Use of Benthic Flux Chambers for the Quantification of Dissolved Mercury and Methylmercury from the streambed of the South River

Benthic flux chambers (BFC) allow the direct measurement of chemical flux from discrete areas of sub-aqueous environments such as sediment deposits and gravel beds. The use of benthic flux chambers to measure mercury fluxes in the South River System can facilitate determination of which sub-aqueous environments are the most important contributors to methylmercury (MMHHg) in the South River system. The resulting data will be used to help our understanding of the mercury cycling in the South River System.

Objectives

The main objectives for the benthic flux chamber work are:

1) Direct measurement of the flux of dissolved total Hg and MMHg from the range of differing sub-aqueous environments ranging from soft sediment deposits to firm rocky gravel beds that may be located in the main stream channel, backwaters, or eddies. Of particular interest are the soft sediment deposits being identified by the geomorphology efforts within the South River System.
2) Direct measurement of the flux of dissolved total Hg and MMHg in transects across the South River with focus on the sub-aqueous environments as close as possible to the wetted shore on both sides and key sub-aqueous environments in between. Of particular interest are the soft sediment deposits along the banks of the South River System.

The use of the BFCs to measure the flux of mercury species from the broad range of sub-aqueous environments on the South River will allow conclusions to be drawn regarding the relative importance of these diverse sub-aqueous environments to the overall mercury budget of South River System.

Methods

The benthic flux chambers that will be used on the South River were developed by DuPont are based upon the BFCs developed at Texas A&M. With input from Dr Gary Gill at Texas A&M (Dr Gill is now at Battelle's Marine Sciences Lab located in Sequim), DuPont advanced the BFC design for measuring flux from a broader range of sediment deposits including very soft sediment and advanced much of the BFC's functional.

All the components of the BFC for the South River that are wetted with the surface water to be sampled are constructed of either Polycarbonate or Teflon. Prior to assembly for field deployment, each component that is wetted by the surface water to be sampled goes through an extensive three week cleaning process. This process includes a soak in Micron 90 solution for one week followed a 10% HCl solution soak for two weeks. In between and after these cleaning solutions the BFCs are thoroughly rinse with distilled water. The BFC is then air dried within a medical type hood that filters the air preventing dust particles from collecting on the BFC. The focus of this cleaning process is to remove potential trace amounts of mercury that may be present on surfaces of the BFC.

There are two types of BFCs; one is transparent and the other is opague, but otherwise they are identical. The benthic flux chambers are typically deployed in pairs, one being transparent and the other being opague. The comparison of the data from the transparent and opague BFCs will aid in the determination of whether or not there is a diurnal cycle regarding the flux of MMHg and inorganic Hg.

The sediment area enclosed by the BFC is rough 974 square centimeters (151 square inches) and has an internal wetted volume of roughly 12.5 liters (3.30 gallons). Each BFC has an internal pump that slowing moves the water within the BFC to avoid concentration gradients within the BFC. The impellar of the pump is inductively coupled via magnets to a motor and gearbox that is powered by two 6 volt batteries wired is series that are contained in a waterproof box. The pump can also pump surface water from the outside of the BFC to the inside of the BFC through a series of valves. This functionality is used primary during the period prior to initiation of sampling events to help maintain the internal water in equilibrium with the external water. The BFC also has three two inch diameter equilization ports that are opened initially to help support the equilibrium processes caused by natural advective force due to currents and wave motion. An additional port has been been engineered for the collection of seepage from within the BFC. The seepage is either collected in a specialized Tedlar seepage collection bag or passes through a developmental electomagnetic seepage meter that directly reads the seepage value.

The BFC has four gauge plates near the bottom of the BFC, a tapered leading edge around the bottom of the BFC, and four ¾ inch diameter spuds all of which help ensure the BFC is appropriately keyed into the sub-aqueous environment of interest. The gauge plates are transparent polycarbonate and visually “wets” when they are in contact with the sediment. The gauge plates are a visual sign the BFC’s tapered leading edge is keyed into the sediment. The spuds anchor into the sediments and ensure that BFC does not move after is properly deployed.

The typical BFC deployment event consists deployment of the BFCs through the use of divers if the water is deeper than a few feet, otherwise deployment can be accomplished via leaning over the edge of a boat or by simply wading. If deployment is accomplished by wading, consideration must be made not to disturb the sub-aqueous area of interest and to stand down stream. After deployment of the BFCs, no further disturbance of the general surrounding sub-aqueous area is permitted. The BFC is then allowed to equilibrate with the surface water for 30 minutes to and a hour depending upon the nature of the sub-aqueous environment. Upon expiration of the equilibration period, the three equilibration ports are closed, the valves to the internal pump are actuated, and the valve to the seepage collection bag is opened.

Once the ports are closed, the valves actuated, and the valve to the seepage collection bag is open, sampling of the BFC begins and continues for 4 or 5 hours. During the sampling period, samples are typically drawn at one hour intervals and continue until the oxygen content of the sample is 50% of the baseline measurement or time expires. Surface water samples are drawn from with the BFCs using six 25 milliliter syringes in order to collect sufficient sample to rinse the sample bottle, measure DO, and fill one 125 milliliter sample bottle with water. All sampling is conducted using ultra-clean techniques, the samples are filtered in the field using a 0.45 micron filter, the samples placed on ice immediately, and shipped for analysis using over night methods.

Samples were analyzed using low level detection methods (roughly 0.05ppt) for filtered total mercury and methylmercury.

Results and Discussion

A pilot test deployment of the benthic flux chambers was conducted in May 2005. The location selected for the deployment was upstream of the Dooms' dam in an eddy zone area containing sediment. Three locations were selected in this area for the pilot deployment tests. The first site selected for deployment was relatively shallow with a fair amount of debris. The second site was deeper than the first site, but similar in general characteristics. The third site that was selected was a close as practical to the bank. All three sites contained a lot of organic matter ranging from decaying organic material as evidenced by the ebullition of gas from the sediments to recently deposited twigs and leaves.

Only the transparent BFC design was used during the pilot deployment test. Two of the BFCs performed well; however, one of the BFCs could not be keyed properly and had poor performance. The BFC at the first site was deployed in the afternoon and sampled at 5:37pm, 7:37pm, 8:10am the following day. The BFC at the third site was deployed in the morning and sampled at 10:12am, 1:50pm, and 4:35pm.

Based upon limited data from the first site, the data appears to indicate that the site had a net positive MMHg flux over the first two hour duration of roughly 19.5 $ng*m^{-2}*hr^{-1}$, roughly 64 $ng*m^{-2}*hr^{-1}$ over the next twelve hours, and 58 $ng*m^{-2}*hr^{-1}$ overall. The total Hg flux over the first two hour duration was roughly 54 $ng*m^{-2}*hr^{-1}$, roughly 62 $ng*m^{-2}*hr^{-1}$ over the next twelve hours and 61 $ng*m^{-2}*hr^{-1}$ overall. During the sampling event the dissolved oxygen showed a trend that was generally decreasing in the samples. Data from the third site was limited as well, but indicated that the site did not have any significant MMHg or total Hg flux. However, at the second site the dissolved oxygen (DO) showed a trend that was generally increasing in the samples. One difference between these two sites could be that the second site was sampled only during the peak sunlight hours of the day and the second site was sampled after the peak daylight hours and overnight. This could possibly mean that the flux from the sediments could have a diurnal cycle at this time. At the first site the DO showed a decreasing trend over night and the third site showed an increasing DO trend overall during the day. This could also indicate that upper zones of the sediment are experiencing a redox cycle caused by the changes in DO throughout the day. The changes in redox could then effect the flux of metals such as iron and manganese from the sediments to the surface water which in turn can effect the flux of mercury.

Path Forward

1) Deploy the transparent and opaque benthic flux chambers in several key sediment deposit locations identified during the geomorphology efforts with emphasis on the reach from DuPont's foot bridge down to Crimora.

2) Deploy the transparent and opaque benthic flux chambers in several key gravel stream beds in key locations of South River with emphasis on the reach from DuPont's foot bridge down to Crimora.

3) Deploy the transparent and opaque benthic flux chambers in transects across the South River in several key locations with emphasis on the reach from DuPont's foot bridge down to Crimora.