Whole River Surface Water Sampling – South River

Spatial and temporal patterns in surface water concentrations of mercury and methylmercury can provide important information about where and when mercury and methylmercury are entering the river, as well as suggesting what phyical and biogeochemical processes are operating. Because surface water conditions can change rapidly, conducting multiple near-synoptic surface water sampling events under different seasonal and flow conditions is necessary. The results discussed here are from sampling events covering the entire length of the South River and completed on the same day. This monograph describes several past and ongoing surface water sampling events that have been conducted in the South River.

Objectives

- Determine the general and detailed distribution of mercury and methylmercury in surface water and in suspended matter in relation to distance along the South River.
- Identify river locations where total mercury or methylmercury concentrations change rapidly, potentially indicating a source or sink.
- Determine loadings [grams per day (g/day)] and fluxes [nanograms per square meter per day (ng/m^2/day)] calculated from measured and estimated discharges and concentrations of mercury and methylmercury being transported down the river under varying conditions.

Primary Team Members

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Methods

Surface water samples were collected in August and September 2004 and in February 2005 at the locations shown in Figure 1. August 2004 samples were collected in warm weather at low flow, September 2004 samples were collected in the middle of a large flood, and February 2005 samples were collected in cold weather with moderate flow. In each sampling event, samples were collected at approximately 14 to 17 easily accessible sampling stations ranging in location from the United States Geological Survey (USGS) gauging station (upstream of the plant) at Waynesboro to the Department of Game and Inland Fisheries (DGIF) launch at Port Republic (mouth of South River). In addition, samples were collected in the North River at Port Republic and often from selected outfalls (plant and municipal sewage treatment plant) and tributaries. In August 2004, water samples were also collected at two locations on the South Fork of the Shenandoah River near McGaheysville.

To obtain a sample, large volumes of water were pumped through C-flex ™ tubing using a battery-operated diaphragm pump. After ample flushing at each station, the unfiltered pump discharge was used to fill bottles for total mercury, total methylmercury, and total suspended solids (TSS) analyses. A high capacity cartridge-type filter was then attached, and the filtered pump discharge was used to fill sample bottles for total dissolved mercury and dissolved methylmercury analysis. At the end of or midway through a sampling event, source (reagent) water and equipment blank samples were prepared to check for contamination.

Samples were analyzed for total mercury and methylmercury (both filtered and unfiltered) using Environmental Protection Agency (EPA) Methods 1631 and 1630, respectively, and high-

resolution TSS [0.45 micron pore size filter, method detection limit (MDL) of 0.1 milligrams per liter (mg/L)] on the three different occasions. Field parameters such as temperature and conductivity were also recorded. Suspended matter concentrations (ng/g dry weight) of mercury (TSS-Hg) and methylmercury (TSS-MeHg) were calculated by dividing particulate mercury and methylmercury concentrations (ng/L) by TSS concentrations (mg/L).

Results and Discussion

As shown in Figures 2 through 4, the unfiltered and dissolved (0.45 micron) concentrations of mercury and methylmercury seem to rise and/or fall in a gradual fashion under normal flow conditions with increasing distance from the plant. August and February results show concentrations gradually rising past the plant to approximately Crimora (river mile 10) and then leveling off or decreasing slightly farther downstream. All concentrations drop abruptly downstream of Port Republic (river mile 25) due to dilution from the North River. Although additional data are necessary to support firm conclusions, current data do not indicate any significant point source locations during non-storm flow conditions. Another monograph on close-interval (1,000-foot) surface water sampling explores the issue of distributed vs. point sources in greater detail and discusses the possible mechanisms of transport. Finally, a monograph on river fluxes applies numerical analysis of flow rates and river dimensions to the mercury concentrations and derives some preliminary estimates of mercury and methylmercury fluxes (loading).

For methylmercury, the expected increase in concentration based on *Corbicula* studies at locations such as the oxbow "wetland" near river mile 2.6 and the depositional pool behind Dooms Dam (river mile 5.3) was not seen in the data. Although elevated methylmercury concentrations (0.87 ng/L in August 2004) relative to nearby upstream South River concentrations (0.45 ng/L in August 2004) were observed in oxbow surface water, total stream flow (from Steele Run that is routed through the oxbow) was too low to alter the overall river concentration at that point. Results from the work described in the monograph on the 1,000-foot interval surface water sampling conform to the trends seen in whole river sampling.

September 2004 results during the flood show that even with orders of magnitude of greater flow, dissolved total mercury concentrations did not decrease significantly. Methylmercury was not measured in most floodwater samples but among the unfiltered samples measured, concentrations are comparable to the August results.

Figure 5 shows the total mercury on suspended matter (TSS-Hg) results. Mercury concentrations on TSS [0.9 to 33 micrograms per gram (µg/g)] are elevated at all South River sampling stations downstream of the plant in comparison to reference results above the plant (0.10 to 0.14 µg/g) and in the North River (0.09 to 0.20 µg/g). The concentrations appear to increase significantly with distance down the river to river mile 3 to 7. The mercury on TSS results are comparable, in order-of-magnitude, to typical impacted area sediment and floodplain soil results—approximately 10 µg/g. Because TSS represent a very fine size fraction of all river system solids, the results are often somewhat higher than 10 parts per million (ppm).

Figure 6 shows methylmercury on suspended matter (TSS-MeHg) results for the three sampling events. As with TSS-Hg, TSS-MeHg concentrations increased with distance downstream from the plant and appeared to reach a plateau of about 100 ng/g below approximately river mile 6 (near Dooms). Upstream concentrations were less than 5 ng/g while maximum concentrations

reached as high as 330 ng/g near river mile 12 during the August 2004 survey. Generally concentration differences were minimal when comparing the warm season and cold season surveys. The two values (8.4 and 13 ng/g) obtained during the flood event suggest some dilution with cleaner suspended matter but the data are very limited and cannot support firm conclusions.

Path Forward

- 1,000-foot interval studies have been conducted to (1) investigate more fully distributed vs. point sources and (2) clarify the possible mercury transport mechanisms along the river.
- An understanding of why dissolved total mercury and methylmercury concentrations did not decrease during the September 2004 flood sampling event is required as most dissolved constituents of surface water typically decrease as discharge increases. Future flood events will be tracked at one to three sampling stations throughout the event. In addition, post-flood event samples will be collected to determine if the relationship of dissolved methylmercury to dissolved total mercury in the water changes, perhaps indicating a loss of methylmercury inventory.
- An additional whole river sampling event was conducted on September 13, 2005; the results are pending. In this sampling event, an additional station was added at Island Ford, the downstream extent of the Natural Resources Defense Council (NRDC) study area.

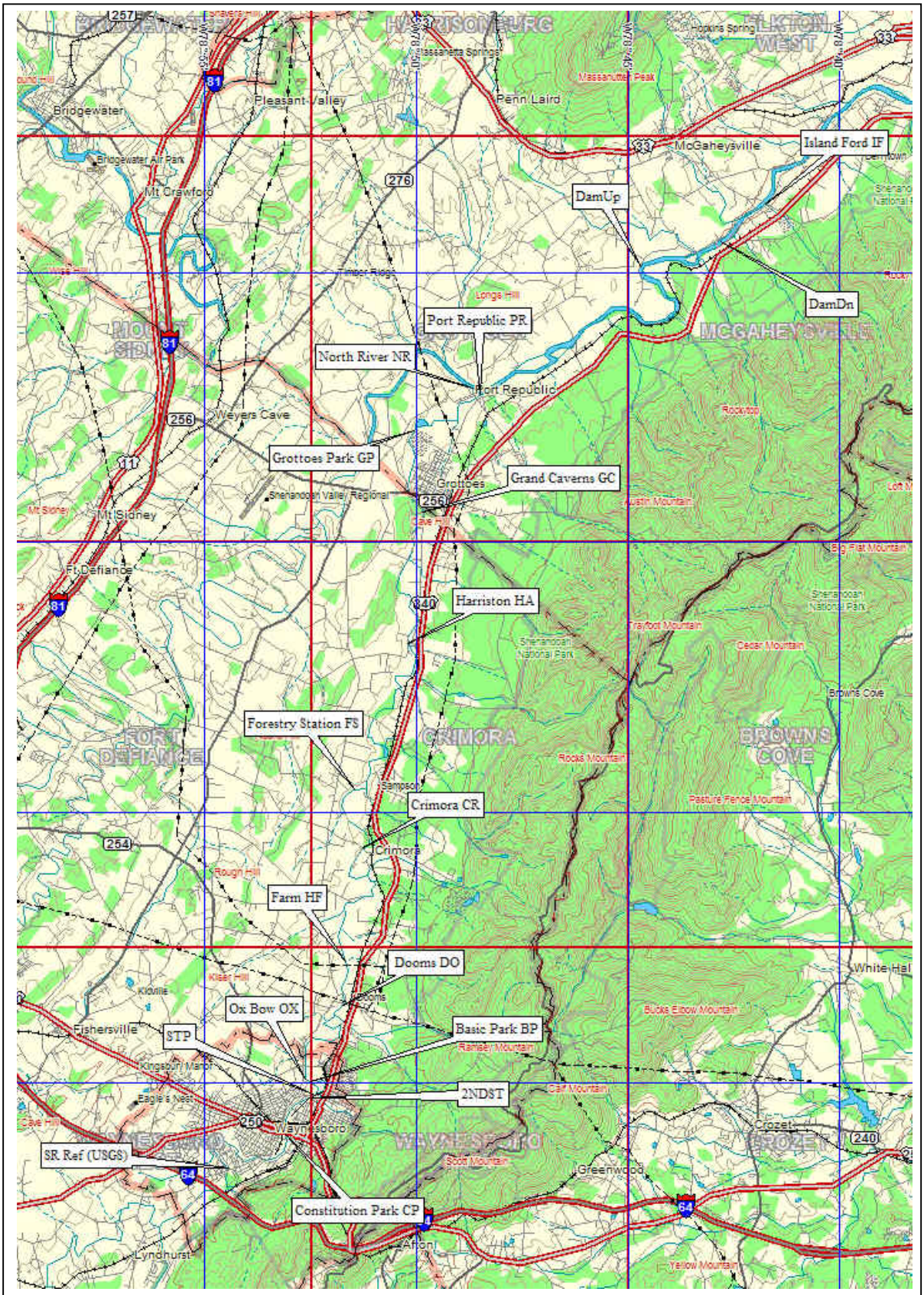

Figure 1. Map of South River surface water sampling locations.

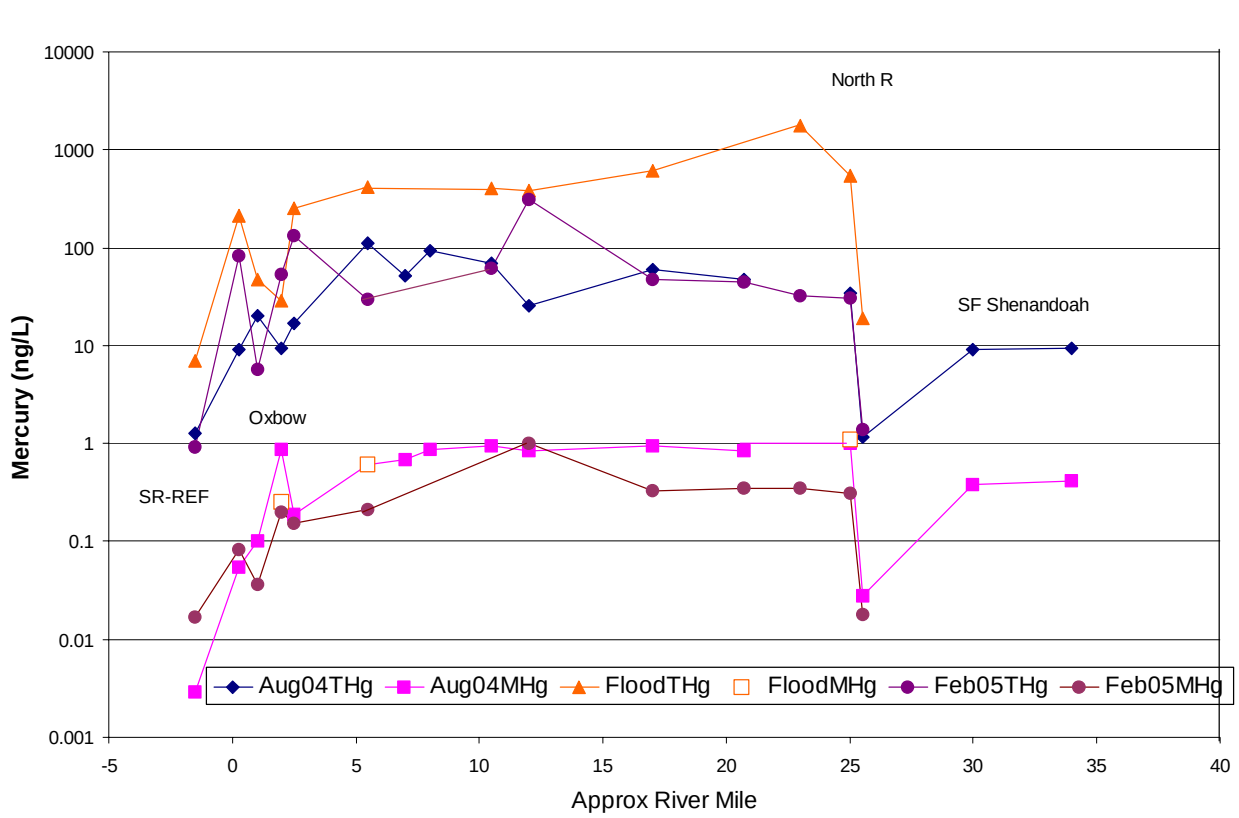

Figure 2. Total (unfiltered) mercury (THg) and methylmercury (MHg) in surface water as function of South River river distance above (-) and below plant and in North River and South Fork Shenandoah.

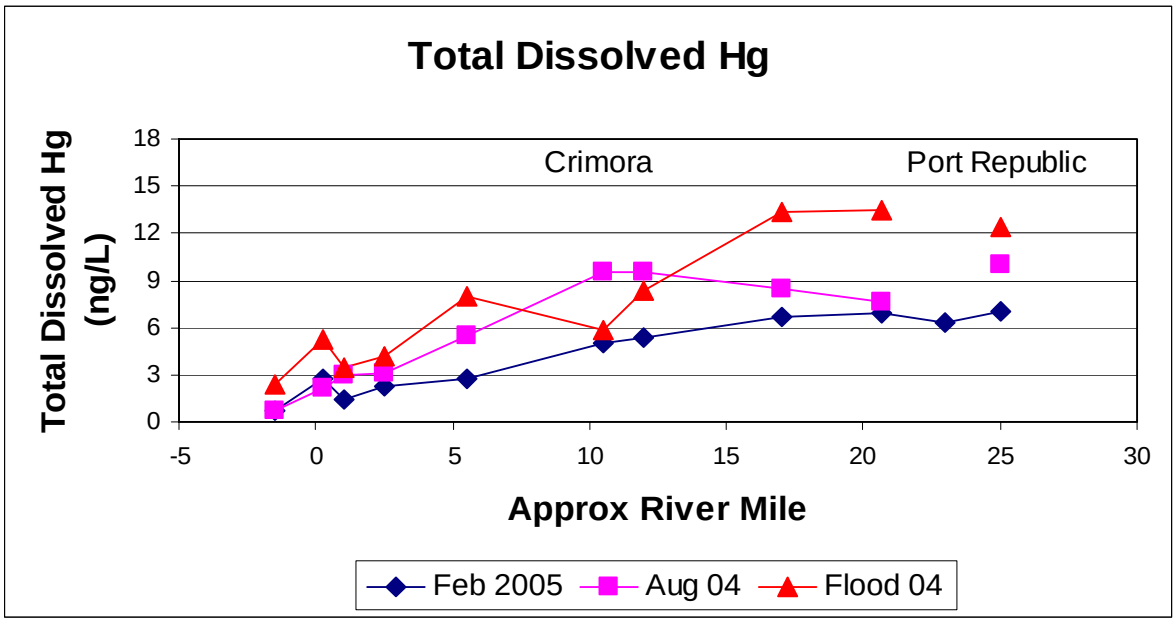

Figure 3. Total dissolved mercury in surface water as function of South River river distance above (-) and below plant.

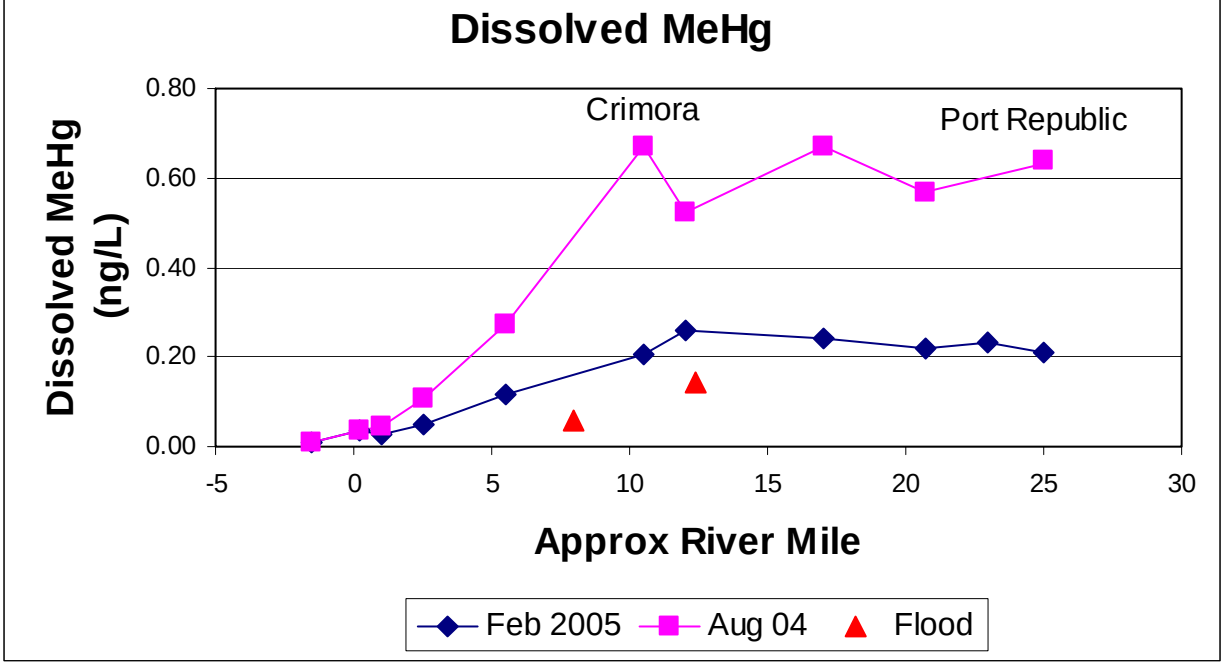

Figure 4. Dissolved methylmercury in surface water as a function of South River distance above (-) and below plant.

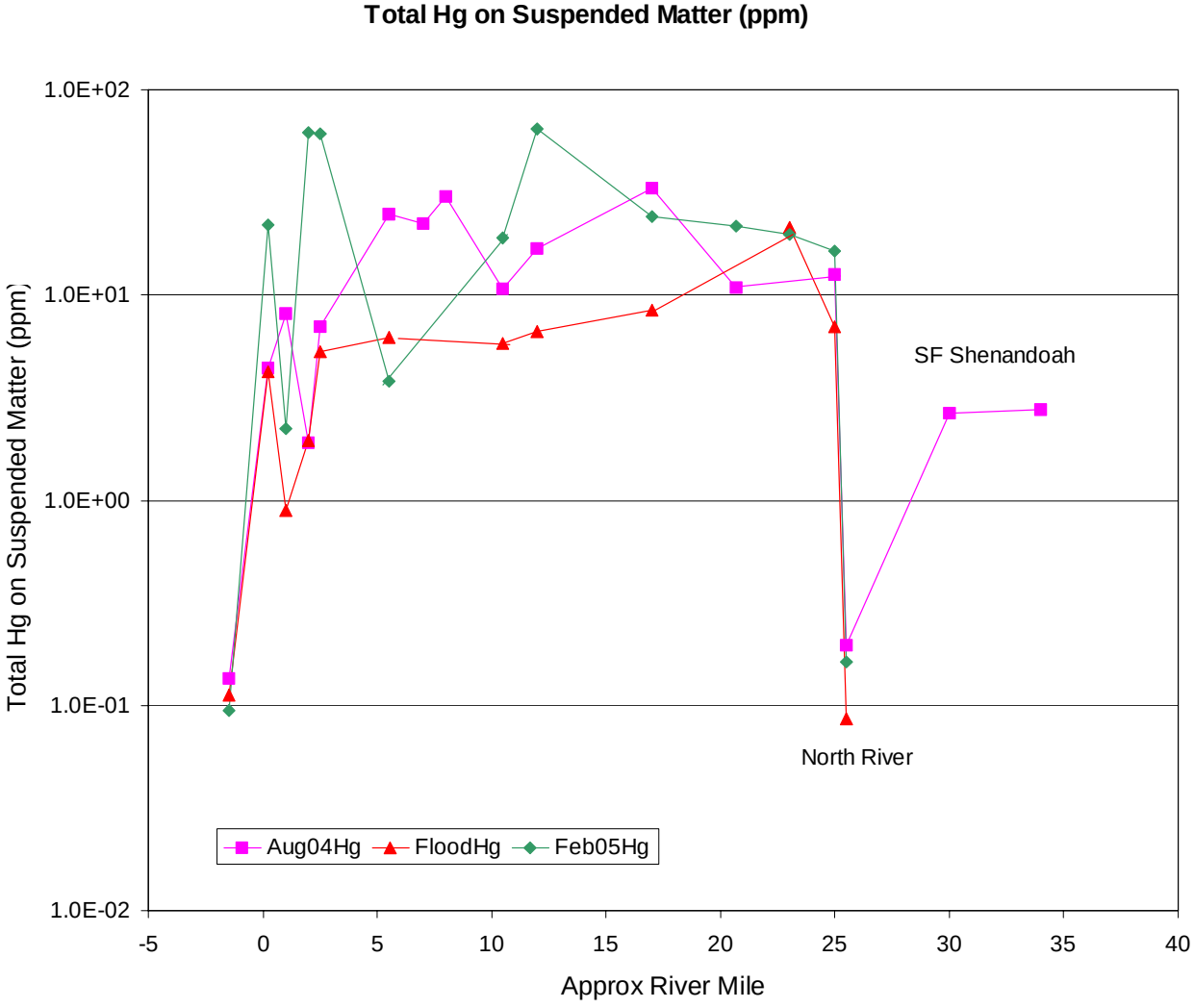

Figure 5. Total Hg on suspended matter (TSS) as function of South River mile distance and in North River and South Fork Shenandoah.

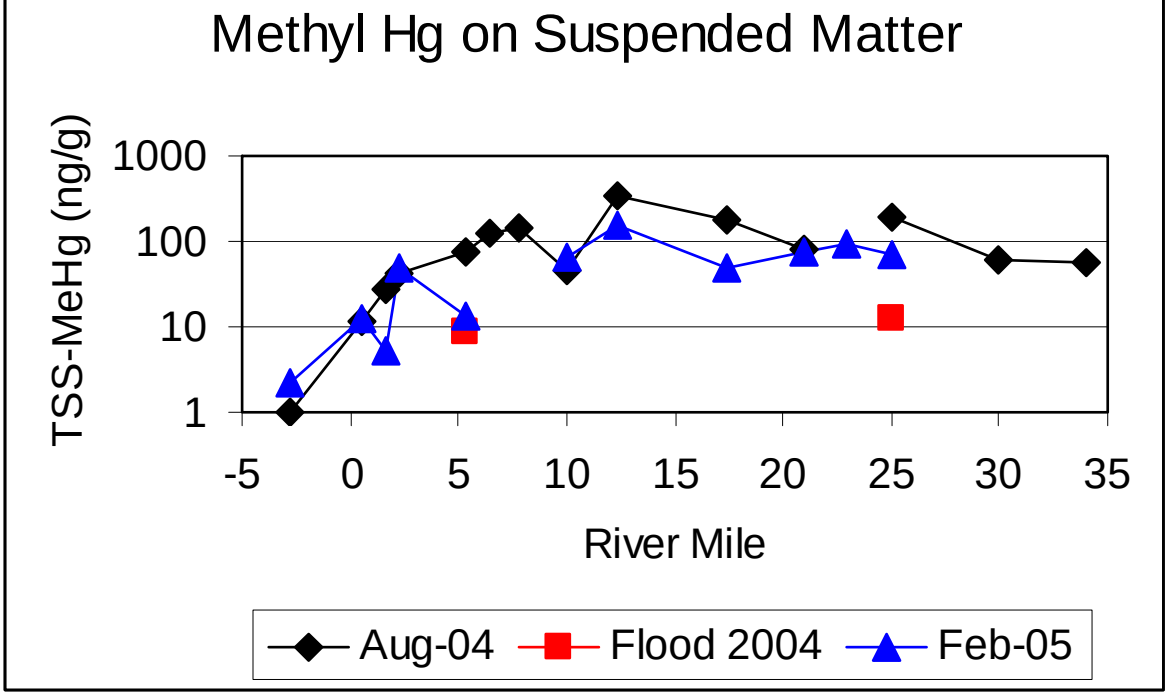

Figure 6. Methylmercury on suspended matter (TSS-MeHg) as function of South River mile distance and in North River and South Fork Shenandoah.