

OPTIMIZATION OF DGT METHYL MERCURY RECOVERY, BANK LEACHING
ASSESSMENT AND EVALUATION OF STABILIZATION EFFORTS ON
MERCURY FATE AND TRANSPORT IN FRESHWATER SYSTEMS

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ABSTRACT

Bioavailable mercury (Hg) in the environment is methylated by bacteria to form methyl mercury (MeHg) a bioaccumulative acute neurotoxin. The ability to quantify Hg and MeHg in sediment pore water may allow for better understanding of mercury mobility, bioavailability and toxicity in the environment. Flooding events in South River, VA have been associated with leaching of pore water total mercury from the contaminated river banks, creating a potentially significant source of mercury to the system. In this research the mobility and availability of Hg in these river banks is assessed through diffusion gradient in thin film (DGT) devices to measure pore water Hg and MeHg.

This research had four main specific objectives. The first objective was to improve the recovery of MeHg from the DGT devices to ensure quantitative recovery. The second objective was to apply DGTs to measure Hg from the pore water leaching from river banks in the South River during inundation/drainage cycles associated with storm events and the associated potential for methylation by assessing redox conditions and MeHg during these cycles. The third objective was assessment of the ability of stabilization and capping of the river bank to reduce Hg flux. The cap was composed of layers of biochar as a Hg sorbent as well as sand and armoring material. The final objective was to predict long term effects of storm events and bank leaching with and without the stabilization and capping.

Studies were done to improve the recovery of MeHg from the DGT resin, resulting in method for extraction of MeHg that improves currently used poorly reproducible extraction recovery in 1-56% range to a reproducible recovery of $91 \pm 9\%$.

Field sampling was done at the Constitution Park and North Park in 2015 during baseline conditions as well as during bank drainage after inundation by a storm event. The results demonstrated that storm event associated leaching introduced an order of magnitude increase in pore water total mercury due to drainage from contaminated banks. Stabilization of the bank and placement of a composite cap led to reduction of pore water concentrations and likely Hg fluxes by 1-2 orders of magnitude, depending on the initial level of contamination at different locations.

Lastly, the inundation and drainage cycle was simulated using a commercial finite element package, COMSOL®. The simulations demonstrated that leaching predominately (90%) occurs near the bank-water interface and allowed estimation of leaching/seepage fluxes. These results were used to simulate long term chemical containment performance of the composite cap during regular 3 and 6 ft flood events for the next 100 years using CapSim®, a modeling environment designed to simulate contaminant transport at the sediment-water interface. The composite cap was predicted to be effective in reducing the pore water concentration and Hg flux at the cap-water interface by more than 93.5% compared to that estimated without a cap layer in place. The maximum Hg flux associated with the flood events was approximately $0.6 \mu\text{g}/\text{cm}^2/\text{yr}$ in the period of 30 to 100 years after the cap implementation.

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LIST OF ABBREVIATIONS

3MFSG	3-mercaptopropyl functionalized silica gel
BMA	Bank Management Area
CH ₂ Cl ₂	Methylene chloride or dichloromethane (DCM)
CP	Constitution Park
DBL	Diffusive Boundary Layer
DDI	Distilled deionized water
DET	Diffusive equilibration in thin film
DGT	Diffusive Gradient in Thin Film
DGT	Diffusive gradient in Thin Film
DOC	Dissolved organic carbon
HRADs	Hg-Release Age Deposits
LSV	Linear Sweep Voltammogram
MDL	Method detection limit
MeHg	Mono methyl mercury
MQL	Method quantification limit
MVG	Mualem Genuchten Model
NHE	Normal Hydrogen Electrode
NOM	Natural Organic matter
NP	North Park
ORP	Oxidation-reduction potential
PA	Polyacrylamide gel
RRM	Reference River Mile
SHE	Standard Hydrogen electrode
SRST	South River Science Team
SWV	Sweep Wave Voltammogram
THg	Total mercury
TU	Thiourea
WLF	Water-level Fluctuation

LIST OF SYMBOLS

A	Area of resin analyzed
a	Atmospheric level solubility ($\mu\text{mol O}_2/\text{L}$)
$A_{\text{bed}}/L_{\text{bed}}$	Bed area per length of stream
Br^-	Bromide ion
BrCl	Bromine monochloride
C	Concentration of oxygen ($\mu\text{mol O}_2/\text{L}$)
C_b	Pore water concentration (ng/L)
Cl^-	Chloride ion
CO_2	Carbon dioxide
C_{pw}	THg pore water
C_w	THg in water immediately above sediment-water interface (ng/L)
d	River depth
D	Diffusion coefficient of THg and MeHg
D_{25}	Diffusion coefficient of ions in water at 25°C (cm^2/s)
D_t	Diffusion coefficient of ions in water at temperature t (cm^2/s)
D_w	Molecular diffusion coefficient in water
Eh	Redox potential (mV)
EtHg	Ethyl mercury
F^-	Flouride ion
Fe^{2+}	Ferrous iron
Fe^{3+}	Ferric iron
FeS_s	Mackinawite
g	Gravitational acceleration
H	Pressure head (cm),
HCl	Hydrochloric acid
HClO	Hypochlorous acid
$\text{Hg}(\text{OH})_2$	Mercury (II) hydroxide
Hg^0	Elemental or metallic mercury
Hg^{2+}	Monovalent or mercurous mercury
Hg_2^{2+}	Divalent or mercuric mercury

Hg _p	Mercury associated with particulate matter
HgS _s	Cinnabar
HSO ₃ ⁻	Hydrogen Sulfite
I ⁻	Iodide ion
J _d	Mass flow rate per length of the river (mass/time/length of river),
k _{bl}	Benthic boundary layer mass transfer coefficient
K _d	Sediment-water partitioning coefficient
m	Manning's coefficient
m	Empirical pore-connectivity parameter
m	Mass accumulated in resin (pg)
Me ₂ Hg	Dimethyl mercury
MeHgCl	Methylmercuric chloride
Mn	Manganese
n	Measure of pore size distribution, greater than 1
NaOH	Sodium hydroxide
NH ₂ OH-HCl	Hydroxylamine-hydrochloride
NH ₃	Ammonia
NO ₃ ⁻	Nitrate ion
OH ⁻	Hydroxide ion
q	Sorption capacity
r _H	Hydraulic radius
S	Salinity (‰)
S ²⁻	Sulfide ion
Sat	Partial pressure of oxygen at max saturation (atm)
Se	Effective saturation value
SH	Thiol group
SnCl ₂	Stannous chloride
So	Zero oxygen partial pressure (atm)
SO ₄ ²⁻	Sulfate
T	Temperature at which profiler was deployed (°C or K)
t	Time of exposure (s)

v_x	River velocity
α	Inverse of the air-entry pressure
Δg	Diffusion and filter layer combined thickness (cm)
ν_w	Kinematic viscosity of water
θ	Volumetric water content (cm^3/cm^3)
θ_r	Residual water content
θ_s	Saturated water content

CHAPTER I

INTRODUCTION

Mercury is a persistent contaminant originating from natural and anthropogenic sources. Fossil-fuel power plants have been identified as the main source of mercury emissions in the environment, releasing approximately 40 tons annually in USA (National Research Council (US) Committee on the Toxicological Effects of Methylmercury, 2000). Methyl mercury (MeHg) is an organic form of mercury that is also a toxin capable of bioaccumulating up the food chain in aquatic systems. Humans are exposed to potentially highly toxic effects of MeHg by consumption of contaminated fish (National Research Council (U.S.). Committee on the Toxicological Effects of Methylmercury., 2000).

River and lake sediment serves as a sink for mercury which is predominately found in an inorganic mercury form (Hg^{2+}) and often associated with organic matter and other elements such as sulfur (e.g. HgS). Mercury in sediments is affected by transport mechanisms such as deposition and erosion that physically relocate sediment particles and associated contaminants. In addition to processes that physically transport sediment particles, sediment is affected by biogeochemical processes, chemical transformation and sequestration and sorption, as well as stable sediment bed processes such as pore water diffusion and advection, bioturbation and desorption to the overlying water (Reible, 2008).

Although a majority of mercury in aquatic sediments is bound to sediments, pore water concentrations may be greater than expected from sediment-water partitioning due

to formation of water-borne complexes such as mercury hydroxides, chlorides, sulfides and natural organic matter and less than expected due to precipitation in effectively insoluble forms such as cinnabar (HgS). The speciation of Hg often leads to a poor correlation between sediment concentrations in solids and biological effects such as organism mortality and growth rate (Di Toro et al., 1991). Measurement of the Hg in pore water may aid in assessing exposure and risks from Hg in sediments by directly assessing the Hg in the most mobile and likely bioavailable phase. The pore water is the first partitioning phase after dissolution or desorption from the sediment and may be better related to the rate of ongoing biogeochemical processes than may be apparent from studies with bulk phase geochemistry (Clarisse, Olivier et al., 2011b). Pore water concentrations may be a better predictor of the pool of more accessible mercury although they are likely not the direct route of exposure for many deposit feeding benthic organisms (Chapman et al., 2002). In order to quantify total and methyl mercury in pore water, diffusion gradient in thin film devices (DGT) were used. DGT devices adsorb and concentrate Hg species that can diffuse through a controlled uptake layer to a strong Hg sorbent. The tool can provide measurements of kinetically labile mercury species in pore water. The tools have proven quantitative for Hg (Bireta, 2015) but there have been challenges in measuring MeHg (Schierz et al., 2014). The recovery of MeHg from DGTs has varied widely and has largely precluded its use to quantify MeHg in pore water.

In the sediment environment, groundwater movement can lead to the greatest fluxes of contaminants through the sediment-water interface. Bireta, 2015 noted that the cyclic inundation and drainage of river banks as a result of the passage of storm events in a watershed can be a significant source of water and potentially Hg from contaminated

banks. Although the potential has been noted there has been little quantification of this mechanism for mercury release from contaminated river banks.

A potential remedy for leaching from a bank during inundation-drainage cycles is *in-situ* capping. *In situ* capping is a process of placing a clean substrate on contaminated sediments to isolate contaminated sediment from the water column and benthic organisms, which typically reside in the top 5-15 cm of sediment (Drott et al., 2008; Skyllberg, 2008). In addition to a physical barrier, a cap can be amended with materials that encourage sorption or transformation of the contaminants and slow or eliminate its migration into the overlying water. Such a cap is characterized as a reactive cap.

Research Objectives

The research presented in this document utilizes laboratory experiments, field and laboratory data and modeling efforts to:

1. Optimize the method of MeHg extraction to achieve quantitative and reproducible recovery of MeHg from DGT resin
2. Perform field sampling during baseline river flow and following a storm event to quantify bank leaching of Hg during inundation and drainage cycles in a freshwater river, South River, in VA
3. Evaluate the effect of bank stabilization and reactive capping on THg and MeHg release at the bank-water interface in the South River
4. Evaluate the long term effectiveness of a reactive cap in reducing THg flux from the bank using modeling

The objectives for the first goal were accomplished using laboratory experiments. The second and third objectives were accomplished using field sampling with DGT passive samplers in the South River at a location where sampling both pre and post bank stabilization was accomplished. A variety of supporting measurements were also conducted including voltammetry and ion specific electrodes to obtain better understanding of redox conditions and dialysis samplers, or peepers, were deployed to better understand pore water constituents affecting speciation of mercury in the system. The final objective was accomplished using COMSOL® for modeling groundwater flow in and out of the river bank and CapSim® to model contaminant transport over 100 years at the bank–water interface. Data obtained both from field sampling, sediment collected from the contaminated bank, and hydrograph data for the South River were used to get a better understanding of the system. The models were used to predict long term Hg leaching from the bank and to compare both pre and post stabilization and capping conditions.

Document Outline

This dissertation is divided into six chapters. The second chapter consists of a literature review on mercury as a contaminant, the health effects associated with uptake of methyl mercury, relevant components affecting mercury fate and transport, the relevance of pore water measurements for understanding mercury fate and transport, sampling techniques used to obtain pore water measurements, and remedial options for mercury containment. The third chapter describes work with optimization of methyl mercury recovery from DGT samplers. The fourth chapter addresses field sampling at South River, VA and evaluation of bank leaching associated with storm events as well as

the effects of bank stabilization on pore water total and methyl mercury during baseline conditions. The fifth chapter contains results of modeling efforts to predict leaching of mercury after the implementation of stabilization efforts as well as long term effectiveness of the placed reactive cap on total mercury leaching from contaminated bank. The sixth chapter summarizes the main conclusions from the work and outlines recommendations for future research based on presented results.

CHAPTER II

LITERATURE REVIEW

2.1. Mercury species

Mercury is a naturally occurring constituent that cycles through the environment while undergoing complex chemical reactions and biologically-mediated transformations. Although naturally occurring, mercury concentrations and biogeochemistry are significantly impacted by anthropogenic perturbations. Mercury is not biodegradable, it is toxic in solution, has high reactivity and affinity to a variety of ligands, making its biogeochemical cycling a complex process (Peijnenburg et al., 2014). Depending on the redox state, mercury exists in three valence states: elemental (metallic, Hg^0), monovalent (mercurous, Hg_2^{2+}) and divalent (mercuric, Hg^{2+}) (Andersson A., 1979; Robinson & Tuovinen, 1984) and is associated with a variety of other minerals and environmental media.

2.2. Health effects of mercury uptake

2.2.1. Toxicity of mercury vs methyl mercury

Although both elemental mercury and inorganic mercury can be taken up into human body, it is methyl mercury that has the greatest impact due to rapid and extensive absorption (EPA, 1997). Mono methyl mercury (MeHg) is a form of mercury that is an acute neurotoxin and it readily bioaccumulates in predatory species of the aquatic food chain. More than 95% of total mercury in the tissue of top predator fish is in the form of MeHg (Feng et al., 2014). MeHg toxicity affects humans, fish, mammals and birds (Anderson et al., 1995; Froelich et al., 1987; Mason, R. et al., 1998; National Research

Council (US) Committee on the Toxicological Effects of Methylmercury, 2000; Scheuhammer et al., 2007).

2.2.2. Consequences of human exposure to methyl mercury

Human exposure to MeHg is mostly through marine fish and freshwater consumption (Fitzgerald et al., 1998). Once absorbed into the body, methyl mercury easily crosses blood-brain and placental barriers. The transfer is carried out with neutral amino acid protein carrier due to similarity of methyl mercury-cysteine complex to methionine. Low dosage effects include IQ deficits, abnormal muscle tone, decrements in motor function, attention and visuospatial performance. Severe effects of methyl mercury neuroexposure include mental retardation, cerebral palsy, deafness, blindness, sensory and motory impairment. Extremely high exposures in Japan (Minamata) and Iraq have led to fatalities and devastating neurological damage (EPA, 1997; National Research Council (U.S.). Committee on the Toxicological Effects of Methylmercury., 2000; Selin, 2009). USEPA criterion for MeHg concentration in fish tissue is set to 0.3 mg/kg, exposure reference dose is 0.1 $\mu\text{g/kg/d}$, whereas half-life of methyl mercury in human body ranges from 44 to 80 days (Eggleston J., 2009; EPA, 1997; National Research Council (U.S.). Committee on the Toxicological Effects of Methylmercury., 2000; USEPA, 2001).

2.3. Mercury fate and transport

2.3.1. Sources of mercury and presence in the atmosphere

Natural sources of mercury Hg^0 release include volcanic and geological activities, as well as various anthropogenic activities. Anthropogenic activities also introduce divalent mercury Hg^{2+} as well as mercury associated with particulate matter Hg_p .

Elemental mercury has low solubility and prefers to be volatilized into the atmosphere and transported over long distances, whereas Hg^{2+} and Hg_p are more soluble in water and are dominant forms during wet and dry deposition. (Andersson A., 1979; Gabriel & Williamson, 2004; Glew & Hames, 1971; Selin, 2009). A sink of Hg^0 in the atmosphere is oxidation of Hg^0 to Hg^{2+} controlled by photochemistry with ozone, $\cdot\text{OH}$ radicals, HClO , HSO_3^- and bromine serving as oxidants (Morel et al., 1998; Selin, 2009).

2.3.2. Mercury in the aquatic systems

During wet and dry deposition, including terrestrial runoff and industrial and municipal point sources, mercury deposits into the aquatic system mostly in inorganic form. The major dissolved mercury forms present in the aquatic systems are elemental mercury, inorganic divalent mercury, and organic mercury. Organic mercury is predominantly MeHg , and in minor quantities dimethyl (Me_2Hg) and ethyl (EtHg) mercury (Andersson A., 1979; Gabriel & Williamson, 2004). Inorganic mercury in aquatic system is often bound to hydroxide, chloride, and organic acids, however sulfide binding has also been observed (Gabriel & Williamson, 2004; Morel et al., 1998). Mercury in the aquatic system can be reduced via photoreduction or microbial reduction and can diffuse back into the atmosphere after being reduced from Hg^{2+} to Hg^0 (Hintelmann, Holger et al., 2000; Ullrich et al., 2001). A small portion of inorganic mercury is methylated in aquatic systems to toxic methyl mercury which is often complexed with chloride in salt waters and hydroxide in fresh waters (Ullrich et al., 2001). Strong associations of inorganic mercury are also formed with natural organic matter or humic substances (Ullrich et al., 2001). Methyl mercury already bioaccumulated in living organisms biomagnifies up the food chain, so concentrations from

phytoplankton, to zooplankton, small and large fish can increase by an order of magnitude (Hintelmann, Holger et al., 2000). The concentration of MeHg in fish can be 10^6 times higher than the MeHg concentration in surrounding water due to the effect of biomagnification (Hsu-Kim et al., 2013). Dimethyl mercury species are unreactive due to partial covalence and hydrolysis reaction (Hintelmann, Holger et al., 2000). The majority of inorganic mercury is bound to particles or precipitates and has very low solubility (Hintelmann, Holger et al., 2000), although substantial amounts may be associated with dissolved and suspended particulate organic matter. Organic matter greatly assists with mercury transport in surface water (Hsu-Kim et al., 2017). Mercury deposited in sediments can serve as a long term source of mercury to surface waters (Gabriel & Williamson, 2004).

2.3.3. Mercury in the sediments

2.3.3.1. Mercury speciation

Sediments at the bottom of water bodies have been found to be major sinks for mercury due to their tendency to bind to particulate matter and settle (Andersson A., 1979; Gilmour, C. C. et al., 1992; Mason, R. P. et al., 1994; Morel et al., 1998; Selin, 2009; Skjellberg et al., 2003; Ullrich et al., 2001). Surficial sediments are of special interest due to the greatest potential of release of methyl mercury into the water column as well as the greatest net rate of mercury methylation (Bloom, N. S. et al., 1999; Korthals & Winfrey, 1987). The sediment-water partitioning coefficient is sometimes used to characterize other conditions under the assumption of linear partitioning and local equilibrium (Lampert & Reible, 2009) (Equation 1).

Equation 1 Sediment water partitioning coefficient

$$K_d = \frac{C_s}{C_d}$$

Where the sediment-water partitioning coefficient (K_d) characterizes the ratio of bulk solid mercury (C_s) to dissolved mercury concentration (C_d) (Di Toro et al., 1991).

The K_d value for THg in estuarine and coastal water ranges from 10^5 - 10^6 L/kg in (Fitzgerald et al., 2007) and 10^5 - 10^7 for freshwater systems (Kocman et al., 2011). K_d for MeHg in oxic surface seawaters is 10^4 - 10^5 L/kg (Fitzgerald et al., 2007), and 10^3 - 10^5 in freshwater systems (Lampert & Reible, 2009). The use of a constant K_d is a crude approximation and does not take into account the various forms of mercury and their solubility and stability. Stable insoluble forms such as cinnabar (HgS), for example, lead to very high apparent K_d 's while other, more soluble forms, lead to much smaller apparent K_d 's.

Mercury(II) in sediments consists of soluble inorganic mercury, soluble organic-associated mercury, mercury(II) adsorbed to inorganic components (such as iron oxides, manganese oxides, and clay minerals), mercury precipitated as insoluble salts (such as HgS) and mercury (II) adsorbed to soil organic matter, with humic and fulvic acids representing predominant dissolved organic matter (Gabriel & Williamson, 2004; Morel et al., 1998; Zhang, H. & Lindberg, 1999). Cinnabar (HgS) has very low solubility and is considered to account for majority of mercury in sediments, particularly under reducing conditions (Bonnissel-Gissinger et al., 1999; Morel et al., 1998). Precipitation of cinnabar is considered to decrease concentrations of all mercury species in solution, but apparently has no effect on their relative concentrations, i.e. the distribution of soluble species in the pore water (Skylberg, 2008). Reduction in soils mostly occurs abiotically via Fe^{2+} , fulvic

and humic acids (Gabriel & Williamson, 2004; Ullrich et al., 2001), but it has also been found to be partially biotically controlled (Fritsche et al., 2008; Porvari, 2003). Although binding to sediments is affected by formation of HgS and other reduced species, oxic conditions in sediment mostly enhance sediment uptake of Hg and MeHg, whereas reduced conditions enhance Hg release from the sediments due to dissolution of oxyhydroxides, Fe and Mn oxides (Ullrich et al., 2001). In terms of strength of complexes, the strongest complexes of inorganic mercury are built with Cl^- , OH^- , S^{2-} , thiol functional groups, and NH_3 . Moderate strength complexes are built with Br^- , I^- , and nitrogenous ligands, and weakest complexes are built with F^- , SO_4^{2-} , and NO_3^- (Gabriel & Williamson, 2004; Schuster, 1991)

Methyl mercury (MeHg) and dimethyl mercury are also present in sediments. MeHg in sediment is commonly bound to chlorides, hydroxides and thiols however is unable to bind to multiple ligands (Gabriel & Williamson, 2004). In general the binding of MeHg to solid phases is less than inorganic Hg. The affinity of MeHg towards common ligands decreases in the following order: $\text{R-S}^- > \text{SH}^- > \text{OH}^- > \text{Cl}^-$ (Dyrssen & Wedborg, 1991; Gabriel & Williamson, 2004).

Mercury complexes exhibit different solubilities. HgCl_2 and MeHgOH are less soluble than MeHgCl and Hg(OH)_2 as indicated by their greater octanol-water partitioning coefficient (Chapman et al., 2002; Gabriel & Williamson, 2004). This also implies that fluxes of MeHgCl and Hg(OH)_2 from sediment into overlaying water are typically greater (Gabriel & Williamson, 2004). MeHg can be directly taken up by living organisms, whereas non-adsorbed mercury can be more readily available for methylation by methylating microorganisms (Gabriel & Williamson, 2004).

2.3.3.2. Net methylation rate

Net methylation rates are determined by the difference between methylation and demethylation rates. The production of methyl mercury (MeHg) depends on the geochemical speciation of biologically relevant inorganic mercury taken up by methylating microorganisms and conditions that encourage methylation. Conditions that encourage methylation include reducing environments and the presence of sulfate and organic matter to drive microbial activity as electron acceptor and donor (Benoit et al., 2002; Berman & Bartha, 1986; Bigham et al., 2016; Gilmour, C. C. et al., 1992; Gilmour, C C et al., 1998; Hintelmann, Holger et al., 2000; Hsu-Kim et al., 2013; Korthals & Winfrey, 1987; Tang et al., 2013; Zhu et al., 2017). MeHg concentrations detected in-situ have been shown to be dominated by methylation processes in the surface sediments (<15 cm), and is more affected by both methylation and demethylation processes in the deeper sediments (Drott et al., 2008; Skjellberg, 2008). The MeHg/Hg ratio depends not only on MeHg and THg, but also on a variety of other factors that affect speciation of Hg and MeHg under changing conditions (Skjellberg, 2008). The following sections address methylation and demethylation processes.

2.3.3.2.1. Methylation

Although there is a possibility of abiotic mechanisms to form MeHg, biochemical methylation accounts for over 90% of overall methylation under anaerobic conditions (Benoit et al., 2002; Berman & Bartha, 1986). Optimum conditions for methylation are found in anoxic conditions near the oxic/anoxic interface few centimeters below the surface (Berman & Bartha, 1986; Gilmour, C. C. et al., 1992; Gilmour, C C et al., 1998; Hintelmann, Holger et al., 2000; Korthals & Winfrey, 1987; Ramalhosa et al., 2006;

Tang et al., 2013; Zhu et al., 2017), although some methylation might be possible in oxic conditions (Robinson & Tuovinen, 1984). Formation of MeHg is typically restricted to the top 15 cm of active surface layer (Sunderland et al., 2004). Methylating microorganisms have presence of *hgcAB* cluster in their genomes encoding for proteins involved in intracellular methylation of inorganic mercury (Parks et al., 2013). This gene pair is not that common in microorganisms but has been mostly found in heterotrophs using sulfate, iron and CO₂ as terminal electron acceptors (Gilmour, Cynthia C et al., 2013). Identification of *hgcAB* genes in these microorganisms builds upon previous understanding of principal methylators being sulfate, iron (Fe³⁺) reducing bacteria, and methanogens (Bigham et al., 2016; Compeau & Bartha, 1985; Fleming et al., 2006; Gilmour, C. C. et al., 1992; Gilmour, C C et al., 1998; Hsu-Kim et al., 2013; King et al., 2000; Selin, 2009). This finding also explains MeHg production in the zones where methanogenesis is a dominant process, although there have been findings that mixed natural sediment populations usually have smaller contributions from methanogenic group as compared to sulfate and iron reducing bacteria (Fleming et al., 2006). It also explains methylation occurring not only in neutral, but also in alkaline and acidic environments. Methylation in surface ocean waters is known to be possible but is still poorly understood since majority of environments with high methylation are anoxic (Gilmour, Cynthia C et al., 2013; Kirk et al., 2008).

Microorganisms are capable of reduction of Hg(II), degradation of MeHg, methylation of Hg(II) and oxidization of Hg(0) to Hg(II) (Porvari, 2003). During methylation, MeHg can cross cell membrane via passive transport and bio-concentrate over a million times in the food chain. Environmental strains found to be capable of

methylation have been identified as proteobacteria, with a few exceptions. Sulfate reducing bacteria, obligate anaerobes using sulfate as terminal electron acceptor, are the most studied microbial methylators (Hsu-Kim et al., 2013). Their activity has been observed with additions of sulfate to stimulate activity and molybdate to inhibit it. In addition to sulfate reducing bacteria, *Shewanella* spp. iron reducing bacteria and *Methanococcales*, *Methanobacterials*, and *Methanosarcinels* methanogens have also been found to be effective methylators (Hsu-Kim et al., 2013).

Microbial methylation is presumed to be an intracellular reaction, which makes transport of bioavailable mercury from extracellular surroundings through outer and inner wall an important step in understanding biological methylation. Hsu Kim et al. presented an overview of 4 different scenarios in which this transport could happen. In the Mer-based transport system, transport protein MerP binds Hg(II) in periplasm after it has passed the outer membrane and passes it to MerT protein allowing mercury to pass the inner membrane and transfer to MerA protein for reduction. In the passive diffusion scenario, neutrally charged complexes such as HgCl₂ and Hg(SH)₂ diffuse through both outer and inner membrane. In the third scenario of facilitated diffusion, neutrally charged or ionic species are transported through transmembrane protein channel. In the active transport scenario such as the one which Gram+ microorganisms are using, mercury is actively transported using energy-dependent transmembrane protein pump. Transport is dependent on the Hg-ligand complexes in extracellular surroundings, periplasm and cytoplasm, type of mechanism occurring, and binding affinities to membrane receptors in the scenarios using it (Benoit et al., 1999; Eckley, Chris S. et al., 2017; Hsu-Kim et al., 2013)

Gene clusters *hgcA* and *hgcB* encode putative coronoid protein facilitating methyl transfer and a ferredoxin carrying out coronoid reduction which causes mercury methylation (Hsu-Kim et al., 2013; Parks et al., 2013). Intracellular methylation of mercury in SRB is followed by rapid transport or diffusion of MeHg outside the cell. Methylation of inorganic Hg(II) is occluding through methyl-cobalamin compounds and acetyl-coenzyme A, although there are other biological pathways. Microbial mercury methylation is most likely using methylcobalmin as methyl donor (Ullrich et al., 2001). The speed of organism growth seems to impact MeHg accumulation, with slow growing and longer lifespan organisms accumulating more MeHg than fast-growing or shorter life-span ones (Bigham et al., 2016). Inorganic mercury uptake may be possible via diffusion of neutral mercury complexes. Mercury present within a cell is usually bound to enzyme or a ligand, as opposed to being a free metal ion (Benoit et al., 2002).

Although abiotic methylation accounts for only a small fraction of methylation in the environment, these process may become important for understanding potential artifacts during extraction periods (Bloom, N. S. et al., 1997; Hintelmann, H. et al., 1997). Abiotic methylation is also correlated to methyl iodide and dimethylsulfide, fulvic and humic acid. Other mechanisms for abiotic methylation include organometallic complexes such as methylcobalamin, methyllead, or methyltin compounds (Celo et al., 2006). In freshwater systems, methylcobalamin is capable of methylating inorganic mercury in acidic pH with low concentration of chloride (Celo et al., 2006).

2.3.3.2.2. *Demethylation*

The main demethylation route are biological due to reduction by *mer* operon mediated pathways, oxidative demethylation predominately via aerobic organisms, and

abiotic due to photochemical decomposition in photic zones of surface waters (Benoit et al., 2002; Bigham et al., 2016; Hintelmann, Holger et al., 2000; Robinson & Tuovinen, 1984; Ullrich et al., 2001). The end product of demethylation is either elemental mercury and methane during reductive bacterial processes, or Hg^{2+} when oxidative demethylation occurs via aerobic organisms (Hintelmann, Holger et al., 2000; Hsu-Kim et al., 2013). Demethylation is generally dominated by methylation in the reducing zone of near surface sediments (<15cm), however appears to be more relevant in oxic sediment and at greater depths (up to 1 meter depth) (Drott et al., 2008)

2.3.3.3. Bioavailability of the mercury

Bioavailability depends on the geochemical speciation of mercury and presence of dissolved ions (Gabriel & Williamson, 2004). There are various approaches for assessment of the amount of bioavailable mercury for uptake by bacteria and methylation, which include thermodynamic modeling, molecular approaches, and chemical extraction (Marvin-DiPasquale et al., 2009). All of the approaches suggest that only a small fraction of total available inorganic mercury pool is biologically relevant (Hsu-Kim et al., 2013; Marvin-DiPasquale et al., 2009). Neutral dissolved species are considered to be available for methylation, whereas the solid and positively charged species inhibit biological uptake (Morel et al., 1998). Natural waters commonly contain Hg^{2+} complexes with chloride, inorganic sulfide, and dissolved organic matter, as well as Hg(II) associated with particles. These phases range from dissolved, colloidal, to particulate phases, with dissolved and colloidal phases associated with natural organic matter. Passive diffusion is the mechanism of transfer of neutral species such as Hg(SH)^0 and HgS^0 into bacteria capable of methylation (Hsu-Kim et al., 2013). In one isotope

study, dissolved mercury sulfide species were found to be more bioavailable than dissolved mercury nitrates, whereas mercury associated with fulvic acids were less bioavailable than mercury nitrates, and thus were methylated at a lower rate as compared to first two species (Hintelmann, Holger et al., 2000).

2.3.3.4. Mercury in the pore water

In order to better quantify biologically relevant and mobile fraction of Hg, dissolved Hg in interstitial pore water is often measured (Bigham et al., 2016; Hsu-Kim et al., 2013; Zhang, Hao. & Davison, 1995). Measurements of interstitial pore water can be considered biologically relevant portions of mercury as they can be ready to be methylated, demethylated and available for biological uptake or can undergo speciation under different conditions to become available for methylation and biological uptake (Benoit et al., 1999; Marvin-DiPasquale et al., 2009). Sediment pore water can also readily release mercury into overlaying water (Randall & Chattopadhyay, 2013)

2.3.4. Sulfur interactions with mercury fate and transport

Sulfur oxidizes to sulfate in the environment and promotes mercury methylation by serving as an electron acceptor for sulfate reducing bacteria (Gilmour, Cynthia C. & Henry, 1991; Morel et al., 1998). Sulfate is reduced into inorganic sulfide, which controls speciation of mercury by forming dissolved polysulfide mercury complexes that can outcompete other ligands due to their higher formation constants ($\text{Hg}(\text{S}_n)\text{SH}^-_{(\text{aq})}$ ($n = 4-6$)) or solid phases ($\text{HgS}_{(\text{s})}$) (Bailey et al., 2017; Benoit et al., 1999; Morel et al., 1998; Orem et al., 2011). As a result, sulfate availability controls the activity of sulfate reducing bacteria, whereas sulfide production and accumulation controls methylation rates (Benoit et al., 2002). Sulfate concentration of 1-20mg/L are considered to be optimal in terms of

promoting maximum MeHg production. Levels below 1 mg/L of sulfate have been found to limit microbial sulfate reduction, whereas levels above 20 mg/L cause buildup of sulfide that inhibits MeHg production (Feng et al., 2014; Gilmour, C. C. et al., 1992; Orem et al., 2011; Oswald & Carey, 2016). Environments with sulfide concentrations lower than 10-50 μM are considered to reach an optimum net MeHg production (Gilmour, C C et al., 1998; Skjellberg, 2008). Oxidation of sulfide results in metal speciation that increases biological relevance and toxicity (Chapman et al., 2002). In the event of high dissolved sulfide concentration, the inhibition of methylation is likely due to enhanced precipitation of HgS, formation of solid thiols depending on sulfide concentration to which Hg is sorbed, or (to a lesser extent) formation of dimethyl mercury from reaction of MeHg with H_2S (Benoit et al., 1999, 2002). Organic sulfides or thiols (e.g. cysteine, glutathione) are known to affect Hg and MeHg speciation. Thiols are able to compete with bisulfides for mercury, so pore water of typical wetland sediment with 50mg DOC/L and 0.15% of DOC composed of thiols with the general form RSH is considered to have Hg equally complexed by inorganic sulfides and organic thiols (Skjellberg, 2008). About 50% of total MeHg near the sediment-water interface has found to be in MeHg-cysteine complexes in one study, with remaining 50% in the form of MeHg sulfide complexes (mainly MeHgS^-) with negligible free MeHg^+ , MeHgOH , and MeHgCl (Zhang, J. et al., 2004). Presence of dissolved sulfide can lead to a variety of complexes forming, such as HgS^0 , $\text{Hg}(\text{SH})_2^0$, $\text{Hg}(\text{SH})^+$, HgS_2^{2-} and HgHS_2^- . As the sulfide concentration increases, speciation shifts towards positively charged complexes, thus reducing presence and diffusion of neutral complexes into sulfate reducing bacteria (Benoit et al., 2002). At $\text{pH} < 7$, the dominant form of sulfide is volatile hydrogen sulfide

(H₂S), whereas at pH>7, the dominant form is readily oxidized sulfide ion (HS⁻), which can rapidly decrease pH (Chapman et al., 2002). In the presence of sulfidic conditions (of less than 10⁻⁴ M total sulfide), HgS⁰ is presumably the major neutral complex available for uptake by bacteria, whereas other forms of dissolved mercury such as HgS(SH)⁻ become important (at total sulfide levels greater than 10⁻⁴M) (Benoit et al., 1999; Hsu-Kim et al., 2013). In the suboxic region, with total S(-II) range from 0.01-10 µM, both inorganic and organic ligands are available for sulfate and iron reducing bacteria uptake (Skylberg, 2008).

Acid Volatile Sulfide (AVS) measurements are often used to predict potential availability of metals in sediments. Acid volatile sulfides are the sulfides released upon acidification of the sediment. Acidification also releases the sulfide bound metals, referred to as the simultaneously extracted metals (SEM). Metals are considered bound to the sediment as sulfides and unavailable if the ratio of AVS to SEM is greater than 1, as there are excess sulfides to bind metals. Although high AVS/SEM ratio indicates unavailability of metals and low toxicity, low ASM/SEM ratio does not necessarily indicate availability of the metals as other binding phases in solid become more important (Reible, 2014).

2.3.5. Chloride interactions with mercury fate and transport

Higher chloride concentrations in sediment are correlated to higher methylation rates expected and increased mobilization of Hg (Benoit et al., 1999; Gabriel & Williamson, 2004; Ullrich et al., 2001). Chloride can enhance desorption of Hg²⁺ by breaking HgS bond and increasing solubility of HgS (Benoit et al., 1999; Gabriel & Williamson, 2004). Surface water chloride concentrations at about 10⁻⁴ M can increase

HgS solubility over 400 times (Schuster, 1991). Chloride presence can reduce inorganic and MeHg sorption capacity of inorganic and organic materials (Gabriel & Williamson, 2004; Reimers & Krenkel, 1974). Higher concentrations of chloride also assist in formation of HgCl_2 , which have been correlated to facilitated diffusion uptake by phytoplanktons and higher permeability through artificial membranes. (Benoit et al., 1999; Hintelmann, Holger et al., 2000) However, at concentrations above 1mM, a decreased bioavailability is likely due to speciation of chloride complexes to negatively charged, unfavorable HgCl_3^- and HgCl_4^{2-} (Feng et al., 2014).

2.3.6. Nitrogen and phosphorous interactions with mercury fate and transport

Nitrogen and phosphorous are both nutrients which can lower MeHg uptake via bio dilution by increasing overall biomass. Oxidic conditions can also be altered using nitrate additions, however overall effect between changing nutrients, carbon loading and oxidic conditions does not have a definite continuous response of the system in change of MeHg concentrations in biota (Hsu-Kim et al., 2017)

2.3.7. Iron and selenite interactions with mercury fate and transport

Iron and selenite both have the ability to decrease bioavailability of inorganic mercury. Iron reduces concentrations of neutral biologically relevant species and promotes reduction of Hg(II) to neutral Hg(0) in a form of mackinawite (FeS_s), whereas selenite forms insoluble Hg selenites (Bigham et al., 2016; Dyrssen & Wedborg, 1991; Winfrey et al., 1990). As opposed to organic substances which are the most effective sorbents in acidic soils ($\text{pH} < 4.5-5$), iron oxides and clay materials are the predominant oxides in neutral soils (Schuster, 1991; Zhang, H. & Lindberg, 1999).

2.3.8. DOM interaction with mercury fate and transport

Dissolved organic matter (DOM) includes high molecular weight compounds formed from condensation of degraded cellular material that forms natural organic colloids such as amino acids. DOM is considered to be smaller than 45 μ meters and is generally considered to be consisting of humic and fulvic acids. DOM presence increases bacterial activity by serving as an electron donor and labile carbon has also been attributed to microbial growth, which has been used to explain positive correlation of organic carbon in sediments and MeHg concentrations observed (Bigham et al., 2016; Hsu-Kim et al., 2013). However, DOM has also been correlated to decreases in methylation rates due to reduction in Hg bioavailability by forming stable Hg-DOM complexes with ionic mercury which decrease speciation and bioavailability of mercury in aquatic environments due to their macromolecular size and hydrophilic nature (Bigham et al., 2016; Hsu-Kim et al., 2013). DOM has been found to inhibit precipitation of metacinnabar (black β -HgS), and to facilitate nucleation to enhance dissolution of cinnabar (red α -HgS) due to similar coordination structure with the metacinnabar which results in formation of amorphous Hg-S-DOM complexes (Bigham et al., 2016; Gabriel & Williamson, 2004; Gilmour, Cynthia C. & Henry, 1991; Hsu-Kim et al., 2013; Schuster, 1991). Organic matter has been shown to affect THg soil-water partitioning coefficient, K_d , where increase in the amount of organic matter in pore water decreases K_d value (Eckley, Chris S. et al., 2017; Liem-Nguyen et al., 2016). Vegetation and organic matter stored in dry sediments provide a great storage and source of dissolved organic matter (Strickman & Mitchell, 2017b). Dissolved organic matter has a large effect on partitioning of mercury species, with fresh waters being more effected than salt

waters due to chloride ion competition. In a fresh water, more than 70% of the MeHg has been found associated with dissolved organic carbon complexes (Ullrich et al., 2001). Humic substances constitute 40-60% of dissolved organic carbon in the system (Thurman, 1985). Humic substances can complex metals and affect metal mobility, solubility, sorption to surfaces, reactivity and biogeochemical processes such as redox reactions and uptake by microorganisms and transformation reactions, including methylation of inorganic mercury (Hintelmann, H. et al., 1997; Nagase et al., 1982), as well as reduction of ionic mercury into elemental mercury during photochemical reactions (Randall & Chattopadhyay, 2013). Both mercury and methyl mercury associate with humic substances, especially in oxic conditions in the absence of sulfide, and this interaction facilitates transport of mercury in the systems from sediments to streams, lakes and groundwater (Hintelmann, Holger et al., 1997; Randall & Chattopadhyay, 2013).

2.3.9. pH effects on mercury fate and transport

pH effects on both microbial activity and partitioning of methyl mercury between sediment and water. A decrease in pH (from 5.5 to 4.5) can cause an increase in HgS solubility, increase in methyl mercury partitioning into water, decrease in Hg solubility into pore water, decrease in demethylation rate and thus higher MeHg net production, and increase in the binding of the organic matter to inorganic mercury (Celo et al., 2006; Gabriel & Williamson, 2004; Gilmour, Cynthia C. & Henry, 1991; Hudson et al., 1994; Ullrich et al., 2001). Increase in the pH of the systems (range 6-8) leads to more rapid Hg(II) reduction and subsequent Hg(0) volatilization which limits substrate availability for methylation (Hudson et al., 1994). pH affects competition between thiols and Hg-

polysulfides, i.e. at pH 7 thiols are outcompeted by Hg-polysulfides, whereas at pH 4 polysulfides are not as competitive, resulting in even speciation between mercury thiols and polysulfides (Skylberg, 2008). In pH range of 4.7-7.5, common forms of MeHg present in the system are MeHgCl, MeHgOH, and free MeHg ions (Gabriel & Williamson, 2004), whereas inorganic mercury is mostly in Hg(OH)₂ and HgOH⁺ form (Randall & Chattopadhyay, 2013). An inverse relationship has been discovered between pH and MeHg present in fish muscle tissue (Benoit et al., 2002). Mercury adsorption decreases as pH decreases due to increased hydrogen ions removing and replacing mercury ions (Gabriel & Williamson, 2004). Moreover, low pH facilitates release of heavy metals and particulate matter from sediments (Randall & Chattopadhyay, 2013). Desorption of MeHg from humic functional groups have been observed at pH of 5.2 (Gabriel & Williamson, 2004). Thiol bound mercury is expected to decrease with lower pH (Andersson A., 1979; Gabriel & Williamson, 2004; Schuster, 1991; Xu, J. et al., 2014). Methylation has been observed in natural waters with pH as low as 5.7 (Gilmour, C. C. et al., 1992). MeHg is found to be more soluble under low pH conditions (Randall & Chattopadhyay, 2013).

2.3.10. Temperature effects on mercury fate and transport

Temperature increases microbial activity by enhancing reducing conditions, resulting in increased net methylation. Increased net methylation is due to methylation in surficial sediment prevailing over demethylation rates (Bigham et al., 2016; Gilmour, C C et al., 1998; Korthals & Winfrey, 1987; Montgomery et al., 2000; Ullrich et al., 2001). Optimum temperature for mercury methylation in freshwater systems is 35 °C (Winfrey et al., 1990). Increased temperature can also decrease mercury adsorption on mineral and

organic surfaces (Gabriel & Williamson, 2004). At higher temperatures, HgCl_2 uses the least amount of heat to be desorbed, as compared to organic complexes and cinnabar (Gabriel & Williamson, 2004). Thus, with increased heat, desorption of HgCl_2 can increase the amount of available Hg. Heat also increases volatilization of Hg^0 from the soil (Gabriel & Williamson, 2004).

2.3.11. Particle size and mercury fate and transport

Finer sediments, such as silt and clay are commonly found to also be associated with reducing conditions and high net methylation rates, whereas more oxic conditions are common in gravelly sediments and lower net methylation rates. Mercury often associates with organic and inorganic particles in fine soil, and finer sediments are associated with higher THg concentrations (Marvin-DiPasquale et al., 2009). Colloids can increase effective solubility of mercury by complexing with ionic mercury and thus increasing mass of mercury available to partition into mobile phase containing water and colloidal matter (Reible, 2008). Colloids are associated with transport of mercury from sediments to streams, lakes, and groundwater due to their greater surface area surface area to volume ratio of particles, thus providing more solid phase binding sites for ionic Hg species (Babiarz et al., 1998; Gabriel & Williamson, 2004; Marvin-DiPasquale et al., 2009; Plourde et al., 1997; Randall & Chattopadhyay, 2013).

2.3.12. The “age” of mercury and mercury fate and transport

There has been some evidence through isotope studies that mercury newly introduced into the environment is more readily methylated, volatilized, reduced and available for ligand exchange in the first 24 hours (Strickman & Mitchell, 2017a). MeHg accumulation was found to be enhanced in the younger wetlands and declines afterwards,

as seen in environments including beaver ponds, wetlands and reservoirs (Strickman & Mitchell, 2017b). The effects of “age” are more likely indicating that size and strength of association of particulate Hg with particles containing sulfides and NOM are important factors controlling bioavailability. “Newer” forms are weakly sorbed, nanostructured particles that are more bioavailable than “older” Hg forms, that are likely indicating strongly sorbed and precipitated reduced phases that are less bioavailable (Bigham et al., 2016; Hsu-Kim et al., 2017).

2.3.13. Water level fluctuations effects on mercury fate and transport

Water-level fluctuations (WLF) have shown to have effects on mercury fate and transport as compared to constantly inundated sediments. During the time where there is lack of water inundating the sediments, sulfide is oxidized to sulfate, and iron(II) to iron (III) (Feng et al., 2014; Gilmour, C. et al., 2004). During water-level fluctuations bank sediment is inundated, providing new nutrients and dissolved inorganic mercury can partition from contaminated bank soil into pore water. The bank sediments are oxic since they were previously unsaturated and exposed to air and thus methylation is discouraged and more soluble forms of mercury are preferred. This mercury can then leach from the contaminated floodplains during the drainage cycle of the storm event (Bigham et al., 2016; Eckley, Chris S. et al., 2017). Water level fluctuations also increase sulfate and labile organic matter present in the system. Once the reoxygenated system gets reduced, sulfate and labile organic matter drive microbial activity, contributing to net increase of methylation of mercury (Feng et al., 2014; Gilmour, C. et al., 2004). A duration of 10-15 days has been found sufficient to observe development of optimum reduced condition resulting in maximum net methylation rate (Brigham et al., 2002). This phenomena has

been observed in hydrologic reservoirs where elevated MeHg concentrations were detected upon reservoir creation (Anderson et al., 1995; Bigham et al., 2016; Brigham et al., 2002; Eckley, C.S. et al., 2015; Eckley, Chris S. et al., 2017; Gilmour, C. et al., 2004; Montgomery et al., 2000; Plourde et al., 1997; Sorensen et al., 2005; Ullrich et al., 2001). A study by Strickman and Mitchell concluded that the effect of repetitive water level fluctuations at a designed wetland was not correlated with increase in MeHg and this phenomena was rather an effect of extreme draughts and rewetting cycles influencing sediments that are not commonly in the zone of water level fluctuations (Strickman & Mitchell, 2017b). In a study by Gilmour et al., rewetting caused increase in sulfate concentration in overlaying soil from <1mg/L to over 200mg/L (Gilmour, C. et al., 2004). This was linked to organic soil oxidizing reduced sulfur species to sulfate which also stimulates methylating bacteria once conditions turn more reduced and stimulate methylation (Eckley, C.S. et al., 2015; Eckley, Chris S. et al., 2017; Gilmour, C. et al., 2004; Orem et al., 2011). The phenomena of the effects of dry/wet cycle has also been observed with measurement of Hg fluxes from sediment into the air. An increase in Hg emissions from soil into ambient air has been observed in deserts following a rainfall event, with the maximum flux out of the sediment appearing in the first 30 minutes after moisture has been added to the sediments (Lindberg et al., 1999).

2.4. Pore water measurements

Pore water is the most available and mobile media in sediments and is considered a key exposure route for contaminants, although it is not the only exposure route (Chapman et al., 2002). Sediment pore water measurements have been correlated to the biological effects such as organism mortality, growth rate, and bioaccumulation (Di Toro

et al., 1991). Moreover, the effects of concentrations found in pore waters were similar to the concentrations found in aquatic systems (Di Toro et al., 1991). Soluble metal concentration measurements in pore water are often greater than predicted values using sediment-water partitioning due to complexation of metals with ligands and numerous interactions between sediment and solid phases (Ankley et al., 1994; Chapman et al., 1998). Pore water concentrations potentially predict overall activity of metal in the sediment environment as they are considered first partitioning phase of contaminant due to desorption or dissolution from the sediment particulates (Ankley et al., 1994; Chapman et al., 2002; Peijnenburg et al., 2014). As a result, the main benefit of having pore water measurements is ability to detect mercury species that might be the most representative of the biologically relevant pool of mercury to benthic organisms (Chapman et al., 2002).

2.4.1. Pore water sampling methods

Pore water sampling methods for mercury include ex-situ and in-situ approaches. Ex-situ sampling includes collection of samples via grab samplers and coring, followed by centrifugation and squeezing extraction techniques. The techniques for pore water extraction can be separated in three approaches, including core collection and sectioning followed by centrifugation and filtration, squeezing of the core or sediment using gas pressure to extract water and lastly passive samplers deployed in-situ (Mason, R. et al., 1998).

In-situ sampling includes passive sampling devices and tube samplers. When analyzing for mercury, the sampling has to be done in a way that minimally disrupts the sample, as this can change speciation of mercury in the sample by changing redox conditions or resuspending solid particles, to which metal contaminants have strong

partitioning preference due to their large K_d value (Fitzgerald et al., 2007). This encourages the use of passive sampling techniques.

2.4.1.1. Core sectioning followed by centrifugation and filtration

Centrifugation involves obtaining sample cores, typically in plexiglass tubes. The issue with coring is the potential introduction of oxic conditions during coring or subsequent processing. Cores are usually frozen, and then sliced into intervals in an anaerobic chamber. Subsamples are centrifuges, for example by placing in 40mL polysulfone and polycarbonate centrifuge tubes with sealing caps in a refrigerated centrifuge at 5000 rpm for 20min. After returning the samples to an anaerobic chamber, the supernatant liquid is placed in a plastic syringe and filtered using 0.45 μ m polysulfone filter (Bufflap & Allen, 1995; Carignan et al., 1985). The advantages of the method are ability to generate relatively large volumes of pore water. The method has issues with sample oxidation which affects the speciation of redox sensitive sample, as well as temperature variations during processing of the sample (Carignan et al., 1985).

2.4.1.2. Squeezing of the core/sediment using gas pressure to extract pore water

Vacuum filtration involves using polyethylene sediment probes to which 0.25in thick porous polyethylene is inserted at different intervals. Polyvinylidene fluoride (PVDF) tubing is inserted to transfer pore water samples from the probe through nylon filter to polyallomar centrifuge tube of an anaerobic jar modified with polypropylene and PVC fittings (Bufflap & Allen, 1995).

The method of vacuum squeezing for pore water extraction uses rubber diaphragm in-line with polysulfone 0.45 μ m filter in combination to compression obtained from nitrogen gas at pressures 20-40psi (Bufflap & Allen, 1995). A moving

piston is used to compress sediment, displacing pore water from sediment which is collected using syringe (EPA & Cantwell, 2013). Both vacuum filtration and squeezing methods have been shown to produce poor chemical results and have issues with implementation, including limited pore water volume extraction and time consuming preparation (Bufflap & Allen, 1995; EPA & Cantwell, 2013)

A Henry's Sampler consists of a tube with sampling openings inserted into the sediment and a vacuum hose attached to a syringe or peristaltic pump to collect pore water. Benefits of Henry's samplers are simplicity, reusability between sites, and relatively low cost. Disadvantages are limited sampling volume, lack of ability for spatial profiling, and potential for interference or disturbance of the sample during sampling since water can be drawn from areas well away from the sampled location. In particular, near surface samples could draw overlying water into the pore water sample (Bireta, 2015; USEPA, 2005).

2.4.1.4. Passive sampling in sediments

Passive sampling methods do not require collection and transport of the environmental media and minimize disturbance, allowing collection of measurements that are more representative of undisturbed site conditions. Passive sampling is beneficial due to its ability to detect episodic events and cyclic changes depending upon the characteristic sampling time of the sampler, reduce sampling artifacts from the disturbance associated with conventional sampling methods, and measure spatial variations depending upon the characterizing sampling scale of the sampler. Potential limitations include detection limit concerns due to the small volume of water sampled and potentially restricted uptake rates. Device design also may introduce limits to

measurements (i.e. lack of sufficient volume collected when using diffusive dialysis membrane), and potential issues introduced during deployment of profilers that may change redox conditions (Peijnenburg et al., 2014).

2.4.1.5. Dialysis samplers (peepers)

A dialysis sampler or peeper is a reservoir(s) covered with a membrane which allows slow equilibration with adjacent sediment pore water, and requires deployment of one week or longer (Mason, R. et al., 1998). In general, any size membrane can be employed as long as diffusion between a sampling chamber and the surrounding medium is the operative uptake process. It was first described in 1976 and developed for use with metals in 1985 (Davison, William, 2016). The peeper frame is commonly made from acrylic (plexiglass) frame and the compartments are filled prior to deployment with deoxygenated ultrapure water. A microbially resistant membrane is placed on top which for mercury might be a 0.2 μ m nominal pore size polysulfone material (Peijnenburg et al., 2014). Peepers are used for measurements of total dissolved concentrations of solutes of interest (Peijnenburg et al., 2014) and measurements have been found to agree well with measurements obtained using centrifugation (Bufflap & Allen, 1995; Carignan et al., 1985). Benefits when using peepers are high vertical resolution and low potential for introduction of artifacts. Issues that might occur when using dialysis membrane is incomplete equilibration (commonly addressed by the implementation of tracer into dialysis cell compartments), membrane breakdown, limiting volume, and charge effects on free diffusion of ions across the membrane (Carignan et al., 1985).

2.4.1.6. Diffusive equilibration in thin films-DET

Diffusive equilibration in thin film technique (DET) was developed in 1991 and is an equilibrium device that uses a thin hydrogel layer, as opposed to the membrane in a peeper. The thin film allows a quicker equilibration than peepers and higher resolution of measurements that is limited by the thickness of the layer (Peijnenburg et al., 2014).

Unconstrained DETs have issues with diffusional relaxation upon retrieval and are preserved in NaOH to minimize these issues although loss of iron and manganese hydroxides is possible (Peijnenburg et al., 2014). Constrained DETs use agarose hydrogel to prevent contact between compartments and allowed for a deployment within days. DET gels allowed for spatial resolution in form of mm scale cuts and analyzed gel could be back-equilibrated for analysis (Davison, William, 2016).

2.4.1.7. DGT

2.4.1.7.1. DGT development

Diffusive gradient in thin film (DGT) technique was adapted from DET technique and was originally developed for measuring zinc in seawater (Davison, W. & Zhang, 1994). Unlike DET devices which need equilibrium between solutes and device solution, DGT devices continuously uptake targeted solute through a well-defined diffusive layer and accumulate solute to a binding layer-resin of functional groups optimized for the uptake of desired analyte (Figure 1) (Davison, William, 2016). DGT devices can be assembled either as a paddle, allowing depth sampling with a vertical resolution of 15 cm, or as a piston, allowing for surface sampling (Figure 2) (Amirbahman et al., 2013).

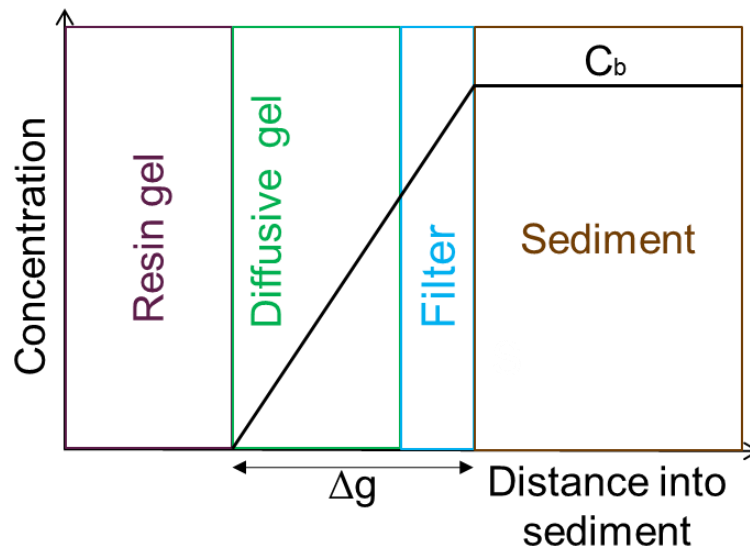


Figure 1 DGT sampler conceptual model (Davison, W. & Zhang, 1994)

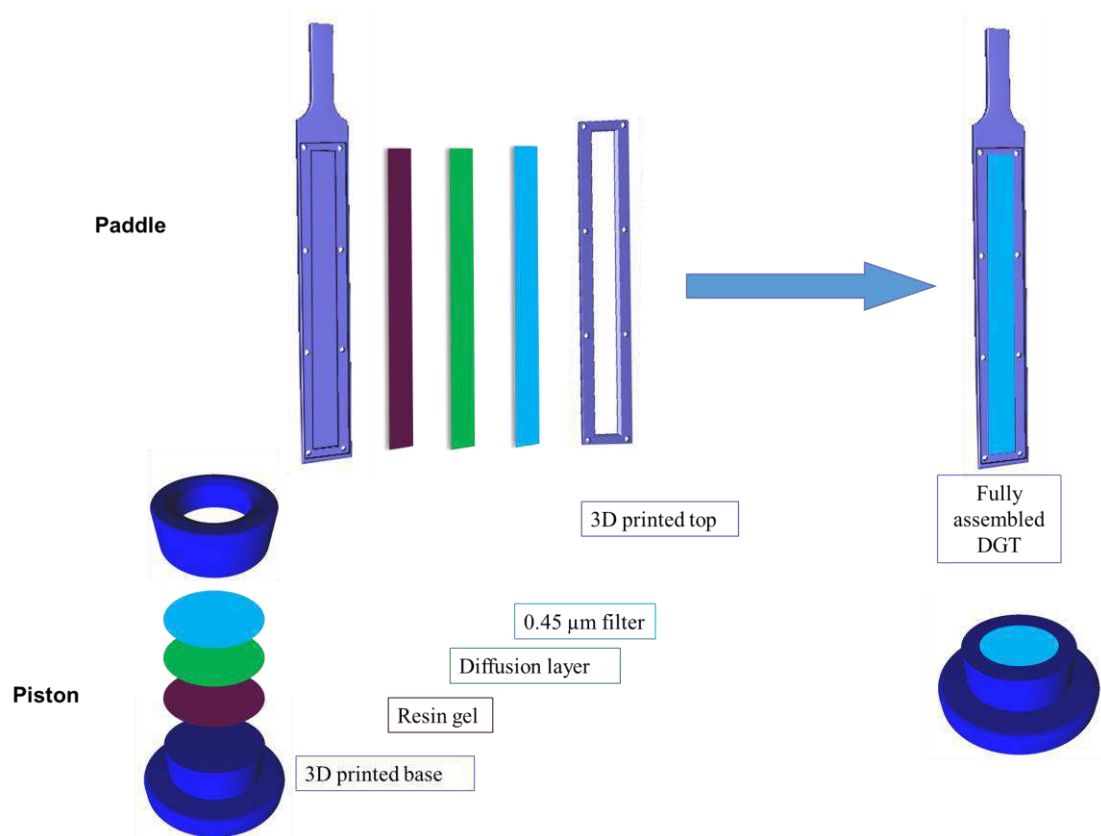


Figure 2 DGT profiler parts, assembled as either a paddle (top) or as a piston (below)

2.4.1.7.2. Assumptions

When using DGT devices and Fick's First Law equation, five assumptions are made (Davison, William, 2016). The first one states that mass accumulated initially during transient period is negligible compared to total accumulated mass (Davison, William, 2016). This limitation is addressed by increasing deployment time. Steady state for DGT samples is achieved within 10-20 minutes, and recommended minimum time for exposure for this purpose is 4 hours (Davison, William, 2016). However, typical deployment is 6 to 72 hrs (Peijnenburg et al., 2014).

The second assumption states that solute uptake is controlled by planar diffusion only (Davison, William, 2016). Depending upon the design of the device, 2 dimensional diffusion may occur near the edges and this should be accounted for (Figure 3) (Davison, W. & Zhang, 2012). For instance, DGT piston with geometric area of exposure of 2.54cm^2 has an effective surface area of 3.08cm^2 due to a diffusion that extend beyond the window exposed to the sediments (Davison, W. & Zhang, 2012).

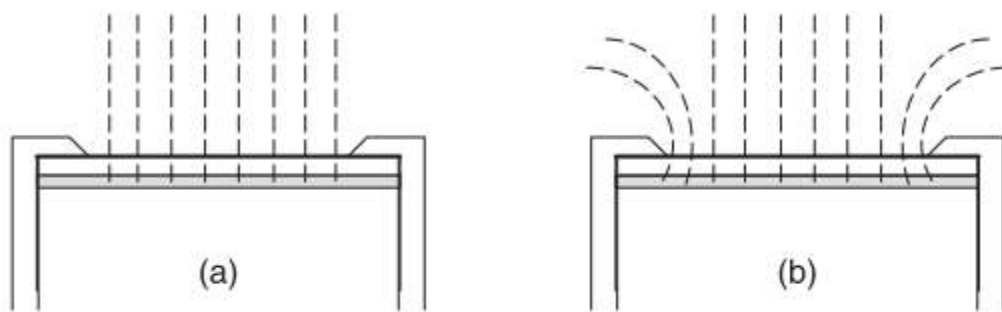


Fig. 2. Two dimensional representation of diffusion pathways into the diffusive gradients in thin films (DGT) device without convection in solution. (a) Assumed for application of Eqn 1 with the physical geometric area. (b) Allowing for lateral diffusion at the edges of the window.

Figure 3 Diffusion pathways into the DGT piston (Davison, W. & Zhang, 2012)

The third assumption states that diffusivity coefficient, deployment time, thickness of diffusive and filter layer, and area of exposure are accurately known (Davison, William, 2016). This is achieved by performing lab studies to determine the diffusivity coefficient in the diffusive layer. The hydrogel diffusive layer can be fabricated by forming the gel within plates of known separation (e.g. utilizing 0.78mm spacers placed between glass plates). The resin layer can be formed the same way although its volume is unimportant as long as it contains sufficient resin to effectively make this layer an infinite sink for the contaminant to be adsorbed. Filter thickness is also known due to prefabricated filter layer of 0.105mm thickness. However, there are also mass transfer resistances at the surface of the DGT. This is typically modeled as a diffusive boundary layer (DBL) which is the effective thickness of a layer in which diffusion is assumed. The effects of the DBL can be significant and need to be accounted for setups with low stirring speeds (Davison, W. & Zhang, 2012). However, the effect of DBL thickness is considered negligible in well mixed solutions and natural waters (Davison, W. & Zhang, 1994). The DBL is also likely negligible in sediments as long as the sediments are effectively an infinite source of the contaminant of interest and therefore maintain contaminant concentrations in the pore water adjacent to the DGT.

The errors associated with assuming planar diffusion through the diffusive layer and neglecting the DBL offset each other and the net error is typically less than 10% of an error in measurements (Davison, W. & Zhang, 2012; Warnken, K. W. et al., 2006). A challenge may occur when system is a poorly mixed solution since a diffusion layer of significant thickness may develop, effectively increasing the thickness of diffusion boundary layer and decreasing flux from the one estimated by diffusion coefficient layer.

For poorly mixed systems, this limitation can be addressed by using DGT devices with varying thicknesses of diffusion layer and using the results to calculate diffusion boundary layer thickness (Davison, W. & Zhang, 2012; Harper et al., 1998; Peijnenburg et al., 2014; Warnken, K. et al., 2005).

The fourth assumption states that charge effects and specific binding between analyte and filter as well as diffusive layer are negligible (Davison, William, 2016). DGT metal uptake was found to be affected by negative charge developing on polyacrylamide gels due to the excess of reagent products during fabrication. This would indicate enhancement of sorption of positively charged metals, which interferes with the concept of free diffusion (Davison, W. & Zhang, 2012). The uptake was also affected by the amount of washing used to remove the excess reagents. Measurements at lower ionic strengths (0.1mM) were affected by a positive charge from hydrogen ions of wash water, inhibiting the uptake of positively charged metals (Kent W. Warnken et al., 2005). However by raising the ionic strength of the gel to 1mM the uptake was no longer affected by washing of the gels due to electrolytic screening of the charge (Davison, W. & Zhang, 2012). This led to the suggestion of raising ionic strength to above 10 mM into process of fabrication of DGTs to eliminate the effects of charge onto uptake of metals into DGT resin (Davison, W. & Zhang, 2012; Warnken, K. W. et al., 2006).

The fifth assumption states that analyte is rapidly sorbed to resin only (Davison, William, 2016). Appropriate choice of resin ensures that the contaminant of concern is adsorbed strongly to the resin. For mercury, 3-mercaptopropyl functionalized silica gel (3MFSG) Isosolute Si-Thiol resin (Biotage) is used (Clarisse, O. & Hintelmann, 2006). Some binding can also occur when fulvic acids are associated with polyacrylamide gel

used as the diffusion layer. This could increase binding of mercury to diffusive layer, which would affect free diffusion of metals into DGT resin. Instead of using polyacrylamide gel, agarose gel is used when fabricating DGTs for mercury measurements (Dočekalová & Diviš, 2005).

2.4.1.7.3. DGT measurements

DGTs are considered tools for measuring kinetically labile fraction of metal present in the system. Labile fraction includes freely dissolved mercury species, mercury associated with fine colloidal matter, and labile or semi-labile ligand complexes readily dissociating during the uptake to resin. However, organic ligand complexes and complexes with DOM with the same diffusion coefficient as freely dissolved species will be also be taken up although larger molecules will do so with slight retardation (Clarisse, O. et al., 2009; Davison, W. & Zhang, 2012; Fernández-Gómez et al., 2015; Peijnenburg et al., 2014; Zhang, Hao & Davison, 1999, 2000). In addition to lability, mobility of labile species is also important with uptake to DGT (Zhang, Hao & Davison, 2000). The uptake of mercury on resin is controlled by the ability of species to pass through diffusive agarose hydrogel, which has average pore-size distribution of 70nm and smaller pore-size distribution of 15nm (Figure 4) (Fatin-Rouge et al., 2004). Without taking into account shape and charge of metal ions, their diffusion coefficient are inversely proportional to the cubic root of their molecular weight (Clarisse, O. et al., 2009). In addition to molecular weight, size of particle also matters, where diffusion of free metal is 10-20 times faster as compared to the same metal bound to humic substances (Clarisse, O. et al., 2009; Zhang, Hao & Davison, 2000). As a result, particles greater than 20-50nm are

likely excluded from DGT measurements and even smaller particles (5-20 nm) are taken up much more slowly than molecules (<1 nm).

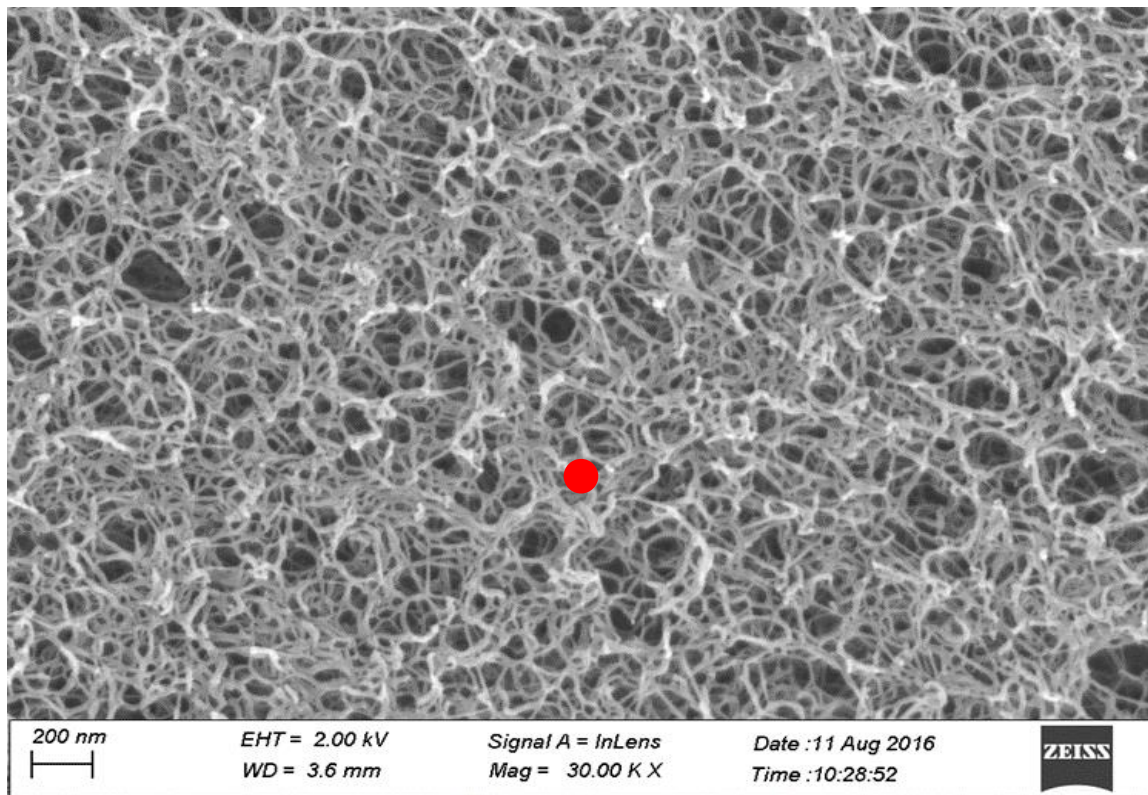


Figure 4 Dr. Bo Zhao and Dr. Haitao Wang of TTU for SEM of the agarose diffusive gel with representation of average pore size particle of 70nm (red dot)

2.4.1.7.4. DGT materials and parts

Filter commonly used on top of the diffusive layer of the DGT device is 0.13-0.15mm thick, 0.45- μ m pore size cellulose nitrate or more commonly polyethersulphone membrane that prevents particles from binding outside of diffusive layer and short-circuiting of diffusion (Davison, William, 2016). A diffusive layer is highly porous hydrogel fabricated with smaller pore size which restricts the entrance of smaller organic metal complexes. Three types of hydrogels are commonly used for diffusive layer of

DGT devices, including agarose, polyacrylamide cross-linked with bis-acrylamide, and polyacrylamide cross-linked with an agarose derivative (Davison, William, 2016; Zhang, Hao et al., 2000). Agarose gel is used for measuring mercury using DGT devices, as covalent binding of mercury to amide groups of polyacrylamide diffusive gel causes competitive sorption between polyacrylamide diffusive gel and Spheron-Thiol resin (Dočekalová & Diviš, 2005). As a result, diffusive layer of DGT profiler used for obtaining mercury measurements is 1.5% agarose solution, creating a gel with pore sizes from 1 to 480 nm, with average values from 35-47nm (Davison, William, 2016). Initial design of resin optimized for mercury uptake implemented Spheron-Thiol resin (Diviš, P. et al., 2005) which is no longer produced (Diviš, Pavel et al., 2010) . There are however other thiol resins that are now used, such as 3-mercaptopropyl functionalized silica gel (3MFSG) Isosolute Si-Thiol resin (Biotage) (Clarisse, O. & Hintelmann, 2006).

Silica gel, an inorganic porous polymer with high specific surface area has been used in a variety of applications such as heavy metal ion adsorption, chromatography, pesticide removal, immobilization of metallic particles and enzymes (Delacôte et al., 2009; Quang et al., 2013). Thiol functionalized silica has been proven effective for adsorption of soft metals, including sorption capacity for mercury ion (Delacôte et al., 2009; Quang et al., 2013). Mesoporous silica functionalized with mercaptopropyl silica group has been shown effective in sorption Hg due to high surface area, open framework, regular structure, high adsorption capacity, fast adsorption uptake, and selectivity of Hg(II) (Bois et al., 2003; Delacôte et al., 2009). Binding properties of mercury species to thiol-functionalized silica resin is affected by pH , and structure of the resin, with ordered structure being better above pH 4 as compared to amorphous gels (Walcarius & Delacôte,

2005). Below this pH, positively charged complexes form in the resin gel, which forms electrostatic forces with mercury ions and reduces uptake process. Variability due to mm sized microniches, where oxidation of labile organic matter can drive reduction of sulfate and affect the speciation (Davison, William, 2016). Complexing ligand such as thiourea increases desorption of Hg^{2+} from resin in 3M and 0.1M HCl medium since 5% of acidific thiourea solutions can elute metal ions from mercapto-functionalized organoclays columns (Walcarius & Delacôte, 2005).

2.5. Remediation options for mercury contaminated sediments

Remediation seeks to remove or otherwise mitigate the risks of mercury contaminated sediments. Options are chosen based on the level of contamination, effects on biogeochemistry changes, speciation of mercury as well as its mobility. Currently, management activities aimed at reducing the impacts of Hg contaminated sediments have mainly focused on actions like dredging and capping (Randall and Chattopadhyay, 2013), or more recently the addition of activated carbon or biochar (Eckley, 2017). Higher levels of contamination are commonly addressed using relocation techniques combined with ex-situ treatment or removal, whereas lower contamination levels are addressed using in-situ treatment and/or immobilization techniques (Xu, J. et al., 2014). Commonly used remediation approaches include monitored natural recovery, dredging and excavation, phytoremediation, and in-situ/ex-situ capping treatments using chemical and biological processes, or the combination of the options listed (Randall & Chattopadhyay, 2013).

2.5.1. Monitored natural recovery

Monitored natural recovery consists primarily of monitoring reduction of contaminants due to naturally occurring process. Cleanup level in a specific timeframe is

usually established and natural processes are observed to evaluate if the cleanup level is achieved in a given timeframe. Processes that can reduce mercury risks that occur naturally include clean sediment deposition (burial), reduction and formation of insoluble and non-bioavailable mercury forms, demethylation and volatilization. Sites where monitored natural recovery is used have about 0.2-1 µg/kg of mercury contamination in the sediments, although the use of monitored natural recovery in Whatcom Waterway at Bellingham, Washington had reported contamination reductions from 4.5mg/kg to 0.5mg/kg (Randall & Chattopadhyay, 2013).

2.5.2. Dredging and excavation

Dredging consists of permanent removal of heavily contaminated sediments from the aquatic environment by hydraulic dredges that use suction and hydraulic action to remove sediments, or by mechanical dredges. There are also hybrid tools including both mechanisms. Hydraulic dredges include rotating cutterhead or a horizontal auger, whereas mechanical dredges include clamshell or cable-arm bucket dredges. Mechanical dredges are preferred in many conditions due to high solids content, low water production, greater accuracy and debris and obstruction containing sites (Reible, 2008). In Japan's Minamata Bay dredging removal was conducted on sediments exceeding 25mg Hg/kg. As a result of dredging efforts, concentrations were reduced from over 600mg Hg/kg to maximum concentrations of 8.75 mg Hg/kg (Randall & Chattopadhyay, 2013). Although this method is effective in removal of high concentrations of mercury, dredging results in resuspension of mercury and leaves residually contaminated sediment at the surface. The residual is typically similar to the concentrations that are dredged but is limited to a thin layer of sediments. Often, dredging is followed by capping or backfill

to control residual contamination at the surface. Capital costs to consider when considering dredging include equipment labor and costs, engineering controls to protect water quality, sediment isolation, dewatering of dredged material and subsequent water treatment, and transport of sediment to treatment or disposal site (USEPA, 2005).

2.5.3. In situ and ex-situ subaqueous capping

Capping is a process of placing covering or isolating material to cover and separate contaminated sediment from the water column (Randall & Chattopadhyay, 2013). Capping creates a physical barrier between contaminated sediments and benthic organisms populating the upper 10-15 cm of sediments, reduces metal fluxes due to organism-induced mixing (bioturbation), stabilizes contaminated sediments to prevent resuspension during high flow conditions, and provides resistance to transport process resulting in chemical release from the sediments (Lampert & Reible, 2009). *In situ* capping refers to placement of capping layer at the contaminated site, while *ex situ* capping refers to capping of contaminated sediment dredged and moved to a separated location (Randall & Chattopadhyay, 2013). A sand or coarse media is often used as a cap layer, which facilitates placement. Great benefits of capping are low cost, low adverse effects, application to multiple contaminants at once, and minimal disturbance to system during remediation implementation. Disadvantages include need for long-term monitoring since the contaminated sediments are not removed from the system. Sediments with mercury contamination in the 430-960 mg/kg range were contained in Hamilton Harbor, Canada using a 35cm thick cap composed mostly of sand. The sampling one year after capping found concentrations in the capping layer to be less than 5µg/kg (Randall & Chattopadhyay, 2013). Due to contaminants often associated with fine

grained particles, these sediment often have low load-bearing capacity and low shear strength, which is a concern that needs to be addressed prior to cap implementation (Reible, 2008) . Capital costs associated with capping efforts include cap material costs, equipment and labor costs, material transport, storage and placement costs (USEPA, 2005).

2.5.3.1. Reactive caps

Reactive cap involves implementation of sorbent material within the capping material and using sorptive properties of contaminant to slow down the migration of the contaminant through cap by accumulation on the clean cap layer (Lampert & Reible, 2009). For example, activated carbon binds inorganic mercury and MeHg compounds and thus decreases its bioavailability and transport and has been used in caps and in geotextile layers as a cap (Randall & Chattopadhyay, 2013). The use of activated carbon adsorption has been previously implemented in the wastewater treatment and has been shown effective in removing more than 99% of ~100ppm mercury levels from the wastewater effluent in 3-11 pH range (Andersson A., 1979).

2.5.4. Phytoremediation

Phytoremediation has also been used to remediate Hg in terrestrial soils through processes of phytostabilization, phytoextraction, and phytovolatilisation.

Phytostabilization limits the mercury movement in the soil through accumulation of Hg in the roots and Hg precipitation in the root zone. Insoluble complexes of mercury with selenium have shown to be important in terms of limiting accessibility, absorption, translocation/bioaccumulation of Hg (Xu, J. et al., 2014). Phytoextraction is the process in which Hg is uptaken by plant roots and further transported into the above-ground parts,

where Hg can be removed by harvesting the plant (Xu, J. et al., 2014). Phytovolatilisation involves Hg taken up by plants transported to xylem and finally released to the atmosphere through cellular tissues. This process is highly affected by light intensity and air temperature (Xu, J. et al., 2014). Main considerations when using phytoremediation are adaptability of the plant to the contaminated site conditions and toxicity of the mercury to the plant roots (Randall & Chattopadhyay, 2013). Plants shown to be effective in preventing mobilization of mercury are *Juncus Maritmus* plant and water hyacinths *Eichhornia crassipes*, as well as *Pteris vittata* and *Sesbania drummondii* (Randall & Chattopadhyay, 2013; Xu, J. et al., 2014). The main considerations when using phytoremediation are adaptability of the plant to the contaminated site conditions and toxicity of the mercury to the plant roots (Randall & Chattopadhyay, 2013).

Other strategies that may be involved in remediation efforts include soil washing with physical separation and chemical extraction, thermal treatment for really high Hg concentration sites (>260 mg/kg), as well as bioremediation using genetically modified microorganisms that has yet to be applied on a pilot scale study (Xu, J. et al., 2014).

2.6. Summary

Understanding the fate and transport of mercury in the aquatic systems is the key for assessing the impact of methyl mercury that readily bioaccumulates in the aquatic food chain and causes human exposure to MeHg through fish consumption (EPA, 1997; Fitzgerald et al., 1998). However, it has been shown that addressing the discharge of contaminants into surface waters doesn't address the persistence of many of the solid-associated contaminants, mercury being one of them. Although mercury in sediments has limited direct connection to human health risks, sediments serve as a sink of mercury in

aquatic systems and can pose significant risk to ecological or human health if the mercury can migrate into biologically active zone near surface (normally 10-15cm in depth) or if it's directly exposed through processes such as erosion (Reible, 2014). Mercury in sediment is often present in weakly bioavailable phases and fate and transport of mercury in sediments is affected by a variety of biological, physical and chemical factors. As a result, remediation of such sites is often expensive by using active options such as dredging. When evaluating risk management strategies, focus is often on ecological risk, so the key in management of mercury in sediments is understanding the risk associated with the contaminated sites. The conventional approach to assessing ecological risk is evaluation of mercury in bulk solids, however an alternative to this approach would be to focus on the most available and mobile fraction of mercury in pore water. DGT devices provide the ability to measure mercury in pore water, however work is needed to ensure quantitative recovery. This is addressed in Chapter 3. Work is also needed to improve the understanding the risks of mercury in bank sediment during inundation drainage cycles. This is addressed in Chapter 4. Remediation of bank soils to reduce the risks of mercury leaching may be accomplished through stabilization and capping/containment. This is also discussed in Chapter 4. Lastly, experimental work can address only some conditions leading to leaching. Long term performance can be addressed through modeling. This is addressed in Chapter 5.

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CHAPTER III

OPTIMIZATION OF DGT METHYL MERCURY RECOVERY

Abstract

Quantification of mercury and its methylated form of mono methyl mercury (MeHg) in sediment pore water allows for better understanding of the most representative biologically relevant pool of this bioaccumulative neurotoxin. The application of diffusive gradient in thin film (DGT) devices provides an in-situ method capable of quantifying pore water mercury and methyl mercury while minimally disturbing the sampled location and the redox conditions present. However, changes in the material availability for fabrication of the 3-mercaptopropyl functionalized silica gel (3MFSG) DGT resins have introduced difficulties in extracting methyl mercury from the deployed resin. As a result of the optimization studies, a method for extraction of MeHg has been developed that improves poor and variable extraction recovery of 1-56% range to a reproducible recovery of $91\pm 9\%$. The improved MeHg extraction from 3MFSG DGT resin with diluted nitric acid allows for more reliable quantification of methyl mercury in the pore water, which provides opportunities for better understanding of overall mercury fate and transport in the environment and its biological relevance.

Introduction

The diffusive gradient in thin film (DGT) devices are an *in-situ* passive sampling technique utilized to measure sediment pore water mercury concentration. Pore water concentration measurements might be the most representative of the biologically relevant pool of mercury to benthic organisms (Chapman et al., 2002). The main advantage of the passive sampling is minimal disturbance of site conditions. *In-situ* sampling also eliminates the physical removal of sediment by coring and obtaining the pore water samples by centrifugation, squeezing, and dialysis. These techniques can interfere with the results by introducing artifacts during sampling, such as introduction of suspended or colloidal particles that can cause artificial increase in a mercury pore water concentration measurements due to inclusion of the colloids and inert complexes (Chapman et al., 1998; Zhang, Hao & Davison, 2000). Additional challenges with the common sampling techniques are contamination during sampling and the small volume of extracted pore water limiting the analysis (Clarisse, Olivier et al., 2011a). The DGTs were developed as a method for measuring cation flux in the near surface sediments and the overlaying water (Davison, W. & Zhang, 2012). The fundamental principle is immobilization of the kinetically labile metal species in a sorbing resin at a rate proportional to pore water concentration by controlling the diffusive uptake through a hydrogel separating the resin and the sediment pore water. The mass of mercury accumulated on the resin is determined analytically. Quantitative relating mass accumulated on the resin to pore water concentration is done using the Fick's First law of diffusion (Davison, William, 2016; Zhang, Hao & Davison, 2000). The DGT devices are a promising tool for estimating the biologically relevant pool of mercury in the system, as benthic

macroinvertebrates MeHg uptake has been found to be correlated to MeHg pore water concentration (Amirbahman et al., 2013; Bejar et al., 2017; Clarisse, O. et al., 2012).

Methyl mercury that is passing into the DGT devices are likely aqueous MeHg^+ ions and the small inorganic MeHg complexes with comparable diffusion coefficients, such as MeHgCl , MeHgOH , MeHg-cysteine , and MeHg associated with DOM complexes much smaller in size than 20nm (Clarisse, O. et al., 2009; Davison, W. & Zhang, 2012; Fernández-Gómez et al., 2015; Zhang, Hao & Davison, 1999).

The resin layer consists of a material with a strong affinity for the mercury, e.g. a thiol modified mesoporous silica gel (Brown et al., 1999; Clarisse, O. & Hintelmann, 2006; Nooney et al., 2001). A variety of sorbents can be used for inorganic Hg but appropriate sorbent resins for MeHg are more limited. Spheron-Thiol was a resin that was initially used instead of Chelex 100 (Diviš, P. et al., 2005; Shade & Hudson, 2005), but is no longer available commercially (Chess, 2010; Diviš, Pavel et al., 2010). More recently, a 3-mercaptopropyl functionalized silica gel (3MFSG) Isosolute Si-Thiol resin (Biotage), has been used as a replacement resin (Chess, 2010; Clarisse, O. & Hintelmann, 2006). The DGT resin with 3-mercaptatypropyl-functionalized silica gel is used for both inorganic Hg and MeHg measurements, where MeHg is accumulated in the pH range of 3-9 (Clarisse, O. & Hintelmann, 2006). The detection limit is 1pg of MeHg on the DGT resin, which is equivalent of 0.05ng/L of MeHg in pore water for 2 day deployment, 2cm^2 resin area and 21°C temperature (Clarisse, O. & Hintelmann, 2006). The 3MFSG resin elution of THg using hydrochloric acid has resulted in 96.5% efficiency (Figure 5), confirming it as an optimum choice for using the DGTs for the detection of THg (Chess, 2010).

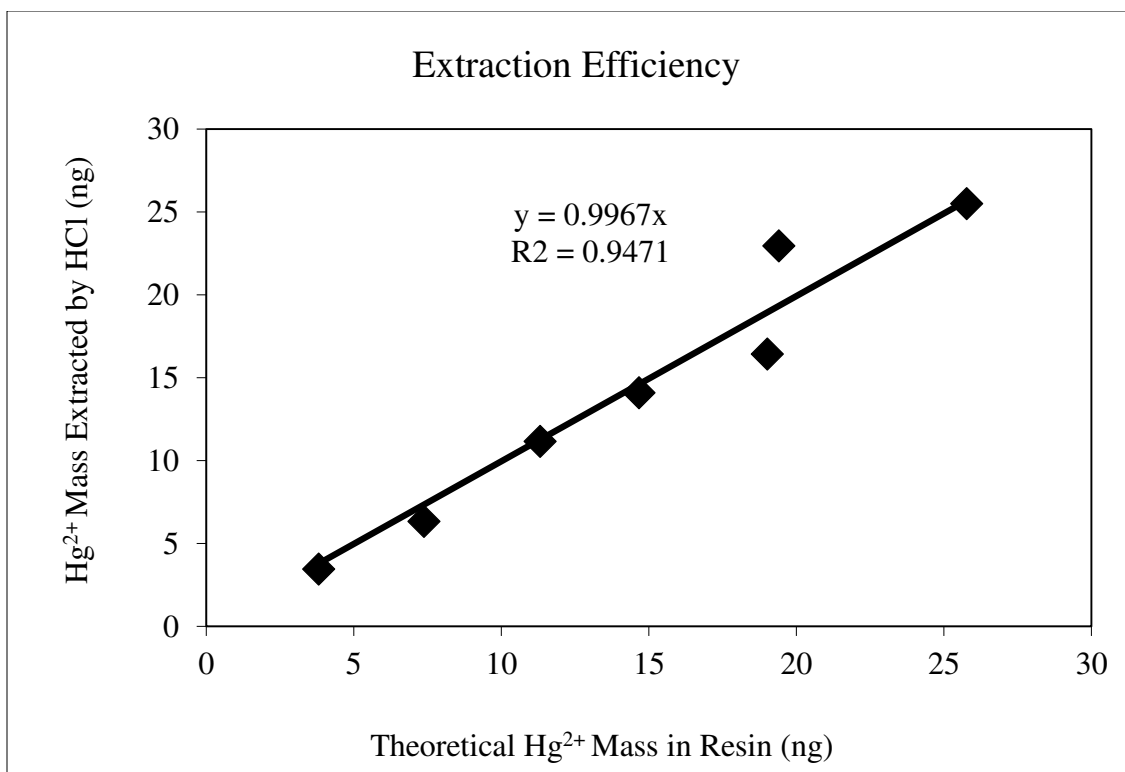


Figure 5 3MFSG in agarose gel THg extraction efficiency (Chess, 2010)

Current method for the elution of MeHg from the 3MFSG DGT resin consists of the thiourea (TU) and hydrochloric acid (HCl). Commonly used concentration for extracting MeHg from DGT samplers is 1.31mM thiourea in 0.1M hydrochloric acid (1.31mM TU/0.1M HCl) (Amirbahman et al., 2013; Blanco et al., 2000; Clarisse, O. et al., 2009; Clarisse, O. & Hintelmann, 2006; Hong et al., 2011; Shade & Hudson, 2005). Thiourea is a neutral ligand with high affinity for soft metals (Shade & Hudson, 2005). 1.31mM TU/0.1M HCl eluent has been demonstrated to extract $91 \pm 3\%$ of MeHg associated with 3MFSG resin in polyacrylamide gel (Clarisse, O. & Hintelmann, 2006). However, when using 3MFSG resin fabricated after 2011 and immersed in agarose gel, the extraction procedure of the MeHg from the resin was found to be below 50% of the spiked MeHg (Figure 6). The issue with unacceptably low extraction efficiency could be

due to a variety of factors such as the strength of TU/HCl eluent (Krishna et al., 2005), potential losses encountered during sample processing or could be associated with the limitations of the method currently used to extract MeHg associated with the resin.

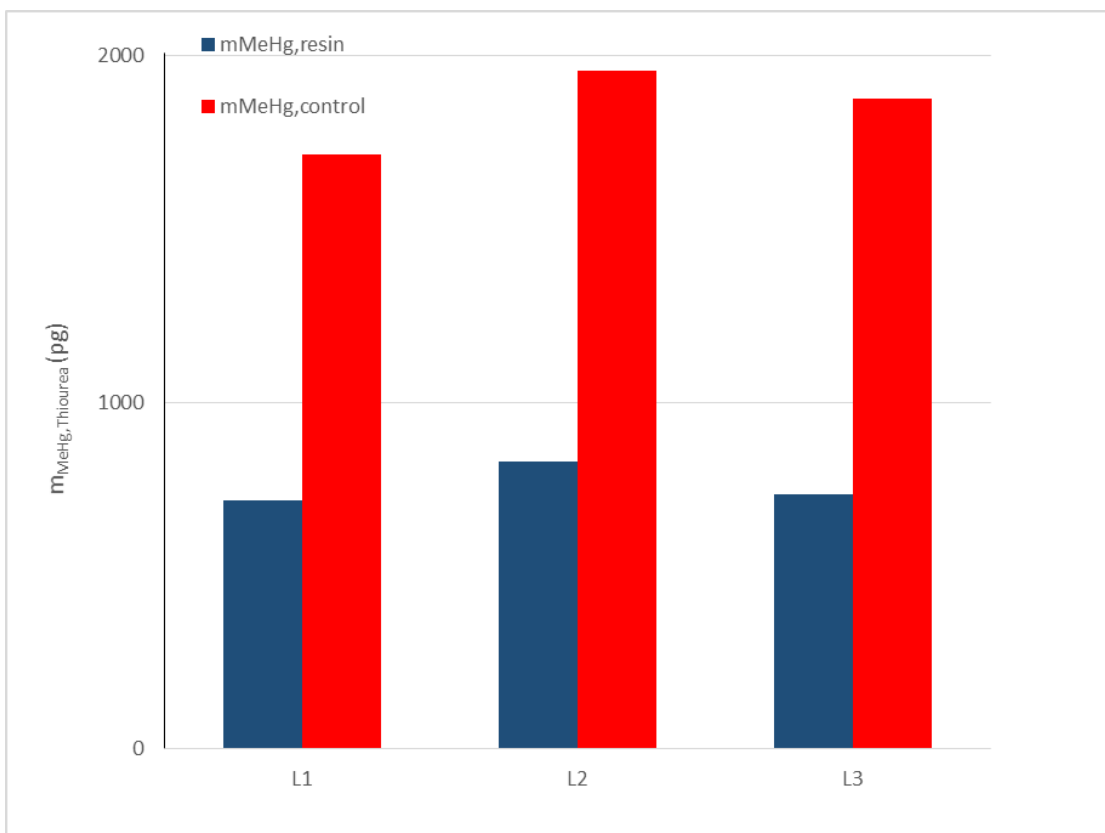


Figure 6 The extraction recovery of 2000pg MeHg spike (Schierz et al., 2014)

As a result of these limitations, the main goal of this study was to improve recovery of MeHg from the 3MFSG resin. This was done by examining the effects of TU/HCl eluent strength, evaluating potential losses of MeHg during the extraction procedure, and identifying optimum recovery method alternatives, including a method based upon nitric acid digestion of biological tissue. The targeted recovery value of $100 \pm 33\%$ was suggested by US EPA Method 1630 (US EPA, 2001). The study objectives were also to obtain reproducibility of the results and avoidance of any significant MeHg formation during the sample processing.

Materials and Methods

The Standard Operating Procedure (SOP) for Fabrication of DGTs can be found in the Appendix A. The reagent water used was 18.2 M Ω -cm ultra-pure water (Thermo Scientific™ Barnstead™ GenPure™ Pro water purification system). The cleanup of the equipment was performed in soapy water (Alconox®) and 10% (v/v) hydrochloric acid baths for 24 hours each, rinsed in between with distilled water. Cleanup of the DGT bodies was done in two 50% (v/v) HCl baths, each for 48 hours followed by ultra-pure water baths until pH was no longer affected by the HCl acidity. The resin gel solution was made with 18.2 M Ω -cm ultra-pure water, 200 g/L 3-mercaptopropyl functionalized silica gel (3MFSG) Isosolute Si-Thiol resin (Biotage 9180-0100) and immobilized in 20g/L of agarose binding gel (Fisher 1356-100). The reagents were stirred on heat before being cast using a glass syringe between the glass plates separated by the 0.78mm gasket and spacer kit (Cole Palmer). Following the solidification, resin beads solidified on the bottom of the binding gel. Piston type resins were fabricated and the resin layer (containing of 3MFSG and Agarose binding gel) was placed into the 40mL Brooks Rand Certified auto sampler vial (Brooks Rand Instruments) with the resin beads on the top using plastic tweezers and a spatula. Although some labs use polyacrylamide gel (PA) during fabrication of DGT devices, agarose gel was chosen over polyacrylamide due to mercury complexes with humic and fulvic acids binding to PA gel amine groups (Davison, W. & Zhang, 2012; Dočekalová & Diviš, 2005). Although these complexes are associated with THg and have not been observed with MeHg uptake (Clarisse, O. & Hintelmann, 2006), these DGTs are used for simultaneous measurements of both THg and MeHg, thus requiring the usage of agarose gel for the diffusive layer. Moreover,

since this study used only the resin layer for MeHg spikes and the resin was completely extracted, the choice of agarose vs PA gel should not affect the recovery of MeHg from the resin.

The resins were spiked inside of the fume hood using dilutions of 1 ppm methyl mercury standard in 0.5% HOAc, 0.2% HCl (Brooks Rand Instruments). The samples were capped tightly, wrapped in aluminum foil, and placed in the dark for 24 hours. Resin gel was separated from the spiked supernatant, followed by resin extraction using the methods described below.

Four methods were used for extraction of MeHg from 3MFSG DGT resin. The first method for extraction of MeHg from 3MFSG DGT resin involved eluent consisting of thiourea and hydrochloric acid. The second method for extraction of MeHg from 3MFSG DGT was done using nitric acid digestion. The third method utilized solvent extraction method. The fourth method involved concentrated hydrochloric acid and is a method commonly applied for THg extraction from DGT resin. The last method is different from the first three as the final result is THg mass as opposed to MeHg mass detected. Concentrated HCl extraction was applied only in the experiment where MeHg was the only form of Hg introduced, so that all of the THg extracted in the experiment originated from a MeHg spike. The following sections further discuss each of the methods used.

Studies of the TU/HCl eluent strength ratio effects on MeHg resin extraction were done using a range of 2-15mL of thiourea/HCl eluent with TU concentrations ranging from 1.31 to 1300 mM, and concentrations of HCl ranging from 0.1M HCl to 1M HCl. The setup of the experiment can be seen below (Figure 7). The resin was spiked with

MeHg standard, and the TU/HCl eluent was added to the spiked resin and kept in dark for 12 to 48 hours to allow for extraction of MeHg from resin to the eluent. The TU/HCl eluent was now presumably complexed with all of the MeHg spiked initially to the resin and it was then separated from the resin that presumably was no longer associated with any MeHg. Then, eluent volumes ranging from 2-15mL were diluted during the preparation of 40mL samples that were analyzed using Merx-M Automated Methyl Mercury CVAFS System (BrooksRands Instruments).

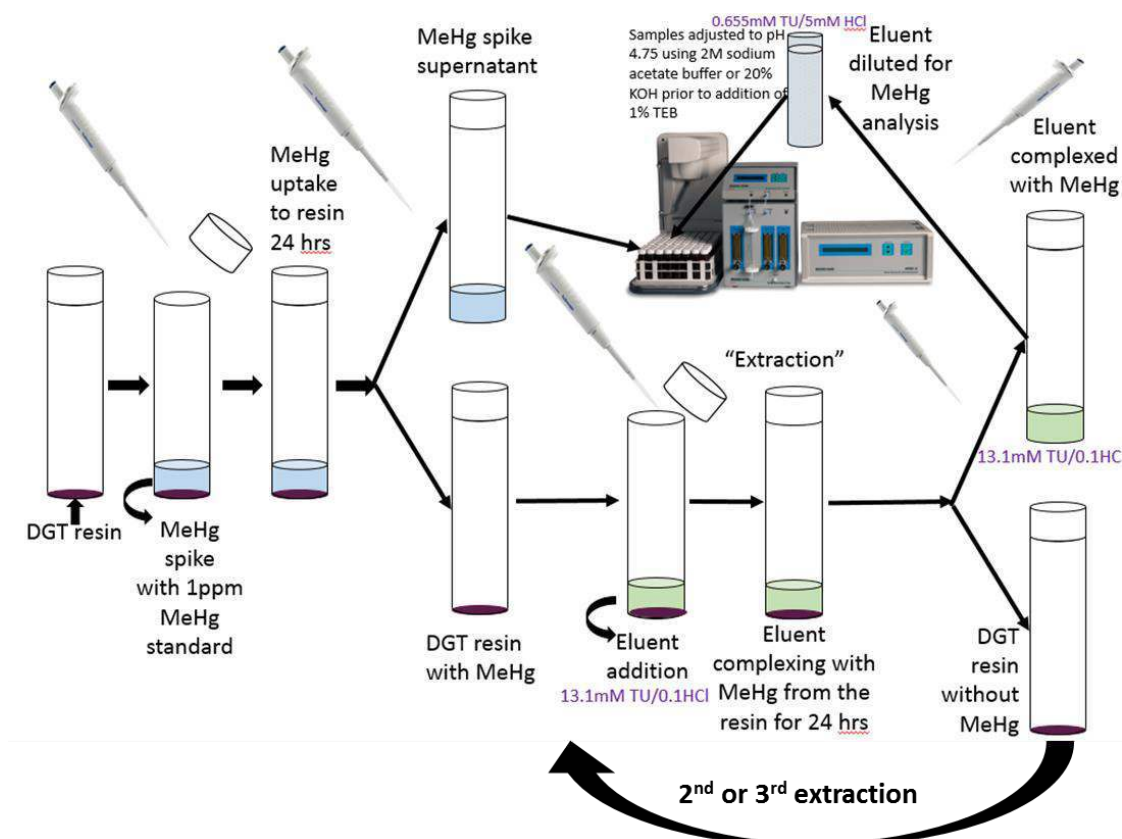


Figure 7 MeHg extraction from 3MFSG DGT resin using Thiourea in hydrochloric acid eluent

The nitric acid digestion was performed by placing 10mL of the 4.73M trace metal grade nitric acid solution to the spiked 3MFSG DGT resin. A sample containing the 3MFSG DGT resin without spike and sample without the 3MFSG DGT resin with

acid only were added for quality assurance. The sample was digested in an oven at 60 °C for 12 hours. Following the digestion, 9 mL of the sample eluent was separated into a 40mL Merx-M Brooks Rand Certified auto sampler vial (Brooks Rand Instruments). The final sample diluted to 0.05M nitric acid was analyzed using Merx-M Automated Methyl Mercury CVAFS System.

The solvent extraction procedure was developed for biological and sediment samples (Baeyens et al., 1999; Bloom, N. S. et al., 1997; Liang et al., 1996). The 3MFSG DGT resin was placed in the Teflon centrifuge tube. 5mL of H₂SO₄ 5% KBr and 1mL of 1M CuSO₄ were added and samples were placed in the dark. Following the addition of 10mL of CH₂Cl₂, samples were wrapped in aluminum foil to prevent light exposure and shaken for another hour. Samples were then centrifuged at 3000rpm for 30 min and CH₂Cl₂ layer was back extracted into 30mL of ultra-pure water. Solution was purged for 30 minutes at 65 °C (Baeyens et al., 1999; Bloom, N. S. et al., 1997; Horvat et al., 1993). The reference material Total Mercury and Methyl Mercury in an Estuarine Sediment ERM-CC580 (Sigma-Aldrich) was used to verify the recovery efficiency for MeHg. The entire volume of the sample was analyzed using Merx-M Automated Methyl Mercury CVAFS System.

During TU/HCl eluent strength optimization studies, resin was also eluted using the method optimized for THg extraction from 3MFSG DGT resin. 3mL of Trace Metal Grade concentrated hydrochloric acid were added to the resin for 24 hours, followed by the application of EPA 1631, Revision E method that included an addition of 1% bromine monochloride causing oxidation of all the Hg species to Hg(II). Samples were then pre-reduced with hydroxylamine hydrochloride and stannous chloride was added for

reduction of all the Hg(II) to elemental mercury. Samples were then analyzed using Merx-T CVAFS system (US EPA, 2002). Since the only Hg present in the system was MeHg that was added as a spike, mass of THg detected using Merx-T SVAFS system was considered as MeHg mass not eluted by TU/HCl eluent.

For the sample analysis using Merx-M Automated Methyl Mercury CVAFS System following US EPA Method 1630, ultra-pure water was added to 40mL Merx-M Brooks Rand Certified auto sampler vial (Brooks Rand Instruments). MeHg sample of interest was added and pH adjustments were done using 2M sodium acetate buffer and daily prepared 20% potassium hydroxide. The additional ultra-pure water was added to fill the vial to 40mL, and 50 μ L of semi-thawed 1% sodium tetraethylborate (BrooksRand) was added before tightly capping the vial and shaking it. The derivatization with sodium tetraethylborate allows the formation of volatile ethylated species that can be separated by gas chromatography and detected by cold vapor atomic fluorescence. The peak areas of MeHg in the samples were normalized by the peak areas of MeHg standards prepared in the ultra-pure water (Bloom, N., 1989; US EPA, 2001). The analysis of samples followed the accepted 9 point calibration run of MeHg spikes prepared in the ultra-pure water. The QA/QC sequence was done in triplicates to account for the three simultaneous traps the Merx Methyl Hg Purge & Trap Module uses. The samples were analyzed in sets of ten, each set followed with three quality control samples from two independent sources and three blank samples. The acceptable range of recovery was $100 \pm 25\%$ for calibration samples, and $100 \pm 23\%$ for quality control samples. The blank values detected in our lab were on average $0.13 \pm 0.2\text{pg}$ (N=143), all below MQL level of 1.09pg . Method detection limit was determined using 7 replicates of lowest

calibration point. The MDL of 0.272 pg was calculated as an estimate of sample standard deviation of 7 lowest calibration point (1pg) replicates using the one sided t-distribution with 99% confidence level for 6 degrees of freedom.

Results and discussion

The effect of TU/HCl concentration on MeHg extraction from 3MFSG DGT resin

To test the efficiency of the MeHg elution, resins were spiked with 20-2000pg of MeHg. The sequential extraction of the resin was done by soaking resin for 24 hours in 3mL of 1.31mM TU/0.1M HCl eluent, as well as 1.31mM TU/1M HCl eluent (indicated as 1. extraction TU). The eluent from the first extraction was separated from the resin and analyzed on the Brooks Rand Merx-M CVAFS system. The second extraction using the same eluent strengths was repeated eluent (indicated as 2. extraction TU). Finally, the resin was extracted using 3mL of concentrated HCl (indicated as 3. extraction HCl). The HCl extraction a method commonly used for the analysis of THg accumulated on 3MFSG DGT resin and using this method inhibits the ability to identify the speciation of mercury analyzed, i.e. MeHg. The results are expressed as mass of MeHg released with each extraction step for the samples (Figure 8). The sequential extraction with 1.31mM TU/0.1M HCl eluent shows less of a MeHg loss during the extraction procedure as compared to a sequential extraction with 1.31mM TU/1M HCl eluent. MeHg spiked to resin is not being lost during the extraction procedure with 1.31mM TU/0.1M HCl, however the eluent is showing inability to outcompete MeHg association with 3MFSG DGT resin, as sequential extraction recovered less than 50% of the spiked MeHg amount.

The final extraction with concentrated hydrochloric acid shows complete recovery of MeHg spiked, however this method cannot be used during deployment with other forms of Hg present, as it is unable to distinguish between MeHg and other Hg forms.

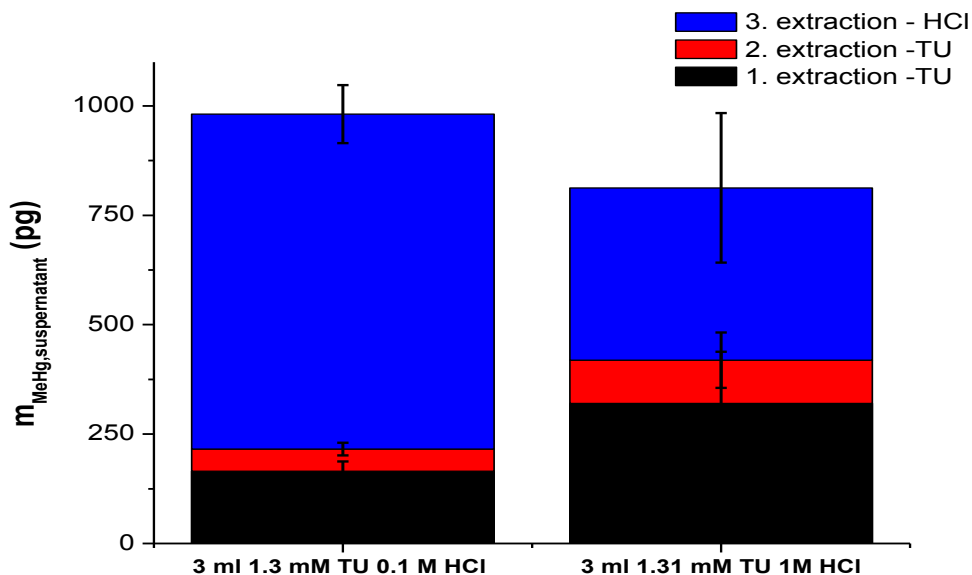


Figure 8 The effect of sequential extraction with two steps of TU extraction (either 1.31mM TU/0.1 M HCl or 1.31mM TU/1M HCl eluent), followed by concentrated HCl extraction step (THg extraction method) on the recovery of direct MeHg spike to the 3MFSG resin (Schierz et al., 2014)

The effect of thiourea concentration on MeHg extraction efficiency was tested by spiking 1000pg of MeHg on the 3MFSG DFT resin and using variable concentrations of thiourea ranging from 1.31mM to 1300mM in 0.1M HCl. The bars represent TU/HCl% eluent recovery of the spiked MeHg amount during the first extraction with TU/HCl eluent and subsequent second extraction with the concentrated HCl for the spiked resin (Figure 9). An eluent with 13.1mM thiourea concentration resulted in improved MeHg efficiency (37.5%) as compared to 1.31mM thiourea (15%) due to its ability to outcompete more of MeHg bounded to the 3MFSG resin. The analytical issue of incomplete ethylation occurred when increasing thiourea concentration to 131mM and

1300mM. The issue of incomplete ethylation is related to the step where tetraethylborate is added to the sample to ethylate MeHg present (Clarisse, O. & Hintelmann, 2006). Further increases in thiourea concentration resulted in strong complexes of sulfur in thiourea with MeHg, resulting in inability of tetraethylborate to completely ethylate the sample. Inability to ethylate the MeHg present in the sample resulted in inability to detect MeHg extracted from 3MFSG resin, so further increases in thiourea concentration greater than 13.1mM were found to be unfitting for the optimization of the 3MFSG resin extraction procedure (Hong et al., 2011). The specific effect of TU/HCl eluent concentration on the recovery of MeHg spiked to the resin is evaluated in the next section.

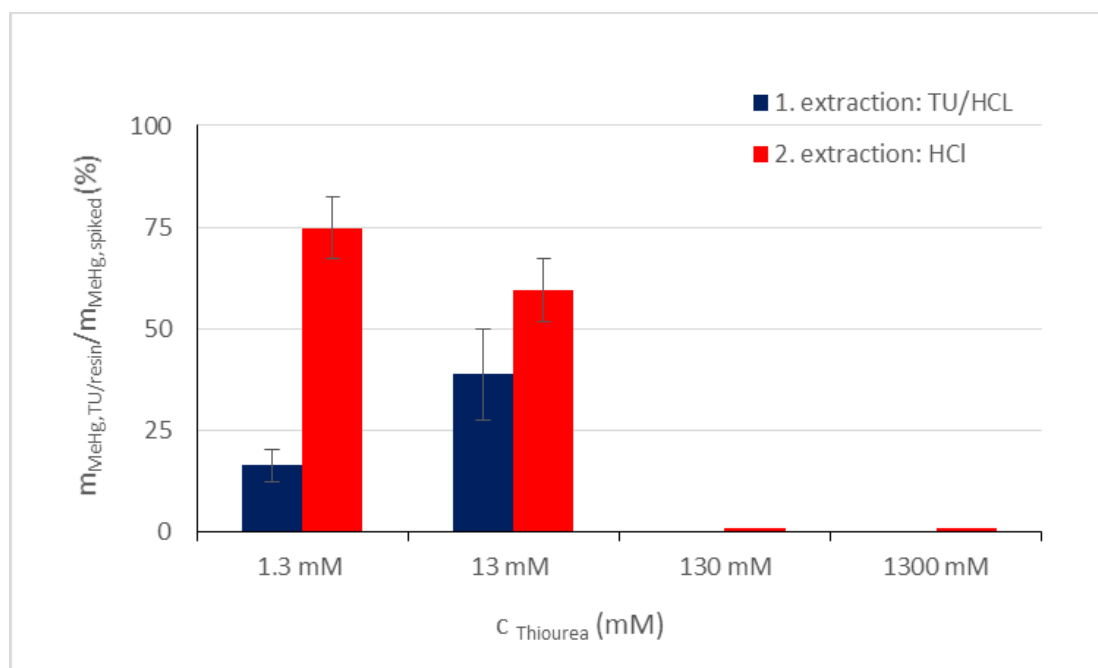


Figure 9 The effect of changing TU concentration of the TU/HCl eluent on the extraction recovery of the MeHg spiked to the 3MFSG resin (Schierz et al., 2014)

The optimum time and volume for soaking the MeHg spiked resin in 13.1mM TU/0.1M HCl eluent was examined using 1000pg 3MFSG DGT resin spikes soaked in 3 and 15mL of eluent for duration of 12 to 48 hours. The results show % recovery of MeHg from the eluent normalized to MeHg spike added to each individual 3MFSG DGT resin (Figure 10). Using 15mL of 13.1mM/0.1M HCl eluent for 24 hours resulted in 51.5 $\pm$ 17.5% recovery, which is the best extraction efficiency achieved using TU/HCl eluent for the MeHg spiked to the 3MFSG resin. However, the extraction efficiency was still below desired 100 $\pm$ 33% recovery of the MeHg spiked to the resin.

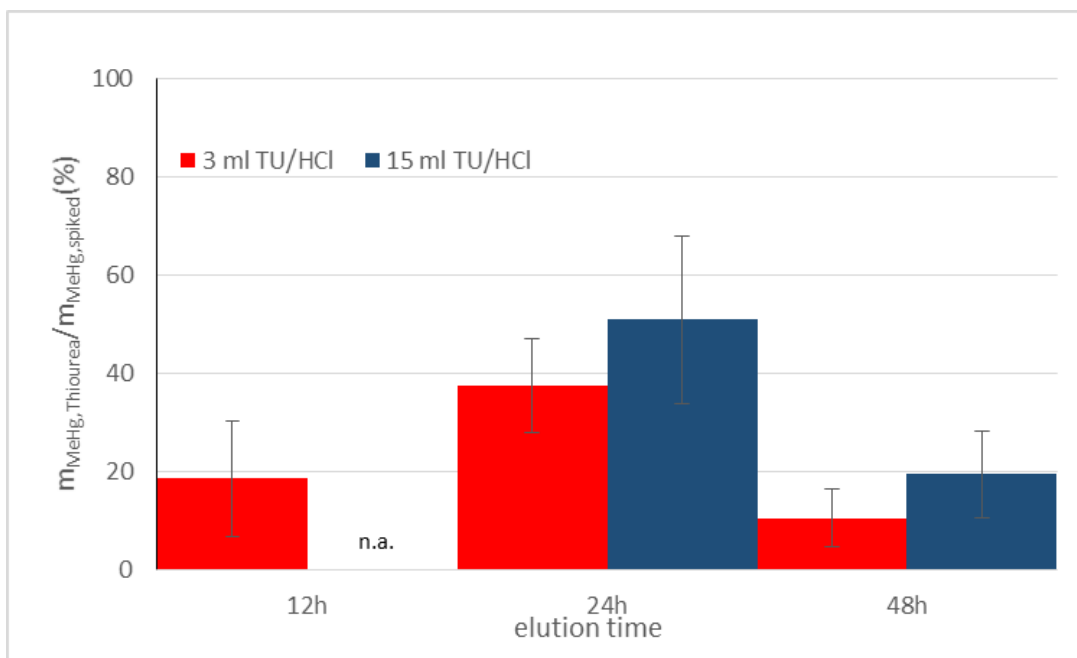


Figure 10 The effect of changing volume and extraction time of 13.1mM TU/0.1M HCl on 1000pg MeHg spike recovery from 3MFSG DGT resin. 15mL eluent recovery after 12 hours was not tested (Schierz et al., 2014)

The effect of TU/HCl dilution on MeHg loss during the analysis

In order to optimize TU/HCl eluent for extraction of MeHg from 3MFSG DGT resin, the effects of TU/HCl dilution on MeHg recovery were examined. This is the step of MeHg recovery procedure following previously discussed extraction step in which the

eluent has already extracted MeHg from the spiked resin and is now separated as a supernatant for the analysis on Merx-M CVAFS (Figure 7). The potential issue examined here is inability to detect MeHg complexed with thiourea after being extracted from the 3MFSG during Merx-M CVAFS analysis. If the concentration of TU/HCl was to interfere with tetraethyl borate derivatization reaction, this could potentially limit the formation of volatile ethylated species from MeHg that could then be separated by gas chromatography and detected by cold vapor atomic fluorescence using Merx-M CVAFS system (Clarisse, O. & Hintelmann, 2006; Gao et al., 2014). The approach to addressing this issue involves optimization of the eluent dilution prior to Merx-M CVAFS analysis to ensure all the MeHg complexed with TU/HCl eluent is detected during the analysis. Direct spikes of MeHg ranging from 25 to 500pg were added to 2, 5, and 15mL of 13.1mM TU/0.1M HCl eluent resulting in final eluent concentrations and recoveries as seen on Figure 1.

Table 1 The effect of final diluted TU/HCl concentration on the recovery of a direct MeHg spike to TU/HCL eluent using Merx-M CVAFS

TU concentration initially used (mM)	13.1	13.1	13.1
HCl concentration initially used (mM)	100	100	100
Eluent volume initially (mL)	2	5	15
Eluent volume prior to TEB addition (mL)	40	40	40
TU concentration prior to TEB addition (mL)	0.655	1.64	4.91
HCl concentration prior to TEB addition (mL)	5	12.5	37.5
Recovery of MeHg spiked directly to the initial eluent concentration and volume (%)	96.95±4.05	83.08±8.16	38.24±12.3

The recovery indicated as the percentage of MeHg detected by Merx-M normalized to MeHg spiked directly to TU/HCl elution show that the optimum concentration for the analysis on Merx-M CVAFS should be 0.655mM TU/5mM HCl eluent, where $96.95 \pm 4.05\%$ recovery was detected (Figure 11). Using one-way ANOVA with $\alpha=0.05$ ($F(2,42)=163.5$, $p=1.15E-20$) indicates statistically significant difference in recoveries based on different TU/HCl strengths. Furthermore, application of Tukey HSD test indicates that different eluent strength recoveries are statistically significantly different from each other. MeHg recovery of increased TU concentration was likely impacted by strong thiourea complexes thiourea formed with MeHg (Hong et al., 2011), resulting in the lack of ethylation following the addition of TEB and subsequently showing lower MeHg recovery.

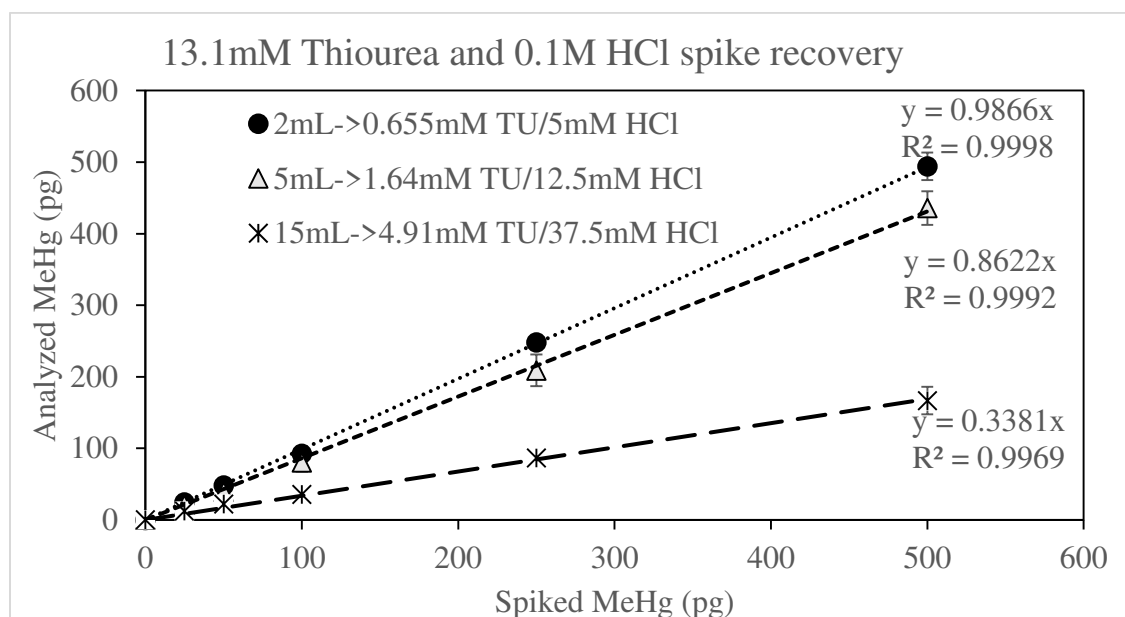


Figure 11 Recovery of MeHg spike to 13.1mM thiourea/0.1M HCl eluent as a result of varying

However, overall extraction of MeHg from 3MFSG DGT resin using 13.1mM TU/0.1 M HCl elution still failed to achieve reproducible $100 \pm 33\%$ recovery from 3MFSG DGT resin. The results presented until now demonstrated that the issue with low recovery is likely originating from the inability of TU/HCl to fully extract MeHg associated with 3MFSG resin. The results demonstrated that the MeHg was completely uptaken by resin, as indicated in Figure 8 and by the analysis of initial spike supernatant. The losses were not associated with the steps following the extraction of MeHg from 3MFSG DGT resin, as the direct spike to TU/HCl eluent was recovered when diluting the eluent to 0.655mM TU/5mM HCl. So in order to achieve reproducible $100 \pm 33\%$ recovery from 3MFSG DGT resin, alternative procedures for extraction of MeHg from DGT resin were examined.

Optimization of the methods for extraction of MeHg from the resin

In order to evaluate if there was a better method for extraction of MeHg from the 3MFSG DGT resin than TU/HCl elution, a couple of alternatives were examined. The first method included solvent extraction with CH_2Cl_2 and back extraction with H_2O commonly used for extraction of MeHg from sediment samples (Baeyens et al., 1999; Bloom, N. S. et al., 1997; Liang et al., 1996). The second method included nitric acid commonly used for extraction of MeHg from the biota samples. The key to this method is diluted nitric acid which strongly binds to MeHg species (BrooksRand Instruments, 2015; Hammerschmidt & Fitzgerald, 2005; Krishna et al., 2005). The nitric acid has also been used to study extraction of 55 elements (Hg not being one of them) from DGT devices composed of Chelex resin immersed in the PA gel (Garmo et al., 2003). The 13.1mM TU/0.1M HCl eluent was used for the comparison to the methods.

Results are showing extraction efficiency expressed as a percentage recovery of the mass detected using each method normalized to 1000pg of MeHg added to the 3MFSG DGT resin (Figure 12). The results are indicating that optimum method for extraction of MeHg from 3MFSG DGT resin are achieved by employing 4.73M nitric acid extraction, as the recovery with nitric acid at $91\pm 9\%$ was considerably better as opposed to the recovery using the 13.1mM TU/0.1 M HCL elute at $57\pm 5\%$, and solvent extraction recovery at $31\pm 7\%$. In order to verify reproducible recovery, the average recovery for the method was calculated on 47 samples, as indicated in the individual recoveries listed in the Appendix A, Table 5. With $91\pm 9\%$ recovery, the application of diluted nitric acid for the extraction of MeHg from the 3MFSG DGT resin satisfies the objective of $100\pm 33\%$ MeHg recovery, as well as the reproducibility of the recovery requirement.

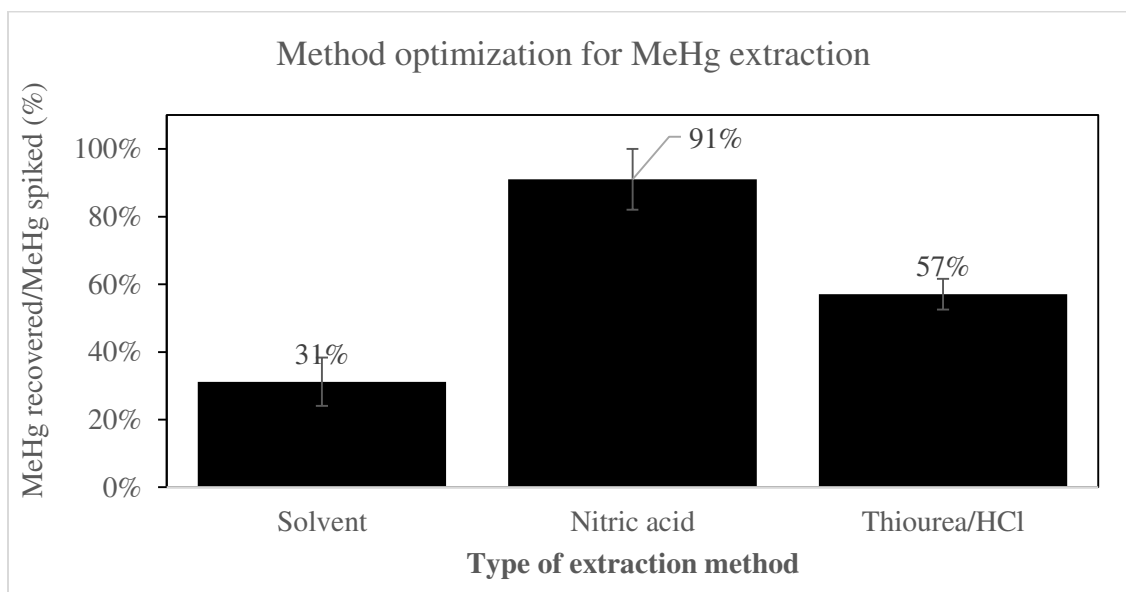


Figure 12 MeHg spike recovery comparison for different extraction methods from the same study

When using nitric acid for MeHg extraction from the sediment samples, quantitative interferences with MeHg measurements can occur during sample processing, such as MeHg being artificially methylated (Hammerschmidt & Fitzgerald, 2001; Leermakers et al., 2005; Mao Tseng et al., 1997). Using nitric acid method to quantify MeHg in fish muscle tissue is likely not affected by artificial MeHg formation as 75-95% of total mercury in fish is in the form of MeHg (Celo et al., 2006; Hsu-Kim et al., 2013). Since natural sediments normally contain only 0.5-2% of THg as MeHg, artificial methylation of ambient mercury can cause significant increase in artificial MeHg (Bloom, N. S. et al., 1997; Hammerschmidt & Fitzgerald, 2001; Hsu-Kim et al., 2013). Potential abiotic methylation during extraction of sediments could be due to humic and fulvic acids, however they would precipitate under acidic conditions (Bloom, N. S. et al., 1997; Hammerschmidt & Fitzgerald, 2001). Fish tissue samples, algae and growth media can have amino acids, peptides, proteins, enzymes, carbohydrates, and their respective degradation products being capable of artificial methylation, mostly observed during alkaline extraction (Hintelmann, H. et al., 1997). As a result of this concern, nitric acid method used for extraction of MeHg from 3MFSG DGT resins was tested for potential artificial formation of MeHg during extraction process. The results of spiking 100-2500pg of THg standard showed that there is no detectable MeHg formation from THg spike addition, as the percentages of MeHg detected over the increases in THg spike range were not correlated to the spikes added (Figure 13). The results were background responses, as the highest spike of 2500pg THg correlated to 0.62% of MeHg detected. As a result of this study, MeHg extraction from 3MFSG DGT resin with nitric acid was not affected by artificial formation of MeHg.

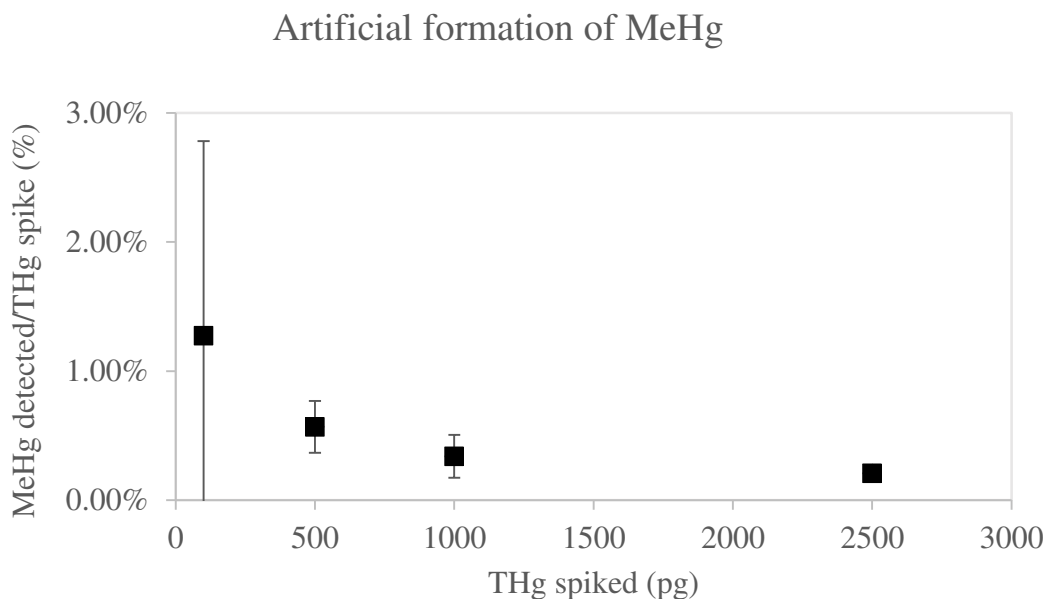


Figure 13 Artificial formation of MeHg from THg spike

In addition to the effects of the artificial MeHg formation, the effects of pH change on optimum methyl mercury recovery (Bloom, N., 1989; Mansfield & Black, 2015) were examined (Appendix A, Figure 60). Maximum average recovery was detected at pH 4.75, however MeHg recovery was found to not be a function of pH in the 4-5.5 range.

To validate that extraction efficiency of MeHg from 3MFSG DGT resin MeHg using nitric acid is independent from the amount of MeHg present in the resin, 3MFSG DGT resins were spiked with the 20-1000pg range and extracted with diluted nitric acid. 20-1000pg correspond to 1-50 ng/L range of DGT MeHg detected for 48 hour exposure, 2cm² area, and 21°C. MeHg mass amount spiked was mostly guided by the detection limit of Merx-M CVAFS analyzer while accounting for 94.6 dilution needed to achieve a final concentration of 0.05M during the analysis from the original concentration of 4.73M

nitric acid that used during 3MFSG DGT resin extraction. The results were plotted as a mass of MeHg detected in eluent and mass of MeHg spiked to 3MFSG DGT resin, and resulted in a linear regression with the coefficient of variation of 0.9995 (Figure 14).

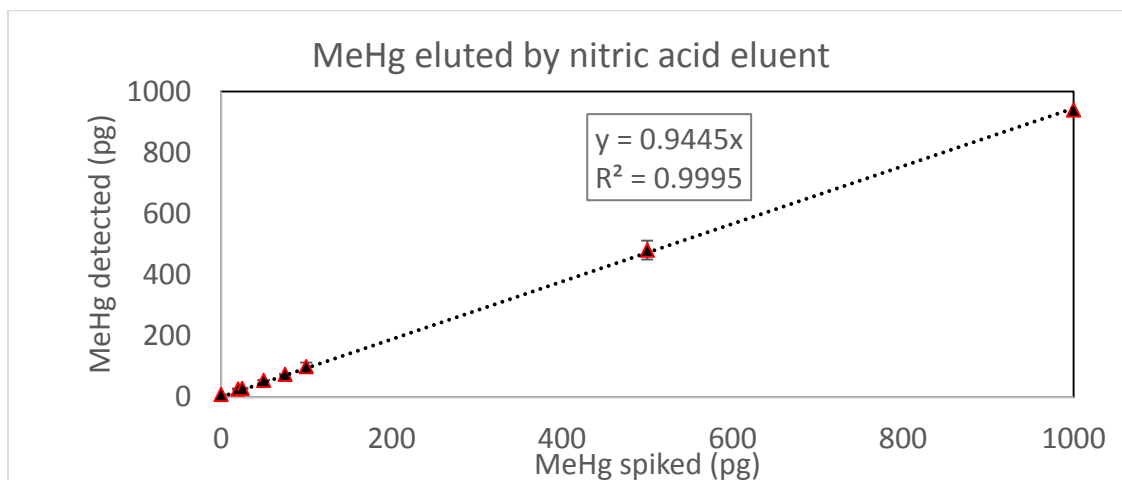


Figure 14 Extraction efficiency of MeHg spiked to 3MFSG resin using nitric acid

As a result of the optimization studied on DGT recovery, nitric acid was found to be efficient in extracting MeHg from 3MFSG DGT resin, resulting in $91 \pm 9\%$ recovery for 47 samples tested (results found in the Appendix A). This extraction efficiency is within the desired recovery for MeHg of $100 \pm 33\%$, making nitric acid digestion the preferred method for extraction of MeHg from 3MFSG DGT resin.

Conclusions and Recommendations

The study demonstrated ability to extract $91 \pm 9\%$ ($N=47$) of MeHg sorbed to the 3MFSG DGT resin by using nitric acid. The recovery achieved accomplished the initial goal of recovering $100 \pm 33\%$ of MeHg spike to the 3MFSG DGT resin, as well as reproducibility of the recovery. There was no evidence of artificial formation of MeHg occurring during the extraction procedure and pH range of 4-5.5 had no significant effect on the extraction efficiency. The method used for accomplishing the objectives of the study indicates that using diluted nitric acid might be a better alternative to using TU/HCl eluent for extraction of MeHg from 3MFSG Isosolute Si-Thiol resin (Biotage). Efforts were done to optimize TU/HCl eluent, demonstrating that the increase in strength of the eluent showed improved MeHg extraction from the 3MFSG DGT resin, however the dilution of eluent to 0.655mM TU/5mM HCl was necessary prior to the analysis to avoid analytical issues.

The recommendations for future work would be to further improve the method by exploring the limits of the detection limit of the diluted nitric acid method. With current method using 4.73M nitric acid for extraction of MeHg from the 3MFSG DGT resin and the dilution of 0.05M nitric acid eluent for analysis, this creates challenges for detection limits that should be addressed in the future research on this topic. Furthermore, the method could be applied to the other DGT resins optimized for MeHg detection.

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CHAPTER IV

EVALUATION OF BANK LEACHING AS A SOURCE OF MERCURY AND EFFECTIVENESS OF STABILIZATION EFFORTS ON MERCURY FATE AND TRANSPORT

Abstract

River banks undergo regular inundation and drainage as a result of flooding after storm events or in estuarine systems as a result of tides. This can enhance releases of any contaminants present in the river banks due to leaching during the drainage portion of the cycle. Pore water sampling of mercury in banks contaminated by historical mercury releases in South River, VA were used to evaluate this mechanism of contaminant release and the effectiveness of mitigation efforts involving stabilization and capping of the banks.

Sampling events during both a low flow condition and after a drainage event in 2015 showed that substantial amounts of biologically relevant mercury could be leaching from the bank areas as result of the post-event drainage. Order of magnitude increases in non-particulate THg pore water concentrations as measured by diffusion gradient in thin file devices (DGTs) were observed during leaching from bank areas. MeHg pore water concentrations decreased likely due to the more oxic conditions observed during leaching.

Efforts to stabilize the bank as well as placement of a cap layer containing biochar led to the observation of dramatically lower pore water concentrations of mercury and corresponding lower Hg fluxes. Although both total and methyl mercury concentrations

were reduced, apparent net methylation rates of available THg were relatively high (leading to 10-50% MeHg in surface DGT measurements) due to reduced conditions developed during baseline flow conditions and high temperatures promoting bacterial activity.

Introduction

The South River in VA was found to be contaminated by mercury during the 1970s when fish concentrations in South River were exceeding the 0.3ppm Virginia Department of Health's guideline for human consumption (Eggleston J., 2009). The cause of contamination was unregulated release of mercuric sulfate that was used as catalyst in the production of acetate flakes and yarn by the DuPont Co. in Waynesboro, VA from 1929 to 1950. In 1984 a monitoring program was set up but did not show satisfactory rates of recovery over the first 20 years and the South River Science Team (SRST) was formed by DuPont and Department of Environmental Quality (DEQ) in 2001 to consider other options. The SRST is an interdisciplinary team of industry, government, academia, citizen groups and private research with the purpose to address the issue of mercury contamination and ensure that the public is properly informed of risks associated with mercury contamination (Virginia Department of Environmental Quality, 2018).

The industrial charges were released into the river at what is now identified as Reference River Mile 0 (RRM 0). The reach from RRM 0 to RRM 3 is characterized by narrow floodplain with low percentage of fine-grained sediment in the channel margins (Anchor QEA, 2013). The main sources of mercury are considered to be erosion of floodplain soils (accounting for 40 to 60% of the THg loading to the river channel system), and historic near-channel deposits "Hg-release age deposits" (HRADs), which contain elevated concentration of mercury deposited from 1929-1950. 47 identified HRADs exist between RRM 0.1- to 23.5, and they are ranging in concentrations from 0.08 to 270 $\mu\text{g/g}$ (Anchor QEA, 2013). A diverse group of iron and sulfate-reducing

bacteria have been found throughout the river that are capable of methylating available inorganic mercury under reduced conditions (Anchor QEA, 2013), causing great concern in terms of accumulation of bioaccumulative neurotoxin methyl mercury in the aquatic organisms (Writer, 2014).

Water-level fluctuations (WLF) have shown to effect mercury fate and transport as compared to constantly inundated sediments. During the time where there is lack of water inundating the sediments, sulfide is oxidized to sulfate, and iron(II) to iron (III) (Feng et al., 2014; Gilmour, C. et al., 2004). Mercury may also be found in more soluble oxidized forms rather than in reduced, low solubility forms such as cinnabar (HgS). During the water-level fluctuations sediment previously depleted of water gets inundated, providing an abundance of nutrients and moving the more soluble mercury forms into the pore water. The bank sediments are oxic since they were previously unsaturated and exposed to air and thus methylation is discouraged and more soluble forms of mercury are preferred. This mercury can then leach from the contaminated floodplains during the drainage cycle of the storm event (Bigham et al., 2016; Eckley, Chris S. et al., 2017). Water level fluctuations also increase sulfate and labile organic matter present in the system. Once the reoxygenated system gets reduced, sulfate and labile organic matter drive microbial activity, contributing to net increase of methylation of mercury (Feng et al., 2014; Gilmour, C. et al., 2004). A duration of 10-15 days has been found sufficient to observe development of optimum reduced condition resulting in maximum net methylation rate (Brigham et al., 2002). WLF phenomena has been observed in hydrologic reservoirs where elevated MeHg concentrations were detected upon reservoir creation (Anderson et al., 1995; Bigham et al., 2016; Brigham et al., 2002; Eckley, C.S. et

al., 2015; Eckley, Chris S. et al., 2017; Gilmour, C. et al., 2004; Montgomery et al., 2000; Plourde et al., 1997; Sorensen et al., 2005; Ullrich et al., 2001). A study by Strickman and Mitchell concluded that the effect of repetitive WLF at a designed wetland was not correlated with increase in MeHg and this phenomena was rather an effect of extreme draughts and rewetting cycles influencing sediments that are not commonly in the zone of WLF (Strickman & Mitchell, 2017b).

In a study by Gilmour et al., rewetting of the soil cores caused 100 times increase in overlaying water sulfate concentrations and an increase in sediment pore water concentrations as compared to the concentrations found in constantly inundated surface waters and sediment pore water (Gilmour, C. et al., 2004). This was linked to organic soil oxidizing reduced sulfur species to sulfate which also stimulates methylating bacteria once conditions turn more reduced and stimulate methylation (Eckley, C.S. et al., 2015; Eckley, Chris S. et al., 2017; Gilmour, C. et al., 2004; Orem et al., 2011). The phenomena of the effects of dry/wet cycle has also been observed with measurement of Hg fluxes from sediment into the air. An increase in Hg emissions from soil into ambient air has been observed in deserts following a rainfall event, with the maximum flux out of the sediment appearing in the first 30 minutes after moisture has been added to the sediments (Lindberg et al., 1999).

These processes were studied at the South River, VA at two locations close to the mercury source (RRM 0.2, Constitution Park, and RRM 1.1, North Park). Pore water concentration measurements were acquired using diffusion gradient in thin film devices (DGTs) and used to infer mercury fluxes from the river banks during normal and drainage conditions.

DGT profilers are in-situ sampling technique used to measure pore water non-particulate mercury (THg) and methyl mercury (MeHg) concentrations. The DGT profilers consist of a sorbing resin hydrogel optimized for sorption of mercury, a diffusive agarose hydrogel of well-defined diffusion coefficient, and a 0.45 μm filter layer. Sorbing resin gel effectively serves as an infinite THg and MeHg sink, keeping a zero concentration on one side of the diffusive gel while the other surface is exposed to sediment pore water concentration of THg and MeHg (Clarisse, O. & Hintelmann, 2006; Dočekalová & Diviš, 2005). Transport of THg and MeHg species through the agarose layer is defined by diffusion (Zhang, Hao. & Davison, 1995). After retrieving DGT profilers and analyzing the resin layer for THg, and MeHg, Fick's first law of diffusion is used to determine mercury concentrations sediment pore water. Mercury species detected in pore water are considered as most representative of the biologically relevant pool of mercury (Ankley et al., 1994; Chapman et al., 2002). THg and MeHg detected using DGT devices include particles operationally defined as dissolved, but may also pass fine particles in the size range of 1-20 nm. The pores of the agarose gel are in the 50-70 nm size range and particles much larger than molecular sizes (<1 nm) are slow to diffuse (Fatin-Rouge et al., 2004).

The potential for bank erosion during high flow events as well as leaching during post-flood drainage led to efforts to stabilize the bank. Initial efforts by Summit Environmental Services were focused on an area of bank along Constitution Park. Portions of the bank were excavated before stabilizing the bank including placement of a leachate control layer. In the areas of lesser erosion and with lower mercury contamination, 6 inch cap including biochar and sand mixture placed within a geocell

was laid, with soil placed on the top to enhance vegetation growth (Figure 15), and erosion control fabric added to prevent possible erosion (Anchor QEA, 2013; SRST, 2016b). After stabilizing the banks with rock toe at the base and adjusting slope by soil lifts, vegetation was replanted to help prevent erosion and woody debris was anchored to rock toe to improve fish habitat (Figure 16) (Anchor QEA, 2013; SRST, 2016b).

Biochar is produced from pyrolysis of biomass and has a large surface area, high porosity and reactivity and has been utilized as an *in-situ* capping amendment to reduce the mobility of the most mobile forms of both organic and inorganic compounds (Beesley et al., 2010; Beesley & Marmiroli, 2011; Gomez-Eyles et al., 2013). Biochar sorption is assumed to be controlled by surface chemistry, with the main sorbing processes including complexation with functional groups, electrostatic interaction, ion exchange precipitation and reduction reactions (Xu, X. et al., 2016). The main advantage of amending uncontaminated natural sediment with biochar is the ability of biochar to effectively sorb MeHg (Gomez-Eyles et al., 2013; Ptacek & Blowes, 2015). Isotherms of both THg and MeHg sorption to the biochar can be fitted with linear models (Gomez-Eyles et al., 2013). Sand amended even with low masses of biochar (3%) has been found effective in removal of THg (Ptacek & Blowes, 2015), however both natural sediment and biochar amended caps have been found to have similar capabilities of THg sorption (Gomez-Eyles et al., 2013).



Figure 15 Implementation of the cap layer on South River site (SRST, 2017)

Objectives of the study

The goal of this study was to evaluate the release of mercury during drainage events through measurement of pore water concentrations of mercury in the bank adjacent to the river and to examine any reductions in mercury release associated with the bank stabilization and capping effort. Sampling of the pore water was done during near-baseline flow as well as following a flooding event to evaluate the effects of storm event related drainage on leaching of non-particulate Hg. Pre-stabilization measurements of non-particulate release from the bank sampled in 2015 were compared to post-stabilization measurements in 2017 to evaluate the effectiveness of bank stabilization efforts on non-particulate associated leaching of THg and MeHg. Evaluation of non-particle related THg and MeHg release was done using diffusive gradient in thin-film (DGT) devices on near surface sediment pore waters (<15cm below sediment-water interface). In addition to DGTs, peeper dialysis samplers were used for evaluation of

anions. Voltammetry and ion specific electrode systems were used for evaluation of oxygen, manganese, iron, sulfides, pH and oxidation-reduction potential (ORP) conditions of near surface sediment. Incorporation of peepers in addition to voltammetry and ion specific electrode systems was used for better understanding of biogeochemical conditions affecting fate and transport of mercury in the system.

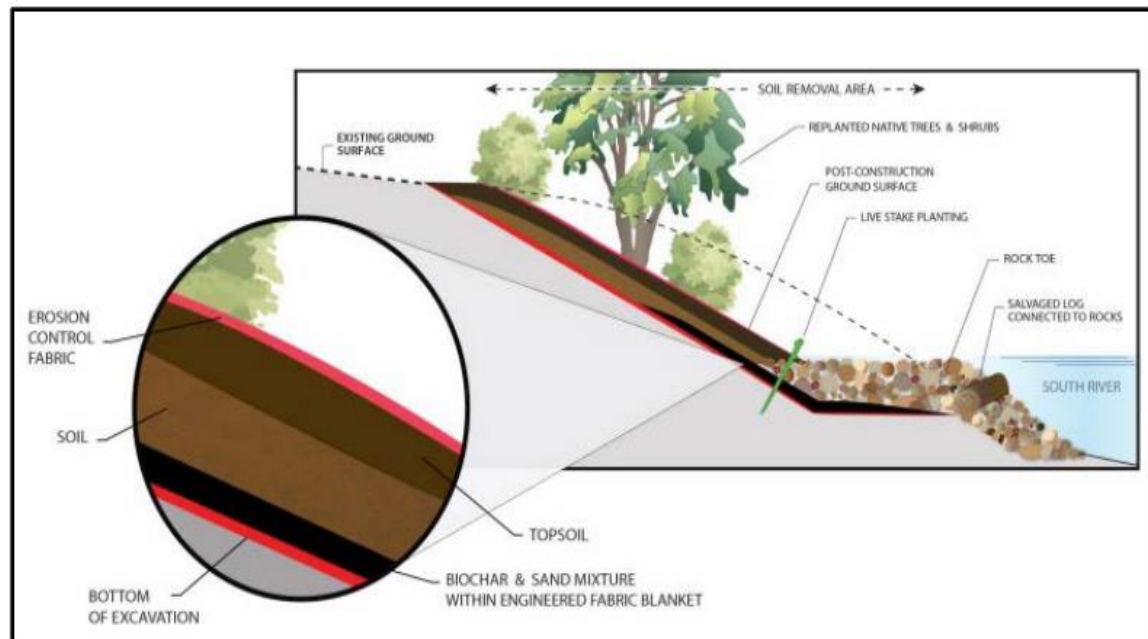
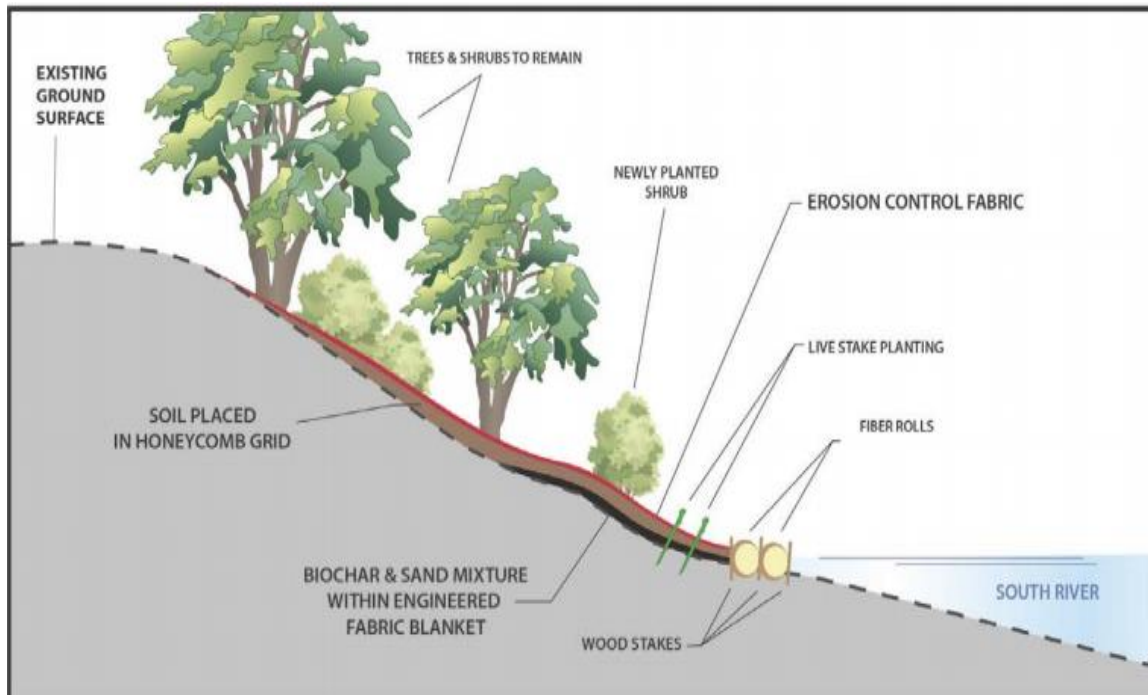


Figure 16 Contaminated Soil Capping Approach implemented at Location 1 of Constitution Park (top) and contaminated soil removal approach implemented at Locations 3 and 5 of the Constitution Park (bottom) (SRST, 2016)

Materials and methods

Sampling timing and locations

The 2015-2017 sampling events were performed at the Constitution Park and North Park in Waynesboro, VA. Two sampling events were done in 2015, the first one from July 20-24, 2015, and second one from October 12-15, 2015. 2015 events were planned to evaluate baseline conditions during July sampling, as well as the potential bank leaching following the storm event that occurred during October sampling. Post stabilization sampling was done from August 15-19, 2017.

Sampling was conducted at 10 locations in 2015, 6 of them were at the Constitution Park (Figure 18), and 4 were downstream at North Park location (Figure 19). North Park was used to illustrate the effects of drainage events at a location that was not subjected to bank stabilization. All the odd-numbered locations were located at the bank of the river, and all the even numbered location were located at the channel of the river. Bank locations were determined as an interface of bank and water during July sampling and were used since water exchange with the bank is the greatest at that point. Channel locations were located 10-15ft off the bank locations to evaluate stream-sediment pore water exchange in the near surface sediments (Figure 17). The initial locations were GPS tracked to enable to perform subsequent measurements at each location. Locations near the bank contain finer grained sediment. Locations in the channel have coarser sediment and gravel. Location numbers increase in the downstream direction.

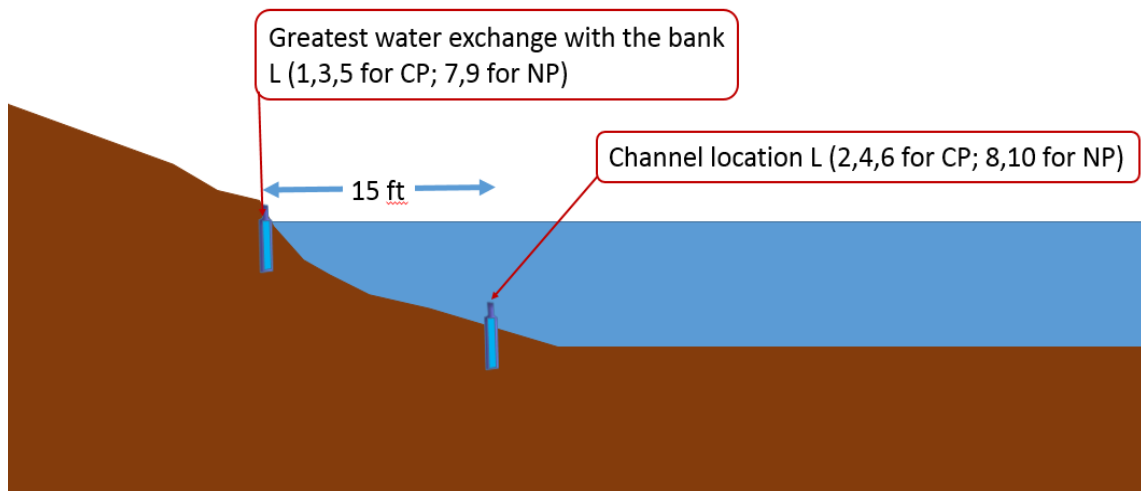


Figure 17 DGT deployment at bank and channel locations

Sampling in the August 2018 was focused only on the Constitution Park due to the stabilization effort implementation at this location. In addition to the previously mentioned six Constitution Park locations, the eleventh location (L0) was chosen as upstream of bank stabilization area to compare the effectiveness of stabilization efforts to adjacent areas (Figure 18).



Figure 18 Constitution park sampling locations (Google, 2016)

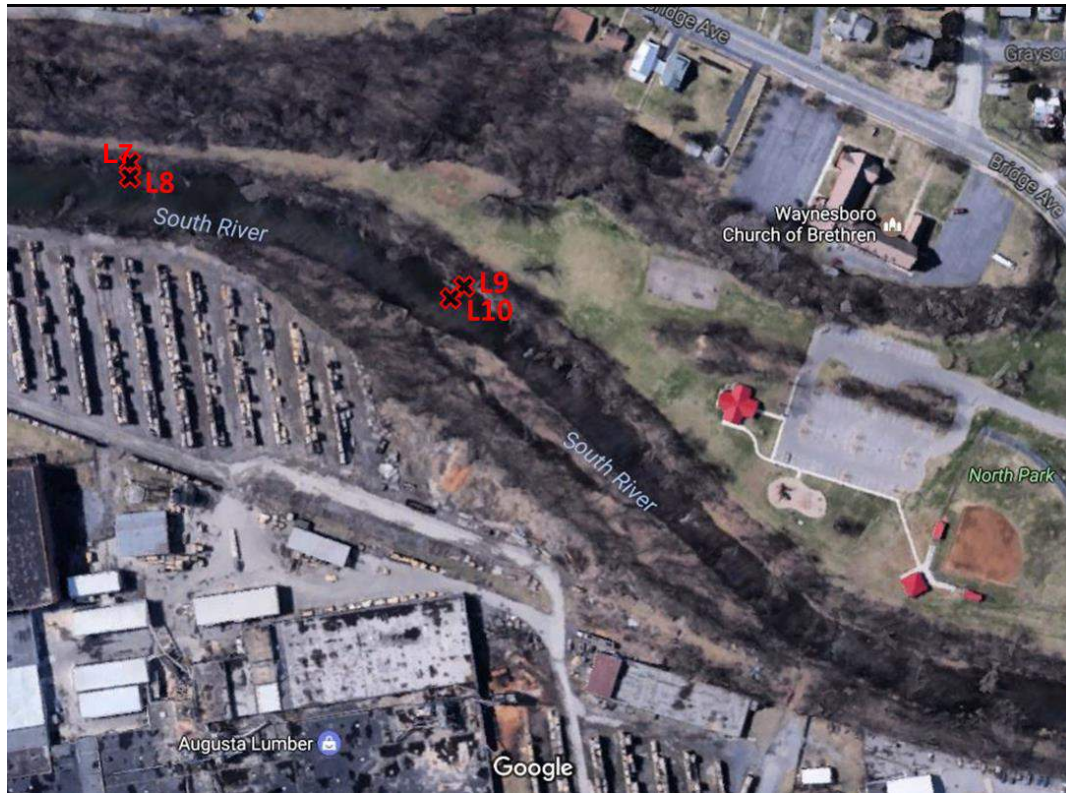


Figure 19 North park sampling locations (Google, 2016)

Table 2 GPS coordinates of the locations tagged in 2015 and 2017 sampling

Time	July 2015		October 2015		August 2017	
GPS °direction	°N	°W	°N	°W	°N	°W
Location L0					38.06621	78.88435
Location L1	36.06633	78.88445	38.06638	78.88442	38.06638	78.8844
Location L2	38.06633	78.88437	38.06635	78.88436	38.06634	78.88432
Location L3	38.06646	78.8844	38.06647	78.88443	38.06647	78.88438
Location L4	38.06649	78.88434	36.06647	78.88437	38.06646	78.88432
Location L5	38.06646	78.88446	38.06661	78.88443	38.06663	78.88441
Location L6	38.06665	78.88432	38.06662	78.88438	38.06662	78.88438

<i>Location L7</i>	38.07654	78.88149	38.07652	78.88152		
<i>Location L8</i>	38.07652	78.88148	38.07652	78.88148		
<i>Location L9</i>	38.07739	78.87996	38.07747	78.87985		
<i>Location L10</i>	38.07739	78.87986	38.07743	78.87983		

With respect to the implemented stabilization efforts, locations in 2017 were chosen to be as close to the originally tracked 2015 GPS locations as possible. Location L1 was right below the implemented wood stakes, whereas locations L3 and L5 were chosen near the rocks that were placed there for erosion control. Water temperature was measured using infrared temperature laser gun.

Diffusive Gradient in Thin Film Devices

The DGT bodies were ordered from the Lancaster University but fabricated at the Texas Tech University. The resin gel (sorbing layer) was made using 3-mercaptopropyl functionalized silica gel (3MFSG) Si Thiol resin (Biotage) immersed in the agarose gel (Fisher). The diffusive gel was also made from the agarose (Fisher), and covered by a 0.45 micron filter (Durapore), which was cut to necessary size for the DGT body. Following the assembly of a DGT (Figure 20), samples were deaerated in sodium nitrate to raise ionic strength, and profilers were bagged inside of an anaerobic chamber and placed on ice until site deployment.

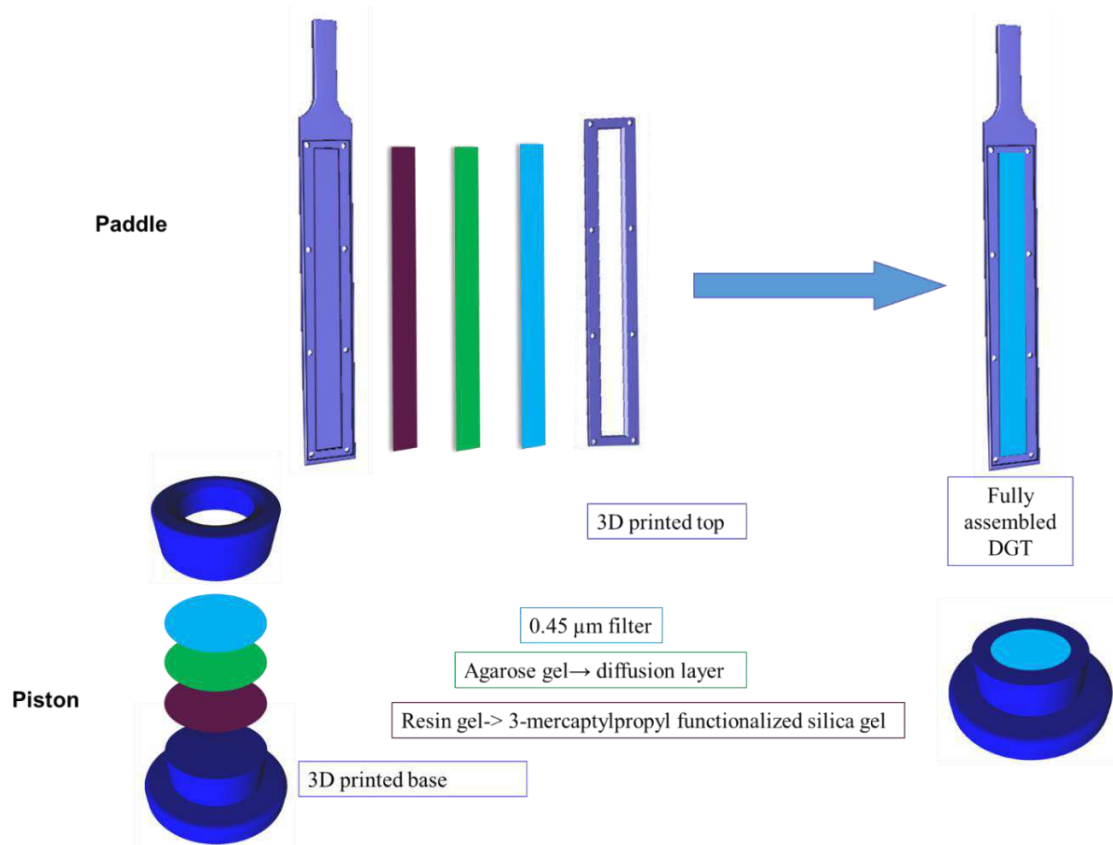


Figure 20 DGT parts and assembly (not to scale)

Multiple DGT paddles were deployed at each location. Each of the DGT paddle replicates was placed at about 1 ft distance from the other DGT device deployed at the same location. During 2017 sampling at bank locations L3 and L5, deployment of paddle replicates was also controlled by positioning of armoring stone, as DGT paddles had to be deployed around the rocks (Figure 21). Pistons were placed at the sediment-water-air interface face down towards the sediment-water interface and covered with a silicon polymer (Silly Putty®) to seal against the sediment. Three pistons were also attached to a channel profiler to measure water column concentrations at different depths of the location 6. DGT profilers were deployed twice during sampling. Both pistons and paddles were deployed for 48 hours.



Figure 21 Bank location L3 DGT paddle profiler deployment during baseline condition July 2015 (left) and August 2017(right) sampling. Notice the differences in L3 location caused by stabilization effort implementation, as well as the deployment of a dialysis membrane at the L3 location during August 2017 sampling

After 48 hours of deployment, DGTs were retrieved, rinsed with DDI water to remove soil particles from piston and paddle bodies and immediately placed in a plastic bag. After retrieving all the samples from the location, DGTs were double bagged and placed on ice. Ice was continuously added to keep the samples cool and the samples were returned to TTU for processing and analysis. During processing for analysis, paddle resin hydrogels were split in half along the depth, and sectioned into 1 cm increments during 2015 sampling and 2 cm increments during 2017 sampling starting in each direction from sediment-water interface (0cm). Increment sizes were doubled during 2017 sampling to lower the detection limit. Piston resins were cut in half for simultaneous THg and MeHg analysis. Each sectioned area was measured separately and noted.

Total mercury resin gels were eluted using 2mL of concentrated trace-metal grade hydrochloric acid for 24 hours, then diluted using 1% bromine monochloride and allowed to digest for additional 24 hours to break down any mercury complexes present (Chess, 2010). Samples were analyzed on a Brooks Rand Merx-T cold vapor atomic fluorescence spectroscopy (CVAFS) using EPA Method 1631, Revision E (US EPA, 2002). Resin gels used for methyl mercury analysis from 2015 sampling were eluted in 15mL of 0.1 M trace metal grade hydrochloric acid with 13.1 mM thiourea. The samples were left for 24 hours and then analyzed on Brooks Rand Merx-M CVAFS system using EPA Method 1630 (US EPA, 2001), modified to adjust to pH to around 4.75 to achieve an accurate analysis. Extraction efficiency of MeHg in the lab by using this method has demonstrated recovery that was less than 60%. However, recovery of MeHg from DGT resins that were first deployed *in-situ* (“sediment exposed resin”), subsequently spiked and tested for recovery was substantially better as compared to DGT resins not deployed *in-situ* and used only during the lab spike recovery studies (“clean”) (Figure 22), indicating that results of *in-situ* deployed DGTs could provide quantitative recoveries. A better recovery was likely due to weaker binding of MeHg onto the resin due to competition of Hg with NOM in the river.

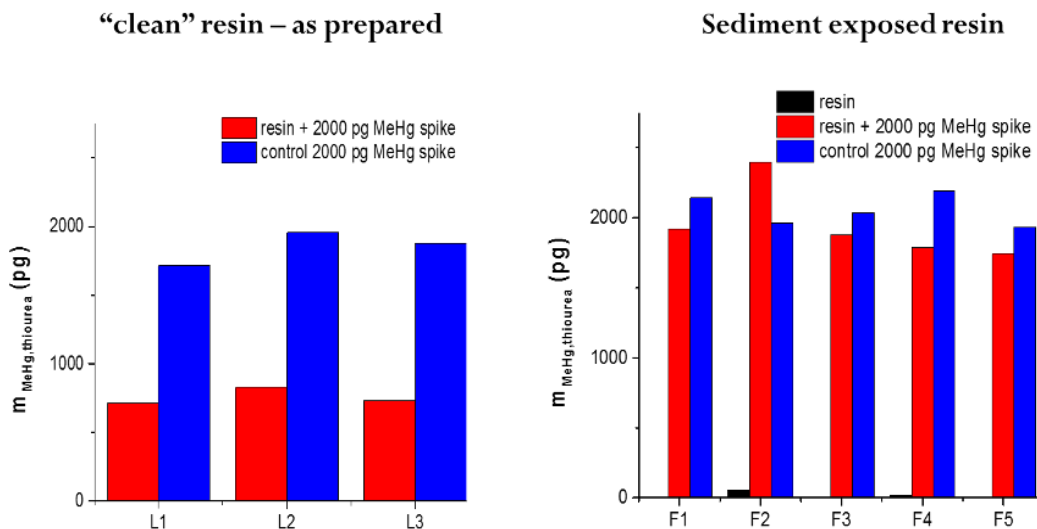


Figure 22 DGT extraction of MeHg with 13.1mM TU/0.1M HCl eluent. On the left are the results of the DGT resin that was spiked with MeHg in the lab and tested for MeHg recovery. On the right are the results of the DGT profiler that has been deployed *in-situ*, spiked with MeHg following the retrieval, and extracted for MeHg (Schierz et al., 2014)

Resin gels used for methyl mercury analysis during 2017 sampling were eluted in 10mL of 30% diluted nitric acid and digested in the oven overnight. This method for extraction of MeHg from DGT resins has been found capable of recovering $91 \pm 9\%$ of MeHg accumulated to the DGT resin due to strong binding of nitric acid and MeHg. The samples were analyzed on a Brooks Rand Merx-M cold vapor atomic fluorescence spectroscopy (CVAFS) using EPA Method 1630 (US EPA, 2001). As a result of change of elution method and differences in recoveries of MeHg from DGT resin for the both methods, comparison of MeHg results between 2015 and 2017 sampling should be done with caution.

In order to calculate pore water concentrations of DGT THg and MeHg, equation describing the mass uptake derived from Fick’s first law of diffusion is used:

Equation 2 Fick's first law of diffusion

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

Where C_b is pore water concentration (ng/L), m is mass accumulated in resin (pg), Δg is diffusion and filter layer combined thickness (cm), D is diffusion coefficient of dissolved inorganic mercury and methyl mercury adjusted for temperature (Equation 3) (cm^2/s), t is time of exposure (s), and A is area of resin exposed and analyzed to obtain mass measurement (cm^2).

Correction for temperature needs to be made for diffusion coefficient value D (Zhang, Hao. & Davison, 1995).

Equation 3 Diffusion coefficient temperature adjustment

$$\log D_T = \frac{1.37023 * (T - 25) + 8.36 * 10^{-4} * (T - 25)^2}{109 + T} + \log \frac{D_{25} * (273 + T)}{298}$$

Where D_T is diffusion coefficient of ions in water at temperature t (cm^2/s), D_{25} is diffusion coefficient of ions in water at 25°C (cm^2/s), and T is temperature at which profiler was deployed ($^\circ\text{C}$).

The practical quantification limit of the Merx-T instrument is 25 pg (lowest calibration mass). This limits the detection limit of DGT devices for 48 hours of exposure and typical sample area to a concentration of around 2.6 ng/L THg for 48 hours deployment, temperature of 21°C and 2cm^2 area of exposure. Samples were “J” flagged if measured concentrations were below the quantification limit for a particular time of exposure and resin area. Quantification limit for Merx-M analyzer used in this study is

1.09 pg which is equivalent to 1.23ng/L for 48 hours deployment, temperature of 21°C and 2cm² area of exposure. Values below these, again accounting for all the other parameters were flagged with “J”. Each set of samples for both total and methyl mercury had appropriate QC checks. Every ten samples analyzed were followed by QC sequence with a blanks and spiked samples. All QC samples were prepared at the same time as the samples. In the event of QC checks not being within acceptable recovery percentage of $\pm 23\%$ and/or substantial blank contamination, the entire set of samples was rejected. DGT profilers were also taken to each sampling event as field blanks as well as left in the lab as a lab blank. One of the field blanks was spiked with THg and MeHg upon return as a trip spike. For DGT QC samples, the average THg detected in field blank samples was 7.24 ± 1.47 pg, which is equivalent to 0.37 ± 0.08 ng/L for 48 hour deployment, 2cm² area, and the same temperature. The average MeHg detected in field blank samples was 0.56 ± 0.06 pg, which is equivalent to 0.029 ± 0.003 ng/L for the same conditions as mentioned above. The average THg detected in lab blank samples was 7.54 ± 1.26 pg (0.39 ± 0.07 ng/L), whereas average MeHg detected was 0.57 ± 0.05 pg (0.029 ± 0.003 ng/L). The similarity between field and lab blanks indicates that there were no contamination issue associated with sample handling during field deployment and transport. As all of these values are below the detection limit for both THg and MeHg. Average recovery of 7 samples spiked with THg was $89 \pm 10\%$. Samples spike with MeHg resulted in $90 \pm 5.9\%$ recovery (2017 sampling).

Diffusion sampler deployment (peepers)

A dialysis membrane allows diffusion of dissolved constituents between sediment pore water and dialysis compartments. The system relies on equilibration of compartment

water and pore water, and had been shown to require deployment of one week or longer (Mason, R. et al., 1998). The peeper frame is commonly made from acrylic (plexiglass) frame with set amount of compartments filled with deoxygenated ultrapure water. A microbially resistant membrane is placed on top and is usually made out of polysulfone material (Peijnenburg et al., 2014). The pore size of the membrane used in the SR deployment was 0.45 μm . Peepers were assembled at the Waynesboro office of the South River Science Team and deployed for 96 hours at the bank locations. Upon retrieval of the peepers, a syringe was used for retrieval of samples from the compartments at known deployment depths. Samples were sent back to TTU and analyzed using ion chromatography to obtain chloride, nitrite, nitrate, sulfate, and fluoride concentrations, while using bromide as a tracer to ensure equilibrium conditions.

Systems for measuring redox conditions

Voltammetry electrodes

Voltammetry scan allow determination of redox profiles in surface and pore water in sediment by detecting current changes over a range of potential (-1.8V to -0.2V). Gold amalgam Au/Hg constructed with PEEK electrode allows for simultaneous measurements of oxygen, ferrous iron Fe^{2+} , manganese Mn^{2+} , and dissolved sulfide species S(-II) in μM limits with mean detection limit of $<0.2 \mu\text{M}$ (Brendel et al., 1995; Grundy, 2013; Luther et al., 2001). The peak for sulfide is the sum of hydrogen sulfide, bisulfide, sulfide, thiols and polysulfide species and is defined as total S(-II), and labile dissolved sulfide (DS) (Brendel et al., 1995; George W Luther III et al., 1985). Ag/AgCl in 3M KCl is used as reference electrode with a potential of 0.210V vs Normal Hydrogen Electrode (NHE) whereas the counter electrode is made out of platinum and reduces drift during the

sampling. A DLK-70 Web PStat potentiostat (Analytical Instrument Systems (AIS), NJ) is used for obtaining current values for a range of potentials and a multiplexer DLK-SM-1 is used to obtain simultaneous measurements from up to 8 working electrodes at the same time (Figure 23).

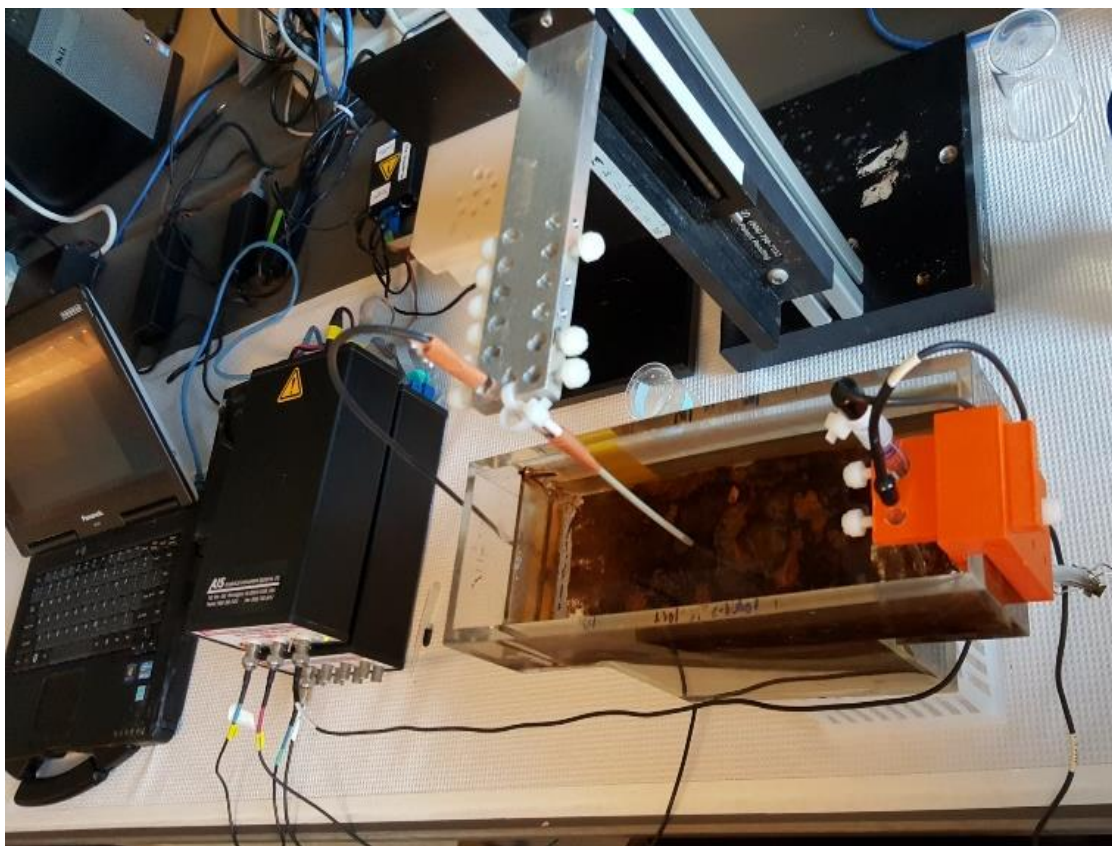


Figure 23 Voltammetry system used in the lab

Oxygen concentrations are obtained using linear sweep voltammogram (LSV), where distance between plateaus is correlated to the oxygen calibration performed in the lab. Ferrous iron, manganese and dissolved species concentrations are obtained using sweep wave voltammogram (SWV), where the peak area is integrated and compared to the calibration performed in the lab. A great advantage of votammetric system is that fabrication is done in the lab, electrodes are robust and sturdy for use with coarser

sediments (such as channel locations of the rivers). The disadvantage of the system is experience necessary to operate the system, calibration correlation to the site conditions is still a matter of discussion and post processing takes a long time. Voltammetry allows for depth-specific measurements, so redox conditions can be associated to the measurements obtained by the DGT devices at the same depth (Harper et al., 1998). Although electrodes made out of Au/Hg could cause a concern to mercury contaminated site concentration measurements, the amalgam is considered to be too strong to diffuse into the sediment (Grundy, 2013).

Since two types of scans are used, two calibrations were obtained prior to the sampling. The LSV scan oxygen calibration is done using 2-points (fully saturated and fully deaerated synthetic freshwater). The SWV scan calibration of remaining analytes is done with Mn^{2+} calibration and “pilot ion method”, where the concentrations of remaining analytes in environmental samples in seawater at a scan rate of 200 mV/s and pulse height of 15 mV were determined using Mn^{2+} slope and constant ratio between slopes for different species, where $\text{Mn}^{2+}=0.070 \text{ nA}/\mu\text{M}$, $\text{Fe}^{2+}=0.025 \text{ nA}/\mu\text{M}$, and total $\text{S}(-\text{II})=2.2 \text{ nA}/\mu\text{M}$ (Brendel et al., 1995). Each electrode was calibrated separately and scans during calibration and sampling were noted based on the association of the electrode with which the scan was obtained. The data collected with AIS software was transferred to MATLAB where VOLTINT, a semi-automated processing program, was used to process geochemical data obtained by voltammetry (Bristow & Taillefert, 2008; Grundy, 2013). Manual peak and plateau separation of voltammograms were used to obtain numerical results.

For LSV scans, the current typically begins at around 0 nA at 0.1V. It then increases to a plateau of 25-40nA at about -0.3-0.4V and at about -1.3V it increases to a plateau usually about twice as high (50-80 nA). The two plateaus indicate reduction of oxygen to hydrogen peroxide, and hydrogen peroxide to water, respectively. In the event of no oxygen detected, there will be no plateaus in the scan (Figure 24). SWV scans have peaks associated with different potential. The locations of peak potentials are used to identify the analytes present in the system, with dissolved sulfide peaks generally occurring at around -0.6V, iron(II) at around -1.4V, and manganese(II) at around -1.55V (Figure 25). These peaks do slightly shift during the run due to pH, temperature and the salinity of solution.

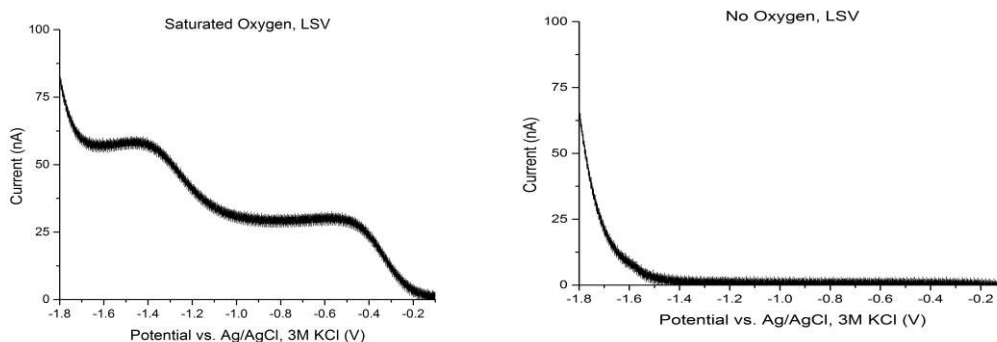


Figure 24 Voltammogram of freshwater with and without dissolved oxygen (left and right, respectively) (Grundy, 2013)

Result from VOLTINT program for LSV scan is a current difference between no oxygen plateau and oxygen plateau. The output of SWV scan is peak area at specific potential. LSV scan results are converted to concentration of dissolved oxygen using Equation 4. For SWV scans, the type of analyte is determined based on the location of the peak and subsequently concentration is determined using related slope and Equation 5 (Bristow & Taillefert, 2008).

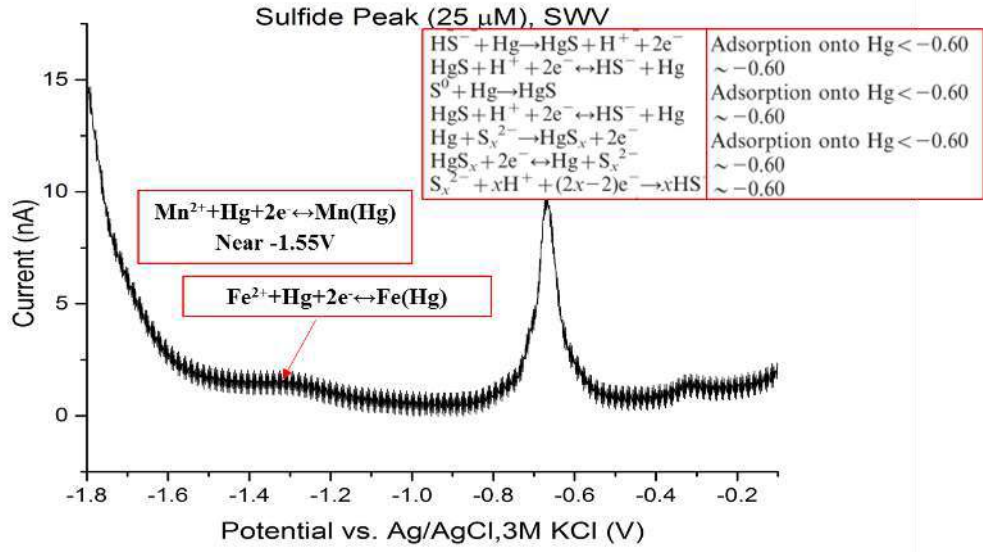


Figure 25 SWV scan used to determine the Mn(II), Fe(II), and S(-II) species (Brendel et al., 1995; Grundy, 2013)

Equation 4 Obtaining DO Concentration from LSV scan

$$C_{O_2} = \frac{\text{current of } O_2 \text{ plateau of sample}}{\text{current of } O_2 \text{ plateau of saturated solution}} * \text{conc. of sat. soln.} \left(\frac{\text{mg}}{\text{L}}\right) * 62.5 \frac{\mu\text{M } O_2}{\text{mg/L}}$$

Equation 5 Obtaining redox species from SWV Scan

$$C = \frac{\text{Peak height (or area)} [\text{nA}]}{\text{Calibration slope} [\text{nA}/\mu\text{M}]}$$

Ion specific electrode

An ion specific electrode system consisted of Unisense Microsensor Multimeter (Version 2.01) coupled with OX-N and H₂S-NP sensors and PH-NP, RD-N and REF-RM electrodes. All probes were modified to include 20meter cables, 2.1x80mm piercing needle, and the weather-proof lemo connection. The system was used for depth specific measurements of oxygen and sulfide concentrations, pH, and redox potential. Probes were calibrated in the lab, calibration was verified on site and electrodes were then

deployed at known depths in 0.5cm intervals. Probing for a given location was completed once the electrodes encountered an obstacle (roots, shells, coarser sand or gravel) due to potential of probes to break. Probes were rinsed with DDI in between the location deployments.

Amperometric electrodes made by Unisense can measure H₂S in the range from 0-300µM. H₂S microsensor has an internal reference, sensing and guard anode. H₂S passes sensor membrane tip, HS⁻ ions formed are oxidized by ferricyanide to sulfur and ferrocyanide. Sensor voltage reading is generated by reoxidation of ferrocyanide. Since the reading is obtained in picoamperes, amplifier is used to obtain measurements. In order to calculate total sulfide concentration, pH measurement is necessary. Calibration is performed prior to sampling using known H₂S concentrations in the 0-300 µM range of values, and pH is calibrated using pH buffers 4, 7, and 10. Once both H₂S and pH measurements are obtained, concentration is calculated using following Equation 6- Equation 12 (Unisense A/S, 2012a):

Equation 6 Obtaining DS measurements

$$[S_{tot}^{-2}] = [H_2S] + [HS^{-}] + [S^{2-}]$$

Which correlated to speciation based on pH is:

Equation 7 Obtaining DS measurements

$$[H_2S] = \frac{[S_{tot}^{-2}]}{1 + \frac{K_1}{[H_3O^{+}]} + \frac{K_1K_2}{[H_3O^{+}]^2}},$$

Where:

Equation 8 Obtaining DS measurements

$$[H_3O^+] = [H^+] = 10^{-pH}$$

Equation 9 Obtaining DS measurements

$$pH = -\log[H^+]$$

Equation 10 Obtaining DS measurements

$$K_1 = 10^{-pK_1}$$

Equation 11 Obtaining DS measurements

$$pK_1 = -98.08 + \frac{5765.4}{T} + 15.04555 * \ln(T) + (-0.157 * (S^{0.5})) + 0.0135 * S$$

At pH range from 4 to 9,

Equation 12 Obtaining DS measurements

$$[H_2S] = \frac{[S_{tot}^{-2}]}{1 + \frac{K_1}{[H_3O^+]}}$$

Where T is temperature in K, and S is salinity (‰).

Oxygen probe is a miniature Clark-type oxygen sensor using external partial pressure to drive oxygen into tip where it is reduced at gold cathode surface at a reduction current that is converted to a signal. Detection limit is 0.3 μM and the calibration of electrodes for oxygen measurements is performed using two point calibration (fully saturated and fully deoxygenated) and Equation 13 to obtain dissolved oxygen concentration measurement (Unisense A/S, 2012b).

Calculation for oxygen concentration is:

Equation 13 Obtaining DO measurements

$$C = a * \frac{S - S_0}{S_{at} - S_0}$$

Where C is concentration of oxygen ($\mu\text{mol O}_2/\text{L}$), S_0 is zero oxygen partial pressure (atm), S_{at} is partial pressure of oxygen at max saturation (atm), and a is atmospheric level solubility ($\mu\text{mol O}_2/\text{L}$).

pH electrode uses difference in electric potential between reference electrode and open ended Ag-AgCl electrode with a gel-stabilized electrolyte. Both reference and pH electrode are calibrated using 3 point calibration with pH buffer 4, 7 and 10 (Unisense A/S, 2017a).

Redox microelectrode is a miniaturized platinum electrode which obtains measurement by measuring electric potential developed between reference Ag-AgCl electrode and redox electrode. Redox potentials are recorded with respect to standard hydrogen electrode (SHE). Calibration is done by performing measurements of potential differences for quinhydrone pH 4 and pH 7 redox buffer and correlating it to known temperature and potential difference with respect to SHE (Table 3) (Unisense A/S, 2017b).

Ion specific electrodes were used as a preferred method for obtaining redox readings to previously used voltammetry system due to ease of use (no need for fabrication of electrode), faster response of electrode minimizing the time needed to be spent on site taking measurements, and the ability to obtain results immediately from

microsensor screen, as opposed to spending months obtaining readings from the voltammetry system.

Table 3 Redox potential for quinhydrone redox buffer provided by Unisense (Unisense A/S, 2017b)

Temperature (°C)	pH 4 buffer	pH 7 buffer
20	470	295
25	462	285
30	454	275

Results and discussion

Hydrographs (USGS gauge 1626000) near Waynesboro showed low flows during July 2015 and August 2017 sampling period (40 cfs), and 150-200 cfs during sampling in October 2015, 7 days after a peak flow of 2200cfs (Figure 26). Water temperature recorded in July 2015 was 28.4°C, whereas October 2015 sampling had water temperature at 16°C. The temperature during August 2017 sampling was 21.1°C. Overall, conditions in July 2015 and August 2017 indicated minimum potential for bank leaching due to the stable low flows and water level. The conditions also indicated potential for high methylation due to the warm temperature. October 2015 sampling indicated potential for evaluating bank leaching since it followed a storm event.

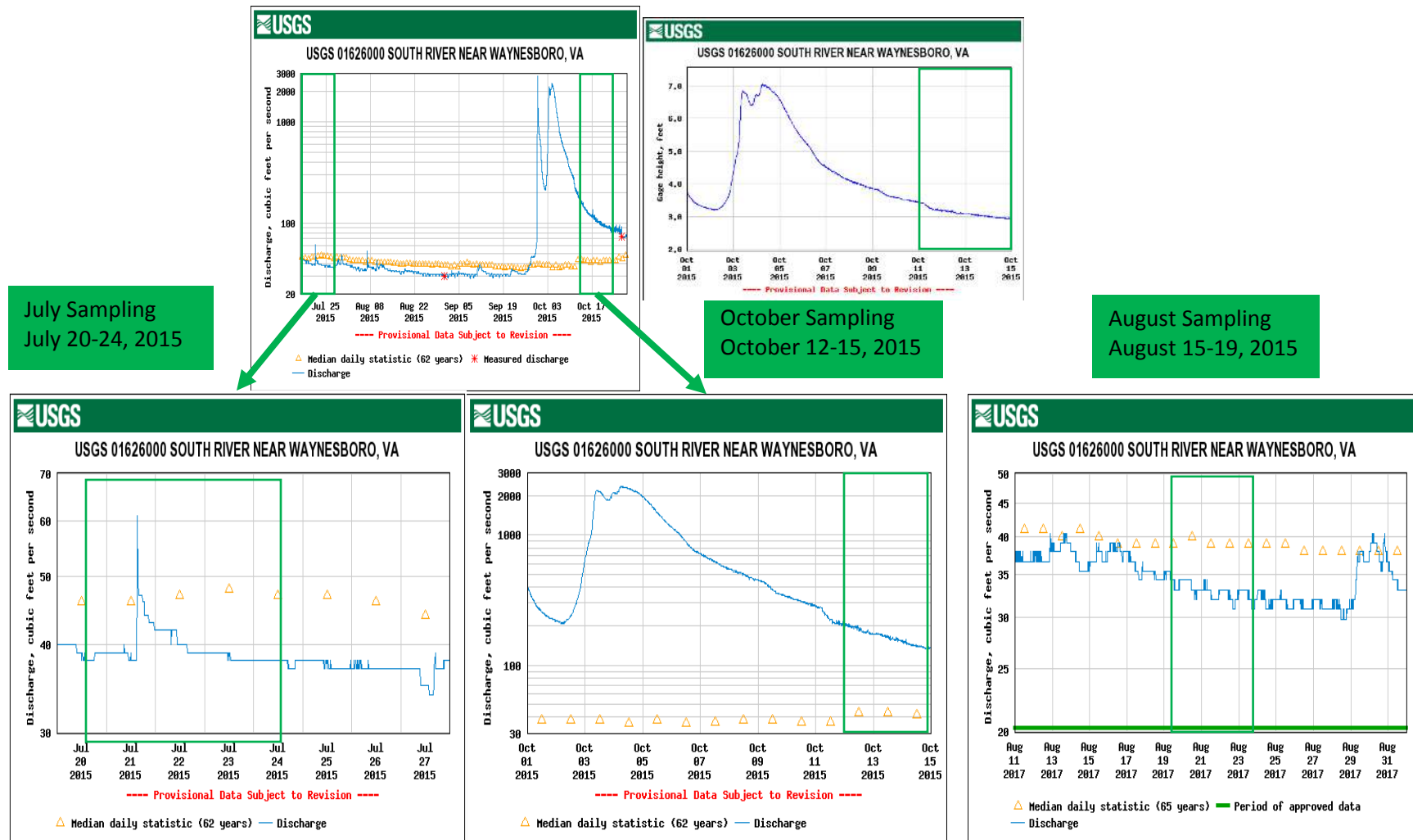


Figure 26 Discharge during sampling events. The sampling event days are marked with a green rectangle (USGS, 2017)

Baseline conditions and mercury behavior

During baseline condition sampling in July 2015, both the Constitution and North Park have shown higher THg and MeHg concentrations at bank locations (odd numbered), as compared to the channel locations (even numbered) (Figure 27).

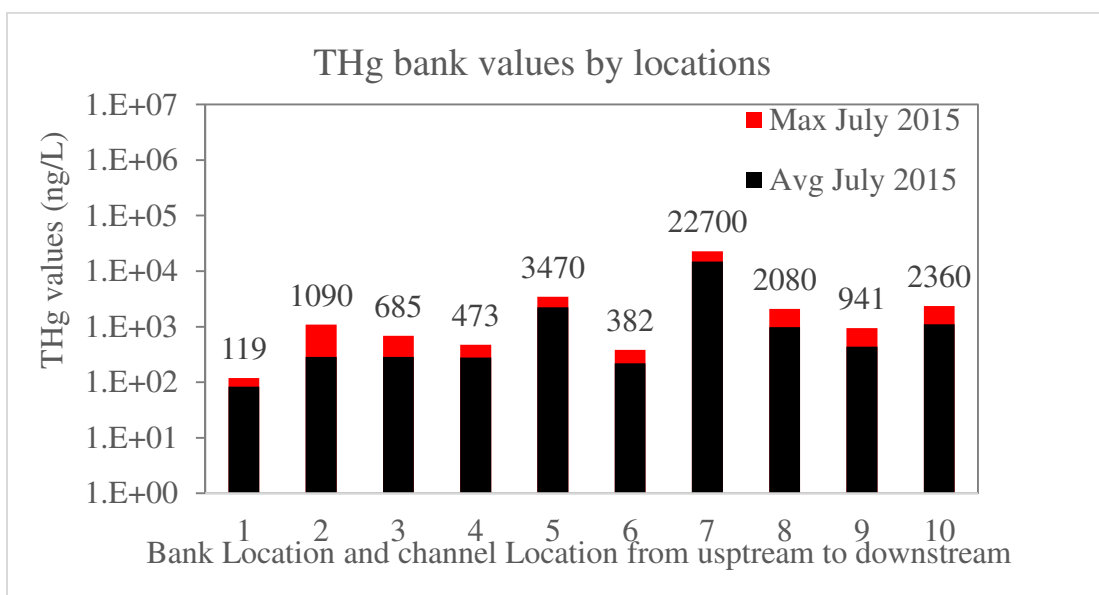


Figure 27 Average and maximum values (indicated on plot) for Constitution Park (L1-6) and North Park (L7-10) locations. Same transect bank and channel location are adjacent to each other and the locations are placed from furthest upstream to downstream

Overall trend of non-particle related THg concentrations during baseline conditions showed an increase towards locations further downstream, with the highest THg concentrations found at the Location 5 of the Constitution Park (CP) and Location 7 of the North Park (NP). The increases in DGT pore water THg concentrations towards downstream locations correlate with solid phase concentration measurements for CP and NP obtained by AECOM (Figure 28 and Figure 29) (AECOM, 2017).

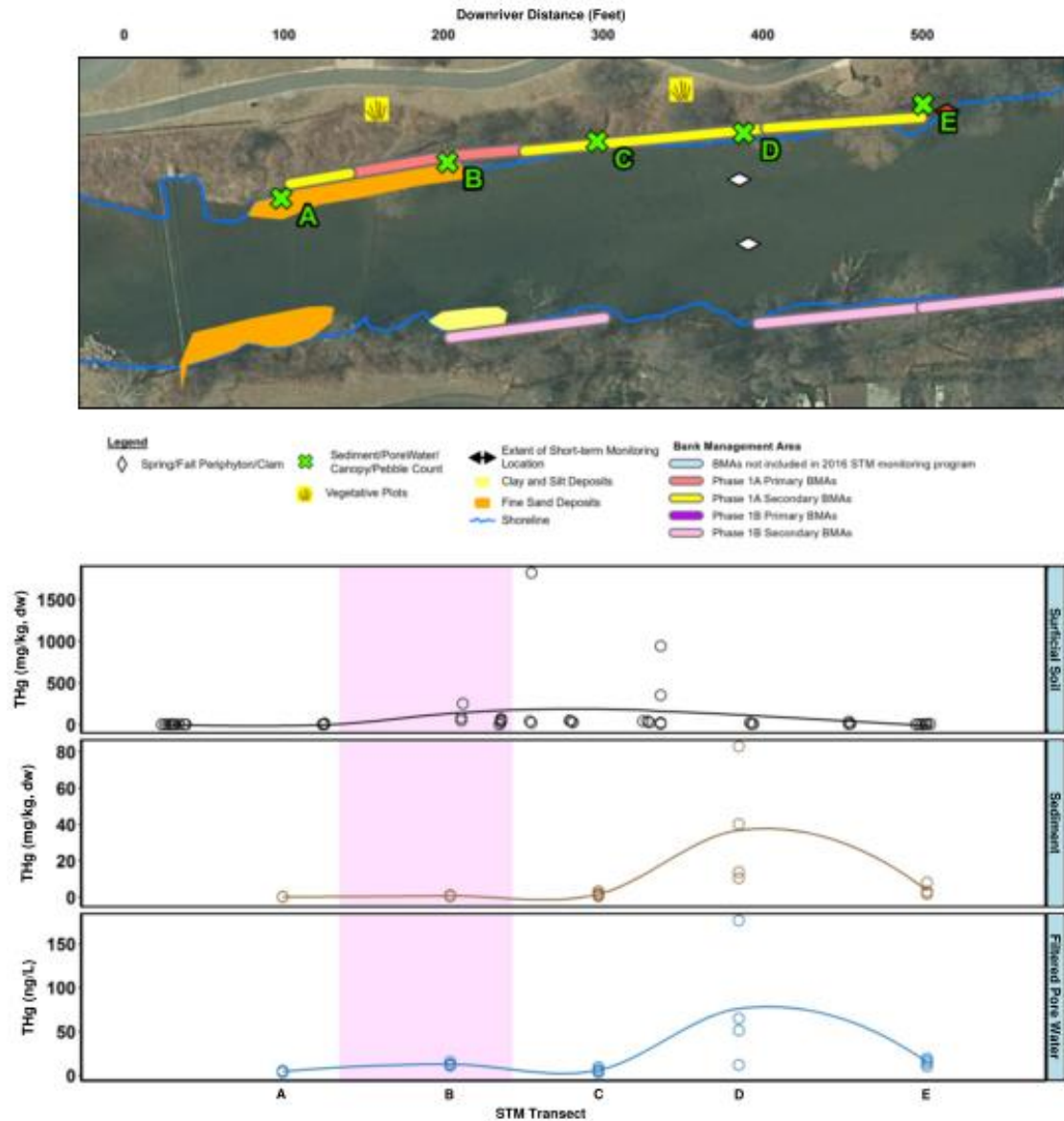


Figure 28 Constitution Park measurements obtained by AECOM, with surficial bank soil measurements in the top figure, sediment measurements in the middle and pore water measurement at the bottom plot. Each set of STM transect corresponds to the locations marked with green x on the top figure (L1=A/B, L3=B, L5=C). Sediment measurements were obtained by pushing 2 inch cores to a 15cm depth at each individual transect. Whereas filtered pore water measurements were obtained with push-point sampler at 5-10 cm below the sediment surface and filtered through 0.45 μ m filters (AECOM, 2017)

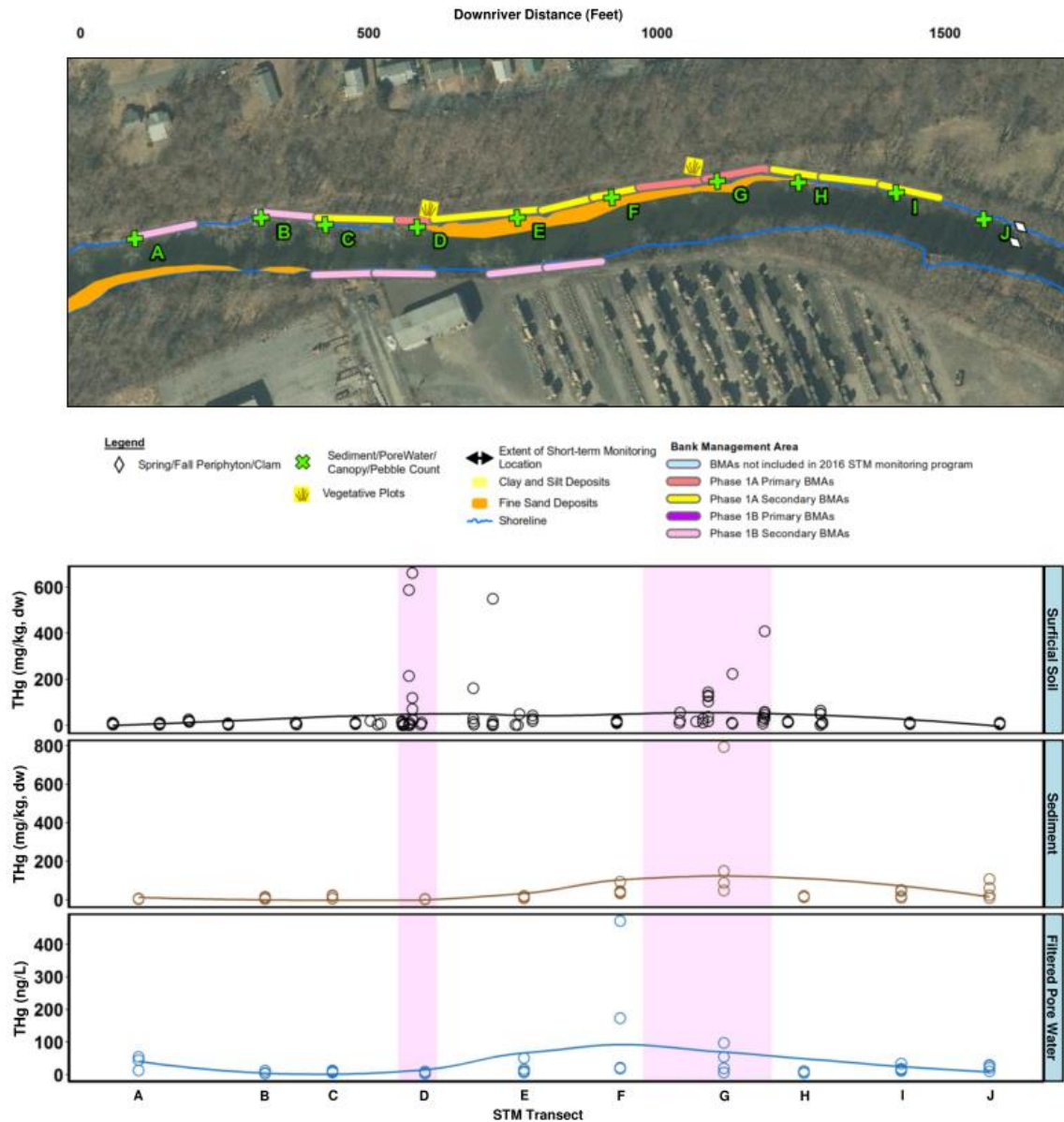


Figure 29 North Park measurements obtained by AECOM, with surficial bank soil measurements in the top figure, sediment measurements in the middle and pore water measurement at the bottom plot. Each set of STM transect points corresponds to the locations marked with green x on the top figure (L7=F/G, L9=J). Sediment measurements were obtained by pushing 2 inch cores to a 15cm depth at each individual transect. Whereas filtered pore water measurements were obtained with push-point sampler at 5-10 cm below the sediment surface and filtered through 0.45 μ m filters (AECOM, 2017)

An average DGT THg concentration during July 2015 sampling was 861 ng/L for the bank locations of Constitution Park and 7,670 ng/L for the bank locations of North Park. A maximum pore water THg concentration detected in upper 15 cm of Constitution Park was 3470ng/L at location 5 at the depth of 8 cm below sediment-water interface (Figure 30). The highest THg pore water concentration at North Park was 22700ng/L at Location L7, likely indicating highly contaminated sediment deposit nearby, as also was observed with solid phase concentrations (Figure 29).

The DGT THg channel concentrations (right, Figure 30) were generally uniform in the upper 10 cm below the sediment, likely due to gravelly nature of channel locations allowing deep mixing throughout the surficial sediment layer. An increase in THg concentration was observed at greater depths of the channel locations, potentially indicating source of higher bulk THg levels deeper in the sediment, with depths greater than 10cm also affected by reduced mixing. The bank locations show elevated THg levels as compared to channel locations, as they are more affected by the historically contaminated river bank. DGT THg profile also looks less uniform (left, Figure 30) as compared to the channel locations due to fine sediment present at the bank locations resulting in reduced mixing.

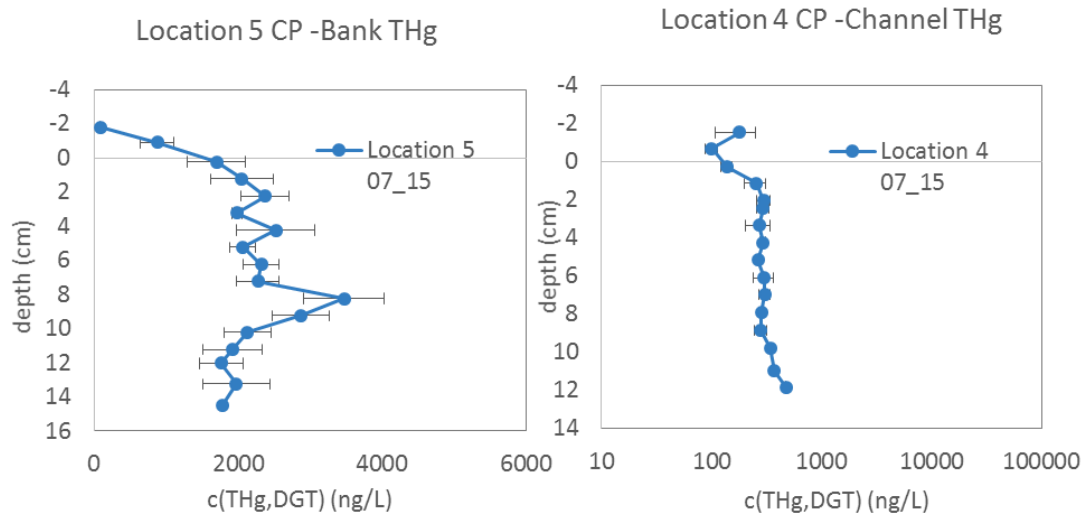


Figure 30 DGT THg profiles for bank and channel locations

DGT MeHg pore water concentrations were also higher at the bank locations as compared to the channel locations (Figure 31). Locations 5 of the Constitution Park and 7 of the North Park showed the highest concentrations. An average DGT MeHg concentration was 29ng/L at the upper 15cm of the Constitution Park Location 5 whereas the maximum value was 37ng/L. The location 7 of North Park showed the highest MeHg concentrations detected, with the maximum values of 71ng/L in sediment pore water, detected 1 cm below the surface.

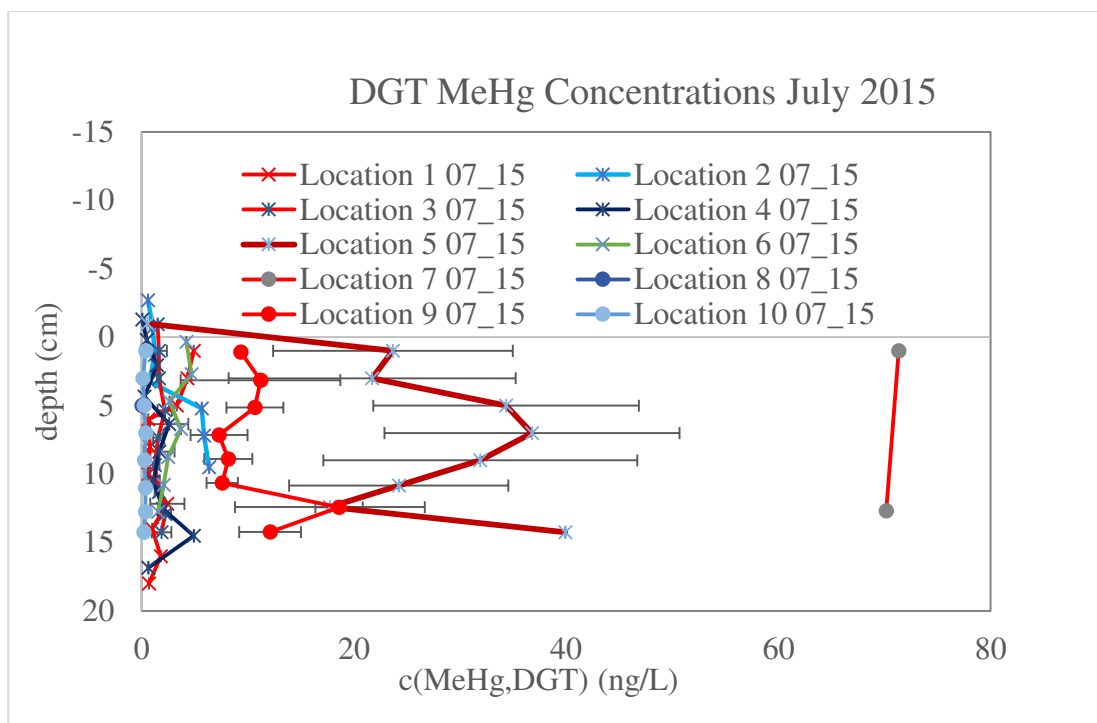


Figure 31 DGT MeHg concentrations during baseline condition sampling in July 2015. Red lines indicate bank locations, whereas blue lines indicate channel conditions. Squares indicate Constitution Park, whereas circles indicate North Park locations.

The trends with increases in MeHg concentration have also been found associated with more reduced conditions. As seen in the Figure 32 below on a typical observed redox profile, bank locations (left) during baseline conditions are subject to more reduced conditions as compared to the channel locations (right). The bank location (L5) profile shows oxygen depleted in the first 2 cm below sediment-water interface and measurable sulfide levels further into the sediment. Manganese reduction was also measured at the bank location displayed below. The channel location (L4) shows more oxic conditions present further into the sediment depth (0-7 cm), subsequent depletion and development of reduced conditions at 7cm of depth with measureable sulfide levels, as well as iron and manganese reduction. MeHg DGT profiles are showing greater MeHg concentrations at the bank location

experiencing more reduced conditions, with the peak MeHg detected 7 cm below the sediment-water interface (left, Figure 32). The peak DGT MeHg pore water concentration, is likely also associated with the highest THg concentrations detected at the same depth, indicating greater THg pool available for methylation (Figure 30).

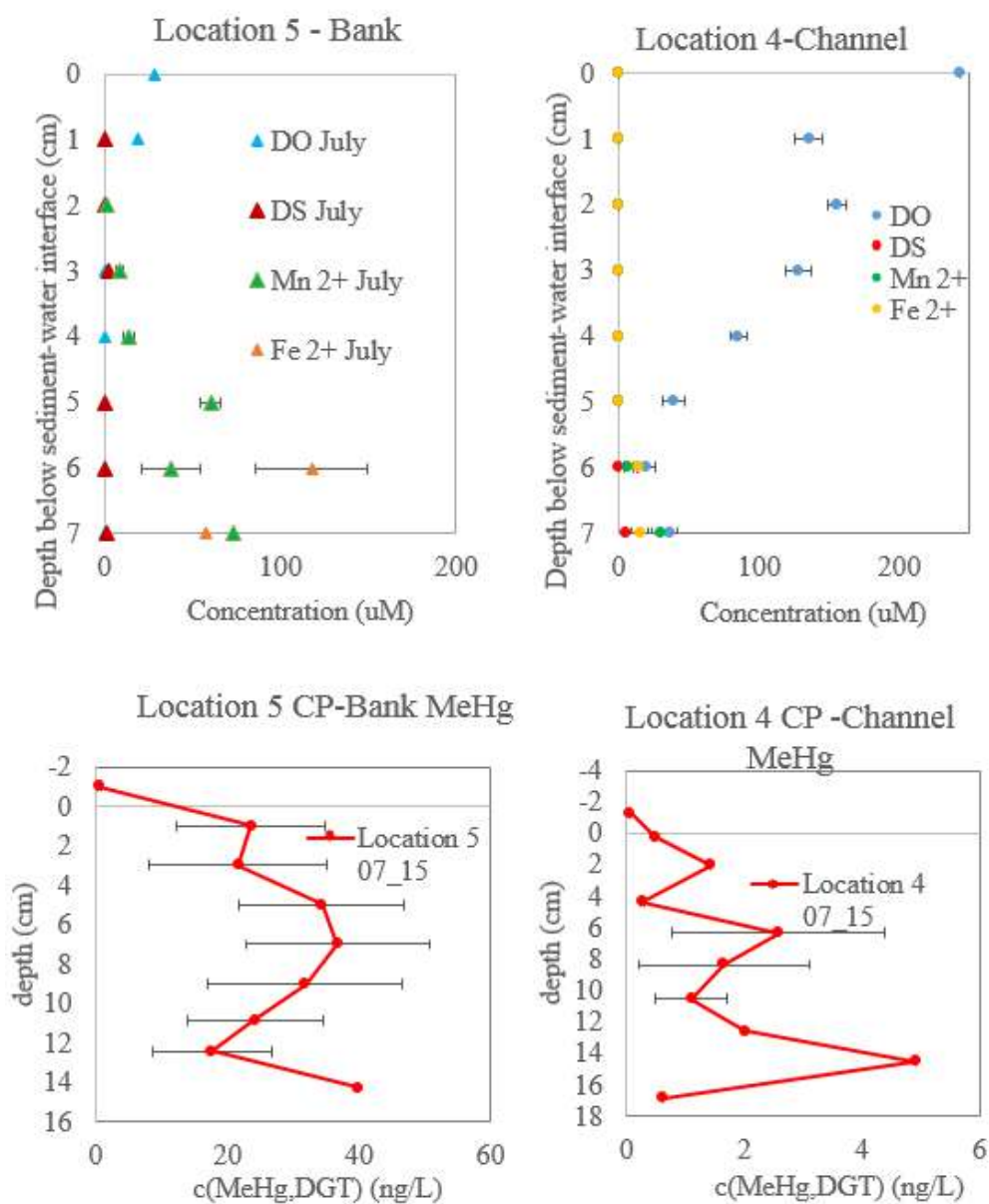


Figure 32 Voltammetry measurements at the bank and channel with the corresponding DGT MeHg profiles

The channel location is showing an order of magnitude lower MeHg concentration profile as compared to the bank location. The peak DGT MeHg concentration for channel locations is detected 14 cm below sediment-water interface at the location L4, which is likely associated with the development of the reduced condition deeper in the sediment (Figure 32, bottom right). Oxidic conditions are present deeper in the sediment at the channel as compared to the bank locations due to gravelly sediment encouraging deeper mixing throughout the sediment. This causes the development of the reduced conditions to be shifted deeper into the sediment, so maximum MeHg concentration is detected at 14 cm below sediment-water interface, as compared to bank locations where maximum MeHg concentration is present 5-8cm below sediment-water interface (Figure 32).

Drainage conditions and mercury behavior

An increase in the non-particle associated mercury in pore water at the bank locations was observed at both Constitution Park and North Park during the sampling in October 2015 where the sampling event was performed 7 days after a storm event with peak flow of 2200 cfs (Figure 26). Average DGT THg concentration in the bank locations of Constitution Park increased from 861ng/L detected during July 2015 to 2,140 ng/L during October sampling. Average DGT THg concentration in the bank locations of North Park increased from 7,670 ng/L detected during July sampling to 11,100 ng/L detected during October sampling.

The increase in pore water DGT THg can be seen when comparing specific locations for July 2015 (baseline conditions) and October 2015 (storm event drainage sampling (e.g. locations 5 and 7, **Error! Reference source not found.**)).

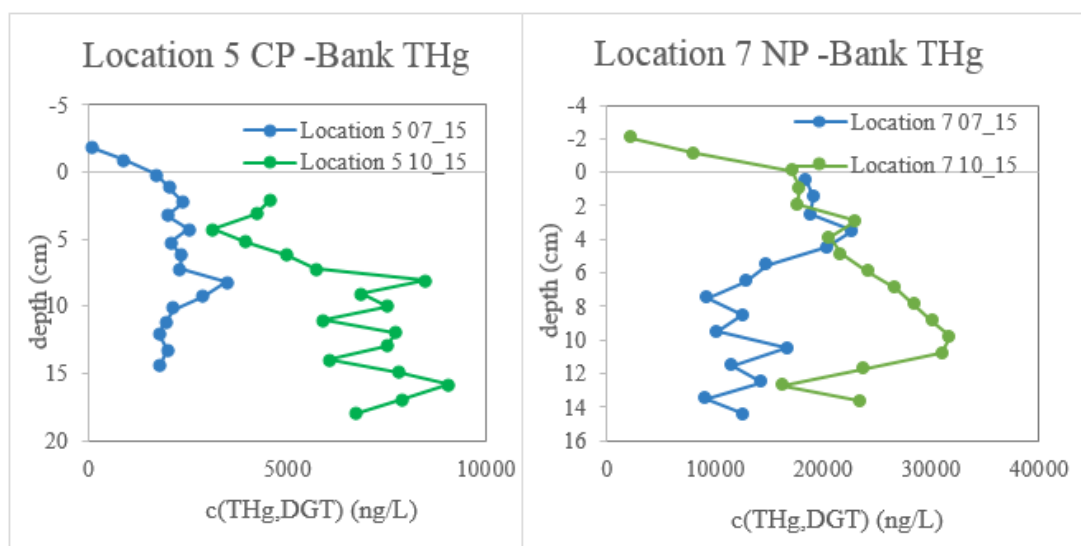


Figure 33 Bank locations L5 of Constitution Park and L7 of North Park indicating the increase in DGT THg concentration during October 2015 sampling following a flooding event as compared to July 2015 sampling performed during baseline conditions

This increase in concentration was likely associated with the storm event where water level in the stream increased as compared to baseline water level conditions which were observed during July 2015 sampling (Figure 34, 1.). The storm event associated rise of water level inundated presumably about 25ft of the previously unsaturated bank (Figure 34, 2.) which now started equilibrating with low partitioning coefficient mercury present in the bank and likely present in more soluble phases in oxic conditions. Water level eventually reached the peak discharge (Figure 34, 3.), and started draining (Figure 34, 4.), causing mercury leaching from temporarily saturated pore spaces, as well as leaching of excess mercury picked up along the way as the draining water passed through highly contaminated near-surface sediment. THg leaching from historically contaminated bank sediment and an order of magnitude increase in non-particulate THg in post-drainage measurements was observed at all bank locations with the highest THg concentrations during July

sampling (Appendix B). Similar behavior of increased DGT THg at the bank locations following a flooding event was observed further downstream during earlier sampling efforts in 2013, where an increase in discharge from 200cfs to 3000cfs caused an order of magnitude increase in DGT THg concentrations (Bireta, 2015).

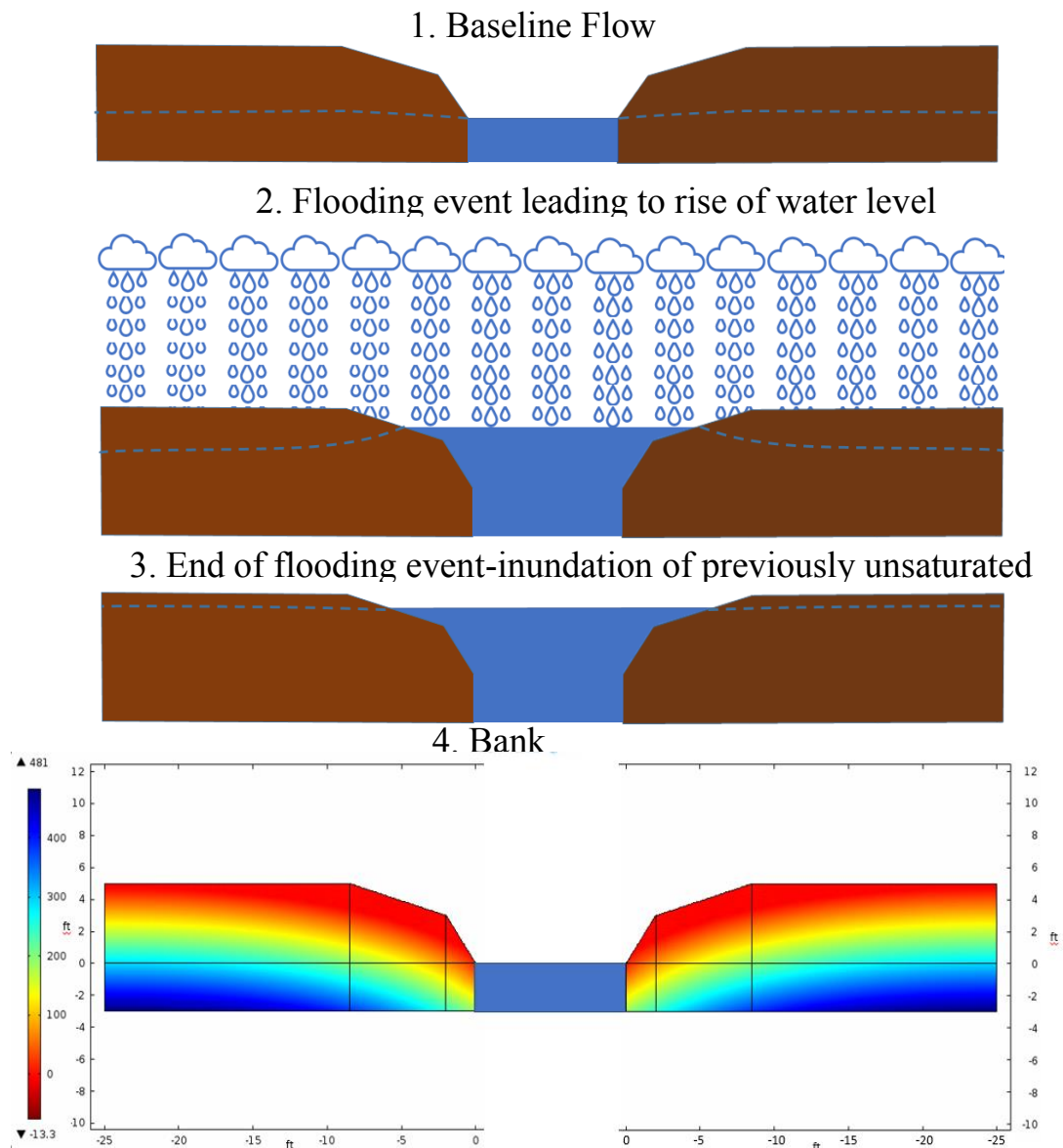


Figure 34 The effects of storm event on non-particulate THg release from the contaminated river bank

Average DGT THg concentration in the channel locations of Constitution Park during October sampling was 59ng/L, which is a decrease as compared to July sampling where average DGT THg concentration was 261 ng/L. The average DGT THg concentration in the channel locations of North Park during October sampling was 905ng/L, again a decrease from July sampling where average DGT THg concentration was 1,040 ng/L. The decrease of THg from July to October sampling in channel locations can be seen when comparing specific locations during July 2015 and October 2015 sampling (e.g. location 6, Figure 35). The decrease is likely due to increase in flow associated with storm event causing more active flushing of the top 10cm of gravelly channel sediment. The increase of the DGT THg at the 13 cm of depth below sediment-water interface during the October sampling indicates reduced mixing at that depth, in addition to possible elevated bulk Hg levels at that depth (Figure 35).

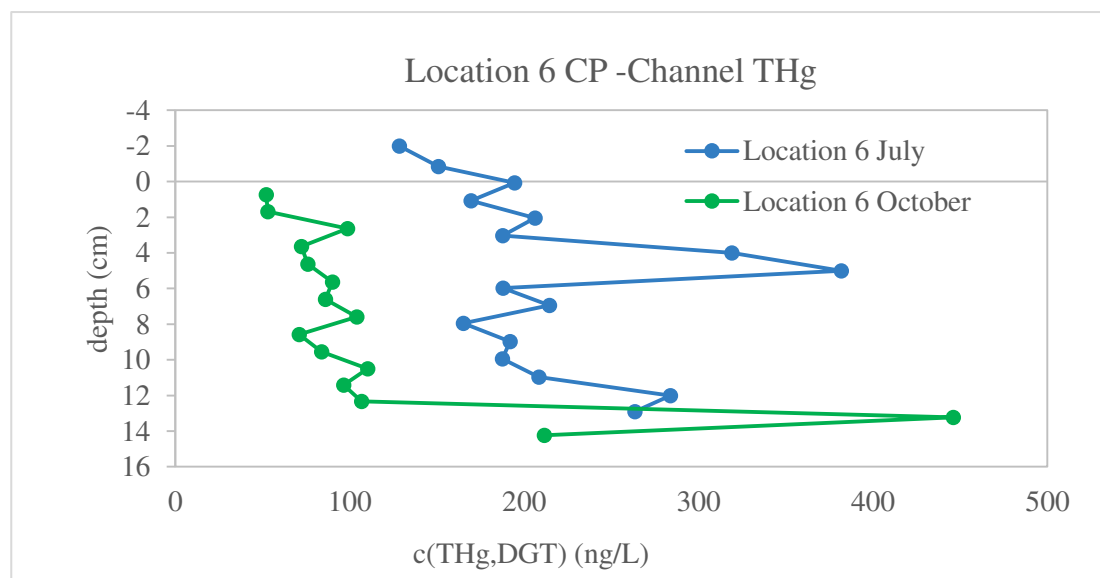


Figure 35 Location 6 Channel DGT THg profile, channel at Constitution Park

Average DGT MeHg concentration at the Constitution Park during October sampling was 1.79ng/L, indicating decrease as compared to average DGT MeHg concentration at Constitution Park during July sampling of 10.9 ng/L. The average DGT MeHg concentration in the bank locations of North Park during October sampling was 3.13ng/L, also indicating a decrease from average DGT MeHg concentrations during July sampling that was 40.7 ng/L. Decrease in bank DGT MeHg concentrations during October sampling as compared to baseline July sampling (Figure 36) was due to more oxic conditions during October, as compare to July sampling (Figure 37). This was likely due both to decreases in temperature, decreasing microbial activity as well as the drainage of water from the oxic bank.

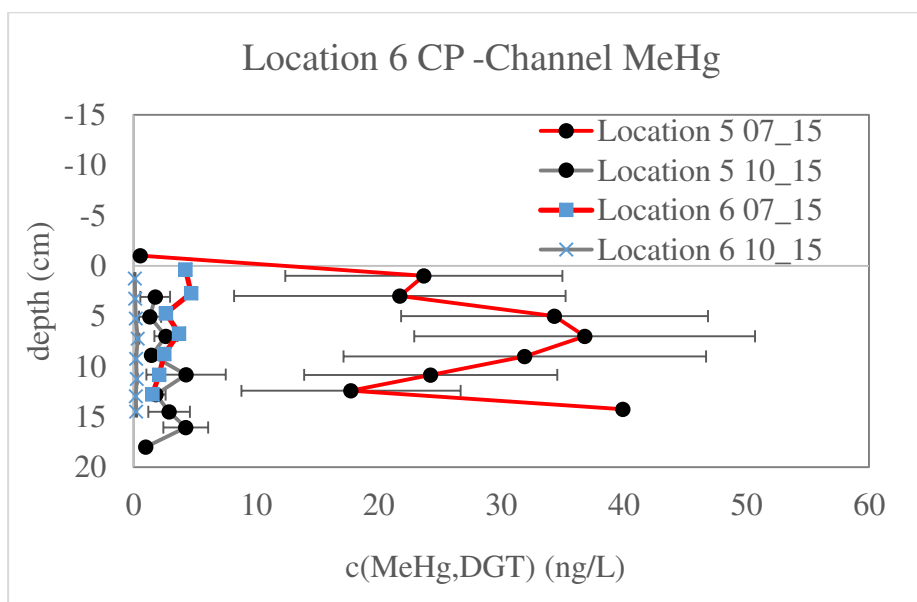


Figure 36 Comparison of DGT MeHg for the bank (circles) and channel locations (squares) of the same transect at the Constitution Park for the sampling events in July 2015 (red line) and October 2015 (grey line)

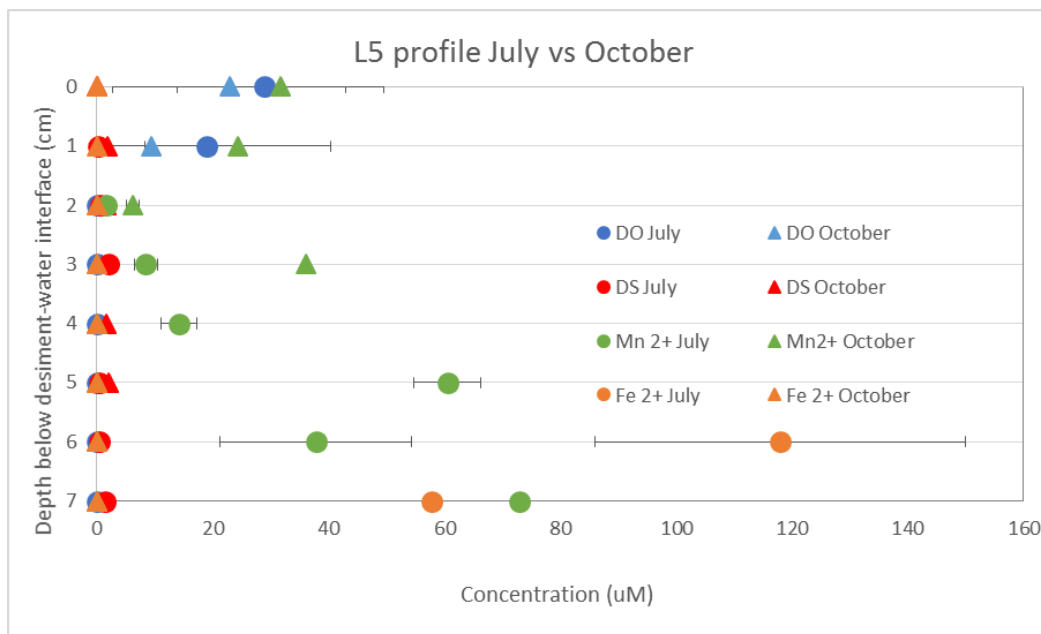


Figure 37 Redox profiles during baseline conditions (July 2015) and draining conditions (October 2015), indicating development of more oxic conditions during October sampling (following storm event), as compared to more reduced conditions developed during July 2015 sampling (baseline conditions)

The same trend of more oxic conditions associated with storm event and a decrease in DGT MeHg concentrations was also observed during previous post-storm event sampling at the location further downstream (Bireta, 2015). In addition to storm event associated reoxygenation, cooler temperatures in October as compared to July likely decreased the activity of methylating bacteria and thus the rate of methylation of the available mercury.

Average DGT MeHg concentration in the channel locations of Constitution Park during October sampling was 0.34ng/L, again a decrease as compared to July sampling where average DGT MeHg concentration was 2.63 ng/L. The average DGT MeHg concentration in the channel locations of North Park during October sampling was 0.65ng/L, which was a slight increase as compared to July sampling where average DGT MeHg concentration was 0.17 ng/L. The significance of this result is

unclear due to the limited data available in the channel and the potential for relatively deep mixing in the channel gravelly sediments. DGT MeHg concentrations were higher at bank locations as compared to channel locations (Figure 36) likely due to higher available THg as measured by DGT and the potential for more reducing conditions and less hyporheic exchange in the fine grained sediments.

There is no information on the depth of penetration of flood waters into the bank and the volume of water draining back out, but an estimate can be made assuming a 3 ft flood inundated 25 ft into the bank soil and drained out of the bank into the stream during the October sampling. The concentrations at each bank location during drainage conditions would be affected by both the bank drainage as well as groundwater advection. An estimate of the flux from the bank surface can be made by Equation 14 which assumes that groundwater advection and benthic boundary layer mass transfer into the river are essentially independent:

Equation 14 Calculation of mass flow rate per area of river for bank locations during active drainage conditions (Boudreau, B. P. & Jorgensen, 2001)

$$J_d = k_{bl}(C_{pw} - C_w) + UC_{pw}$$

During baseline flow conditions when the advection due to drainage is negligible,

Equation 15 applies.

Equation 15 Calculation of mass flow rate per length of river for channel locations and bank locations during baseline conditions (Boudreau, B. P. & Jorgensen, 2001)

$$J_d = k_{bl}(C_{pw} - C_w)$$

Where J_d is mass flow rate per length of the river (mass/time/length of river), k_{bl} is a benthic boundary layer mass transfer coefficient of the sediment-water interface (calculated below), C_{pw} is THg pore water concentration (average concentration for

depth profilers under sediment-water interface), C_w is a THg in water immediately above sediment-water interface (ng/L), and U is seepage velocity (cm/hr).

Equation 16 Calculation of benthic boundary layer mass transfer coefficient river (Reible, 2014)

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

Where k_{bl} is benthic boundary layer mass transfer coefficient (cm/hr), v_x is river velocity, m is Manning's coefficient, g is gravitational acceleration, d is river depth, D_w is molecular diffusion coefficient in water, r_H is hydraulic radius, and v_w is kinematic viscosity of water. All the specific values used for each of the locations during all sampling events are listed in the Appendix B.

The estimated THg flux from the Constitution Park sediment bed during July 2015 sampling is about $16 \mu\text{g}/\text{m}^2/\text{hr}$ for bank locations and $9.4 \mu\text{g}/\text{m}^2/\text{hr}$ for channel locations. The estimated THg flux from the Constitution Park sediment bed during October 2015 sampling is approximately $190 \mu\text{g}/\text{m}^2/\text{hr}$ for bank locations and $4.7 \mu\text{g}/\text{m}^2/\text{hr}$ for channel locations. The estimated THg flux from the North Park sediment bed during July 2015 sampling is approximately $160 \mu\text{g}/\text{m}^2/\text{hr}$ for bank locations and $20 \mu\text{g}/\text{m}^2/\text{hr}$ for channel locations. The estimated THg flux from the North Park sediment bed during October 2015 sampling is approximately $1100 \mu\text{g}/\text{m}^2/\text{hr}$ for bank locations and $81 \mu\text{g}/\text{m}^2/\text{hr}$ for channel location (Figure 38). Bank fluxes calculated for October 2015 sampling have increased as compared to July 2015 sampling due to flooding event leaching mercury into the banks as well as increasing groundwater flow contributing to THg flux from the sediment bed. North Park bank locations show greater increase in THg flux likely due to higher bulk Hg

present in the bank and increased impact of flooding event on contamination of the leachate.

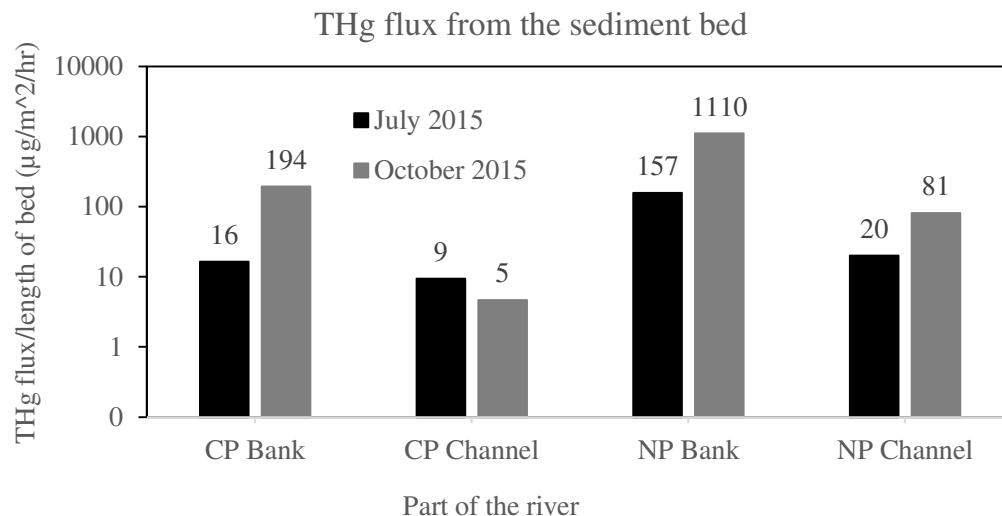


Figure 38 THg fluxes in July and October 2015 from the sediment bed for both Constitution Park (CP) and North Park (NP)

Channel location fluxes of the Constitution Park are not being affected by the bank drainage. This is expected, as the bulk of the water drainage from the bank would be expected to occur at the seepage face at the bank-water interface. The flux of mercury from sediment bed at channel locations appears to be more affected by the increased river flow and the exchange between pore water in gravelly sediment and the overlying water. While Constitution Park THg flux from sediment bed is showing decrease, the North Park channel locations are showing increase in THg flux from the sediment bed. This is likely an indication of the bank leaching having a predominant impact on the entire local river system, while the exchange between pore water and overlaying water is still present, but contributes less than the first factor to overall THg flux from the sediment bed at North Park channel locations.

Baseline conditions post-stabilization

In order to evaluate the effects of stabilization efforts, sampling was performed in August 2017. The streamflow was 40 cfs during the sampling event, indicating baseline conditions that could be compared to pre-stabilization baseline conditions sampled in July 2015. No rain event happened prior nor during sampling, so results of August 2017 sampling do not account for active drainage period from the associated bank (Figure 26). Subsequent sampling during active drainage was not possible and remains a recommendation for future sampling work.

Stabilization efforts were implemented on the bank associated with Constitution Park locations 1, 3 and 5, which is where stabilization was conducted. Location 1 associated bank was subject to amended capping only, whereas bank associated with locations 3 and 5 was subject to sediment removal followed by amended capping (Figure 16). Location 0 was chosen upstream of stabilization area to compare areas with stabilization efforts to the adjacent ones (Figure 18). When comparing THg DGT pore water concentrations (Figure 39), it is evident that bank stabilization efforts have shown to be effective in decreasing non-particulate THg in pore water from baseline concentrations as high as 3500 ng/L to values generally in 10-20 ng/L range with the highest concentrations detected being lower than 50ng/L and the depth average value of bank locations of 17.7 ng/L (Figure 39). For the previously most impacted location 5 (furthest downstream) with depth averaged concentrations of 2220 ng/L in July 2015, the depth average concentration now detected was 15.4 ng/L, indicating a decrease in THg pore water concentrations of 2 orders of magnitude (Figure 40). Concentrations at location 0 were also low but

somewhat higher than the stabilized bank locations. Based upon the presumption of low Hg levels at this location, the pore water concentrations along the stabilized bank are equal to or lower than this reference location (Figure 39). Channel locations with average THg depth value of 9.32ng/L did not seem to be affected by the bank stabilization efforts.

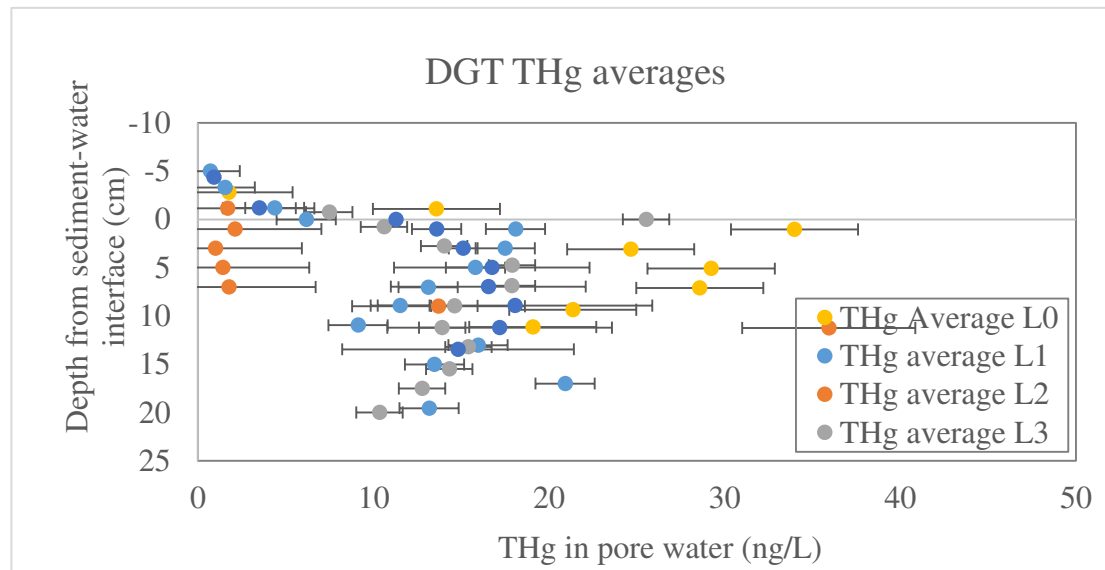


Figure 39 Comparison of THg DGT results at the Constitution Park areas during post stabilization August 2017 sampling

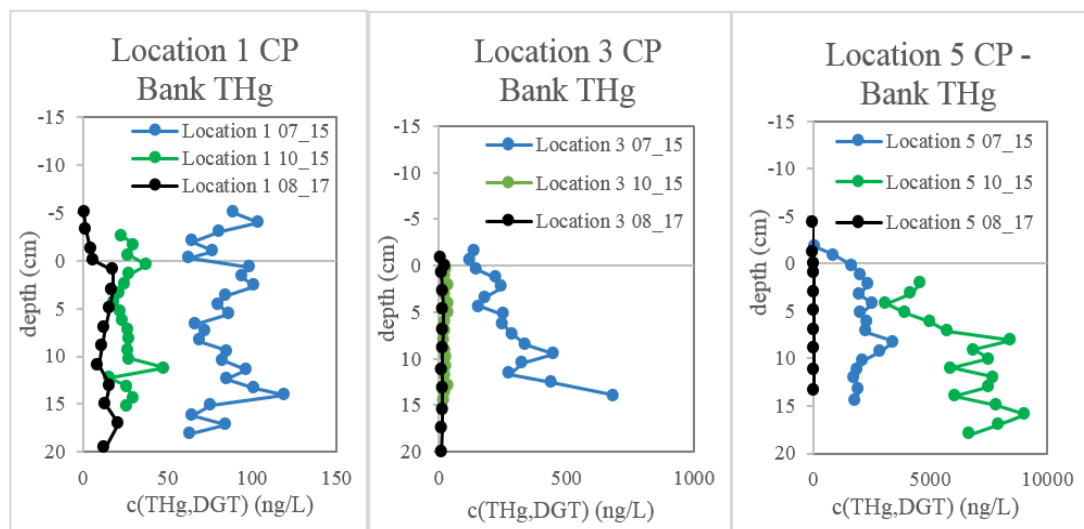


Figure 40 Change in THg concentration as the result of stabilization efforts sampled in August 2017 as compared to pre-stabilization efforts during July 2015 sampling (baseline conditions) and October 2015 sampling (flooding event)

MeHg concentration profiles (Figure 41) exhibit peak methyl mercury in the near surface of the bank locations and at a depth of 10 cm below sediment-water interface in the channel location. The deeper peak in channel locations is typically observed due to the greater hyporheic exchange in the near-surface of the coarse channel sediments. MeHg values, post-stabilization, are approximately 20% of pre-stabilization baseline values at the upper 15cm of the Constitution Park Location. Thus MeHg reductions were apparently less than THg reductions. The fraction %MeHg/THg is an indicator of net methylation of the available THg and is relatively high post-stabilization, with average peak values around 50%. This could be a result of a combination of factors, including high water temperatures and discharge below historical average, both encouraging reduced conditions to develop near the sediment-water interface. Comparison to previous MeHg concentrations and percentages, however, should be done cautiously due to the change in extraction in the analysis of these samples.

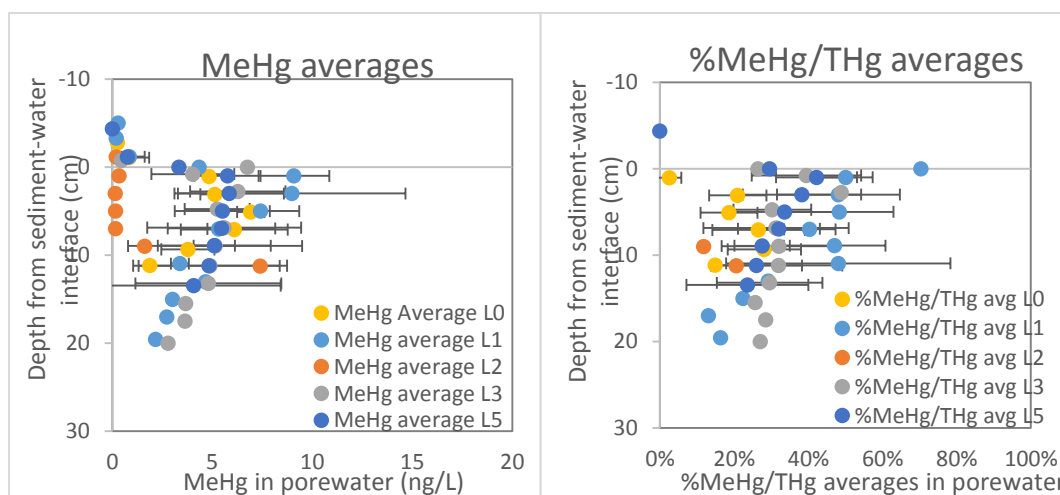


Figure 41 Comparison of MeHg and %MeHg/THg results at the Constitution Park areas

In addition to MeHg concentration measurements obtained using DGTs, peeper results assist in understanding biogeochemical factors affecting net methylation. Sulfate profiles obtained using peeper samples (Figure 42) show presence of sulfate concentrations in overlaying water, and a sharp depletion in the first 10 cm of sediment at the bank, likely indicating microbial activity of sulfate reducing bacteria using sulfate as electron acceptor (Cynthia C. Gilmour & Henry, 1991; Morel et al., 1998). Sulfate concentration of 1-20ppm are considered optimal in terms of promoting maximum MeHg production, which is the range measured below at bank locations (Feng et al., 2014; C. C. Gilmour et al., 1992; Orem et al., 2011; Oswald & Carey, 2016). Comparing sulfate concentrations ranges obtained by peepers and %MeHg/THg measurements obtained by DGTs is indicative of bank locations of Constitution Park exhibiting favorable conditions for MeHg production during baseline flow conditions.

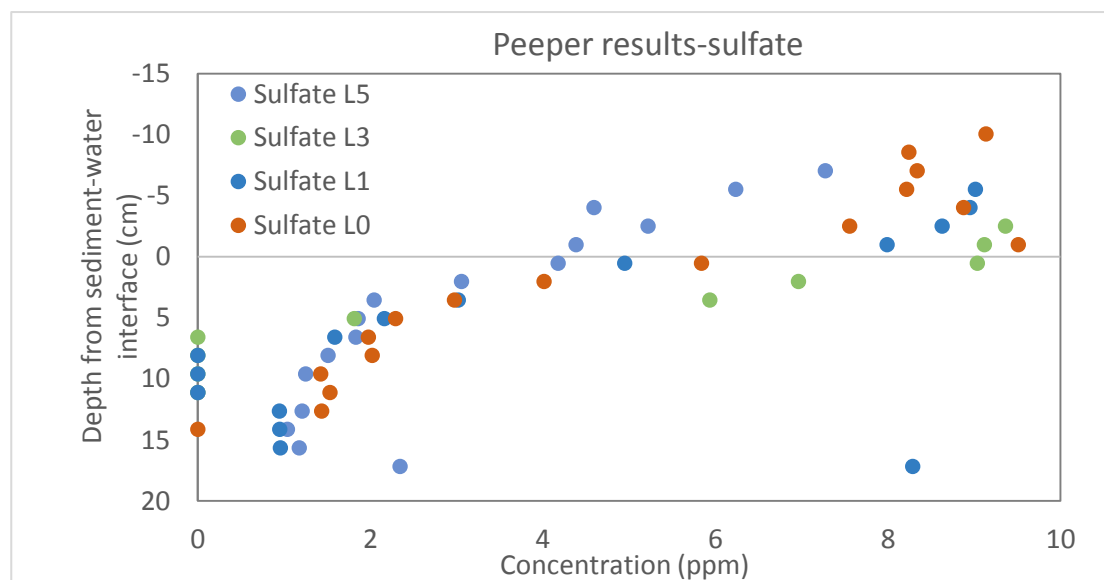


Figure 42 Sulfate concentrations for CP bank locations

Oxygen levels appear depleted within the first few cm of sediment depth (Figure 43), followed by peak MeHg detection, which correlates well to expectation of peak activity of methylating bacteria at the oxic/anoxic interface (Figure 43).

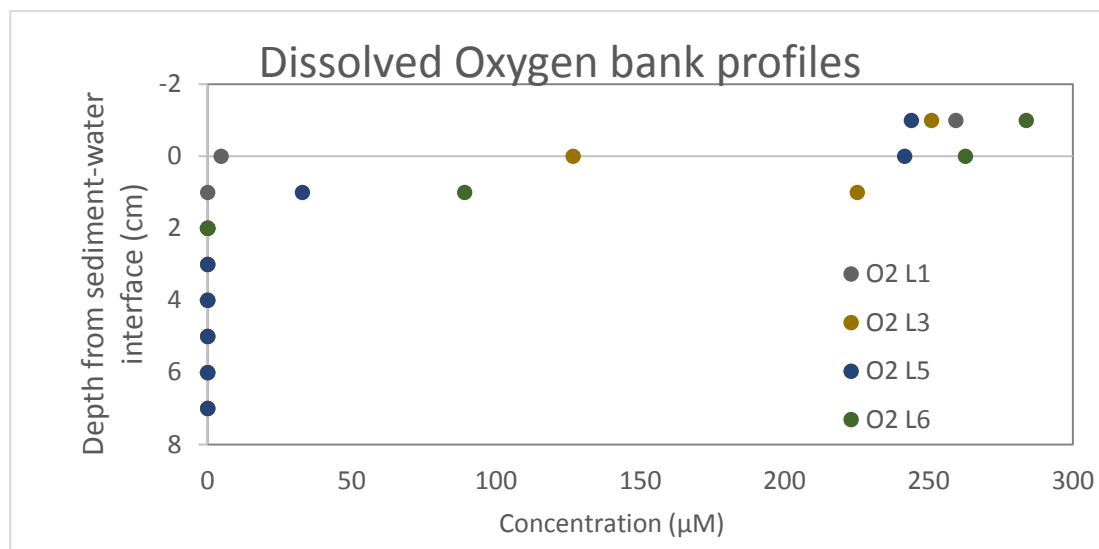


Figure 43 Dissolved oxygen at the Constitution Park bank locations

Chloride concentrations detected via peeper sampling indicate different degree of hyporheic exchange for different locations. These exchanges may include seep and advective transport (Thibodeaux, 1996). Locations 0, 1 and 3 all show elevated chloride with depth indicating groundwater at these locations (Figure 44). Location 5, however, shows chloride levels that are more consistent with the surface water, suggesting that groundwater is not moving through that portion of the bank during these baseline flow conditions or that the surface water-bank exchange is relatively efficient near the surface of the bank. Higher chloride concentrations ($>3.5\mu\text{g/L}$) in sediment have been correlated to higher methylation rates, increased

mobilization of Hg and solubility of HgS, resulting in increased availability of mercury (Benoit et al., 1999; Gabriel & Williamson, 2004; Ravichandran et al., 1999; Schuster, 1991; Ullrich et al., 2001). Although chloride concentrations detected deeper in the sediment may increase available Hg, there is little indication of that in the measured mercury profiles (little difference between mercury concentrations between Location 5 and the other bank locations), indicating that relative differences in chloride do not directly correlate to available Hg. The presence of chloride near the surface, however, may be encouraging different mercury speciation and potentially the elevated % ratio of pore water MeHg/THg.

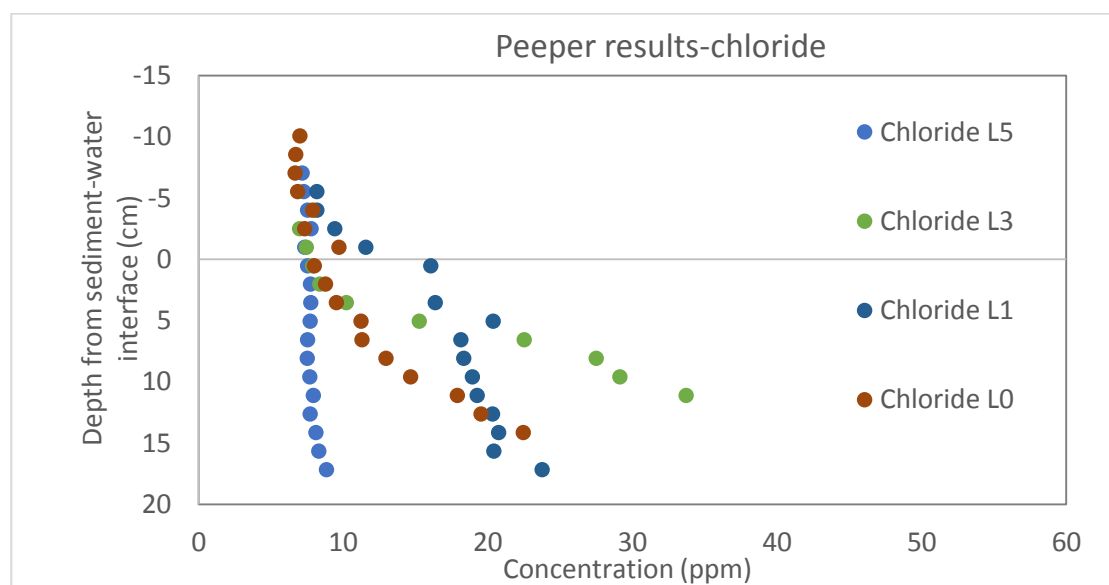


Figure 44 Chloride Concentrations at CP bank locations

Average THg fluxes were estimated to be $0.3 \mu\text{g}/\text{m}^2/\text{hr}$ for bank locations and $1.2 \mu\text{g}/\text{m}^2/\text{hr}$ for channel locations, showing that that stabilization efforts resulted in decrease of flux at both bank and channel location. Considering almost two orders of magnitude decrease of THg fluxes at bank locations and an order of magnitude decrease at channel location, stabilization efforts have shown to be effective in reducing mercury flux from the contaminated river bank.

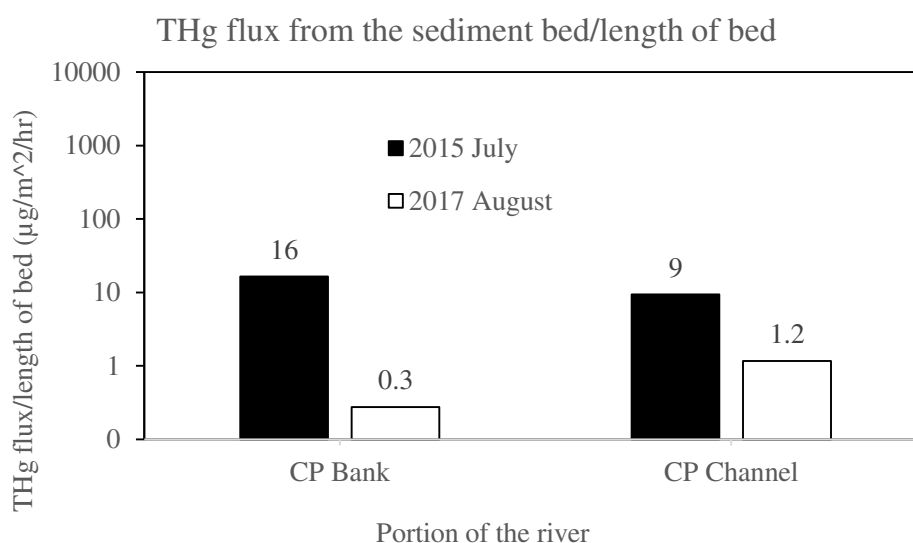


Figure 45 THg fluxes for Constitution Park during baseline conditions before (July 2015) and after stabilization efforts implementation (August 2017)

Conclusions

Historical releases of mercury in Waynesboro, VA has led to contaminated sediments in the river and along the banks of the South River. Studies were undertaken at the direction of the South River Science Team which was established in 2001 to understand why fish tissue remains elevated and to evaluate feasible remedial options. The primary concern for mercury that has accumulated in the river banks is particle-associated mercury release as a result of erosion during flood events.

As a result, stabilization of some banks has been proposed to reduce mercury release to the river during flood events. An additional mechanism for mercury release, however, is non-particle associated mercury release during bank drainage after flooding events. Past studies in the river indicated this might be a significant source of mercury release in some portions of the river. This mechanism was evaluated at the Constitution Park and North Park locations that were under consideration for bank stabilization. Bank stabilization efforts are part of the remediation approach to address elevated concentrations of MeHg in the fish tissue and included in-situ remediation-reactive capping of contaminated sediment in the South River. The primary target of bank stabilization efforts was erosion control and particle associated THg. However, stabilized bank has potential to leach and introduce biologically relevant non-particle related total mercury (THg) and methyl mercury (MeHg) into the water. Non-particle mercury release and redox conditions were evaluated using DGTs, voltammetry, ion specific electrodes and peepers.

Pre-stabilization sampling events performed at Constitution Park and North Park areas of the South River were used to evaluate the effects of bank inundation and drainage associated with flooding effects. Non-particle related pore water THg and MeHg concentration measurements indicated that flooding events could introduce leaching of potentially significant source of mercury from the bank areas. Redox measurements indicated more reduced conditions during baseline conditions and more oxic conditions following the flooding event, which corresponded to elevated net methylation rate during baseline study, as compared to post-flooding measurements.

DGT sampling of Constitution Park following the implementation of bank stabilization efforts demonstrated the effectiveness in reducing non-particulate associated THg by orders of magnitude, depending on the location. The greatest reduction was seen at the location furthest downstream that used to be the most contaminated, and all the detected DGT concentrations were less than 50ng/L. Although the amount of THg available for methylation decreased, system was still productive in terms of net methylation rate potential due to baseline flow allowing for development of reduced conditions, as well as higher temperature increasing microbial activity. Average THg fluxes following the stabilization efforts decreased by a couple of orders of magnitude at the bank locations.

As a part of future efforts, we recommend sampling the same locations of Constitution Park following a flooding event to examine the maximum non-particulate THg leaching from the stabilized bank area as we were not able to sample after a storm event in the 2017. Furthermore, the effectiveness of the stabilization efforts over the longer period of time should be examined in terms of non-particulate THg concentrations to ensure that bank stabilization efforts provide efficient tool for managing non-particulate THg leaching from contaminated bank areas of South River, VA.

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CHAPTER V

PREDICTING LONG TERM EFFECTIVENESS OF BANK STABILIZATION EFFORTS ON BANK LEACHING MERCURY INPUT

Abstract

Observations in the South River, VA have shown that substantial Hg leaching from banks can occur as a result of inundation and drainage after watershed storm events. Observations were limited to a single baseline flow event and a single drainage cycle after a storm event. Bank stabilization and capping, including a biochar-sand cap, were implemented in an effort to reduce the observed Hg leaching and an additional monitoring event was conducted after bank stabilization. Modeling efforts were implemented to interpret the observations and to make long-term predictions of the bank stabilization and capping effort based upon the normal frequency of watershed flooding events.

The modeling was undertaken in two phases, a commercial finite element model, COMSOL Multiphysics®, was employed to estimate the inundation and drainage volume and rates due to a common event (3 foot flood stage) and the annual maximum flooding event (6 foot flood stage). These flows were used to simulate contaminant transport over a 100 year period using CapSim, a model of chemical behavior at the sediment-water interface. CapSim was used to predict THg concentrations in the river bank and fluxes to the river. Simulations suggest that a composite cap with biochar should effectively eliminate THg fluxes from the

contaminated bank to the river for the first 3 years after the biochar-sand cap implementation. The simulations also showed that the THg flux from the contaminated bank should be reduced by approximately 60% 100 years after the biochar-sand cap implementation.

Introduction

The pore water sampling of mercury in historically contaminated banks of South River, VA have shown the effect of storm event bank inundation-drainage cycle on release of non-particulate THg from contaminated river bank (Chapter 4). Stabilization efforts were implemented following the flood event monitoring and baseline conditions post the implementation of stabilization efforts were monitored. However, due to inability to monitor storm event associated bank leaching, modeling efforts were implemented.

Bank profile

The bank site for the Constitution Park of South River, VA (Figure 46) was modeled using field borings to define the structure of the bank (Figure 49) as well as assumptions about permeability, porosity and storage coefficient used by AECOM, Aquanty and SRST (Appendix A, Figure 99) (AECOM & Mudrick, 2017).

The bank consists of two general layers (Figure 49). The bottom layer is highly permeable and composed primarily of sand that is not contaminated from historical releases. The top layer is a fine sediment silt/clay layer with lower permeability with a surface layer that is contaminated by historical mercury deposits (Bireta, 2015). Considering the stabilization efforts implementation schematic of the

bank slope (Figure 48), a model was built to include implemented stabilization efforts. The stabilization efforts included an addition of 15cm layer consisting of sand and biochar overlaid by 15cm of top soil (modeled as silt/clay).

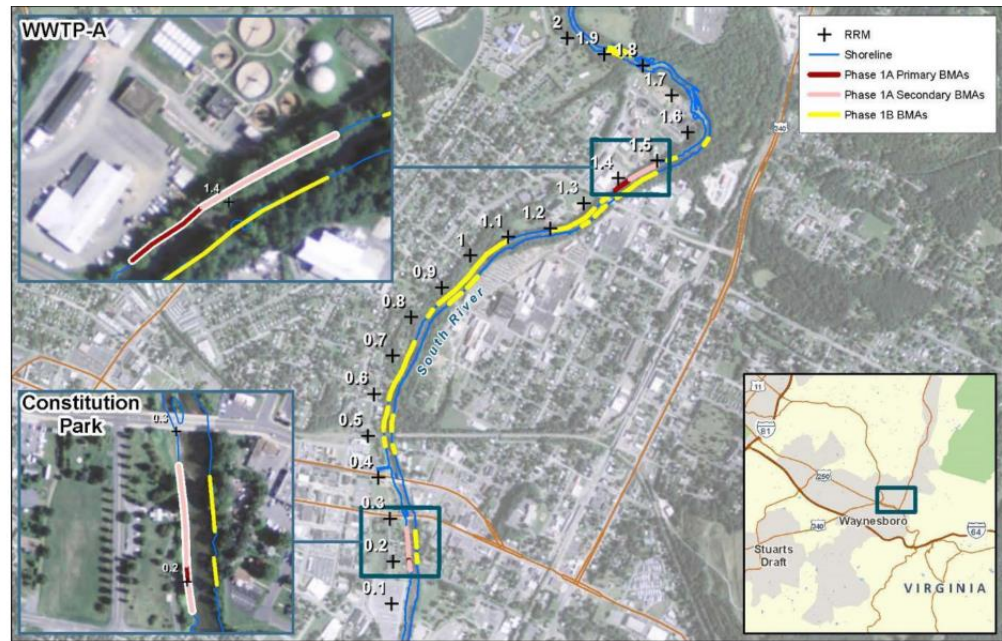


Figure 47 Constitution Park of South River, VA



Figure 46 Implemented stabilization efforts: close up of reactive cap layer (left, AECOM & Collins, 2017) and overall implemented efforts 6 months later (right)

Schematic of Cover Design

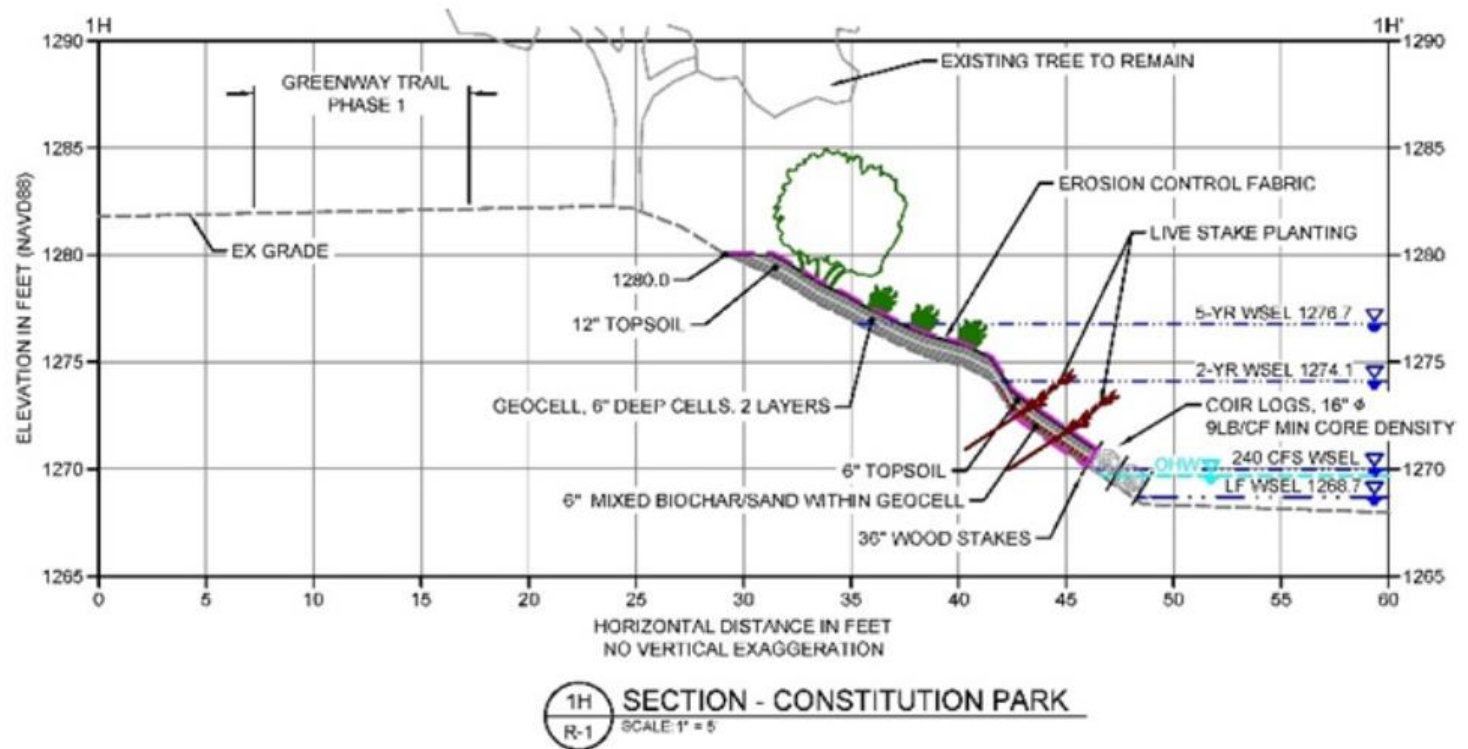
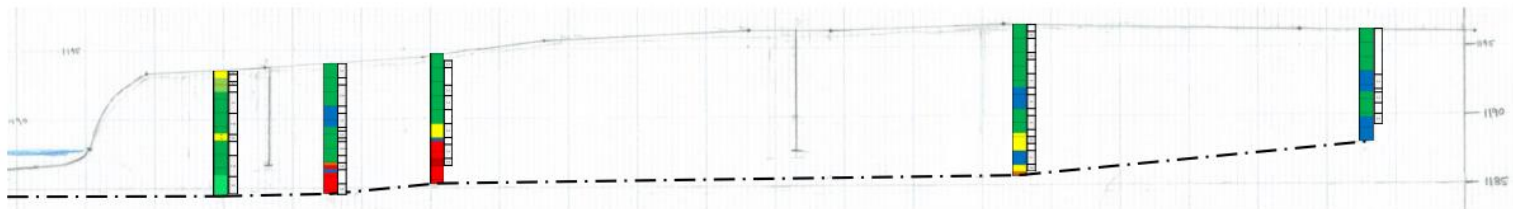
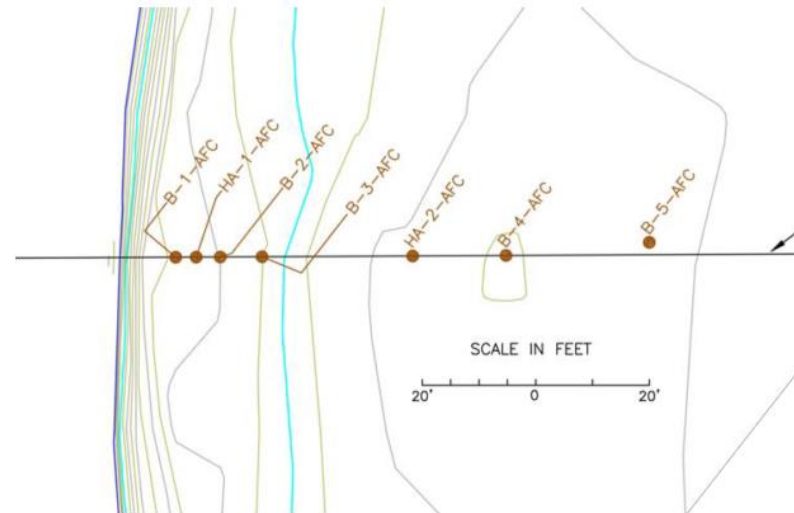
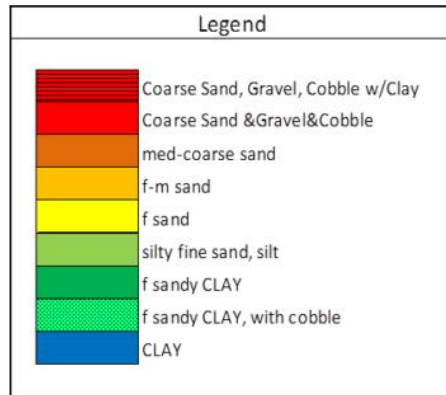


Figure 48 Schematic of cap design used for characterizing capping layer used in modeling (SRST, 2016a)



Borings



Cross-section

AECOM

Figure 49 Cross section of the bank with boring results used in bank (AECOM & Mudrick, 2017)

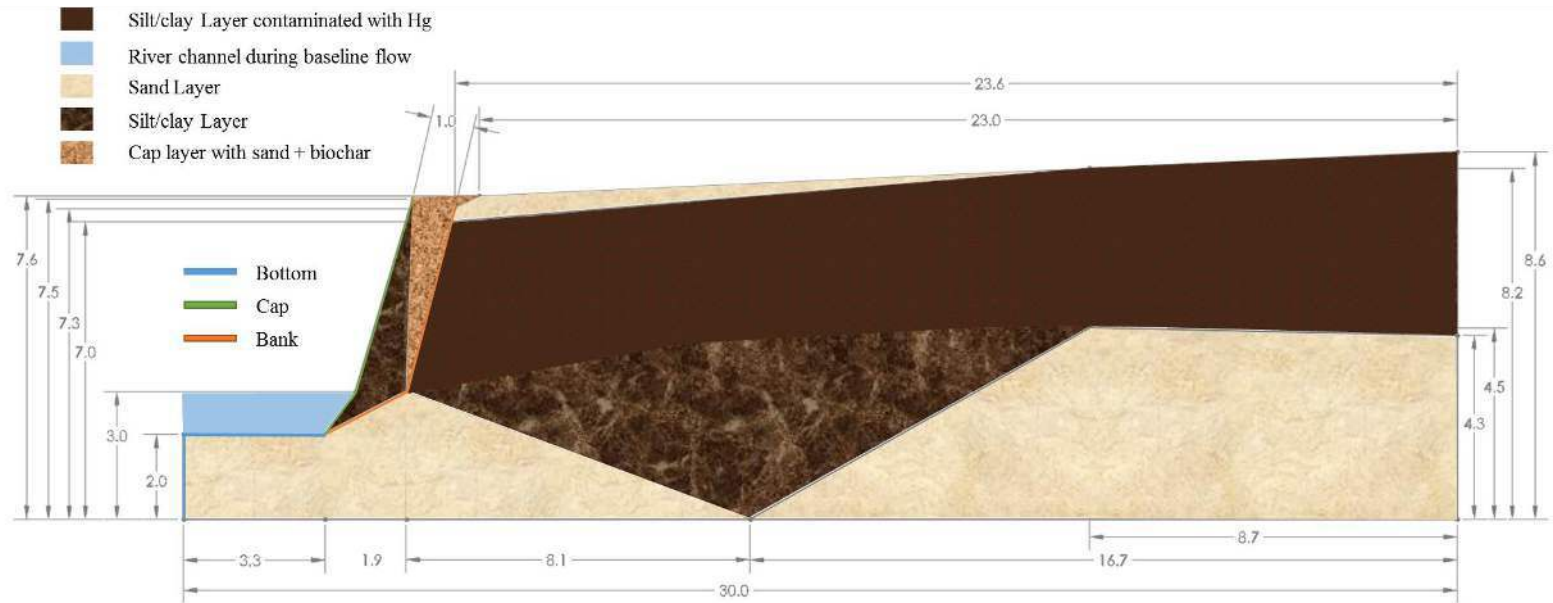


Figure 50 Model sketch of the bank created in SolidWorks made based upon the boring results showed above. All the measurements noted are in ft

Flooding event frequency was estimated from historical hydrographs, indicating 3 ft flood stage event as a common event, and 6 ft flood stage event as an annual maximum flooding event (Table 4) (Anchor QEA et al., 2015). In the simulation of flow, inundation 30 ft into the bank (Figure 50) associated with the common flooding event (3ft) and maximum flooding event (6ft) was assumed to be at the end of the inundation cycle (i.e. bank was fully saturated and starting elevation was 3 or 6 ft above river channel height during baseline flow). Simulation was used to estimate drainage rate and volume from the saturated bank.

Table 4 Return frequency and bank drainage volume for different size flooding events (Anchor QEA et al., 2015)

Flood Stage (ft)	Return Frequency (events/yr)	Drainage Volume (L/ft of bank)
1.5	18	49
3	3.5	102
6	1	260
Total/yr	22.5	1499

A commercial finite element model, COMSOL Multiphysics®, was used for storm event drainage simulation from an inundated bank. Integrated hydrological modeling was performed using Richards Equation in the Earth Science Module with rainfall infiltration and seepage faces implemented in simulations (Chui & Freyberg, 2007). Richards Equation Solver with Earth Science Module is used for variably-saturated subsurface flow modeling, where Darcy's laws and conservation of mass are included (Chui & Freyberg, 2007). Mualem Genuchten Model (MVG) is used for

simulating fluid and mass transport in the unsaturated zone and assumptions are that all excess surface water on the surface runs off immediately and there is no ponding (Schaap & van Genuchten, 2006; van Genuchten, 1980)

With the return frequency and bank drainage volume for different size flooding events given, Darcy velocity could be estimated and used to estimate Hg migration and fluxes. CapSim® modeling software was developed as a tool for modeling behavior of contaminants in the contaminated sediments and allow for prediction of the effectiveness of remedial efforts. CapSim® was used to predict short term and long term fluxes of THg from the contaminated silt/clay layer through the reactive cap of *in-situ* stabilization efforts. In addition to THg fluxes through the stabilized bank, THg concentration profiles in the bank could also be predicted. The model relies on the chemical migration of contaminants in the porous media, where media is separated into multiple layers and each layer is defined as 1-D porous media system with specific properties and boundary conditions (Shen, 2017). In addition to chemical migration in well-defined porous media, the model also accounts for bioturbation, burrowing and dredging activities, and the mass transport across the sediment-water interface. This considerations are important, as the activity of benthic organisms in the first few cm of sediment alter physical and chemical characteristics of sediments. Likewise, sediment-water interface has turbulent motions in overlaying water which can cause mixing and dilution by the overlaying water. As a result, CapSim® modeling of contaminant fate and transport accounts for the impacts of sorption/desorption, redox conditions, bioturbation, oscillated advection and deposition (Shen, 2017) .

Objectives of the study

The study was focused on achieving two objectives. The first one was to examine the effects of a typical (3ft) and yearly maximum (6ft) flooding events on bank drainage while accounting for the implemented stabilization efforts. In this simulation, the bank was assumed to initially be fully saturated as it would presumably be at the end of a flooding event (Figure 34, 3), as the drainage from the bank is starting to occur. The simulation provides estimates of drainage rate and volume associated with typical and yearly maximum flood event.

The second objective was to examine the long term performance of the reactive cap with sand and biochar implemented at Constitution Park. The performance of implemented bank stabilization efforts was examined in terms of long term flux of THg from the bank following the flooding events, as well as spatial resolution of THg throughout both the contaminated sediment and reactive cap.

Methods

Flow modeling

Bank drainage was modeled assuming an initially saturated bank at the end of the inundation period of the common flooding event (3ft) and maximum flooding event (6ft). The inundation was modeled to seep 30 ft into the bank (Figure 50), and subsequently drains out completely before the next inundation-drainage cycle. The volume of water draining was assumed to be 25% of the volume of the bank. River level was modeled as hydraulic baseline level at 1 ft above bottom of the channel, although this level during actual drainage event would start above that height and gradually decrease until reaching 1 ft river level. Seepage and no flow boundaries were defined as seen on the Figure 51

below. Layer specific properties were evaluated using the data from borings (Figure 49) (AECOM & Mudrick, 2017) and estimating percentage of constituents of each layer. Bank layer porosity, storage capacity, specific yield, and alpha values were estimated using percentage of constituents of each layer or estimate based on the previous application of modeling parameters (Duffield, 2016; Geotechdata.info, 2013; Schaap & van Genuchten, 2006). Table 10 and Table 11 in the Appendix C indicate specific properties used for each layer.

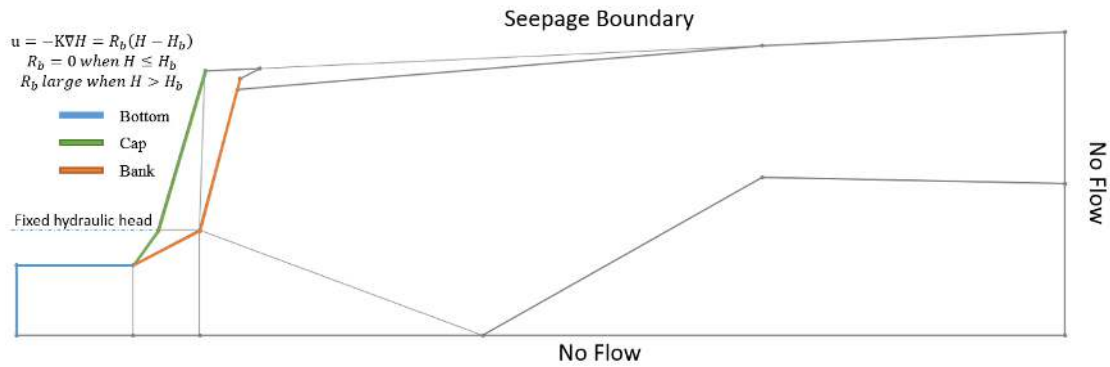


Figure 51 Boundary conditions for the model used in COMSOL

The modeling was done using Mualem-van Genuchten Model (MVG) which includes following equations to describe unsaturated soil hydraulic properties over a wide range of hydraulic heads, H , while accounting for small minimum capillary height to address limitations of Equation 17 and Equation 20 below caused by mathematical properties on the description of conductivity near saturation (Schaap & van Genuchten, 2006; van Genuchten, 1980; Yang & You, 2013):

Equation 17 MVG Model soil-water retention equation

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

Equation 18 MVG Model effective saturation equation

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

Equation 19 MVG Model

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

Equation 20 MVG Model hydraulic conductivity function

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

Where θ is volumetric water content (cm^3/cm^3), H is pressure head (cm), θ_r and θ_s indicate residual and saturated water contents, respectively (cm^3/cm^3), α is related to inverse of the air-entry pressure and is a positive number (1/cm), n is a measure of pore size distribution and is greater than 1, m is related to n value using following relationship: $n=1-1/n$, l is an empirical pore-connectivity parameter and is usually fixed at 0.5, Se is an effective saturation value (Schaap & van Genuchten, 2006).

From the equations above, governing equations are Richards' equation (silt layer) and Storage Equation (sand layer):

Equation 21 Richards' Equation governing silt/clay layer

$$\left(\frac{C_m}{\rho g} + S_e S_{silt}\right) * \frac{\partial H}{\partial t} = \frac{\kappa}{L\mu} \nabla^2 H, \quad \text{Where } \kappa = K_{silt} K_r \epsilon, \quad K_{silt} = 0 \text{ when } H_p < 0$$

Equation 22 Storage equation governing sand layer

$$(S_{sand}) * \frac{\partial H}{\partial t} = \frac{K_{sand}}{L} \nabla^2 H$$

Long term evaluation of the stabilization efforts

Based on the Table 4, the flow in and out of the bank during bank inundation/drainage was simulated as a sinusoid that provides 22.5 periods per year and leads to 1499 L/ft into the bank during inundation and the same volume out of the bank during drainage. Sinusoid model is given by:

Equation 23 Sinusoidal model representing average drainage volume (Reible et al., 2017)

$$Q = 4709 \frac{L}{ft} \sin \frac{2\pi t}{\tau} \quad \tau = 0.044yr$$

Darcy velocity could be estimated using return frequency and bank drainage volume for different sizes of flooding events (Table 4) by assuming a 1 ft high seepage face (Reible et al., 2017):

$$V = 5069 \frac{cm}{yr} \sin \frac{2\pi t}{\tau} \quad \tau = 0.044yr$$

Darcy velocity was used in CapSim® model as the advective component of the THg flux.

The cap was composed of biochar and sand. The effective partitioning coefficients were determined by lab sorption tests where mercury in the form of mercury nitrate was added to the small amounts of biochar and sand. Sorption was assumed to be

linear, with $q=K_d \cdot C$ isotherm. Change between initial and final concentration was measured after 24 hour equilibration at 20 °C. The effective partitioning coefficient value, K_d , from the sorbent isotherm was estimated to be 1310 L/kg for biochar, and 6 L/kg for sand. Therefore, a biochar-sand cap with 11% biochar by weight had a K_d value of 150 L/kg. Thickness of the cap was obtained from bank stabilization plans (Figure 48), where 15 cm of biochar and sand layer is placed on top of contaminated soil, in addition to 15cm clean sediment layer. As a result, thickness modeled was 15 cm. Clean layer of sediment on top was also modeled as 15 cm, with hydrodynamic dispersivity of 1.5cm.

The properties of sand-clay layer were obtained from mesocosm (T-cell) study performed with homogenized sediment obtained from the bank location of the Constitution Park. The Constitution Park sediment concentration from the mesocosm study was found to be 3.3mg/kg, with DGT THg value of 2274 ng/L resulting in Log K_d value of 3.16. As a result, silt/clay sediment layer was considered to be uniformly contaminated with 2.3 µg/L of THg in pore water. The thickness of the contaminated sediment layer modeled was assumed to be 130 cm, a conservative estimate based on the sediment grab samples obtained during field sampling at the Constitution Park bank locations. Tortuosity correction for sediment was Boudreau (Equation 25) since it a fine grained sediment, whereas tortuosity correction for mixture was calculated using general correction model for porous media Millington & Quirk (Equation 24). Tortuosity and porosity are used for correcting effective diffusivity coefficients in the sediments due to the effect of porous media, finite void fraction, and random structure of solid paths on the diffusion pathway (Shen, 2017).

Equation 24 Effective diffusivity for tortuosity correction model (Millington & Quirk, 1961)

$$D_{n,i} = \varepsilon_i^{4/3} D_{w,n}$$

Equation 25 Effective diffusivity for tortuosity correction model for fine-grained sediments (Boudreau, Bernard P., 1996)

$$D_{n,i} = \frac{\varepsilon_i D_w}{1 - \ln(\varepsilon_i^2)}$$

Bioturbation or enhanced hyporheic exchange was modeled with a Gaussian distribution with depth with 5cm Gaussian model coefficient, 10 cm²/yr particle biodiffusion coefficient and 100 cm²/yr pore water biodiffusion coefficient. Bank water effective mass-transfer coefficient was calculated to be 1.83 cm/hr. All the input parameters are summarized in the Table 12 Input parameters for CapSim model of the Appendix C.

Results and Discussion

Flow modeling

6 ft flood event

Using the 6 ft flood modeling, accumulative discharge volume through bottom, bank and cap layer was estimated as 31.9 ft³/ft, 43.3 ft³/ft and 3.9 ft³/ft, respectively. The discharge from contaminated bank layer is mostly draining into the channel layer, as opposed to the cap (Figure 52). Since the volume discharged through bottom and cap layer in 15 days of modeling is 35.6 ft³ per ft of river width, relative contributions of volume associated with the 6 ft flooding event are 89.8% from the bottom, uncontaminated layer and 10.2% from the contaminated sand-silt layer.

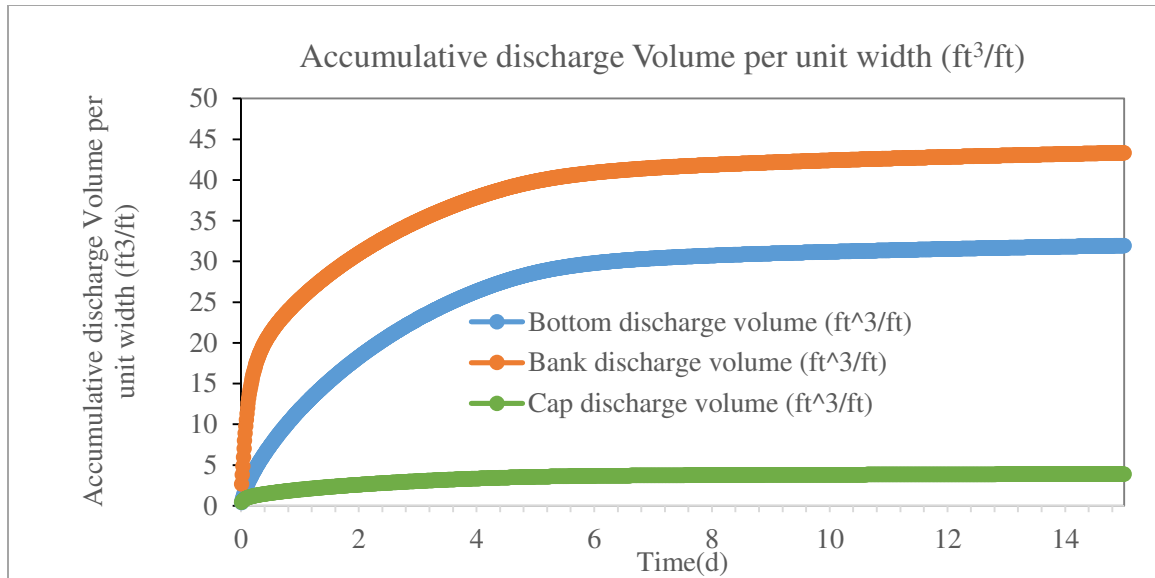


Figure 52 Accumulative discharge volume per unit width for 6 ft flooding event

Velocity through each of the layers was calculated by using Darcy velocity magnitude ft^2/d normalized to a length of bottom, bank and cap interface of 5.3ft, 7.2ft, and 5.9ft, respectively. Average velocity through a bottom, bank and cap layer were 0.4 ft/d, 0.39ft/d, and 0.04ft/d, respectively. Maximum velocities in bottom, bank and cap layers are 7.75ft/d, 16.3ft/d and 2.71ft/d, respectively, and total volumetric flow rate for bottom, bank and cap per width for river bank adding up to 28.6ft³/ft, 38.3 ft³/ft, and 3.3 ft³/ft for the first 5 days when maximum leaching is occurring.

Drainage simulation of 6 ft flood event, as seen on Figure 53 shows 6ft flood event drainage at different time points. The simulation shows that the inundated bank volume from the finer grained silt/clay layer drained predominately into the underlying sand layer and the volume drained into the river channel mostly from the sand layer. This is due to properties of the sediments, where fine sediments such as silt and clay ($<64\mu\text{m}$) have high porosity but low permeability and hydraulic conductivity, whereas sands

(>64 μ m) have lower porosity but higher permeability and hydraulic conductivity (Chapman et al., 2002). The effect of 6ft flooding event simulation is indicative of the maximum drainage occurring in the first day following the maximum inundation associated with the storm event, and the majority of drainage is completed within the first 5 days. The quick drainage through fine sediment into porous sediment is indicative of oxic conditions associated with the storm event not getting reduced as the drainage through the bank is occurring. The 5 day duration of drainage, with the peak discharge occurring in the first day also indicate that devices capable of capturing non- particulate mercury associated with leaching should be able to be deployed for less than 5 days in order to capture full effect of bank leaching, such are diffusive gradient in thin-film (DGT) devices (Zhang, H. et al., 1995). However, the initial conditions for the model are assuming 6 ft water level in the bank and 1 ft baseline water level in the river channel at the beginning of the simulation (day 0). Considering the water level in the river would be slowly declining as opposed to being 1ft initially, the actual drainage is likely occurring for a longer time duration (about seven days based on the location hydrographs).

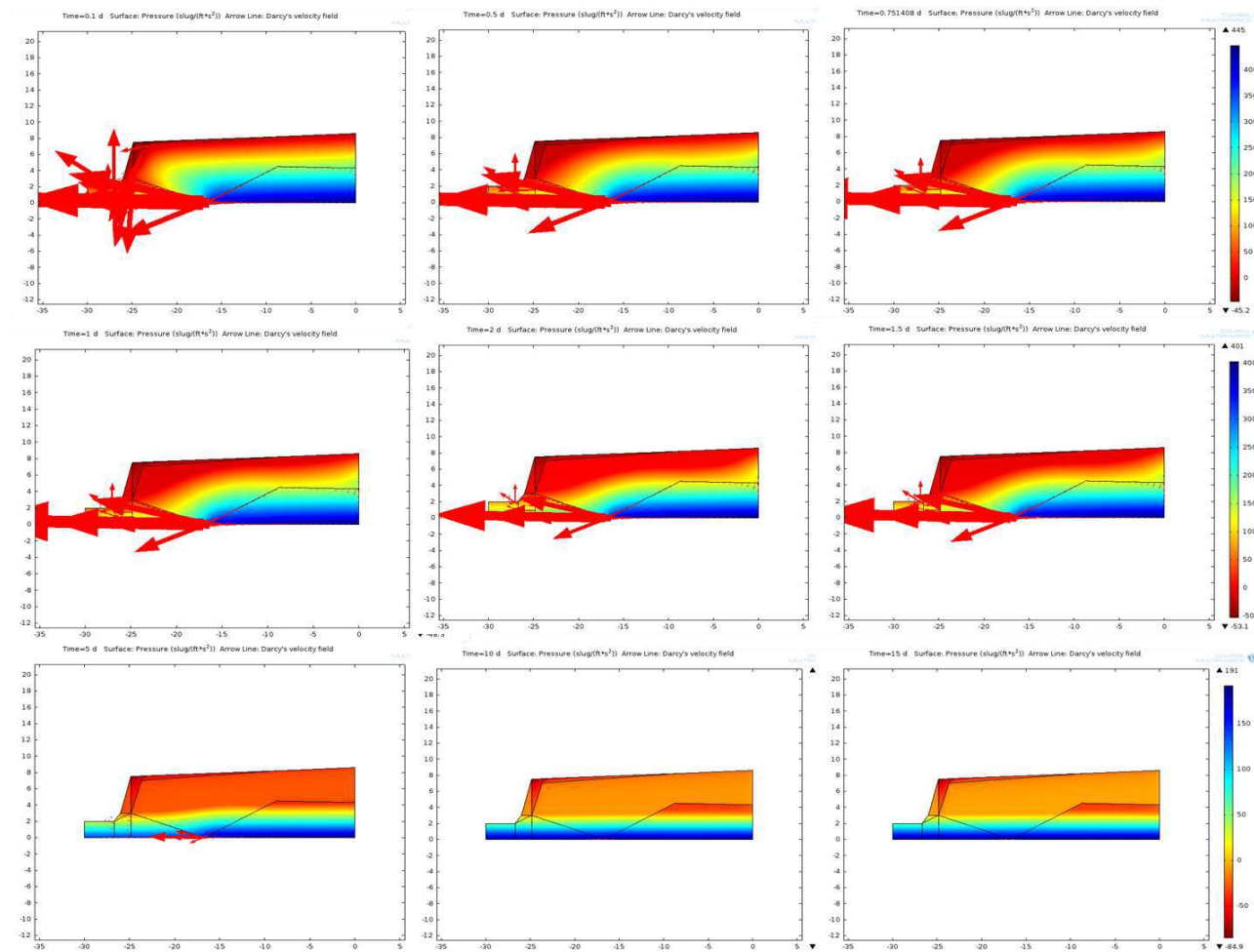


Figure 53 6 ft flood event drainage simulated for the first 15 days after the flooding event, shown as 0.1d, 0.5d, 0.75d, 1d, 1.5d, 2d, 5d, 10d, and 15d (left to right, top to bottom). Notice maximum drainage from the upper, contaminated layer occurring at the bank-water interface, and greater drainage occurring from the “midpoint” of the uncontaminated bottom layer red arrows and their size)

3 ft flood event

A 3 ft flooding event was also simulated. In terms of accumulative discharge volume (Figure 54), the trends are similar to the 6ft flood event, although the volumes are smaller due to a smaller size of flooding event simulated. Accumulative discharges volumes per unit width of bank for bottom, bank and cap layer interface are 7.9 ft³/ft, 9.11 ft³/ft, and 0.9 ft³/ft, respectively. When only considering the cap and bottom layer that are discharging directly into the river system, this amounts to total volume of 8.82 ft³/ft, with bottom sandy layer discharge contributing to 89.3% of this volume, and cap layer contributing to 10.7% of the total volume per unit width of the river. When compared to 6 ft volume, the volume have been reduced by 75% of the accumulative discharge volume from a 6 ft food.

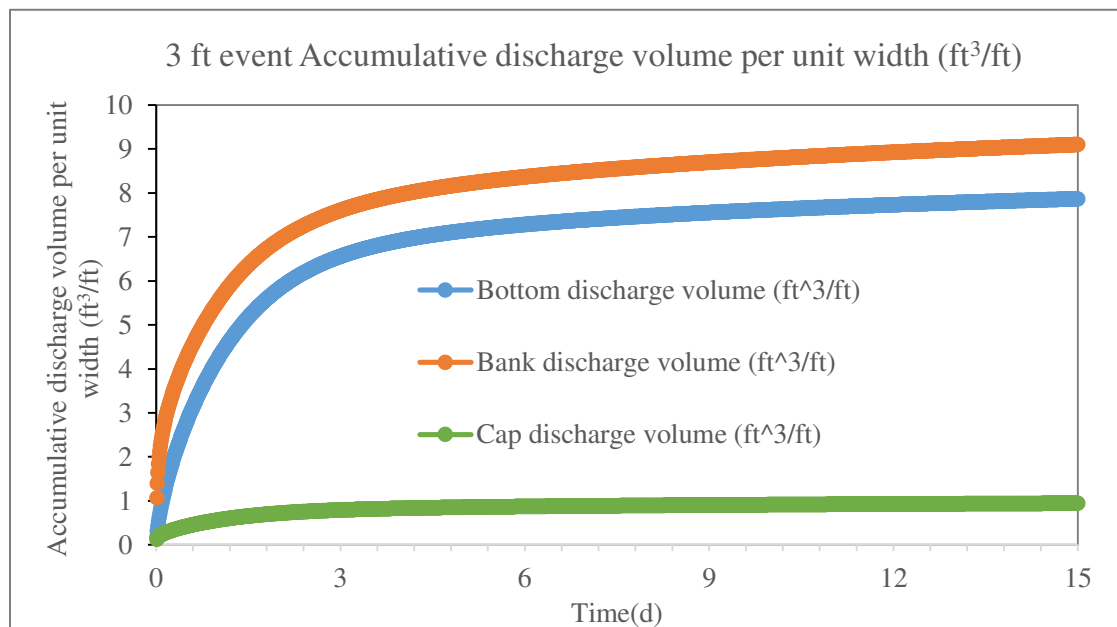


Figure 54 Accumulative discharge volume per unit width for 3 ft flooding event

Average velocity through bank, bottom, and cap layer were calculated to 0.099 ft/d, 0.0785ft/d, and 0.0098ft/d, respectively. The velocity shows that that majority of the

volume is again draining from bank into the channel, as opposed to cap layer. The velocity of 3 ft flood is reduced by 75% as compared to 6 ft flood. Maximum velocities in bottom, bank and cap layers are 3.39ft/d, 6.14ft/d and 0.724 ft/d, respectively. Total volumetric flow rate for bottom, bank and cap added up to 5.8 ft³/ft/s, 8.5 ft³/ft/s, and 0.9 ft³/ft/s for the first two days when maximum leaching is occurring.

Similar to 6 ft flooding event, the volume associated with 3 ft flooding event is draining quickly (<2 days) through silt/clay layer and mostly draining into the underlying sand layer, with the sand layer contributing the majority of drainage volume into the river as indicated on Figure 55. This also indicates that pore water mercury mostly associated with the silt/clay is also predominantly leaching into the bottom sand layer. Main difference from the 6 ft flooding event is the majority of discharge occurs in shorter time period. After the period of two days, the main draining remaining is the one from the bottom layer (Figure 55). Total discharge through bottom and cap interface is 8.82 ft³/ft for 3 ft storm, which is equivalent to 250L/ft. This value is greater than the 102 L/ft drainage volume reported in the Table 4, which is likely a result of initial conditions with 3 ft water level in the bank and 1 ft initial river water level quickening the drainage from the bank. It also indicates that the drainage from the bank with the river water level slowly declining to the baseline conditions would slow down seepage out of the system as compared to the values obtained by the model.

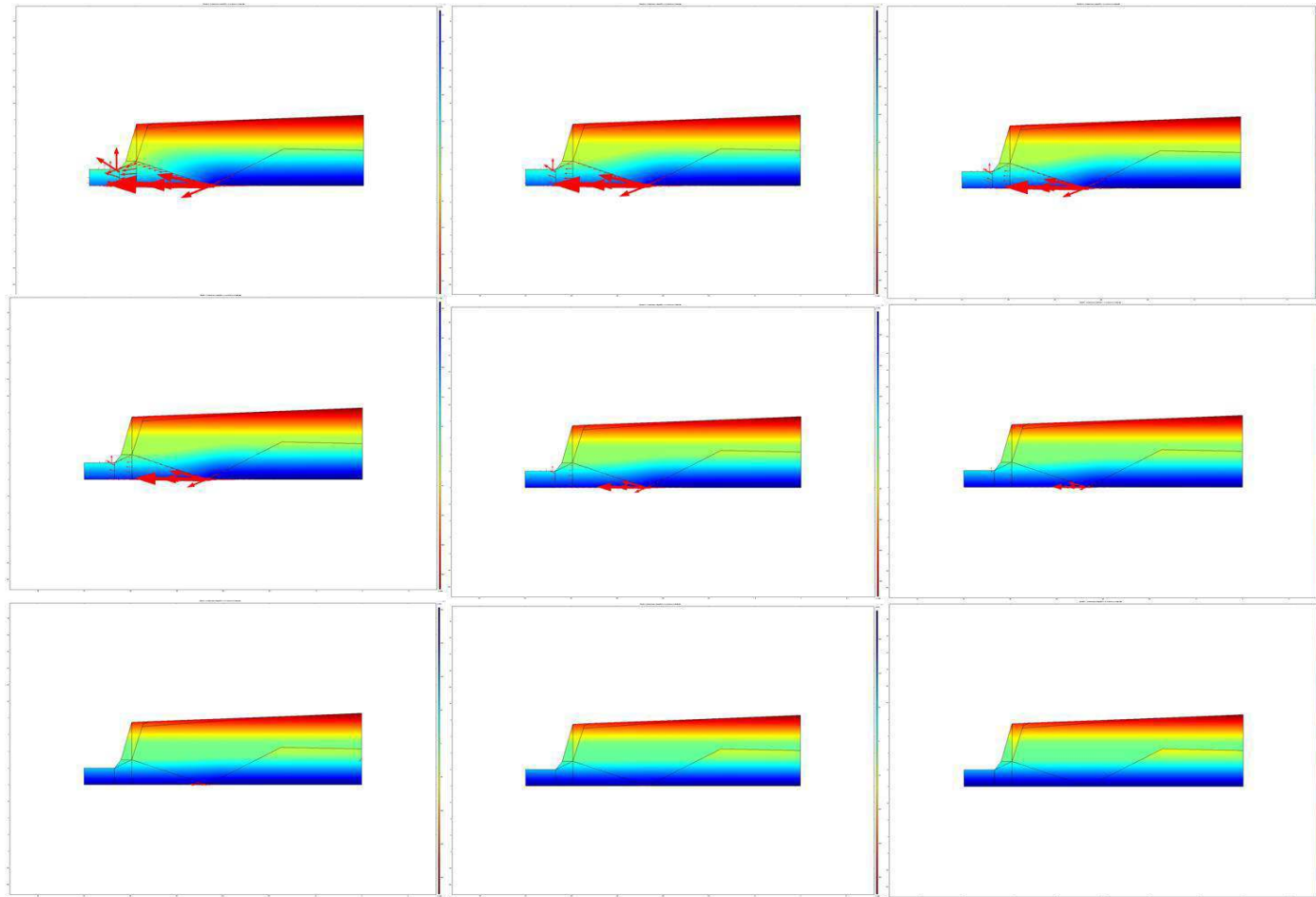


Figure 55 3 ft flood event drainage simulated for the first 15 days after the flooding event, shown as 0.1d, 0.5d, 0.85d, 1d, 1.5d, 2d, 3d, 5d, 15d (left to right, top to bottom). Notice maximum drainage from the upper, contaminated layer occurring at the bank-water interface, and greater drainage occurring from the “midpoint” of the uncontaminated bottom layer (red arrows and their size)

Long term evaluation of the stabilization efforts

CapSim ® modeling was used on the bank with implemented stabilization efforts assuming average flood event and its associated advective groundwater flow and THg flux. As seen from the Figure 56 below showing THg flux at sediment-water interface, the reactive cap implemented as a part of stabilization efforts prevents any THg flux from entering overlaying water in the first 4 years after the implementation of the cap. In the following 26 years THg flux from the contaminated sediment through reactive cap keeps increasing until storm event upwelling fluctuations reach a maximum expected THg flux of $0.6 \mu\text{g}/\text{cm}^2/\text{yr}$. For the following 70 years THg flux reduces to an average value of $0.5 \mu\text{g}/\text{cm}^2/\text{yr}$ and stays there until 100 years after reactive cap implementation. This decrease is likely due to depletion of mercury from the underlying contaminated sediment providing resupply of pore water mercury concentration by partitioning from the solid phase.

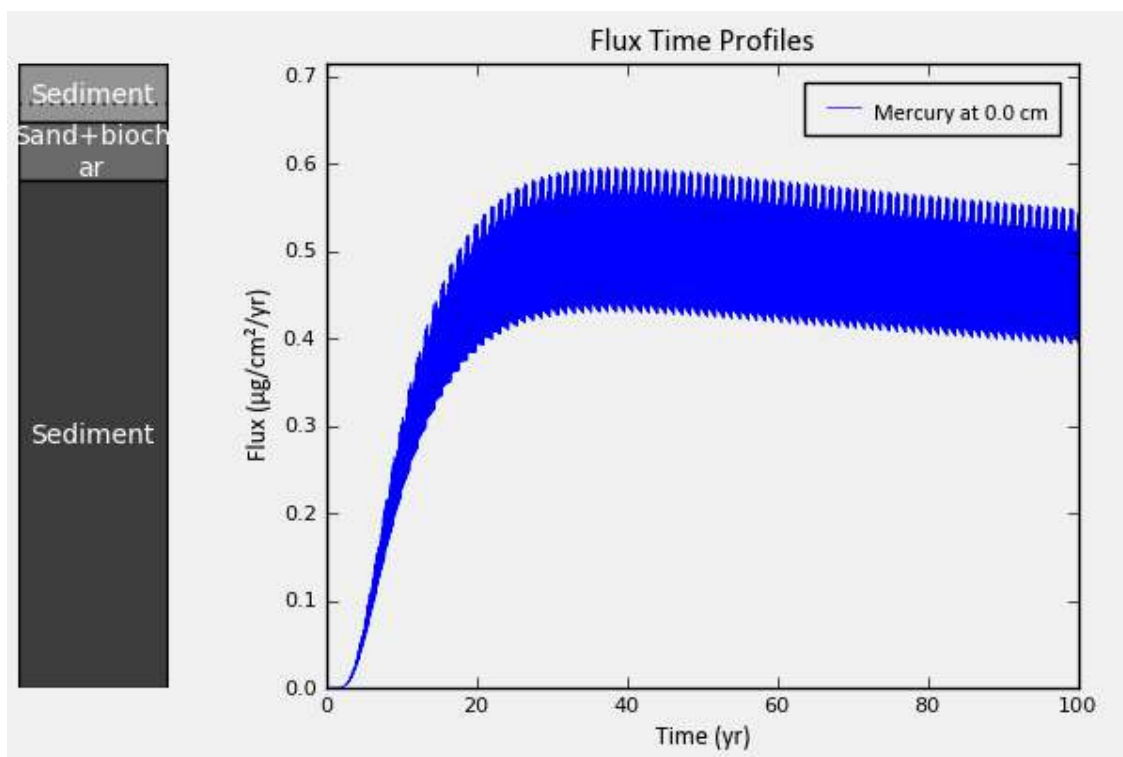


Figure 56 The effect of the average annual storm size and frequency on the flux of mercury in the first 100 years of stabilization implementation

Using CapSim ® modeling also allowed prediction of spatial profile of pore water mercury throughout the cap and contaminated sediment for 100 years following the reactive cap implementation (Figure 57). As seen from the profile below, the cap is very effective at preventing the majority of THg flux in the first 3 years. Even once the pore water concentration migrate through the sediment-water interface, the concentrations remain below 20ng/L in the first 10 years and below 30ng/L in the first 100 years since the implementation of the reactive cap (Figure 58). Considering the initial pore water THg concentration in contaminated sediment of 3500ng/L, the reactive cap shows reduction in surface sediment pore water concentrations by 99.1%. This is likely due to ability of the capping to enhance reduced conditions and alter the speciation of mercury.

Also, biochar in the reactive cap has high affinity for mercury sorption, contributing to overall effectiveness of the cap, particularly during the first 3 years.

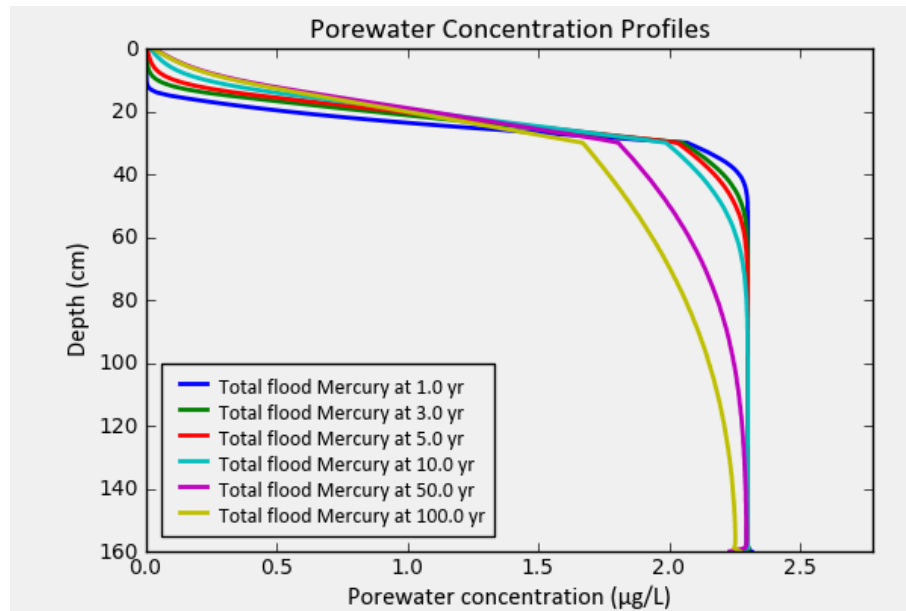


Figure 57 Spatial profile of mercury pore water concentrations with the implemented cap

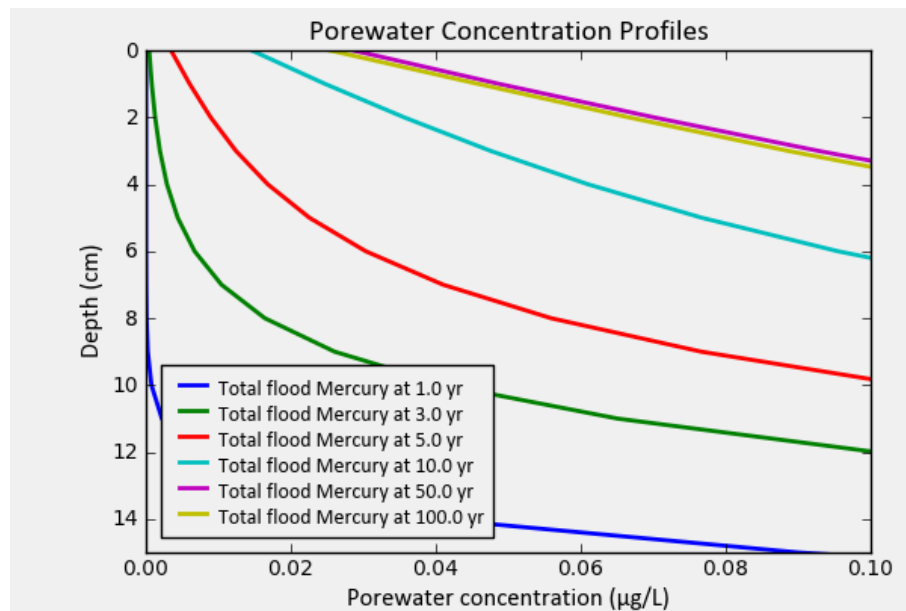


Figure 58 Spatial profile of mercury pore water concentrations in the first 15 cm below sediment-water interface

Lastly, long term evaluation of THg flux through implemented reactive cap was compared to the evaluation of THg flux through a sediment without stabilization efforts to evaluate the effectiveness of the stabilization efforts. As seen on the Figure 59 below, reactive cap is effective at completely immobilizing pore water THg for the first 3 years, whereas the contaminated sediment without implemented reactive cap is showing THg fluxes as high as $24 \mu\text{g}/\text{cm}^2/\text{yr}$. Moreover, the effectiveness of the reactive cap to reduce THg flux is substantial in the first 100 years. There is a rapid decline in THg flux in the first 20 years likely due to a depletion of the contaminated bulk mercury source in the contaminated river bank (about 90% THg flux reduction in no cap scenario).

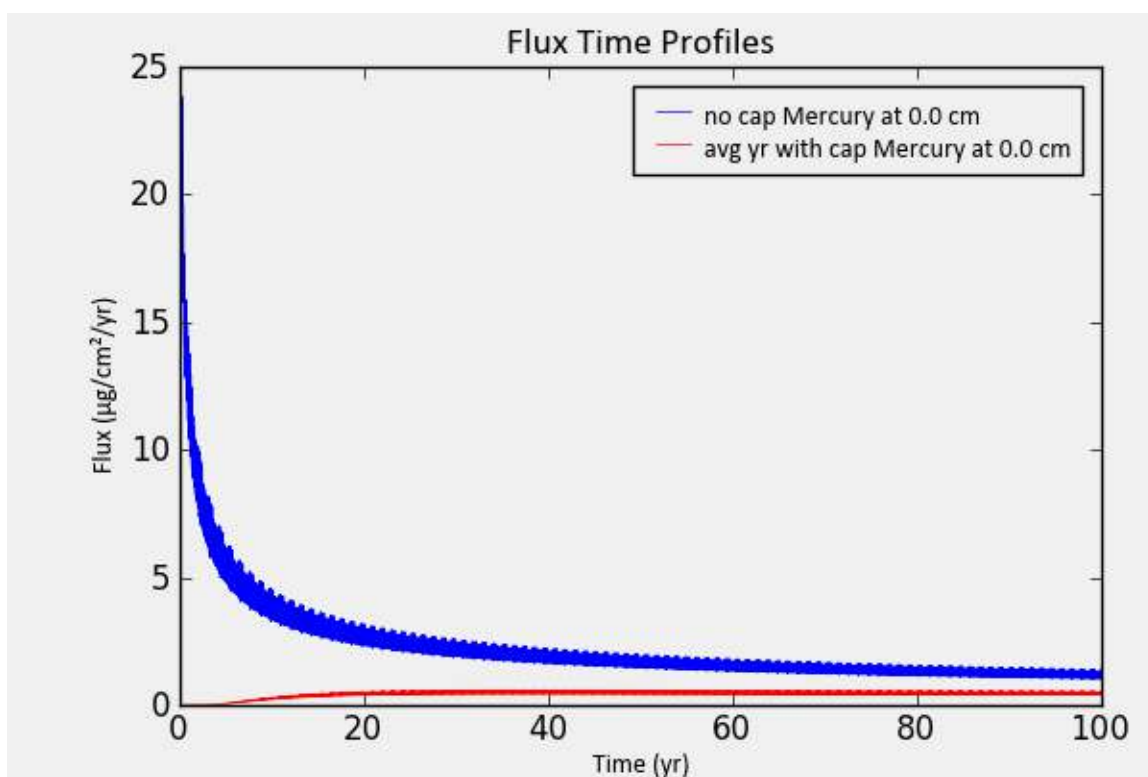


Figure 59 Flux of THg as a result of the average of the flooding events in the first 100 years for the no cap and reactive cap implemented scenario

Stabilization efforts continue to effectively reduce THg fluxes from contaminated sediments in the first 100 years, with 100 year THg flux from capped scenario of 0.5

$\mu\text{g}/\text{cm}^2/\text{yr}$ showing 61.5% reduction in THg flux as compared to the sediment without implemented stabilization efforts with 100 year THg flux of $1.3 \mu\text{g}/\text{cm}^2/\text{yr}$.

Conclusions

Modeling efforts were undertaken to simulate drainage from inundated bank following the storm event using COMSOL®. The models of a common event (3ft flood stage) and annual maximum event (6ft flood stage) demonstrated that drainage is occurring within 5 days from the start of the drainage cycle for the 6 ft flood and 2 days for 3 ft flood. Slow water level decreases after the peak flood would slow the seepage out of the system. The volume of the drained volume is predominately in the bottom sand layer (~90% for both flood events simulated), as compared to the bank layer (~10%). This indicates that sampling to monitor the full extent of a flood event requires sampling devices able to obtain samples in less than 2 days such as DGT profilers. The pattern of drainage also indicates that oxic conditions are likely to remain in the system due to quick passage of drained volume through silt/clay layer and introduction into the river system through a coarser sand layer.

Bank leaching associated with storm event flooding of contaminated bank has been found to be a significant source of non-particle related mercury. CapSim® modeling was used to simulate pore water THg transfer in the first 100 years from the stabilization efforts implementation with the reactive cap. The reactive cap was found effective at reducing pore water concentration of THg from leaching from the contaminated sediment through the reactive cap. Maximum THg flux breakthrough is expected to be $0.6 \mu\text{g}/\text{cm}^2/\text{yr}$ 20 years after the implementation of a biochar-sand cap and subsequently decreasing to $0.5 \mu\text{g}/\text{cm}^2/\text{yr}$ for the following 80 years. A biochar-sand cap was also

found to be efficient in reducing pore water concentrations of THg via sorption to the biochar of biochar and sand layer. The placement of reactive cap is predicted to reduce pore water concentrations in the next 100 years from $2.3\mu\text{g/L}$ to values lower than 30ng/L , indicating 99.1% reduction in sediment pore water THg concentration. Lastly, the results of implemented biochar-sand cap were compared to sediment without implemented stabilization efforts (no cap scenario). A biochar-sand cap placement demonstrated substantial improvements in reduction of THg Flux, especially in the first 20 years. Estimated reduction in THg flux as a result of a biochar-sand cap placement in 100 years is 61.5% as compared to uncapped contaminated bank sediment. In the areas where a biochar-sand cap has not yet been placed, bank leaching associated with storm events might present a significant source of non-particulate THg drainage.

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CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Summary and Conclusions

Quantifications of mercury and methyl mercury in sediment pore water with DGT devices allow for better understanding of the most available and mobile fraction of this persistent contaminant and bioaccumulative neurotoxin. Difficulties with the extraction of MeHg from the 3MFSG DGT resin were resolved by the application of nitric acid extraction method. The utilization of nitric acid for extraction of MeHg from the 3MFSG DGT resin resulted in reproducible $91 \pm 9\%$ methyl mercury recovery, suggesting that switching to digestion of DGT resin with diluted nitric acid might be preferred to commonly used TU/HCl extraction method.

Field sampling at South River, VA demonstrated that storm event associated inundation and subsequent flooding could leach biologically relevant mercury from the contaminated river bank. The effects of leaching were greater at the bank locations as compared to the channel ones. MeHg concentrations following the storm event were lower as compared to baseline conditions due to the storm event associated reoxygenation of the system. However, increased amount of mercury in the system could increase methylation potential following a development of more reduced conditions. The implementation of stabilization efforts at the Constitution Park containing biochar has resulted in substantial decrease in pore water mercury concentration as well as the associated Hg fluxes. High temperatures and reduced conditions developed during baseline conditions have indicated increased methylation rates.

The observations of substantial Hg leaching from contaminated river bank at the Constitution Park following a flooding event were characterized by monitoring under baseline conditions and during a drainage event after a storm. The ability to control the post event drainage with bank stabilization including a chemical sorbing layer of biochar, was evaluated by monitoring under baseline conditions after bank stabilization. Since further monitoring events were not possible, modeling efforts were undertaken to predict the THg fluxes into the river after the stabilization efforts. In order to achieve that, a commercial finite element model was used to estimate the velocities and volumes associated with storm event inundation and drainage. The model described the location and timing of the maximum drainage associated with a common and maximum annual flooding event. The CapSim® model was used to predict THg fluxes at sediment-water interface, as well as depth specific THg concentrations in the bank accounting for implemented stabilization efforts. CapSim® modeling showed that stabilization efforts eliminated THg fluxes for the first 3 years after reactive cap implementation and even after 100 years, THg fluxes were reduced by 61.5% as compared to the bank without implemented reactive cap. Concentration profiles at sediment-water interface showed 99.1% reduction in THg concentrations as a result of reactive cap placement. Maximum fluxes associated with stabilization efforts were $0.6 \mu\text{g}/\text{cm}^2/\text{yr}$, with the long term (100yr) average of $0.5 \mu\text{g}/\text{cm}^2/\text{yr}$.

Recommendations

The main limitation with the new method for extraction of MeHg from the DGT resin is its detection limit so the main recommendation for future work would be to address this issue. Using current procedure and MQL of Merx-M analyzer shows capability of detection of 1.02 ng/L of DGT MeHg in pore water for the diffusive layer thickness, area and time of exposure currently used. This creates an issue for the applications where MeHg in pore water concentration is expected to be below 1 ng/L. For such applications, further development of this method is needed. The detection limit of MeHg could be reduced by altering the concentration of nitric acid currently used, either by decreasing the initial concentration of nitric acid used for the 3MFSG DGT resin extraction (currently 4.73M), or by increasing the final concentration of the nitric acid analyzed (currently 0.05M). Current concentrations were determined based on the application of the method for the analysis of MeHg in biota (Brooks Rand Instruments, 2017; USGS-Mercury Research Laboratory, 2016). The main concern with this would be the ability of less concentrated nitric acid to elute MeHg from the 3MFSG DGT resin and the sensitivity of Merx-M analyzer to increased nitric acid concentration. Parameters such as time of exposure and area are fairly simple to extend in order to increase MeHg accumulation onto the resin. A final alternative would be to work on lowering detection limit on Merx-M analyzer. According to its specifications on Brooks Rand Instruments websites, Merx-M should be able to detect 0.005ng/L, which is more than 5 times lower than the 0.0273ng/L limit currently achieved in the conditions used (1.09pg for 40mL of sample). This may require isolating the machine into a separate room, replacing system

parts such as quartz cell and using specific cleaning protocols to ensure background levels of reagents low enough to achieve this MQL.

Recommendation for future work would be to perform another field sampling to capture full effects of storm event after the stabilization. It would be very useful to capture non-particulate THg leaching after the stabilization efforts, preferably immediately before the storm, during the storm, and within the first week of leaching. The key with using DGTs for obtaining pore water THg measurements is the ability to deploy samples for 48 hours allowing the capture of the peak increase in THg associated with the flood event. The efforts to capture maximum bank leaching would likely detect really low MeHg concentrations due to oxic conditions associated with a storm event, which could be addressed by deploying a few profilers for longer time period. These results could then be used to optimize modeling efforts presented in the Chapter 5. In order to successfully perform such sampling, timing around the storm event is the key to capturing maximum THg DGT pore water effects associated with flooding event mercury leaching.

For the future modeling efforts, parameters of input into the model could be enhanced. A better understanding of soil properties and more accurate hydraulic conductivity values could be obtained for the locations modeled. A potential that the remedial cap sorptive capacity will be reduced over time should be evaluated, as such decrease has not been implemented into this model. Continuous monitoring, particularly after 4 years would be beneficial for comparing predicted values to monitored ones. Overall, the utilization of CapSim® could be a very useful tool for predicting long-term performance of bank stabilization efforts on the reduction of THg release.

APPENDIX A. SUPPORTING INFORMATION FOR CHAPTER 3

A.1. Agarose Diffusive Gradients in Thin-Film Probe Fabrication

Texas Tech University (TTU)

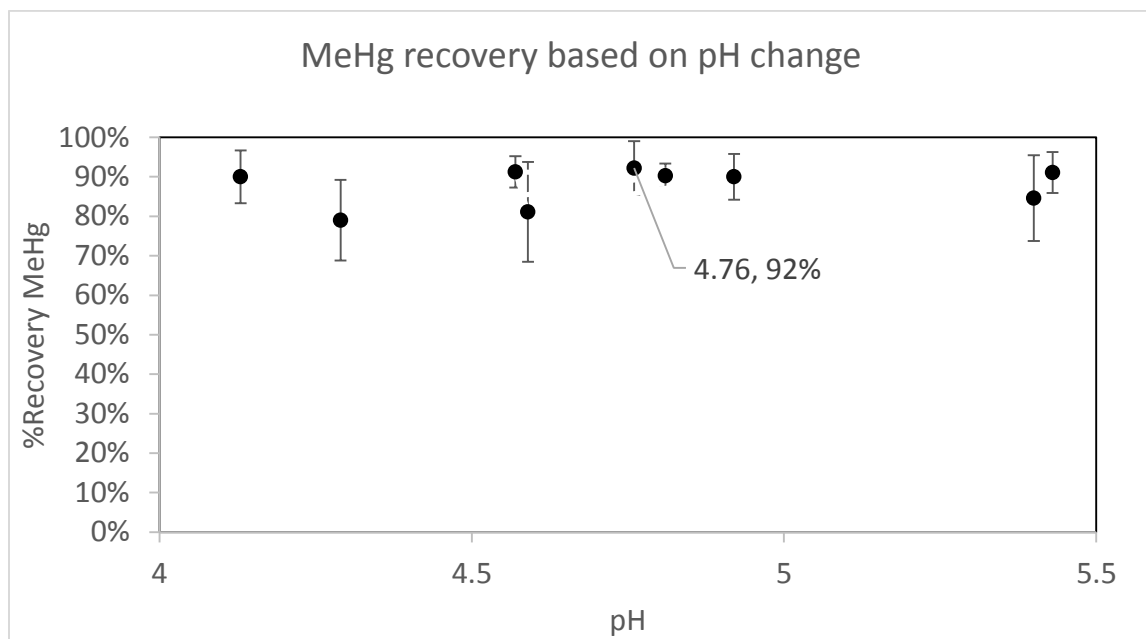


Figure 60 Effect of pH change on the recovery of the spike

SCOPE AND APPLICATION

- 1.1. This method is an operating procedure for preparing the resin and diffusive layer of DGTs, as well as, assembly of the DGT body.
- 1.2. DGTs can be used in mercury and trace metal uptake studies in the sediment and porewater.
- 1.3. This method was adapted from the following references: The method is mainly an adaption of Amirbahman et al. Typically, polyacrylamide gel is used to impregnate the resin beads (see other references for details). However, this procedure describes steps to fabricate agarose based resin-gel layer.
 - 1.3.1. Amirbahman et al., (2014). Assessment of mercury bioavailability to benthic macroinvertebrates using diffusive gradients in thin films (DGT). *Environ. Sci. Processes Impacts*, 2013 (15), 2104
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 - 1.3.4. Practical Guide for Making Diffusive Gel and Chelex Gel. From www.dgtresearch.com.
 - 1.3.5. Practical Guide to Assemble DGT Devices. From www.dgtresearch.com.

- 1.3.6. How to make DGTs videos and this document (Dropbox→Reible
Group→SOPs) made by Michelle Bejar

SUMMARY OF METHOD

- 1.1. Fabricating agarose resin and diffusive layers require ultra-pure water, resin beads, and agarose. Glass plates for casting and gel manipulation will be used, as well as, the type of DGT being fabricated.
- 1.2. This method prepares resin gel samples that can be run on ICP-MS, Merx-T and Merx-M.

INTERFERENCES

- 1.3. Interferences largely arise from working in an area that is suspected to have high mercury concentrations or mercury contaminated tools and glassware.
- 1.4. Historically, most Hg contamination has occurred during clean-up and N₂ purging steps of the DGTs

APPARATUS AND MATERIALS

All glassware and in some cases plasticware must be soap and acid washed with the acid bath in the DGT room.

- 1.5. Glass plates, two different widths (TTU Chemistry Glass Shop, or can be bought)
- 1.6. Glass Beaker
- 1.7. Glass stirring rod
- 1.8. Teflon magnetic stir bar
- 1.9. Hot plate and stirrer
- 1.10. Vial cap that is similar in diameter to the piston body
- 1.11. Fume hood

- 1.12.0.78 mm gasket and spacer kit (Cole Palmer EW-28573-31, EW-28573-04)
- 1.13. Plastic clamps (Cole Palmer EW-28565-30)
- 1.14. Glass Syringe, 10 cc
- 1.15. Clean Oven set to 105 °C
- 1.16. Plastic spatula and tweezers (Fisher 14-518, Cole Parmer EW-06443-27)
- 1.17. Gel staining box, Nalgene® (VWR 28196-306)
- 1.18. Probe holders, piston and sediment shape
- 1.19. Filters, 0.45 µm, Millipore® – Durapore®, 25mm diameter, polysulfone: for piston probes (Millipore HVLP02500)
- 1.20. Filters, 0.45 µm, Millipore® – Durapore®, membrane filter sheet, polysulfone: for sediment probes (Millipore HVLP00010)
- 1.21. DGT Bodies (Pistons or Depth Profilers, or Sediment Probe)
- 1.22. Nylon rivets for Depth Profilers

REAGENTS

- 1.23. Ultra-pure water (resistivity~18Ω.cm)
- 1.24. ISOLUTE Si-Thiol (Biotage, 9180-0100)
- 1.25. Agarose, Broad Spectrum Range for DNA/RNA (Fisher 1356-100)

PROCEDURE

- 1.26. Resin Gel Construction:
 - 1.26.1. For the resin gel solution, use the following:
 - 1.26.1.1. ISOLUTE Si-Thiol resin - 1 gram per 5 mL of ultra-pure water
 - 1.26.1.2. 2% Agarose – 0.2 gram per 10 mL of ultra-pure water

- 1.26.2. 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).
- 1.26.3. Collect a glass syringe and find a plunger that will fit inside the syringe as well as move freely within the syringe. After a plunger has been found, put the glass syringe (not plunger) in the Clean Oven (set to 105°C) to warm up while the resin gel is being prepared.
- 1.26.4. Combine agarose with desired amount of ultra-pure water into an acid washed beaker. Add a small teflon magnetic stir bar. Set stir setting to maximum setting and set the heating setting to 7. Place a folded paper towel over the top of the beaker to prevent cooling to the upper portion of the agarose solution.

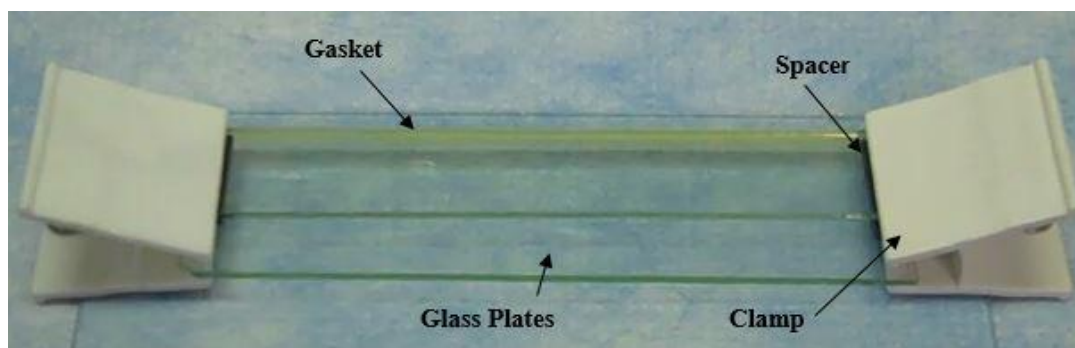


Figure 61 Glass plates, spacers, and gasket ready for gel casting.

- 1.26.5. The solution will appear cloudy in the beginning. As the agarose solution warms up, the solution becomes clear, like water.

- 1.26.6. As soon as the solution starts to become clear, retrieve the glass syringe from the oven. Place the plunger in the syringe and set aside.
- 1.26.7. Remove the beaker once the solution is clear. Add the resin to the beaker. While adding, use an acid washed glass stir rod to mix in the resin. Place the beaker back onto the hot plate and continue to mix the solution for less than 30 seconds.
- 1.26.8. Once the solution is well mixed, place the beaker near the glass plates. Use an acid washed glass syringe to collect more than 7 mL of solution. Tap the syringe on the beaker to move any bubbles from the spout of the syringe.
- 1.26.9. Tilt the glass plates while casting the resin gel solution at a constant speed. Casting can be performed from left to right or vice versa depending on what is comfortable.
- 1.26.10. Repeat if making multiple resin gel strips [1 gel strip = 1 sediment probe or 6 piston probes]
- 1.26.11. Let the resin get for 45 minutes at room temperature.
- 1.26.12. Remove clips and any excess resin that is not in between the glass plates. Remove spacers, and gasket and carefully separate glass plates with a plastic spatula; separating slowly as not to tear the new resin gel strip. If the strip is difficult to remove from the glass plates, spray some ultra-pure water in between the glass plates to re-hydrate the resin gel.
- 1.26.13. After solidifying, the resin beads have settled down on the bottom of the resin gel.
- 1.27. Diffusive Gel Construction:

- 1.27.1. 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).
- 1.27.2. Collect a glass syringe and find a plunger that will fit inside the syringe as well as move freely within the syringe. After a plunger has been found, put the glass syringe (not plunger) in the Clean Oven (set to 105°C) to warm up while the resin gel is being prepared.
- 1.27.3. Add 0.15 grams of Agarose per 10 mL of DI water into a beaker and bring to a boil. Round up to the nearest 10 mL to ensure there is enough gel for casting. While boiling, use a paper towel to cover the beaker to ensure even heating throughout the Agarose/DI solution. 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.
- 1.27.4. The Agarose gel will begin bubble as it heats, so during this time retrieve the glass syringe from the oven. Place the plunger in the syringe and set aside. The Agarose gel is ready to be cast when the solution begins to boil rapidly.
- 1.27.5. Using a glass syringe and extract Agarose/DI solution from beaker and cast between the glass plates. Use the same technique employed for casting the resin gel.
- 1.27.6. Let gel solidify for 30 minutes at room temperature.
- 1.27.7. Using the plastic spatula tool, cut off any excess Agarose that is not in between the glass plates. Remove the top glass plate and cut diffusive gel into the desired shape.

- 1.27.8. Construct probes immediately when diffusive gel is solidified.
- 1.28. Piston Construction:
 - 1.28.1. Using a large glass plate, first carefully transfer the resin gel onto the glass plate (ensure that the resin beads are face-up during the transfer).
 - 1.28.2. Using a centrifuge cap, press the cap down into both layers and slowly twist. Repeat for more discs from the strip.
 - 1.28.3. Transfer the resin gel discs onto the piston body. Ensure that the resin beads are face-up when it is placed on the body.
 - 1.28.4. Next, transfer the agarose gel on top of the resin gel.
 - 1.28.5. Cut out discs in the same manner as the resin gel strip.
 - 1.28.6. Place the agarose gel disc on top of the resin gel disc and ensure both are aligned properly.
 - 1.28.7. Apply the filter with sterile plastic forceps. Then place the probe cover down onto the piston body.
- 1.29. Depth Profiler Construction:
 - 1.29.1. Rinse the profiler body with distilled de-ionized (DDI) water and place on a large glass plate.
 - 1.29.2. Carefully transfer the resin gel strip to the profiler body (ensure that the resin beads are face-up during the transfer).
 - 1.29.3. Carefully transfer the agarose gel strip to the profiler body.
 - 1.29.4. Align the two gel layers until they are both lined up within the indented region of the profiler body. Cut off any remaining resin and agarose.

1.29.5. Using two sterile forceps, place the filter paper on top of the agarose layer.

If there are any air bubbles visible, it would be best to run the spatula over the bubbles and push them to the edge of the filter paper.

1.29.6. Align the probe retaining wall onto the profiler body and push down. 8

nylon rivets will be used to hold the probe retaining wall in place. Simply place the rivet over the hole and push down until secure.

PROBE CONSTRUCTION TIPS

A1.1. Ensure resin gel is sufficiently wet, apply extra ultra-pure water, when cutting resin on large glass cutting plate.

A1.2. To identify which side of the resin gel has the settled resin beads, gently scrape the surface of each side of the resin gel. If the resin gel feels coarse as opposed to smooth, then the coarse side contains the settled resin beads.

A1.3. See Figures 2A and 3A for completed probes dissected by each layer.

A1.4. There are a variety of sediment probe sizes, designed for laboratory or field use. Choose the appropriate probe for your desired use.

A.15. 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.

A1.6. Probes MUST BE de-aerated before use in 10 mM Sodium Nitrate solution with Ultra High Purity Nitrogen gas.

CLEANING PROCEDURE

A2.1. New DGT Bodies

A2.1.1. Etch the DGT bodies with any symbol, number, and/or letter to denote their use for a particular project.

A2.1.2. Log each etched DGT body into the designated DGT Log Book. See A2.2. for the information needed to be logged. An additional digital log book will need the same information and can be found on the MERX-T desktop.

A2.1.3. Soap wash the bodies in an Alconox® soap solution for 24 hours in a clean container. If the DGTs were deployed in sediment, scrub the bodies with a bristle brush until most of the sediment particles are removed before placing in them in the soap bath. Rinse the bodies with DDI water until no soap remains on the body.

A2.1.4. Place the bodies into a 50% acid bath for DGT bodies and allow the bodies to sit for 2 days. Use a container that will solely be used for acid washing DGTs. Some batches of DGTs will need to be rinsed successively to achieve background $\leq$ 100 pg. Monitor the acid bath to by taking subsamples of the acid bath and analyzing.

A2.1.5. Rinse the DGT bodies with DDI water, or the DGT bodies should be placed in a container and filled with DDI water. The pH of the water that the DGT bodies have been soaking in should be checked with a pH strip or pH probe. The pH should be between 5-6. If the water is very acidic, change the water bath and allow the DGTs to sit in the water bath for about 4 hours before checking the pH again.

A2.1.6. Once the DGTs are dried, they must be returned to their storage container in the DGT room (or other personal storage location).

A2.2. Used Lab and Field DGT Bodies

A2.2.1. Log in the DGT Log Book:

A2.2.2. Date Received

A2.2.3. Project Name

A2.2.4. DGT ID number (or Symbol)

A2.2.5. Damage to the body

A2.2.2. Disassemble the DGT bodies. Dispose of all nylon rivets removed from the DGT (These rivets cannot be acid washed. If they are acid washed, they will either deform or become brittle and break during DGT assembly)

A2.2.3. If the DGT bodies are heavily soiled or show discoloration, use a bathtub brush to scrub the DGT bodies of any sediment particles.

A2.2.4. Soap wash the bodies in an Alconox soap solution for 24 hours.

A2.2.5. Rinse the bodies with DDI water until no soap remains on the body.

A2.2.6. Place the bodies into a designated 50% acid bath for DGT bodies and allow the bodies to sit for 2 days.

NOTE: If O-Rings were used for Lab Piston bodies, do not place the O-Rings in the acid bath. The acid will weaken the O-Ring elasticity.

A2.2.7. Place the bodies into a 2nd designated 50% HCl acid bath for DGT bodies and allow the bodies to sit for another 2 days. (If there is no 2nd designated acid bath, then simply drain the acid and refill the acid bath container.)

A2.2.8. Rinse the DGT bodies with DDI water. The DGT bodies should be placed in a basin and filled with DDI water. The pH of the water that the DGT bodies have been soaking in should be checked with a pH strip or pH probe. The pH should be

between 5-6. If the water is very acidic, change the water bath and allow the DGTs to sit in the water bath for about 4 hours before checking the pH again.

A2.2.9. Once the DGTs are dried, they must be returned to their storage container in the DGT room to prevent the deposition of dust and to maintain organization.

A2.3. Cleaning and storage of non-DGT body related items

A2.3.1. All glass and plastic ware (to include probe holders) should be soaked in soapy water (Alconox®) for 24 hours. Glass plates and tools are acid washed after they have been soap washed overnight. Ensure an acid bath designated for DGT glassware and tools is used and not the general acid bath. Although contamination is minimal with the DGT acid bath, check the acid bath every 3 months.

A2.3.2. Glass and plastic ware should then be dried in a dust-free environment. To minimize the collection of dust during drying, cut a large sheet of bench paper and cover the drying items.

A2.3.4. All reagents should be stored in a mercury free environment to minimize contamination. Agarose and resin can be stored in the DGT Fabrication room. To minimize contamination, designate a plastic spatula for weighing for agarose and resin.

A2.3.5. All reagents should be reordered annually as some lose reactivity over time.

PREPARATION OF DGTs AFTER FABRICATION

A3.1. DGTs Used for Anaerobic Solutions or Sediments

A3.1.2. Use a container that is large enough to accommodate the number of DGTs fabricated.

A3.1.3. Prepare a 10 mM sodium nitrate purging solution in a container. Always prepare fresh purging solution! Never reuse previously used or old purging solution!

NOTE: Ensure that the container is not filled to the top. Depending on the number of DGT bodies that have been fabricated, displacement of the purging solution will vary. All DGT bodies must be fully submerged during purging.

A3.1.4. Prior to placing the DGTs into the purging solution, take triplicate subsamples for background analysis. This value should be less than 1 ng/L.

A3.1.5. Place resin gel strip scraps into the purging solution (scraps equivalent to 1 whole resin gel strip or more is sufficient).

A3.1.6. Place the DGTs into the purging solution. Note the time the DGTs began to purge.

A3.1.7. Place the bubbler stone into the purging solution and begin purging. Purge overnight with fast bubbling.

A3.1.8. After the DGTs have been purged, turn off the gas and remove each body and place into a Ziploc bag. Note the final time the DGTs were kept in the purging solution.

A3.1.9. Once all the DGTs have been removed, take triplicate subsamples of the purging solution and run immediately on MERX-T to ensure that the DGTs are not possibly contaminated. The working criteria for the purge solution after DGTs have been purged is 5 ng/L. If the purge solution is > 5 ng/L than the DGTs cannot be trusted and will need to be disassembled and acid washed again.

A3.1.10. If the DGTs will not be used immediately or will be used in the field, this protocol should be used. Take all the purged DGTs to an anaerobic chamber, along with clean Ziploc bags, and place them in the airlock chamber. Ensure that all the Ziploc bags, including the ones with DGTs, are open in the airlock chamber. Begin the airlock control.

A3.1.11. After the airlock chamber is anaerobic, begin to transfer 3 DGT profilers (or 1 piston) per Ziploc bag. Ensure that the profilers are not stacked on top of each other. Seal the Ziploc bag as airtight as possible.

A3.1.12. Place the Ziploc bag with DGTs into another Ziploc Bag.

A3.1.13. Repeat the bagging process until all DGTs have been doubled bagged.

A3.1.14. Place all double bagged DGTs into the airlock chamber for removal from the anaerobic chamber.

A3.1.15. Store the DGTs in a sealable plastic container in a 4 °C room until they are ready to be deployed.

A2.3.2. Small Scale Oxidic Ex-Situ Experiments

A2.3.2.1. After DGTs have been fabricated, place them in a Ziploc bag with a small amount of DDI water.

A2.3.2.2. Place the Ziploc bag in another Ziploc bag and place the DGTs in a sealable plastic container in a 4 °C room until they are ready to be deployed.

Table 5 Recoveries of MeHg extraction with nitric acid

<i>N</i> <i>replicate</i>	Recovery (%)		
1	112%	25	93%
2	108%	26	85%
3	107%	27	85%
4	99%	28	96%
5	99%	29	97%
6	101%	30	92%
7	98%	31	71%
8	99%	32	95%
9	94%	33	90%
10	93%	34	90%
11	88%	35	97%
12	70%	36	95%
13	73%	37	96%
14	68%	38	90%
15	90%	39	94%
16	86%	40	93%
17	84%	41	92%
18	85%	42	81%
19	77%	43	83%
20	92%	44	83%
21	99%	45	95%
22	94%	46	93%
23	95%	47	82%
24	93%		
		Average	90.9%
		Standard deviation	9.4%
		N samples	47

APPENDIX B. SUPPORTING INFORMATION FOR CHAPTER 4

DGT THg and MeHg spatial profiles for individual locations

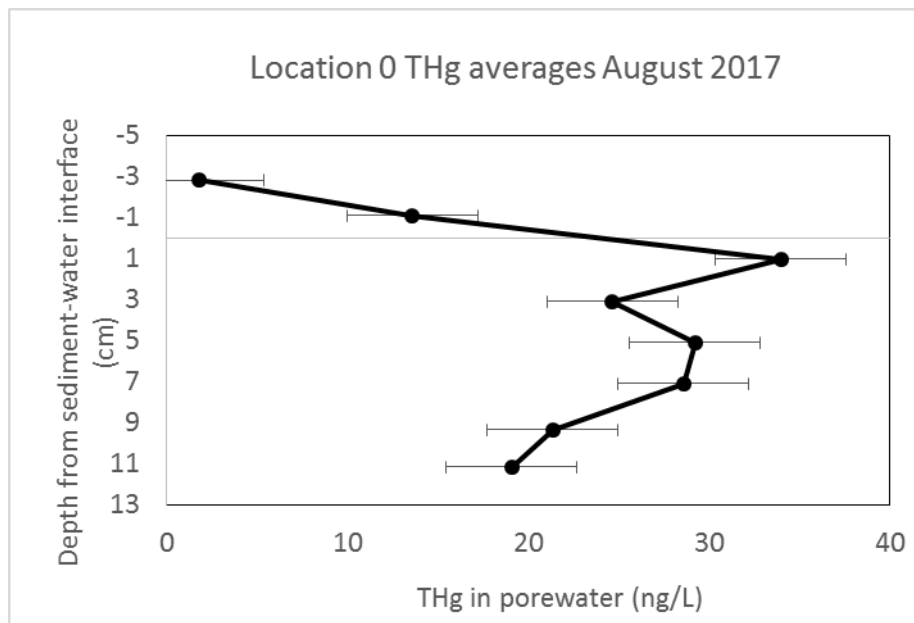


Figure 62 Location 0 avg THg

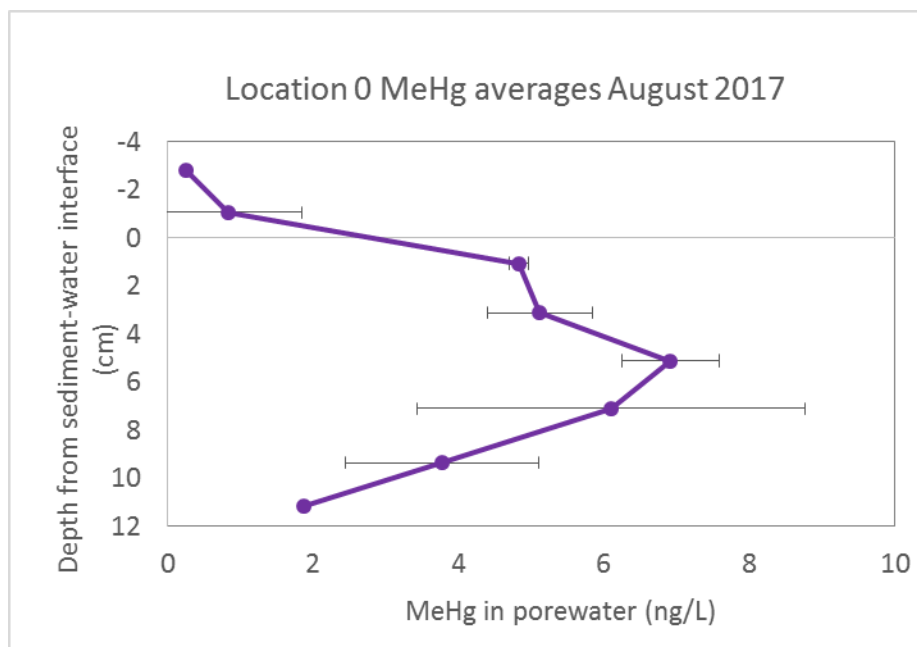


Figure 63 Location 0 avg MeHg

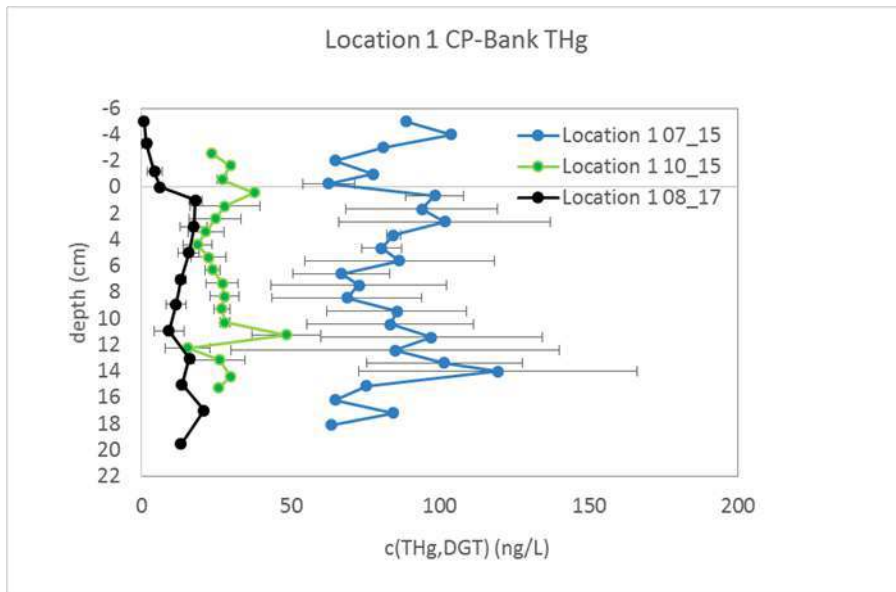


Figure 64 Location 1 avg THg

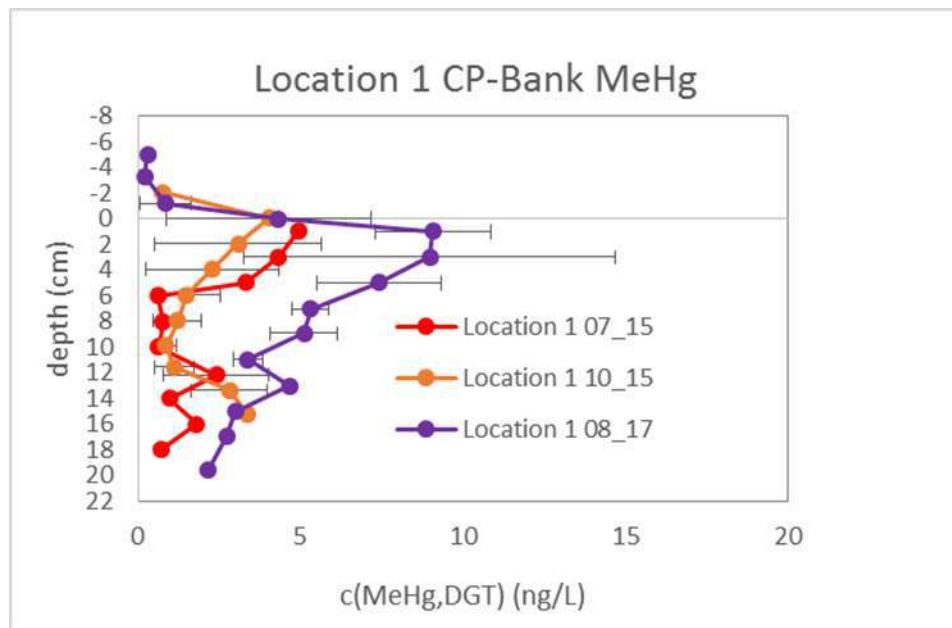


Figure 65 Location 1 avg MeHg

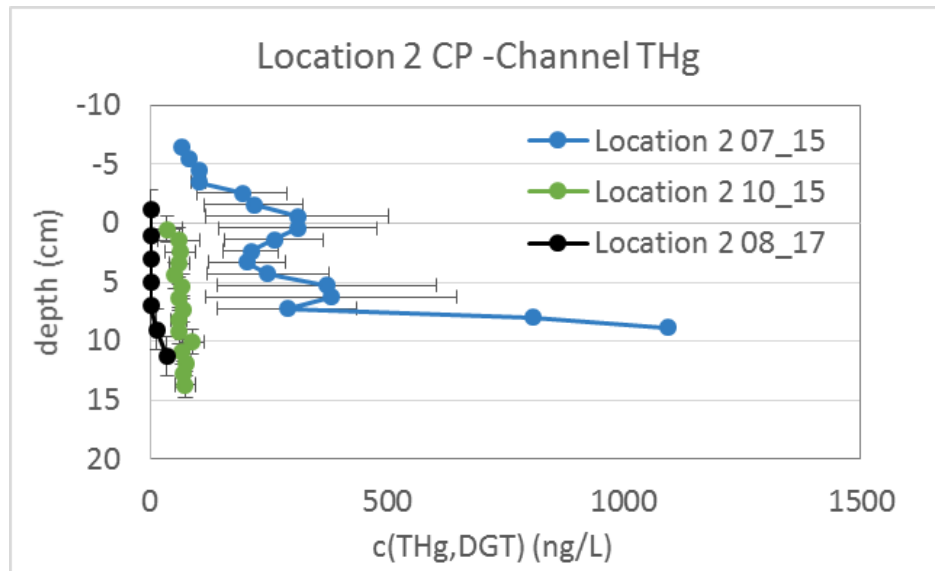


Figure 66 Location 2 avg THg

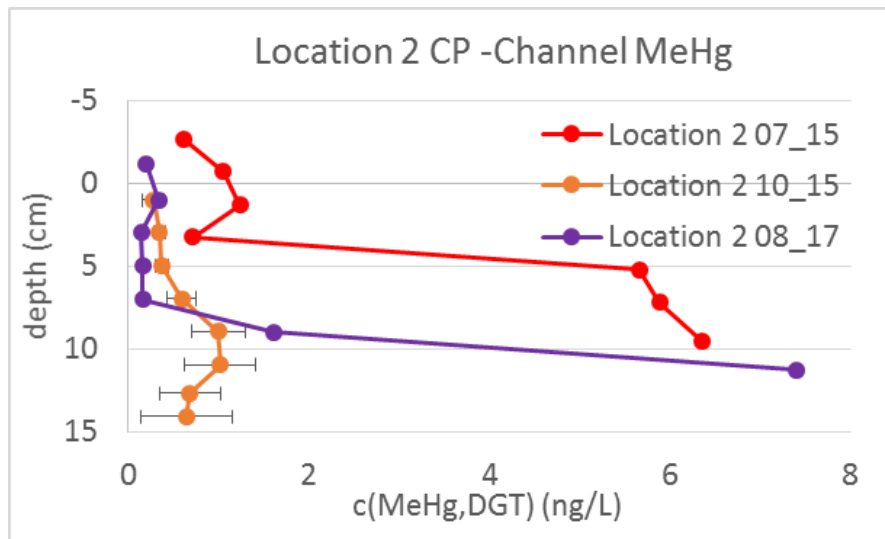


Figure 67 Location 2 avg MeHg

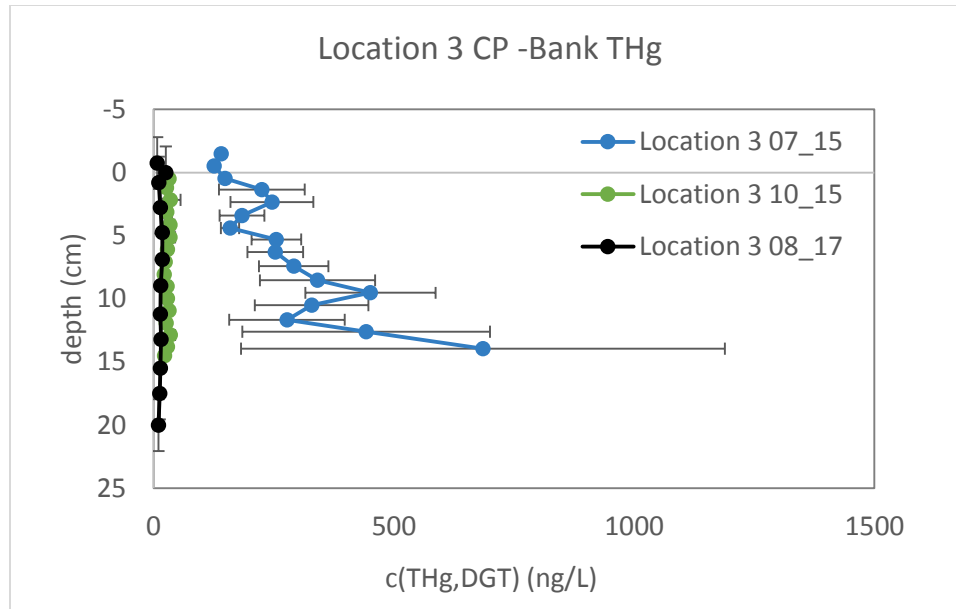


Figure 68 Location 3 avg THg

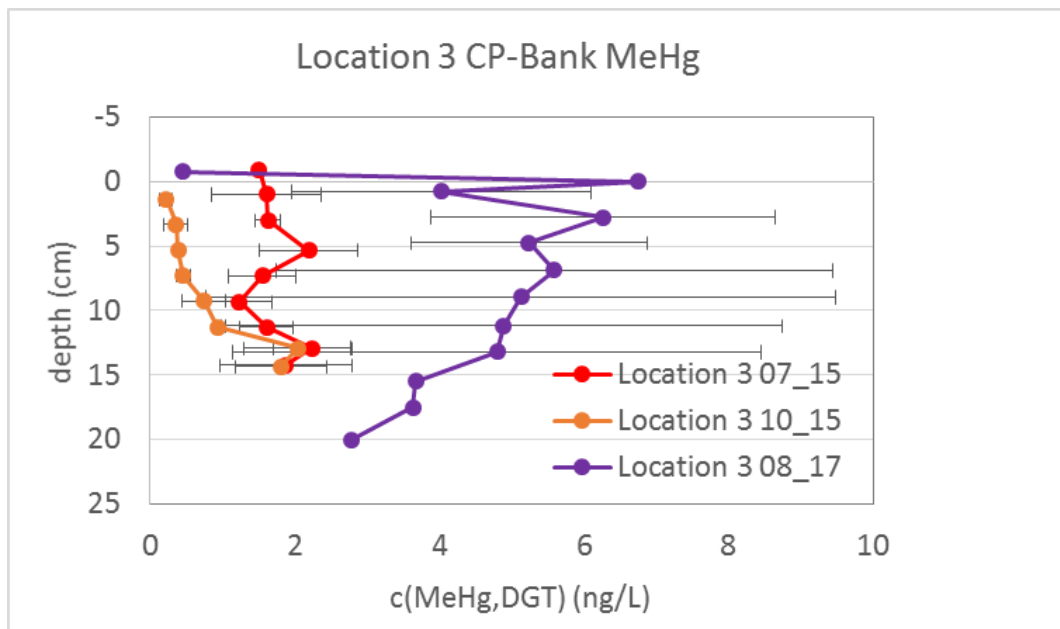


Figure 69 Location 3 avg MeHg

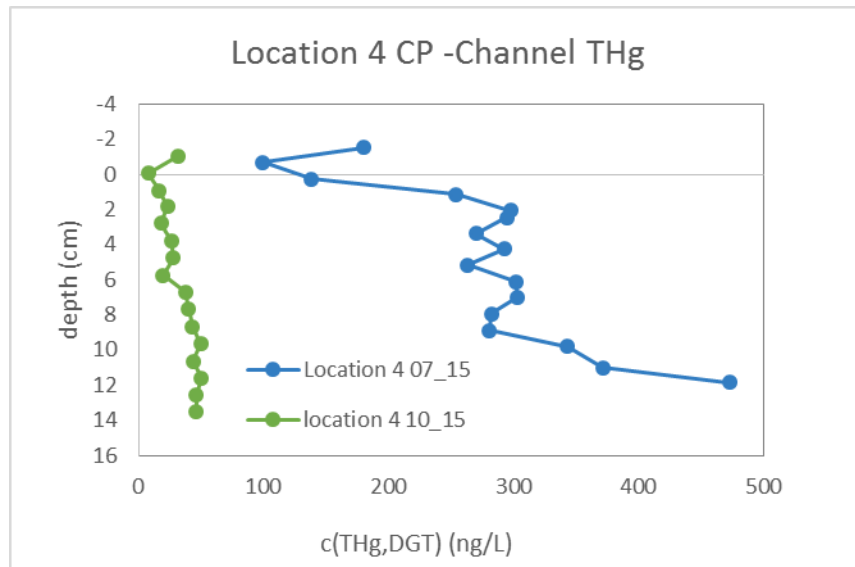


Figure 70 Location 4 avg THg

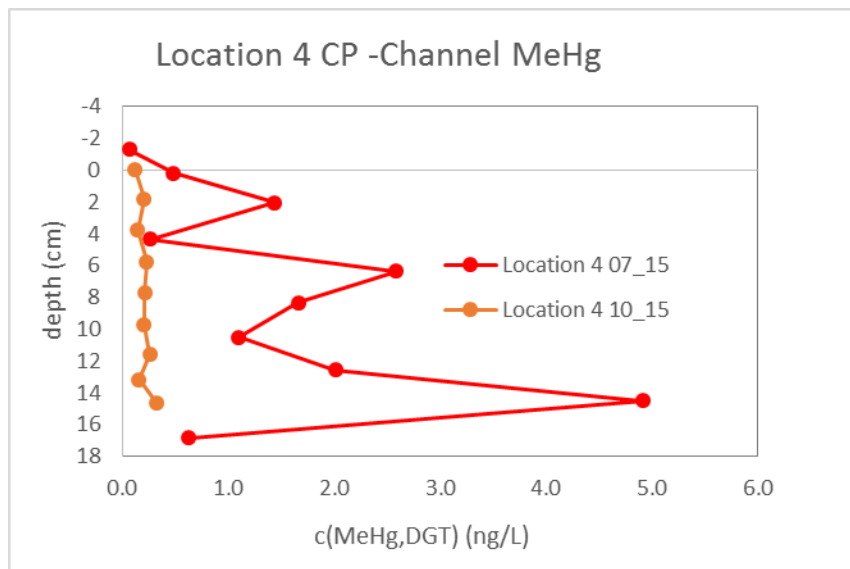


Figure 71 Location 4 avg MeHg

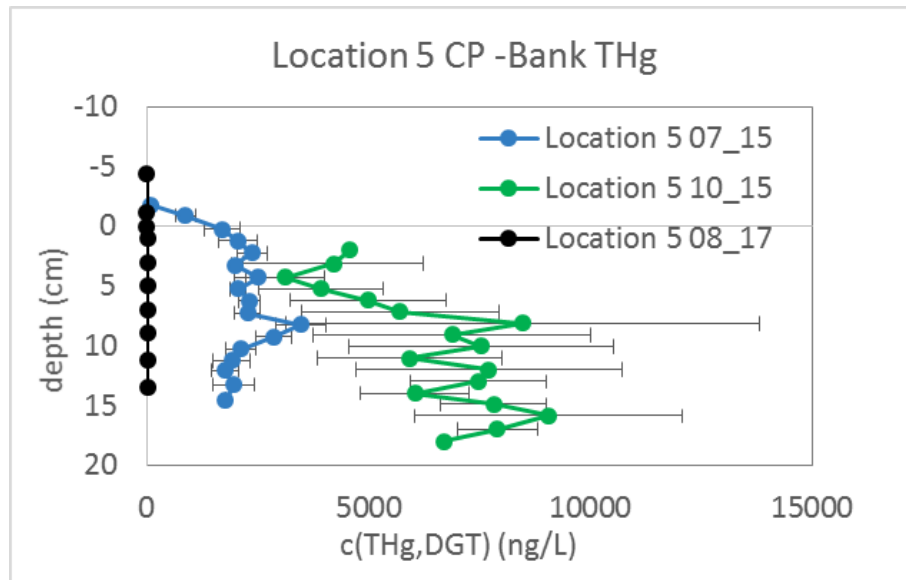


Figure 72 Location 5 avg THg

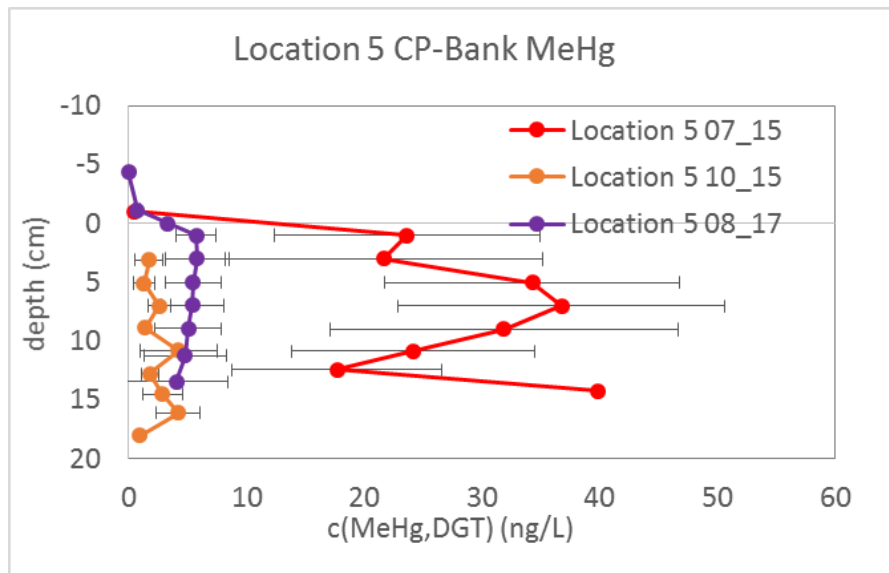


Figure 73 Location 5 avg MeHg

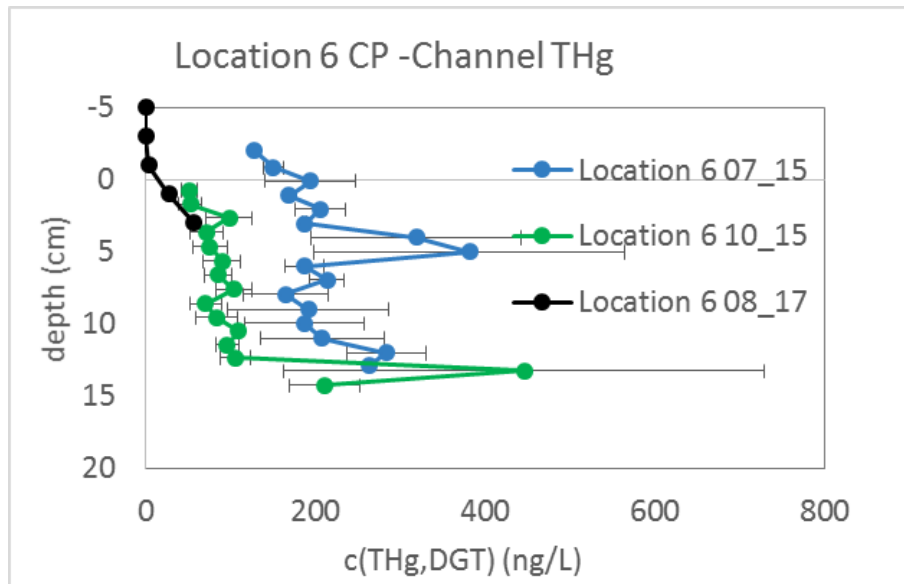


Figure 74 Location 6 avg THg

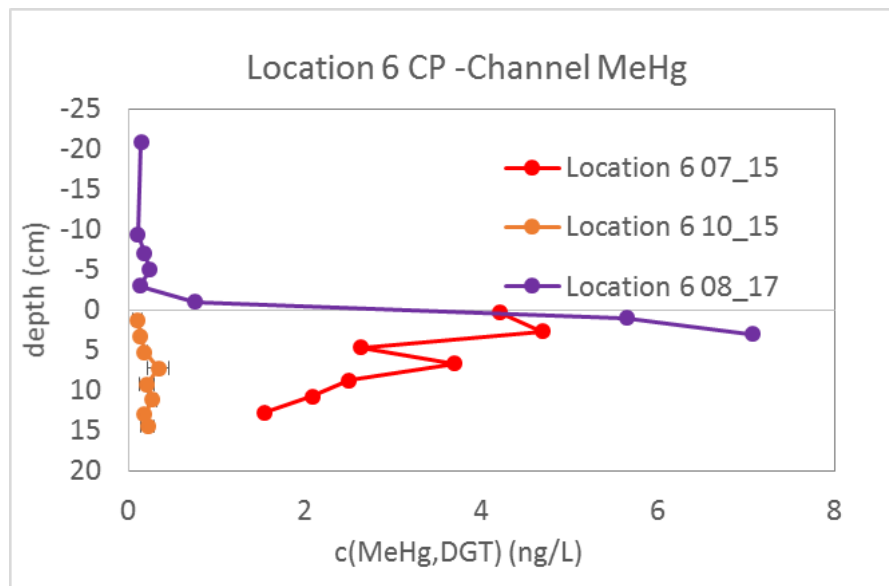


Figure 75 Location 6 avg MeHg

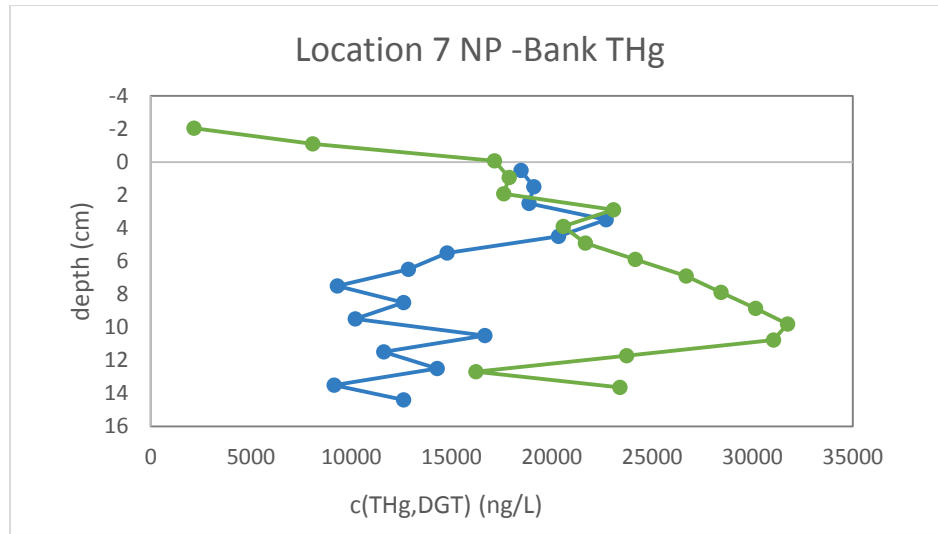


Figure 76 Location 7 avg THg

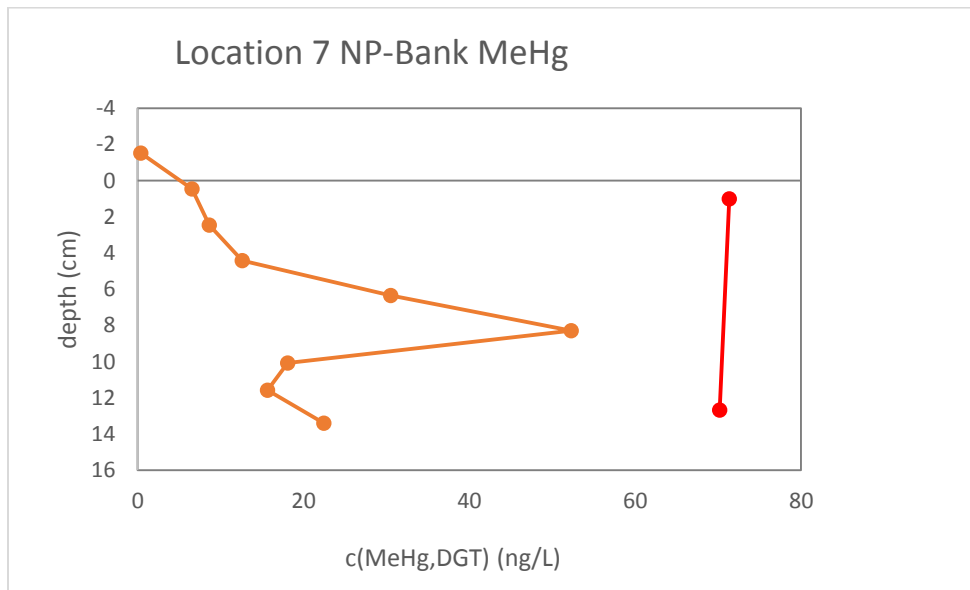


Figure 77 Location 7 avg MeHg

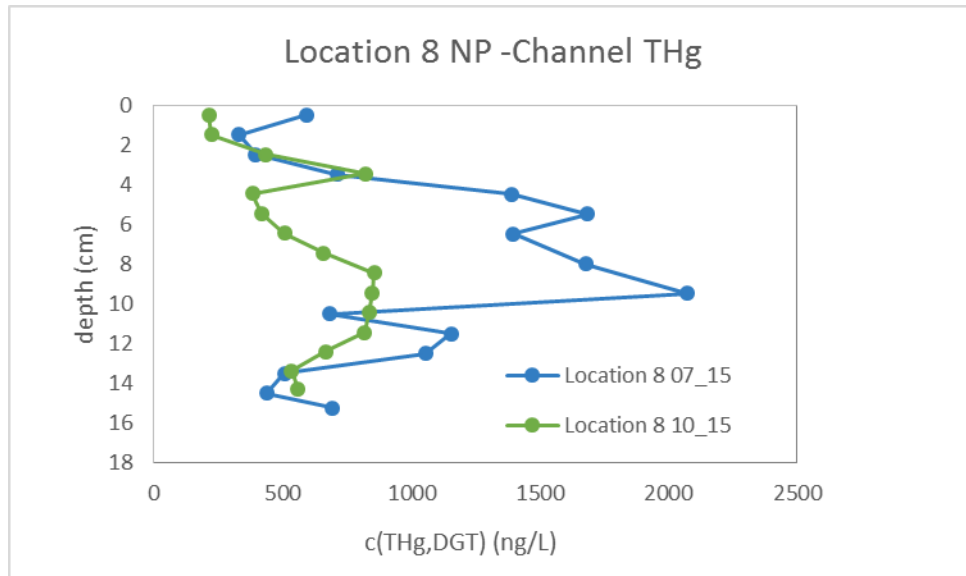


Figure 78 Location 8 avg MeHg

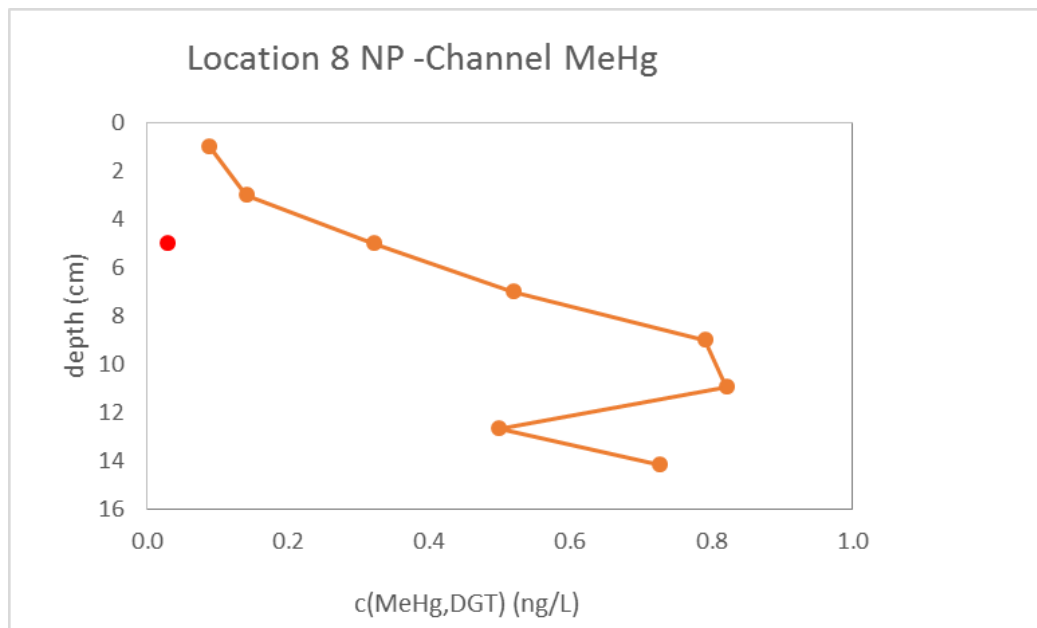


Figure 79 Location 8 avg MeHg

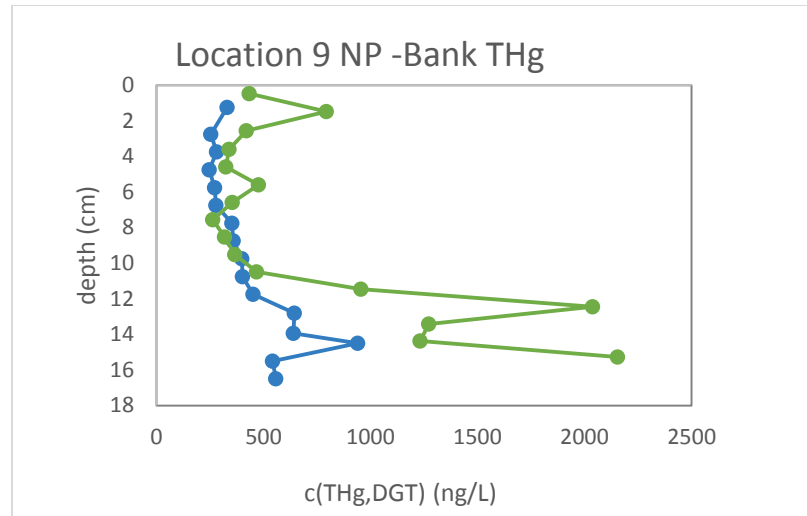


Figure 80 Location 9 avg THg

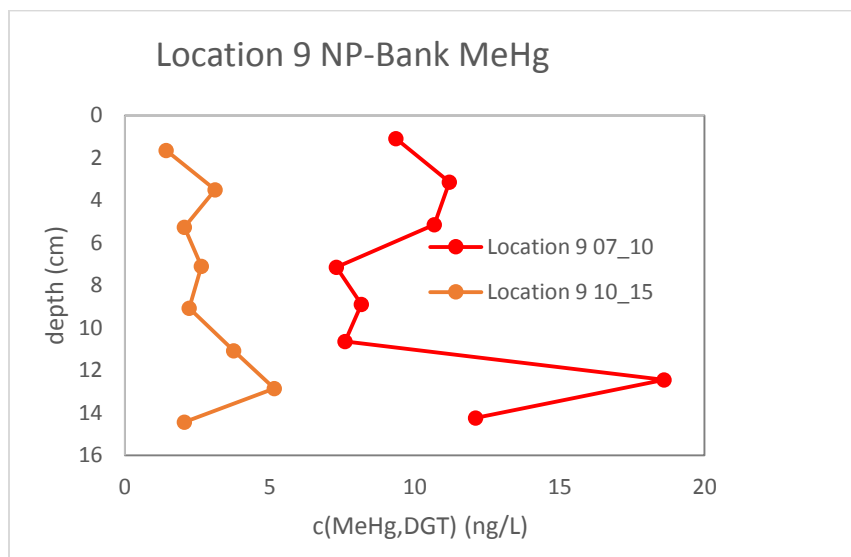


Figure 81 Location 9 avg MeHg

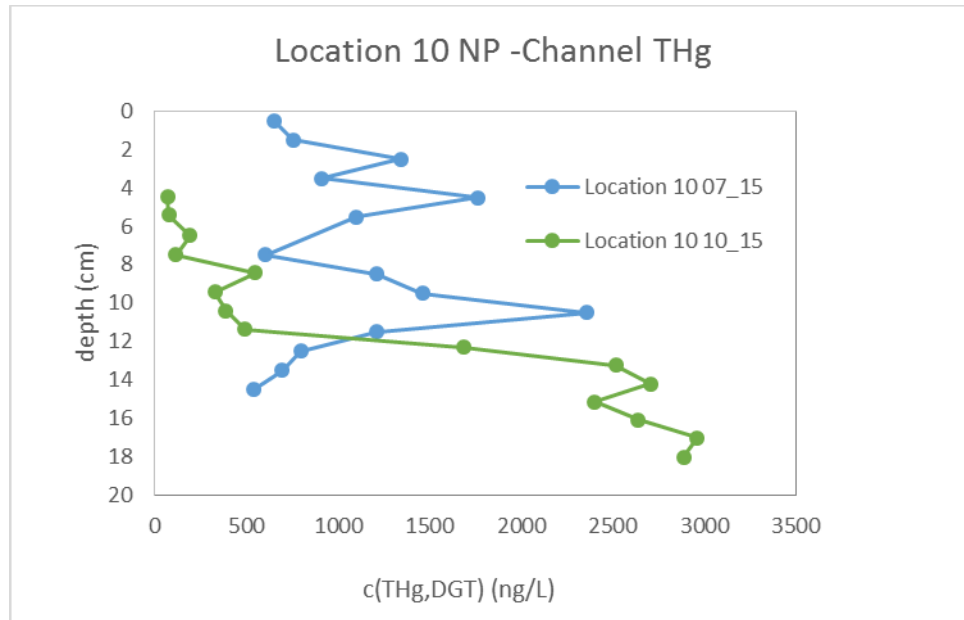


Figure 82 Location 10 avg THg

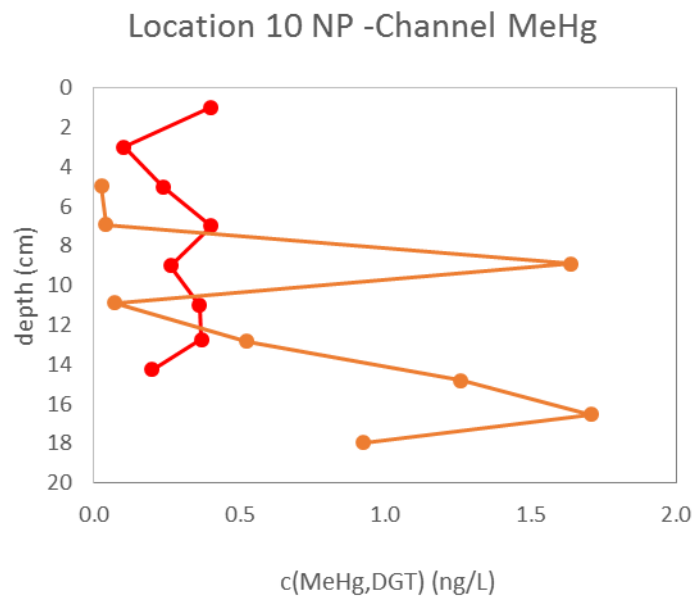


Figure 83 Location 10 avg MeHg

Redox measurements at South River, VA

Ion specific electrodes

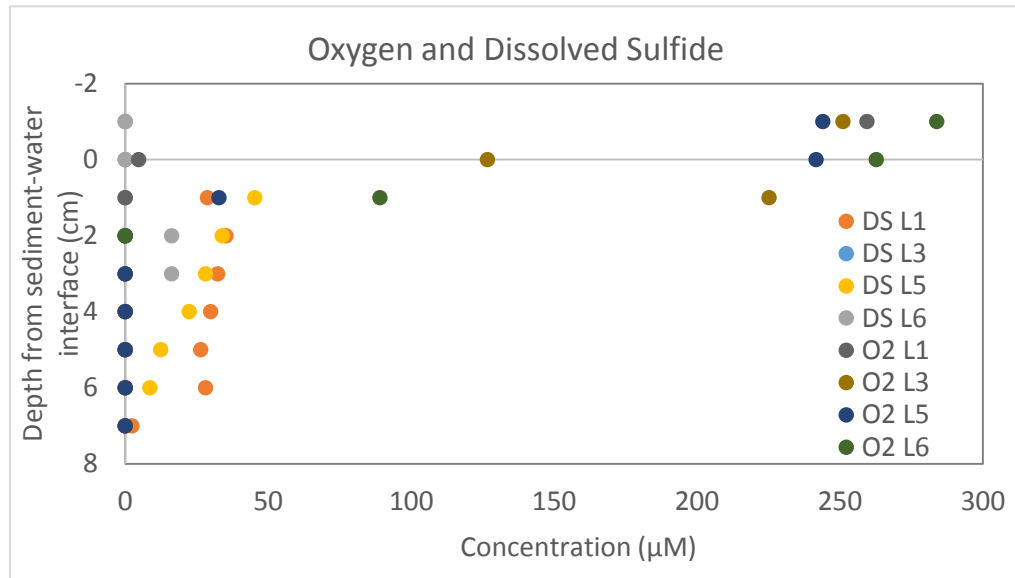


Figure 84 The measurements of DO and DS with ion specific electrodes during August 2017 sampling

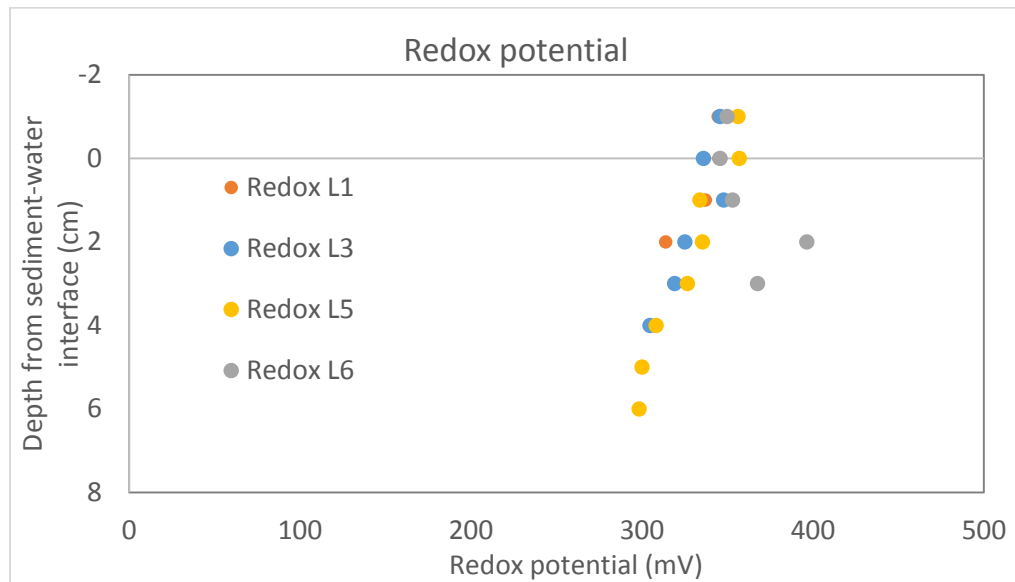


Figure 85 Redox measurements with ion specific electrodes during August 2017 sampling

Peeper results

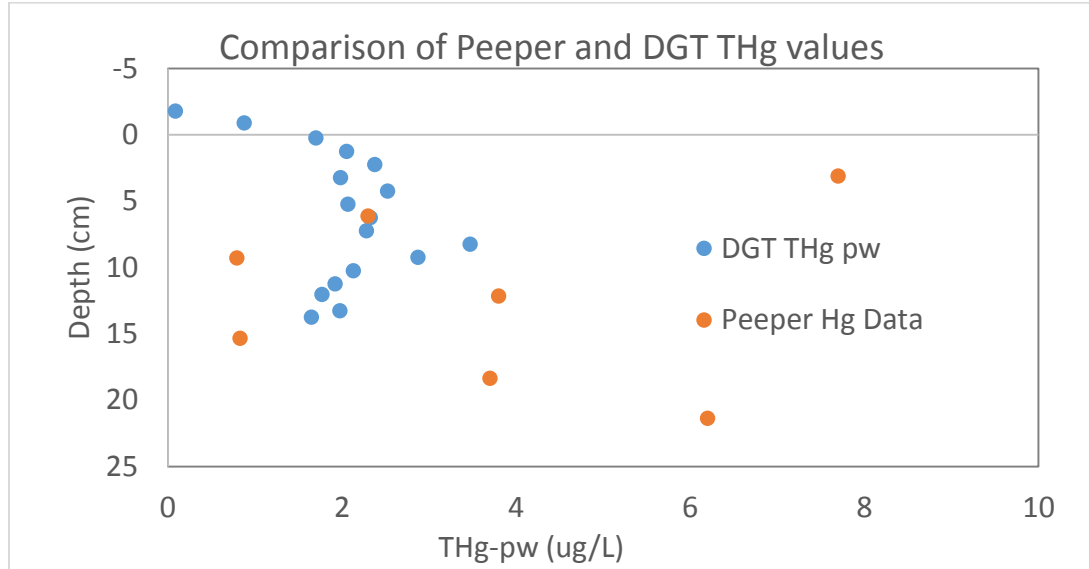


Figure 86 Comparison of Peeper and DGT THg results

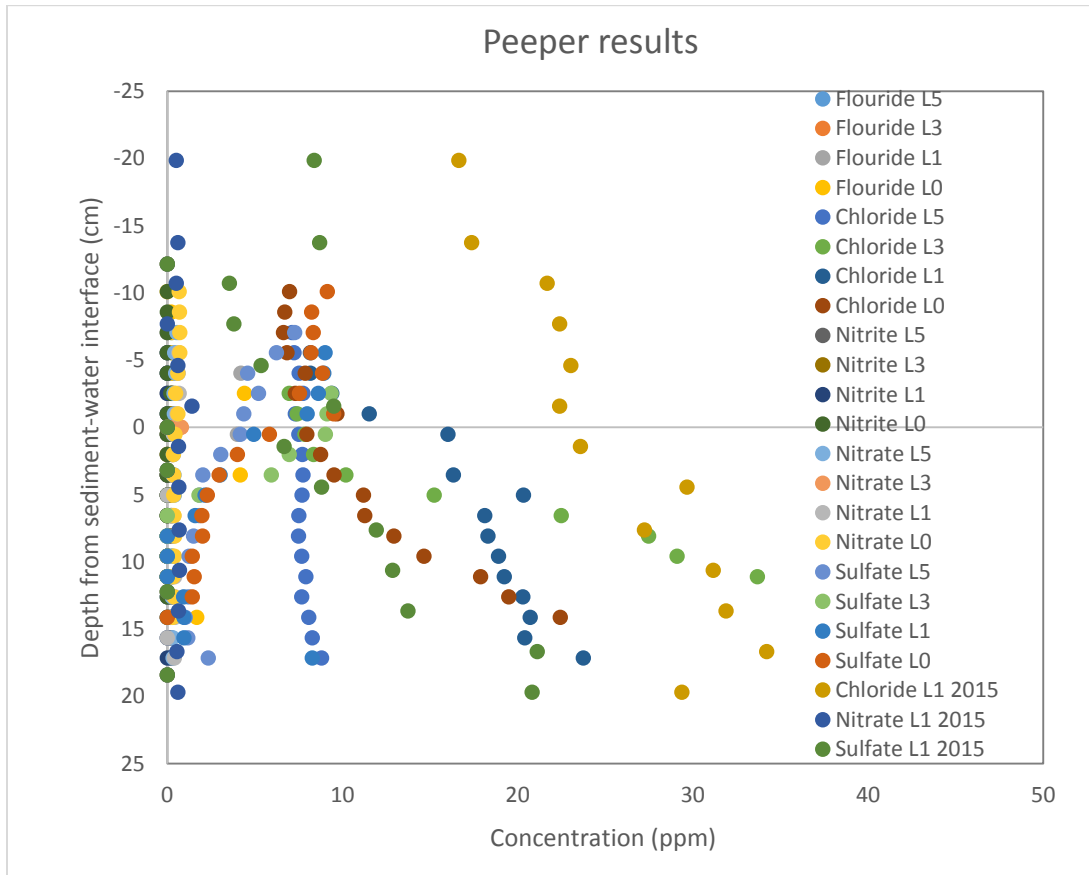


Figure 87 Peeper results from baseline 2015 and 2017 sampling

Voltammetry

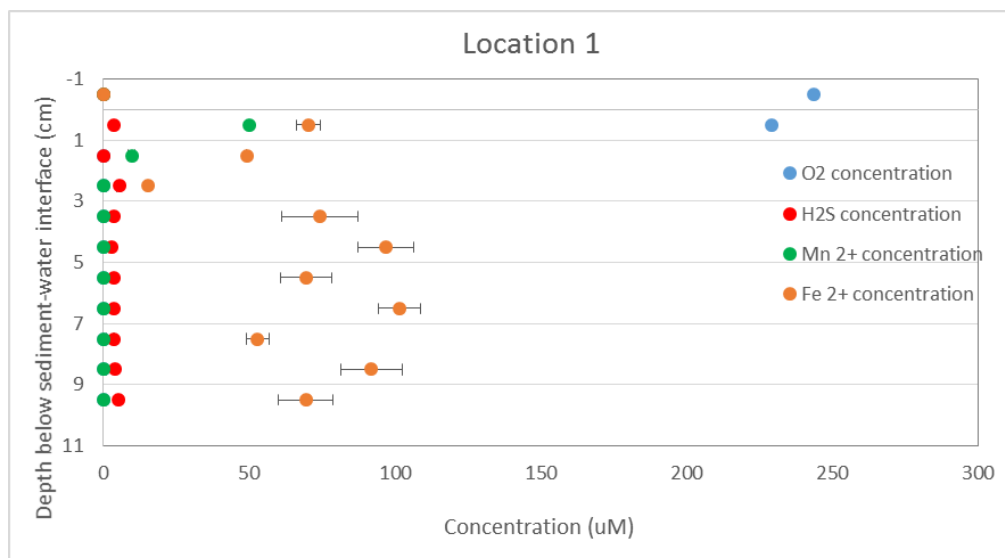


Figure 88 Voltammetry results for location 1

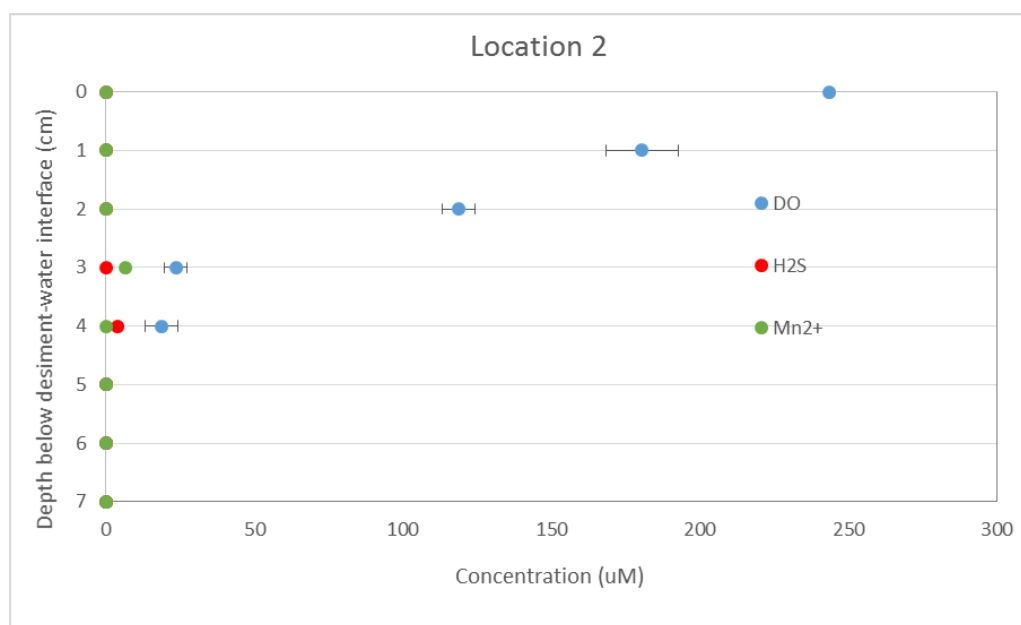


Figure 89 Voltammetry results for location 2

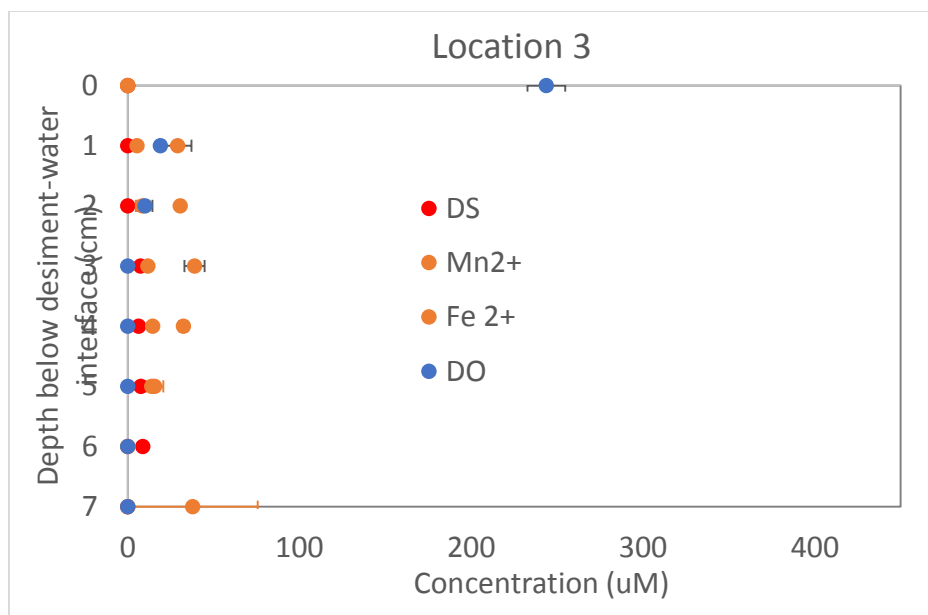


Figure 90 Voltammetry results for location 3

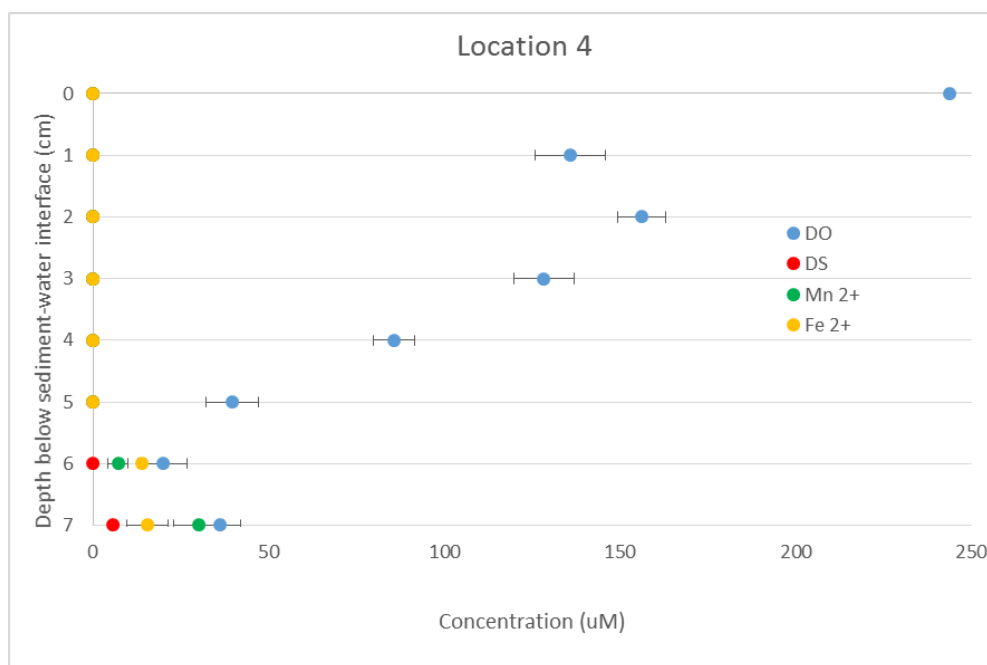


Figure 91 Voltammetry results for location 4

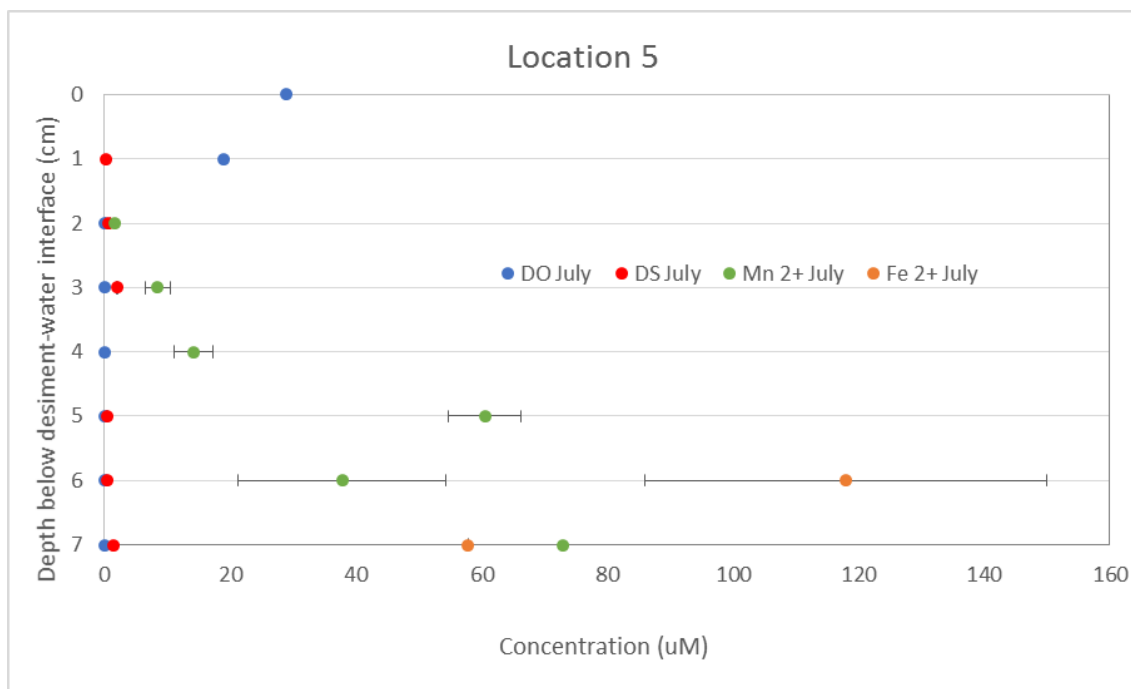


Figure 92 Voltammetry results for location 5

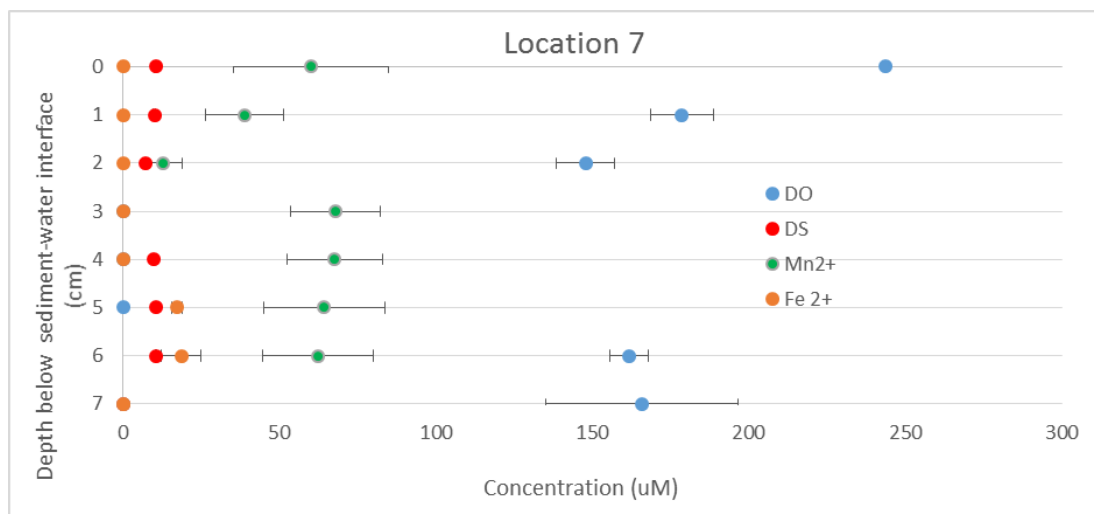


Figure 93 Voltammetry results for location 7

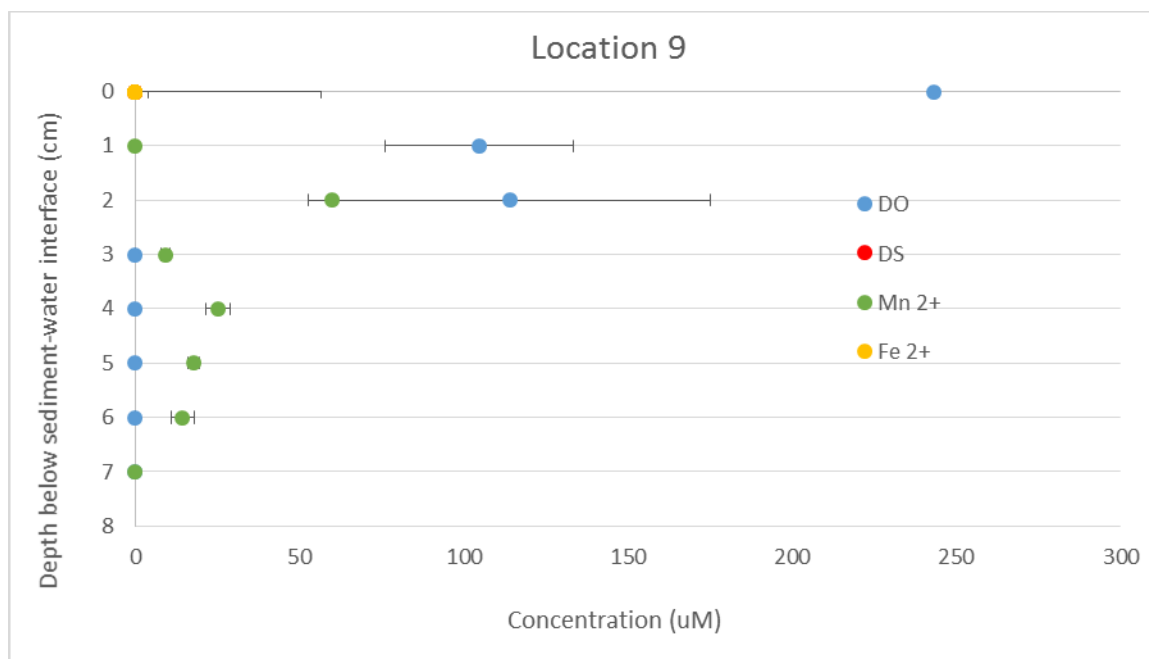


Figure 94 Voltammetry results for location 9

Bacteria by type during July 2015 sampling

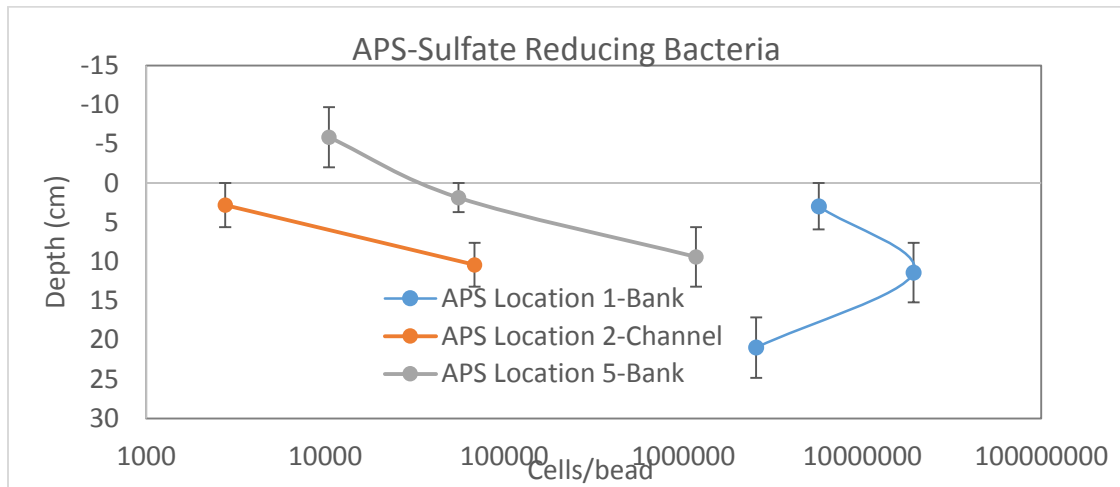


Figure 95 APS Sulfate reducing bacteria at Constitution Park in July 2015

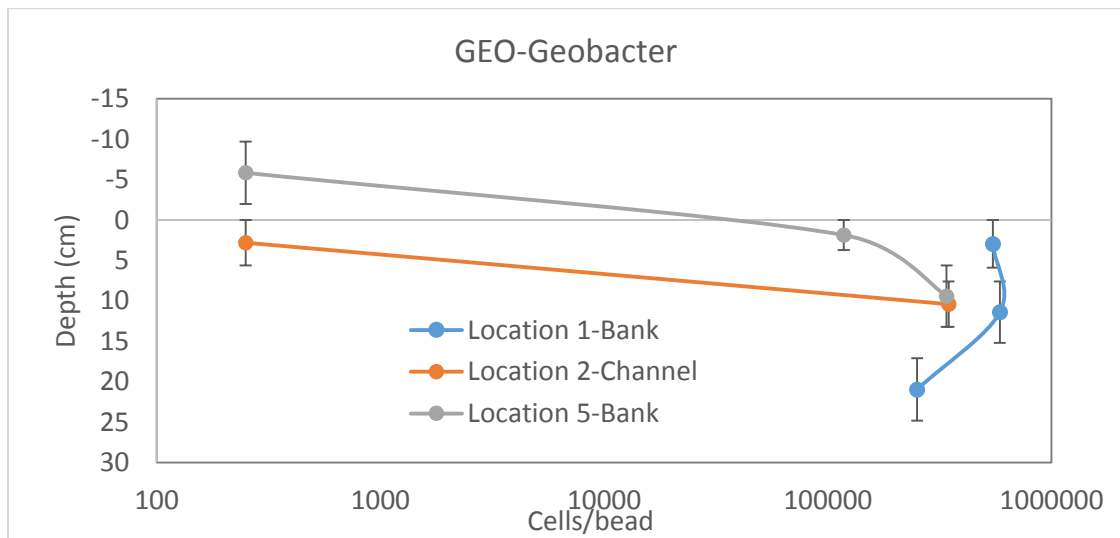


Figure 96 Geobacter bacteria at Constitution Park in July 2015

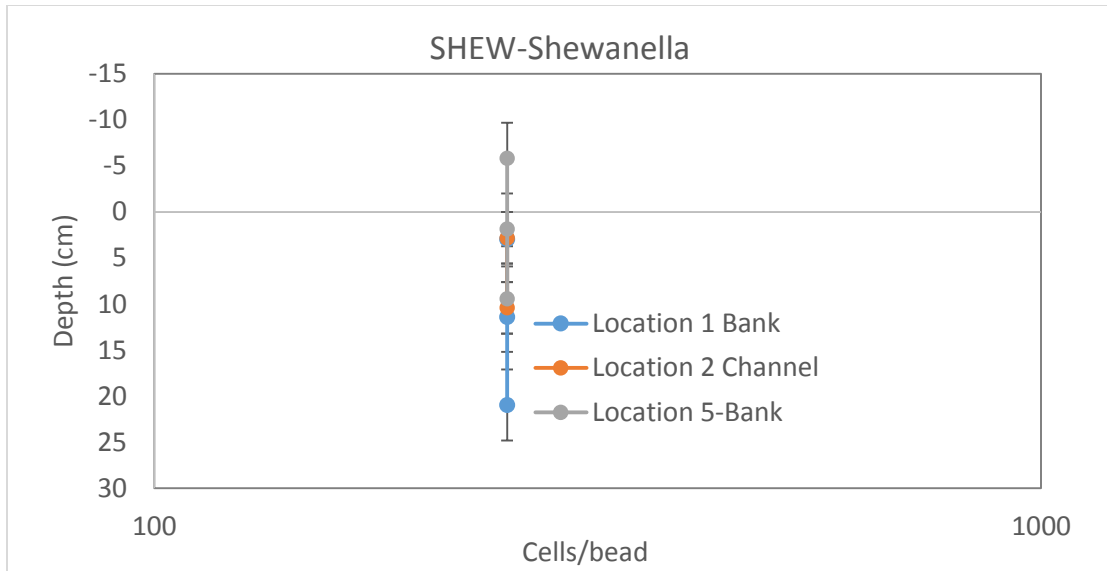


Figure 97 Shewanella bacteria at Constitution Park in July 2015

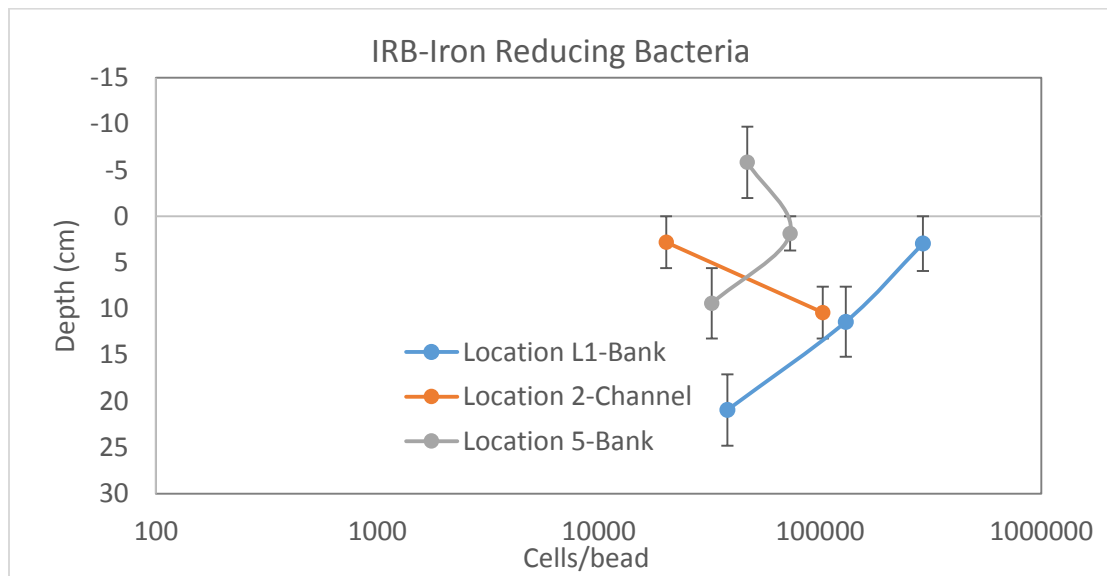


Figure 98 Iron reducing bacteria at Constituion Park in July 2015

THg flux measurements

Table 6 THg flux measurements July 2015

<i>parameter</i>	Unit	Location 1	Location 2	Location 3	Location 4	Location 5	Location 6	Location 7	Location 8	Location 9	Location 10
v_x	m/s	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
n		0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035
g	m/s ²	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8
d	m	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
D_w	cm ² /s	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06
r_h	m	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
v_w	m ² /s	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06
k_{bl}	cm/hr	2.1	4.8	2.1	4.8	2.1	4.8	2.1	4.8	2.1	4.8
Q	ft ³ /s	40	40	40	40	40	40	40	40	40	40
Q	m ³ /s	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13
U	ft/d	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
U	cm/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$Area/lengt$ h	(m ² /m)	0.3	20	0.3	20	0.3	20	0.3	20	0.3	20
C_{pw}	(ng/L)	84.93	430	306.36	297.53	2215	225.82	14898.81	986.46	434.96	1100.97
C_{pw}	(ng/m ³)	84930	430000	306360	297530	2215000	225820	1489881 0	986460	434960	1100970
C_w	(ng/L)	79.75	84	133.24	139.84	84	139.69	331	595	331	652
C_w	(ng/m ³)	79750	84000	133240	139840	84000	139690	331000	595000	331000	652000
J_d	ng/m ² /hr	111	16551	3704	7543	45589	4120	311650	18726	2224	21477
J_d	(ng/m/hr)	33	331027	1111	150866	13677	82403	93495	374520	667	429541
J_d	(ug/ft/d)	0	2422	8	1104	100	603	684	2740	5	3142

Table 7 THg flux measurements October 2015

<i>parameter</i>	Unit	Location 1	Location 2	Location 3	Location 4	Location 5	Location 6	Location 7	Location 8	Location 9	Location 10
v_x	m/s	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
n		0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035
g	m/s ²	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8
d	m	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
D_w	cm ² /s	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06
r_h	m	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
v_w	m ² /s	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06
k_{bl}	cm/hr	4.9	10.9	4.9	10.9	4.9	10.9	4.9	10.9	4.9	10.9
Q	ft ³ /s	150	150	150	150	150	150	150	150	150	150
Q	m ³ /s	4.25	4.25	4.25	4.25	4.25	4.25	4.25	4.25	4.25	4.25
U	ft/d	3.39	0.00	3.39	0.00	3.39	0.00	3.39	0.00	3.39	0.00
U	cm/hr	4.31	0.00	4.31	0.00	4.31	0.00	4.31	0.00	4.31	0.00
$Area/length$	(m ² /m)	0.3	20	0.3	20	0.3	20	0.3	20	0.3	20
C_{pw}	(ng/L)	27.01	65	29.08	38.84	6359	117.24	23561	586.76	763.52	1334.41
C_{pw}	(ng/m ³)	27010	65000	29080	38840	6359000	117240	23561000	586760	763520	1334410
C_w	(ng/L)	26.77	20.01	26.77	20.01	52	52	214	214	214	214
C_w	(ng/m ³)	26770	20010	26770	20010	52000	52000	214000	214000	214000	214000
J_d	ng/m ² /hr	1175	4891	1364	2047	580424	7093	2149516	40526	59590	121810
J_d	(ng/m/hr)	352	97825	409	40944	174127	141856	644855	810521	17877	2436195
J_d	(ug/ft/d)	3	716	3	300	1274	1038	4717	5929	131	17821

Table 8 THg flux measurements August 2017

<i>parameter</i>	Unit	Location 0	Location 1	Location 2	Location 3	Location 5	Location 6
v_x	m/s	0.11	0.11	0.11	0.11	0.11	0.11
n		0.035	0.035	0.035	0.035	0.035	0.035
g	m/s ²	9.8	9.8	9.8	9.8	9.8	9.8
d	m	0.1	0.1	0.5	0.1	0.1	0.5
D_w	cm ² /s	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06
r_h	m	0.5	0.5	0.5	0.5	0.5	0.5
v_w	m ² /s	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06
k_{bl}	cm/hr	2.1	2.1	4.8	2.1	2.1	4.8
Q	ft ³ /s	40	40	40	40	40	40
Q	m ³ /s	1.13	1.13	1.13	1.13	1.13	1.13
<i>Area/length</i>	(m ² /m)	0.3	0.3	20	0.3	0.3	20
C_{pw}	(ng/L)	26.14	14.07	9.32	15.2	15.41	42.68
C_{pw}	(ng/m ³)	26140	14070	9320	15200	15410	42680
C_w	(ng/L)	7.67	2.2	1.72	7.48	2.19	1.64
C_w	(ng/m ³)	7670	2200	1720	7480	2190	1640
J_d	ng/m ² /hr	395	254	364	165	283	1963
J_d	(ng/m/hr)	119	76	7271	50	85	39264
J_d	(ug/ft/d)	1	1	53	0	1	287

Table 9 Avg THg flux measurements

<i>Jd (ug/m²/hr)</i>	CP Bank	CP Channel	NP Bank	NP Channel
<i>2015 July</i>	16	9	157	20
<i>2015 October</i>	194	5	1105	81
<i>2017 August</i>	0.27	1.2		
<i>Jd/ft-river (ug/ft/d)</i>	CP Bank	CP Channel	NP Bank	NP Channel
<i>2015 July</i>	36	1376	344	1728
<i>2015 October</i>	426	684	2424	11875
<i>2017 August</i>	1	170		
<i>Jd (ug/cm²/yr)</i>	CP Bank	CP Channel	NP Bank	NP Channel
<i>2015 July</i>	14	8	137	18
<i>2015 October</i>	170	4	968	71
<i>2017 August</i>	0.24	1.02		

APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER 5

Objective – Validation of Model Results



Modeled Surface Water Inundation Results for Different Hydraulic Conductivity Values

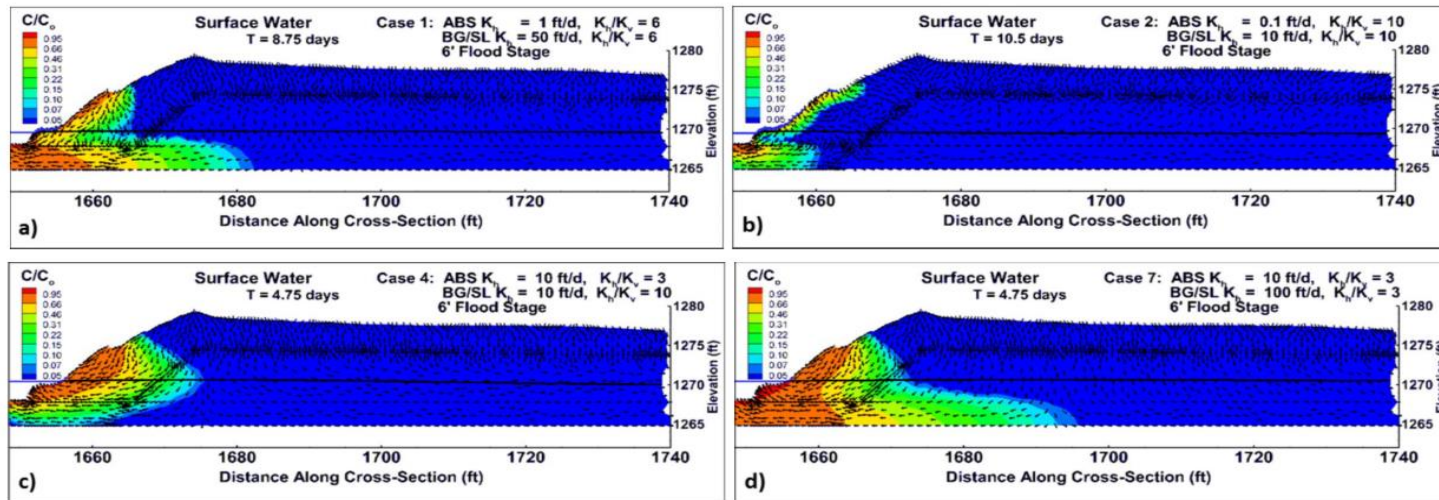


Figure 25. Snapshot of maximum surface water inundation into the bank for each case. a) Case 1 at $t = 8.75$ days; b) Case 2 at $t = 10.5$ days; c) Case 4 at $t = 4.75$ days; and, d) Case 7 at $t = 4.75$ days.

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Figure 99 HydroGeoSphere modeling results used for estimate of hydraulic conductivity and flood stage height (AECOM & Mudrick, 2017)

Table 10 Properties based on material type used to estimate properties of the bank layout

	porosity	storage capacity S	specific yield	alpha (cm)	Alpha (ft)
<i>Coarse sand, gravel</i>	0.32	2.30E-05	0.28	0.598	18.2
<i>Med coarse sand</i>	0.345	5.05E-05	0.3	0.598	18.2
<i>Sand</i>	0.375	2.30E-04	0.32	0.598	18.2
<i>Silty fine sand</i>	0.37	2.30E-04	0.33	0.529	16.1
<i>Sandy clay</i>	0.42	3.35E-04	0.2	0.819	25.0
<i>Clay with cobble</i>	0.43	5.85E-04	0.06	0.320	9.75
<i>Clay</i>	0.66	3.49E-03	0.06	0.320	9.75
<i>Source</i>	(Geotechdata.info, 2013)	(Duffield, 2016)			

Table 11 Input parameters for bank model

<i>Areas</i>	A-top sand	B-clay	C-sand	D-cap sand +biochar	E-Cap- silt/clay
<i>Coarse sand, gravel (%)</i>	0.00E+00	0.00E+00	5.50E-01	0.00E+00	0.00E+00
<i>med coarse sand (%)</i>	0.00E+00	0.00E+00	5.00E-02	0.00E+00	0.00E+00
<i>sand (%)</i>	3.33E-01	1.59E-02	3.00E-01	1.00E+00	1.59E-02
<i>silty fine sand (%)</i>	6.67E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00
<i>sandy clay (%)</i>	0.00E+00	8.89E-01	0.00E+00	0.00E+00	8.89E-01
<i>clay with cobble (%)</i>	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
<i>clay (%)</i>	0.00E+00	9.52E-02	1.00E-01	0.00E+00	9.52E-02
<i>Porosity</i>	3.72E-01	4.42E-01	3.72E-01	3.75E-01	4.42E-01
<i>Storativity (ft⁻¹)</i>	2.30E-04	6.34E-04	4.33E-04	2.30E-04	6.34E-04
<i>Thickness (ft)</i>	1.50E+00	8.00E+00	3.00E+00	1.00E+00	8.00E+00
<i>Specific Yield</i>	3.27E-01	1.89E-01	2.71E-01	3.20E-01	1.89E-01
<i>Storage Capacity</i>	3.27E-01	1.94E-01	2.72E-01	3.20E-01	1.94E-01
<i>Alpha (ft) (Yang & You, 2013)</i>	16.82	23.41	17.38	18.23	23.41
<i>n(Yang & You, 2013)</i>	1.32	1.32	1.46	1.37	1.32
<i>I</i>	0.5	0.5	0.5	0.5	0.5
<i>Kh Scenario (ft/d)</i>	50	1	50	50	1

Table 12 Input parameters for CapSim model

<i>Parameter</i>	<i>Value</i>	<i>Unit</i>
<i>Contaminated sediment pore water concentration</i>	2.3	µg/L
<i>Temperature</i>	20	°C
<i>Sand-biochar thickness</i>	15	cm
<i>Sand-biochar hydrodynamic dispersivity</i>	1.5	cm
<i>Clean sediment thickness</i>	15	cm
<i>Clean sediment hydrodynamic dispersivity</i>	1.5	cm
<i>Contaminated sediment thickness</i>	130	cm
<i>Contaminated sediment hydrodynamic dispersivity</i>	13	cm
<i>Gaussian model coefficient</i>	5	cm
<i>River depth</i>	10	cm
<i>Darcy velocity</i>	5069	cm/hr
<i>Bank water effective mass-transfer coefficient</i>	1.83	cm/hr
<i>Molecular diffusivity in water</i>	6.3E-06	cm ² /s
<i>Particle biodiffusion coefficient</i>	10	cm ² /yr
<i>Pore water biodiffusion coefficient</i>	100	cm ² /yr
<i>Sand+biochar bulk density</i>	1.07	g/cm ³
<i>Sediment bulk density</i>	1.25	g/cm ³
<i>Mercury molecular weight</i>	200.95	g/mol
<i>Sand Kd linear sorption</i>	6	L/kg
<i>Biochar Kd linear sorption</i>	1310	L/kg
<i>Sand Kd linear sorption</i>	6	L/kg
<i>Sediment Kd</i>	1445	L/kg
<i>River velocity</i>	0.11	m/s
<i>Kinematic viscosity</i>	1.E-06	m ² /s
<i>Contaminated sediment Concentration</i>	3.3	mg/kg
<i>tau</i>	0.044	yr
<i>Simulation duration</i>	100	yr
<i>Sand+biochar porosity</i>	0.476	
<i>Sand+biochar organic carbon fraction</i>	0.11	
<i>Sediment porosity</i>	0.5	
<i>Sediment organic carbon fraction</i>	0.01	
<i>Sediment clean tortuosity correction</i>	Bourdreau	
<i>Sediment contaminated tortuosity correction</i>	Bourdreau	
<i>Sand+biochar tortuosity correction</i>	Millington & Quirk	
<i>Modeling bioturbation</i>	Depth Dependent	

<i>Modeling consolidation</i>	None	
<i>Upwelling groundwater flow</i>	Period oscillation	
<i>Manning's n</i>	0.035	
<i>Hydraulic Radius R_H</i>	0.5	
<i>Overlaying waterbody type</i>	River	
<i>Steps in output files</i>	3000	
<i>Time step options</i>	Implicit	
<i>Mass balance options</i>	Track	
<i>Oscillation output</i>	Instantaneous and average	
<i>Number of grid points</i>	160	
<i>Time step per oscillation circle</i>	16	
<i>Discretization options</i>	Specify Manually	
<i>Benthic surface boundary</i>	Mass transfer	
<i>Underlying sediment boundary</i>	Flux-matching	