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Mercury Source Tracing and Mechanistic Studies
Status for October 2008 Expert's Meeting

Purposes of Studies:
1) Characterize mechanisms by which non-filterable (<0.45 micron) mercury and methyl mercury enters the river and water column.

2) Develop/provide investigative tools and methods for later phases of the ecostudy. These may include field or laboratory protocols to better characterize mechanisms and/or forms of mercury.

Specific locations/objectives of study:
1) Plant reach, from Wayne Avenue to Main Street (RRM -0.5 to RRM 0.3). Under higher flow conditions, this reach consistently shows greater loading than has been accounted for, thus far, from plant outfalls and groundwater. The objective has been to determine the origin of the additional loading.

2) Basic Park (RRM 2.0). This location is within a section of the river consistently showing a high loading of total dissolved mercury to the water column and includes areas for ecostudy baseline monitoring, geomorphology special studies (LIDAR) and benthic flux chamber research. Desorption of inorganic mercury from bank soils and/or bed sediments are the chief suspects. Understanding the nature and extent of the desorption process has been a continuing objective. More recently we have begun to measure vertical profiles in methyl mercury concentration in gravel substrates and to examine the desorption process of methyl mercury from bed sediments.

Status of studies at plant reach:
No additional studies were conducted within the plant reach in 2008. Results of all previous studies have been summarized in previous briefing papers and presentations to the Science Team.

Status of studies at Basic Park:
Gravel Bar Hyporheic Water - Stainless steel probes have been used to sample hyporheic water within a large gravel bar at Basic Park. Surface water flow over the bar produces zones of upstream entry to, and downstream exit from, the interstitial space (hyporeheic zone) of the bar. Some, but not all, pressure head measurements across the Basic Park bar show negative heads upstream and positive heads downstream and thus generally support the conceptual model of flow through the bar. Hyporheic water extracted from the bar at 6 to 12 inches below the gravel surface has been consistently higher in dissolved mercury than surface water flowing over the bar. In contrast, dissolved methyl mercury concentrations in this deeper, and less oxic, hyporheic water has been consistently lower than in overlying surface water, suggesting that any methylation that might occur in the bar is occurring at shallower depths than sampled initially by the probes. In 2008 we began a program of collecting hyporheic water at three depths (3, 6

and 12 inches) in the Basic Park gravel bar. These data have confirmed that methyl mercury concentrations are indeed highest in the uppermost, and more oxic, portion of the hyporheic zone, both in pore fluid and fine-grained sediments. Generally dissolved oxygen has been lower (but never zero) in deeper hyporheic water than surface water, but especially where the direction of flow is suspected to be out of the gravel bar. *A reliable means to quantify the contribution of gravel bars to whole river loading of mercury and methylmercury remains elusive, although calculated estimates might be possible based on more intensive characterization of porewater mercury profiles, pressure heads and thermal gradients.*

Desorption Kinetics of Methyl Mercury – It is important to define whether releases of methyl mercury to surface water during benthic flux measurements are due to active methylation during the flux measurement or to desorption of methyl mercury formed earlier or even at a different location in the river. Batch extraction of sediment to define desorption potential and kinetics of methyl mercury is confounded by likely changes in redox conditions and even the generation or degradation of methyl mercury during the extraction. To address the desorption vs production issue in 2008 we ran some pseudo-column style desorption experiments using fine-grained sediments recovered from the gravel bar at Basic Park that were quickly loaded onto a high capacity inline filter and then "leached" slowly with river water. These experiments were short-term (<2 hr) and designed to simulate the flow of surface water with both local elevated (Basic Park) and upstream background (Lyndhurst) concentrations of methyl mercury. Not all analytical results are available yet but those that are suggest that this may be a useful tool.

Wider Area Investigations:

Longitudinal Profile in Hg(II) Concentrations – Mercury in surface water that is easily reducible by tin citrate (at native pH) was hypothesized to be a better index of sources of mercury to the South River. Accordingly we measured this operationally-defined form of mercury in 2008 at several intervals along the river, in two outfalls (001 and Waynesboro STP). Results of surveys conducted in April and June 2008 showed that Hg(II) tracked filter-passing Hg reasonably well but did not support the usefulness of the measurement of Hg(II) to identify non-point sources.

Hyporheic Zone Profiling – The method of characterizing vertical gradients in temperature, dissolved oxygen, mercury and methyl mercury in hyporheic porewater has been extended to two other sites (RRM4.4) and RRM9.8 on the river. Patterns very similar to those at Basic Park were observed.

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