mercury into stream systems. In a New Jersey stream, isolated groundwater seeps were found to have up to 5,000 ng/L of mercury. The relative influence of groundwater is also dependent on stream flow conditions. For a river in South Carolina, it was found that the main source of mercury during baseline flow conditions was groundwater but that during flood events there were hydraulic connections to other source areas (Bradley et al. 2010). Groundwater mercury and methylmercury have been found to correlate strongly with dissolved organic carbon (DOC), but less so with sulfate and redox potential. The impact of mercury contaminated groundwater depends on the hydraulic characteristics of the river system (Vidon et al. 2013). This research shows the importance of understanding site-specific hydrology. Mercury in groundwater is also affected by speciation within the plume. In deep groundwater systems, redox changes can develop across the plume, both vertically and horizontally (Lamborg

et al. 2013). These redox changes can alter the mobility of mercury across the plume so it is important to understand the groundwater geochemistry across the whole source area.

2.6 Summary

Understanding mercury in aquatic systems is important due to their actions as a sink for mercury, a source for methylmercury, and their potential exposure risk to biota and humans (Fitzgerald, Lamborg, and Hammerschmidt 2007). Sediment systems are an integral part of mercury fate and transport in aquatic systems. Sediment systems have a mixture of physical, biological, and chemical processes controlling mercury behavior. Dissolved mercury species in the porewater are available for transport and methylation. The complex interactions between mercury and the solid-phase in sediment systems make bulk mercury measurements inadequate primarily due to the fact that sediment-water partitioning coefficients range over several orders of magnitude. Traditional sampling techniques have significant shortcomings in porewater sampling for mercury. They are unable to measure mercury concentrations in-situ and transport and sediment processing can change porewater chemistry which in turn affects mercury speciation. Passive samplers, especially diffusive gradient in thin-film samplers, can address many of these shortcomings and yield a more accurate dissolved mercury porewater concentration. DGT samplers have been primarily used as a laboratory tool; however, there is a need for protocol development for their use as a field tool.

Chapter 3 – Diffusive Gradient in Thin-Film Use for Mercury in Sediment Porewater

3.1 Introduction

The goal of this chapter is to further develop the existing method for DGT samplers to measure mercury and methylmercury for use in field sampling of sediment porewater. In order for DGT samplers to be more widely used as a field tool, a more fully developed QA/QC protocol is needed and this work addresses this need. DGT samplers are compared to other porewater sampling techniques both in the field and laboratory to show that conventional techniques overestimate porewater concentrations when measured unfiltered and underestimate porewater concentrations when measured filtered. DGT samplers have been in use since the early 1990's for measurement of cations and methods for their preparation and deployment are well developed. While DGT samplers for mercury have shown significant potential, methods and sampling protocols are still under development. The most frequently cited protocol for DGT measurement of mercury was developed by Clarisse and Hintelmann in 2006. Their method was developed for laboratory and field use of DGT samplers in natural waters. Laboratory verification studies for DGT sampler performance for mercury in sediment porewater were performed by Chess and Hong in 2010. Their work included a limited field trial using DGT samplers in the South River (Virginia, USA) to test the DGT samplers in a real environment (Chess 2010). This work builds upon these trials and expands the use of DGT samplers in the South River. The methods used for DGT sampler fabrication and use are described in this chapter.

3.2 Materials and Methods

There are two types of DGT samplers that have been commonly used, a depth profiler, which allows for sampling of up to 14 cm in depth, and a piston sampler for point measurements at a specific depth. The DGT depth profiler sampler, shown in Figure 3, is used to measure porewater concentrations in sediment over depth. The samplers used for this work have a sampling depth of 14cm, this depth is sufficient for most sites as the active zones for porewater mercury dynamics and mercury methylation typically occur in the top 10 cm of sediment.

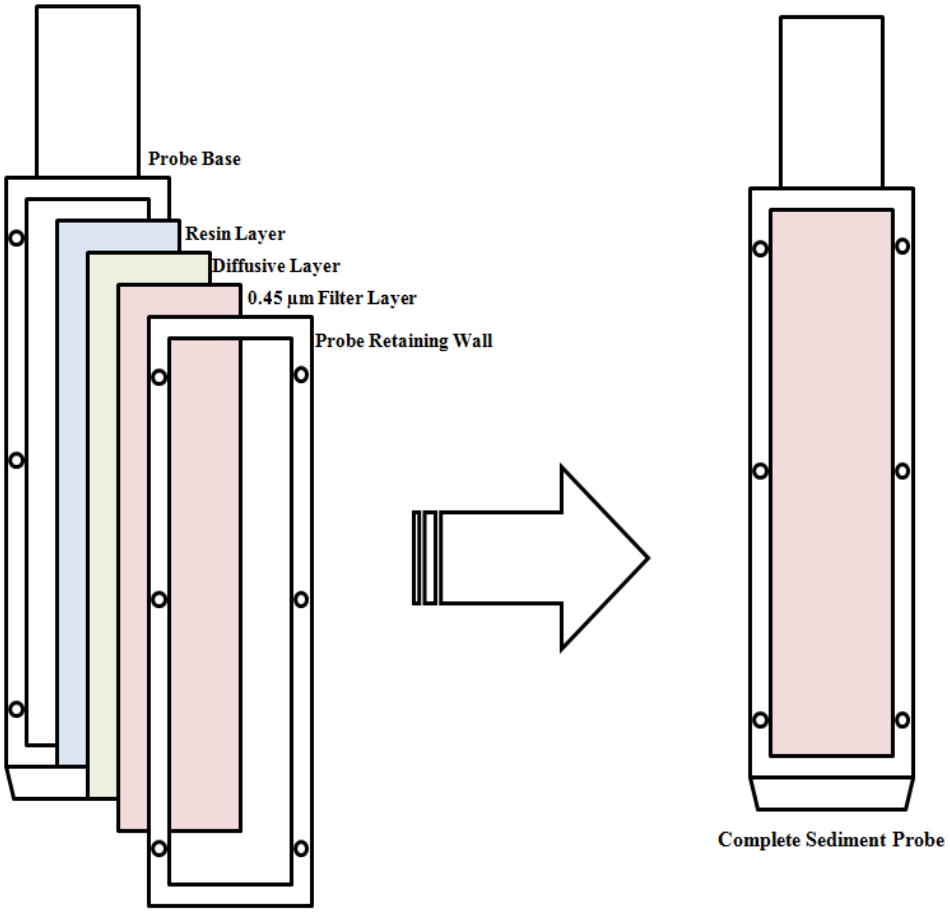

Figure 3 – Schematic of a DGT Depth Profiler Sampler

The second type of DGT sampler, the piston sampler, is shown in Figure 4. The piston sampler gives a point measurement for a specific depth or location but has more flexibility in placement. The piston sampler can be deployed in sediment, the water column, sampling wells, or in glassware in the laboratory. For sediment sampling, the piston sampler is placed gel-side down into the sediment and provides a measurement for the upper 2cm of porewater concentrations. For water column sampling, the piston sampler is suspended at the desired depth, e.g. using fishing line, a weight, and a float. To sample sampling wells, the piston sampler can be lowered down the well to the water surface. To use the piston samplers in the laboratory, an o-ring is attached to the sampler so that it will seal in the opening of a flask. A variety of glassware can be used depending on the sample volume needed. The exposure area for DGT piston samplers used in this work is 3.14 cm^2.

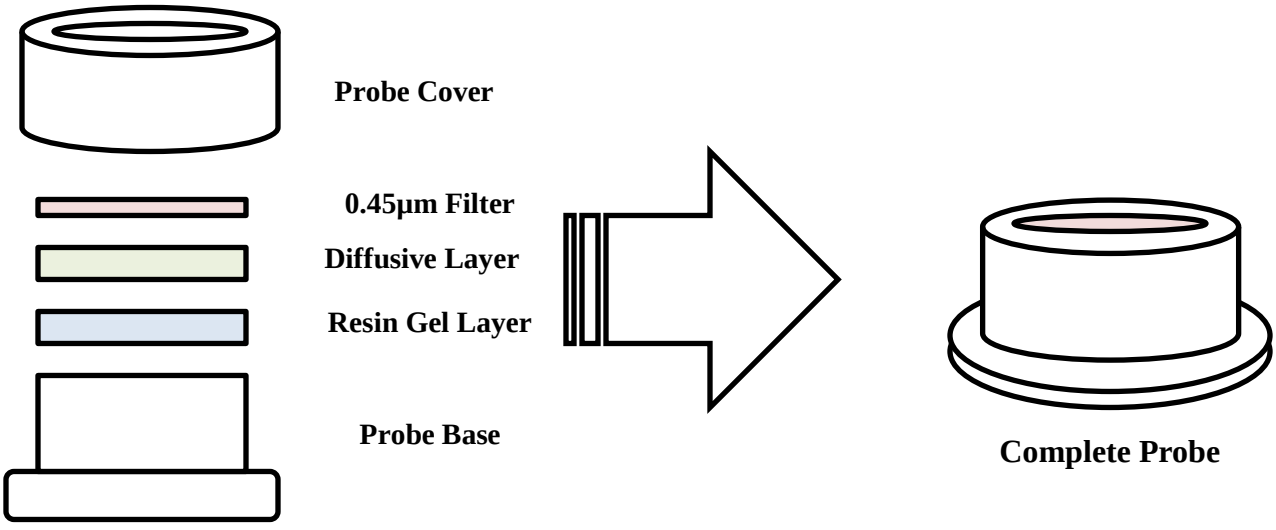

Figure 4 – Schematic of DGT Piston Sampler

The DGT samplers are fabricated in-house using commercially available chemicals. DGT samplers for mercury have generally not been available commercially necessitating in-house production. However, fabricating the samplers in-house allows for better quality control for important factors such as total mercury contamination. The DGT samplers are made in three steps, resin gel casting, diffusion gel casting, and construction. The standard operating procedure for DGT fabrication can be found in the appendix.

The first step in DGT fabrication is the casting of the resin gel. The resin gel layer acts as the sink for mercury in the DGT sampler. The resin layer consists of a thiolated resin bound in a polyacrylamide or agarose gel, with polyacrylamide gels being used more often. The thiolated resin used in this research was 3-mercaptopropyl functionalized silica gel (Sigma Aldrich) and Isosolute SI-Thiol (Biotage). The resin gel solution is made up of 15% acrylamide with 0.3% DGT cross-linker. The cross-linker is a patented product obtained from DGT Research Ltd. in the United Kingdom. The thiolated resin beads are then mixed into the gel solution at a ratio of 1 gram per 5mL of solution. An ammonium persulfate 10% solution is used as a gel activator along with tetramethylethylenediamine as a catalyst. The gel is mixed and then cast between glass plates at a thickness of 0.075cm. The gel sets at room temperature for 45-60 minutes. It is then hydrated in deionized water for at least 24 hours. The resin gel expands during this hydration step and impurities diffuse out of the gel. After hydration the gel is stable and ready for use in DGT samplers.

The second step is the casting of the diffusion gel. The diffusion gel is made up of 1.5% broad-spectrum agarose (Fisher). The agarose gel is boiled in deionized water and then immediately cast between glass plates at a controlled thickness. The most commonly used thickness for this work was 0.075cm. The agarose gel sets at room temperature for 30-45

minutes. The agarose gel is ready for use immediately after cooling. Most commercial DGTs employ polyacrylamide diffusion gels but these are not appropriate for mercury due to their tendency to sorb mercury.

The final step for DGT sampler fabrication is sampler construction. The resin gel is cut into the proper shape and placed into the DGT sampler body. The diffusion gel is then cut into the same shape and placed over the resin gel. Both gels are then covered with a 0.45 μm polysulfone filter (Millipore). The filter layer protects the resin gels from particulates. The DGT sampler body cover is then snapped on to hold the gels and filter in place. DGT samplers are stored at 4^{o}C until they are deployed.

Prior to use, the DGT samplers are deaerated in 10 mmol/L sodium nitrate for 12-24 hours. This step removes oxygen from the samplers which can be introduced into the sediment when the DGT samplers are deployed. The sodium nitrate is necessary to raise the ionic strength of the diffusion gel. The sodium nitrate increases the reproducibility of metal ion diffusion (Zhang 1999). DGT samplers should not be exposed to oxygen prior to deployment. If the DGT samplers need to be transported prior to deployment, the samplers should be transferred to double-bagged plastic bags in an anoxic atmosphere. The deaeration step should be completed as close to deployment as possible as oxygen can diffuse back into the samplers over time. The DGT samplers are then deployed in the media to be measured. If they are being deployed in water samples, the DGT samplers must be in the liquid and have the gel face exposed. In laboratory experiments, slow mixing is recommended to reduce any diffusion boundary layers at the surface of the sampler. For sediment, the samplers are pushed into the sediment. Piston DGT samplers are placed at the surface of the sediment and can be sealed with putty to ensure that the

gel face remains in contact with the porewater. Depth profiler DGT samplers can be inserted by hand or using an insertion tool. Insertion tools are discussed in Chapter 4.

The DGT samplers are left exposed in the media for a known amount of time. In sediments, this time is typically 1-7 days and for water samples this time is typically 1-21 days. The deployment time will vary depending on the range of concentrations that are being measured. Lower concentrations require a longer deployment to allow the samplers to accumulate a measurable amount of mercury. Higher concentrations should not be deployed too long as the sampler can accumulate enough mercury to disrupt the linear concentration gradient across the gel causing non-linear uptake. In addition, in mixing limited systems, long deployment times can deplete concentrations in the vicinity of the sampler and limit the applicability of constant flux in the analysis. When the DGT samplers are removed, they should be thoroughly rinsed with distilled or deionized water. For sediment sampling, all residual solids need to be cleaned from the exterior of the sampler as they can contaminate the gels during processing.

The DGT samplers are then ready to be processed. The gels are cut out from the sampler body using a Teflon® coated razor blade. The filter and diffusion gel can be discarded. If any solids penetrated the filter layer and made direct contact with the resin gel, the resin gel should be discarded. Direct contact with the sediment will contaminate the resin gel and would result in overestimation of porewater concentrations. The resin gel is then sectioned. The resin gel can be split to allow for simultaneous measurement of total mercury and methylmercury. For depth profiler DGT samplers, the resin gel is sectioned over depth to give porewater concentrations over depth. The depth profilers are typically sectioned at 0.5 or 1.0 cm resolution but sections have been taken as low as 0.1 cm. As long as there is a detectable amount of total mercury or

methylmercury in each section, the area chosen will not affect the estimated porewater concentration.

For total mercury elution, each resin section is then eluted in 3mL of concentrated trace-metal grade hydrochloric acid for 24 hours. Resin gels should not be left in the acid for longer than 24 hours as the gel will break down and can interfere with analysis. Once the acid is removed from the gel, it is ready for analysis. A subsample of the acid is diluted in 1% bromine monochloride and digested for at least 24 hours. This digestion step is necessary to break down any mercury complexes that were contained in the sampler. For samples that were exposed to high dissolved organic carbon, 2% bromine monochloride can be used as the DOC will react with some of the bromine monochloride. If the samples have turned clear after 24 hours, add additional bromine monochloride and digest for an additional 24 hours. The samples are then analyzed according to EPA Method 1631, Revision E. The volume of acid used to dilute should be chosen in order for the samples to fall within the calibration range of the analysis. For this work, the total mercury samples were analyzed on a Brooks Rand Merx-T cold vapor atomic fluorescence spectroscopy (CVAFS) system or a Tekran 2600 CVAFS.

For methylmercury elution, each resin piece is eluted in 15mL of 0.01 molar trace-metal grade hydrochloric acid with 13.1 mM thiourea. Resins should be eluted for 24 hours, but these resins should not break down after elution as with the total mercury samples. The acid-thiourea sample can be directly analyzed for methylmercury following removal of the resin gel. The samples are analyzed for methylmercury according to EPA Method 1630. There is one important change from the EPA method for these samples as the pH needs to be adjusted above 2.9 for accurate analysis. The pH can either be adjusted with addition of 0.01 M sodium hydroxide or by increasing the volume of sodium acetate buffer used in the EPA Method. The EPA Method calls

for 0.3 mL of buffer to be added to each sample but these DGT extract samples require addition of 5.0 mL of buffer. A pH check was performed for each set of samples to ensure that the pH was high enough for effective analysis. Dilutions are typically not necessary for methylmercury analysis. For this work, methylmercury analysis was performed on a Brooks Rand Merx-M CVAFS system or a Tekran 2600 CVAFS.

It is important to analyze quality control checks during use of DGT samplers. There are several types of QC samples that are run with every DGT sampler batch. The first sample is a laboratory blank. A laboratory blank is a check on the mercury contamination contained in the resin before it is assembled into a DGT sampler. Mercury contamination in the resin can come from chemical contamination, especially the thiol resin beads, glassware, or storage solutions. A laboratory blank is taken from each set of DGT resin gels cast for a sampling event. The second QC sample is a deaeration blank. The deaeration blank is taken after the DGT samplers are deaerated in sodium nitrate but before they are taken out into the field. The deaeration solution contains a small amount of mercury from the ambient atmosphere and chemicals used. The DGT samplers will accumulate a small amount of this mercury during the deaeration process. The deaeration blank will check that this mercury contamination is not significant compared to the mercury accumulated during sampling. Field blanks are also taken as a QC sample. The field blanks are DGT samplers which are deaerated and then transported along with all deployed DGT samplers. The field blanks will measure any mercury contamination accumulated during transportation, storage, and field use of the DGT samplers.

The detection limit is an important factor when considering what sampling technique to employ. A detection limit for total mercury using DGT has been proposed at 0.7 ng/L (Hong 2011). This detection limit was calculated for a DGT sampler that is deployed for 21 days and analysis is done using inductively coupled plasma mass spectrometry (ICP-MS). It is assumed that the analytical detection limit will control the detection limit of the DGT sampler. This calculation does not take into account mercury contamination in the DGT sampler and how that will affect the detection limit. For the detection limit of 0.7 ng/L, the DGT resin would contain 0.01 ng of total mercury. As an example, in field use in the South River, the average mercury contamination mass in a DGT piston sampler was 0.40±0.18 ng. It would be impossible to quantify accumulation as low as 0.01 ng from deployment of the sampler with that contamination level. The detection limit of the sampler was controlled by the contamination mass not the analytical detection limit. Using a typical CVAFS analyzer, masses as small as 0.005 ng can be detected, but this is not useful when the contamination mass is so much higher. In order to quantify the mass accumulated in the DGT from deployment, this accumulated mass must be greater than the mercury contaminant mass. Parameters of the DGT deployment will determine the equivalent porewater concentration for different accumulated masses. For these calculations, the parameters used were the same as was used in field deployment of DGT in the South River. The diffusion gel thickness was 0.075cm and the deployment time was varied The first set of detection limits calculated are the theoretical detection limits based on the analytical detection limits of the Brooks Rand Merx-T CVAFS. The sampling times used were 2, 7, and 21 days. Deployment times in the field ranged from 2-7 days. 21 days was chosen since it was used by Hong to calculate the 0.7 ng/L detection limit. The second set of detection limits was calculated using the average contamination mercury mass of 0.4 ng. The detection limit was the

necessary porewater concentration needed to accumulate mercury mass equal to that contaminant mass. The third set of detection limits were calculated so that the accumulated mass would be at least equal to the average plus two standard deviations of the mercury mass contamination. Using this detection limit would ensure that the accumulated mass would be sufficient to insure that the mercury contamination did not interfere. All calculated detection limits are shown in Table 1. Lower detection limits are possible in controlled laboratory settings where mercury contamination is lower. Future improvements in lowering mercury contamination in DGT samplers will lower the detection limit for field sampling.

Table 1 – DGT Total Mercury Detection Limits

Deployment Length (days)	Theoretical Detection Limit (ng/L)	Detection Limit to Equal Average Contamination (ng/L)	Detection Limit to Equal Average +2SD Contamination (ng/L)
2	0.032	13.1	25.0
7	0.009	3.8	7.2
21	0.003	1.3	2.4

The stability of mercury in the resin and extract solution are important parameters for good analytical quality control. It is important to understand how long the mercury is stable in the resin before processing and in the extract before analysis because sample loss can lead to underestimating measured porewater concentrations. When these samplers are used in the field, it may not be possible to process the samplers immediately so stability is an important consideration for real-world use. In order to assess the stability of mercury in the DGT resin gel,

a set of 60 DGT piston samplers were spiked with mercury and processed after various times and under varied storage conditions. Solutions were spiked with mercury(II) chloride stock (Brooks Rand) to 10 ug/L and buffered with 10 mM sodium nitrate. The DGT piston samplers were then exposed to this solution in order to spike the samplers with mercury. The DGT samplers were removed from the solution and split into six subgroups with ten samplers each. The first group was processed immediately and served as the baseline for storage comparisons. Four of the groups were stored at 4^{o}C for 3, 7, 14, and 35 days respectively. The final group was frozen at -20^{o}C and stored at that temperature for 3 days. The samplers were then analyzed for total mercury to see if there was substantial sample loss over these storage times. The results for this experiment are shown in Figure 5. No losses were observed after only 3 days of storage at 4^{o}C and only 2.5% loss under the frozen conditions. The samplers stored for 7 and 14 days at 4^{o}C showed only 2-5% loss. The DGT samplers stored for 35 days lost over 20% of spiked mercury. This storage condition is the only one that showed significant loss. DGT samplers should be processed within 2 weeks and be stored at 4^{o}C from retrieval to processing.

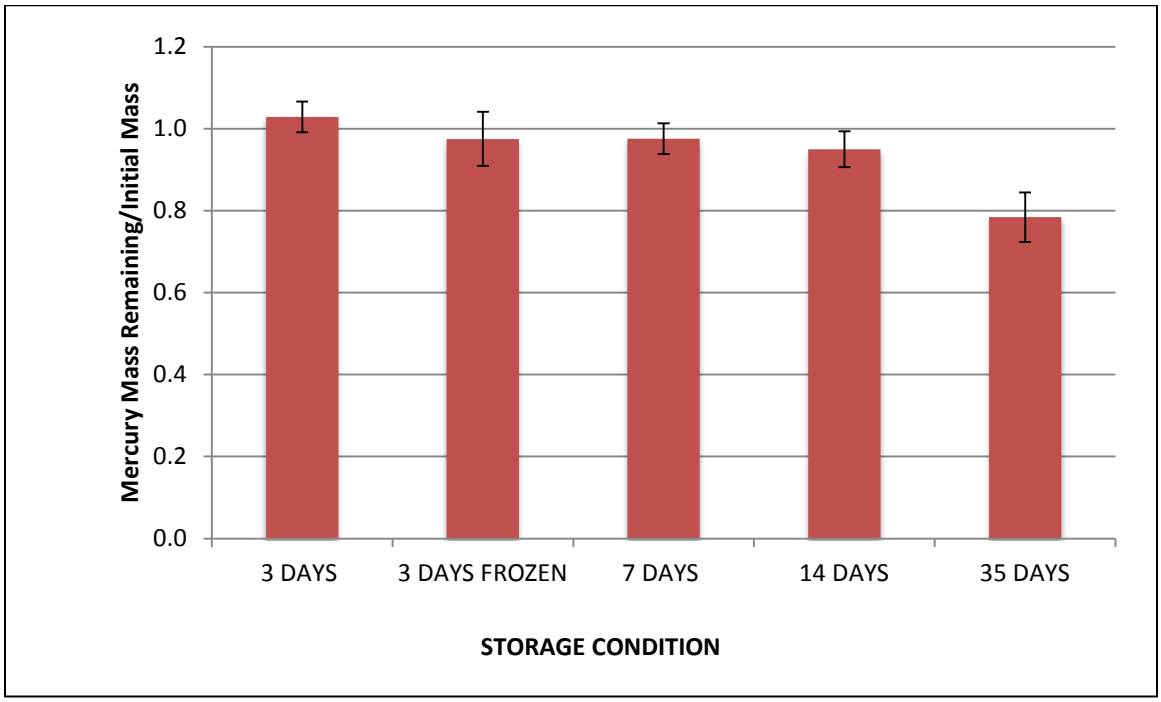

Figure 5 – Storage Stability of Polyacrylamide based DGT Resin at 4°C and -20°C. Error Bars are Standard Deviation form 10 Replicates.

Polyacrylamide resin gels are stable for at least 14 days but some resin gels use an agarose base instead. Further experiments were needed in order to compare the stability of the agarose gels relative to the polyacrylamide gels. Polyacrylamide and agarose DGT samplers were spiked using the same method described previously and stored at 4°C for 14 and 28 days. The results from these tests are shown in Figure 6. Both gels showed similar stability when stored for 14 days. The polyacrylamide resin loss was minimal, which matched the losses tested previously. The agarose resin also showed no detectable loss over the 14 day storage. However, the agarose gel lost 10% of spiked mercury at 28 days and showed greater variability compared

to the polyacrylamide resins. Agarose resin gels should also be processed within 14 days of retrieval and stored at 4°C from retrieval to processing.

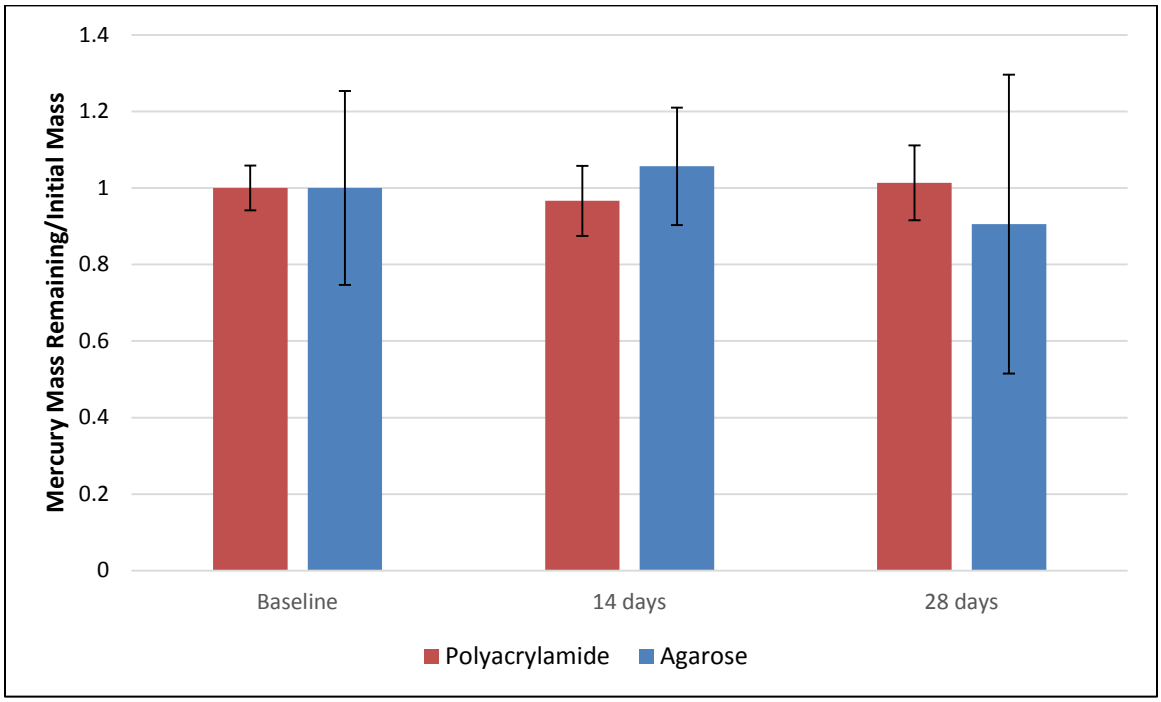

Figure 6 – Comparison of Polyacrylamide and Agarose based DGT Resins storage stability at 4°C. Error Bars are Standard Deviation form 6 Replicates.

Storage of the DGT extract solution is another possible route for sample loss. Even if the DGT samplers are processed with 14 days, mercury could still be lost from the hydrochloric acid extract solution over time. In order to determine the stability of this solution, a set of 129 DGT field samples were reanalyzed after a variety of storage times. All of these samples were originally analyzed within days of processing. They were then reanalyzed after 1, 7, and 10

months. The results are shown in Figure 7 with the total mercury mass normalized by the baseline measurement. After 1 month of storage at 4°C, the extract solution showed only 1% mercury loss. At 7 months, the extract solution showed 15% mercury loss with slightly more variability. The extract samples had almost 40% sample loss after 10 months. In order to minimize mercury loss during extract solution storage, the DGT extract samples should be analyzed within 1 month of processing. If this timeline is followed, no practical sample loss should be observed.

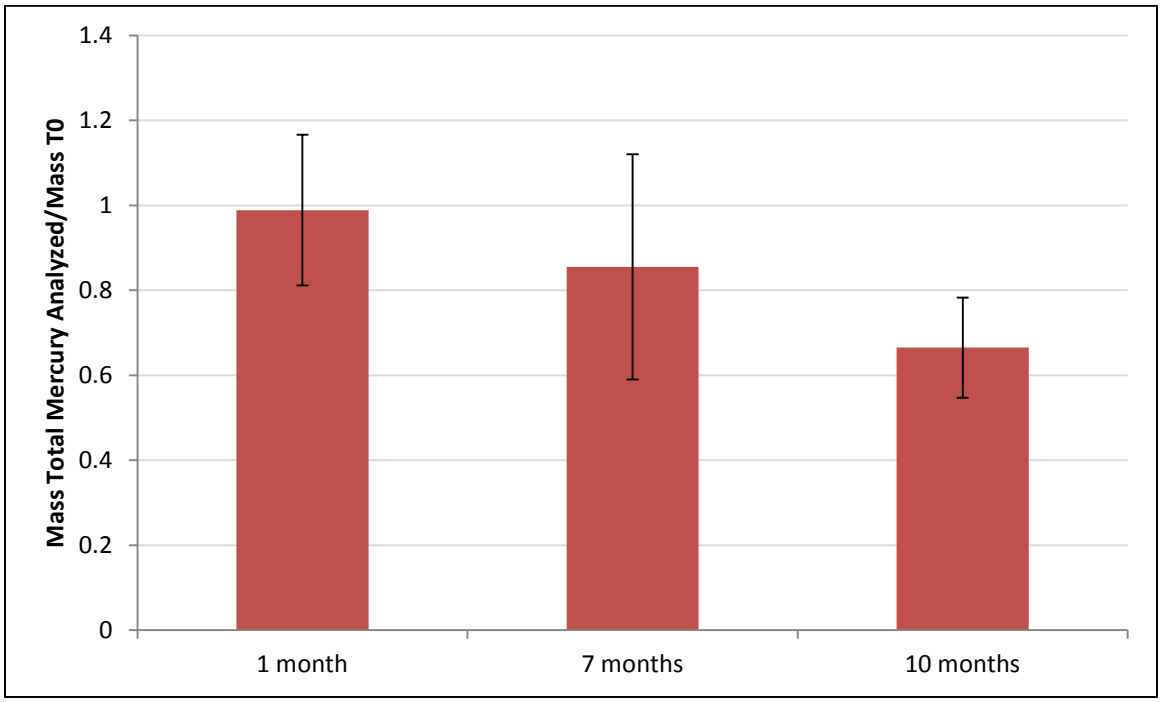

Figure 7 – Storage Stability of Hydrochloric Acid Total Mercury DGT Extract at 4°C. Error Bars are Standard Deviation form 77 Replicates.

DGT samplers have been used for measuring a variety of dissolved analytes but are relatively new for mercury sampling. In order to give context for the comparison of DGT samplers with other porewater sampling techniques, an understanding of how DGT samplers perform with mercury is needed. Chess 2010 performed laboratory testing and optimization of DGT samplers for mercury, DGT samplers were exposed to a variety of solutions of known mercury concentrations ranging from 100 to 700 ng/L. The solutions were spiked with a certified mercury-chloride standard and buffered at a neutral pH with sodium nitrate. For each DGT sampler exposure, a theoretical mercury mass uptake was calculated. The DGT samplers were processed and analyzed for total mercury and the comparison between the analyzed and theoretical masses is shown in Figure 8. Ideally, the slope for this curve would be 1 and the actual slope is very close to this at >0.99. The fit is very good with the coefficient of determination of 0.94. This experiment demonstrates that the DGT samplers made using the method described above can successfully uptake mercury according to theory and that mercury can be eluted off the resin.

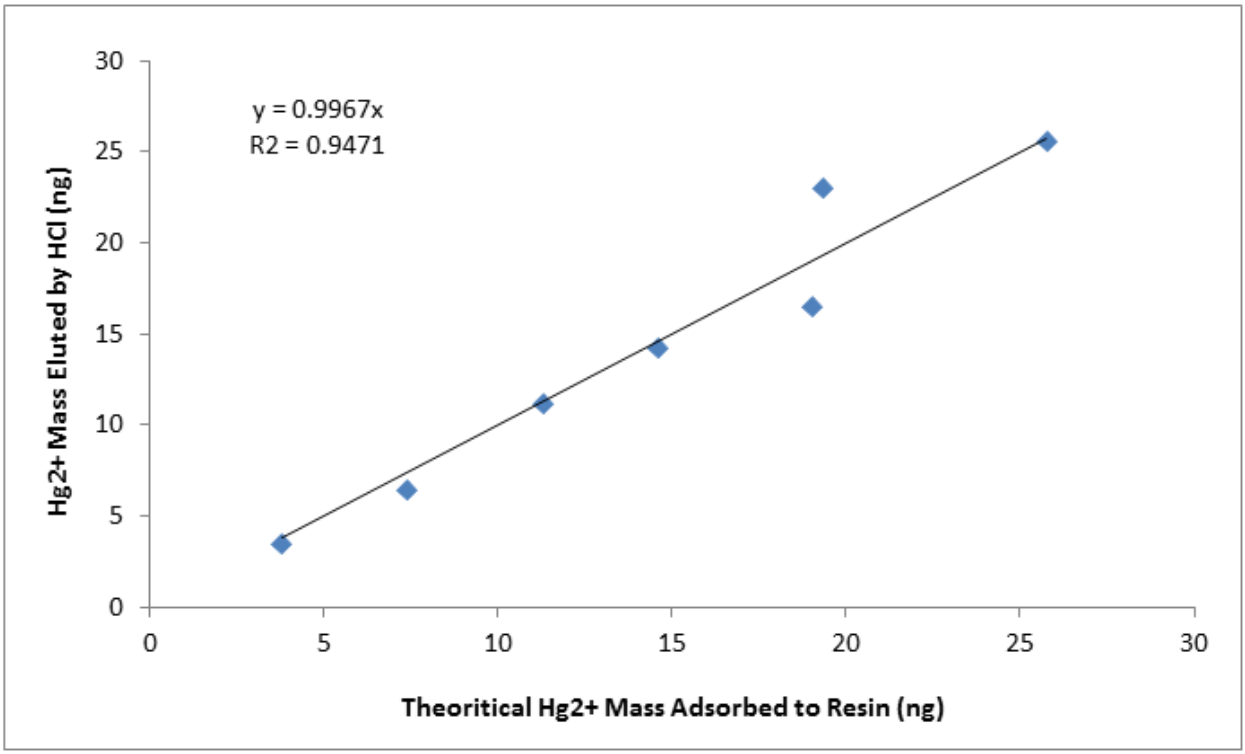

Figure 8 – DGT Sampler Total Mercury Uptake and Elution Performance
(Chess 2010)

Sediment porewater was collected using Henry's Samplers in a small test section of the South River in 2011. Samples were collected by URS Corporation and analyzed by a commercial laboratory. Sampling was conducted at 0, 4, and 16 weeks and for each sampling event, three sampling locations were selected. Henry's Samplers were pushed into the sediment and samples were collected using syringes. Both unfiltered and filtered samples were analyzed. The filtered samples were filtered through a 0.45µm filter immediately after sampling and preserved with trace-metal grade hydrochloric acid. Piston and depth profiler DGT samplers were deployed at the same sampling locations. The DGT samplers were deployed and processed in the same

manner described earlier in this section. The DGT total mercury porewater concentrations were averaged over the top 4cm in order to include both the depth profiler and piston sampler data.

Sediment porewater was collected by centrifugation for comparison with DGT samplers from South River bank sediment. The sediment was allowed to equilibrate and reduce for the first sampling event. The sediment was then mixed in order to oxidize for the second sampling event. The sediment was then allowed to equilibrate and reduce for the final sampling event. The set-up of this experiment is described in greater detail in section 4.2. For centrifugation, sediment was collected under an anoxic atmosphere and loaded into Teflon centrifuge tubes. The samples were then centrifuged at 7,000 RPM for 30 minutes. The supernatant was then collected from the centrifuge tubes. A portion of the sample was taken off for unfiltered analysis. The unfiltered sample was diluted in 2% bromine monochloride. The rest of the sample was filtered through a 0.45µm polyethersulfone filter. The sample was then diluted in 2% bromine monochloride. Both samples were analyzed on a Brooks Rand Merx-T CVAFS system according to EPA Method 1631, Revision E. 15 DGT piston samplers were deployed into the sediment under each condition and sampled at 0, 24, 48, 72, and 96 hours. The mass uptake rate was used to calculate the equivalent porewater mercury concentration.

South River bank sediment was loaded into columns in order to collect sediment porewater by displacement. The columns used were Kontes Chromaflex columns and were 4.8cm in diameter and 30cm long. The bed supports used at the end of the columns and all tubing were polytetrafluoroethylene to minimize mercury loss. A flowrate of 0.375 mL/min was used in order to minimize disturbance of the solids in the column with a retention time of six hours and a linear darcy velocity of 0.048 cm/min. Porewater was collected in a glass jar and split for analysis. Half of the porewater was kept unfiltered and half was filtered with a 0.45 µm

polyethersulfone filter. Both the filtered and unfiltered porewater was diluted in 2% bromine monochloride and analyzed for total mercury using a Brooks Rand Merx-T CVAFS system according to EPA Method 1631, Revision E. DGT piston samplers were deployed in unfiltered and filtered porewater respectively as shown in Figure 9. The DGT were deployed for 12 hours and then analyzed as described earlier in this chapter. The porewater concentration was then calculated for the DGT samplers exposed to the filtered and unfiltered porewater. This allowed for comparison of not only unfiltered and filtered direct porewater analysis but also allowed testing to determine whether the DGT samplers reacted differently to the two sample types. Ideally, the DGT samplers should measure the same porewater concentrations in both samples since it only measured freely dissolved mercury. Freely dissolved mercury should not be removed by the filtration process since the sample was collected with minimal disturbance.

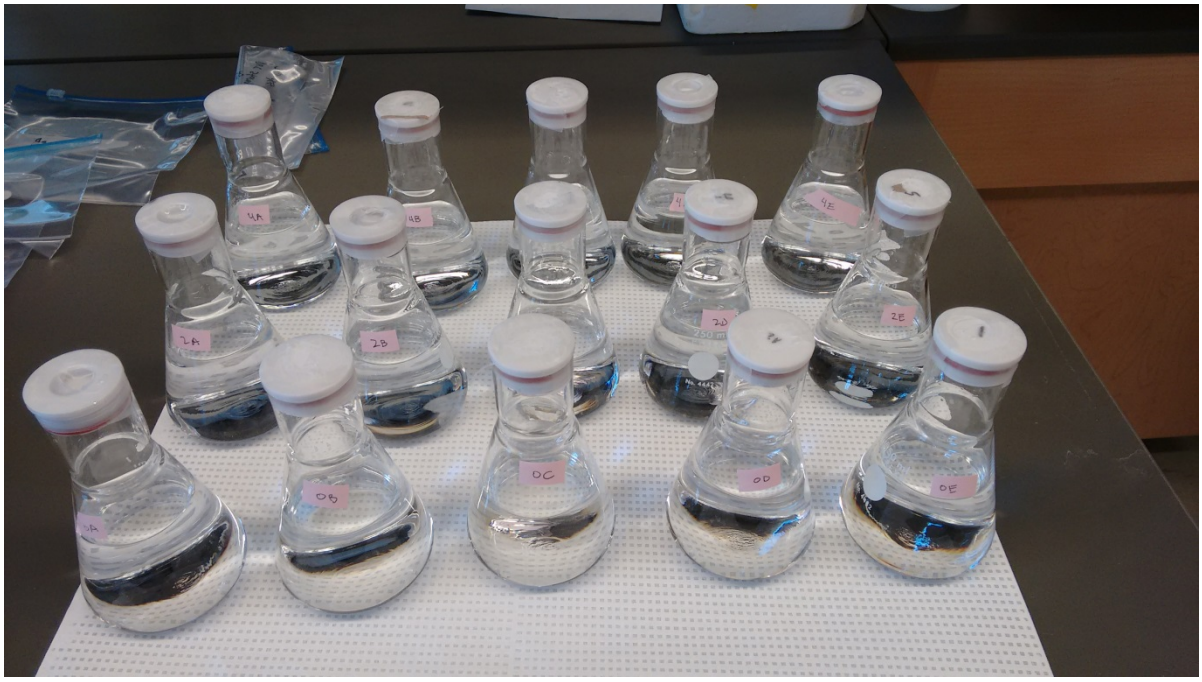

Figure 9 – Comparison of Filtered and Unfiltered Displaced Porewater DGT Experiment Set-up

Dialysis samplers were used in the South River in order to compare the measurements of DGT samplers to the passive sampling approach. Dialysis samplers, or peepers, allow a given volume of water to equilibrate with the adjacent porewater. The dialysis membrane behaves similarly to the diffusion layer in the DGT, but the sampling time and dimensions of the equilibrating water cell are adjusted to ensure equilibration. The peeper used for this sampling is shown in Figure 10. Each sampler contained 37 cells, each measuring 1x6x2 cm and containing 3mL of sampler. The samplers used a 0.45µm polysulfone membrane covered with a 5 µm nylon mesh for protection. Bromide was used as a tracer in order to follow the approach to equilibrium. Samples were processed in the field immediately after removal of the dialysis samplers from the sediment. Samples were preserved with 0.5% trace-metal grade hydrochloric acid in the field and then diluted in 2% bromine monochloride once received in the laboratory. The samples were run for total mercury on a Brooks Rand Merx-T according to EPA Method 1631, Revision E. Samples were run for bromide on a Dionex IC system with IS25 Isocratic pump, a CD20 conductivity detector, and AS40 autosampler. The samples were run according to EPA Method 300, Revision 2.1.

Figure 10 – Dialysis Membrane Peeper Deployed in South River

3.3 Results and Discussion

3.3.1 Henry's Samplers

The DGT samplers were deployed in parallel with Henry's Samplers porewater collection over three sampling events at the South River. The comparison between the DGT samplers and the Henry's Sampler are shown in Figure 11. The DGT measured concentrations are shown in blue and the Henry's Sampler filtered porewater is shown in red. The DGT samplers measured significantly higher mercury concentrations over all sampling events and locations. The Henry's Sampler collected samples were not analyzed unfiltered so it is difficult to assess if filter losses

may have significantly lowered these concentrations. To better understand what may be affecting the Henry's Sampler, a comparison to the surface water is needed.

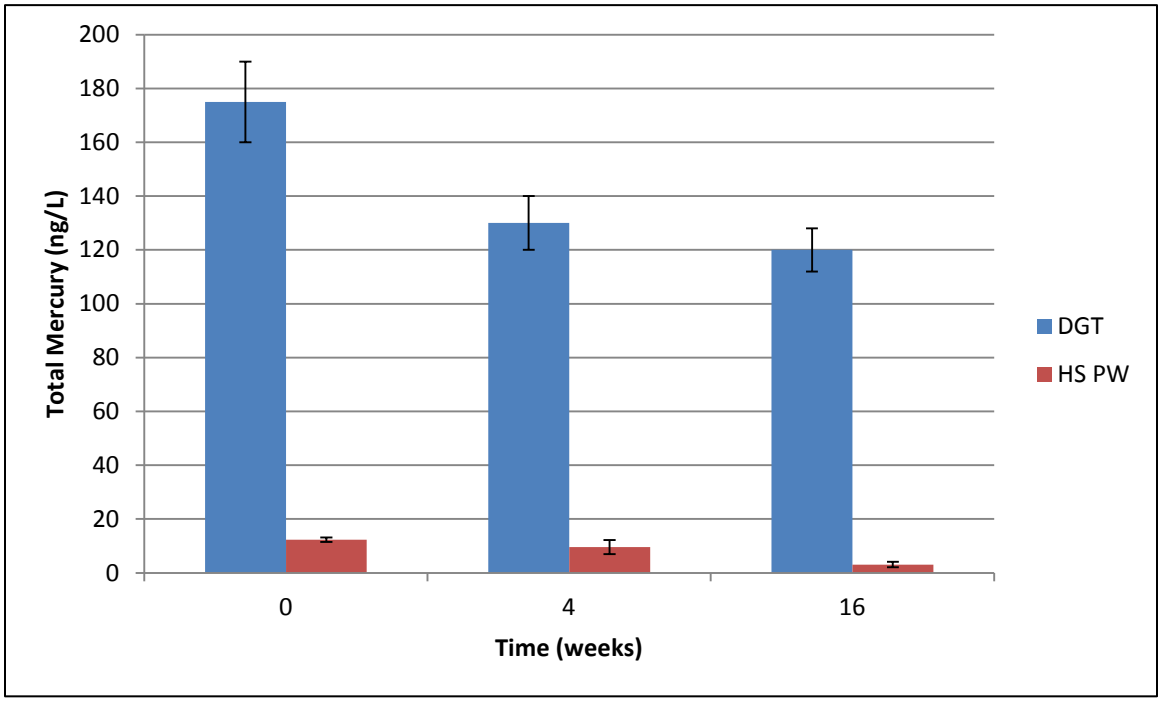

Figure 11 – Porewater Sampling Comparison between DGT Samplers and Henry's Samplers. Errors Bars Represent Standard Deviation for Replicate Samples.

The Henry's Sampler filtered porewater and surface water results are shown in Figure 12. Comparing these results without the DGT results makes it easier to see how close the two concentrations are. The sediment porewater should be significantly higher than the overlying surface water. However, the measured porewater collected with the Henry's Probe and surface water are very similar. This sediment area sampled is mostly rocky without fine-grained consolidated sediments. One of the major disadvantages with the Henry's Sampler is that you

cannot determine where the collected sample is flowing from. The water will flow from the path of least resistance, even if that is not from the sediment porewater. In this case, the gravel substrate made flow easiest from the surface water. It is likely that the Henry's Sampler collected mostly surface water instead of porewater based on the concentrations in Figure 12, but it is difficult to say that conclusively, which reinforces the major disadvantage of the sampling technique. Henry's Samplers have been tested for surface water seepage with dye tests and it was shown that they did not collect surface water (MHE 2003), however this previous research was for porewater collected deeper in consolidated sediments. For more heterogeneous matrices, the Henry's Sampler does not appear to be an appropriate sampling technique as there can be significant influence from surface water.

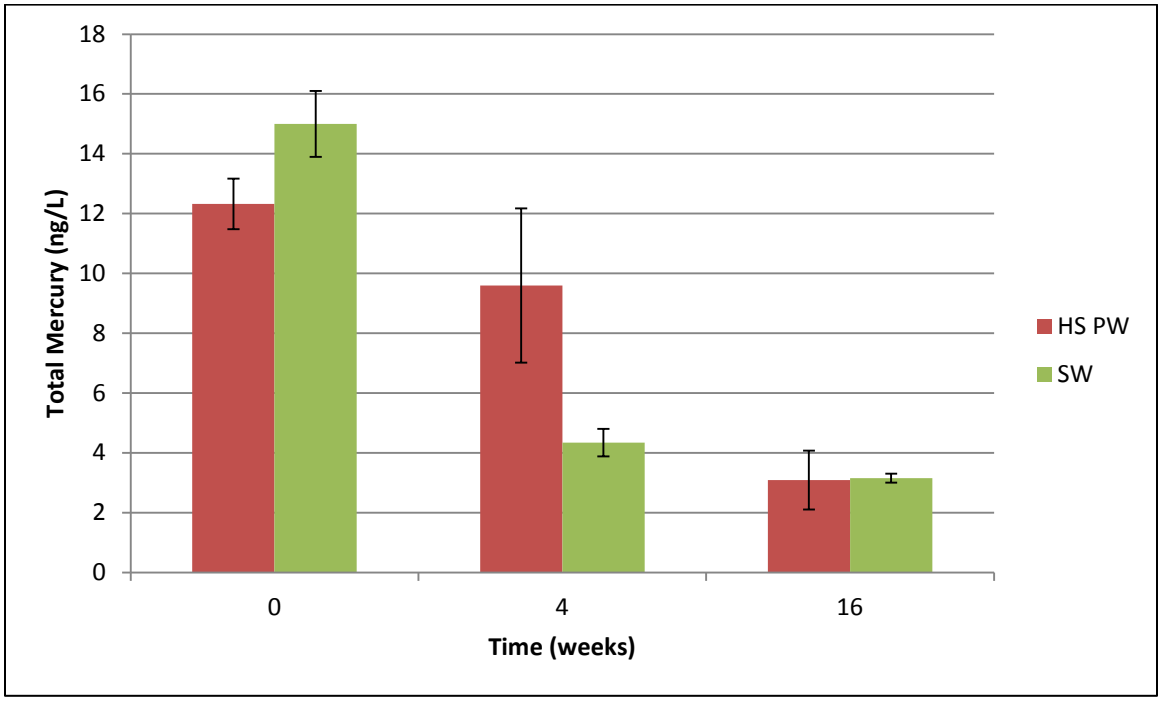

Figure 12 – Comparison between South River Porewater Collected via Henry's Sampler and Surface Water. Errors Bars Represent Standard Deviation for Replicate Samples.

3.3.2 Centrifugation

Centrifugation and filtration of sediment samples is the most commonly used porewater collection technique. Bulk sediment samples were exposed to varying redox conditions to determine the impact of redox on mercury concentrations. As part of this experiment, sediment samples of South River bank sediment were centrifuged and the collected porewater was measured both filtered and unfiltered. DGT samplers were deployed in the same sediment samples for comparison. The results for these three measurements under three different conditions (Reduced 1, Oxidized, and Reduced 2) are shown in Figure 13 with a more complete description of this experiment discussed in Chapter 5. The centrifuged, unfiltered porewater is significantly higher than both the DGT and filtered porewater. The unfiltered samples vary from 60 to 300 times greater than the unfiltered samples. Note the logarithmic scale for the porewater concentrations. This difference is expected since both the DGT and filtered samples exclude, at a minimum, anything greater than 0.45µm via the external filter layer. The agarose gel would exclude even smaller particles either by pore size restriction or by the limited diffusion rate of larger particles. The high concentrations in the unfiltered samples are most likely due to suspended particles that are generated during the centrifugation step. These particles would not normally be present in the porewater and thus the unfiltered concentrations significantly overestimate mercury concentrations in the system.

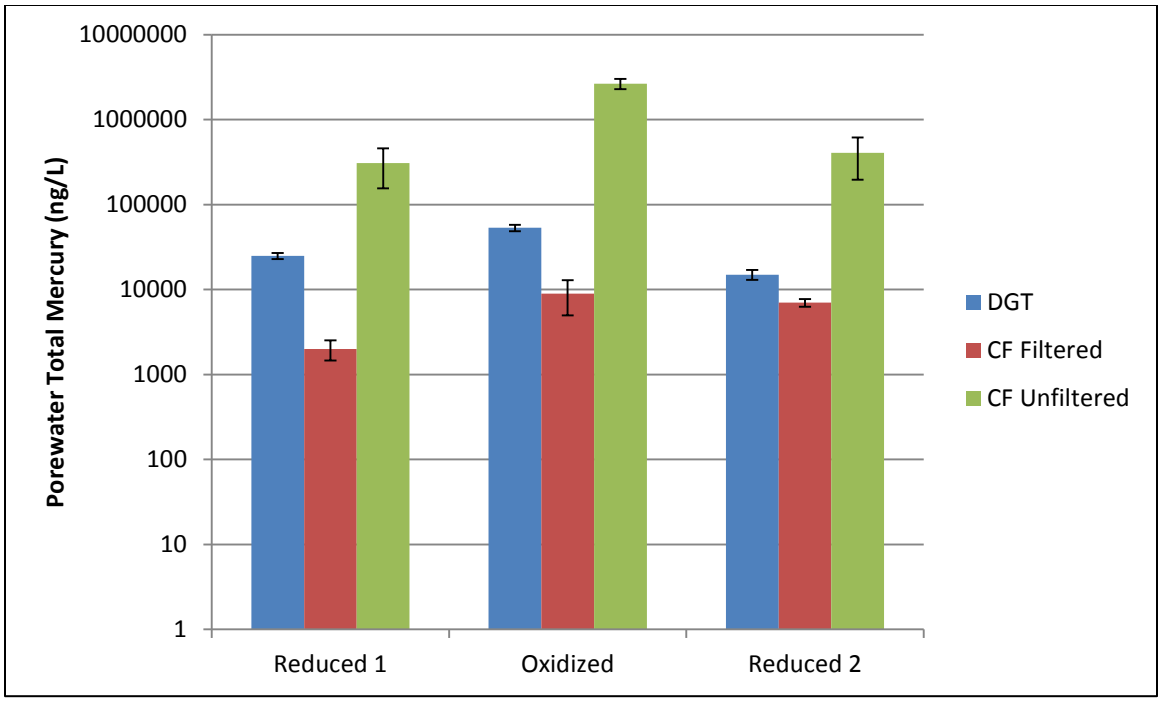

Figure 13 – Comparison of Bulk Sediment Experiment Total Mercury Porewater Measurements from DGT, Centrifuged Filtered Porewater, and Centrifuged Unfiltered Porewater. Errors Bars Represent Standard Deviation for Replicate Samples.

The more relevant comparison for standard sampling techniques is between the DGT and filtered centrifuged porewater samples as the unfiltered porewater is not commonly used. The comparison between these two techniques is shown in Figure 14, note that these results are shown on a linear scale. The DGT measurements are significantly higher than the filtered samples. This supports the hypothesis that suspended particles generated during the centrifugation step can scavenge porewater mercury from the porewater leading to an underestimation of mercury concentration and risk.

Centrifugation and filtration as a sampling technique disturbs the sample during collection and during processing. The data suggest that unfiltered samples contain much higher

amounts of suspended particulate matter and mercury. Filtration of the samples can remove some of the extra particulates but also some of the mercury, suggesting a redistribution of mercury between the particulate and water phases during centrifugation. Neither filtered nor unfiltered centrifuged samples give an appropriate indication of mercury in the in-situ porewater. Use of these concentrations in modeling or risk calculations would lead to incorrect decisions for sites. The DGT samplers have less risk of sampling artifacts and the measurement is linked directly to the chemical activity of the mercury species, not the physical sampling techniques.

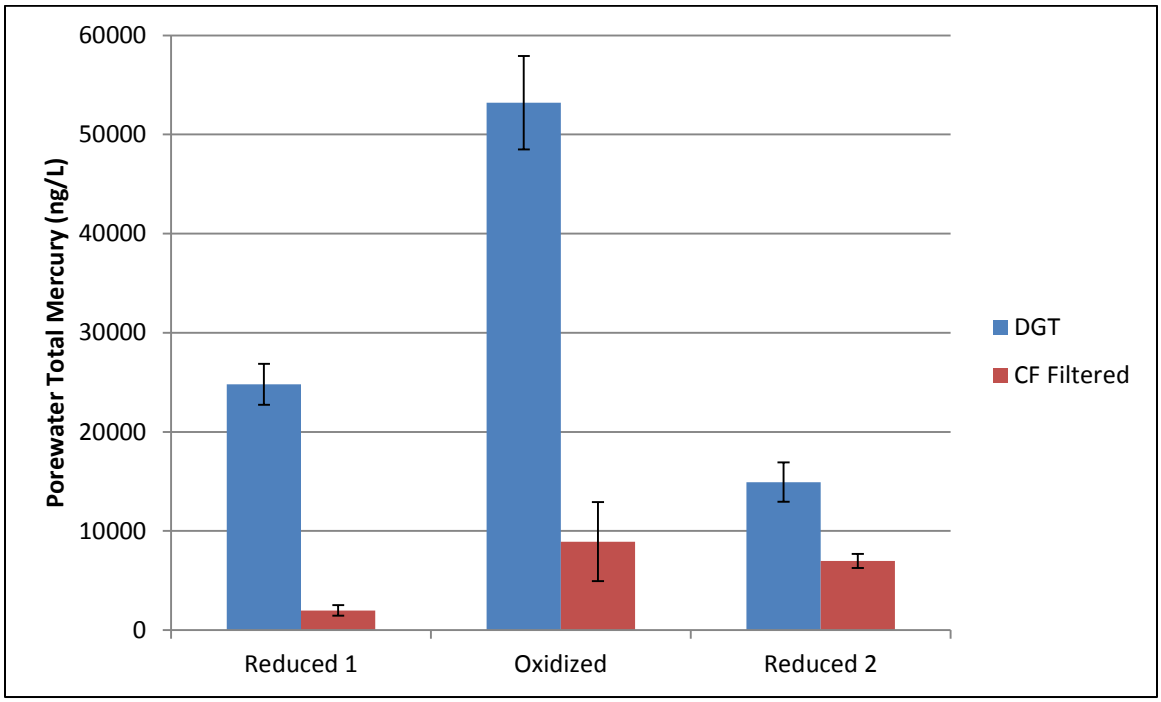

Figure 14 – Comparison of Total Mercury Porewater Measurements using DGT and Centrifuged Filtered Porewater. Errors Bars Represent Standard Deviation for Replicate Samples.

3.3.3 Displacement

Displacement is another commonly used porewater collection technique but it is more time consuming that centrifugation and requires more equipment for porewater collection. The South River bank sediment column was pumped slowly with synthetic freshwater to collect porewater. The collected porewater was analyzed directly both filtered and unfiltered. DGTs were exposed directly to the collected porewater, again both filtered and unfiltered. The results for all these measurements are shown in Figure 15. As with other sampling techniques, the unfiltered porewater sample that was collected via displacement was significantly higher than any other measurement. Significant amounts of mercury were associated with suspended particulates either reflecting in-situ conditions or generated by the porewater displacement process. Even if the total mercury displaced accurately reflected the porewater conditions, the association with large suspended particles suggest that it is not reflective of the mercury available for biological uptake or methylation.

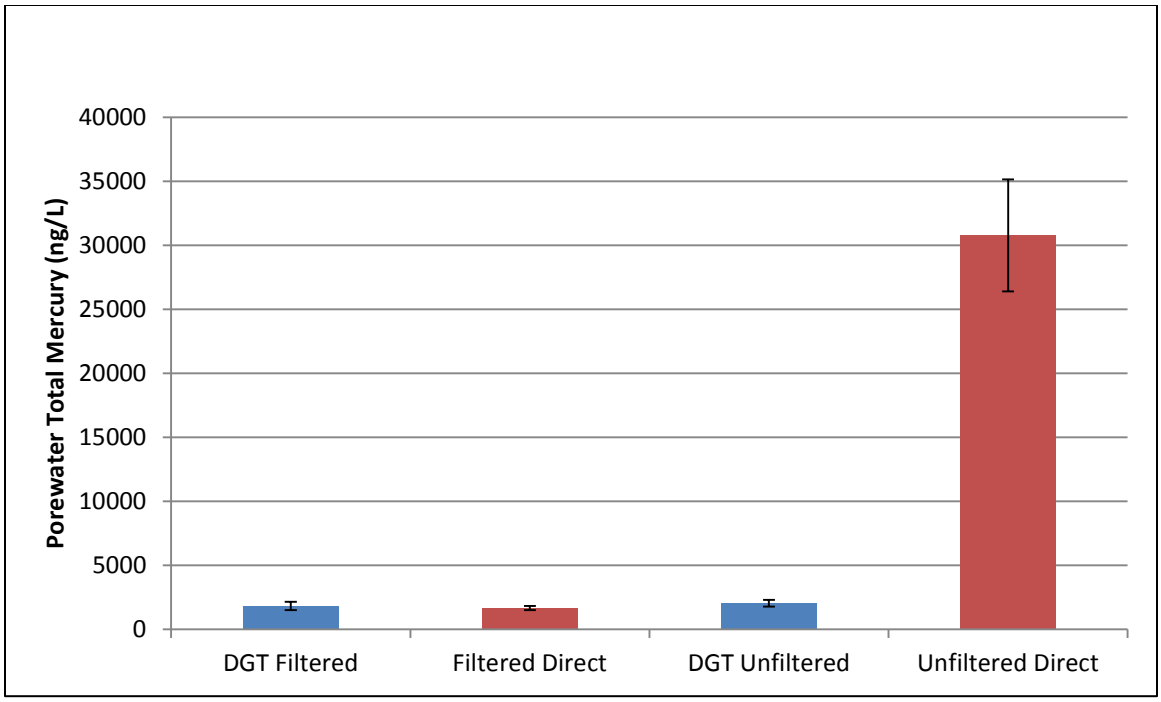

Figure 15 – Comparison of Total Mercury Porewater using DGT, Filtered Displaced Porewater, and Unfiltered Displaced Porewater. Errors Bars Represent Standard Deviation for Replicate Samples.

The DGT measurements and displaced filtered measurement are shown in Figure 16. The first important comparison is between the DGT samplers that were deployed in filtered and unfiltered porewater, both shown in blue. The DGT samplers exposed to the unfiltered porewater were not significantly higher than those exposed to the filtered porewater, despite the unfiltered sample containing more bulk mercury. The unfiltered direct analysis showed that there was significant mercury associated with particulates in the sample; however the DGT samplers were not affected by these particulates. This is important as it shows that the DGT samplers are not greatly affected by the disturbed particulates in porewater or surface water samples, a good indicator that DGT samplers only measure the chemically available mercury

concentration. The other comparison is between the DGT filtered measurement and the displaced, filtered porewater measurement. The two sampling technique measured similar mercury concentrations in the porewater, which was not the case for the other sampling techniques tested. This sampling technique minimized disturbance of the porewater by pumping the porewater out as slowly as possible. There is still potential for losses from sample collection or dilution with feedwater but those were not significant in this case, especially since the DGT were exposed to collected samples. The slow displacement did not produce as many suspended particulates as other techniques, which lowered the influence of filtration. For centrifugation, the filtered samples were significantly lower than DGT measurements, likely due to the more disturbed porewater.

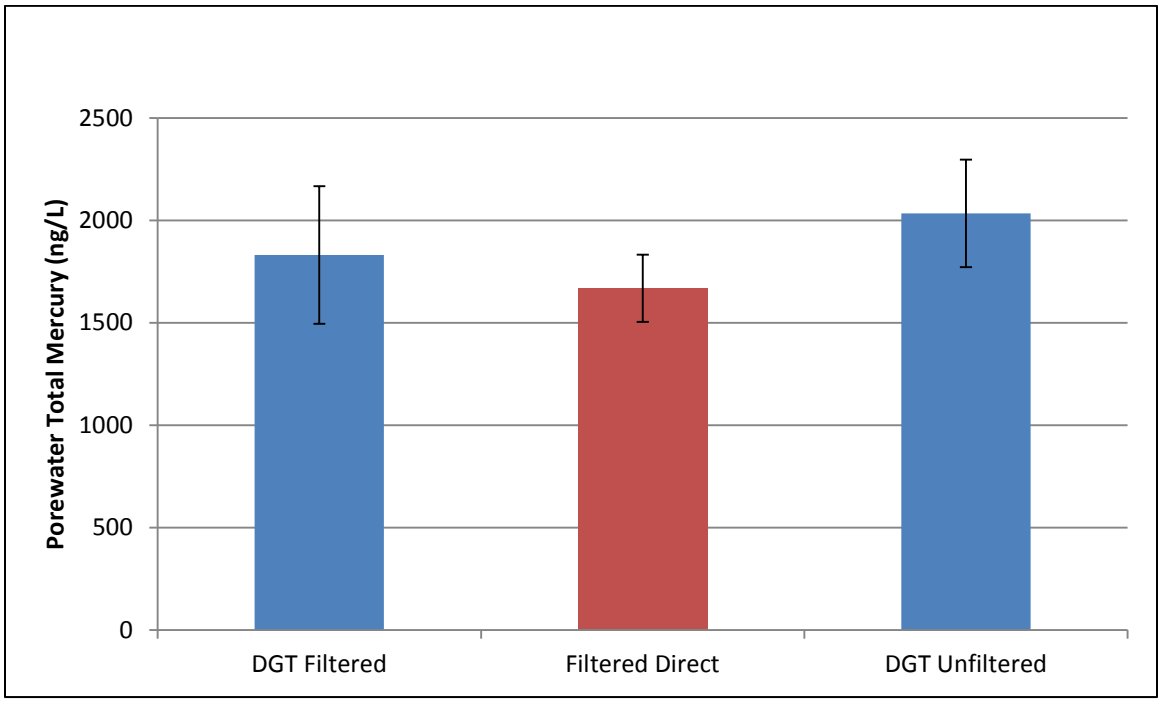

Figure 16 – Comparison of Total Mercury Porewater using DGT and Filtered Displaced Porewater. Errors Bars Represent Standard Deviation for Replicate Samples.

3.3.4 Dialysis Samplers

Dialysis samplers and DGT samplers are both in-situ passive sampling techniques for porewater mercury concentrations. They share many of the same advantages and disadvantages. Sediment samples do not need to be collected and shipped to a laboratory. The samples undergo minimal processing which can lead to sampling artifacts. The measurement of the mercury is based on diffusion into the sampler, a more direct chemical measurement of the dissolved mercury species. For one sampling event in the South River, dialysis samplers, and DGT were deployed in parallel at the base of a bank during a bank drainage event for verification of both sampling techniques. The results for one location in the RRM3.5 bank are shown in Figure 17. The dialysis sampler measured concentrations ranged from approximately 4,000 to 11,000 ng/L. In the same bank area, two DGTs were placed. The width of the zone sampled by the dialysis sampler is approximately 15 cm while the DGT samples only a width of about 2 cm. As a result, DGTs were placed on each side of the dialysis samplers. The DGTs measured concentrations ranged from 1,600 to 11,000 ng/L. One DGT exhibited concentrations between 1600 and 4000 ng/L while a second exhibited concentrations between approximately 5000 and 10000 ng/L. This is a reflection of the spatial variability of mercury concentrations during the drainage event. The average concentration between the two DGTs is 6600 ng/L, which is essentially equivalent to the average of 5760 in the more integrative dialysis sampler. The porewater concentration in the DGT and dialysis sampler peak at approximately 6cm depth and then is lower as the depth increases. Since this comparison was done as part of a field sampling deployment, there is not enough data for a statistical comparison, which would be difficult even with more samples due to the heterogeneity. However, there is good semi-quantitative comparison between the two types

of samplers. Unlike DGTs versus other conventional porewater analyses, the DGT and dialysis samplers are within the same order of magnitude of each other.

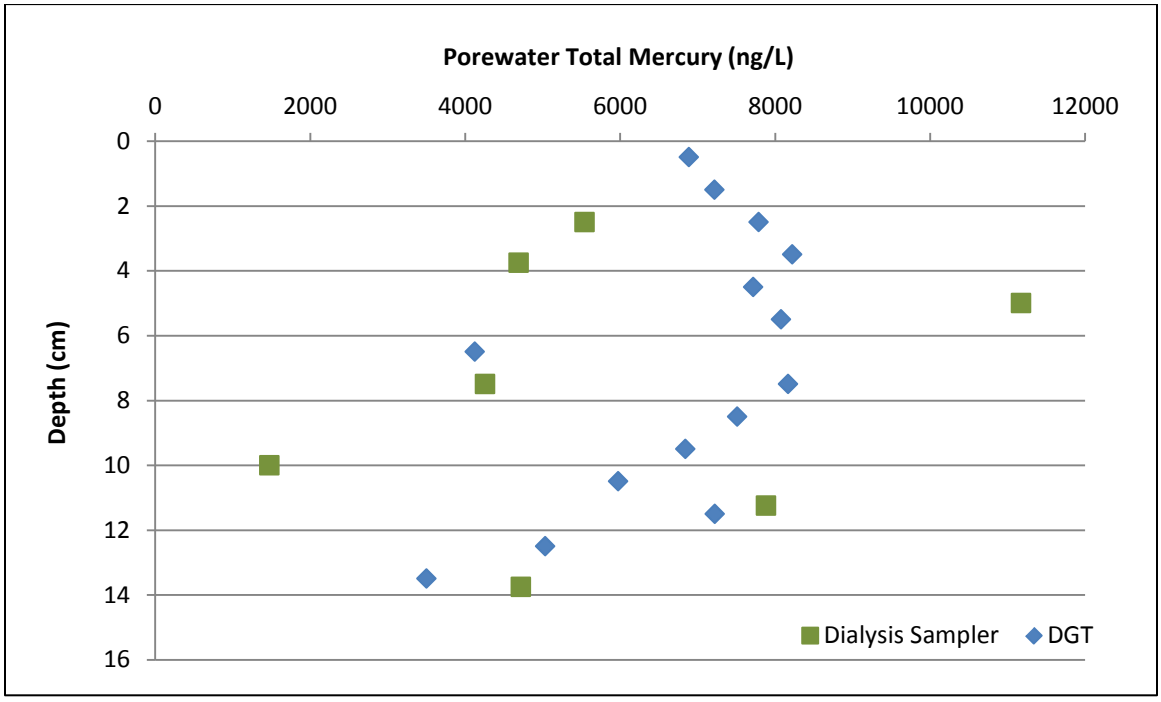

Figure 17 – South River RRM3.5 Comparison of Field Total Mercury Sediment Porewater Profiles using DGT and Dialysis Samplers. Average of 2 DGT Samplers Shown

3.4 Conclusions

The results of this chapter suggest that DGT samplers for mercury in sediment porewater have promise. The methods for fabrication, deployment and storage developed in this chapter provide a protocol that minimizes error due to background mercury contamination, sampling, processing, and storage. In this research, QA/QC protocols for DGT sampler use in sediment porewater sampling were established. Background mercury contamination, and its impact on

sampler detection limits, was quantified in order to better understand the limitations of this method. Field use of DGT samplers, as opposed to use in a controlled system requires the transportation and storage of samplers after use. The impact of these practical necessities were quantified and it was found that the impact can be minimized by processing samplers within two weeks of retrieval and analyzing samples within four weeks of processing.

A number of methods were evaluated for their potential for analyzing mercury concentrations in porewater and compared to the DGT method. Many of the reported shortfalls of conventional techniques were evident in the data collected during this investigation including sample dilution, introduction of suspended particles, and filter losses. Of the techniques tested the dialysis sampler method was the only technique that produced results that were not influenced by these shortcomings as these samplers are deployed in-situ and do not require the removal and processing of the sediment. Comparison of DGT to dialysis samplers showed similar porewater concentrations. While Henry's Samplers, centrifugation, and displacement showed significant differences between filtered and unfiltered samples, DGT results were similar prior to and after filtration suggesting that DGT samplers are not influenced by the presence of suspended particles in the porewater. Of the conventional methods evaluated that involve sample processing, displacement can be accomplished with much less disturbance of the sediment sample compared to other methods such as centrifugation. The filtered displaced water samples were effectively identical to concentrations measured by DGT. If conventional sampling is needed, displacement is preferable to centrifugation and filtration due to the ability to collect porewater with lower less suspended particles.

Of particular note with respect to the conventional samplers, is that they suffer from limitations due to requirement of removing the porewater from the sediment. For example, the

pumping of porewater using Henry's Samplers causes water to flow from the path of least resistance, which may or may not be from the porewater surrounding the sampling location. In field sampling using both DGT samplers and Henry's Samplers, the porewater concentrations using Henry's Samplers were very similar to those of the surface water and lower than those from the DGT, likely suggesting surface water dilution. The other commonly used porewater sampling techniques, centrifugation and displacement, physically separate the porewater from the sediment in the laboratory. This adds the extra step of sediment sampling and transportation to the laboratory. Removing the sediment can disrupt in-situ redox conditions and significantly alter porewater chemistry. Processing of the samples in the laboratory is another opportunity for disturbance. Centrifugation can displace flocs and small particulates into the porewater which can change porewater chemistry and introduce mercury into samples than is not available chemically or biologically. These suspended particles can also scavenge mercury from the dissolved phase which is then removed from the sample during the filtration step. This leads to inaccurate concentrations, either artificially high when measured unfiltered or low when measured filtered. This was seen in the comparison between DGT samplers and centrifugation using South River bank sediment. The unfiltered centrifuged porewater was significantly higher than both the filtered and DGT concentrations. This is explained by the resuspension of particulates into the porewater. The centrifuged and filtered porewater concentrations were significantly lower than those measured with the DGT samplers presumably due to mercury scavenging by the filtered particles. In contrast, unfiltered yielded higher values compared to DGT and filtered sample as significant mercury was associated with particulates in the sample.

DGT samplers are not only more accurate for measuring porewater concentrations but they have the potential to overcome many of the challenges associated with traditional sampling

techniques. DGT samplers can be placed in a variety of sediment types and obtain porewater concentrations at fine resolution. DGT samplers obtain porewater concentrations from the sediment close to the sampler as opposed to from a bulk porewater gathered from processing. The DGT sampler's small size gives them the ability to be placed in a variety of environments. It does not require a large volume of sediment to be available for collection and processing which limits the areas that can be sampled. The DGT samplers measure porewater concentrations based on the diffusion of mobile mercury species. This chemical measure is more applicable to other models such as toxicity, methylation potential, or bio-uptake models. One of the potential issues for DGT samplers is the possibility of mercury complexation affecting the diffusion into the samplers. The dialysis samplers are an equilibrium sampling device and would not be influenced by kinetic limitation of mercury availability from solids or semi-labile dissolved complexes. The DGT sampler measurements are consistent with the dialysis sampler concentration, which shows that the DGT samplers are not influenced by these limitations. The DGT samplers were not influenced by the filtration of suspended particles in the displacement comparison. This shows that the DGT samplers are not affected by the presence of these complexes which do not directly diffuse into the sampler. These conclusions enhance the viability of DGT samplers for sediment porewater. Additional work is needed for low-level mercury monitoring using DGT samplers as the detection limit is currently controlled by the mercury contamination in the DGT resins not the analytical detection limit. Careful efforts to avoid contamination of samplers may reduce this detection limit and would be needed for routine measurements in relatively clean (low-mercury) waters.

Chapter 4 – Field Use of DGT in the South River

4.1 Introduction

The goal of this field work was to use the technique of DGT samplers for porewater mercury and methylmercury to assess the potential sources of mercury at a field site and determine if these samplers improve on data collected using conventional porewater sampling techniques. DGT samplers have been primarily used as a laboratory sampling technique or surface water field sampling technique in the past. They have not been widely used as field sediment porewater sampling devices. The field site for this research work is the South River, located in central Virginia (USA). Waynesboro, VA is the site of a former DuPont factory, where the first synthetic fabric was invented. Mercury was used as a catalyst in production from 1929 to 1950. Elevated mercury levels were discovered in the 1970's and as part of the clean-up effort, the South River Science Team was established in partnership between DuPont, the Virginia Department of Environmental Quality, the Virginia Department of Health, and the Virginia Department of Game and Inland Fisheries. The purpose of the group is to identify, manage, and reduce risk to the public from mercury contamination in the South River and provide technical direction for the monitoring of mercury in the South River.

Prior field sampling in the South River was done using a variety of the conventional sampling techniques described in Chapter 3. From that work, a conceptual model for the movement of mercury and methylmercury in the river was developed. A visual representation of the current site conceptual model is shown in Figure 18.

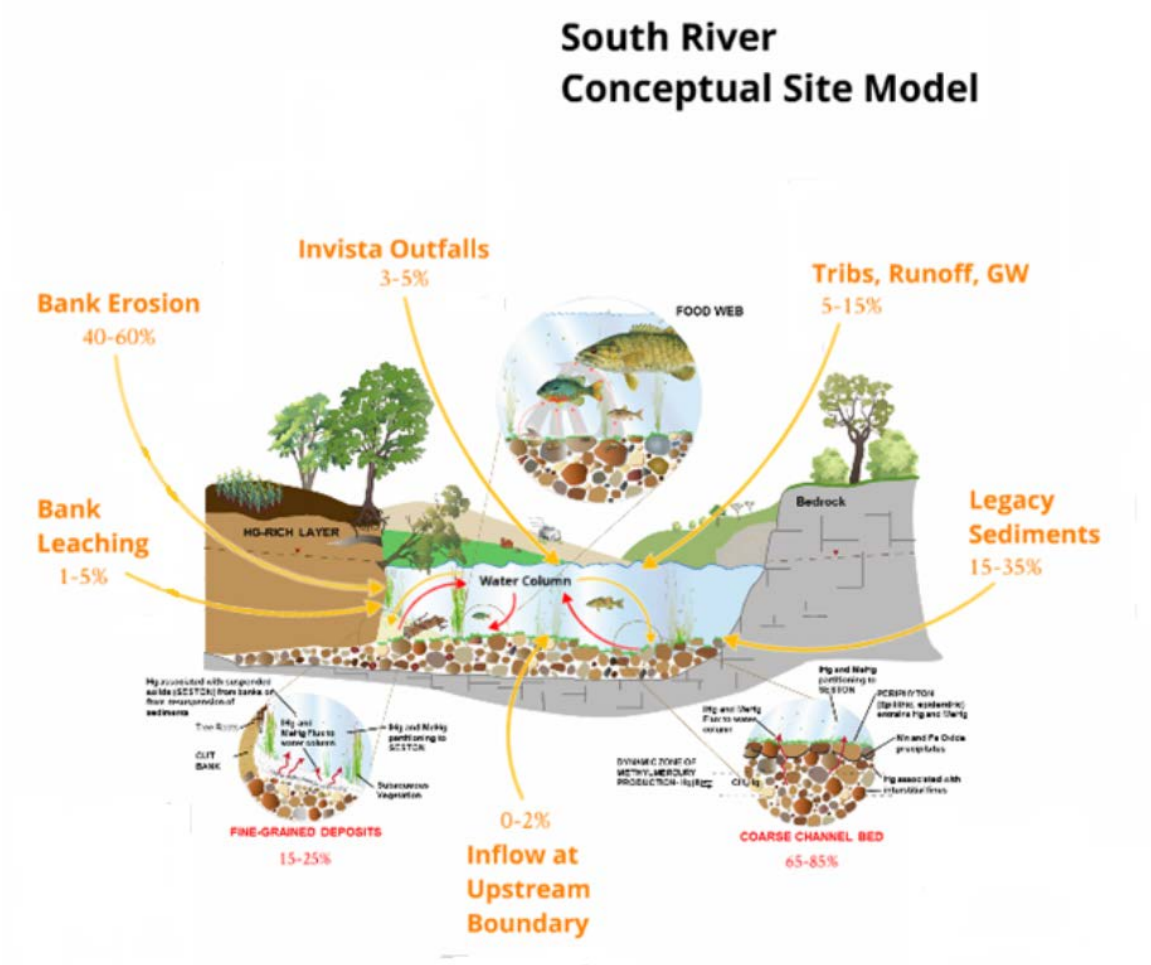

Figure 18 – Conceptual model of mercury sources into the South River (South River Science Team, unpublished)

According to this model, the greatest sources of mercury into the river channel are bank erosion and legacy sediments. However, this model is based on several assumptions and results from conventional sampling techniques. It is assumed that all mercury from eroded bank and floodplain soil is equally available for transport and methylation. However, it is not possible to directly measure the contribution of mercury from erosion and so the estimates of the contribution from erosion are based on ex-situ tests and models. Bank leaching has been estimated to only account for 1-5% of mercury flux into the river. As a result of the expected

source, preliminary remedial plans being considered for the river are focused on stabilizing the banks and reducing solid erosion.

Using traditional measurements, however, it has been difficult to directly measure mercury flux from bank erosion and leaching. Due to the lack of direct measurements of either mechanism in the field, it is difficult to differentiate between bank erosion and leaching. If bank leaching contributes more to mercury flux into the river, remediation focused on bank stabilization may not be effective. The objective of the field sampling with DGTs is to better assess the significance of bank leaching.

The site conceptual model was developed for baseline flow (<300 CFS) in the river channel. Elevated flow events can change mercury behavior in several ways. Higher flow rates can increase erosion of contaminated banks. Increased river stage also increases the portion of the river bank that is inundated, changing the water flow and chemistry in those bank areas. Surface water is pumped into the bank during these high river stage events. There are both chemical and physical changes in the bank system during high flow events. Surface water flows into the banks which can change the porewater chemistry. These changes in the bank systems may only last hours to days which make them difficult to assess using conventional sampling techniques as these require the removal, transportation, and processing of samples. However, just because these high flow events are temporary does not necessarily mean that they have a small impact on the overall mercury flux into the river. The contribution of mercury to the river from these flood events is currently unknown. Figure 19 shows the 2013 hydrograph for the South River. There are many of these high flow events each year, and their cumulative impact could significantly alter understanding of how mercury moves from the banks to the river channel. Flooding events have been identified as a cause of metals release through the

dissolution of iron, manganese, and sulfate minerals. Frequent changes in geochemistry, like those caused by frequent flooding, result in mineral phases which are freshly precipitated and more available for dissolution in subsequent flood events (Lynch, Batty, and Byrne 2014).

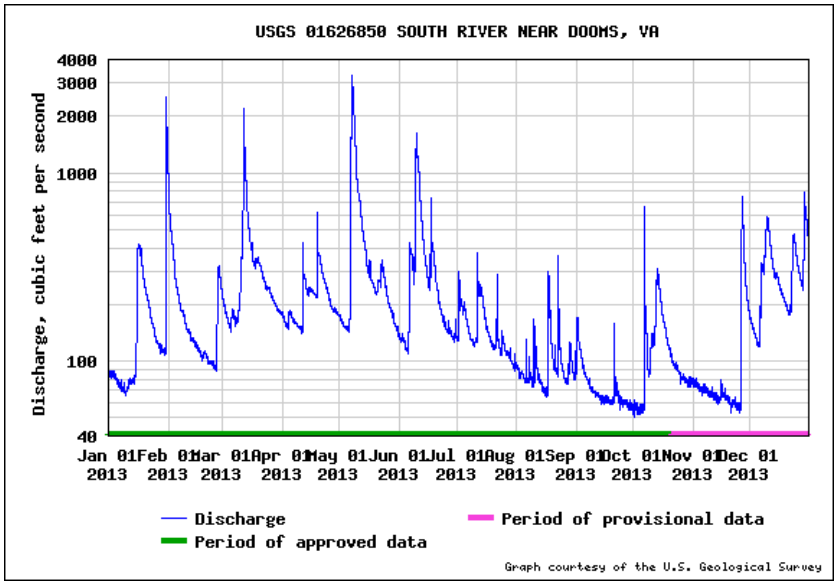

Figure 19 – 2013 Hydrograph for South River near Dooms, VA (USGS)

In order to better understand how mercury porewater concentrations are contributing to mercury flux into the river, a model was constructed in order incorporate groundwater flow through the bank system. The bank system has a silt layer overlaying a sand layer. The silt layer contains the elevated mercury loadings. The sand layer has a higher hydraulic conductivity than the silt layer and so the flow through the two layers will vary. The goal of the model was to determine how much of the water will flow through the silt and sand layers during drainage of an inundated bank. These volumes are then used to calculate a mercury mass flux budget from the bank into the river channel during an idealized bank drainage event. DGT mercury porewater concentrations measured in the field are used for the water draining through the silt and groundwater grab samples are used for the sand layer.

4.2 Materials and Methods

DGT samplers were used to measure mercury porewater concentrations at a variety of locations in the South River. The DGT samplers were fabricated in-house as described in Chapter 3. The thiol resin used was 3-mercaptopropyl functionalized silica gel from Sigma Aldrich from 2010 to 2013. For 2014-2015, Isosolute SI-Thiol resin beads from Biotage were used. There was no difference in performance or mercury contamination measured between the different suppliers. The change in suppliers was prompted by a lack of availability from Sigma-Aldrich stemming from changes in their manufacturing process.

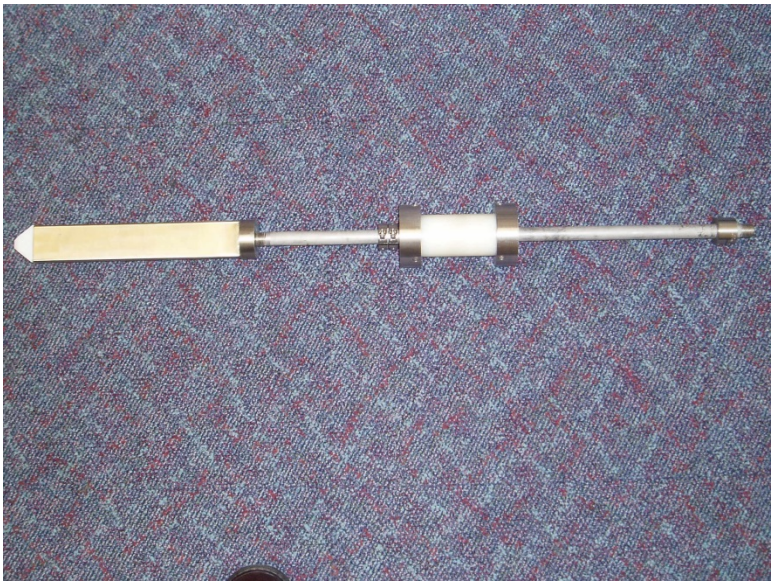

Figure 20 – Slide Hammer DGT Insertion Tool

DGT depth profilers and pistons were both used for sampling. The DGT sampler housings were made of polycarbonate and custom made using a 3D printer. All design and fabrication was done by DuPont. The depth profilers were inserted into the sediment using

insertion tools which were designed to both protect the DGT sampler during insertion and allow for sampling of gravel substrates. If the gels are ripped during insertion, the samplers are compromised and cannot be used. The insertion tools enclose the DGT sampler in a stainless steel sheath during insertion and then the sheath is removed, exposing the sampler to the sediment porewater. An example of one insertion tool, the slide hammer tool, is shown in Figure 20. The slide hammer insertion tool allows for DGT depth profiler insertion into rocky sediment in which the sampler cannot be easily inserted by hand. The DGT depth profiler is inserted into the stainless steel sheath shown on the left. A tip cover is placed at the end, protecting the DGT sampler. The tip is placed in the sediment location to be sampled and the slide hammer is used to pound the sampler to the proper depth. A rod is used to hold the DGT sampler at that depth while the tool and sheath are removed. DGT piston samplers are held in place using a Silly Putty® disc. A 3 inch diameter disc of Silly Putty® is placed on the back of the DGT piston sampler and when the sampler is placed in the sediment, the putty is pushed in around it. This ensures that the DGT sampler gel face will remain facing the sediment and that surface water will not short-circuit the sampler. In initial deployments of the DGT piston samplers, some samplers would be found in the water column instead of the sediment where they were deployed. With the Silly Putty® sealing in samplers, all piston samplers stayed in place. Analyses of the Silly Putty® showed that it neither contributed mercury to the analysis nor scavenged mercury from the surrounding area. An example of the putty discs used can be seen in Figure 21.

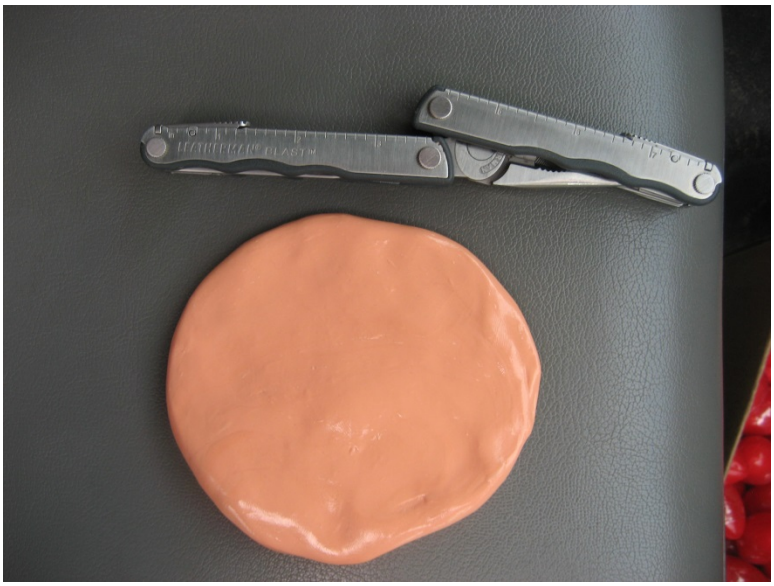

Figure 21 – Silly Putty® Disc used to Seal DGT Piston Samplers in Place

The DGT samplers were processed and analyzed for total mercury as described in Chapter 3. The analysis was performed on a Tekran® 2600 CVAFS from 2010-2013. In late 2013, a Brooks Rand Merx-T CVAFS was purchased and all subsequent analysis was performed using it. There was no change in the processing procedure over the sampling events.

Cyclic voltammetry was used to measure dissolved redox sensitive species in the sediment porewater on some sampling trips to indicate the degree of reduction versus depth. The sampling was done using a DLK-70 Potentiostat from Analytical Instrument Systems (Ringoes, New Jersey). The electrodes used were a mercury/gold amalgam with a PEEK body and 100µm diameter gold plating. The detection limits for this set-up were 5µmol/L for manganese, 10 µmol/L for iron, and 0.1 µmol/L for sulfide. Cyclic voltammetry is a method to measure redox

sensitive, dissolved species in-situ at a sub centimeter resolution. The method uses a solid-state gold amalgam microelectrode to measure dissolved oxygen, Fe(II), sulfide, and Mn(II) (Brendel and Luther 1995). A range of voltages is applied across the microelectrode and the resulting electron flow is measured. A sample of a voltammogram using this method is shown in Figure 22.

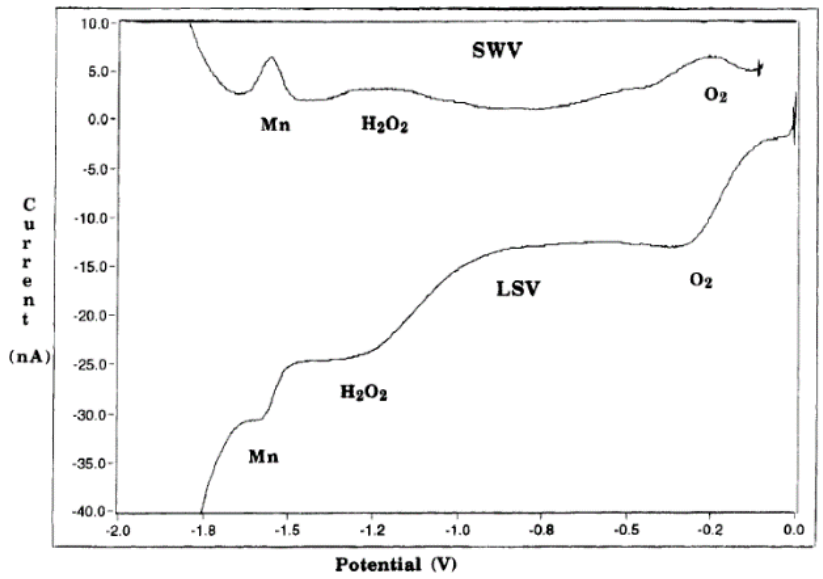

Figure 22 – Representative voltammogram with both square wave (SWV) and linear sweep (LSV) voltammetry measurements (Brendel and Luthy 1995)

For a given redox reaction, the reaction is driven, causing a flow electrons, when the applied voltage matches the reaction's redox potential. The flow of electrons can be quantified in order to measure the concentration of the dissolved species. For the sample voltammogram shown in Figure 21, in the SQV at top, the area under the peaks are integrated to quantify the electron flow, for the LSV at bottom, the plateau current is measured to quantify the electron

flow. This method allows these redox sensitive species to be measured without disturbing the sample, lowering the chances of oxidizing the sample.

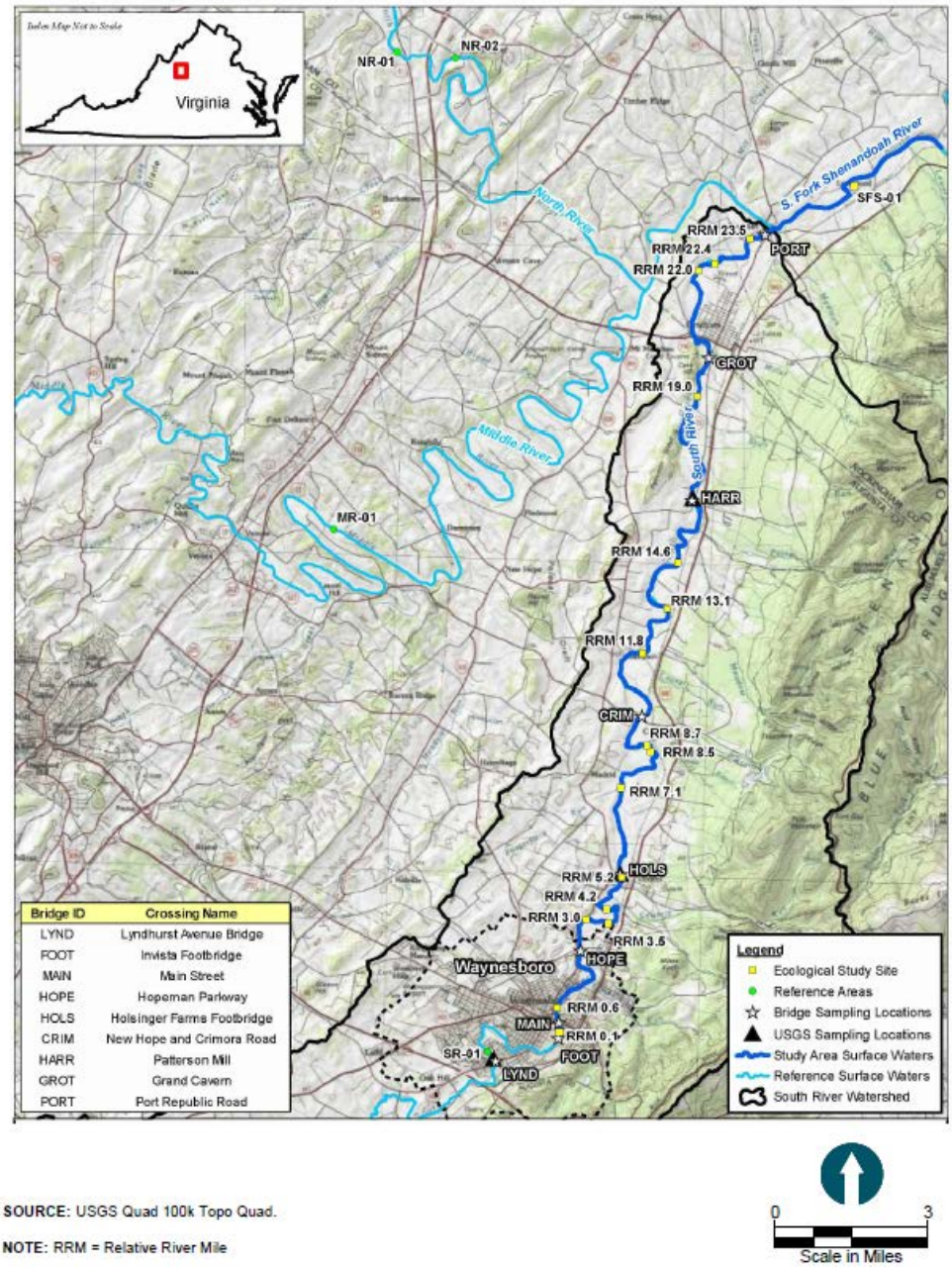

Figure 23 – South River Area Map (Anchor QEA, URS Corporation, and E.I. du Pont de Nemours and Company 2013)

The South River study area includes impacted areas as well as up-stream and downstream locations to capture all areas impacted. The river locations are denoted by the distance from the source of original mercury contamination and are measured by relative river mile (RRM) from the source. RRM 3.5 has been identified as a historical deposit area for mercury contamination and a source area for mercury into the river. The area of RRM3.5 that was sampled extensively for this work includes the bank, a near bank area approximately 10 feet into the channel, and the main channel bed approximately 20 feet into the channel. The bank is an area of active erosion into the river and this erosion has been identified as a potential mechanism of mercury movement into the river. RRM 11.8 is downstream of this source area and was not historically impacted by mercury contamination. Solid-bound mercury and dissolved mercury can both be transported downstream by the river. The area at RRM 11.8 is a depositional environment and viewed as potentially impacted by the upstream mercury contamination.

Figure 24 – South River Relative River Mile 3.5 Sampling Area

4.3 Field Results

The DGT samplers were deployed in the main channel of the South River. A summary of findings from DGT sampling is discussed in this section. The majority of DGT sampling events took place during baseline flow conditions for the South River, with a photo showing the RRM3.5 sampling location during baseline flow conditions shown in Figure 25. The baseline river flow in the South River is less than 200 CFS. The low river flow makes sampling easier and safer. In order to sample the South River, DGT samplers were inserted by hand and required wading into the river, which was easier during the baseline flow.

Figure 25 – South River Relative River Mile 3.5 Bank during Baseline Flow

For example, one sampling event took place in October 2013 when the river flow was low. The hydrograph for this sampling event is shown in Figure 26. The river flowrate was below 100 CFS and did not change over the sampling duration which is shown shaded in blue.

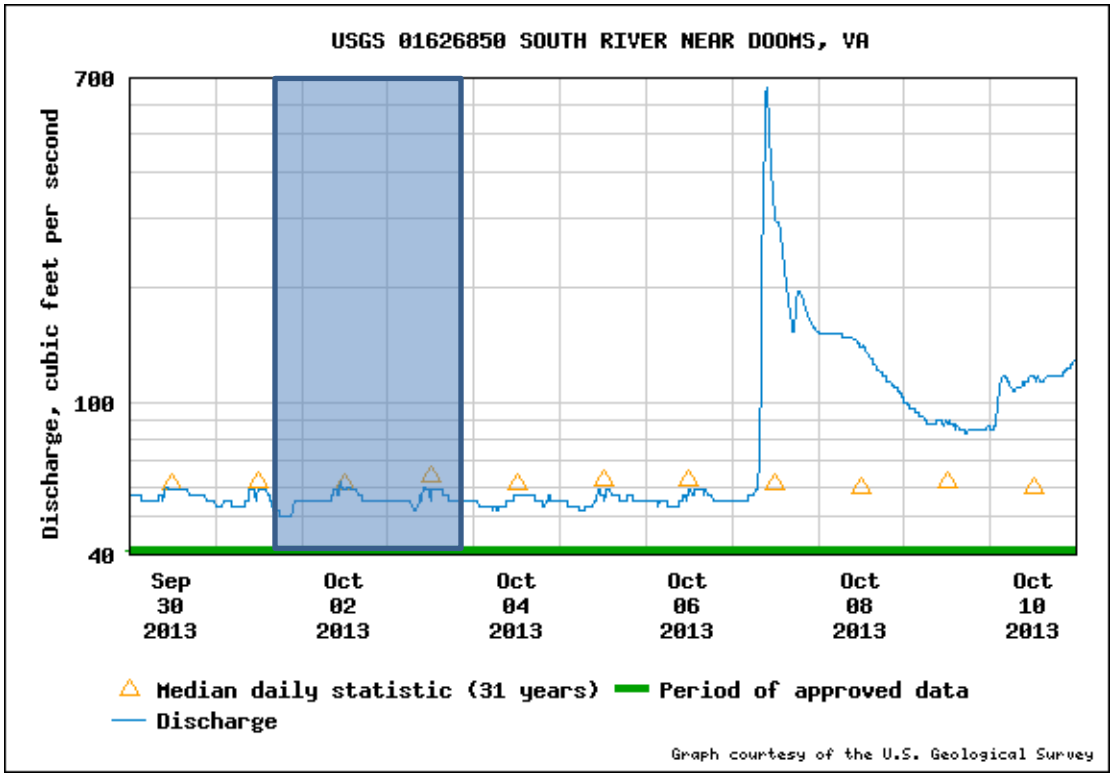

Figure 26 - USGS stream flow data for South River in October 2013 with DGT Sampling Period Shaded in Blue (U.S. Geological Survey)

During this sampling event, the DGT samplers were deployed at both RRM 3.5 and RRM 11.8. At each location, DGT samplers were placed at the bank, 10 feet into the channel, and 20 feet into the channel. The mercury data obtained from this sampling event for samples collected at RRM 3.5 are shown in Figure 27. At RRM 3.5, the mercury concentrations measured in the bank were significantly higher than measured in the channel. The mercury concentrations were 3,000-5,000 ng/L in the bank but under 1000 ng/L in the channel. This fits with the current site

conceptual which shows that the terrestrial soils at RRM 3.5 are a source of mercury into the river channel. Although the concentration is lower in the main channel, the much larger area of the river bottom versus the bank (e.g. 50-100 ft in width versus approximately 2-5 ft of wetted bank) also suggest that the river bottom is an important source of mercury to the river. Mercury is transported from the terrestrial soil through bank erosion and bank groundwater seepage into the river channel. Some of that mercury is deposited back into the channel bed sediments, as seen at 10 and 20 feet from the bank. There is no discernable difference between the concentrations measured 10 and 20 feet from the bank which, along with the lower concentrations measured away from the bank, suggest that the channel sediments are not a significant source of mercury to the channel.

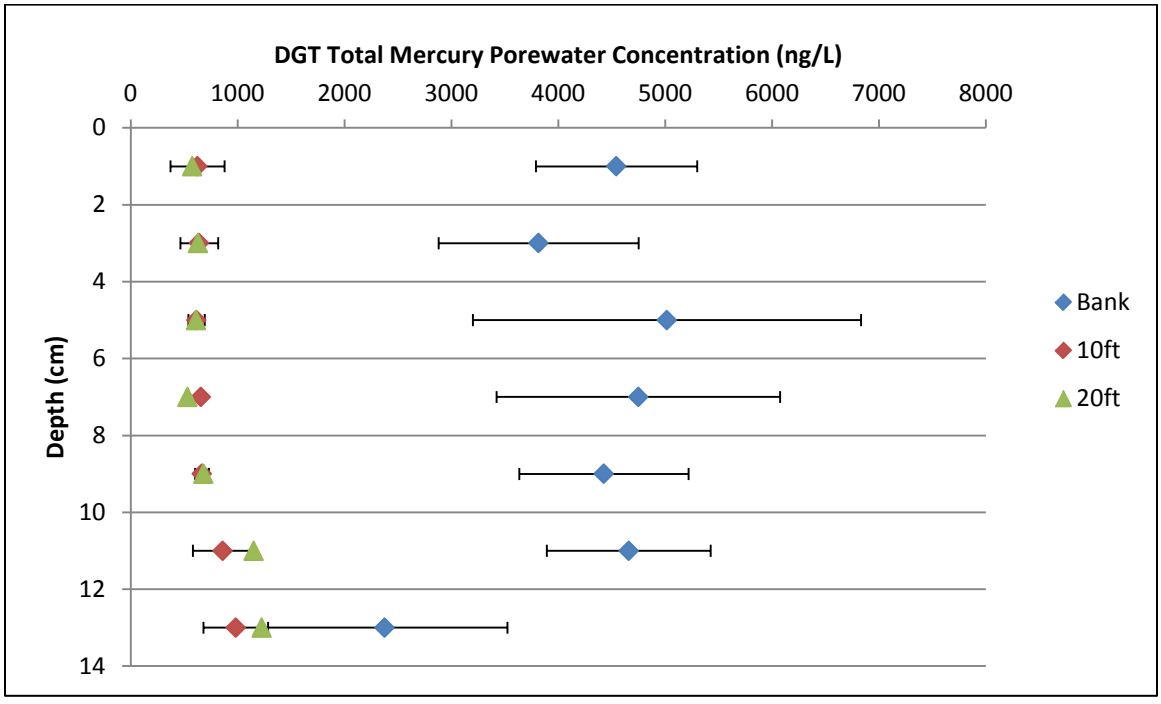

Figure 27 - South River RRM 3.5 DGT Total Mercury Porewater Concentrations, October 2013. Error Bars Represent Standard Deviation from Replicate Samples.

DGT sampling was also performed at RRM 11.8 which is located downstream from RRM3.5. DGT samplers were again deployed at the bank, 10 feet from the bank, and 20 feet from the bank. The depth profiles measured in October 2013 are shown in Figure 28. At this location, the mercury porewater concentrations in the bank are lower than those measured in the channel sediments. Mercury porewater concentrations are similar 10 and 20 feet from the bank, with both between 600 and 1000 ng/L, an order of magnitude lower than the bank sediments at RRM 3.5. The porewater concentrations in the bank are even lower, suggesting that mercury is not migrating from the banks to the channel. This data suggests that the terrestrial soil at RRM11.8 is not as significant a source for mercury into the river channel compared to RRM 3.5. The physical conditions at RRM 11.8 are such that sediment appears to deposit in this area during periods of low flow and mercury contaminated sediments are likely accumulating in this area. The porewater concentrations at the bank are slightly lower than in the channel, likely due to more limited deposition on the bank except during high water periods.

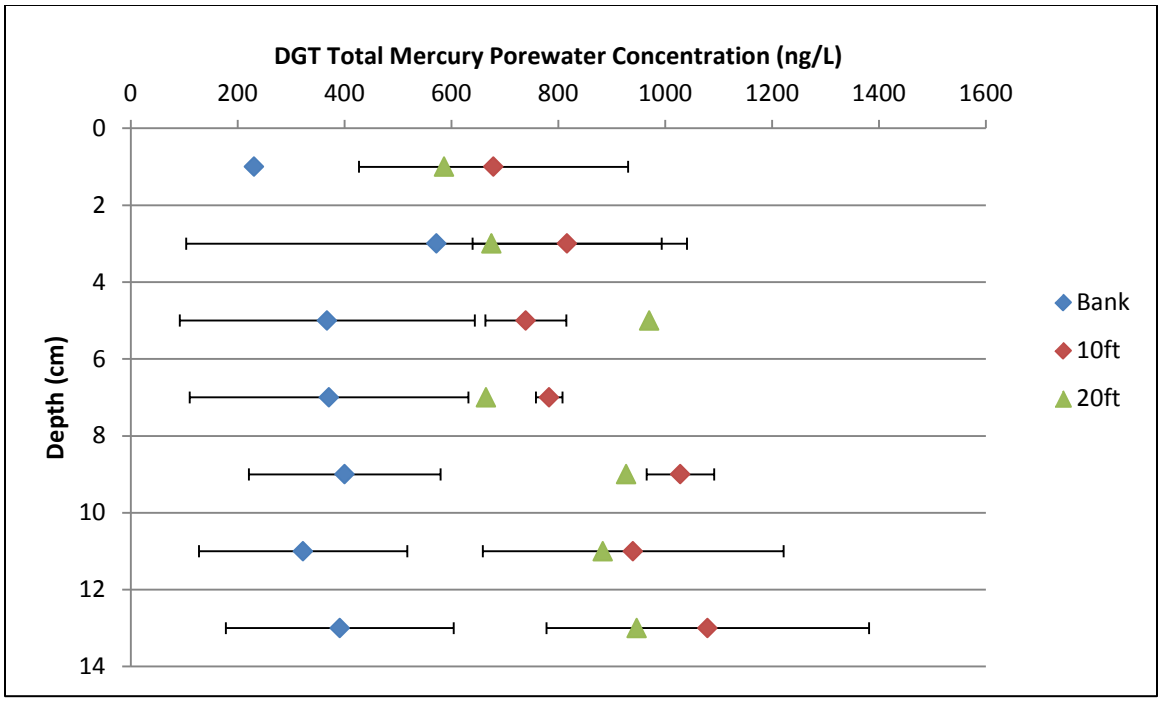

Figure 28 - South River RRM 11.8 DGT Total Mercury Porewater Concentrations, October 2013. Error Bars Represent Standard Deviation from Replicate Samples.

Figure 29 – South River Relative River Mile 11.8 Sampling Area

Figure 30 – South River Relative River Mile 11.8 during High River Stage, May 2013

The sampling event in May 2013 was different from the majority of other sampling events. Most DGT sampling had occurred while the river was at or near baseline flow. This was not done intentionally; weather was not taken into account when scheduling sampling events. The May 2013 sampling trip coincided with a large storm event which caused the peak river flow to reach over 3000 CFS, compared to the baseline flow of approximately 200 CFS with the hydrograph for that period shown in Figure 31.

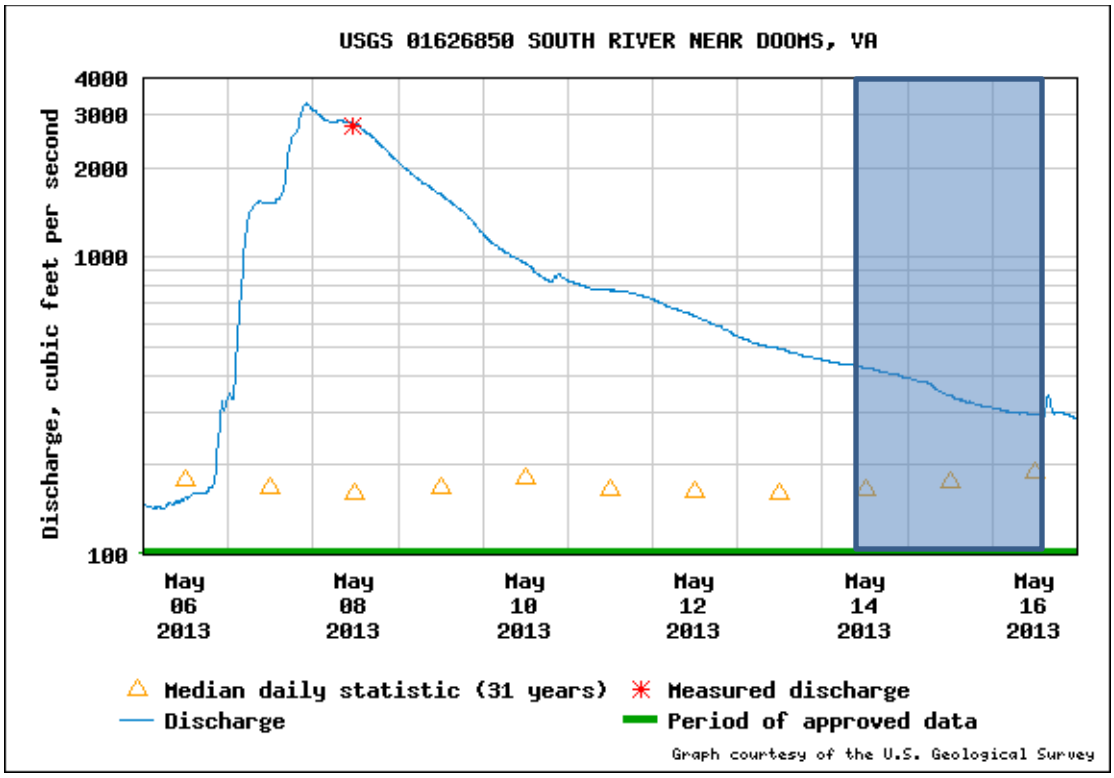

Figure 31 – USGS stream flow data for South River in May 2013 with DGT Sampling Period Shaded in Blue (U.S. Geological Survey)

The bank environments at RRM 3.5 and 11.8 were both inundated with water. The DGT samplers were deployed just after the river flow had crested and so they obtained porewater data that was averaged over the first two days of the declining river stage, while the bank was draining. Voltammetry was also performed during the bank drainage period. The DGT porewater data from RRM 3.5 is shown in Figure 32. The mercury concentrations measured in the bank porewater were significantly higher than had been measured previously. Elevated mercury concentrations were measured over the entire 14cm sampled. The peak mercury concentration measured in the bank porewater was over 120,000 ng/L, more than 10x higher than

measured during the low flow conditions in October 2013. The concentrations were more spatially variable as well, reflecting the location and magnitude of drainage through the bank soils.

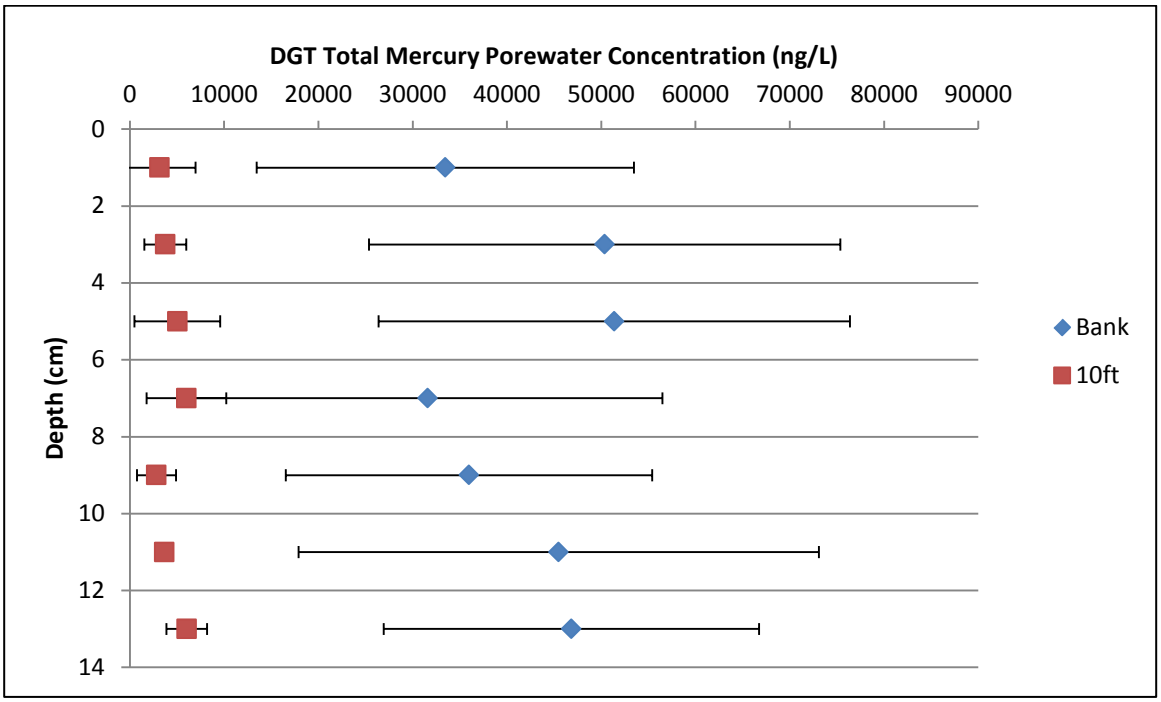

Figure 32 – South River RRM 3.5 DGT Total Mercury Porewater Concentrations during Bank Drainage, May 2013. Error Bars Represent Standard Deviation from Replicate Samples.

Voltammetry data from the bank at RRM 3.5 is shown in Figure 33. There was no reduced iron or sulfide detected at any depth within the bank; however, a small amount of reduced manganese was measured but only at 8-10 cm. These results suggest that there was no significant reduction occurring in the sediment bank during this sampling event, especially at depths less than 8 cm. If significant reduction was occurring high concentrations of manganese would be expected as well as reduced iron. Dissolved oxygen was not measured during this

sampling event but it was likely that oxygen would have been detected over the entire profile. The relatively low extent of reduction noted is consistent with the flooding of a previously unsaturated (and therefore air filled) bank immediately prior to the sampling period.

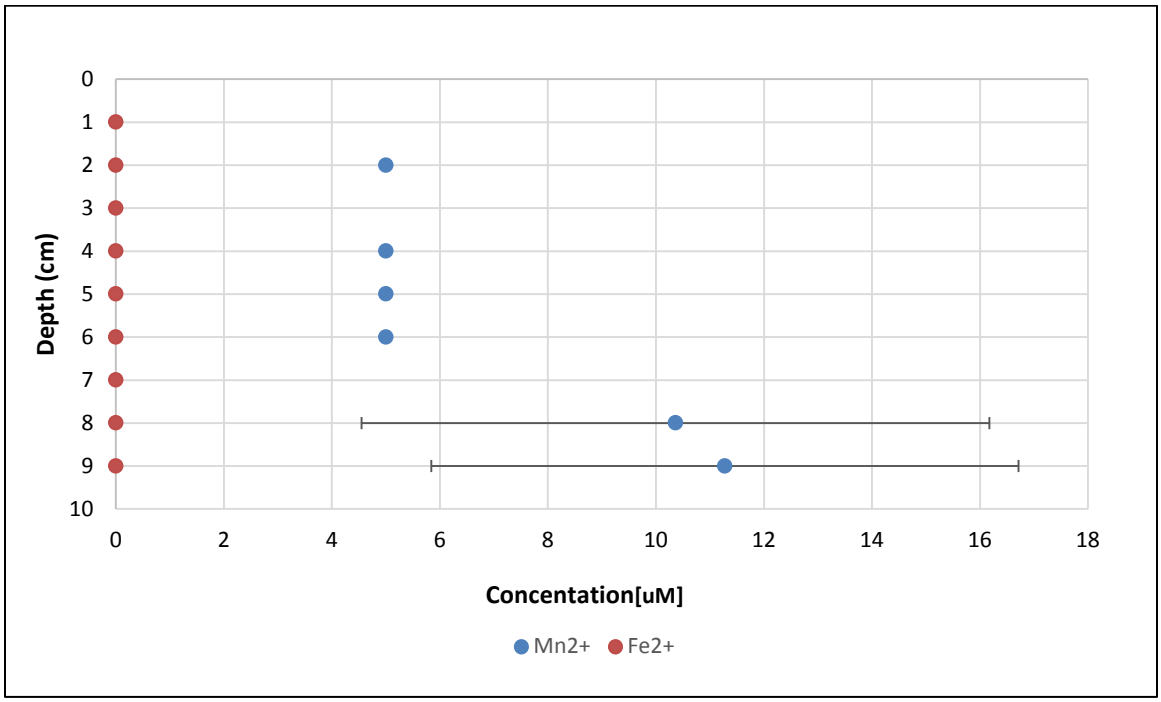

Figure 33 – South River RRM 3.5 Cyclic Voltammetry Porewater Measurements in Bank during Bank Drainage, May 2013. Error Bars Represent Standard Deviation from 3 Replicate Electrodes.

Methylmercury porewater concentrations were also measured in the RRM3.5 bank using DGT samplers. Methylmercury concentrations were not detected during the October 2013 sampling event due to the low temperature likely leading to low microbial activity. Methylmercury porewater concentrations from the bank drainage period in May 2013 are shown in Figure 34. The methylmercury concentrations are relatively low and have no significant trend

with depth. This is likely due to the flushing of the banks with oxic water during the flood event. Any methylmercury in the bank system would be mixed over the sampling depth.

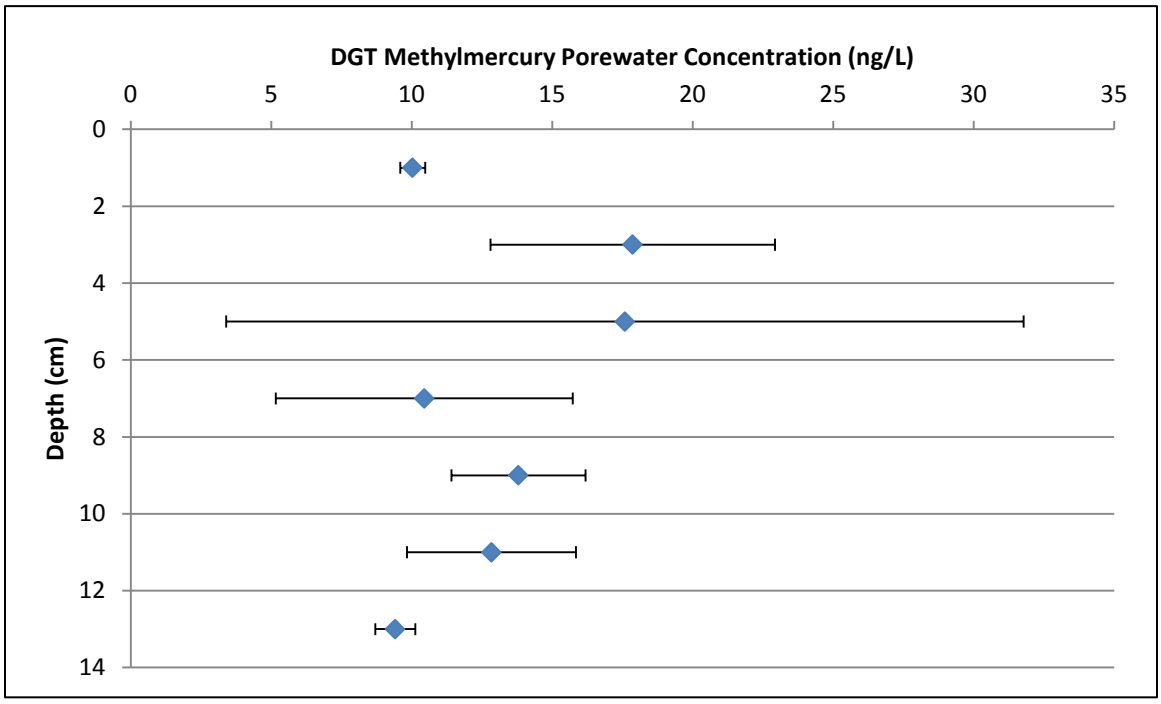

Figure 34 - South River RRM 3.5 DGT Methylmercury Porewater Concentrations during Bank Drainage, May 2013

The ratio of methylmercury to total mercury in the porewater is shown in Figure 35. The methylmercury percentages also show that there is either very little methylation occurring or that demethylation is dominating. There is no trend with depth for the percentage of methylmercury. The percentages measured here would be indicative of a low productivity sediment system with regards to methylmercury production. This result is also consistent with the relatively oxic conditions in the bank waters in that methylation is most rapid under reduced conditions.

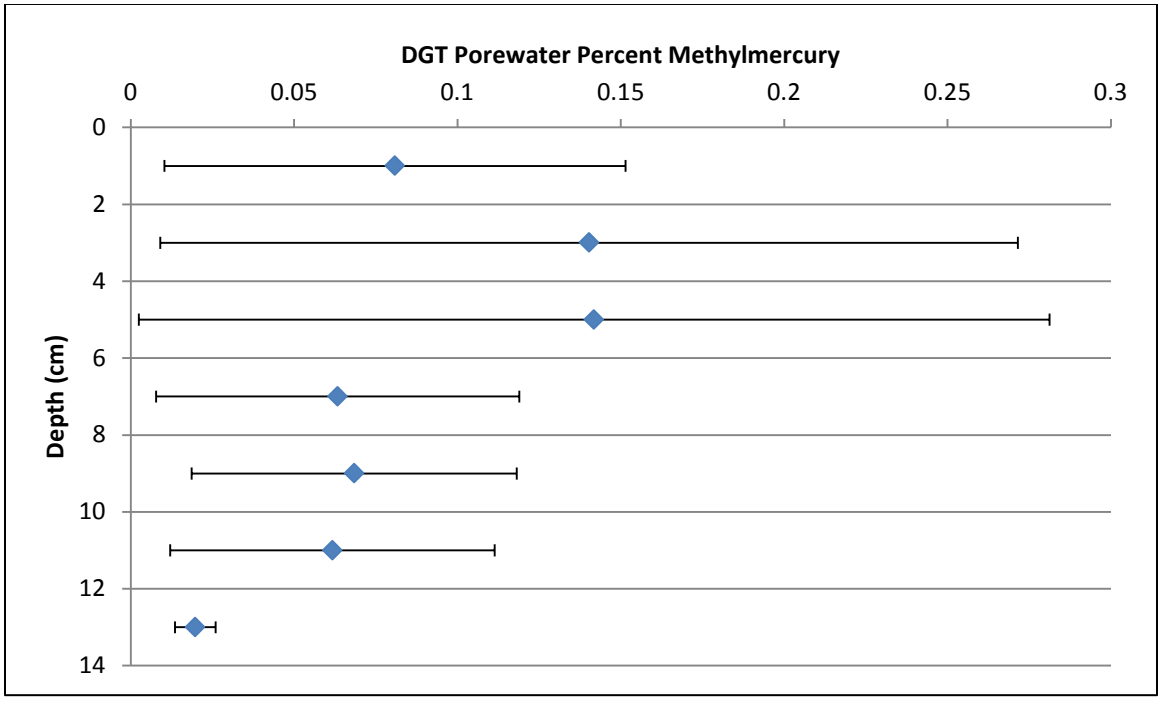

Figure 35 - South River RRM 3.5 DGT Porewater Percent Methylmercury during Bank Drainage, May 2013.

Figure 36 – South River Relative River Mile 3.5 Bank during Baseline Flow

A field sampling event occurred in July 2013 and included both DGT samplers and voltammetry. This sampling event occurred while the river was near baseline flow, as shown in Figure 37. The bank environment at RRM 3.5 was above the river stage height, unlike during the May 2013 sampling event. The photo in Figure 36 shows the RRM 3.5 bank environment during baseline flow.

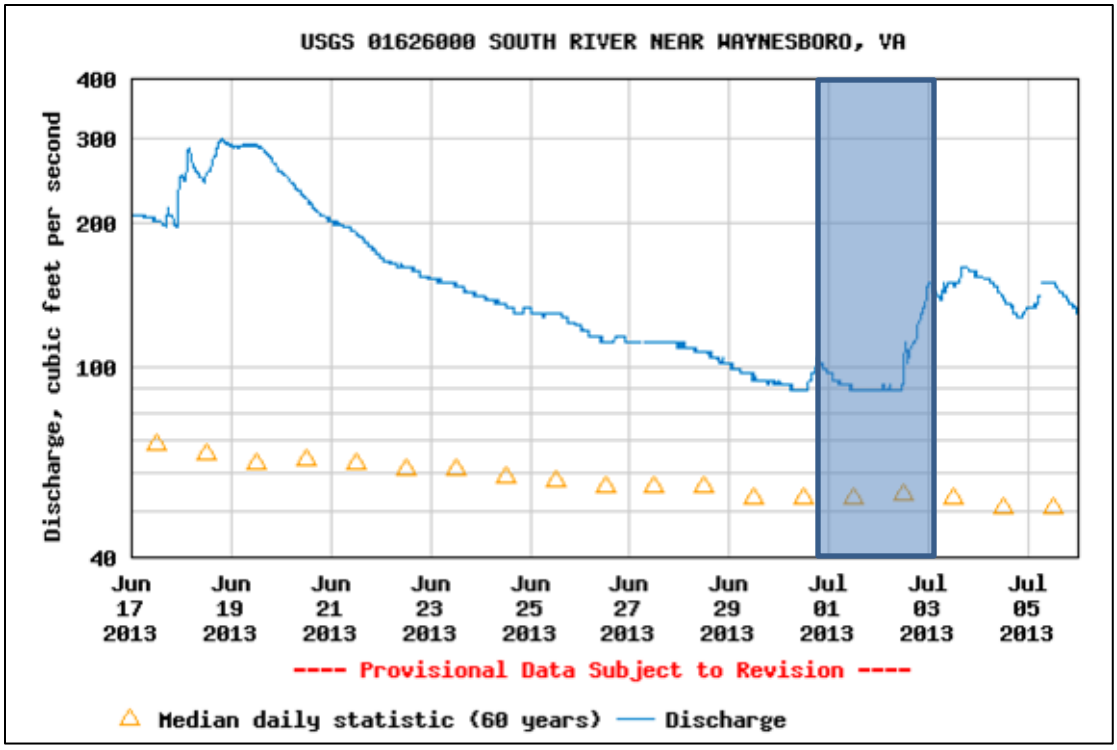

Figure 37 - USGS stream flow data for South River in July 2013 with DGT Sampling Period Shaded in Blue. (U.S. Geological Survey)

Figure 38 shows the DGT total mercury porewater data measured at RRM 3.5 in July 2013. The total mercury porewater concentration peaked at approximately 6cm depth into the bank, similar to the May 2013 data. However, the peak concentration was approximately 18,000 ng/L, compared to 120,000 ng/L in May 2013. However, since the comparison is between sampling events that are months apart, there could be other factors affecting the mercury behavior. The air and water temperature were higher in July which could impact both porewater chemistry and biology. Ideally, measurements would be taken during the baseline flow before a storm and then again as the flow is declining.

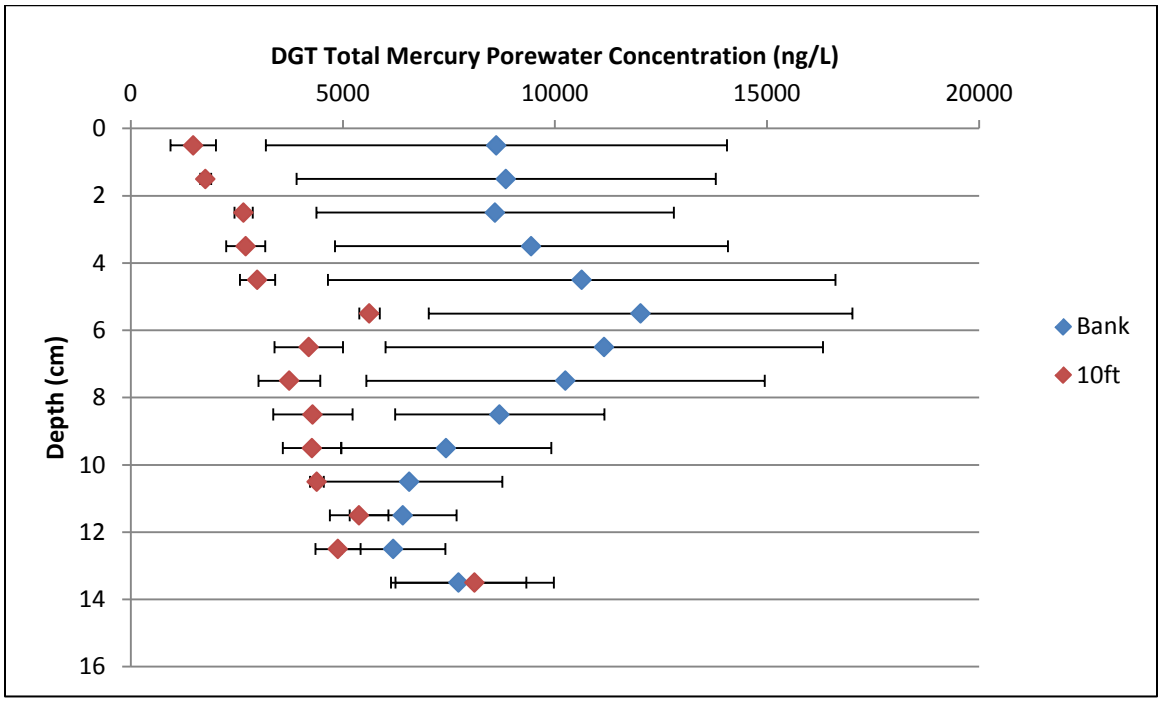

Figure 38 - South River RRM 3.5 DGT Total Mercury Porewater Concentrations during Baseline Flow, July 2013

Methylmercury porewater concentrations were measured in the bank during this sampling event and are shown in Figure 39. The concentrations measured are significantly higher than measured during the bank drainage period. Methylmercury concentrations are higher in the upper 6 cm of the bank than at deeper depths, but this trend is not strong and there is significant variability. The higher methylmercury is consistent with the observed reducing conditions, which should enhance methylation rate.

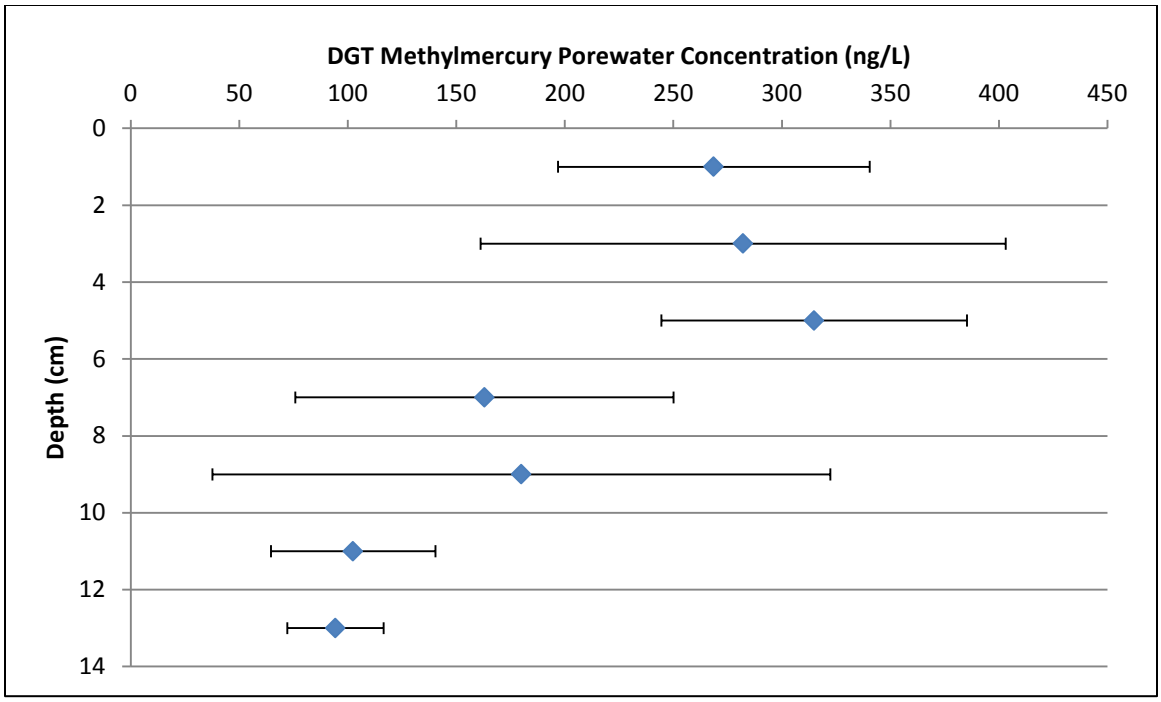

Figure 39 - South River RRM 3.5 DGT Methylmercury Porewater Concentrations during Baseline Flow, July 2013

The methylmercury percentages in the RRM3.5 bank porewater over depth are shown in Figure 40. The methylmercury percentages are significantly higher than measured during the bank drainage period in May 2013 but do not suggest of a highly productive system in terms of methylation. In highly productive sediment systems, porewater methylmercury percentages can reach over 80%, meaning that the majority of available mercury has been methylated (Kannan et al. 1998).

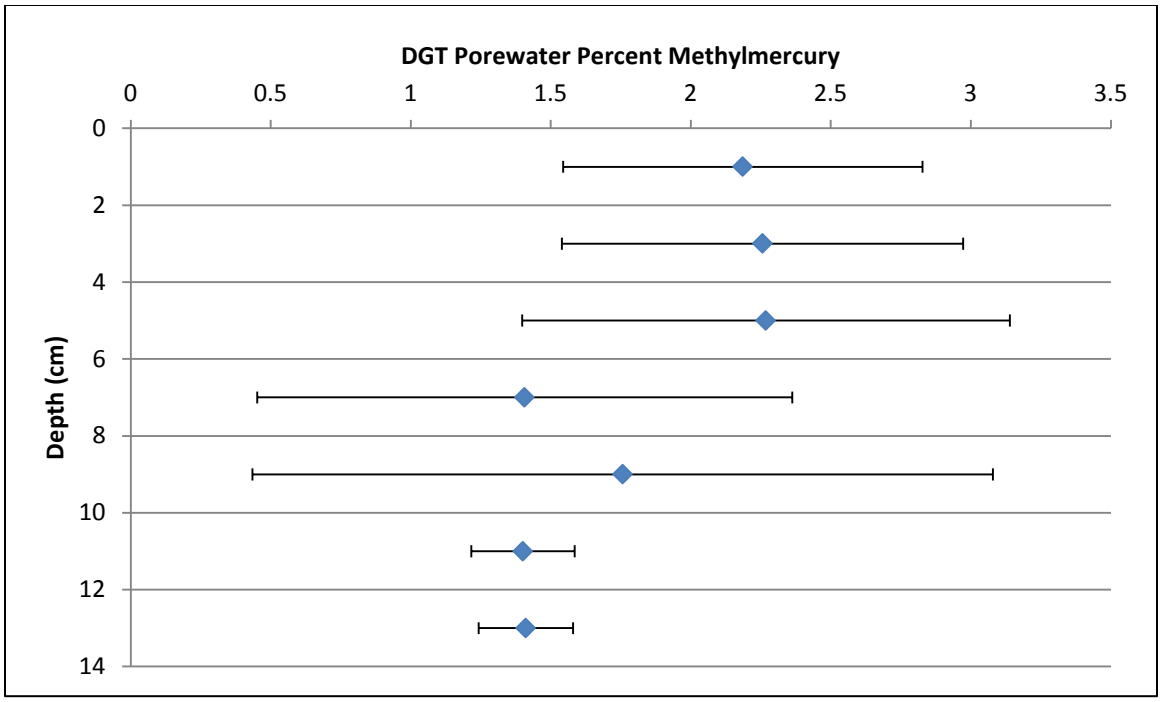

Figure 40 - South River RRM 3.5 DGT Porewater Percent Methylmercury during Baseline Flow, July 2013

Redox sensitive, dissolved species were measured in the bank porewater using voltammetry and these can help explain the total mercury and methylmercury behavior observed with the DGT samplers. The voltammetry results for reduced manganese, iron, and sulfide are shown in Figure 41. Reduced manganese and iron are observed the entire sampling depth. Sulfide is only detected at one sampling depth, 3cm, and could not be quantified, indicating a concentration significantly below the detection limit of 0.01 µmol/L. There was significantly more reduction measured during this sampling event than in May 2013, yet it is still a mildly reduced system. In a more fully reduced system sulfate reduction would be occurring and, along with it, the iron and manganese reduction would taper off. This system does not reach that level of reduction over the 8cm of sampled depth.

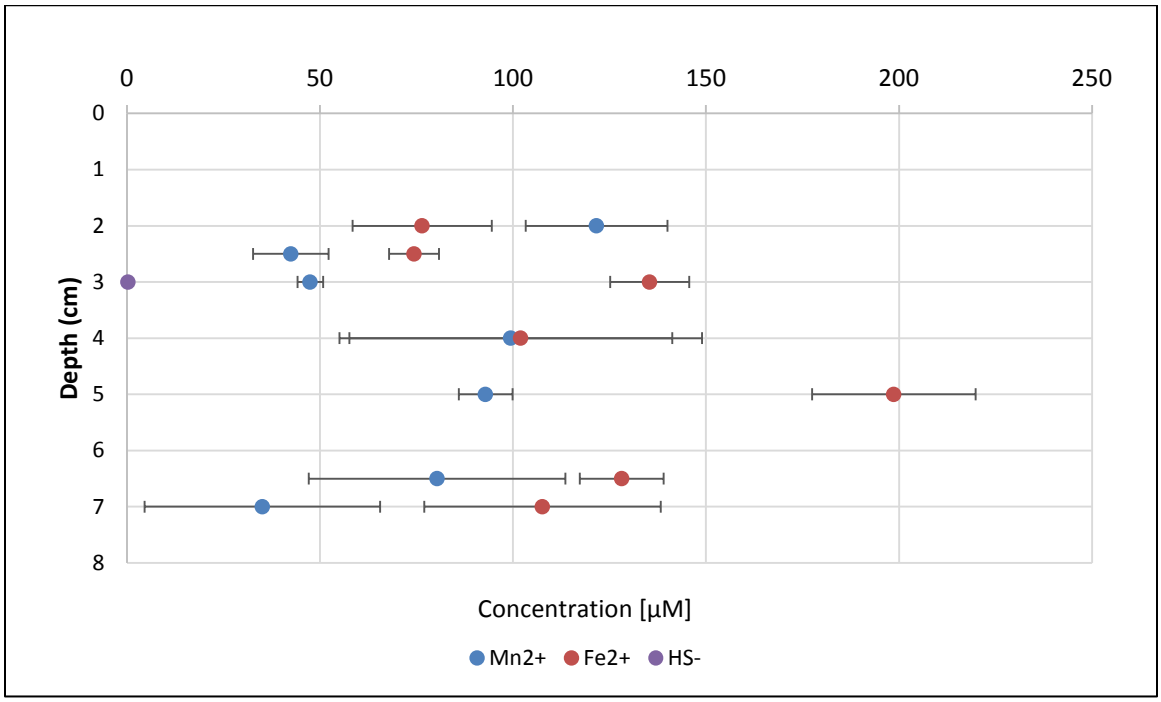

Figure 41 - South River RRM 3.5 Cyclic Voltammetry Porewater Measurements in Bank during Baseline Flow, July 2013. Error Bars Represent Standard Deviation from 3 Replicate Electrodes.

The sampling data in July 2013 show significant differences from the May 2013 sampling event data. The total mercury concentrations measured in the RRM3.5 bank were significantly lower than in May 2013 and similar to those measured during baseline sampling events. The methylmercury concentrations and percentages were higher than in May 2013, but still indicative of a low-productivity system. The voltammetry also shows this to be a low-productivity system as the bank was only mildly reduced, with only iron and manganese reduction occurring, even during baseline flow. It is difficult to draw conclusions from the

comparison of the May 2013 and July 2013 sampling events as they occurred months apart and other factors may contribute to the differences observed.

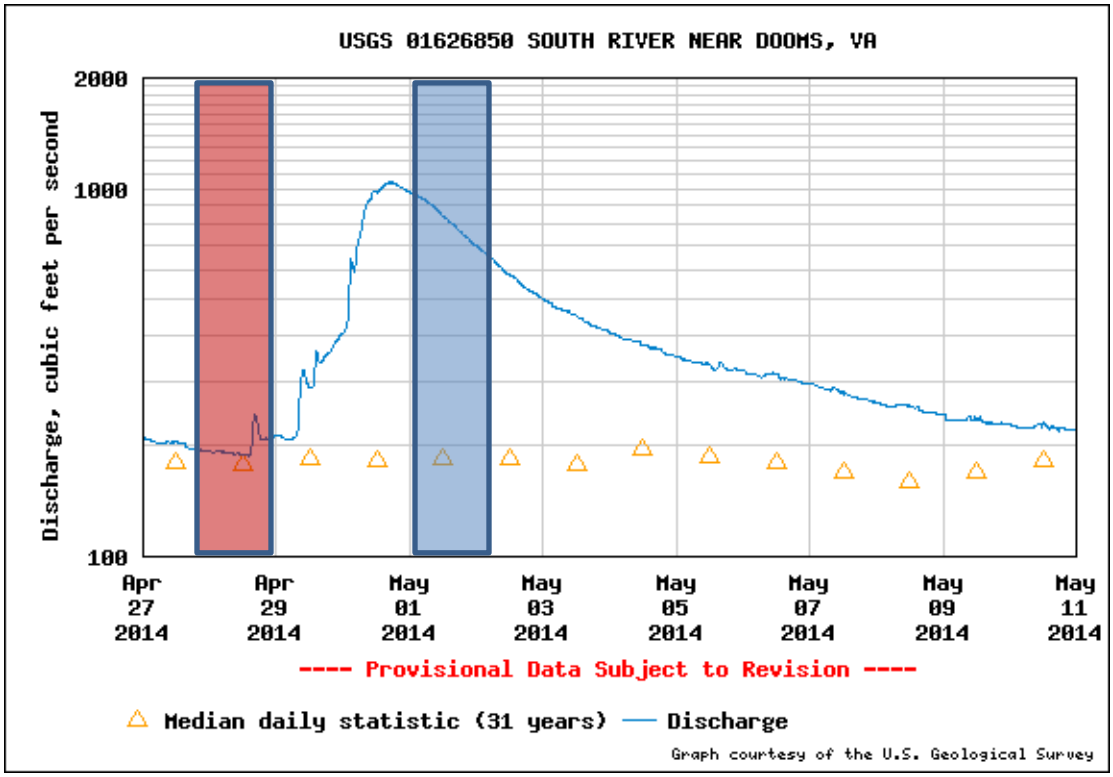

Figure 42 – South River USGS Stream Flow Data, May 2014 with DGT Baseline Flow Sampling Period Shaded in Red and Bank Drainage Sampling Period Shown in Blue (U.S. Geological Survey)

Field sampling took place in late April and early May 2014 and included DGT samplers and voltammetry. This sampling event took place around the same time as a large storm event, making it possible to sample at both baseline flow and during the bank drainage period. A comparison can now be made between these different bank flow regimes at a close time interval. The hydrograph for the South River during this sampling event is shown in Figure 42. DGT

samplers were deployed during the baseline flow and retrieved before the river started to rise. Voltammetry was also performed on the bank system during the baseline flow period.

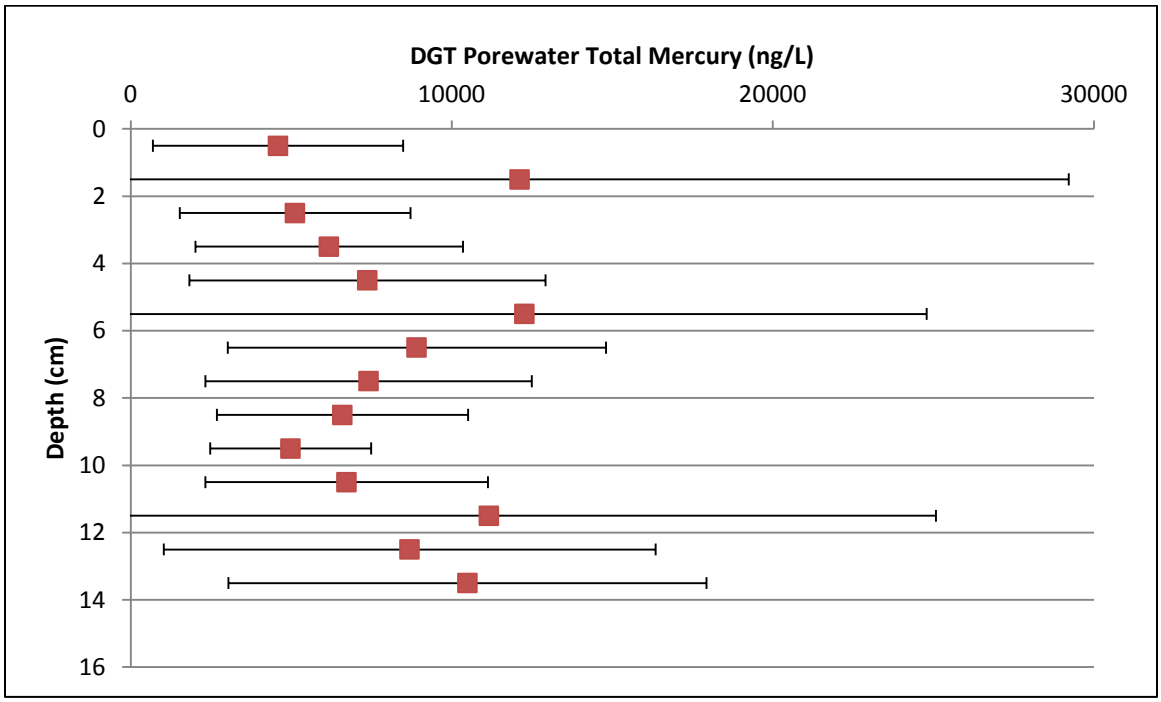

Figure 43 – South River RRM 3.5 DGT Total Mercury Porewater Concentrations in Bank during Baseline Flow, May 2014

The DGT porewater data from the bank at RRM 3.5 during the baseline flow period is shown in Figure 43. The concentrations measured were comparable to what has been measured in previous sampling events. The average bank porewater ranged from 4,000 to 12,000 ng/L over depth. The mercury concentration peaked at 6cm depth, as seen during baseline flow sampling, but the concentration was also elevated near the surface. There was variability in the concentrations measured at each depth but no clear trends. These variations may simply be the result of heterogeneity in the bank.

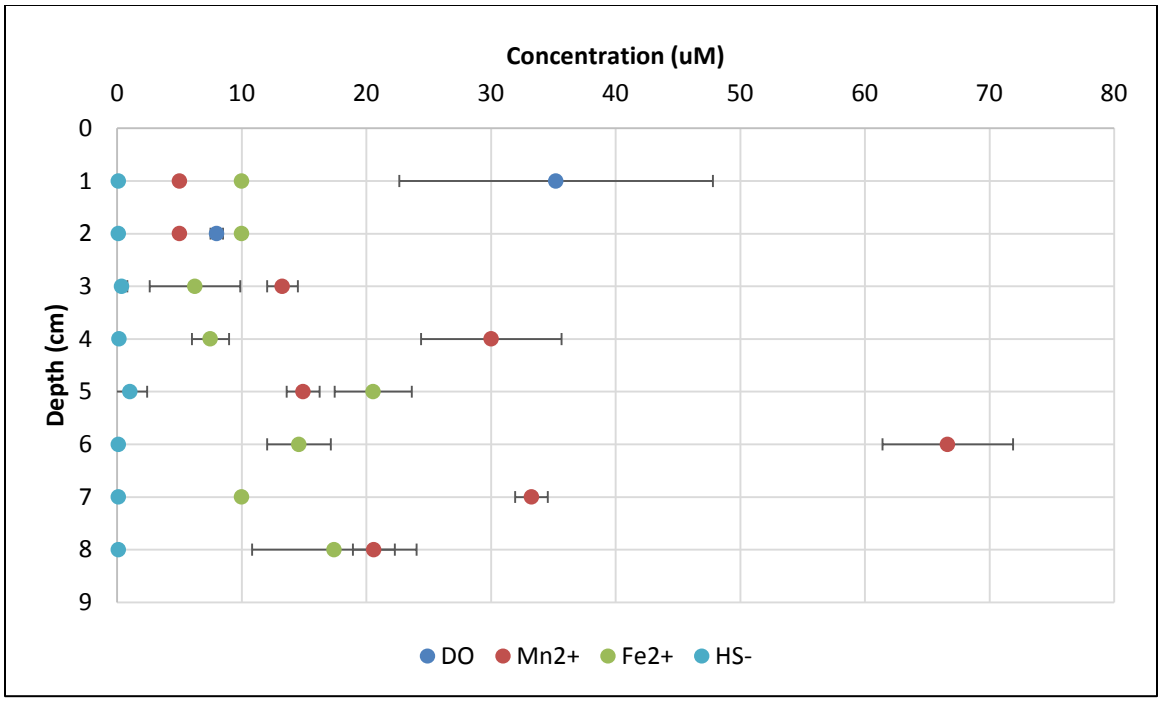

Figure 44 – South River RRM 3.5 Cyclic Voltammetry Porewater Measurements in Bank during Baseline Flow, May 2014. Error Bars Represent Standard Deviation from 3 Replicate Electrodes.

The redox conditions measured during the baseline flow event were very similar to those measured in July 2013. Figure 44 shows the reduced species and dissolved oxygen voltammetry data from the baseline flow period in May 2014. Dissolved oxygen was depleted within the first 2cm of depth. Reduced manganese and iron were measured over the entire depth after oxygen depletion. Sulfide was detected at only one sampling depth, 5 cm, which is what was also measured in July 2013. The absolute concentrations of reduced species are lower than were measured in July 2013, likely due to the lower temperatures during this sampling event which decreased biological activity. The bank system can again be described as mildly reducing with dissolved oxygen being depleted quickly and very little sulfate reduction occurring.

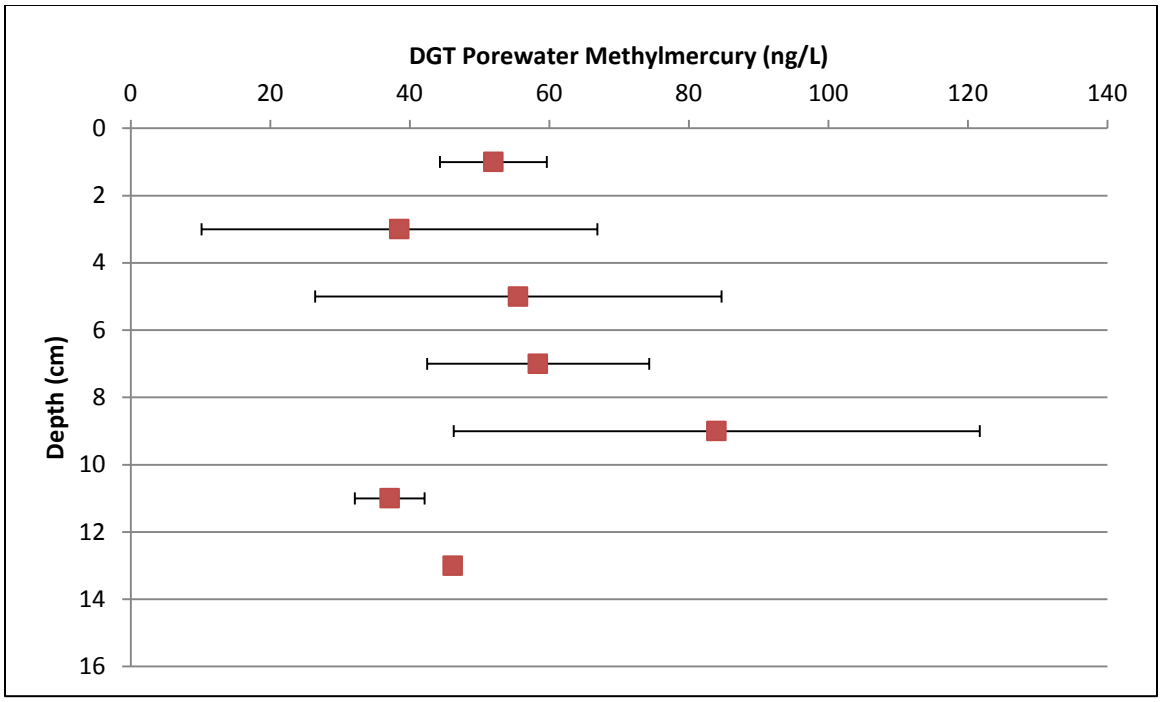

Figure 45 - South River RRM 3.5 DGT Methylmercury Porewater Concentrations in Bank during Baseline Flow, May 2014

Methylmercury porewater concentrations were measured using the DGT samplers during baseline flow and the average concentrations over depth are shown in Figure 45. The methylmercury concentrations are lower than measured during the July 2013 baseline flow sampling event. This is likely due to the lower temperature during May 2014 as this would slow microbial activity. The lower microbial activity is supported by both the voltammetry and methylmercury concentrations as these are all biologically mediated. The methylmercury concentration peaks at 9cm depth into the sediment. Voltammetry sampling was not captured at depths greater than 8cm and so it is unknown if this increase is methylmercury concentrations is related to increases in reduction at greater depths.

Immediately following the baseline flow sampling, a large rain event occurred in the area which caused South River channel flow to increase to over 1000 CFS as shown in the

hydrograph in Figure 42. The bank at RRM3.5 was partially flooded during the elevated flow. The river stage stared to decrease and a second sampling event was conducted during the bank drainage period. DGT samplers were again deployed in the RRM3.5 bank with the period of DGT deployment shown in the hydrograph in Figure 42 in blue. Cyclic voltammetry was performed while the DGT samplers were deployed.

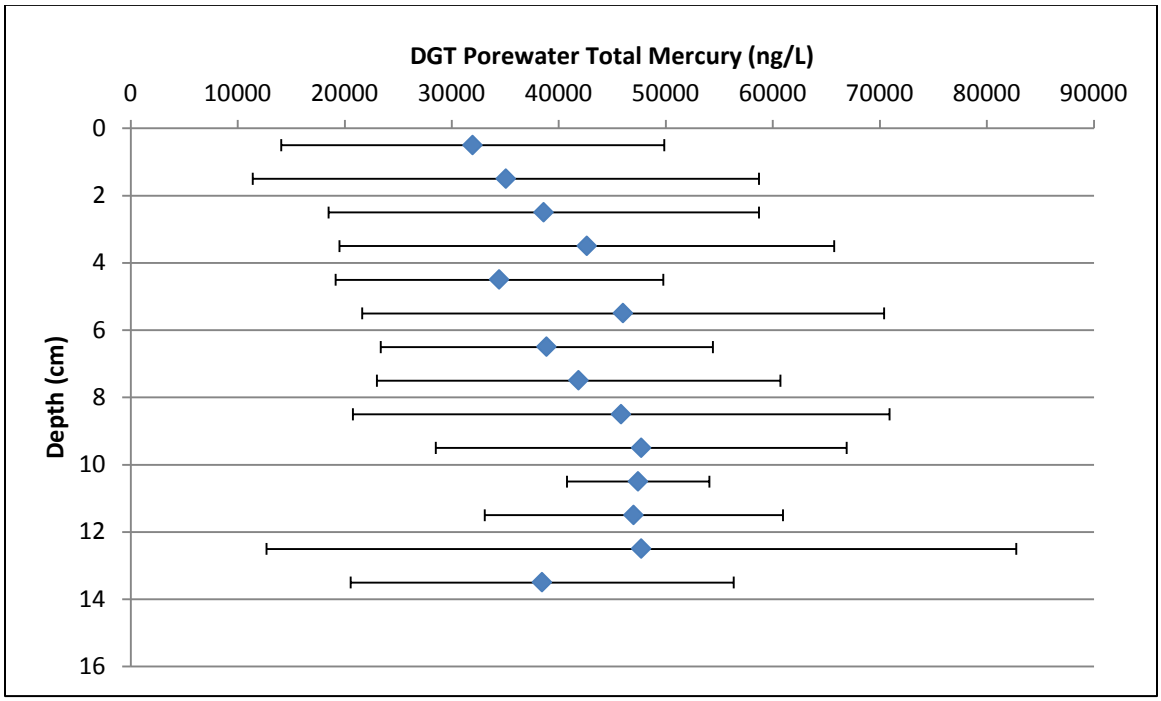

Figure 46 – South River RRM 3.5 DGT Total Mercury Porewater Concentrations in Bank during Bank Drainage, May 2014

Porewater mercury concentrations measured during this bank drainage period were approximately 10x higher than measured just a few days earlier. This data confirms the elevated mercury porewater observed in the bank in May 2013. The two sampling events in May 2014 occurred only 3 days apart and so there were fewer variations, such as temperature and seasonal

variability, than between the May and July 2013 sampling events. The total mercury porewater depth profile measured here is similar to the one seen in May 2013. The porewater mercury concentrations increase over the top few centimeters and then stay elevated over the rest of the sampling depth.

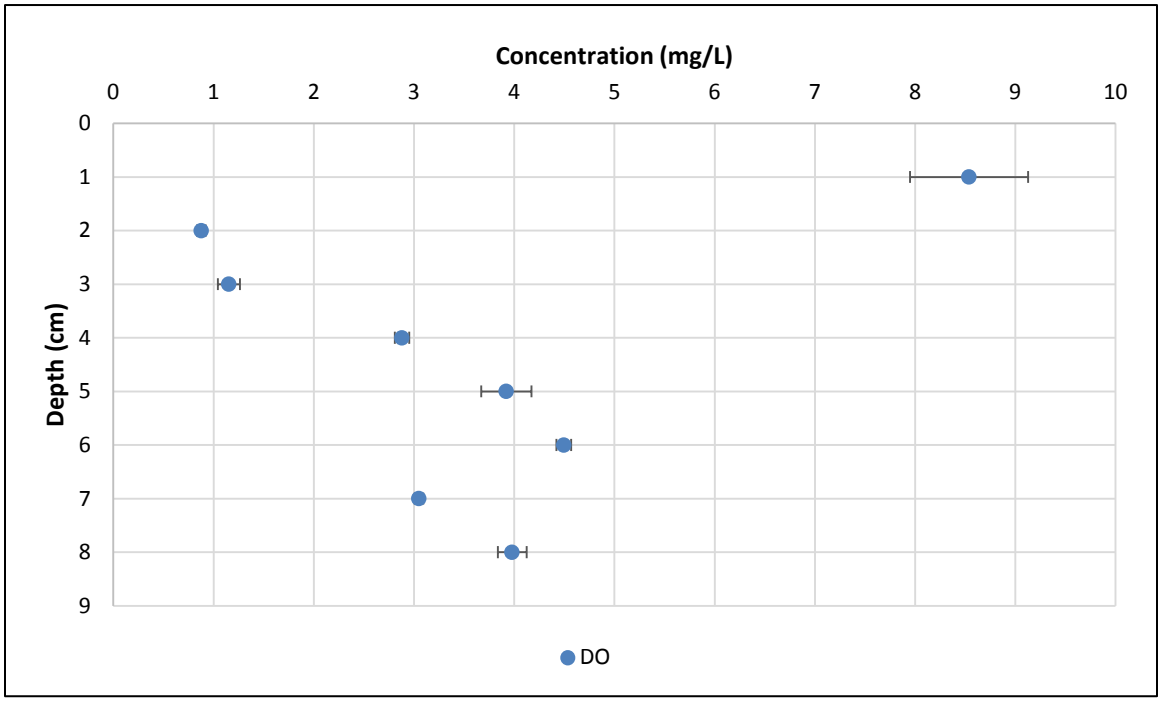

Figure 47 – South River RRM 3.5 cyclic voltammetry measurements in bank during bank drainage in May 2014. Error Bars Represent Standard Deviation from 3 Replicate Electrodes.

Cyclic voltammetry measurements were repeated during the bank drainage period. During this sampling, no reduced metals were detected. Dissolved oxygen was measured over the entire depth with the results shown in Figure 47. The dissolved oxygen depth profile measured during the bank drainage period was significantly different than what was measured during baseline flow conditions. Dissolved oxygen was detected over the entire 8cm depth sampled as opposed to being depleted within the top 2cm. Not only is the dissolved oxygen

present over the entire depth, the concentrations are higher. The dissolved oxygen concentrations ranged from 1 to 8 mg/L instead of being less than 1 mg/L as seen during baseline flow conditions. Although the shape of the profile changed along with the concentrations, it is difficult to draw conclusions from this change. The concentrations did not decrease with depth as was seen previously, but this may have been due to heterogeneities in hydraulic conductivity over the sampling depth. The lower dissolved oxygen measured from 2 to 4 cm in depth may be due to that area not being as permeable for the high dissolved water to flow through. The more important observation is that there is dissolved oxygen present over the entire depth. The river water that inundated the bank during the high flow likely had very high dissolved oxygen concentrations prior to entering the bank. This dissolved oxygen was continuously resupplied as new water was flushed through the bank. The sediment oxygen demand was not high enough to deplete this dissolved oxygen over the first few days of the bank drainage event.

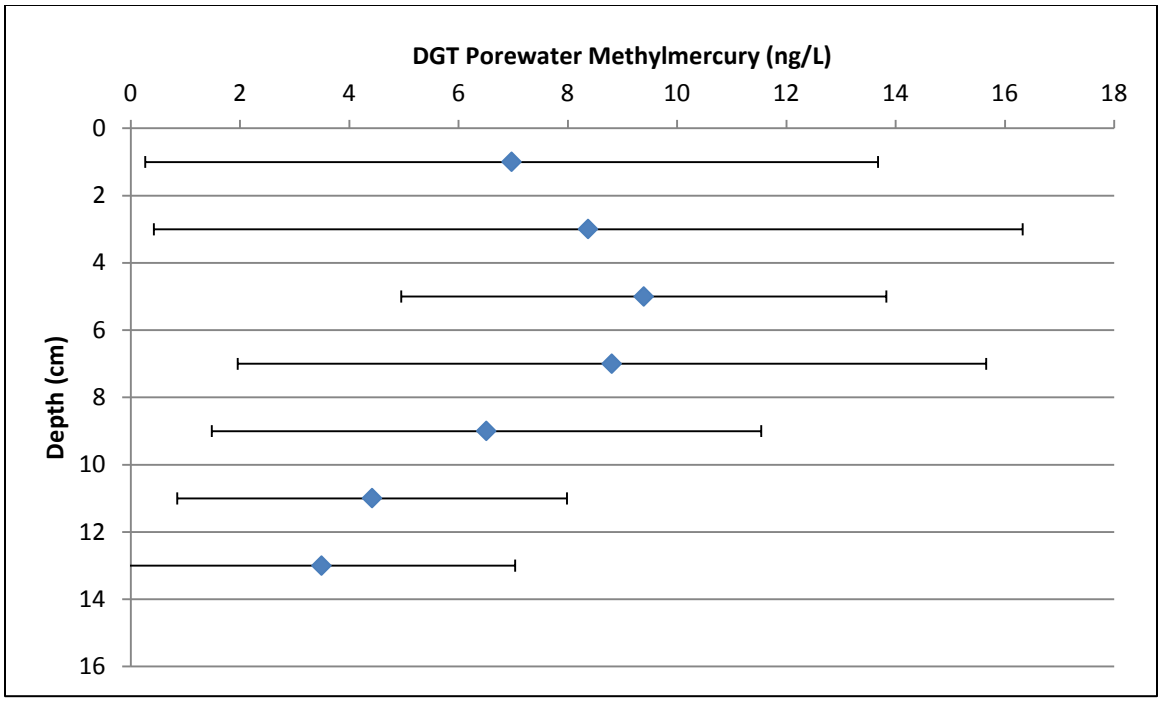

Figure 48 - South River RRM 3.5 DGT Methylmercury Porewater Concentrations in Bank during Bank Drainage, May 2014

The methylmercury bank porewater concentrations measured using DGT samplers during the bank drainage period are shown in Figure 48. The methylmercury concentrations in the bank decreased from baseline sampling just a few days prior. The methylmercury concentration peaks at 6cm depth into the bank but the range of concentrations measured is very narrow. Over the 14 cm depth sampled, the methylmercury concentration varied from 5 to 10 ng/L so there is little variability over depth. The low methylmercury concentrations are expected with the voltammetry results showing no reduced species and dissolved oxygen present over the entire sampling depth. The lack of reduction occurring means that conditions for methylation were unfavorable, even with the higher concentrations of available total mercury, and the dissolved oxygen is likely contributing to an increase in the demethylation rate.

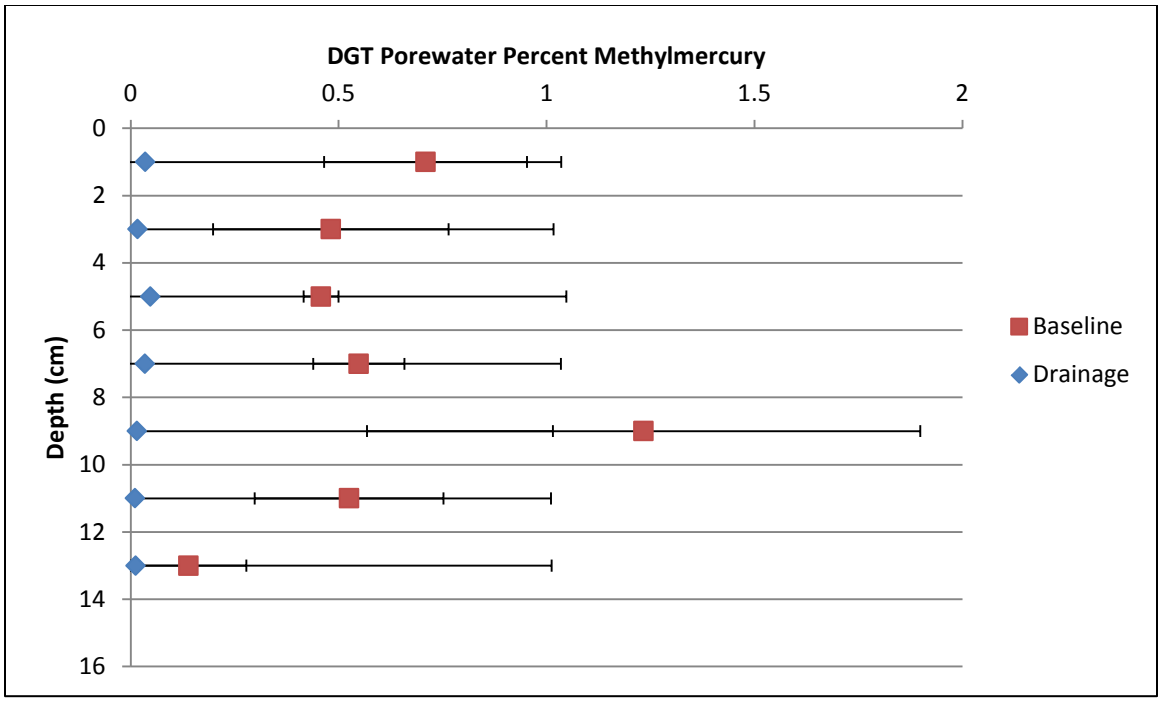

Figure 49 - South River RRM 3.5 DGT Porewater Percent Methylmercury in Bank during Baseline Flow and Bank Drainage, May 2014

The comparison of methylmercury percentages in the porewater between the baseline flow and bank drainage period is shown in Figure 49. The porewater methylmercury percentage decreased after the bank flushing and drainage. The percentage was low to begin with during the baseline flow sampling but decreased to near zero. The bank system is not a productive methylmercury system likely due to the limited reduction occurring. The extremely low percentages measured during the bank drainage period are caused by the low methylmercury concentrations and elevated total mercury concentrations. The mild reduction that was occurring in the bank during baseline flow ceased during the bank drainage period and so the low methylmercury production that was caused by this reduction also reduced significantly . During the bank drainage period, the bank is not a significant source of methylmercury into the river channel system.

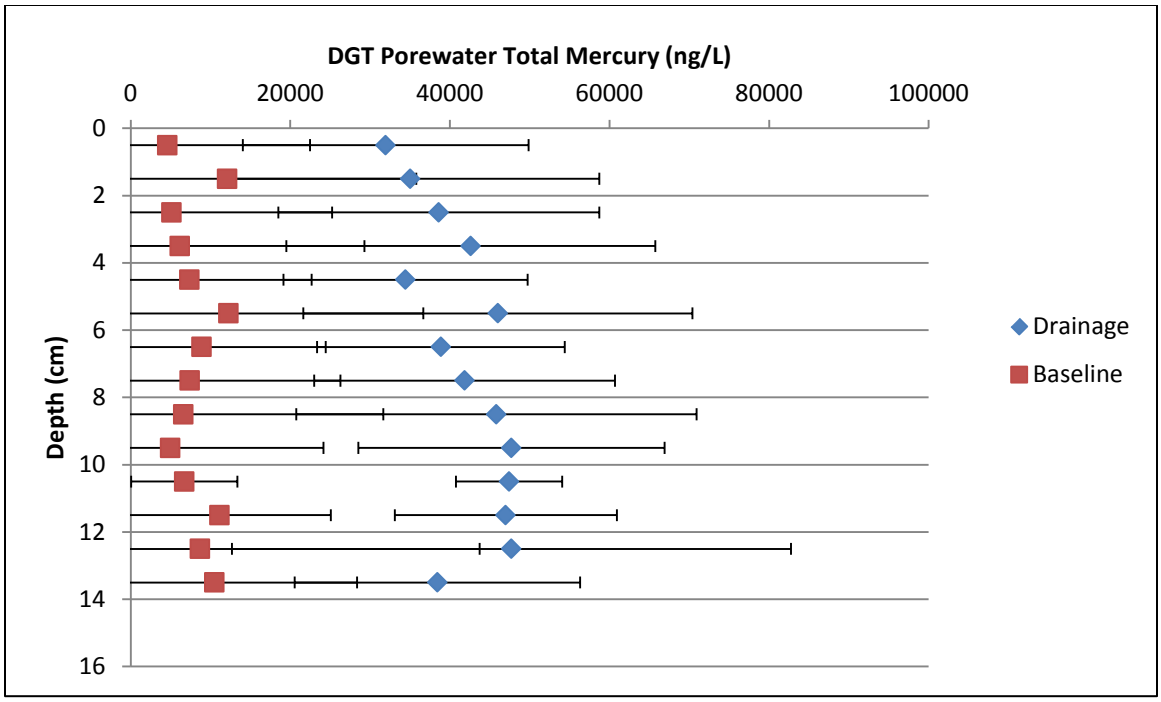

Figure 50 - South River RRM 3.5 DGT Total Mercury Porewater Concentrations in Bank during Baseline Flow and Bank Drainage, May 2014

In summary, at low flows there is little exchange between groundwater and surface water at the bank-water interface and the water level within the bank is stable. Under these conditions, the porewater shows indications of reduction that generally increase with depth. Porewater mercury at RRM 3.5 is generally in the range of 1-10,000 ng/L. Methylmercury constitutes 1-10% of the total mercury in the porewater indicating moderate methylation activity.

In summary, the data suggest that after storm events in which the river flow increases dramatically, water will inundate the adjacent bank. The water will fill the previously air-filled unsaturated zone and potentially mobilize mercury in the pore space within that zone. After the storm event, the river flow and depth decreases and the bank begins to drain back to the river. Under these conditions, the draining porewater shows oxygen over the entire measured depth (10 cm) and as a result, there is little evidence of methylation. Methylmercury constitutes much less

than 1% of the total mercury in the porewater. Total mercury on the other hand is very high and in the range of 50,000-100,000 ng/L or more. This is potentially due to the mobilization of the mercury in the previously air-filled unsaturated zone. The oxidized state of the previously unsaturated zone soils suggests that mercury is unlikely to be associated with reduced precipitated phases.

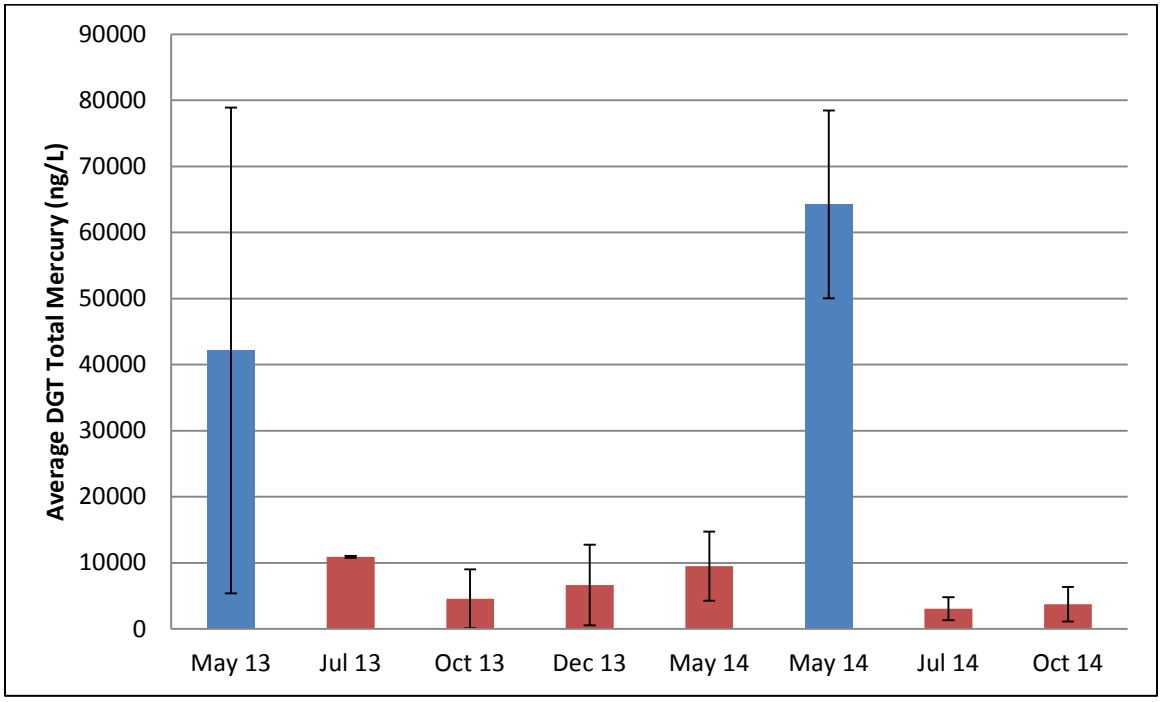

Figure 51 - South River RRM3.5 Average Bank Sediment Porewater Total Mercury Concentrations Measured via DGT 2013-2014

Through the use of DGT samplers, elevated mercury porewater concentrations were detected in the South River banks during bank drainage periods. The average mercury porewater concentration measured at the bank at RRM3.5 is shown in Figure 51. The maximum measured porewater concentration at the bank at RRM3.5 is shown in Figure 52. There is a clear increase in both the average and maximum concentration for the two sampling events conducted during

bank drainage periods. These elevated concentrations would not have been detected using conventional sampling techniques. Capturing dynamic events, such as the bank drainage period, is difficult using other sampling techniques. All conventional sampling techniques use grab sampling and only give a snapshot of a single time point. The DGT samplers capture a time-integrated average concentration over their entire deployment, which allows better monitoring of dynamic systems. River flooding has been identified as a cause of metals release in systems containing iron, manganese, and sulfate minerals. Systems which have frequent changes in river stage and redox, as happens in the South River, have more recently precipitated minerals which are more available for dissolution and release of metals (Lynch, Batty, and Byrne 2014).

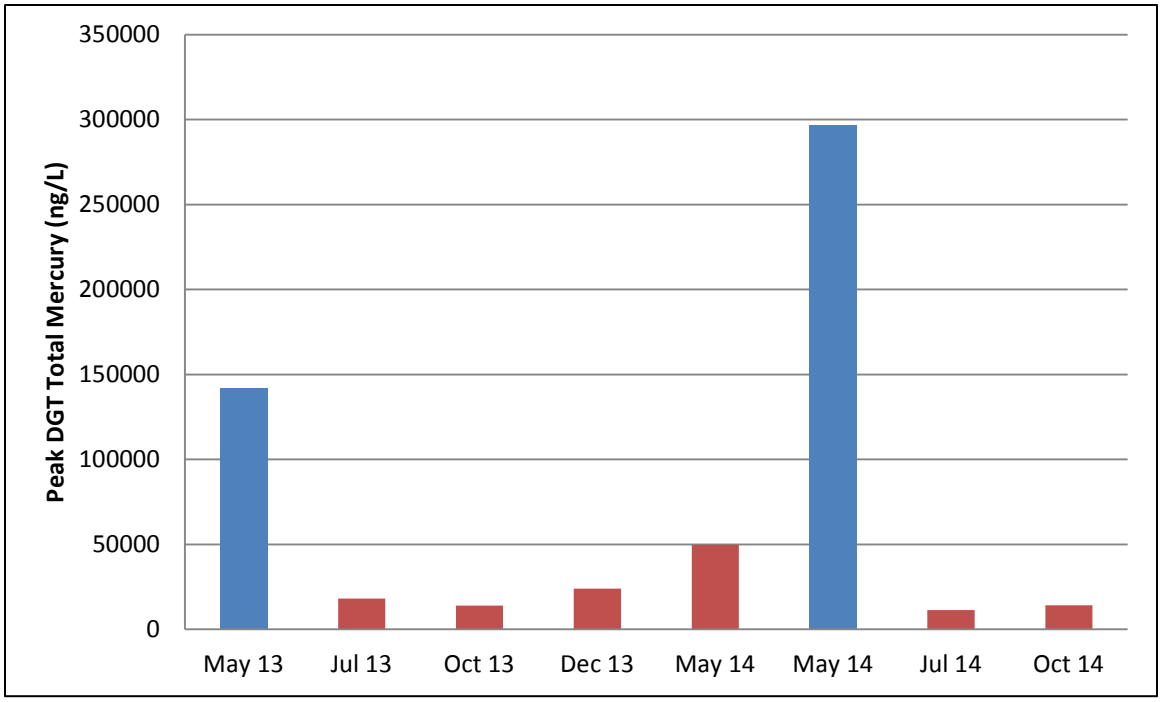

Figure 52 – South River RRM3.5 Maximum Bank Sediment Porewater Total Mercury Concentrations Measured via DGT 2013-2014

4.4 Transport Model and Budget

This field sampling gives us mercury porewater concentrations in the bank porewater but this data alone is not enough to determine if bank leaching is a significant contributor to mercury flux into the river. In order to better assess the contribution of bank leaching, a numerical model of water flow out of the bank at RRM 3.5 during a drainage cycle was made. The modeled bank system consists of two layers called silt and sand. The silt layer is modeled to replicate the bank soil near the channel and the sand layer is modeled to replicate the underlying sand formation. A conceptual model of the system is shown in Figure 53. The goal of the model is to determine how much of the water will drain out of the silt and sand layer faces respectively under a variety of conditions. The contaminated solids are largely located on the outer layer of the silt, shown in red in Figure 53. The DGT samplers deployed in the bank of RRM3.5 were located in the elevated silt layer. Groundwater monitoring wells located in the bank of RRM3.5 are screened in the sand layer and grab sample concentrations from these groundwater monitoring wells were used in the budget for the sand layer.

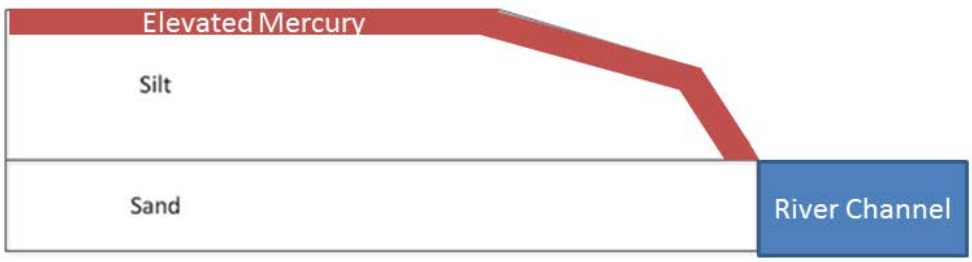

Figure 53 – Conceptual Model of RRM3.5 Bank Drainage System

For this model, water that enters the river channel through the silt faces, marked A and B in Figure 54, is counted as silt drainage volume as it will pass through the contaminated solids. Any water that enters the channel through the sand face, marked C in Figure 54, is counted as sand drainage, even if it drained from the overlying silt layer. This accounting of drainage volumes assumes that the drainage water's mercury concentration is controlled by whether or not it flows through the contaminated silt faces. The volumes from the model are then coupled with field measurements to calculate a mercury mass loading to the river per length of bank for the modeled drainage event.

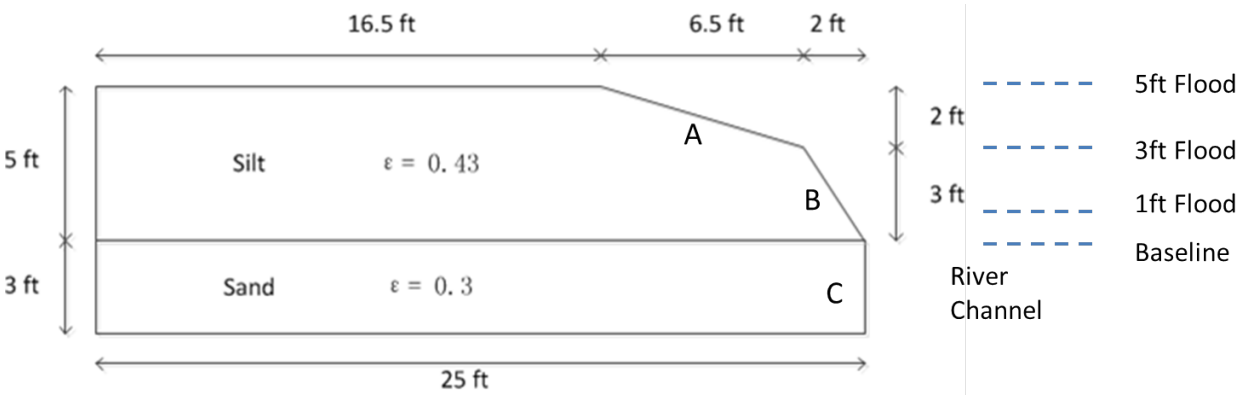

Figure 54 – Schematic of RRM3.5 Bank Drainage Model

The model was designed to simulate drainage from an inundated bank after a flood event. The physical layout for the model was taken from core samples taken by URS Corporation. The silt and sand parameters were taken from a combination of experimental and literature sources and a more complete discussion is found in the appendix. The hydraulic conductivity of the sand layer was modeled as eight times higher than the silt layer. For the model, the bank is assumed

to be saturated at the beginning of the run. The river level is modeled as the bottom of the sand layer for the entire duration of the model. The river level would lower more gradually but this time dependent boundary condition could not be modeled. The bank inundation height was modeled as 1, 3, and 5 feet to determine how flood events of varied sizes would affect bank drainage. The horizontal length into the bank was chosen as 25 feet. This length was also modeled as 10 and 50 feet to ensure that this parameter is not important to the results. A model run duration of 10 days was used for all scenarios. The output of the model was the cumulative discharge volume per foot of bank through the silt and sand layers respectively.

The base case for the model was an inundation height of 5 feet and a bank depth of 25 feet. This case represents a flood event similar to the one that occurred during the field sampling event of May 2013. The discharge results from this case are shown in Figure 55 with the sand discharge shown in blue and silt discharge shown in red. Several important results can be observed from this case. The first conclusion is that the majority of water drains from the sand layer and not the silt layer. Over the 10 days, only 7% of the water volume drains through the silt layer. The hydraulic conductivity of the sand layer is higher so it can be expected that more water would drain through this layer. The second conclusion form this base case is that the silt drainage occurs quickly. For this case, over 95% of the silt drainage occurs in the first two days. The silt layer is located above the sand layer and as the drainage occurs the saturated level in the bank is dropping down. At some point, this saturated level drops below the bottom of the silt later and all subsequent drainage goes through the sand layer. This shows that any water that drains through the silt layer would not go anoxic before draining.

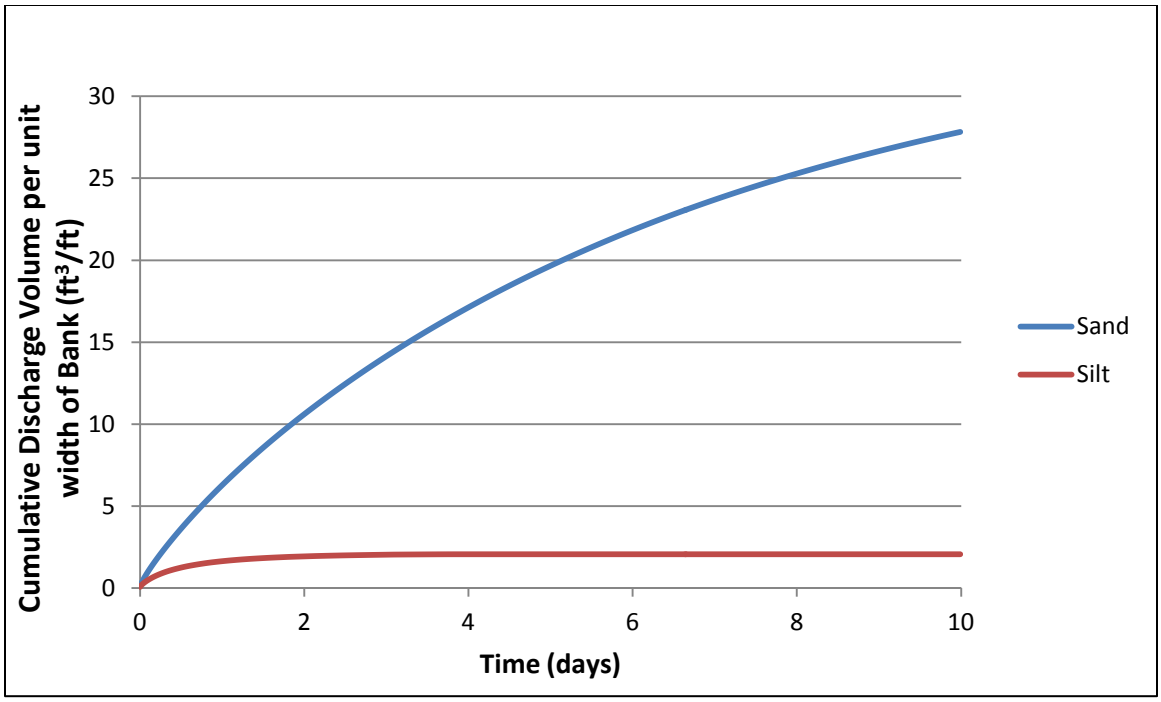

Figure 55 – Cumulative Discharge Volume for RRM3.5 with 5' Inundation Height and 25' Horizontal Inundation Length over 10 Days

The model was run with inundation heights of 1, 3, and 5 feet to examine how smaller flood events would impact bank drainage. For these runs, all parameters were held consistent with the base case except for the starting height of saturation within the bank. The modeled drainage volumes for these cases are shown in Table 2. The silt drainage volume does not trend linearly with the inundation height. A large portion of the water drains down to the sand layer before draining out. When the inundation height is raised, this will increase the amount that flows through the silt face but it will also increase the amount that flows into the sand layer and it will not affect these two volumes linearly. The sand volume trends linearly with inundation height as the majority of water drains through this layer. The total drainage volume will increase

linearly with inundation height and that volume ends up draining mostly through the sand layer. The small changes in silt drainage volume do not have a large impact on the sand drainage volume since it is a small percentage of the total.

Table 2 – Model Drainage Volumes for RRM3.5 with Varying Inundation Heights over 10 Day Drainage Period

Inundation Height (feet)	Silt Drainage Volume (ft^3/ft)	Sand Drainage Volume (ft^3/ft)
1	0.0027	5.61
3	0.627	16.7
5	2.07	27.8

The horizontal length into the bank was also varied to determine if this would affect the bank drainage. The base case was run with a horizontal length of 25 feet. The flood event in May 2014 saturated the bank at least 25 feet in from the bank based on the water height observed in groundwater sampling wells. It is possible that the bank was saturated further back from the channel but monitoring wells were not installed further away than 25 feet. The model was run with a horizontal length of 50 feet to examine if the additional length would change the silt drainage significantly. The model was also run with a horizontal length of 10 feet to examine how smaller flood events would affect bank drainage. The results from these three horizontal lengths are shown in Table 3 for both the silt and sand layers. For the 50 feet length, neither the silt or sand volumes changed significantly. For the silt layer, beyond a certain length, the water will drain down to the sand layer before it reaches the bank face. Increasing the length of the model will not change this and so there is very little sensitivity to this parameter. In the sand

layer, the drainage volume is limited by the time and so increasing the length doesn't significantly increase the sand drainage volume.

Table 3 – Model Drainage Volume for RRM3.5 with Varying Horizontal Inundation Lengths over 10 Day Drainage Period

Horizontal Length (feet)	Silt Drainage Volume (ft^3/ft)	Sand Drainage Volume (ft^3/ft)
10	1.39	9.73
25	2.07	27.8
50	2.11	31.3

The mercury concentrations used are different for the silt and sand layers. The silt layer uses DGT measurements, either maximum or average concentrations, taken from the bank face during drainage events in May 2014. The highest bulk mercury concentrations are found at the bank face, not throughout the silt layer. This concentration is only applied to the water that drains through the silt face, not water that drains from the silt to the sand before draining. The sand layer uses measurements taken from groundwater monitoring wells during a drainage event in May 2014. These groundwater monitoring wells are screened in the sand layer. The mercury concentrations used in the model are shown in Table 4.

Table 4 –Mercury Concentrations used for Mercury Budget during Modeled Drainage Event

Model Layer	Average Concentration (ng/L)	Maximum Concentration (ng/L)
Silt	64,235	296,353
Sand	152	279

Using the volumes from the model and the concentrations from field measurements, a mercury mass flux budget was made. The silt and sand volumes varied with flood height and so a budget was calculated for 1, 3, and 5 feet inundation heights. The mass flux is expressed in a mercury mass per unit width of bank. The budget results are shown in Table 5 for all conditions. For the base case with an inundation height of 5 feet, the mercury mass results differ greatly from the drainage volume results. The sand drainage volume is higher than the silt but more mercury mass drains from the silt layer for both the average and maximum concentrations. This is also the case for the 3 feet inundation height, although the difference is not as great. Only for the 1 foot inundation height is the sand mercury flux greater than the silt flux.

Table 5 – Mercury Mass Flux Budgets for Bank Drainage under Varying Flood Heights

Flood Height	Silt Drainage Volume	Silt Mercury Flux – Max	Silt Mercury Flux – Average	Sand Drainage Volume	Sand Mercury Flux – Max	Sand Mercury Flux – Average
Ft	ft^3/ft	µg/ft	µg/ft	ft^3/ft	µg/ft	µg/ft
1	0.0027	22.7	4.9	5.6	44.3	24.2
3	0.627	5262	1141	16.7	132	71.9
5	2.07	17371	3765	31.9	252	137

The bank is also a source of mercury to the river channel during baseline flow via leaching from the porewater. The flux during baseline flow gives better context for the bank drainage values to be compared to. This flux can be modeled using a mass-transfer coefficient (Boudreau and Jorgensen 2001), which depends on site specific parameters, and an average porewater concentration. An empirical correlation for the benthic layer mass-transfer coefficient was developed for river systems and is shown below (Thibodeaux 1996).

$$k_{bl} = 88.4 v_x n \sqrt{gd} \left(\frac{D_w}{r_H \nu_w} \right)^{2/3}$$

k_{bl} = benthic boundary layer mass transfer coefficient (cm/hr)
v_x = river velocity (m/s)
n = Manning's coefficient
g = gravitational acceleration (m^2/s)
d = river depth
D_w = molecular diffusion coefficient in water (cm^2/s)
r_H = hydraulic radius (m)
ν_w = kinematic viscosity of water (m^2/s)

A full description of parameters used for this system can be found in the appendix. The diffusive flux rate per unit width of bank can be calculated using the benthic boundary layer mass-transfer coefficient, the porewater concentration, and bank geometry parameters. This relationship is shown below and a full description of parameters is shown in the appendix.

$$J_d = k_{bl} C_{pw} \frac{A_{bank}}{L_{bank}}$$

J_d = Diffusive Flux (ng/m-hr)
k_{bl} = benthic boundary layer mass transfer coefficient (cm/hr)
C_{pw} = mercury porewater concentration (ng/cm^3)
A_{bank} = bank area (cm^3)
L_{bank} = bank length (cm)

This relationship gives a diffusive flux rate per unit bank width which can be used for a comparison with the model results. The average bank porewater concentration over all baseline sampling events, 6400 ng/L, was used. For this system, the benthic boundary layer mass-transfer coefficient was calculated as 10.2 cm/hr. This gives a diffusive flux of 21.4 µg/ft/day. The model run duration for all parameters was 10 days; the diffusive flux during this same duration is

214 µg/ft. This flux is greater than the drainage flux only for the 1-foot flood. For both the 3 and 5 foot floods, the diffusive flux is not significant compared to the mercury mass draining from the banks. The total mass flux from the 5-foot drainage event, 4017 µg/ft, is equal to the diffusive flux for 188 days. The site conceptual model only considers baseline flow conditions for bank leaching and therefore underestimates the mercury contribution from bank leaching by not including bank drainage.

4.5 Conclusions

DGT samplers were successfully deployed in the South River to better understand mercury fate and transport. The DGT samplers were able to measure mercury porewater concentrations in both the gravel channel bed and silty river banks. The DGT mercury porewater concentrations measured were higher in the banks than channel sediments, which agrees with the site conceptual model with the terrestrial soils being the major source of mercury into the river system and the channel sediments being a long-term sink. The mercury porewater concentrations measured in the channel downstream at RRM11.8 were lower than those measured at RRM3.5. RRM3.5 is a known source area of mercury into the river system and the DGT measurements again agree.

The porewater methylmercury percentage was low to begin with during the baseline flow sampling but decreased to near zero during the bank drainage period. The bank system is not a productive methylmercury system likely due to the limited reduction occurring. The extremely low percentages measuring during the bank drainage period are caused by the low methylmercury concentrations and elevated total mercury concentrations. The mild reduction

that was occurring in the bank during baseline flow ceased during the bank drainage period and so the low methylmercury production that was caused by this reduction also terminated. Other changes could have contributed to the decrease in methylation such as a decrease in dissolved organic carbon to act as a carbon source for microbial activity. During the bank drainage period, the bank is not a significant source of methylmercury into the river channel system. The methylmercury percentages also support the idea that the bank geochemistry is changed significantly by the bank drainage and that changes in geochemistry may be the cause of the increase in total mercury porewater concentrations observed.

There is a relationship between the mercury porewater concentrations measured in the bank and the redox measured by cyclic voltammetry but it is unclear whether there is a causal relationship between these measurements. The shift in redox conditions are not the only change occurring during the flood event. The rise in river stage wets bank sediment that was previously partially saturated. This partially saturated bank sediment is oxidized during baseline flow and so the availability of mercury on the solids may be different. Understanding this behavior will be important in making remediation decisions. The mercury budget shows that the elevated concentrations in the bank are significant for larger flood events and so it must be taken into account for future sampling and remediation treatments.

This work successfully showed the DGT samplers can be used to measure mercury sources from sediment porewater in the field. The DGT samplers were successful over a wide range of porewater concentrations, ranging several orders of magnitude. The DGT samplers were deployed over a wide range of temperatures and worked well in all temperatures. Techniques were developed to better deploy DGT piston and depth profiler samplers. Piston samplers needed to be sealed to keep them properly oriented towards the sediment. A 4-inch

Silly Putty ® disc was able to keep the DGT piston samplers in contact with the sediment, lowering any potential impacts from surface water. A variety of insertion tools were developed by DuPont for DGT depth profilers. DGT depth profilers can be inserted into soft or hard sediment without damaging the samplers.

The mercury budget gives context for the DGT sampler measurements. For the system modeled, only larger flood events would potentially mobilize higher mercury from the banks. The mercury from the banks does not scale linearly with flood height or drainage volume. The mercury draining from five 1 foot floods would not equal one 5 foot flood. The depth of flooding likely does not impact mercury flux from the banks as long as it saturates at least 25 feet of the banks. The mercury porewater concentrations alone can be deceiving. One could incorrectly assign the high concentrations found in the bank to the entire bank drainage volume and overestimate the mercury flux to the river. The drainage model without the DGT sampler data is also flawed. The drainage volumes alone would suggest that the sand layer is the larger source of mercury into the river. Using conventional sampling techniques for mercury, such as the groundwater grab samples, the mercury flux from the bank drainage event would be underestimated. The porewater chemistry and physical dynamics complement each other to better the understanding of the mercury behavior in the banks. It is unknown how these mass fluxes compare to other sources as we don't know if these values hold for the rest of the river. These results show that bank leaching needs to be reconsidered as part of the site conceptual model, highlighting the effective use of DGT samplers to monitor mercury sources.

Chapter 5 - Mercury Behavior during Bank Drainage

5.1 Introduction

Field measurements using the DGT sampler technique highlighted the importance of processes in the river banks during high flow events to mercury flux into the river. However, several questions still remain unanswered relative to the processes contributing to the mercury release from the banks. In order to better understand this behavior, laboratory experiments were conducted under more controlled conditions than possible in the field. Field sampling provided good measurements of porewater mercury and redox-sensitive species, but it is difficult to determine causes and processes of trends observed with only those parameters. A better understanding of the mercury release behavior from the bank is required in order to properly incorporate this source into the site conceptual model. Specifically, laboratory studies were conducted in order to further understand and describe mercury flux from the bank sediments during bank drainage cycles.

The experiments were carried out in three parts. The first set of experiements were designed to determine if the porewater concentrations measured with DGT in the laboratory are similar to those seen in the field and if increased dissolved mercury concentrations could be replicated by manipulating the redox conditions of bank sediment in bulk. For these experiments, only DGT samplers were used. The second experiment better replicates field conditions. A mesocosm was filled with bank sediment and allowed to equilibrate, establishing a redox gradient over depth. The mesocosm was sampled with both DGT samplers and cyclic voltammetry as was done in the field. After equilibrium was reached, the mesocosm was flushed with oxic water and then drained to simulate what occurs in the bank during a flood event and

bank drainage. The mesocosm was again sampled using DGT samplers and cyclic voltammetry. This experiment replicates the field sampling done in May 2014 with the bank environment sampled just before and after a flood event. The final experiment was designed to better understand the porewater chemistry that is controlling the mercury release during bank drainage. In field sampling and the first two experiments, only DGT samplers and cyclic voltammetry were used. For this experiment, a column set-up is used and effluent is collected for more thorough chemical analyses. This experiment was designed to identify the cause of increased mercury porewater concentrations during bank drainage events. While it may not be possible to provide a mechanistic explanation of mercury release from this experiment, the results can be used to develop a better understanding of the mercury behavior than could be achieved with only DGT samplers and cyclic voltammetry.

5.2 Materials and Methods

For these studies, bank soil was collected from RRM 3.5 at the South River in October 2014. The sample was collected from the same study area as was sampled extensively from 2010-2014. The sample was sieved at ¼" to remove rocks and root material and then stored at 4^{o}C until the start of the experiments.

The bulk sample was analyzed for total mercury and total organic carbon. Bulk total mercury analysis was performed according to EPA Method 1631, Revision E. Solid samples were digested in Aqua Regia for 24 hours. The acid was then analyzed on a Brooks Rand Merx-T CVAFS system. Total organic carbon was analyzed according to EPA Method NCEA-C-1282. Analysis was performed using a Vario Cube analyzer.

Selective sequential extraction was performed on the homogenized, oxic bank soil. Selective sequential extraction is a method to determine what soil phases mercury is associated with and how easily the mercury can be released and mobilized. This is achieved by extracting mercury from the sample with increasing strength solutions. It is not a quantitative measure of mercury speciation but can be a useful tool for comparing the availability of solid bound mercury. The method used was developed in order to determine which mercury solid fraction was biogeochemically relevant (Bloom et al. 2003). The five extraction solutions used are shown in Table 6. Each extract fraction was analyzed for total mercury on a Perkin Elmer Elan DRC-e ICP-MS according to EPA Methods 1631, Revision E. Samples which were below 1 µg/L on the ICP were reanalyzed using the Brooks Rand Merx-T CVAFS, also according to EPA Method 1631, Revision E.

Table 6 - Selective Sequential Extraction Solutions (Bloom et al. 2003)

Fraction	Extraction Solution	Qualitative Description
F1	Deionized water	Water soluble
F2	0.01 M HCl + 0.1 M CH_3COOH	Human stomach acid soluble
F3	1 M KOH	Organo-chelated
F4	12 M HNO_3	Elemental mercury
F5	Aqua regia	Mercuric sulfide

The first set of experiments were run using bank soil in bulk to determine how the mercury porewater concentrations compared to field conditions using DGT. Approximately 2kg of homogenized, saturated bank soil was loaded into a PVC container. The bank soil was tested under two general conditions, reduced and oxidized. For the reduced condition, the bank soil was allowed to sit undisturbed in the container in an anoxic glovebox for 3 weeks prior to sampling. This first set of results is referred to as 'Reduced 1.' 15 piston DGT samplers were deployed in the bank soil and sampled in triplicate at 0, 24, 48, 72, and 96 hours. The DGT samplers were processed and analyzed as described in section 3.2. Solid samples were taken and porewater was collected using centrifugation for comparison. The collected porewater was sampled both unfiltered and filtered. The filtered samples were filtered using a 0.45 μm polyethersulfone filter. The samples were diluted in 1% bromine monochloride and analyzed as described in section 3.2. After the reduced sampling was completed, the bank soil was mixed vigorously under oxic conditions for several minutes in order to oxidize the sample. The data gathered after mixing is referred to as 'Oxidized' in the results section. 15 piston DGT samplers were then deployed in the bank soil and sampled in triplicate at 0, 24, 48, 72, and 96 hours. A second sampling of the oxidized bank soil was conducted using agarose based resin DGT samplers. The bank soil was again mixed vigorously prior to DGT deployment and removed in triplicate at 0, 24, 48, 72, and 96 hours. Solid samples were again taken and porewater was collected via centrifugation. The porewater was measured both unfiltered and filtered. The bank soil was then allowed to sit for an additional 3 weeks in an anoxic atmosphere to reduce again. This final set of data is referred to as 'Reduced 2' in the results section. A final set of 15 DGT samplers were deployed after 3 weeks and sampled in triplicate at 0, 24, 48, and 72 hours. Solid

samples were collected and porewater was collected via centrifugation. The porewater was analyzed both unfiltered and filtered.

Figure 56 – DGT Batch Experiment Set-up

The next laboratory experiments were designed to examine mercury fate in the bank soil under field conditions. The previous experiments took bulk measures of porewater mercury but did not mimic field conditions such as sediment density and redox profiles. Mesocosms experiments allow us to monitor the mercury behavior under conditions which are more representative of field conditions, but allow increased monitoring relative to field monitoring. These experiments allow us to validate the behavior seen in the batch studies and verify that the conditions we observed in Chapter 4 under field conditions are consistent with the laboratory tests. Homogenized bank soil was placed into 5cm x 15cm acrylic mesocosms (Wang et al.

1991). The mesocosms contained 8cm depth of bank soil and a 5cm water column. The water column consisted of synthetic freshwater made up 0.4 mM calcium chloride, 0.5 mM sodium chloride, 0.5 mM potassium chloride, and 0.2 mM sodium bicarbonate. The water column was circulated over the bank soil with a residence time of approximately 5 hours during the 4 week equilibration period. The equilibration period was designed to allow redox gradients to stabilize in the mesocosm that mimic field conditions. The redox conditions were measured using cyclic voltammetry as described in section 4.2. When a steady-state redox condition had been established, DGT samplers were deployed into the mesocosms to measure a baseline porewater mercury profile. The DGT samplers were deployed and analyzed as described in section 3.2. After DGT measurements were completed, the mesocosm was drained through a sample port as shown in Figure 57. The collected porewater was measured for unfiltered and filtered total mercury. The filtered samples were filtered using a 0.45µm polyethersulfone filter. Samples were diluted in 1% bromine monochloride and analyzed on a Brooks Rand Merx CVAFS Total Mercury Analyzer. The approximate porewater volume of the mesocosm was 240mL. Collected porewater was limited to the first 100mL drained in order to minimize dilution with overlying water.

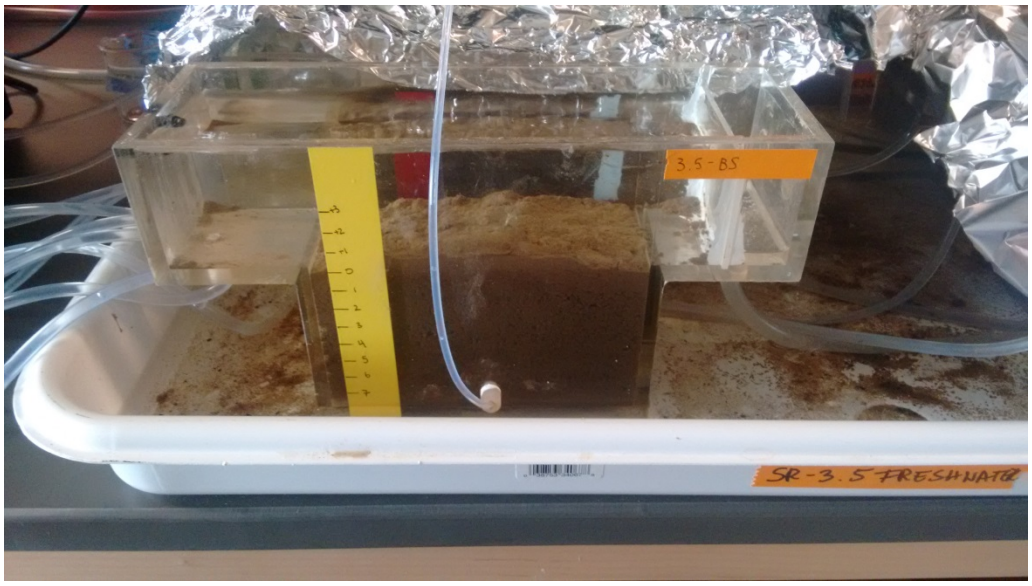

Figure 57 – South River RRM3.5 Bank Sediment Mesocosm

After porewater collection was completed, oxic water was pumped through the bank soil in order to simulate what occurs prior to bank drainage cycles in the field. The water was pumped at a seepage rate of 0.05 cm/min, which was consistent with velocities modeled during bank drainage, for a period of 15 days. After 15 days, pumping was stopped and the oxic water was allowed to equilibrate with the bank soil for 3 days. DGT samplers were deployed again in the mesocosm to measure mercury porewater concentrations over depth. The dissolved oxygen profile over depth was measured using cyclic voltammetry at the same time. Immediately following, the porewater was again drained and collected. The porewater was measured both unfiltered and filtered for comparison.

The final set of experiments run was designed to better quantify porewater chemistry to identify possible causes of the mercury release. Column experiments were run using the bank soil to study the effect of redox change on porewater chemistry. The release of mercury from the bank sediments is likely due to the mobilization of mercury by the flow of oxic water through the banks. The goal of these column studies is to see how mercury is released under specific conditions and how porewater chemistry can explain this release.

The column was filled with homogenized bank soil and was circulated with de-aerated water until a stable mercury concentration was measured in the outlet. The feedwater consisted of synthetic freshwater and the flow-rate was chosen to replicate flow conditions modeled in the bank during bank drainage periods as shown in the model section later in this chapter. After a steady mercury concentration was achieved, the feed water was changed to aerated freshwater. The outlet water was then tested over time for a variety of geochemical parameters as shown in Figure 58 . Unfiltered samples were collected from the effluent and analyzed for pH and sulfide. The samples were then filtered through a 0.45µm polyethersulfone filter. The sample was then split for ICP, IC, DOC, and CVAFS analyses. ICP samples were preserved with 2% trace-metal grade nitric acid and stored at 4^{o}C until analysis. ICP samples were run on a Perkin Elmer Elan DRC-e ICP-MS according to EPA Methods 1631, Revision E and 200.7. IC samples were stored at 4^{o}C until analysis. IC samples were analyzed on a Dionex IC system with IS25 Isocratic pump, a CD20 conductivity detector, and AS40 autosampler. The samples were run according to EPA Method 300, Revision 2.1. DOC samples were preserved with 0.2% trace-metal grade hydrochloric acid and stored at 4^{o}C until analysis. Analysis was performed on a Shimadzu TOC-Vcsh with ASI-V autosampler. Analysis was done according to EPA Method 415.3, Revision 1.1. CVAFS samples were immediately diluted in 1% bromine monochloride

and stored at 4^{o}C until analysis. These samples were run according to EPA Method 1631, Revision E.

Table 7– Sampling Parameters for Column Studies

Parameter Measured
Mercury
Sulfide/Sulfate
Iron (II)/Iron (III)
Manganese (II)/Manganese(IV)
Dissolved Organic Carbon
pH

It has been shown that pH and organic matter may influence metal release for oxidized sediments and so it will be seen if those are controlling factors. This will help to determine if the oxic feedwater caused elevated mercury in the porewater phase. Geochemical parameters, such as Iron(II)/Iron(III), will help measure the changing redox conditions in the column. If mercury release correlates with changes in these parameters, it can suggest possible processes contributing to the release. The feedwater was changed back to de-aerated water after 4 days and the outlet was sampled for an additional 5 days.

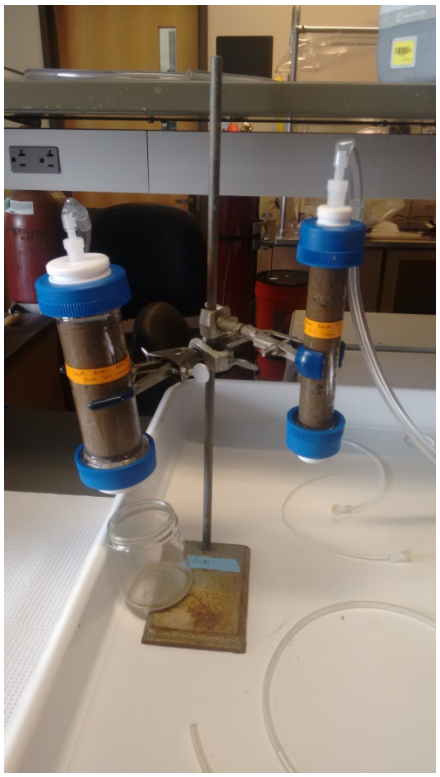

Figure 58 – South River RRM3.5 Bank Sediment Column Experiment Set-up

5.3 Results and Discussion

Preliminary characterization of the bank soil used in the experiments was conducted on a homogenized sample of the material collected from RRM 3.5 in October 2014. The sample was analyzed for total mercury and total organic carbon, and by selective sequential extraction. The bulk total mercury was measured as 151±25 mg/kg dry weight. This is consistent with the conceptual model that the bank at RRM 3.5 is a source area for mercury into the river. The total organic carbon was determined to be 2.05±0.19%. This organic concentration suggests that the

bank sediment is not organic-rich, which makes sense since it is flushed periodically and labile carbon is continually removed from the system.

The results for the selective sequential extraction are shown in Figure 59 as a percentage of total mercury extracted. Even though this method is not quantitative, it is useful for understanding the basic break down of how mercury is partitioned in the solid phase upon changes in redox conditions that occur during bank drainage events. The F1 and F2 fractions account for 0.5% and 1.9% of the mercury in the solid phase, respectively, and could be easily released during bank flushing. The F1 and F2 fractions are comprised of solid complexes which are easily dissociated such as mercury (II) chlorides and mercury sulfates on the solid surface and mercury contained in porewater. The complexes that are mobilized in the F1 fraction are characterized by high water solubility and the complexes mobilized in the F2 fraction are associated with complexes that are easily disassociated in an acidic solution, as this the pH of this extract is near 1. The F3 fraction accounts for 5.5% of the total mercury, respectively, and should also be easily released with minimal changes, such as oxidation of the soils. The F3 fraction contains organo-chelated mercury including humic-associated and methylmercury. These organic complexes are solubilized by the high pH of the F3 extract solution. The F4 fraction in this sample accounts for 7% of the total mercury. This fraction is predominantly made up of elemental mercury as the F4 extract solution oxidizes Hg^0 to Hg^{2+} which increases their solubility. The F5 fraction accounts for the majority of total mercury in this sample at 79.6%. The majority of this fraction is made up of mercury sulfide solids which are oxidized by the aqua regia extract solution.

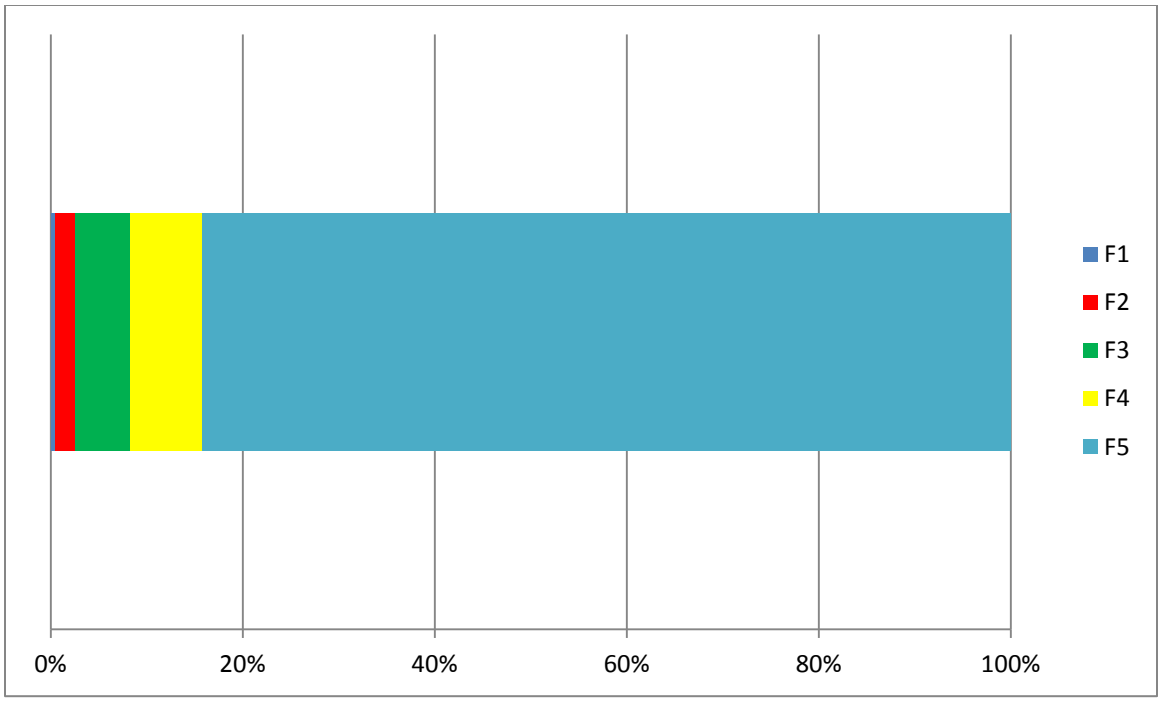

Figure 59 – South River RRM3.5 Bank Sediment Sequential Solid Extraction Fractions as a Percentage of Total Mercury Extracted

If it is assumed that the F1 and F2 fractions can readily partition into porewater under all conditions and that the F3 fraction can partition into porewater only after sediment oxidation, the ratio fraction of F3 suggests that oxidation of the sediment would increase the porewater mercury by a factor of approximately 3 ([5.5+1.9+0.5]/[1.9+0.5]) . If the F1 fraction can partition under baseline conditions and the F2 fraction is released, the increase would be approximately 5 ([1.9+0.5]/0.5). If only the F1 fraction can partition into the porewater and that oxidation of the sediment releases both the F2 and F3 fractions, the increase in porewater would be approximately 15 ([5.5+1.9+0.5]/0.5). These ratios bound the increased porewater concentrations observed during bank flooding and drainage (of the previously unsaturated oxidized soil) relative to the concentrations in saturated more reduced soils, with that fraction ranging from 4.5 to 16. The F5 fraction accounts for the largest portion at 79.6%. If any

substantial portion of this fraction is released as a result of soil oxidation, this could also lead to very large releases of mercury. This data may not definitively test the release process but can be used to support or dispute observations in subsequent experiments.

The sequential solid extraction results can also be used to determine the potential for DGT samplers to deplete the available mercury in sediment porewater. As discussed in Chapter 3, DGT samplers can deplete sediment porewater of the analyte being measured if the analyte is diffusing into the sampler faster than it is being resupplied by the surrounding porewater or solids. If depletion occurs, the diffusive uptake into the DGT samplers will be slower as it is linearly related to the porewater concentration. To determine the potential for depletion of mercury in porewater by DGT samplers, the mercury mass accumulated in the DGT samplers is compared to the mercury mass in F1 fraction of the solids immediately surrounding the sampler. These comparisons are done assuming a sediment system with a solid loading of 151 mg/kg, a porewater concentration of 10,000 ng/L, and an F1 fraction of 0.5% of the total solid loading. As a conservative assumption, the solids within 1 cm of the DGT sampler are available to replenish mercury porewater. For a two day exposure, the DGT samplers will accumulate 98 ng/cm^2. The F1 fraction of the solids near that sampler contains 167 ng/cm^2. Even if only the most soluble solid-associated mercury is available for replenishing the porewater, a conservative assumption, the DGT samplers will not deplete the surrounding porewater.

5.3.1 Batch Sediment DGT Studies

The first laboratory experiment run with the bank soil was conducted in a batch method in order to determine whether the mercury porewater concentrations observed in the field could

be replicated in the lab. The DGTs were sampled over a range of deployment times to get the most representative measure of porewater concentrations. The results from the first deployment of DGT in the Reduced 1 bank soil are shown in Figure 60. The mass uptake for the DGT was very linear showing that the porewater in the soil was relatively homogenous within the batch set-up. Taking the slope of the mass uptake over a series of timepoints also removes any possible interference from mercury contamination in the DGT or non-linear uptake from equilibration or saturation. From the measured mass uptake rate of 15.976 nanograms per hour, the equivalent porewater concentration of 24,800 ng/L can be calculated from the DGT equation in section 3.2. The DGT porewater concentrations for the Oxidized and Reduced 2 batches of bank soil were calculated in the same way.

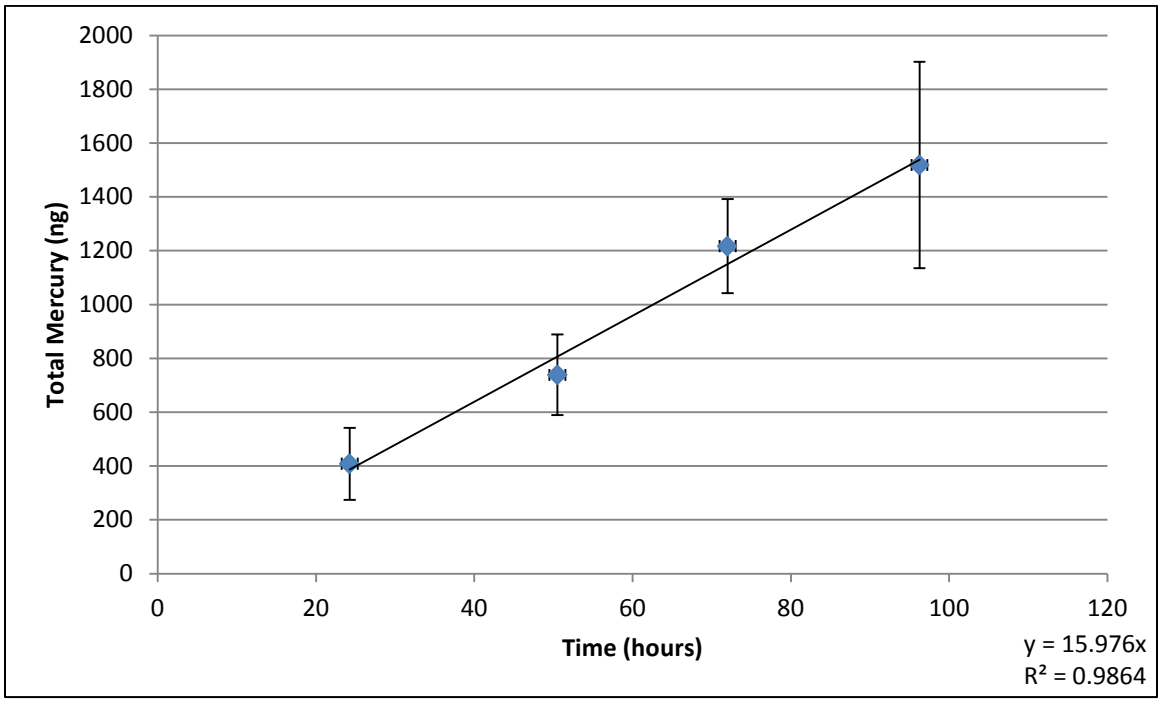

Figure 60 –DGT Mass Uptake of Reduced 1 South River RRM3.5 Bank Sediment

Table 8 – Comparison of Total Mercury Porewater Measurements with DGT, Centrifugation, and Centrifugation with Filtration

	Reduced 1	Oxidized	Reduced 2
DGT (ng/L)	24,800±2000	53,000±4700	15,000±2000
Centrifuged – Filtered	2000±530	9000±4,000	7,000±700
Centrifuged - Unfiltered	307,000±152,000	2,645,000±364,000	405,000±208,000

The DGT results from these batch experiments are generally consistent with data observed in the field. Although this set-up was not designed to replicate field conditions, the range of mercury porewater concentrations are similar to those seen under field conditions, particular the oxidized sediment porewater concentration. The mercury concentration under reduced concentrations, however, are at least 3 times larger than typically observed under somewhat reduced conditions during baseline flow conditions in the field. This may suggest that the reduced conditions don't represent as reduced a condition as was observed in the field. Under the baseline flow conditions in the field, where the bank system is mildly reduced, the average bank porewater concentrations ranged from ~3,000-10,000 ng/L with a peak concentration measured of approximately 50,000 ng/L. It is also possible that this is simply a reflection of bank heterogeneity and differences between the samples and the sediment actually sampled in the field. The Reduced 1 batch was allowed to equilibrate in an ambient atmosphere while the Reduced 2 batch equilibrated in an anoxic atmosphere. It can be assumed that Reduced 1 would have less reduction as it was being slowly resupplied with oxygen diffused in from the atmosphere. This may explain why the porewater concentrations in Reduced 1 were higher than Reduced 2. The Oxidized batch porewater concentrations matches values measured

in field sampling. In the two bank drainage periods sampled in the field, the average porewater concentrations in the bank were approximately 42,000 and 64,000 ng/L respectively and lab value of 53,000 ng/L fits between those averages.

5.3.2 Mesocosm Studies

The mesocosm experiments were designed to provide a better understanding of mercury behavior under more site representative conditions. The batch experiments only measured one value of porewater mercury under each condition and did not measure any accompanying porewater chemistry. In the mesocosm experiments, redox gradients were expected to form over depth and then measured using cyclic voltammetry. Pumping oxic water through the mesocosms replicated the river flood conditions better than the bulk mixing in the batch experiments. The combination of DGT total mercury and cyclic voltammetry dissolved oxygen porewater measurements were compared to the field observations.

The baseline DGT total mercury porewater measurements are shown in red in Figure 61. The mercury porewater concentrations increased over the first 3cm of depth and ranged from approximately 9,000 ng/L to 30,000 ng/L. The concentrations leveled off after 3cm and remained between 30,000-36,000 over the remaining depth. This concentration range at depth is comparable to both the values measured in the field under baseline flow conditions and in the batch experiments. The cyclic voltammetry dissolved oxygen baseline measurements are shown in red in Figure 62. Dissolved oxygen was detected in the top 2cm and not detected starting at 2.5cm depth. The mesocosm had deeper oxygen penetration than observed in field conditions which typically showed oxygen depletion within 1cm. The mesocosms had oxic water flowing

over the sediment during the equilibration period which explains both the lower mercury concentrations and higher dissolved oxygen concentrations measured in the upper portion of the mesocosm. This may also reflect that the overflowing water was flushing through the surface few cm of the sediment. The upper 2cm of the mesocosm are not representative and so we will focus on the lower portions of the profile as an indication of porewater mercury in somewhat reduced zones in saturated soils.

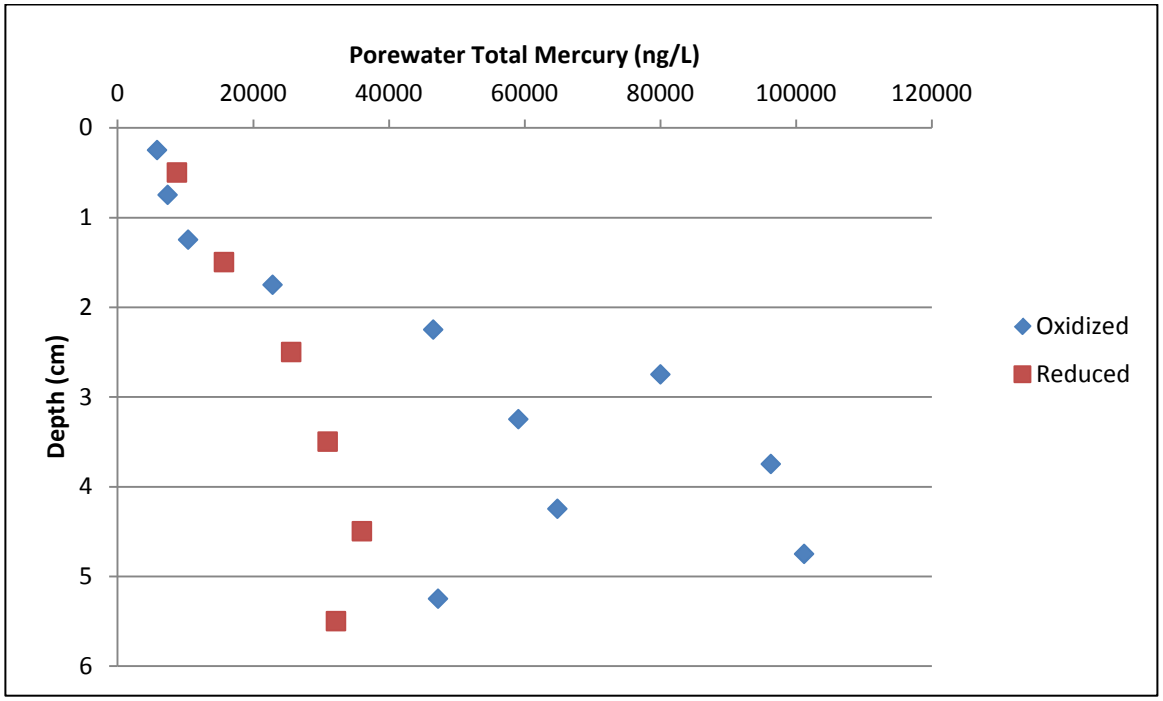

Figure 61 – South River RRM3.5 Bank Mesocosm DGT Total Mercury Porewater Depth Profiles under Oxidized and Reduced Conditions

After the baseline condition was measured, the mesocosms were pumped with oxic water from top to bottom. This was meant to simulate a flood event in which oxic water from the channel would move into parts of the bank system that were previously mildly reduced. The DGT porewater mercury depth profile is shown in Figure 61 in blue. The total mercury concentrations did not change in the upper 2cm of the mesocosm. This was expected as that area was already oxic and probably being controlled by diffusion and mixing with overlying water. The reduced cyclic voltammetry sampling found dissolved oxygen in the upper 2cm so the flushing likely did not significantly change the redox conditions in that area. At all depths greater than 2cm, the porewater mercury concentrations increased, at some depths by as much as triple the baseline concentrations. The dissolved oxygen depth profile is shown in blue in Figure 62. The dissolved oxygen was detected all the way to 5cm depth, the entire depth of the mesocosm that was measured. This also matches what was observed in field measurements during the May 2014 bank drainage event, although the dissolved oxygen concentrations at depth in the field were higher than measured in the lab. This is likely due to allowing the mesocosm to equilibrate after pumping and deploying DGT samplers before sampling dissolved oxygen. The dissolved oxygen was depleted during this time. However, in the field, it was being resupplied as the bank was still draining during measurements. The dissolved oxygen concentrations during the DGT deployment would have been at least as high as measured with cyclic voltammetry and likely slightly higher, perhaps closer to matching field conditions.

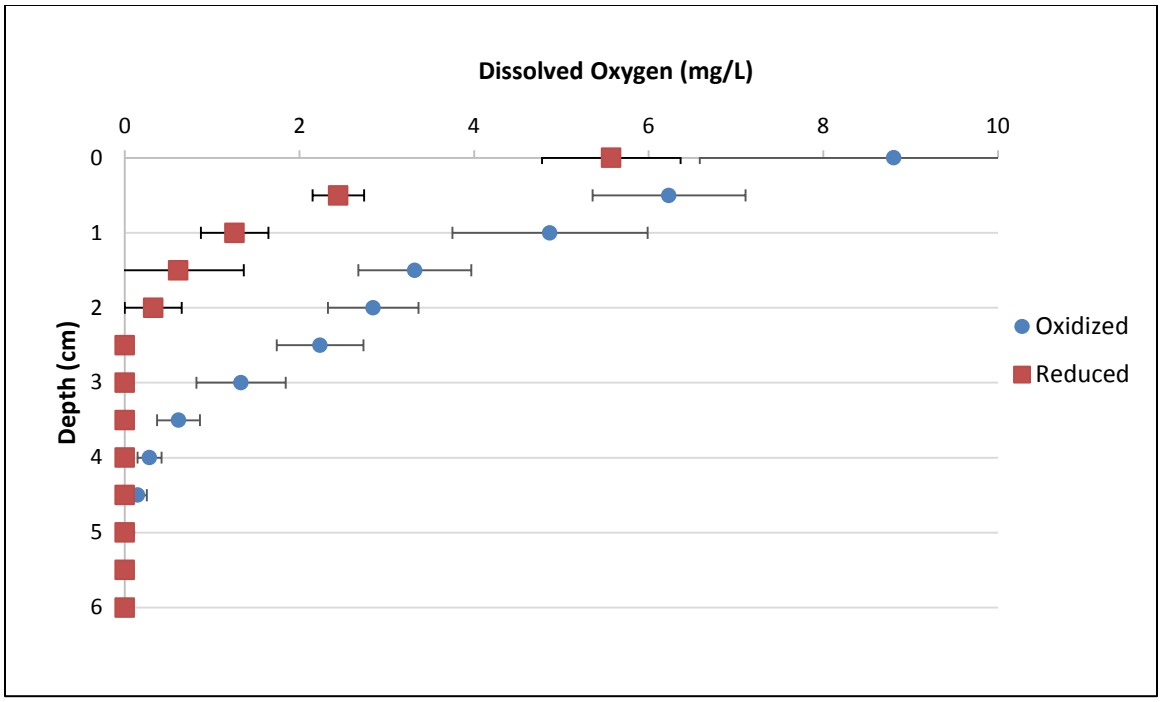

Figure 62 – South River RRM3.5 Bank Mesocosm Dissolved Oxygen Depth Profile under Oxidized and Reduced Conditions

This mesocosm experiment shows that the DGT and cyclic voltammetry measurements made in the field can be duplicated in the laboratory. The concentrations measured in the laboratory were less scattered as the mesocosm system was controlled while the field bank environment has heterogeneity in biological and physical processes as well as bulk sediment mercury loadings. The DGT concentrations give a better measure of the amount of available mercury that is moving through the bank face during drainage events than the unfiltered or filtered drained water samples. It is difficult to tell where the collected water came from within the mesocosm and the difference between unfiltered and filtered is great and operationally controlled. The DGT sampler is measuring the porewater in-situ so there is less uncertainty as to where the sampled porewater is located and the measured value is controlled by the chemical

activity of the dissolved mercury species rather than the collection technique. The cyclic voltammetry measurements were also similar to what was observed in the field. When the mesocosm was allowed to achieve reducing conditions, mercury porewater stabilized over the 2-6cm depth and dissolved oxygen was not found at depth. When the system was flushed with oxic water, as happens during a flood event in the river, dissolved oxygen penetrates deeper in the sediment and mercury porewater concentrations increase. These experiments reinforce field measurements and show a correlation between dissolved oxygen and mercury porewater concentrations but they do not give a complete understanding of the chemistry that is controlling the mercury behavior. In order to better understand this chemistry, another set of experiments were run in which the porewater chemistry was better quantified to examine possible processes for mercury release.

5.3.3 Column Studies

The column experiments with South River bank sediment were designed to more accurately capture the effects of porewater chemistry parameters compared to the field or mesocosm experiments. Field measurements only included DGT samplers for all sampling events and cyclic voltammetry for most sampling events. The batch DGT experiments did not include any additional porewater measurements other than DGT samplers, as they were designed to test if the heightened porewater concentrations could be replicated in the laboratory simply by changing the redox conditions. The mesocosm experiments were designed to replicate field conditions to test if the same mercury behavior was observed in the laboratory as was seen in the field, but by replicating field conditions, additional porewater chemistry measures were not able

to be collected. The sampling parameters chosen for the column studies included those that have been shown to be important for metals release and speciation. Mobilization of metals has been shown to be strongly influenced by pH and dissolved organic carbon. Total Manganese and Iron were sampled in order to test if other metals were released in the same manner as mercury. These metals are also redox sensitive and their behavior is indicative of the redox conditions within the column. Reduced iron, Fe^{2+}, was sampled during the equilibrium period and until it was under the detection limit for several days during the experiment. Anion samples were measured but were not above detection limits for the majority of the experiment and were not included. These include sulfide, sulfate, nitrate, nitrite, and phosphate. Chloride was the only anion that had sample concentrations above the detection limit for the entire experiment. Samples were analyzed for sulfide but no samples were above the detection limit. The parameters which were not useful (total iron, reduced iron, and chloride) are shown in the appendix.

The column was allowed to equilibrate for two weeks and was sampled periodically during this period. The columns were considered to be at steady-state when the sampled parameters stabilized for several days, most importantly total mercury. The data for this equilibrium period can be found in the appendix. A sample was collected just prior to switching the column influent to oxygenated synthetic freshwater and the values from this sample were used as the time zero values for the experiment. Samples collected with anoxic influent are shown in all graphs in red. Samples collected while the oxygenated influent was employed are shown in blue in all graphs.

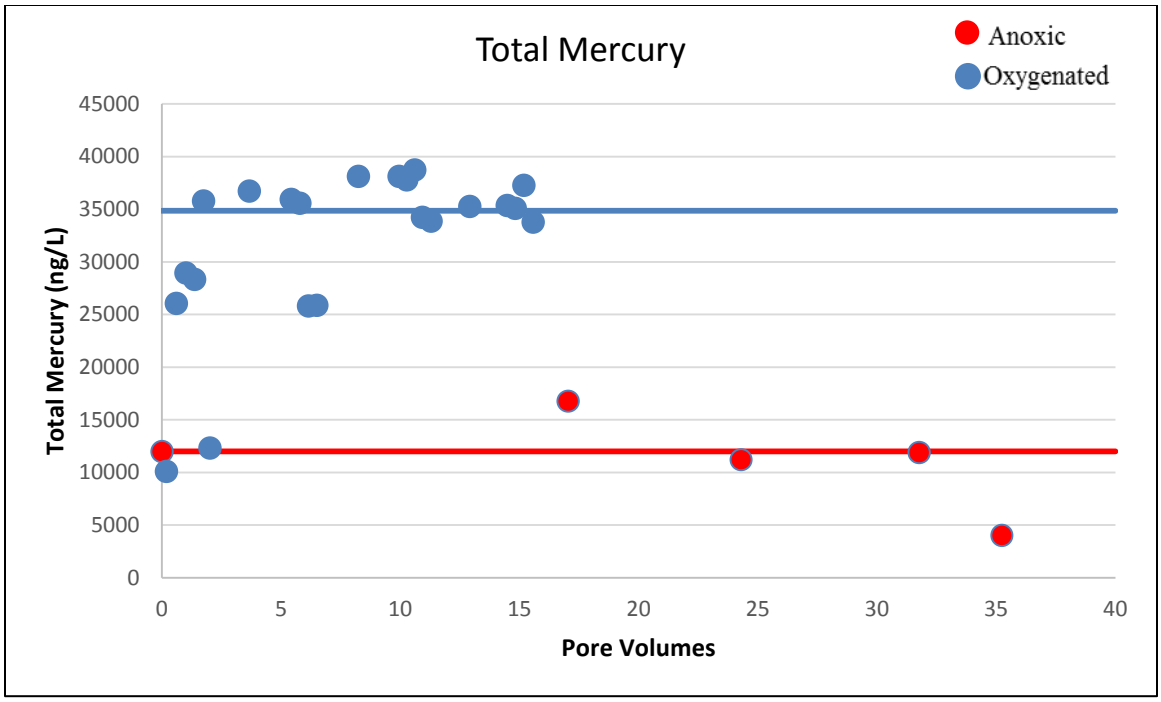

Figure 63 – South River RRM3.5 Bank Column Effluent Filtered Total Mercury

The total mercury column effluent results are the most important as they represent the mercury that would be mobilized by bank oxidation. These results are shown in Figure 63. During the equilibration period, total mercury concentrations stabilized at approximately 10,000 ng/L. This concentration is comparable to concentrations measured in the field with DGT samplers during baseline flow conditions. This is also close to concentrations measured in other laboratory experiments under reduced conditions. The batch DGT experiments yielded mercury concentrations of approximately 14,000 ng/L when the sediment was allowed to equilibrate in an anoxic atmosphere, as the column was in this experiment. However, the ratio of total mercury concentrations in reduced and oxidized conditions is consistent between all these measurements. The oxidation of the bank sediment increased the total mercury porewater concentrations by 2-4 times in all these samples. The total mercury

concentrations were lower when the anoxic inlet water was restarted in the column. The mercury concentration returned to approximately 10,000 ng/L and stayed in this range for the remainder of the anoxic period. This change occurred quickly as the first sample after the inlet change was taken less than 2 pore volumes later.

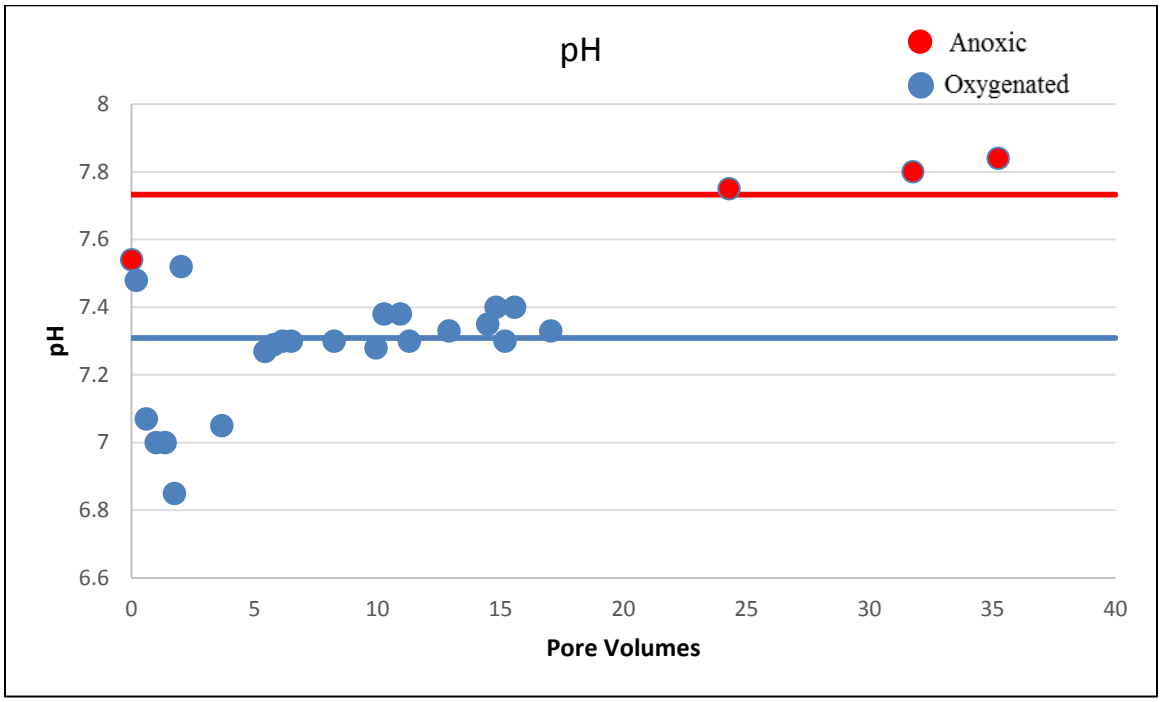

Figure 64 – South River RRM3.5 Column Effluent pH

The pH of the porewater can have a strong effect on mercury speciation and chemistry and so it is important to measure pH and compare it with the mercury concentrations measured. Changes in pH may be the result of oxidation of other species rather than the cause of that oxidation. During the equilibration period, the pH of the column effluent stabilized at 7.5 and this value was used as the initial condition for the column. After changing the column influent

back to anoxic freshwater, the pH climbed quickly to 7.8 and stabilized at that level throughout the experiment.

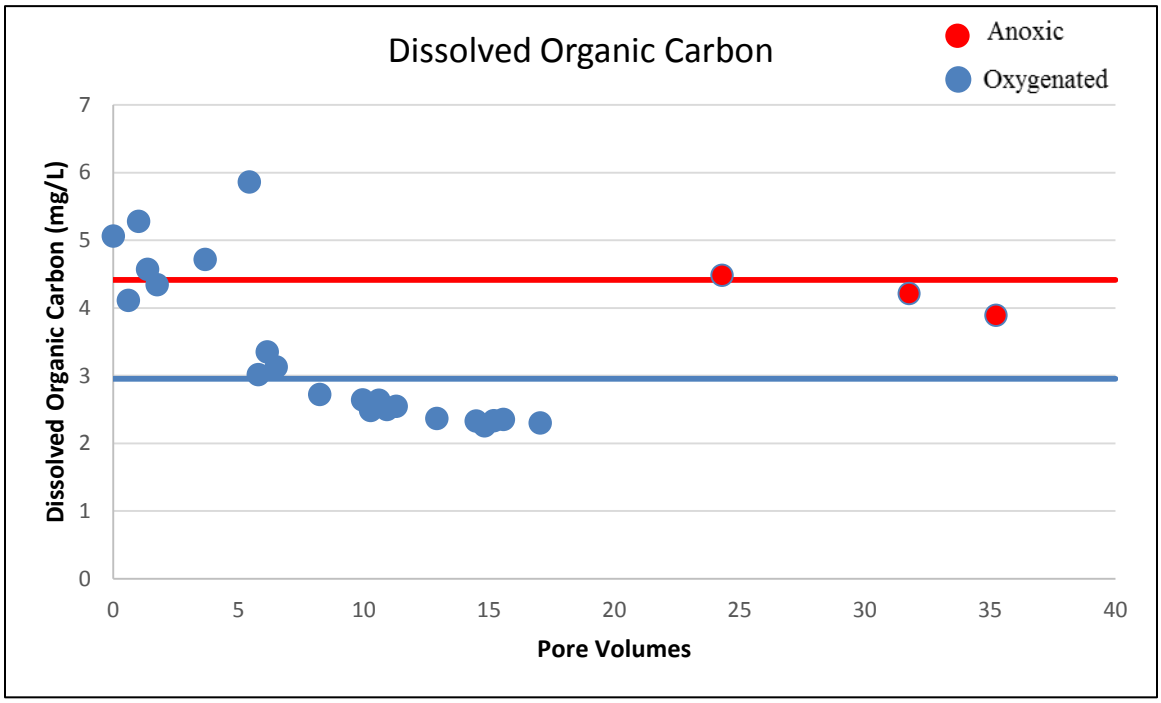

Figure 65 – South River RRM3.5 Bank Column Effluent Dissolved Organic Carbon

Dissolved organic carbon has also been shown to be important to mercury speciation and mobility. The dissolved organic carbon was measured at 5.07 mg/L after the equilibration period. This value did not change as dramatically as total mercury or pH after the change to oxygenated inlet water. The dissolved organic carbon concentration varied between 4 and 6 mg/L over the first 5 pore volumes before slowly decreasing to almost 2 mg/L. The dissolved organic carbon concentrations increased after changing back to anoxic inlet water and reached levels similar to those seen during the equilibration period.

Manganese was measured in the column outlet over the entire sampling period and the results are shown in Figure 66. The total manganese concentration was 722 µg/L at the end of the equilibration period. The manganese increased over the course of the equilibration period before stabilizing. After changing the inlet to oxygenated water, the manganese concentration slowly decreased over time, reaching as low as 493 µg/L. The total manganese concentration never stabilized during the experiment and may have continued decreasing if the oxygenated water was run for longer. The concentrations increased when the anoxic water was reintroduced into the column, reaching a similar concentration as was measured prior to oxidation. The total manganese concentrations decreased when the column was oxidized, the opposite shift of total mercury. This is consistent with previous research which shows that manganese is mobilized under reduced conditions, in contrast to mercury (Huerta-Diaz, Tessier, and Carignan 1998). Manganese is more mobile in its reduced form and so the oxidation of the system lowers the dissolved concentration (Lynn and Bonatti 1965).

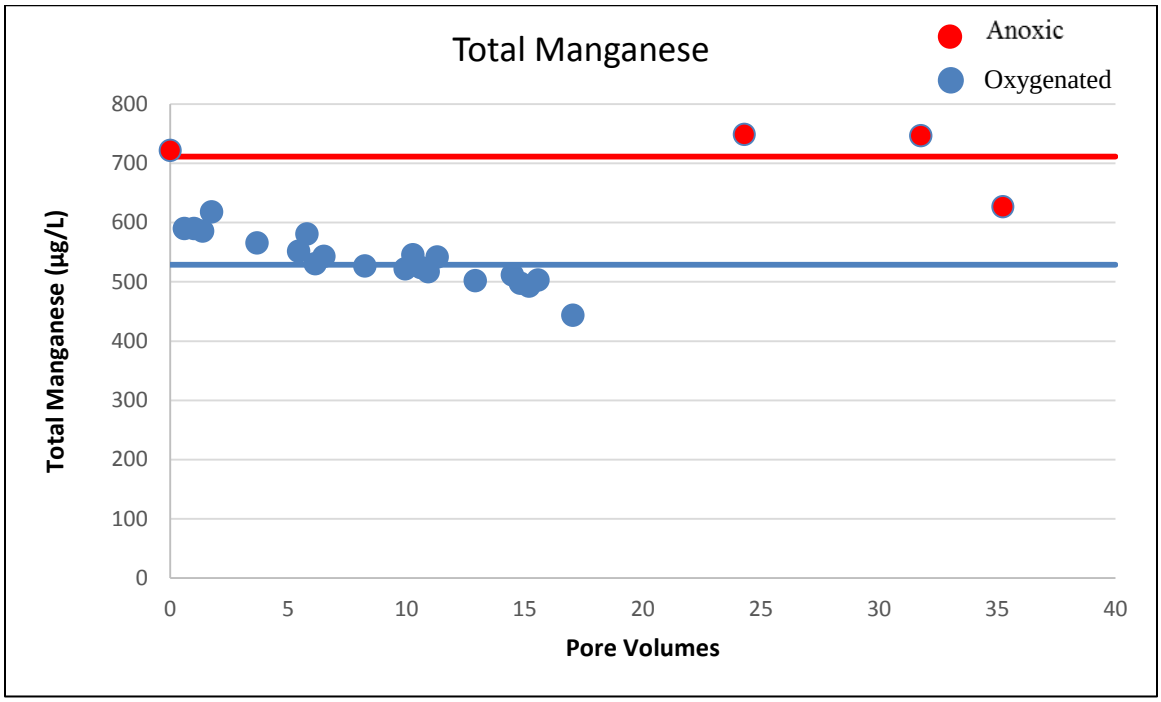

Figure 66 – South River RRM3.5 Bank Column Total Manganese

These experiments show a more complete picture of the porewater chemistry in the South River banks during a bank drainage event. The additional chemical measurements were not possible in field sampling or prior experiments so we could not determine causes or processes of the mercury release. Through these experiments, some potential processes explaining the mercury release can be excluded. Mercury release is commonly seen in systems with oxidation of sulfides, both dissolved and solids. Mercury can be complexed with these sulfides and then contained in the matrix of the solids or can be complexed on the surface of these solids. When the sulfides are oxidized, mercury is released and mobilized. However, in this system, sulfides are not generated in large concentrations. In field measurements, sulfides are rarely detected in the bank porewater. In the column effluent, sulfide was not measured above the 0.5 µmol/L

detection limit at any time. With no detectable sulfide, it is not possible for sulfide solids to be formed extensively. In addition, sulfide oxidation would likely end as the pool of available sulfides is exhausted. Eventually, the dissolved mercury concentrations would decrease after the column is flushed long enough. In this experiment, the mercury concentration did not spike up past the stable concentration reached at the end of the oxidized phase of the experiment. A similar argument can be made about the oxidation of reduced iron and its impact on mercury release. The dissolved reduced iron fell below the detection limit within 4 pore volumes of oxygenated water flowing through the column. If oxidation of iron was a significant contributor to mercury release, the mercury concentrations should have decreased after all the reduced iron was oxidized. However, the mercury concentration stayed elevated until the feedwater was changed back to anoxic.

Dissolved organic carbon has also been shown to impact solid-partitioning of mercury in a variety of systems. As dissolved organic carbon increases, the dissolved mercury concentrations increase as more mercury is complexed by the DOC. However, in this experiment, the dissolved organic carbon did not trend positively, or correlate well with, the dissolved mercury, as shown in Figure 67. Dissolved organic concentrations ranged from 2.5 to 6 mg/L under oxic conditions. The dissolved organic carbon concentrations under reducing conditions were between 4 and 5 mg/L, which fell well within the range of the oxic samples. The change in dissolved organic carbon may have changed mercury speciation but this change did not control the mobile fraction of total mercury. The change in dissolved organic carbon measured from oxidation is small and this change may not have been enough to significantly change the mercury-solid interaction.

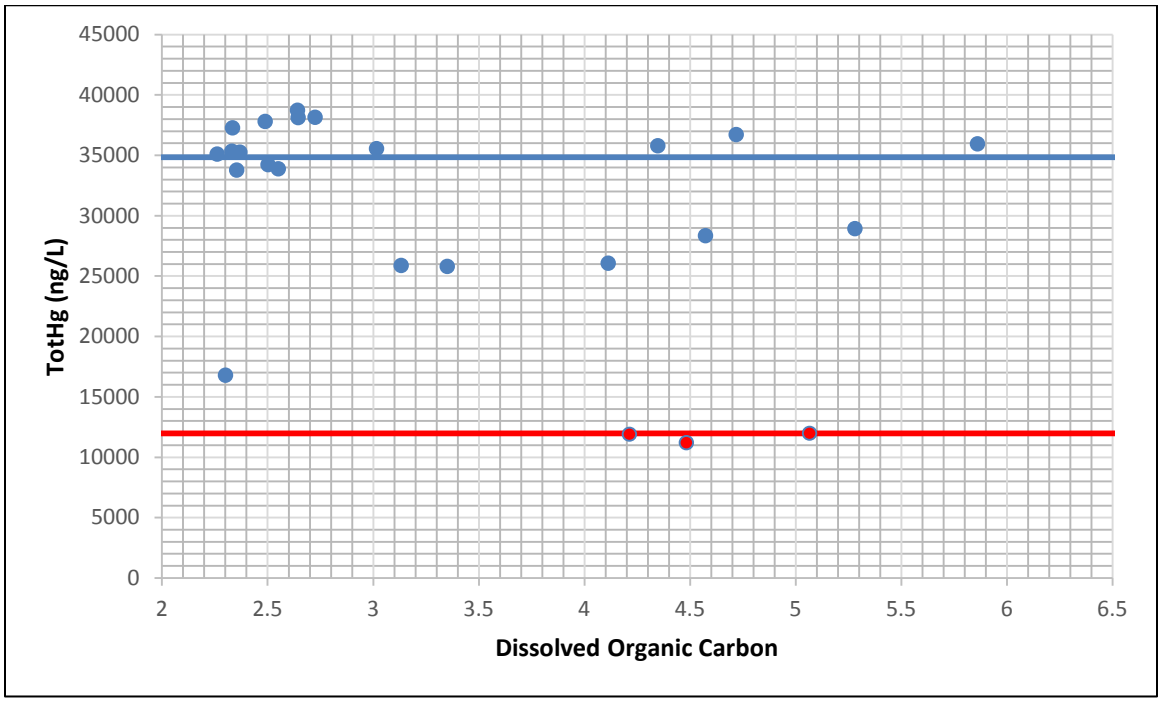

Figure 67 – South River RRM3.5 Bank Column Total Filtered Mercury versus Dissolved Organic Carbon

Based on this experimental work, the most influential factor for mercury release and mobility is pH. The results comparing total mercury and pH are shown in Figure 68. The pH of the oxic samples ranged from 6.85 to 7.52 while the anoxic samples from 7.54 to 7.84. There was no overlap between the pH values measured during the oxic and anoxic periods. The total mercury correlates more with pH, as shown in Figure 68, than it does with DOC. The high pH values measured during the reduced portion of the column test also contained the lowest mercury measured. A variety of processes can explain the drop in pH during oxidation. Oxidation of sulfides, organic compounds, and iron solids all have been shown to change pH in sediment systems (Calmano, Hong, and Forstner 1993). The pH change can also be caused by new

microbial activity that is spurred by the introduction of oxygen into the system. The pH is not the sole driver of dissolved total mercury, as there is a spread of total mercury concentrations at the most commonly measured pH value of approximately 7.4.

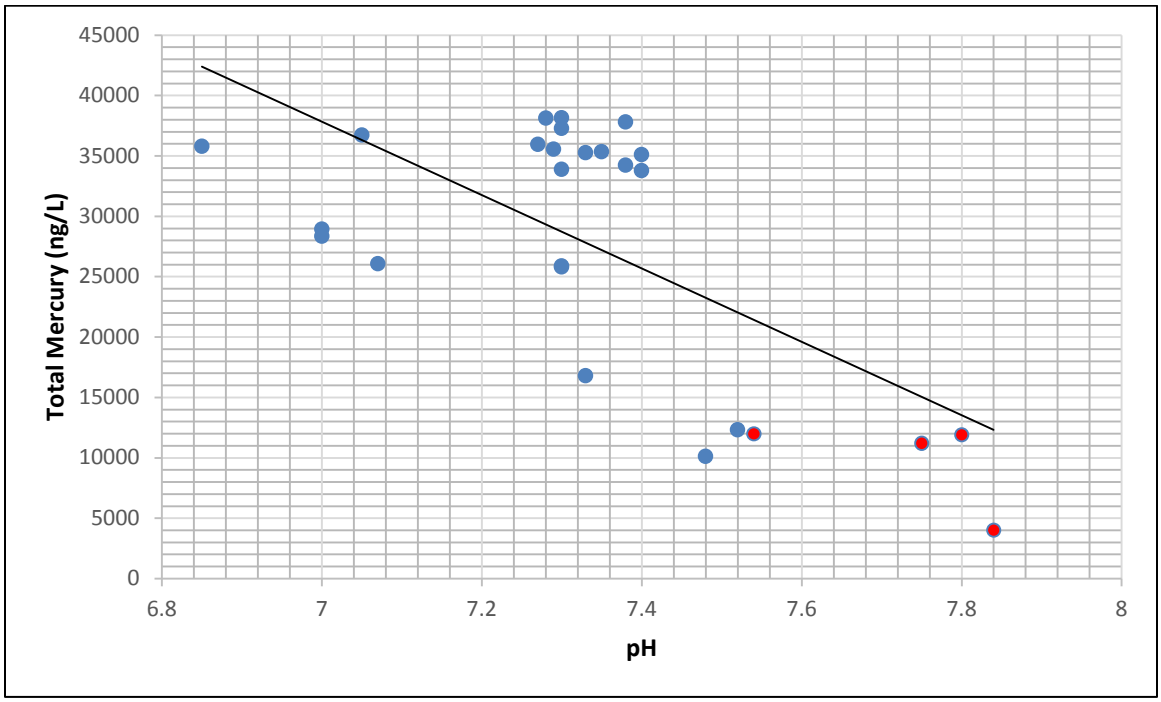

Figure 68 - South River RRM3.5 Bank Column Total Filtered Mercury versus pH

We can see the correlation between total mercury concentrations and pH, but this does not tell us the mechanism of mercury release. These experiments may not definitively show this mechanism but some can be hypothesized. The first way that higher pH may be mobilizing mercury is a change in the interaction between the dissolved and solid phase mercury. In this system, the majority of mercury is contained in the solid phase. A slight change in the partitioning coefficient between the solids and porewater will have a large impact on the absolute

porewater concentration. Mercury partitioning is greatly affected by both the porewater and solid phase chemistry (Schartup, Balcom, and Mason 2014). The solid phase chemistry changes the redox environment changes, such as oxidation or reduced iron solids or sulfide solids. These mineral phases have a high affinity for mercury and their presence will lower dissolved mercury concentrations (Benoit et al. 1999). If these solids are present, even in small quantities, their dissolution would increase dissolved mercury concentrations. However, the dissolution process may not sustain elevated mercury concentrations as seen in the column experiment. In this system, the pH values only ranged over approximately one pH unit. In other river systems, a pH increase from 7.8 to 8.8 lowered the K_d by over one order of magnitude (Kocman et al. 2011). The smaller pH changes measured in this system fit into a similar order of magnitude change in K_d. Changes in salinity and DOC also impacts the partitioning of mercury to solids, but consistent trends were not observed between those parameters and dissolved mercury concentrations in these experiments. Salinity has also been shown to impact solid-phase partitioning for mercury but to a lesser degree than pH (Turner, Millward, and Le Roux 2001). An increase in salinity increase Kd, but from 0 to 35 mg/L salinity, the increase in Kd is less than one order of magnitude. For the laboratory experiments, the feedwater salinity remained constant over the reduced and oxidized sampling. During a flood event in the field, the high flow could lower the salinity in the river bank, as the water flowing through the bank during baseline flow is groundwater. This shift may not be drastic as this is a freshwater system. A decrease is salinity would increase the mercury release even more than was observed in the laboratory experiments, as the salinity was not altered when the redox was changed. The changes in solid partitioning do not have a large impact on the absolute mass loading on the solid phase, so only a small change in K_d would be needed to increase the dissolved mercury

concentrations by the amounts seen in these experiments. Other work on metals-impacted sediments has shown that sustained metals release is caused by the sustained oxidation of the sediment. In sediments with lower solids mercury loadings, approximately 2 mg/kg, increased mercury mobility was observed after oxidation, but release was not sustained (Caille et al. 2003). In these experiments, the mercury release was sustained and the total mercury loadings were significantly higher at 151 mg/kg. This suggests that oxidation of solid-bound mercury is the source of elevated mercury in the porewater and this source is limited by the amount of mercury bound to the solids prior to oxidation.

Alternatively, pH may increase mercury mobility in the system through a shift in mercury speciation. The pH of solution is known to have a strong influence on the speciation and mobility of mercury, but research into this effect is typically examined over a wider range of pH values. Dissolved mercury concentrations can increase by orders of magnitude in systems in which the pH varies from several pH units. In this system, the pH only ranged over 1 pH unit (6.8-7.8). The smaller range of pH measured in this system is likely due to the buffering capacity of the sediment solids. Although sulfides were not detected in this system, they may have been present at very low concentrations. Even at low micromolar concentrations, sulfide can control the speciation of mercury (Benoit et al. 1999). These sulfides could be oxidized and not be detected in either direct sulfide measurement or sulfate measurements. The oxidation of trace sulfides would decrease pH and change mercury speciation.

5.4 Conclusions

The laboratory experiments in this chapter build upon the results of the South River field sampling. The DGT samplers used in field sampling were able to identify different mercury behavior occurring in the RRM3.5 banks during bank drainage. The laboratory testing confirmed these observations and then advanced the understanding of this behavior through a series of controlled experiments that ranged from batch tests to a mesocosm study to a column experiment.

The first experiments on the bulk system looked at the RRM3.5 bank sediment under generalized conditions to replicate and verify the field experiments. The concentrations measured in the laboratory were similar to those measured in the field which supports the DGT sampler technique. The increased mercury concentrations in the field were not solely due to heterogeneity in the sediment. The bulk system experiments showed that DGT sampler measurements changed as a result of oxidation.

The mesocosm experiment builds upon the batch system results and better replicates field conditions. The mesocosms develop redox gradients which were not quantified in the batch systems. The mesocosms are oxidized by pumping oxic water through the sediment not mixing with air, which better replicates what occurs in the banks. Not only are the conditions similar to those in the field, the sampling techniques used on the mesocosms are the same used in the field. The bulk system experiments helped to reinforce DGT sampler measurements found in the field, the mesocosm experiments did the same for both DGT samplers and cyclic voltammetry. The mesocosm experiment showed that both DGT sampler measurements and cyclic voltammetry measurements changed when the sediment from the bank oxidized. This experiment does not

show a definitive link between the redox and porewater mercury concentrations, but it strongly suggests that they are related.

The column experiment provides more information on what may be causing the elevated porewater mercury concentrations during the bank drainage events. By measuring more chemical parameters than was possible in the field, a more complete understanding of the porewater chemistry was achieved. The dissolved oxygen increase in the bank porewater not only changes the mercury chemistry in the porewater, but it alters redox conditions which affects a number of geochemical parameters including speciation, pH and total organic carbon concentrations in the porewater. The column experiment does not give a complete understanding of the porewater chemistry but the important parameters relating to mercury such as DOC, sulfate, and reduced iron were measured. None of these parameters were correlated with the dissolved mercury concentrations. No sulfide was detected at any time during the experiment, and even if it was present in trace amounts, it would have been oxidized quickly. The reduced iron was oxidized early in the experiment. The dissolved mercury concentration stayed elevated even after these reduced species were oxidized so it was not the loss of these species which mobilized the mercury. The only parameter which seemed to correlate with the dissolved mercury concentration was pH. The pH dropped when the dissolved oxygen was introduced into the system and rose when it was changed back to anoxic feedwater. A small change in pH can result in a large change in the dissolved mercury concentration. The most likely cause of this rise in dissolved mercury is the pH dependency of partitioning to the bank sediment. The change in pH could mobilize mercury through a variety of processes. The sequential solid extraction results show that only a small percentage of solid-bound mercury, 0.5%, is water soluble under neutral conditions. The F1 fraction has been shown to not fully mobilize all soluble complexes

such as mercury (II) chlorides and sulfates (Bloom 2003). The decrease in pH will more completely mobilize these complexes. The decrease in pH could also mobilize a small fraction of mercury-sulfide species, which account for the majority of solid-bound mercury at 79.6% of the total mercury. A mercury concentration change by a factor of 3 to 10, as seen in this work, would not significantly change the solids mercury loading as the majority of mercury is contained on the solids. If the solid loading is constant, a relatively small change in K_d, less than an order of magnitude, would change the porewater mercury concentrations significantly.

Chapter 6 - Conclusions and Recommendations

6.1 Summary

DGT samplers were successfully used to measure mercury porewater concentrations in both field and laboratory applications. The DGT method is well-established for other analytes in water but this work shows the success of a modified DGT method for mercury use in sediment porewater. Reliable use in the field required resolution of a variety of potential contamination sources including deaeration of DGTs in baths that might release contamination from the sampler bodies. Storage and transportation of DGT samplers also increased the potential for mercury contamination in the samplers and led to the increased use of field blanks as well as careful isolation of transported samplers. Any contamination can lead to an inability to detect low concentrations in sediment porewater, particularly because short time durations (2-4 days) are normally required to insure linear uptake in the samplers. Using the average residual mercury contamination in a sampler routinely achieved in this work, 0.40±0.18 ng, and considering a two day environmental exposure, the minimum detectable total mercury concentration was estimated to be 25 ng/L. This is adequate for the field program undertaken herein but additional efforts, including working to achieve longer deployment times, may be necessary at other sites.

Studies were also undertaken to assess mercury loss during storage of DGT samplers and from sampler resin extract solution. DGT samplers could be held at 4 °C for 14 days between retrieval in the field and processing without significant loss of mercury. DGT samplers stored for 28 days showed significant mercury loss. After processing the DGTs into a hydrochloric acid resin extract solution, minimal mercury loss (<2%) was observed after 1 month of storage at 4^{o}C. The loss increased to 15% after 7 months of storage and to almost 40% after 10 months. As a

result samplers should be stored at 4^{o}C and processed within 14 days of retrieval from the field and the extract analyzed within one month.

The deployment of DGT samplers in the field required the use of stronger, polycarbonate DGT sampler bodies than are commercially available and which can withstand insertion into rocky sediments. DGT pistons samplers need to be sealed into the sediment, this work used mercury-free Silly Putty®, to avoid surface water dilution of porewater on the face of the sampler. The DGT depth profiler samplers can be more easily inserted into a variety of media using insertion tools developed for this work. The insertion tools protect the delicate gel face of the sampler from being torn during the insertion process.

DGT samplers were compared with a variety of traditional sampling. DGT samplers were initially shown to provide an accurate measurement of mercury standards, prepared without suspended particulate matter, indicating their ability to measure freely available and unassociated mercury. DGT samplers were compared to Henry's Samplers for field porewater collection and analysis. The DGT samplers measured significantly higher mercury porewater concentrations than filtered samples from the Henry's Samplers. The Henry's Samplers were impacted by dilution with surface water.

The DGT samplers were also compared against porewater collection using laboratory centrifugation and filtration. South River sediment samples were centrifuged to collect porewater which was analyzed for mercury both unfiltered and filtered. DGT samplers were deployed in the same sediment. The unfiltered samples via centrifugation were much higher than the filtered samples, typically by two orders of magnitude, due to the introduction of suspended solids by the centrifugation process. These solids also scavenged mercury from

solution when filtered. The porewater concentrations measured using DGT samplers were between the unfiltered and filtered concentrations for all samples, suggesting that the disturbance of the sample by centrifugation led to misleading estimates of porewater concentrations.

DGTs were also compared to sediment porewater collected by displacement and analyzed both unfiltered and filtered. DGT samplers were deployed in both the filtered and unfiltered porewater. The direct measurement of mercury in the unfiltered displaced porewater was much higher than measured by DGT while the directly measured filtered displaced porewater was similar to that measured by DGT in both filtered and unfiltered porewater. This suggests that DGTs can measure available mercury in porewater with or without the presence of particulate matter while accurate estimates by direct measurement were only possible after filtration.

The final comparison was between DGT samplers and dialysis samplers deployed in the South River. The comparison was qualitative as only a few samplers were deployed, but the dialysis samplers and all DGT samplers measured very similar mercury concentrations. The DGT samplers were easier to insert and process, and could be deployed in far more places and with greater spatial resolution but are expected to provide similar measures as dialysis samplers.

The DGT samplers were deployed extensively in the South River to better characterize mercury porewater behavior and assess the potential for this sampling tool to identify sources of mercury flux into the river. Hundreds of DGT samplers were deployed over a dozen sampling events from 2011 to 2014. DGT samplers were deployed in different areas of the river including a known source area, RRM3.5, and a non-source area downstream, RRM11.8. The mercury porewater concentrations measured at both areas were consistent with the current understanding of mercury behavior in the river. Concentrations measured at RRM3.5 were higher than those

measured downstream, which is consistent with its status as a source area due to historical deposition of discharges from the facility. Within the RRM3.5 sampling area, the mercury concentrations measured close to the bank were higher than those measured in the channel sediments. The terrestrial soil and banks are thought to be a significant source of mercury into the river and these measurements are consistent with this. The mercury concentrations measured using DGT samplers were higher than measured with other sampling techniques (all filtered samples that led to the scavenging by particulate matter indicated previously). The field sampling also identified processes that may be a significant contributor of mercury to the river.

A field sampling event took place in May 2013 which occurred immediately after a flood event in the South River. The river stage rose and inundated the banks at RRM3.5. DGT samplers were deployed into the bank as the river stage was declining. The mercury concentrations measured in the bank were higher than measured in any previous sampling event, with the average concentration in the bank at over 40,000 ng/L, with this average being under 10,000 ng/L for the more typical conditions at low flow with more limited exchange between the banks and river. The changes in the mercury behavior in the river banks were not anticipated and were not detected with other sampling techniques. Changes were also detected in the redox conditions of the bank porewater. No reduced metals were detected in the bank during this sampling event. Dissolved oxygen was not able to be measured during this sampling event. Another sampling event was carried out in July 2013 when the river was back down to low-flow baseline flow conditions. Mercury concentrations measured with DGT samplers were much lower than measured in May. The average concentration measured in the bank was approximately 10,000 ng/L, consistent with other sampling during baseline river flow. This

suggested that the flood event was responsible for the elevated mercury concentrations but there may have been other variables between the May and July sampling events.

A sampling event was carried out in May 2014 to sample the bank for mercury porewater concentrations and redox conditions immediately prior to the flood event and then again as the bank was draining. This would reduce the potential for other factors than the flooding to be controlling mercury behavior in the banks. The mercury concentrations measured prior to the flood event were consistent with those measured during other baseline flow events with a bank porewater average of approximately 9,500 ng/L. Reduced metals were detected in the banks and dissolved oxygen was depleted within the upper 2 cm of the bank. The sampling event was then repeated after the river flooded the banks from the storm event and began to drain back to the river. The mercury concentrations measured in the bank were much higher than measured just days earlier at an average of 64,000 ng/L. No reduced metals were detected in the bank using cyclic voltammetry and dissolved oxygen was measured over the entire depth measured. These measurements confirm the behavior measured in the May 2013 sampling and suggest that the flood event is responsible for the increased mercury measured in the banks. The DGT samplers were able to identify this mercury behavior in the bank, which was underestimated using conventional porewater sampling techniques.

In order to better understand the implication of the elevated mercury concentrations measured in the bank, a mathematical model of water drainage from the bank was developed. The RRM3.5 bank system has a silt layer overlying a gravel-sand layer. The silt layer is thought to contain the high mercury concentrations measured with DGT samplers while the sand layer contains lower concentrations. The model was designed to find out how much water would drain from each layer. The flood height was varied to determine the sensitivity of the drainage to the

size of the flood event. For the base case, with a fully inundated bank with a height of 5 feet, the majority of water drained from the sand layer. This was also the case for the smaller flood heights of 1 and 3 feet. However, the silt drainage volumes did not scale linearly with the flood height. The volumes from the model were combined with field measurements of mercury concentrations to calculate the mercury mass flux from the silt and sand layers during drainage events. The budget was calculated using both average concentrations measured during a flood event and the maximum concentrations measured. The drainage volumes from 1, 3, and 5 feet flood heights were also used in the budget. The mass flux was higher for the silt layer for the base case, even though the sand layer flow was significantly higher. The silt mass flux was also higher for the 3 feet flood height. Only for the 1 foot flood height was the mass flux from the sand and silt layers comparable. The modeling suggested that the drainage from the silt layer after high flood events was likely the dominant process leading to mercury release to the river if the bank was not eroding.

Laboratory experiments were carried out to further understand mercury behavior in the river banks during flood events. Bank soil sediment was collected from RRM3.5 and used for all experiments. The first experiment was done as a bulk system to determine if the increased mercury concentrations observed during the flood events could be replicated. Bank sediment was allowed to equilibrate and reduce before DGT samplers were deployed which measured an average concentration of 25,000 ng/L. The sediment was then oxidized and DGT samplers were redeployed with an increased concentration measured of over 53,000 ng/L. The sediment was then allowed to reduce again and the final DGT sampling gave an average of 14,000 ng/L. This experiment showed that the mercury increase in banks and subsequent decrease could be replicated in the lab. A mesocosm experiment was then run to replicate this behavior at in-situ

conditions, allowing a redox gradient to form in the sediment. The mesocosm was sampled for mercury with DGT samplers and for dissolved oxygen with cyclic voltammetry, the same sampling techniques used in the field sampling. The total mercury concentrations stabilized at depth near 30,000 ng/L. with the dissolved oxygen was depleted within the top 2cm of the mesocosm. The mesocosm was pumped with oxic water to simulate the bank drainage during a flood event and the DGT sampling and cyclic voltammetry measurements were then repeated. The dissolved oxygen was measured to a depth of 5cm. The mercury concentrations increased after oxidation, but only at depths that were previously anoxic. The increase in dissolved mercury concentration is again linked with oxidation with this experiment showing it occurring in conditions similar to the field.

In order to better understand the link between oxidation and mercury behavior, an experiment was run in order to get a more complete picture of porewater chemistry. A column experiment was run using RRM3.5 bank sediment. The column was allowed to equilibrate with anoxic water pumping through it to simulate the bank environment during baseline flow. The mercury concentration stabilized at approximately 10,000 ng/L and the mercury concentrations more than tripled when the column was oxidized. The dissolved organic carbon decreased slightly but did not trend well with the dissolved mercury concentration. The iron was oxidized quickly and the total iron did not change significantly after oxidation. The total manganese decreased slightly after oxidation. The most significant change in porewater chemistry after oxidation was a drop in pH. The pH stabilized near 7.5 prior to oxidation. This value dropped after oxidation and stabilized near 7.3. The pH value increased again, up to 7.8, after the inlet was changed back to anoxic. The pH values trended with the total mercury concentration during both the oxic and anoxic periods of the experiment. The pH change affects several processes

that are pH dependent, most notably, mercury speciation and solid-partitioning. Only a small change in the sediment-water partitioning coefficient is needed to explain the increase in porewater mercury concentrations. This change could be caused by the drop in pH observed.

6.2 Conclusions

DGT samplers are a promising tool for better understanding mercury in sediment systems due to their ability to more accurately measure porewater concentrations. Conventional sampling techniques, when using filtration, typically underestimate dissolved porewater concentrations, which is more harmful as the toxicity and bioavailability will also be underestimated. An accurate measurement of porewater is important to understanding mercury fate as the dissolved mercury is more available for methylation and transport. Porewater sampling for mercury is, however, difficult as mercury is sensitive to many factors and typically present at low concentrations in porewater. Mercury is sensitive to redox conditions within the sediment sample and can be transformed by chemical, biological, and physical processes. Conventional sampling of sediment requires it to be removed and transported, which can change the redox chemistry in the porewater and leads to disturbance and potentially sediment resuspension. In general, separating porewater for analysis can't be accomplished without changing the porewater that is being sampled. These problems are overcome with DGTs due to their passive measurement of porewater concentrations.

The DGT samplers can be cheaper and easier than conventional sampling techniques. The chemical analysis is the same for conventional and DGT sampling. Both only require a total mercury measurement using CVAFS or ICP. DGT samplers require only a simple extraction to

prep for analysis. Conventional sampling has many extra steps which increases costs and opportunity for errors. DGT sampling is a simpler technique, especially if the samplers become commercially available. The fabrication of samplers is more difficult than the deployment and processing. If reliable DGT samplers can be produced commercially, their use would become more widespread.

Successful field use of DGT is important to the promotion of more widespread use. This work is an example of effective use of DGT samplers in the field to measure mercury availability and mobility These samplers identified mercury behavior in the South River banks that was not found with conventional sampling techniques. The DGT samplers allowed areas to be sampled that couldn't be sampled with other techniques. The samplers allowed increased spatial resolution and specific areas could be sampled with fine depth resolution. The DGT samplers sample over the deployment time and can give a clearer picture of dynamic systems than grab samples.

All of these advantages led to the identification of elevated mercury concentrations during bank drainage. The bank system is difficult to access during flood events. The model shows that the silt layer may drain substantially in 1 to 2 days and accurate sampling of the bank seepage is difficult in that narrow of a time frame. The experimental measurements indicated that bank seepage from the silt layer can contribute significantly to mercury flux into the channel. This may be underestimated by the current site conceptual model, which attributes the majority of mercury from the banks to erosion. It is difficult to directly measure the contribution of mercury from bank erosion but the DGT samplers are the first tool that can give an accurate, direct measurement of the impact of bank leaching.

Understanding of the processes of mercury release from the banks is important for designing effective remediation systems which reduce mercury flux into the river. Having a better understanding of mercury behavior is important before making these remediation decisions. Any remediation design must address the sources that are responsible for mercury and methylmercury movement into the river. Passive sampling using DGT samplers will help to improve the understanding of mercury behavior, not only in the South River, but all sites. Passive sampling techniques directly measure parameters in-situ and will give better data to shape the understanding of mercury behavior in aquatic systems. Understanding mercury behavior in this bank system can help the understanding of the fate of other redox sensitive metals in non-static systems. Short-term hydrologic changes in these systems can impact metal fate which may not be captured in conventional sampling.

6.3 Recommendations for Future Work

This works shows the potential for DGT samplers to be effective tools for field sampling of mercury in sediment porewater but further work is needed to enhance the understanding of the data obtained. The only mercury speciation currently available with DGT samplers is differentiating between total mercury and methylmercury. The extraction method for total mercury destroys the speciation of the porewater mercury. The mercury fraction that is measured using DGT samplers is described as 'labile' mercury. While this definition has a chemical basis as it only includes mercury species which can pass the filter layer and diffuse through the agarose gel, it is less clear which mercury species it includes. Mercury speciation is complex and can be impacted by sulfates, DOC, and nanoparticulates. DGTs clearly exclude

larger (>100nm) particles containing mercury but it is unclear how much of the colloidal and dissolved mercury is taken up. It is not known how these complex species affect DGT measurements. Nanoparticulate mercury species would be counted as 'dissolved' using a standard filtering technique but it is unknown if they would be taken up by DGT samplers.

Research is currently underway on this question but is still in the introductory phase. As the speciation of mercury changes, the chemical characteristics such as diffusion rate can be affected. In system with high DOC, the majority of mercury will be complexed and the molecular weight of the dissolved species will increase. The diffusion of these species will then decrease which will affect their measurement using DGT samplers. A better understanding of how speciation impacts uptake into DGT samplers is needed. If DGT samplers are to be widely accepted, a better understanding of what mercury species DGT samplers are including is needed.

Work is also needed to make DGT samplers more easily accessible as tools for academic, industry, and regulatory use. Currently, the majority of DGT samplers are made in-house by academic groups. DGTs are available in small quantities semi-commercially from the inventors of the approach in the United Kingdom. These can be difficult to obtain in the United States as their supply is low and they must be transported safely. Mercury DGTs from this source have been available in very small numbers and have historically contained a substantial mercury contamination. For producing DGT in-house, a proprietary gel crosslinker is used which can only be procured from DGT Research. This crosslinker is not manufactured in commercial quantities so any DGT production is limited by its supply. Alternative DGT resin gels have been used with the thiol resin beads held in an agarose gel instead of the standard acrylamide gel. The initial results using these alternative DGT have been promising but further work is needed to prove their performance and reliability.

There is also variability in the thiol resin used in mercury DGT samplers across groups producing them. The standard thiol resin used was produced by Sigma Aldrich® but their manufacturing process changed in 2013 which may have changed the resin performance. The change was made to Biotage® Iso-Solute thiol resin beads after this change was found but there has not been a consensus reached. Many labs produce their own thiol resin beads. Some labs use Chelex® 100 resins but it has relatively poor performance for mercury. In order for DGT samplers to be produced at a larger scale, a standard resin material needs to be chosen which has good mercury uptake and recovery and low mercury contamination. Any resin material chosen would ideally also perform well for methylmercury. Preliminary studies with the new Sigma Aldrich® and Biotage® resins suggest poor recovery of methylmercury from the resins but further studies are needed. One major potential advantage of DGT samplers is their ability to measure total mercury and methylmercury simultaneously. In order to utilize this advantage, a resin needs to be chosen which performs well for both total mercury and methylmercury.

There are also open questions related to the mercury behavior in the banks in the South River and how best to use DGT in concert with other tools to assess that behavior. It is unknown how representative the site of primary focus here, RRM3.5, is for the rest of the South River. All laboratory experiments were also performed with bank sediment from RRM3.5. Decisions cannot be made for the entire river based on only one sampling location. Further field sampling is planned for 2015 which includes new sampling locations to try and address this question.

A better understanding of the specific physico-chemical mechanisms controlling mercury behavior during bank drainage is needed. The banks have been identified as a major source of mercury to the river channel but the chemical processes that causes the observations is not known. If these processes are better understood a more appropriate remedial approach can be

design. Stabilization of the banks is envisioned to be a primary remedial approach, but bank stabilization would not decrease mercury entering the river system through bank leaching. The bank stabilization system could, however, include sediment amendments which target the processes of mercury release. In order to accomplish this, the release processes need to be better understood so that the bank amendments can be properly chosen. Studies of the effectiveness of the remedial approaches could also be undertaken.

Appendix

DGT Probe Fabrication SOP

Preparation:

1. References:

    a. Davison, W., & Zhang, H. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the In Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry , 67* (19), 3391-3400.

    b. Clarisse, O., & Hintelmann, H. (2006). Measurements of Dissolved Methylmercury in Natural Waters Using Diffusive Gradients in Thin Films (DGT). *Journal of Environmental Monitoring , 8*, 1242-1247.

    c. *Practical Guide for Making Diffusive Gel and Chelex Gel.* From www.dgtresearch.com.

    d. *Practical Guide to Assemble DGT Devices*. From www.dgtresearch.com.

    e. How to make DGT video (see Reible Group external hard drive).

2. Cleaning and Storage:
    a. All glass and plastic ware (to include probe holders) should be soaked in soapy water (Alconox®) for 24 hours. Glass plates and tools should be acid washed periodically (approximately every 6 months)
    b. Glass and plastic ware should then be dried in a dust-free environment
    c. All reagents should be stored in a mercury free environment to minimize contamination
    d. All reagents should be reordered annually as some lose reactivity over time

3. Materials:
    a. Glass plates, two different widths (TTU Chemistry Glass Shop)
    b. 0.75 mm gasket and spacer kit (Cole Palmer EW-28573-31, EW-28573-04)
    c. Plastic clamps (Cole Palmer EW-28565-30)
    d. Glass Syringe, 10 mL
    e. Plastic spatula and tweezers (Fisher 14-518, Cole Parmer EW-06443-27)
    f. Gel staining box, Nalgene® (VWR 28196-306)
    g. Probe holders, piston and sediment shape
    h. 3-Mercaptopropyl-Functionalized Silica Gel (Biotage 9180)
    i. Cross-Linker (DGT Research LTD.)
    j. 40% acrylamide/bis 37.5:1 ratio solution (Fisher BP14101)
    k. N,N,N', N' – Tetramethylethylenediamine (TEMED) (Fisher BP150-20)

l. Ammonium Persulfate (Fisher BP179-25)
m. Agarose, Broad Spectrum Range (Fisher 1356-100)
n. Filters, 0.45 µm, Millapore® – Durapore®,, 25mm diameter, polysulfone: for piston probes (Millipore HVLP02500)
o. Filters, 0.45 µm, Millapore® – Durapore®, membrane filter sheet, polysuflone: for sediment probes (Millipore HVLP00010)

Resin Gel Construction:

1. For the Gel Solution (100 mL), mix the following and maintain in the 4°C room:
    a. 15 mL Cross-Linker (they come in 15 mL vials)
    b. 47.5 mL DI water
    c. 37.5 mL 40% acrylamide/bis 37.5:1 ratio solution

2. Fresh (within a few hours of making resin gel) Ammonium persulfate solution has to be made:
    a. Add 0.05 g of Ammonium persulfate to 0.5 mL of DI water in a 2 mL centrifuge vial
    b. Vortex for 30 seconds (located in Lab 253F)

3. Two glass plates, of two different widths (3 and 4.1 cm), should be laid flat on one another separated by the desired width PVC spacers and rubber gasket, all held in place with the white plastic clamps (see Figure 1).

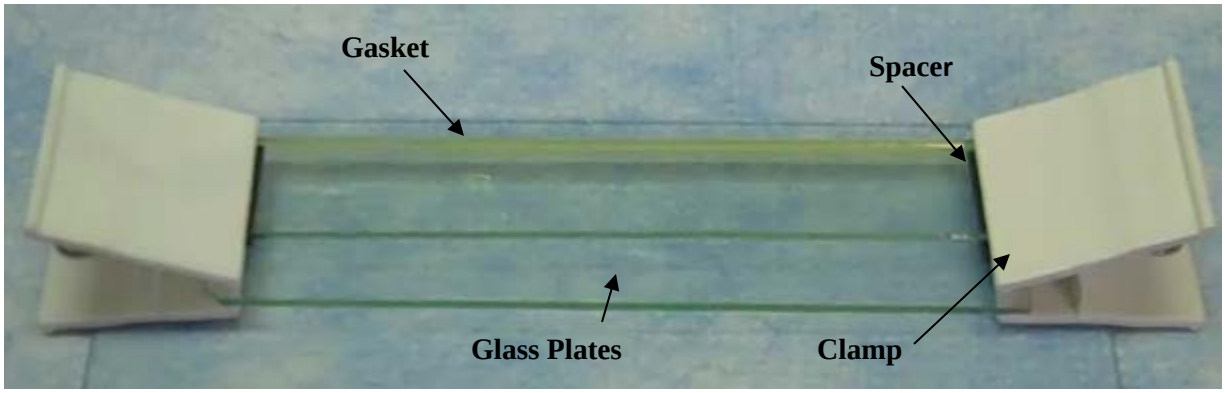

Figure 1: Glass plates, spacers, and gasket ready for gel casting

4. A 10 mL glass syringe should have its spout wrapped in Parafilm® and placed in a tube rack with the spout facing down

5. For 1 gel strip of 0.75 mm thickness, add the following to 1 syringe in the exact order:
    a. 5.5 mL gel solution
    b. 1.1 g 3MFSG resin
    c. Insert syringe plunger and shake/mix well
    d. 33 µL Ammonium persulfate solution
    e. 8.25 µL TEMED

f. Re-insert syringe plunger, mix well, immediately cast between the plates starting from the left and moving to the right
g. Repeat if making multiple gel strips [1 gel strip = 1 sediment probe or 5 piston probes]

6. Let resin gel sit for 45 minutes at room temperature

7. Remove clips, spacers, and gasket and carefully separate glass plates with a plastic spatula; separating slowly as not to tear the new resin gel strip

8. Remove gel strip from glass plates and place in a clean gel staining box filled with Milli-Q water, let gel strip hydrate for 24 hours before placing in a probe holder

9. The resin gel strip will curl up after being hydrated. The resin beads settled down during solidification, they are on the inside of the curled surface (see Figure 2 for depiction). This is the surface that needs to be facing towards the bulk liquid/sediment pore water for proper adsorption of mercury/MMHg.

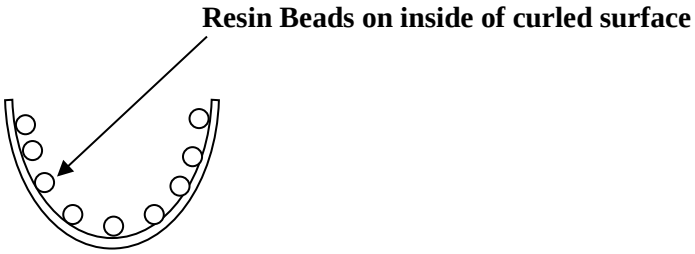

Figure 2: Resin bead location after solidification (not to scale, resin beads are not that large).

Diffusive Gel Construction:

1. Two glass plates of two different widths (3 and 4.1 cm), should be laid flat on one another separated by the desired width PVC spacers and rubber gasket, all held in place with the white plastic clamps (see Figure 1).

2. Add 0.15 grams of Agarose per 10 mL of DI water into a flask and bring to a boil. Round up to the nearest 10 mL to ensure there is enough gel for casting. 5 mL of Agarose/DI solution will create 1 x 0.75 mm diffusive gel layer but it is best to cast with 6-7 mL of gel in the syringe. This will ensure that no air bubbles are cast between the plates.

3. Using a disposable plastic syringe, extract Agarose/DI solution from flask and cast between glass plates.

4. Let gel solidify for 30 minutes, then remove the top glass plate and cut diffusive gel into the desired shape. Use glass centrifuge bottle cap for exact piston shaped cuts. For sediment probes, put into holder first, then cut off extra.

5. Construct probes immediately when diffusive gel is solidified.

Probe Construction Tips:

- Ensure resin gel is sufficiently wet, apply extra Milli-Q water, when cutting resin on large glass cutting plate
- Because resin is curled up, it is easier when making sediment probes to lay diffusive gel flat on large glass cutting plate and then spread resin gel over the top. After you have flattened out the resin gel over the diffusive gel, place sediment probe body over the two layers and flip the glass plate over. The sediment probes are more easily constructed by two people
- See Figures 2 and 3 for completed probes dissected by each layer.
- There are a variety of sediment probe sizes, designed for laboratory or field use. Choose the appropriate probe for your desired use.
- There are two types of piston probe holders, laboratory and field. Laboratory piston holders have a groove along the outside of the cover to hold an o-ring. Field piston probe holders do not have this groove and have holes drilled in the back of the base for tying markers to probes.
- Probes must be de-aerated before use in 0.1 Molar $NaNO_3$ solution with $N_{2(g)}$. In order to minimize background mercury accumulated during deaeration, add scrap resin strips to solution. Deaerate for at least 12 hours.
- Probes can be stored at 4^{o}C for up to six months. Long-term storage can increase background mercury so it is best to construct probes as close to sampling as possible.

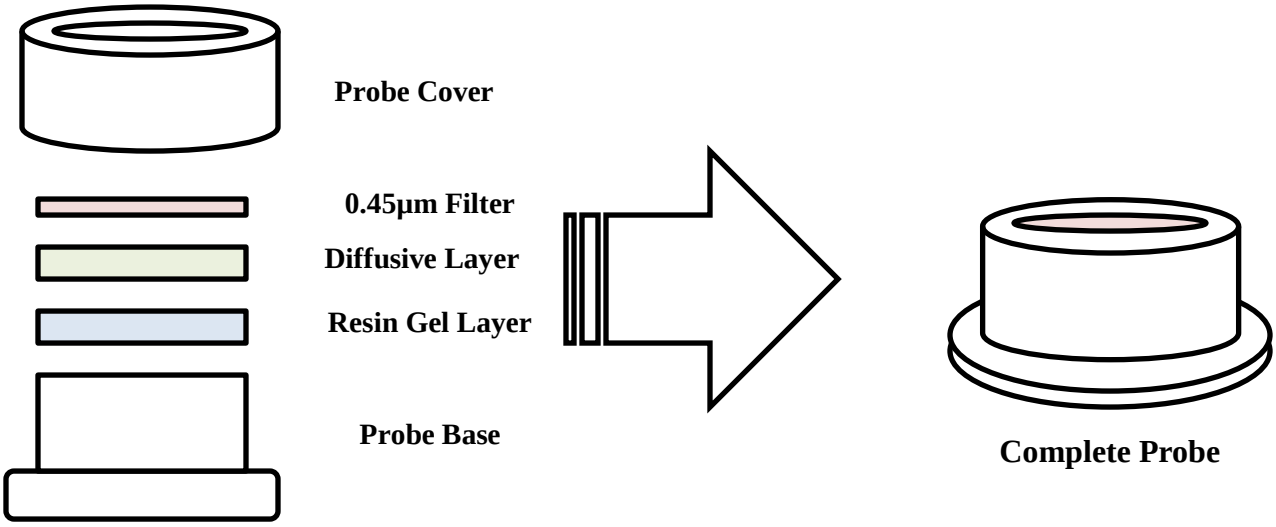

Figure 2: Completed piston probe by layer.

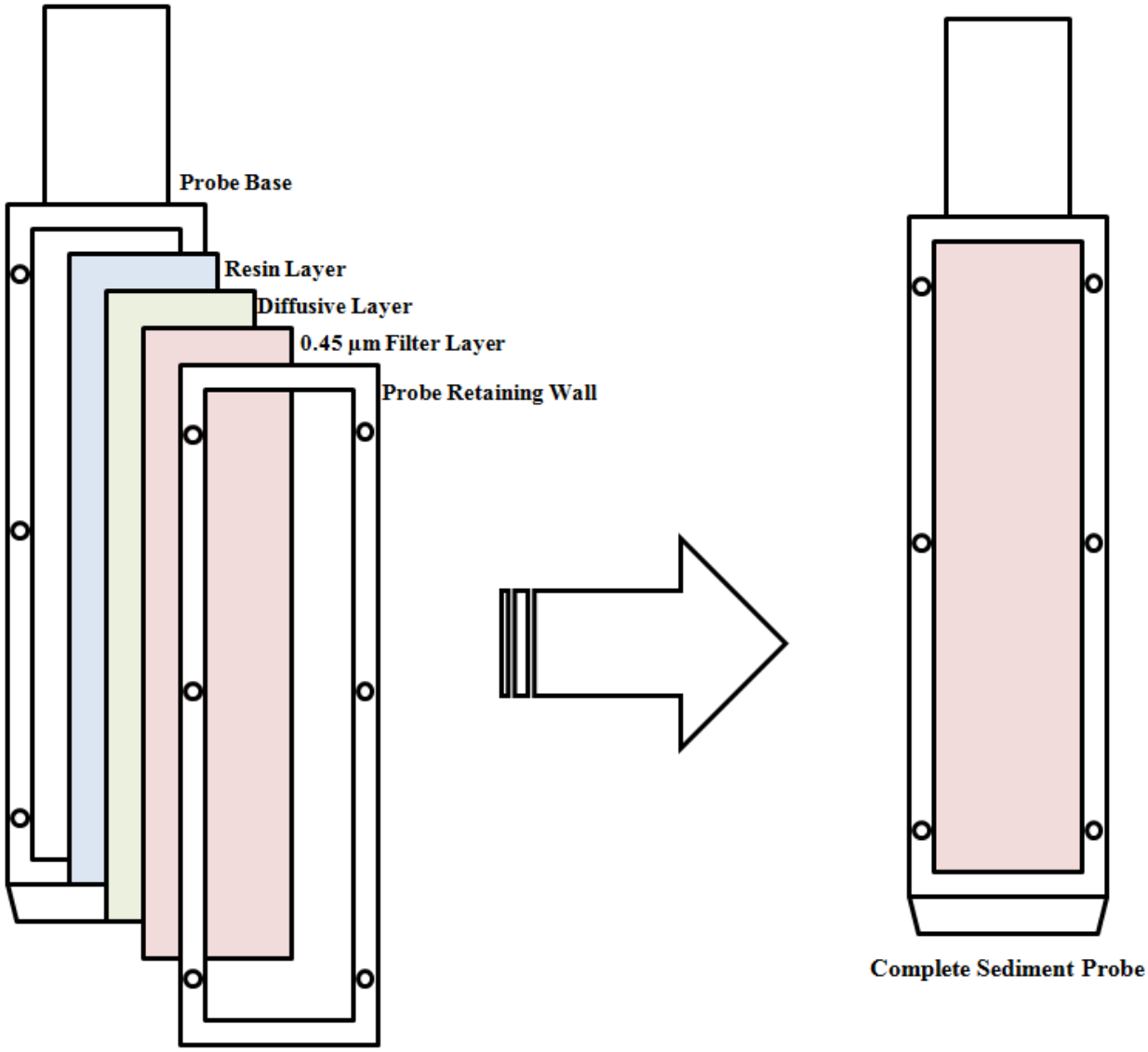

Figure 3: Completed sediment probe by layer.

DGT Bulk Laboratory Experiments

The uptake curves for the Oxidized, both polyacrylamide and agarose gel samplers, and Reduced 2 bulk DGT experiments are shown below. The slope, (M/t) in the below equation, of the uptake curve is used to calculate the equivalent porewater concentration as measured using the DGT samplers. All parameters are defined in Chapter 2 in the DGT sampler theory section.

$$C_{pw} = \frac{M\Delta g}{AtD_{eff}} = \left(\frac{M}{t}\right)\frac{\Delta g}{AD_{eff}}$$

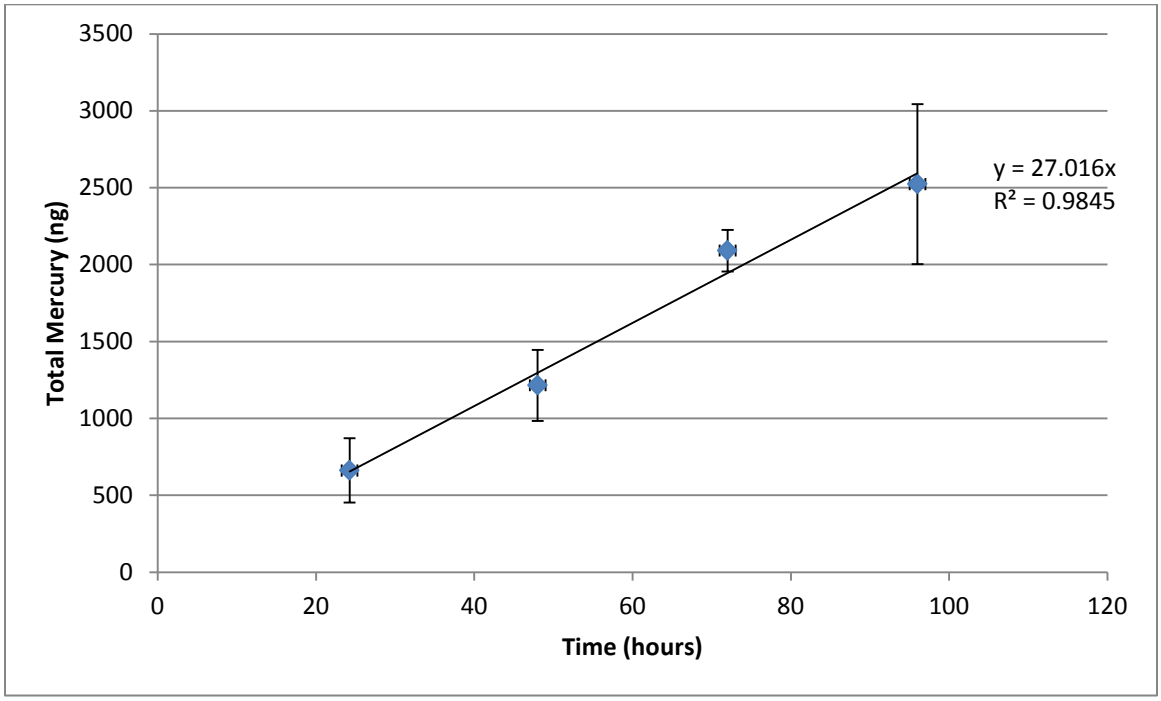

Figure 69 - DGT Mass Uptake of Oxidized South River RRM3.5 Bank Sediment

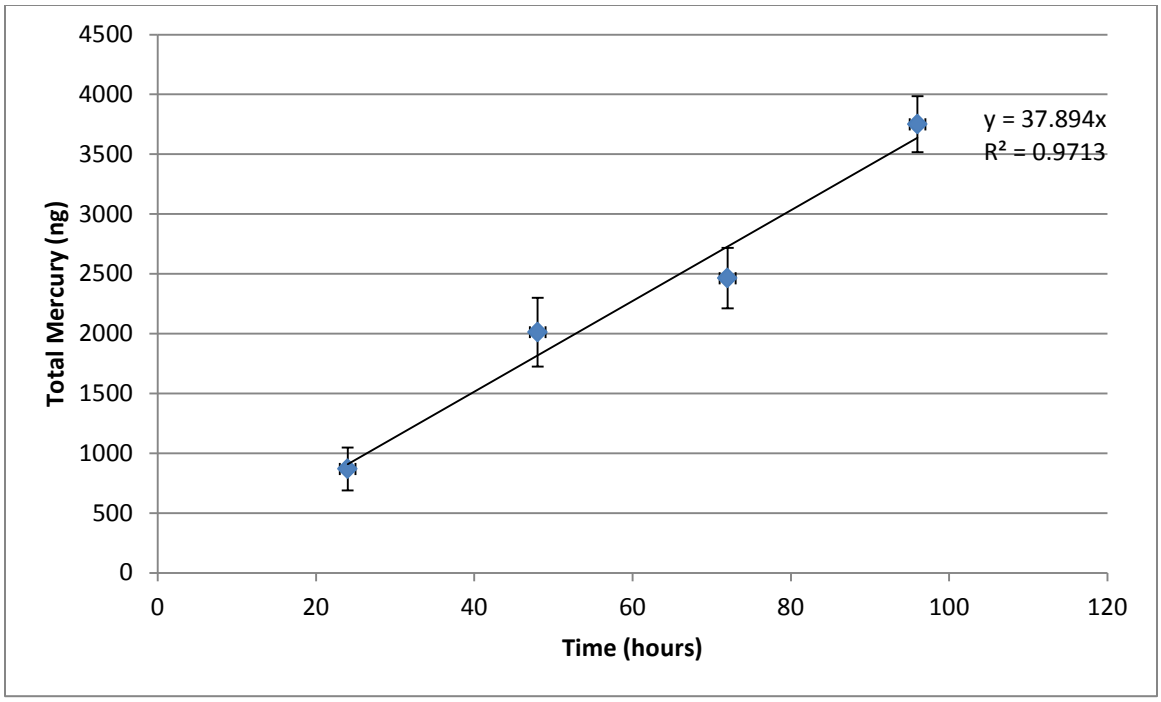

Figure 70 - DGT Mass Uptake of Oxidized - Agarose South River RRM3.5 Bank Sediment

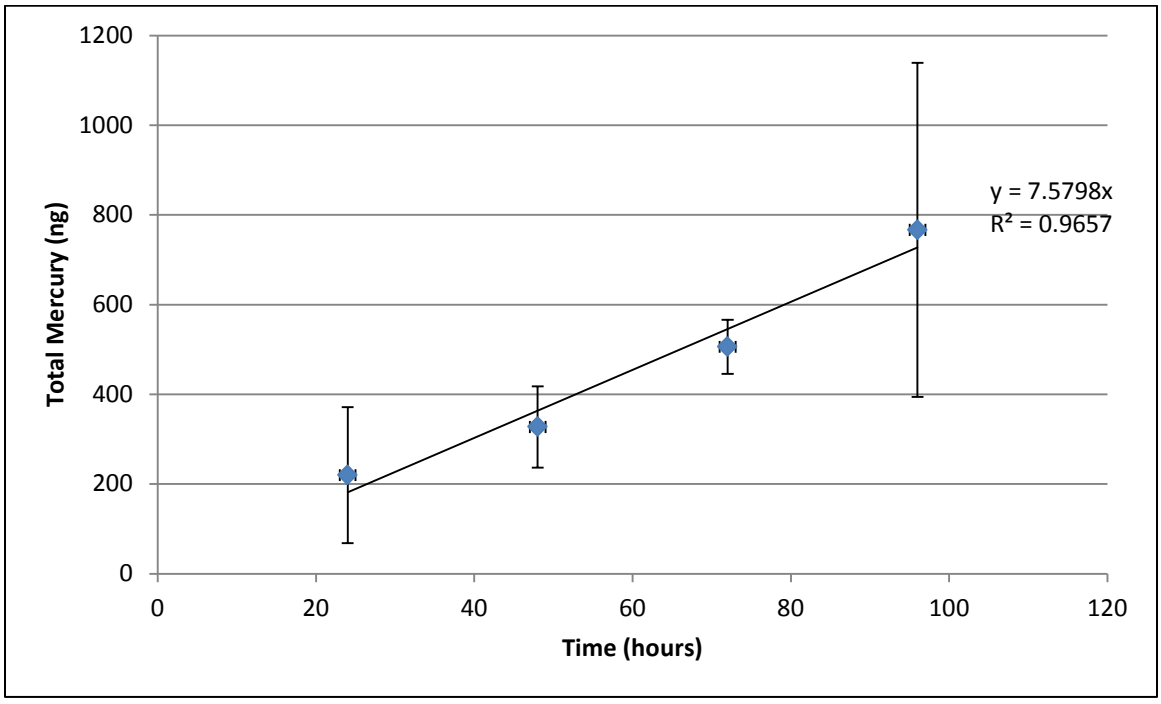

Figure 71 - DGT Mass Uptake of Reduced 2 South River RRM3.5 Bank Sediment

Bank Drainage Model Parameters

Richards' Equation: $\left(\frac{C_m}{\rho g} + S_e S_{silt}\right)\frac{\partial H}{\partial t} = \frac{\kappa}{L\mu}\nabla^2 H$

Storage Equation: $S_{silt}\frac{\partial H}{\partial t} = \frac{K_{silt}}{L}\nabla^2 H$

$$\theta = \begin{cases} \theta_r + \mathrm{Se}(\theta_s - \theta_r) & H_p < 0 \\ \theta_s & H_p \geq 0 \end{cases}$$

$$\mathrm{Se} = \begin{cases} \dfrac{1}{[1 + |\alpha H_p|^n]^m} & H_p < 0 \\ 1 & H_p \geq 0 \end{cases}$$

$$C_m = \begin{cases} \dfrac{\alpha m}{1-m}(\theta_s - \theta_r)\mathrm{Se}^{\frac{1}{m}}\left(1 - \mathrm{Se}^{\frac{1}{m}}\right)^m & H_p < 0 \\ 0 & H_p \geq 0 \end{cases}$$

$$k_r = \begin{cases} \mathrm{Se}^l\left[1 - \left(1 - \mathrm{Se}^{\frac{1}{m}}\right)^m\right]^2 & H_p < 0 \\ 1 & H_p \geq 0 \end{cases}$$

Other Model Parameters (Yang 2013, Genutchen 1980)

α = 15.24 ft^{-1}
m = 1.26
l = 0.5

The equations and parameters used for the baseline flow diffuse flux are shown below. The river velocity, river depth, and hydraulic radius were estimated based on site experience. The Manning's coefficient was chosen as the normal value for a clear, winding channel with some weeds and stones (Chow 1959). The bank area per unit width was calculated for the chosen river depth.

$$k_{bl} = 88.4 v_x n \sqrt{gd} \left(\frac{D_w}{r_H \nu_w} \right)^{2/3}$$

k_{bl} = benthic boundary layer mass transfer coefficient (cm/hr)
v_x = river velocity (m/s)
n = Manning's coefficient
g = gravitational accelearatoin (m^2/s)
d = river depth
D_w = molecular diffusion coefficient in water (cm^2/s)
r_H = hydraulic radius (m)
ν_w = kinematic viscosity of water (m^2/s)

$$J_d = k_{bl} C_{pw} \frac{A_{bank}}{L_{bank}}$$

J_d = Diffusive Flux (ng/m-hr)
k_{bl} = benthic boundary layer mass transfer coefficient (cm/hr)
C_{pw} = mercury porewater concentration (ng/cm^3)
A_{bank} = bank area (cm^2)
L_{bank} = bank length (cm)

Parameter	Value	Units
V_r	0.25	m/s
n	0.045	-
d	0.45	C
D_w	8.6e-6	cm^2/s
r_H	0.8	m
ν_w	1.004e-6	m^2/s
A_{bank}/L_{bank}	0.45	m

Supplemental Column Results

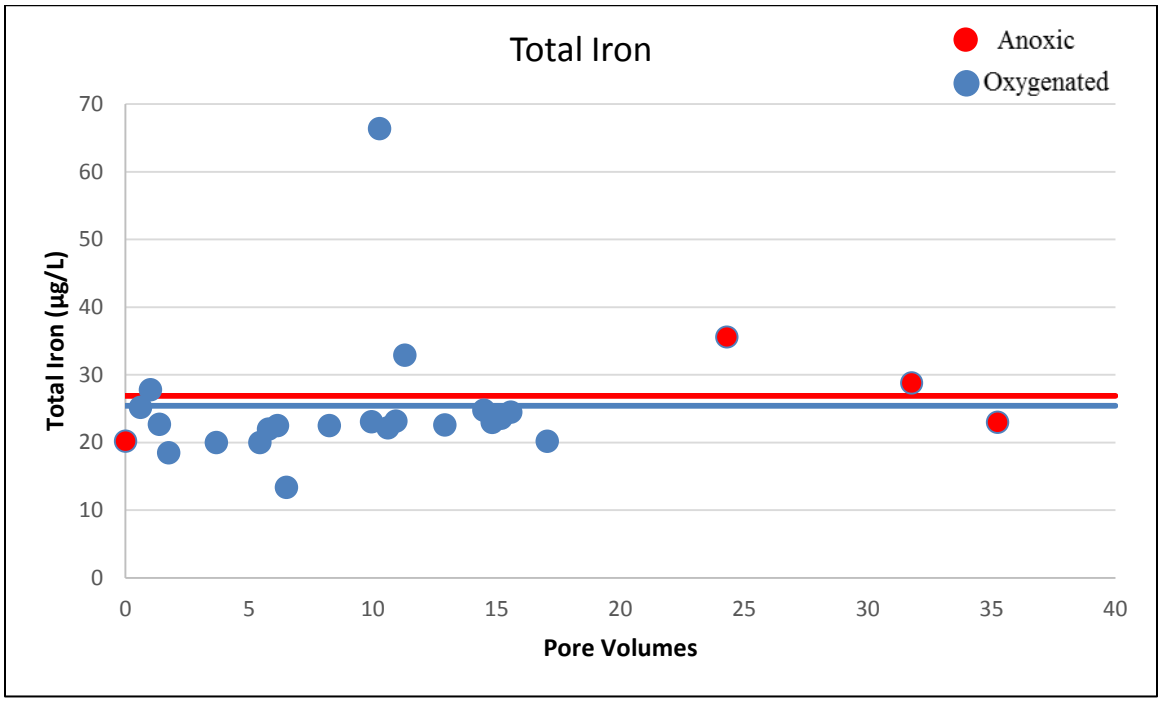

Figure 72 – South River RRM3.5 Bank Column Effluent Total Iron

Total iron and reduced iron(II) were measured in the column effluent. The iron measurements are important both to quantifying metal release and redox conditions. The total iron is a good measure of the mobilization of iron from both dissolution of iron solids and iron bound to mineral surfaces. The reduced iron is the best measure for redox conditions of the column, especially since sulfide was never measured above the detection limit. The total iron concentration was 20 µg/L after the equilibration period and stayed close to that value for most of the experiment. The total iron spiked for one sample midway through the experiment, reaching 66 µg/L, but stayed between 20 and 20 µg/L for almost all other samples. After changing back to anoxic inlet water, the total iron increased to 35 µg/L before lowering back to

near 20 µg/L. The reduced iron concentrations were very different than the total iron concentrations. The reduced iron was 11.3 µmol/L at the end of the equilibration period. This value would not be expected to stabilize during the equilibration period as iron reduction was ongoing. The concentrations measured in the column were lower than measured in the field with cyclic voltammetry but within the same order of magnitude. The reduced iron fell below the detection limit within the first 4 pore volumes after switching to oxygenated inlet water. Sampling for reduced iron was stopped after 10 total pore volumes due to none being detected for several samples.

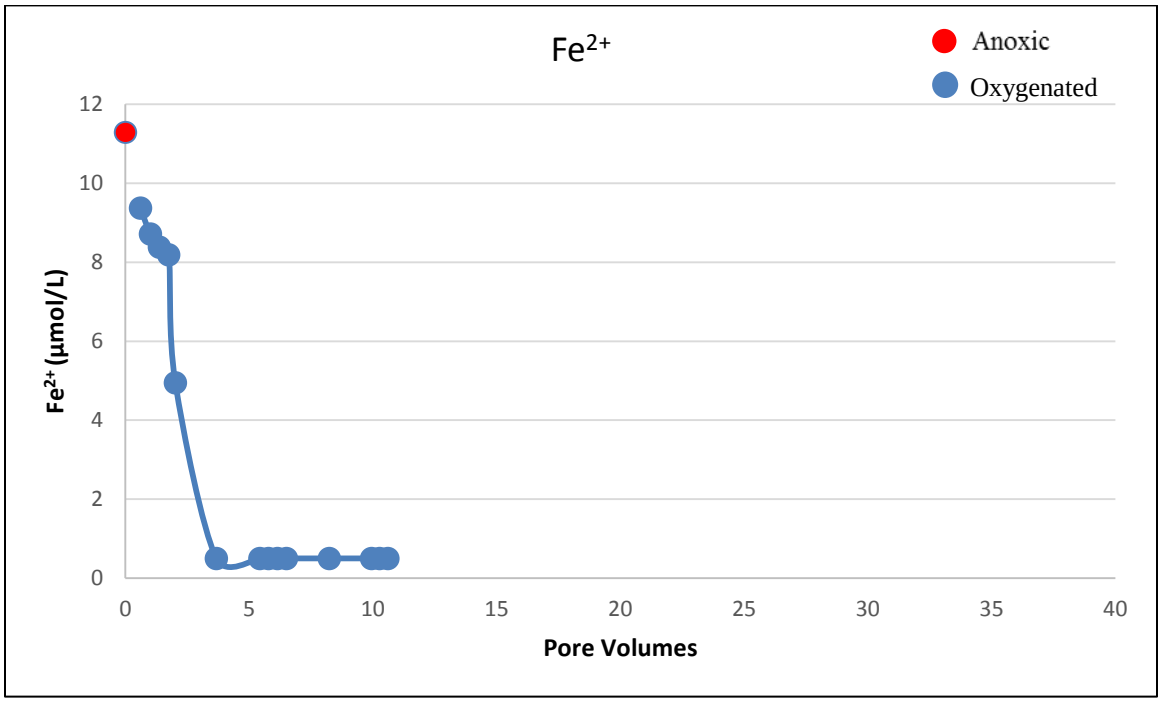

Figure 73 – South River RRM3.5 Bank Column Effluent Iron(II)

Chloride was the only anion that was detected in all samples measured from this column experiment and results are shown in Figure 74. Chloride decreased over the equilibration period before stabilizing at 65 mg/L. Chloride concentrations dipped initially after changing to

oxygenated inlet water but quickly stabilized at 75 mg/L. This concentration did not change until the feedwater was changed back to anoxic and even then it took nearly 20 pore volumes for the chloride concentration to decrease. The chloride concentration did not change significantly over the course of the experiment, which can be expected as the composition of the feedwater was not changed. The same synthetic freshwater feedwater was used for both the oxygenated and anoxic feedwaters.

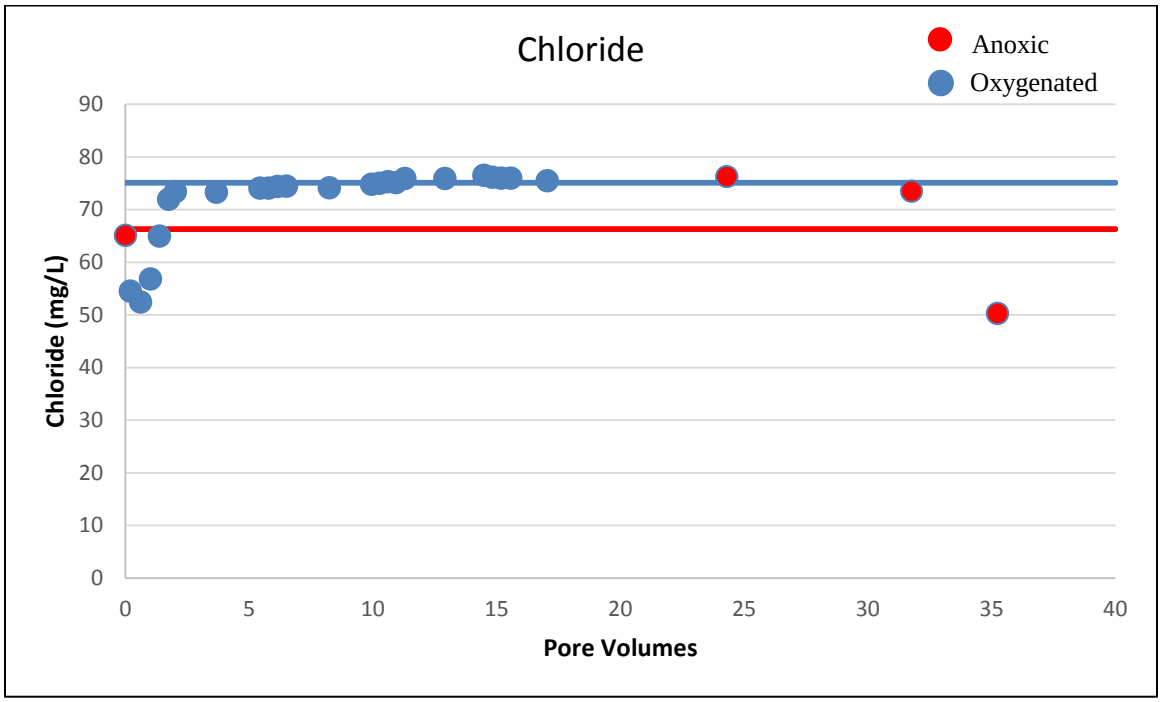

Figure 74– South River RRM3.5 Bank Column Effluent Chloride

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