

SOURCE, TRANSPORT, AND FATE OF ARSENIC IN THE POCOMOKE RIVER BASIN, A POULTRY DOMINATED CHESAPEAKE BAY WATERSHED

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The source, transport, and fate of several arsenic compounds are being investigated in water, soil, and sediment of the Pocomoke River Basin in Maryland and Delaware, an area in the Chesapeake Bay Watershed that has a high concentration of poultry-feeding operations and where arsenic feed amendments are used extensively. Organic arsenic compounds are commonly added to the feed of animals, particularly poultry and swine, in the United States to control parasites, thereby improving animal growth rates. Poultry manure, which is typically spread on agricultural fields for disposal and as fertilizer, can contain from 15-35 mg/kg total arsenic (Morrison, 1969). An estimated 600 million chickens are raised annually on the Delmarva Peninsula (based on 1992 U.S. Department of Agriculture data); these animals produce more than 1.5 billion kg of raw manure (Sims and Wolf, 1994). Therefore, about 20-50 thousand kg of arsenic are delivered annually to the Delmarva peninsula. The fate of these arsenic feed amendments in the environment is not well understood.

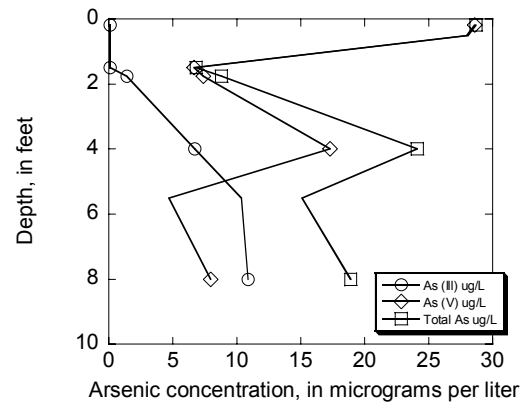
The Pocomoke River Basin includes agricultural land (row crop and poultry operations) interspersed with woodlands. The area is flat with poorly drained soils underlain by unconsolidated Coastal Plain sediments. The shallow aquifer system is characterized by complex heterogeneous hydrogeology with short, shallow ground-water flow paths (Hamilton and others, 1993). A relatively thin sandy surficial aquifer, which is overlain by poorly drained soils, contains the shallow water table. This surficial aquifer overlies a discontinuous confining bed composed of fine-grained sediments and organic matter, which in turn overlies a semi-confined sandy aquifer that is a source of drinking water for small public supplies. Extensive ditches drain the agricultural fields and form the headwaters of streams. Due to the lack of vegetation, manure particles and agricultural contaminants mobilized by storm runoff are likely transported in the ditches and along short ground-water flow paths. The agricultural ditches connect to the Pocomoke River, which has had documented cases of fish lesions, fish kills, and harmful algal blooms like *Pfiesteria piscicida*.

We are conducting reconnaissance sampling to determine if there are measurable concentrations of arsenic in poultry manure, ground water, surface water, agricultural ditch water, agricultural soil, forest soil, bed sediment, and cored sediments of the Pocomoke River Basin. In addition, we will determine if the observed concentrations are related to land use, such as proximity to agricultural fields, that receive poultry waste for fertilizer or to a potential natural source of arsenic. Lastly, we are examining the effects of hydrogeology in order to understand the mechanisms by which arsenic reacts and is transported in the basin.

Concentrations of total arsenic in fresh poultry manure collected from the Pocomoke River Basin were as high as 27 mg/kg, whereas older, composted manure contained less than 2 mg/kg total arsenic. It is likely that some arsenic in composting manure is leached into water during rain events and volatilized. Rutherford and others (2000) performed an extraction experiment in which poultry litter was amended with a known amount of an organic arsenic feed additive. After the litter was shaken with de-ionized water, more than 70% of the total arsenic added was recovered as inorganic As (V) in the water. We found 1-2 mg/kg total arsenic in agricultural and forest soil of the Pocomoke River Basin; these soils had similar concentrations of total arsenic as the older, composted manure sample. Base-flow concentrations of arsenic in suspended particles and in bed sediment in the Pocomoke River and its tributaries were 0.8-21 mg/kg in both 1997 and 1999 (Miller and others 2000); these concentrations are moderate to high when compared to national averages for river samples (Rice, 1999).

Although the initial input of arsenic from poultry waste to the basin is in the form of organic arsenic compounds, we found mostly inorganic arsenic (As III and As V), and lower concentrations of methylated arsenic in pore water from cored sediments collected beside an agricultural field. Total arsenic in pore water from sediments collected at land surface and at depths to 8 feet ranged from below detection limits to as high as 29 ug/L in surface sediments (fig. 1). The As (V) concentrations were elevated (29 ug/L) in pore water from the near-surface sandy soil and from an iron-rich clay silt layer at depth (24 ug/L). As (III) was not detected in the near-surface sediments, but increased with depth to 11 ug/L.

Figure 1. Arsenic concentrations and speciation in pore water from core sediments near an agricultural field in the Pocomoke River Basin.



Concentrations of total dissolved arsenic (0.45 microm filtered) in water samples from the Pocomoke River did not exceed 1.6 microg/L during base-flow (table 1). Base-flow concentrations of total dissolved arsenic were within the ranges found in other tributaries of the Delmarva Peninsula that are dominated by agriculture, but have a lower density of poultry operations. Concentrations of total dissolved arsenic in agricultural ditches and the in main stem of the Pocomoke River increased during high flow, presumably due to runoff.

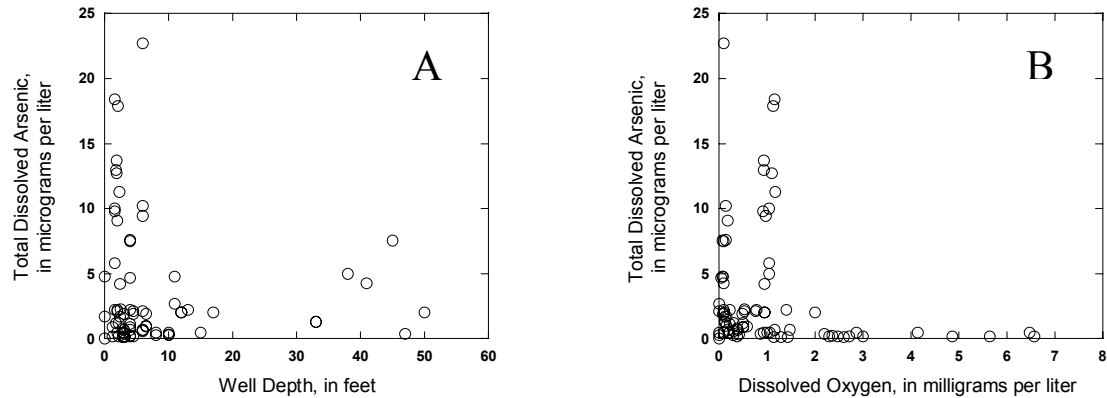
Table 1. Ranges of total dissolved arsenic concentrations in waters of the Pocomoke River Basin. ¹Lower level detection limits vary depending on laboratory and method.

Sample Type	Location	Range of concentrations ¹
Surface Water		
Base flow	Pocomoke River, lower basin, tidal	0.4 - 0.8 ug/L
Base flow	Pocomoke River, upper basin, non-tidal	<1.0 - 1.6 ug/L
Storm flow	Pocomoke River, upper basin, non-tidal	1.6 - 3.4 ug/L
Base flow	agricultural Ditch, upper basin	0.5 ug/L
Storm flow	agricultural Ditch, upper basin	10.4 ug/L
Ground Water		
Well	deep	<1.0 - 7.6 ug/L
Piezometer	shallow	<0.1 - 22.7 ug/L
Core	shallow pore water beneath agricultural field	6.8 - 28.7 ug/L

Shallow ground water from piezometers near agricultural fields, which had total dissolved arsenic concentrations as high as 23 microg/L (fig 2A), appears to be an important reservoir for arsenic cycling in the Pocomoke Basin. Water from a deeper, semi-confined part of the surficial aquifer system, which is a drinking water source, had total dissolved arsenic concentrations as high as 8 microg/L (fig 2A) (The U.S. Environmental Protection Agency has proposed to reduced the arsenic drinking water standard from 50 to 10 microg/L). This deeper ground water also had relatively high concentrations of dissolved iron (25-29 mg/L) and did not contain any obvious signs of agricultural influence (for instance, nutrient concentrations were low and few pesticides were detected). This suggests two sources of arsenic in the basin; poultry waste spread on land, and a natural source associated with iron-rich sediments, particularly at depth. Elevated arsenic concentrations were observed in ground water with low (less than 1 mg/L) dissolved oxygen content (fig 2B), and under these reducing conditions, ground water has the potential to mobilize arsenic from the reduction of metal oxides. Several mechanisms can mobilize arsenic from minerals or coatings, including bacterially mediated reduction of iron (III) to soluble iron (II), which can liberate co-precipitated arsenic that is adsorbed onto iron oxides (Cummings and others, 1999; Zobrist and others, 2000).

To understand all the potential sources and sinks of arsenic in the basin, we will analyze total arsenic concentrations in soil and bed sediment samples representing varying intensities of agricultural land use. Core sediment collected from various locations and representing various land uses in the basin will be analyzed for total arsenic, carbon, and sulfur. In addition, grain-size analyses and sequential partial extractions will be performed to characterize the sediments. We will collect a storm-runoff samples for measurement of total arsenic and arsenic speciation in both whole water and dissolved (filtered) samples. Sampling also will be expanded to other tributaries in the Chesapeake Bay Watershed affected by high-density poultry operations.

Figure 2. Concentrations of arsenic in relation to well depth (A) and dissolved-oxygen concentrations (B) in ground water of the Pocomoke River Basin.



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