Close-Interval Surface Water Sampling of the South River

Surface water samples were collected from the entire length of the South River in August and September 2004 and in February 2005. 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 (Invista plant, the Waynesboro 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. These results are reported in a separate monograph about whole river surface water sampling.

Although these sampling results showed no significant spikes in dissolved total mercury and methylmercury concentrations in specific river reaches or river locations, the longitudinal spacing was large between sampling locations. Therefore, close-interval surface water sampling was performed and encompassed the entire South River below the Invista plant. This monograph describes the past and ongoing close-interval surface water sampling events performed between previous sampling stations both down the length of the river (longitudinal) and across the direction of flow (transverse).

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Objectives

- Identify potential longitudinal or tranverse patterns in mercury concentrations that might suggest a local input or source of mercury or methylmercury.
- Clarify the mercury transport mechanisms in the river system.

Methods

In January 2005, samples were collected at 1,000-foot (sometimes closer) intervals from Constitution Park to Dooms, with particular emphasis near the oxbow wetland and near the pool at Dooms Dam (see Figure 1). In March 2005, similar samples were collected at 1,000-foot intervals from Dooms to Crimora and near selected corresponding riverbanks (see Figure 2). In May 2005, the entire South River below the Invista plant (25 river miles) was sampled at varying intervals from 500 to 4,000 feet, concentrating primarily below Crimora (see Figure 3). This latter sampling was conducted during a two-day float of the river to obtain near-synoptic data.

Samples were collected mid-stream and well above the river bottom in all locations with sufficient water depth. To obtain a sample, large volumes of water were pumped [at approximately 3 gallons per minute (gpm)] through C-flex™ tubing using a battery-operated diaphragm pump. After ample flushing of the pump and tubing at each station, a high capacity cartridge-type filter was 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. Water samples were stored and shipped on ice to Studio Geochimica where analysis for total dissolved mercury and total dissolved methylmercury was performed using EPA Methods 1631 and 1630, respectively. Additional details for sampling events are as follows:

- January 2005
  Different filter porosities (0.45, 0.2, 0.1 microns) were tested at two locations to determine the effect on the measured "dissolved" concentration. This test explored the true nature of "dissolved" as measured operationally by the normal 0.45-micron filtration.
- March 2005
  In addition to the standard 1,000-foot interval sampling, samples were collected at four locations near the left or right riverbank between Dooms and Crimora. This sampling method is designated hereafter after "transverse" close-interval sampling. An additional near-bank sample was collected at a badly eroded/undercut bank with recently eroded soil lingering in a pile beneath the water.
- May 2005
  Because January 2005 results indicated a possible increase in total dissolved mercury concentrations between Hopeman Parkway and Dooms, this river reach was studied in greater detail in May 2005. Samples were collected in 500-foot intervals in this reach and additional samples were collected from the small tributary inflow opposite the Genicom ditch and from the Genicom ditch. In addition, higher concentration results for near-banks in March 2005 were investigated in May 2005 using a detailed study of two fixed transects. The center stream was sampled as usual, but additional samples were collected near both banks—one sample from just above the river bottom and one very near the surface. [Note: These transverse (transect) results will be described in a separate monograph with additional results from September 2005.]

The close interval data, coupled with known river dimensions and flow rates, were used to calculate average fluxes of total mercury and methylmercury for the major river intervals (see the South River as a flux chamber monograph for more detail).

Results

- January 2005
  Figures 4 and 5 show the January 2005 results and indicate only a single location where significant dissolved total mercury *might* be entering the water column [i.e., between Hopeman Bridge (river mile 2.5) and the Genicom Ditch (river mile 3)]. The increase is small when compared to the overall change from the plant to Dooms. Otherwise, total mercury concentrations seem to increase more gradually along the entire length of river between the plant and Dooms. No corresponding increase in methylmercury concentrations was present at Hopeman Parkway. In addition, no increase in methylmercury concentrations was present at the oxbow. Specific river sections (e.g., below the Genicom ditch) showed highly variable concentrations of total dissolved mercury. Variable concentrations can be explained by mercury or clean water inputs along the specific river reaches that are not well mixed. [Detailed temperature measurements (not reported here) were obtained at several transects below the Genicom ditch, but results were inconclusive.]

Filter porosity results are shown in red in the January plots at Constitution Park and Dooms. Except for the two anomalous results for methylmercury at Constitution Park, the 0.2- and 0.1-micron filters produced lower dissolved results, indicating that not all of the "dissolved" mercury measured using the typical 0.45-micron filter pore size is truly dissolved. It is unlikely that the anomalous results for methylmercury at Constitution Park are accurate; rather, they may reflect the leakage of unfiltered water through the smaller pore size filters.

- March 2005

  Figure 6 shows the dissolved total mercury and methylmercury results for March 2005 on a single semi-log plot. This figure also shows the results of the five transverse samples collected at riverbanks adjacent to normal center stream samples and at a badly eroded bank location. Results confirmed that concentrations of both dissolved total mercury and methylmercury are higher near the bank versus the center stream (see the yellow triangles and blue circles in Figure 6). These elevated concentrations could be a result of (1) mercury inputs from the banks or the bottom or (2) the banks being a source of methylmercury production.

  Figure 7 combines the results from January and March 2005 into a single semi-log plot. Note the minor step change at Dooms between the January and March results. This change may be due to the difference in river flow between the two sampling events [423 cubic feet per second (cfs) versus 322 cfs at Harriston gauge] or it may be related to water temperature differences between January (3°C) and March (8°C).

  Unlike the January results, no unusual amounts of total mercury or methylmercury appeared to be entering the water column in March at any longitudinal locations.

- May 2005

  Figure 8 shows the results of all three close-interval surface water sampling events on a single semi-log plot. A moderate increase in dissolved total mercury concentrations between Waynesboro and Crimora can be seen when comparing samples collected during the cold temperatures in January and March to those samples collected during the warm temperatures (14°C) in May. [There was also less river flow (190 cfs at Harriston) in May than in either January or March.] By comparison, there was a significant increase in dissolved methylmercury in May versus January and March, and this higher trend continues to Port Republic. Contrary to earlier results from the whole river surface water surveys where concentrations seemed to peak or plateau near Crimora, the concentrations in May 2005 of both dissolved total mercury and methylmercury continued to increase all the way to Port Republic.

  Figure 9 shows that the small tributary inflow opposite the Genicom ditch ("Corn") is relatively clean and could not contribute to the distinct increase in total mercury or methylmercury observed in this reach. The Genicom ditch, however, is elevated in both total mercury and methylmercury concentrations relative to the river. The ditch flow was less than 10 gpm (0.022 cfs), making the ditch an unlikely significant contributor to the concentration increase observed in this reach. The closer-interval mid-stream samples collected in May did not replicate the distinct increase observed in total dissolved

mercury in January 2005. It is unknown if lower flow in the Genicom ditch in May compared to January explains this difference.

The two fixed transect sampling results confirmed the higher concentrations at the two banks. It is not clear if the higher concentrations observed near the banks in March and May are the result of dissolution from river solids near the banks or from elevated mercury groundwater entering the river near the banks.

Figures 10 and 11 show the relationship between dissolved methylmercury and total mercury for both close-interval and whole river surface water sampling events. Figure 10 shows only the January and March results. In both figures, for the 1000-foot interval samplings, the linearity and low data scatter are remarkable, demonstrating that the methylmercury and total mercury concentrations vary together from sampling to sampling, location to location, and season to season. These results suggest that increased dissolved total mercury is closely related to and may be causing increased dissolved methylmercury. In warm months, dissolved total mercury may be providing the substrate for conversion to methylmercury. In cold months, the close linear relationship is more surprising as methylation is expected to be less effective or even absent at low winter temperatures. The samples collected during the whole river sampling events, whose results are also shown in these figures, were generally obtained from nearer the bank and near the river bottom. These samples seemed to be relatively higher in total mercury and lower in methylmercury, suggesting that methylation in these samples has not had as much time to convert inorganic mercury to organic mercury as for the midstream samples.

Path Forward

- Continue the close-interval longitudinal and transverse sampling for selected reaches of the river under contrasting flow and temperature conditions as well as where a source is suspected.
- In September 2005, additional whole river surface water samples were collected at 17 locations, including a new location at Island Ford on the South Fork Shenandoah. In addition, nine new transects were sampled for dissolved total mercury and methylmercury at the following five locations: left bank, right bank, left bottom (1/4 width), right bottom (3/4 width), and center stream above the bottom where deep enough. All transect (transverse) results will be reported in a separate monograph following receipt of September results. Hydrosol samples (i.e., the top fluffy layer of sediments) were collected at most transect locations and submitted for analysis of total mercury and methylmercury, moisture, and loss on ignition (LOI).

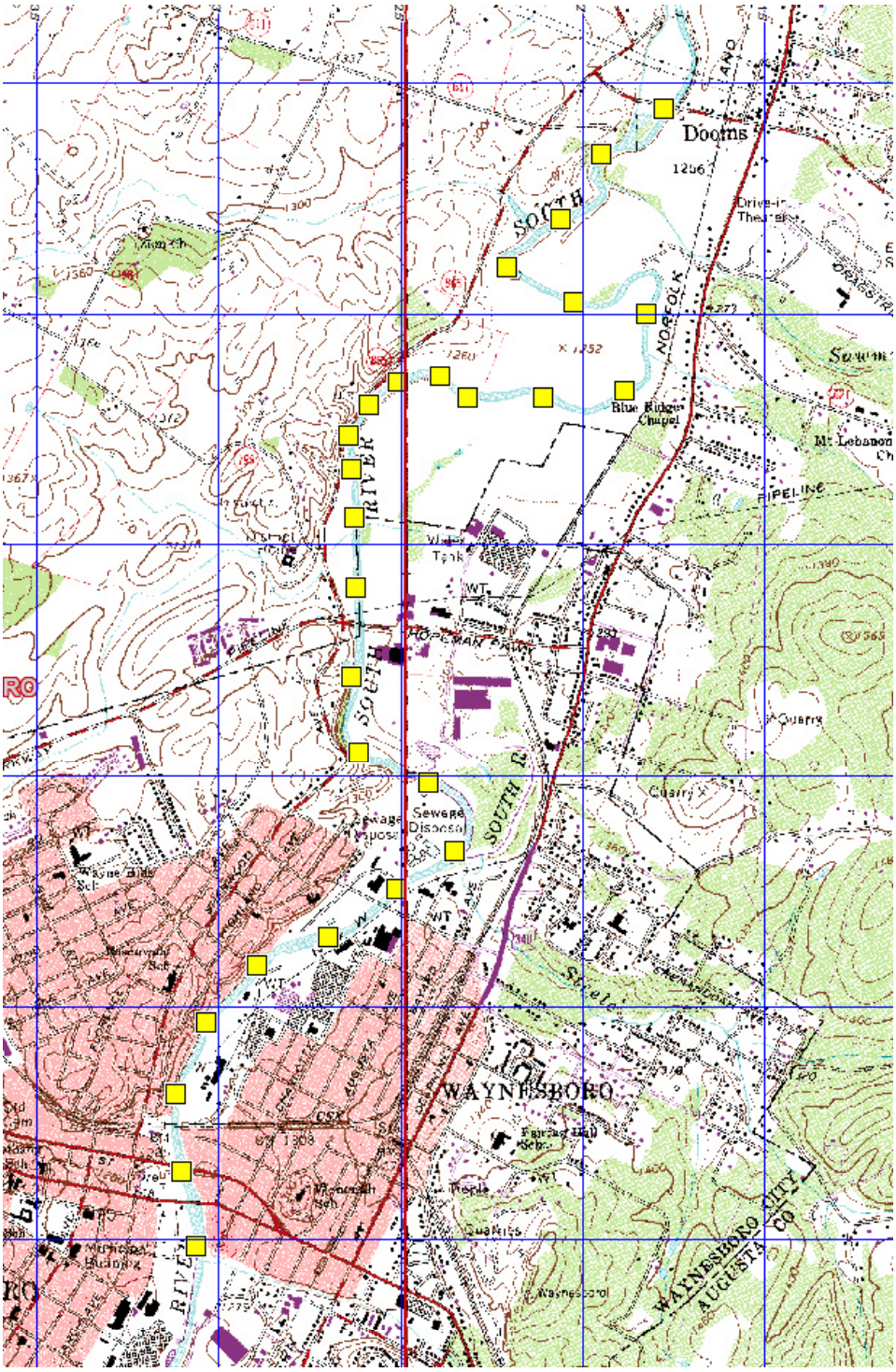

Figure 1. Sample locations in January 2005.

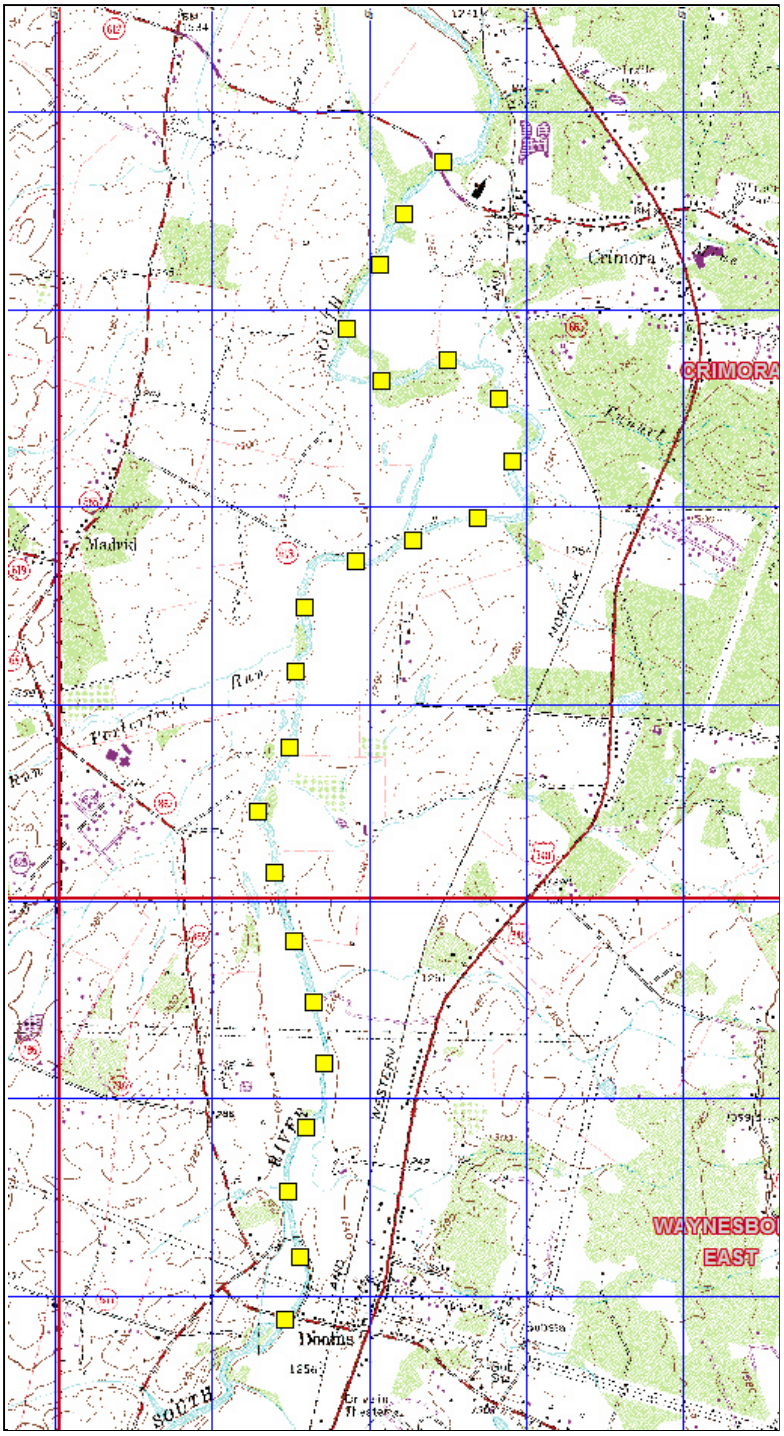

Figure 2. Sample locations in March 2005.

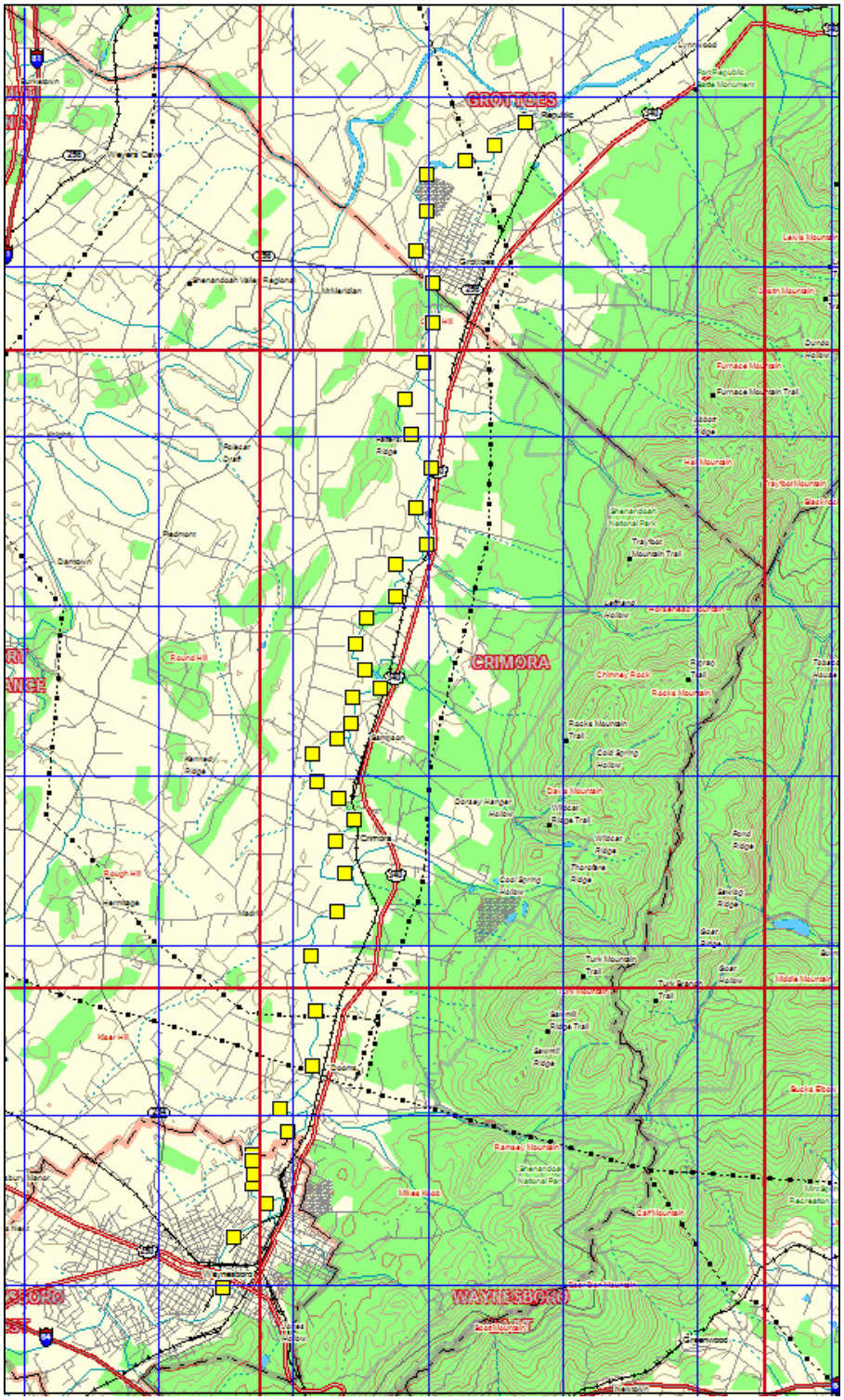

Figure 3. Sample locations in May 2005.

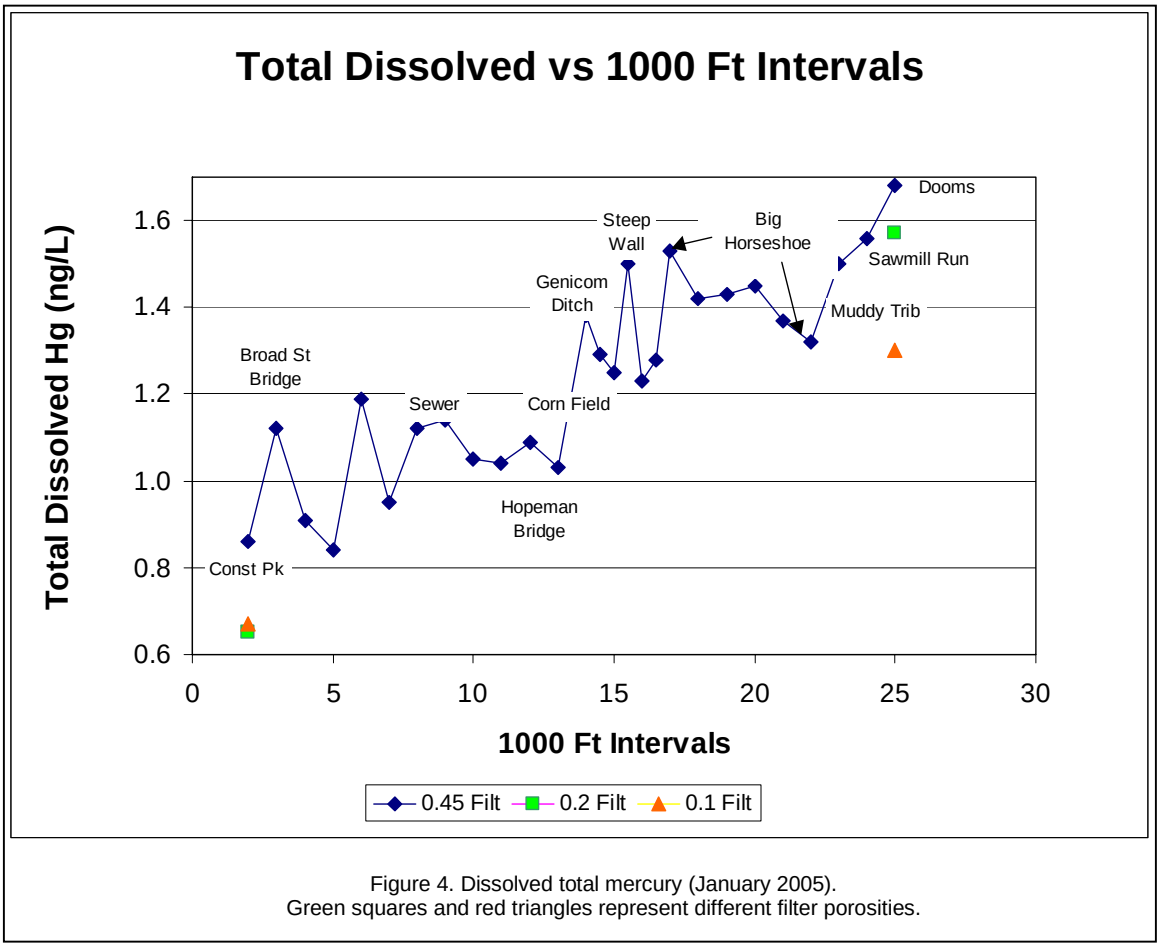

Figure 4. Dissolved total mercury (January 2005).
Green squares and red triangles represent different filter porosities.

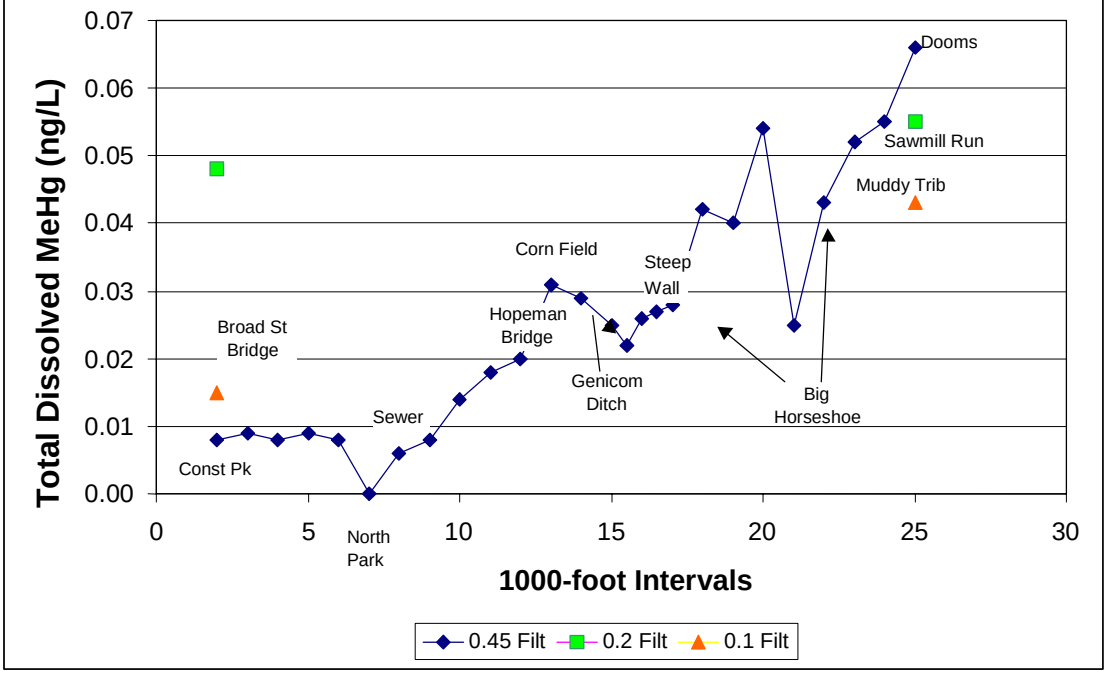

Figure 5. Dissolved methylmercury (January 2005). Green squares and red triangles represent different filter porosities.

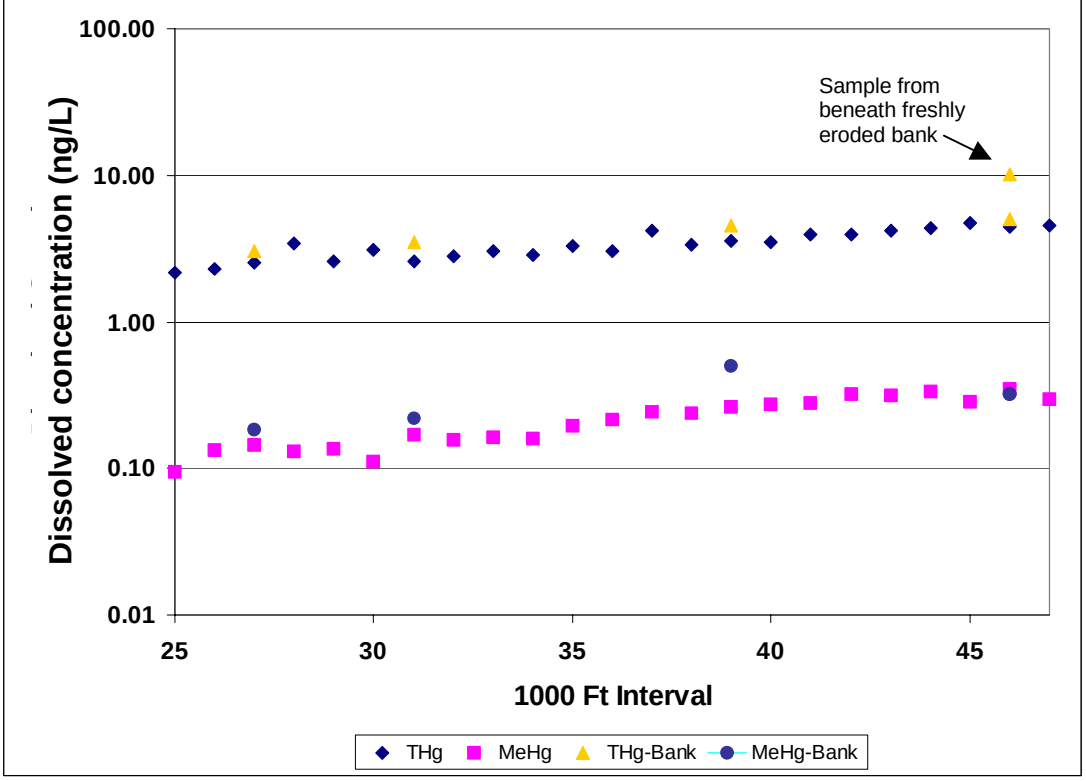

Figure 6. Dissolved total mercury and methylmercury (March 2005).
Yellow triangles and blue circles are near-bank results

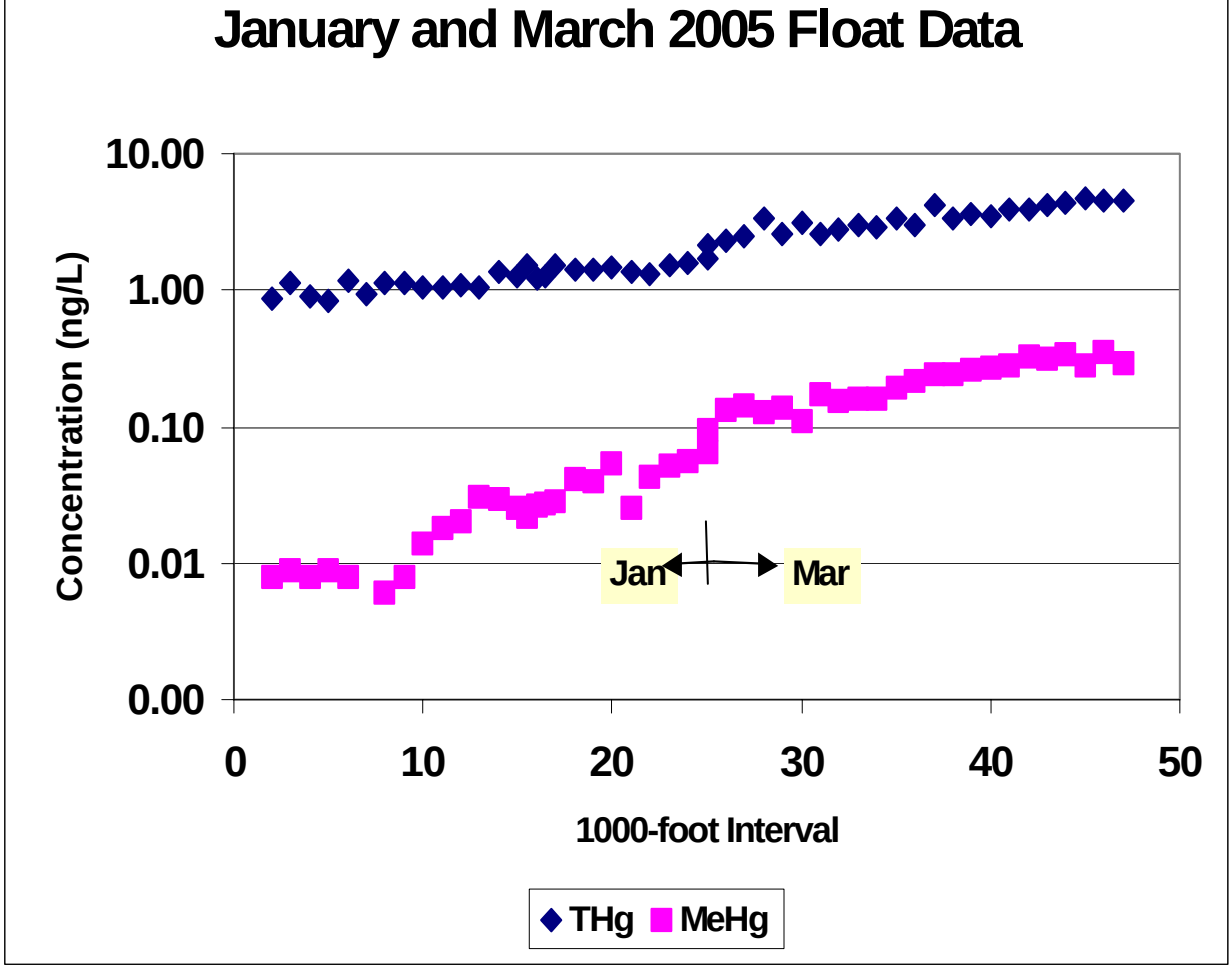

Figure 7. Dissolved total mercury and methylmercury (January and March 2005).

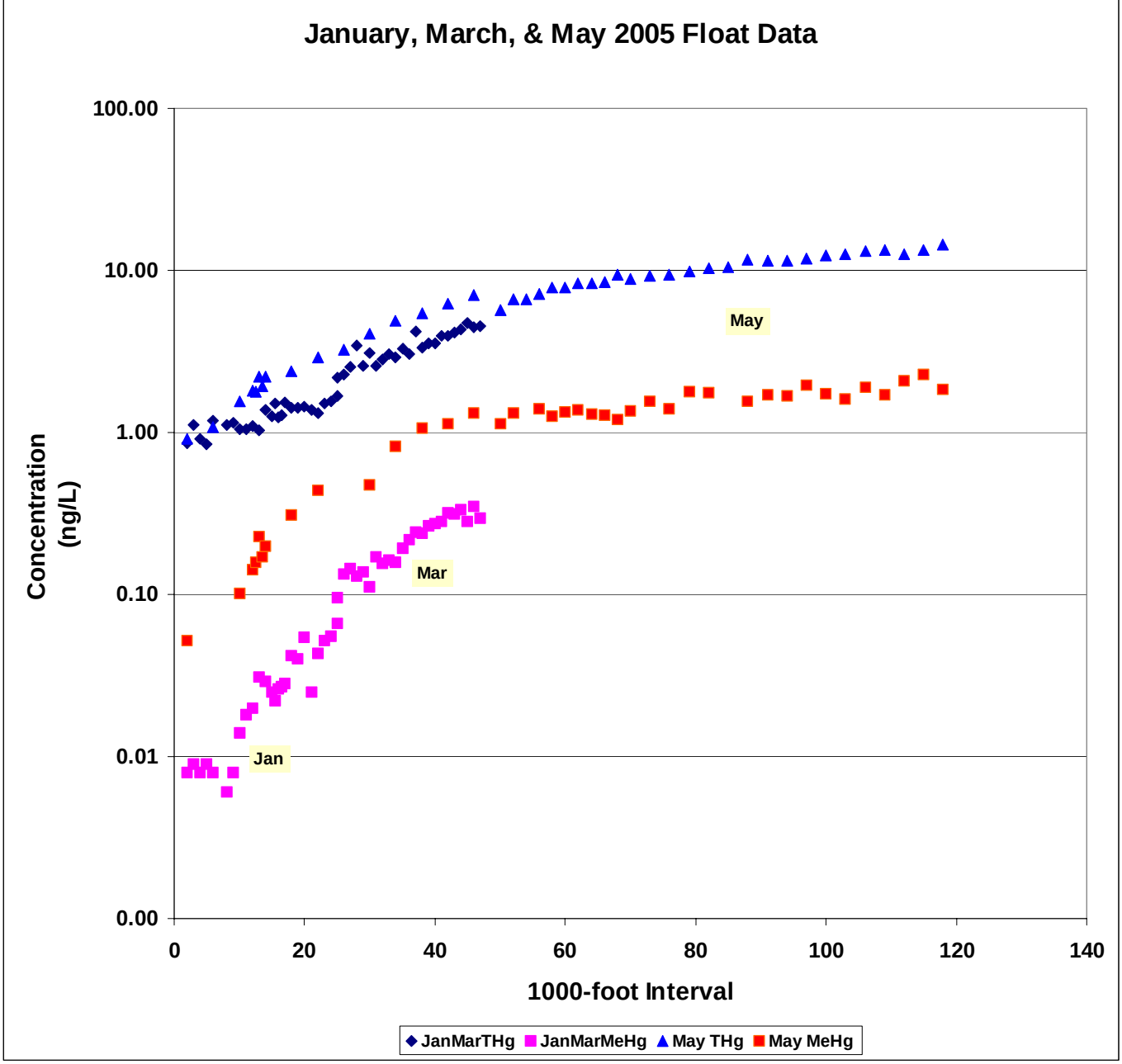

Figure 8. Dissolved total mercury and methylmercury in January, March, and May 2005.

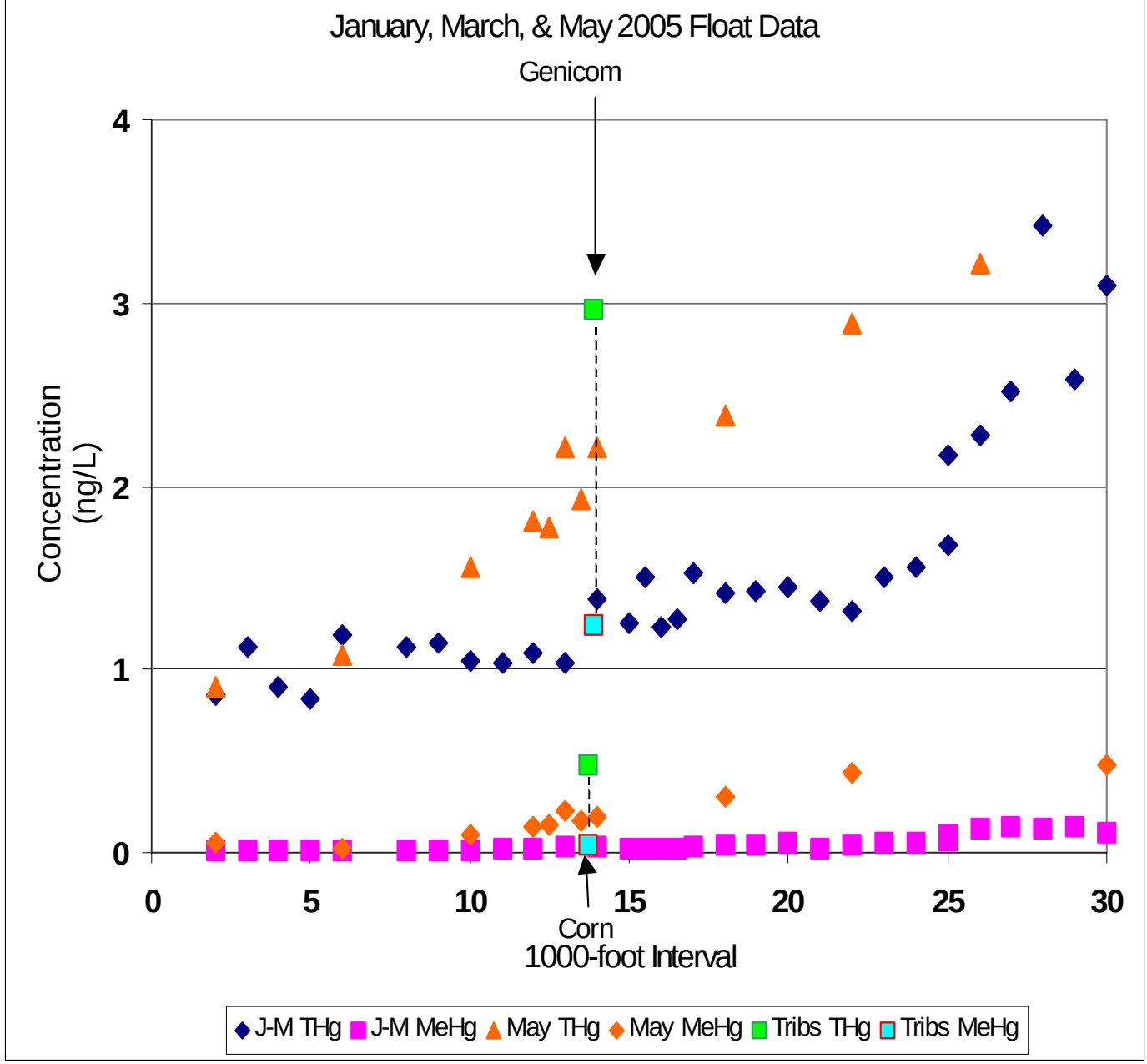

Figure 9. Dissolved total mercury and methylmercury in January, March, and May 2005 (zoomed in on Genicom ditch area).

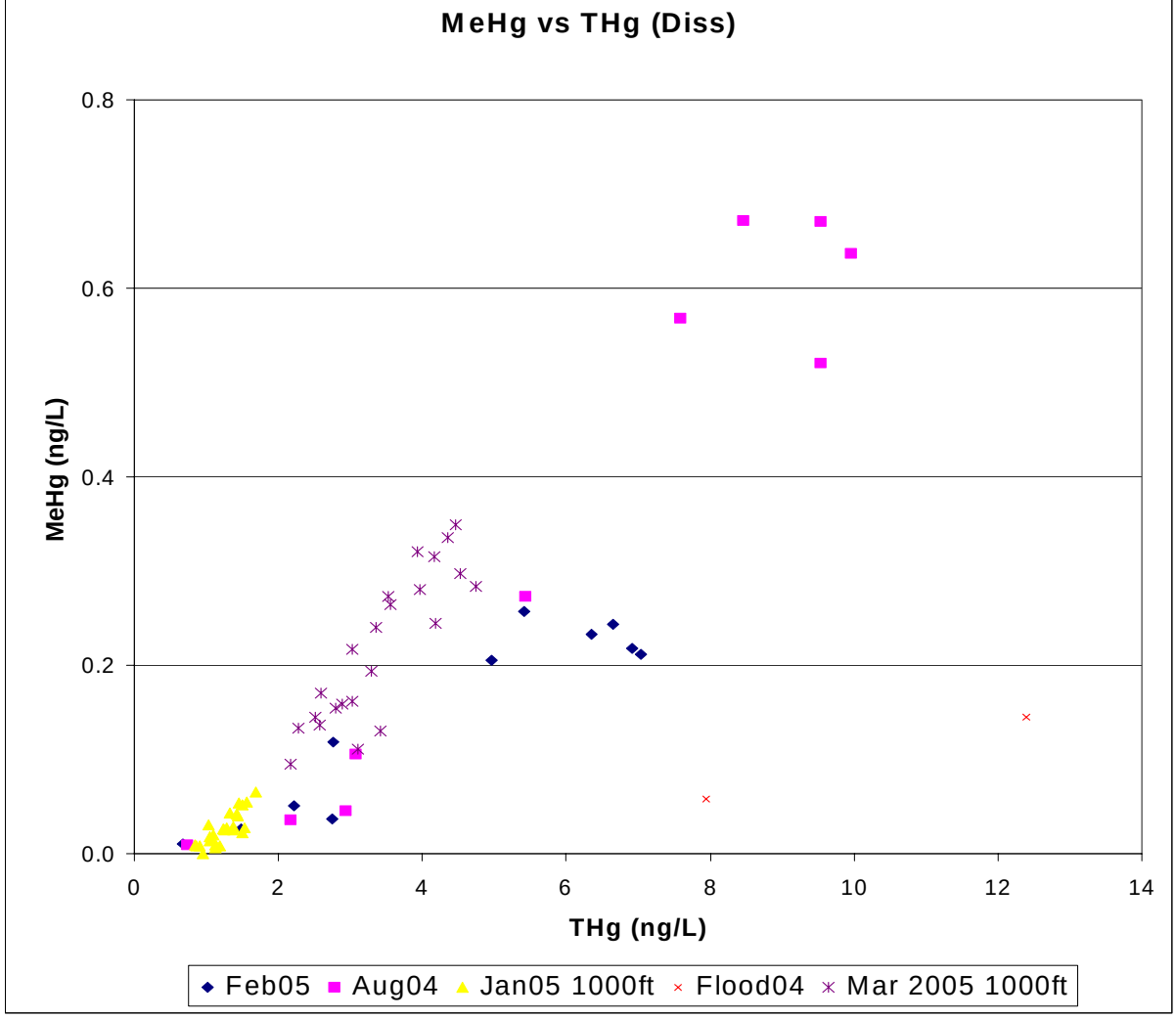

Figure 10. Dissolved methylmercury vs. dissolved total mercury.
(January and March 2005 close interval and prior whole river samples)

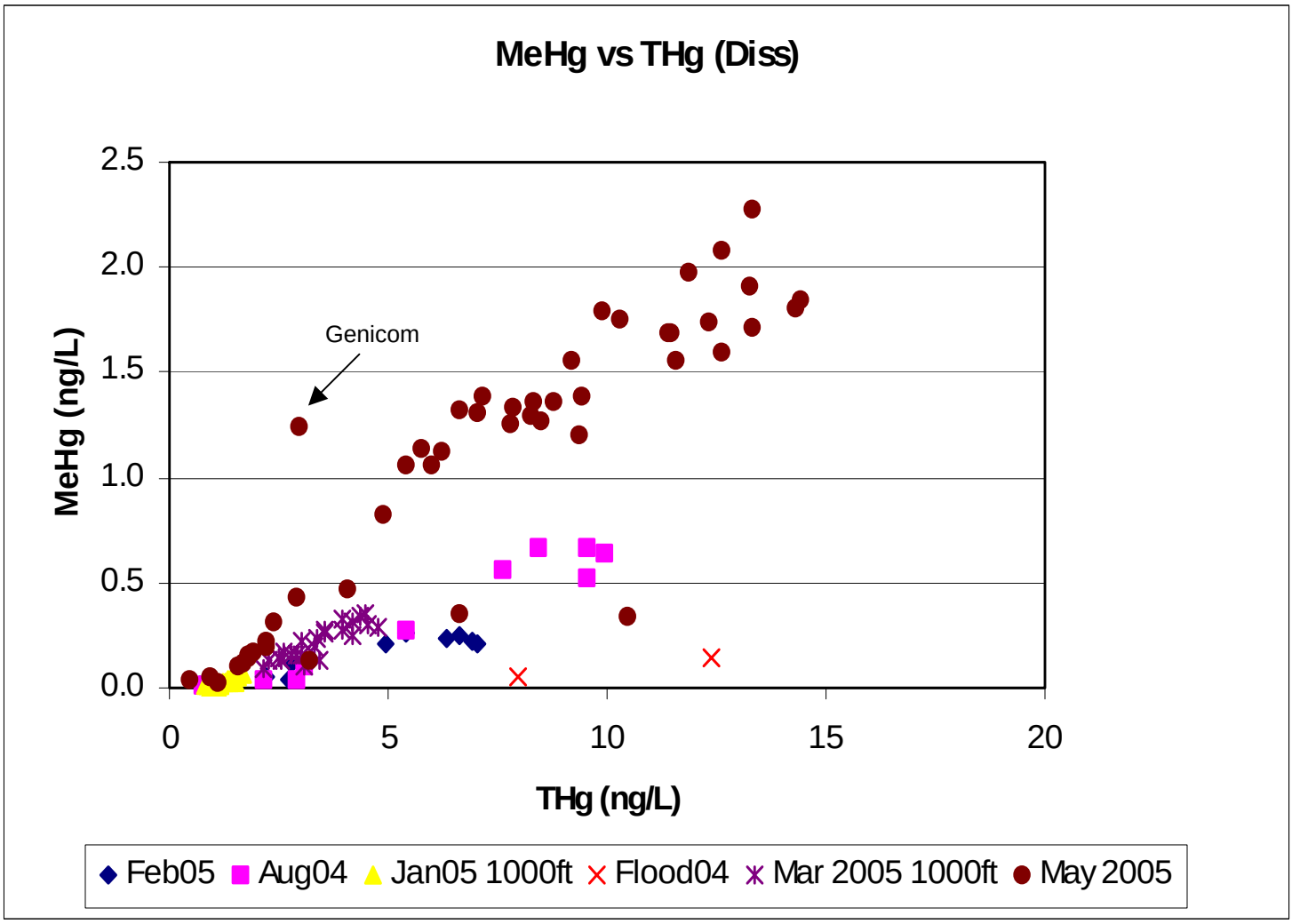

Figure 11. Dissolved methylmercury vs. dissolved total mercury (January, March, and May 2005 close interval and prior whole river samples)