

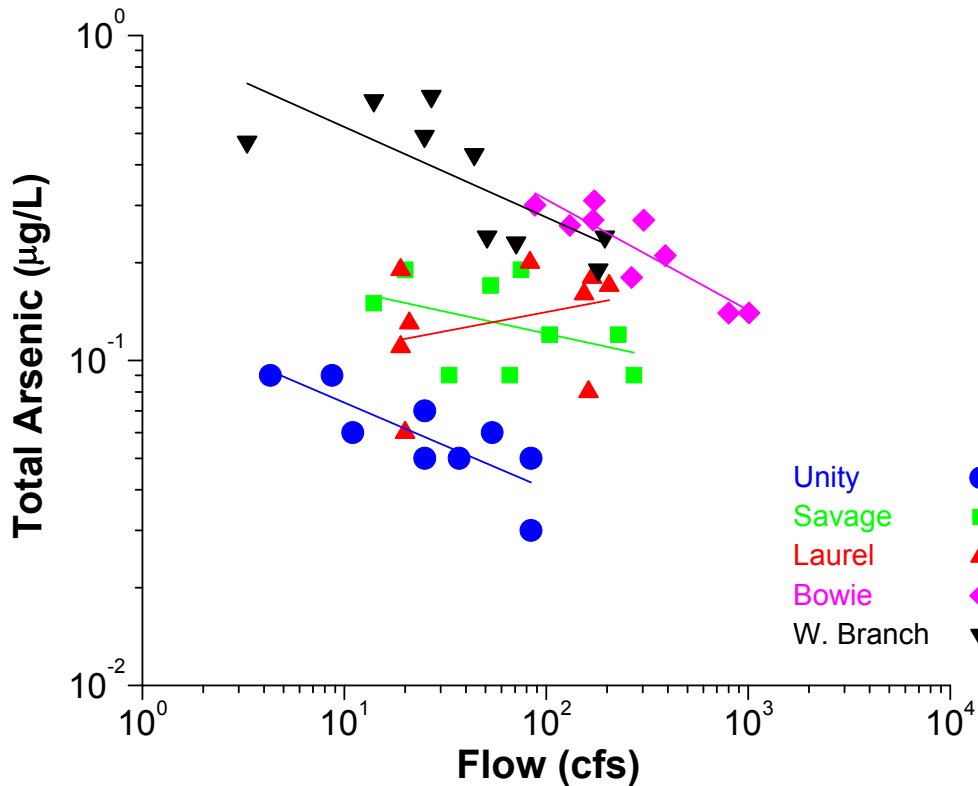
# ARSENIC IN CHESAPEAKE BAY TRIBUTARIES

G. F. Riedel<sup>1</sup>

<sup>1</sup>Academy of Natural Sciences, Estuarine Research Center, St. Leonard, Maryland

Sampling for dissolved and suspended particulate arsenic was carried out in several Chesapeake Bay Tributaries, including the Anacostia, Patuxent, Patapsco, Pocomoke, Wicomico Rivers using high sensitivity, species specific analytical techniques. The most extensive data set is from the Patuxent River, in which samples were taken from 5 riverine sites and 10 tidal sites on nine occasions over three years (Riedel et al., 2000). In the non-tidal freshwater portions of the Patuxent, total arsenic concentrations ranged from 0.02 to 0.7  $\mu\text{g L}^{-1}$ , and were significantly inversely related to river flow (Fig. 1), which suggests that a relatively fixed source, such as groundwater, was predominant.

**Figure 1. Concentration of total dissolved arsenic at 5 riverine sites in the Patuxent River watershed plotted versus the average daily flow (USGS 1998).**

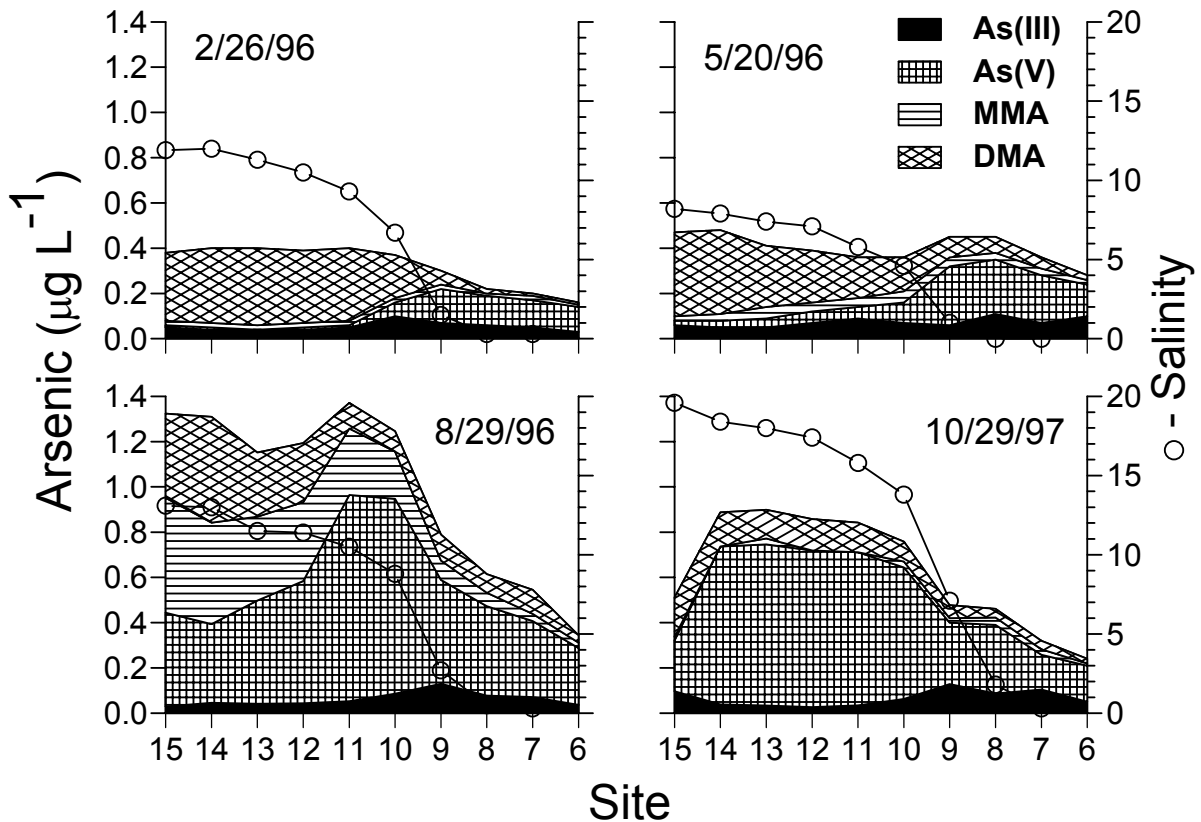


One major tributary of the Patuxent, the Western Branch, was a significantly greater source than the remainder of the Patuxent. This appears to correlate to the widespread out cropping of a glauconitic stratum, the Aquia Greensands formation,

across the watershed. In all cases, the inorganic forms of arsenic, As(III) and As(V) predominated in the freshwater portions of the river.

In the estuarine portions of the river, arsenic concentrations were generally more elevated in the more saline areas, up to  $1.5 \mu\text{g L}^{-1}$ , reflecting the input of relatively high arsenic Atlantic Ocean seawater (Fig. 2). However, dissolved arsenic was non-conservative with salinity, showing evidence of input at the low salinity end. During the summer, a substantial input of inorganic arsenic appeared to come from the sediment as a result of low oxygen conditions in the bottom waters of the Patuxent River estuary and main stem Chesapeake Bay. In winter and spring, most of the arsenic in the estuarine portion of the river was found to be in the form of mono- and dimethylarsenic (MMA and DMA). These organic forms of arsenic appeared to have been formed in situ, and in the main stem of Chesapeake Bay, by the action of phytoplankton under phosphorus limiting conditions.

**Figure 2. The concentration and speciation of arsenic in the Patuxent River estuary over the course of an annual cycle, from the tidal freshwater (Site 6) to the river mouth at the Chesapeake Bay (Site 15).**



The highest concentrations of arsenic in suspended solids ( $22.5 \pm 4.7 \mu\text{g g}^{-1}$ ) in the freshwater regions of the river also occur in the Western Branch in association with

the glauconitic soils, with substantially lower concentrations (5-10  $\mu\text{g g}^{-1}$ ) occurring in the other regions of the Patuxent drainage. In the Patuxent River estuary, arsenic in suspended particles increased from ca. 11  $\mu\text{g g}^{-1}$  in the freshwater end to ca. 17.2  $\mu\text{g g}^{-1}$  at the Chesapeake Bay end, generally consistent with the rise in arsenic concentration with salinity (Table 1).

Table 1. Concentrations of arsenic in suspended particles (mean  $\pm$  Std. Dev.) collected from the Patuxent River watershed.

| Site                               | As<br>( $\mu\text{g g}^{-1}$ ) |
|------------------------------------|--------------------------------|
| 1 Patuxent River at Unity          | 5.4 $\pm$ 0.7                  |
| 2 Patuxent River at Laurel         | 9.9 $\pm$ 3.7                  |
| 3 Little Patuxent at Savage        | 6.4 $\pm$ 0.9                  |
| 4 Patuxent River at Bowie          | 7.6 $\pm$ 1.0                  |
| 5 Western Branch at Lower Marlboro | 22.5 $\pm$ 4.7                 |
| 6 tidal freshwater                 | 10.8 $\pm$ 3.8                 |
| 7 upper estuary                    | 12.9 $\pm$ 0.9                 |
| 8 upper estuary                    | 13.4 $\pm$ 1.0                 |
| 9 salinity transition zone         | 13.2 $\pm$ 2.9                 |
| 10 salinity transition zone        | 14.1 $\pm$ 3.3                 |
| 15 lower estuary                   | 17.2 $\pm$ 11.8                |

Using the concentration of dissolved arsenic as a function of flow, the concentration of arsenic in suspended particles, the concentration of suspended particles as a function of flow, and the daily mean flows of the river at Bowie and Western Branch the annual input of arsenic to the Patuxent River estuary from the Patuxent River was estimated. These are compared to several other estimates of arsenic inputs to the estuary derived from several sources (Table 2). Atmospheric deposition supplies sufficient arsenic to the watershed surface to supply all the arsenic in the river. Analytically determined point sources are insufficient to supply much of the arsenic found in the river, but estimated point sources from sewage treatment plants could potentially supply more arsenic than was actually found.

Results from others Chesapeake Bay tributaries, including the Anacostia, Patapsco, Pocomoke, and Wicomico Rivers showed similar patterns of concentration and speciation of arsenic.

Table 2. A comparison of potential sources of arsenic to the Patuxent River drainage.

| Source  | As<br>(kg yr <sup>-1</sup> ) | Reference                 |
|---|------------------------------|---------------------------|
| Atmospheric Deposition <sup>a</sup><br>Total Watershed Area<br>Water Surface        | 510<br>48                    | Scudlark et al. (1994)    |
| Point Sources Estimates<br>EPA Inventory <sup>b</sup><br>NOAA Estimate <sup>c</sup> | 0 - 7.6<br>980               | EPA (1999)<br>NOAA (1993) |
| Urban Runoff <sup>d</sup>   | 140                          | NOAA (1993)               |
| “Fall Line” Load <sup>e</sup><br>Filterable<br>Particulate                          | 69 ± 32<br>No data           | EPA (1996)                |
| Filterable Yield (This study)<br>Main Branch<br>Western Branch                      | 93<br>70 ± 22<br>23 ± 6      | Riedel et al. (2000)      |
| Particulate Yield (This study)<br>Main Branch<br>Western Branch                     | 240<br>50 ± 30<br>190 ± 100  | Riedel et al. (2000)      |

References:

- National Oceanic and Atmospheric Administration. 1993. Point Source Methods Document for the Virginian Province. National Ocean Service.
- Riedel, G. F., S. A. Williams, G. S. Riedel, C. C. Gilmour and J. G. Sanders. 2000 Temporal and Spatial Patterns of Trace Elements in the Patuxent River: A Whole Watershed Approach. *Estuaries* 23: 521-535.
- Scudlark, J. R., K. M. Conko and T. M. Church. 1994. Atmospheric wet deposition of trace elements to Chesapeake Bay: CBAD study year 1 results. *Atmospheric Environment* 28: 1487-1498.
- United States Environmental Protection Agency, Chesapeake Bay Program. 1996. Chesapeake Bay Fall Line Toxics Monitoring Program 1994 Final Report.
- United States Environmental Protection Agency, Chesapeake Bay Program. 1999. Chesapeake Bay Toxics Loading and Release Inventory.
- United States Geological Survey. 1998. Water Resources Data - Maryland and Delaware, Water Year 1997.