



Organic Compounds and Trace Elements in the Pocomoke River and Tributaries, Maryland

Open-File Report 99-57
(Revised January 2000)

In cooperation with

George Mason University
and

Maryland Department of the Environment

U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY



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By Cherie V. Miller, Gregory D. Foster, Thomas B. Huff, and John R. Garbarino

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U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

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CONTENTS

Abstract.....	1
Introduction.....	1
Background	2
Description of Study Area	4
Acknowledgments	4
Sample Collection and Handling	5
Analysis of Samples	7
Field Conditions at Time of Sampling	16
Results of Trace-Element Analysis	16
Results of Organic-Compound Analysis	26
Summary and Implications	30
References Cited	32

FIGURES

1. Locations of water-quality sampling stations in the Pocomoke River and tributaries. Locations of three areas in the Lower Eastern Shore of Chesapeake Bay that experienced fish-kill events in 1997 are also indicated.....3

TABLES

1. Locations and station descriptions of Pocomoke River sampling stations.....5
2. Quality assurance results for dissolved trace elements determined by Inductively Coupled Plasma- Mass Spectrometry (ICP-MS)
 - a) Dissolved trace-element concentrations measured in field blanks and replicate field samples by ICP-MS.....8
 - b) Dissolved trace elements determined for USGS standard reference water samples by ICP-MS.....9
3. Quality-assurance results for dissolved trace-element measurements determined by Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS)
 - a) Dissolved arsenic and selenium concentrations measured in field blanks by GGF-AAS.....10
 - b) Dissolved trace elements determined in USGS standard reference water samples – analyses by GF-AAS.....10
4. Quality-assurance results for dissolved trace-element measurements in chelation extracts determined by Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS)
 - a) Quality-assurance blank-subtracted results for dissolved trace-element measurements in chelation extracts using ICP-MS.....11
 - b) Blank-subtracted results for dissolved trace elements determined in chelation extracts of USGS standard-reference water sample T145 by ICP-MS.....11
5. Quality-assurance results for particulate trace-element measurements.
 - a) Precision of particulate-trace-element, total-organic-carbon, and total-sulfur measurements in water samples collected on September 30, 1997 (station 01485730) and on April 10, 1998 (Chesterville Branch, USGS station 01493112).....13

b) Results of analyses for particulate trace elements in selected standard reference materials.....	14
6. Gas Chromatograph-Mass Spectrograph parameters used in the analysis of steroids in samples of sediment and chicken manure from the Pocomoke River Basin.....	15
7. Field-measured parameters for sampling stations in the Pocomoke River Basin	
a) Field-measured parameters and suspended-sediment concentrations for sampling stations in the Pocomoke River Basin on September 30, 1997.....	17
b) Field-measured parameters and suspended-sediment concentrations for sampling stations in the Pocomoke River Basin on February 12, 1999.....	17
8. Laboratory determinations for major-ion concentrations, specific conductance, and pH for samples collected in the Pocomoke River Basin on February 12, 1999.....	18
9. Dissolved trace-element concentrations from water-column samples collected in the Pocomoke River Basin	
a) Dissolved trace-element concentrations for direct-injection Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analysis on water-column samples collected in the Pocomoke River Basin on September 30, 1997.....	19
b) Dissolved trace-element concentrations for direct-injection Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analysis on water-column samples collected in the Pocomoke River Basin on February 12, 1999.....	20
c) Dissolved arsenic and selenium concentrations determined by Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS).....	21
d) Blank-subtracted dissolved trace-element concentrations determined in chelation-extracts by ICP-MS.....	21
10. Particulate-trace-element, total-organic-carbon, and total-sulfur concentrations from water column samples collected in the Pocomoke River Basin	
a) Particulate trace-element, total organic-carbon, and total sulfur concentrations from water-column samples collected in the Pocomoke River Basin on September 30, 1997.....	22
b) Particulate trace-element, total organic-carbon, and total sulfur concentrations from water-column samples collected in the Pocomoke River Basin on February 12, 1999.....	23
11. Bed-sediment-trace-element, total-organic-carbon, and total-sulfur concentrations from samples collected in the Pocomoke River Basin on September 30, 1997.....	24
12. Selected pesticide and pesticide-metabolite concentrations for samples collected in the Pocomoke River Basin on September 29, 1997.....	27
13. Selected Polyaromatic Hydrocarbon (PAH) concentrations from samples collected in the Pocomoke River Basin on September 29, 1997.....	28
14. Gas-chromatogram peak-area counts for cholesterol in samples collected in the Pocomoke River Basin in 1997.....	29
15. Mean concentrations of steroidal lipids in Pocomoke River bed sediment collected near the shoreline at station 01485705 on December 13, 1997.....	29

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ABSTRACT

In response to concern about recent blooms of the dinoflagellate, *Pfiesteria piscicida*, samples of sediment and water were collected from the lower Pocomoke River Basin and were screened for trace elements, pesticides, and other organic compounds. A large group of steroid and fatty acid methyl-ester compounds was detected in streamwater using gas chromatography/mass spectroscopy in scan mode. Some of these steroid compounds have been identified and further quantified in bed-sediment extracts. Spatial patterns of the concentrations of cholesterol suggest that these compounds are linked to the runoff of animal wastes into the river. Many of the organic compounds found in the Pocomoke River sediments have not yet been identified, but at least several are in the class of hormone compounds related to estradiols and have the potential to promote endocrine-disrupting effects in aquatic life. Particulate forms of arsenic and zinc are slightly elevated above normal levels for streams, but the sources for these elements are still undetermined. Several pesticides were found in low, parts-per-trillion concentrations, but were within the ranges commonly found in streams of this region.

INTRODUCTION

Fish kills and human-health advisories in several tributaries of the Chesapeake Bay on the Eastern Shore of Maryland in 1997 have been attributed to blooms of the dinoflagellate *Pfiesteria piscicida*, and may be tied or linked to nutrient pollution that stimulates the growth of this organism. Sampling in the Pocomoke River by State and other agencies has been limited to a select suite of constituents, primarily phosphorus, nitrogen, and major-use pesticides (Eskin and others, 1997). The study described here is the first seeking evidence of other forms of contamination in the affected areas by measuring the concentrations of a large suite of trace elements and by use of gas chromatography/mass spectroscopy (GC/MS) in scan mode to search for non-target compounds.

This report presents trace-element, pesticide, and organic-compound concentration data for samples of water and sediment collected in the fall of 1997 at selected stations in the mainstem of the Pocomoke River and on several small tributaries or ditches in this basin. Additionally, a sediment sample and a chicken-manure sample, both collected within the study area, were compared to identify similar organic compounds. Some stations were resampled for trace-element analysis in February 1999 to verify earlier results. These data were evaluated in the context of the recent fish kills in this and other tributaries, with the hypothesis that chicken manure may be a source of trace-element and/or organic-compound contaminants to the Pocomoke River. Numerous inorganic and organic compounds are used as commercial poultry-feed additives (Animal Health Institute, 1996), and are assumed to be transferred to the watersheds through the disposal of poultry litter.

This report, originally released in January 1999, has been revised due to artifacts with analytical methods for dissolved arsenic and selenium by the direct-injection Inductively Coupled Plasma-Mass Spectrometry method (ICP-MS), that were identified after publication of the original report. Because of these earlier problems with the data, a detailed review of the methodologies used and quality-assurance data has been added to this report.

Background

Water-quality data for the southern end of the Delmarva Peninsula (the peninsular part of Maryland, Delaware, and Virginia; fig. 1) are limited. For the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) study of the Delmarva Peninsula, 100 samples for analysis of pesticides and nutrients were collected from drinking-water wells across the peninsula from 1988 through 1990. In that study, the most commonly detected organic compounds in ground water were the triazine and acetanilide herbicides and degradation products from these compounds, but few detections exceeded 3 µg/L (micrograms per liter) (Koterba and others, 1993). Trace levels of arsenic, selenium, and cadmium also were detected in approximately 18 percent of the surface- and ground-water samples analyzed for trace elements (Shedlock and others, 1999).

Gupta and Karuppiah (1996 a,b) studied interstitial pore waters and whole sediments collected in the Pocomoke River and concluded that the sediments were anthropogenically enriched with zinc, lead, copper, arsenic, and cadmium, with concentrations in porewaters exceeding the freshwater acute criteria for aquatic life for zinc, lead, and cadmium. Their evidence was based on a decrease in concentrations moving away from agricultural sources and a decrease with depth into the sediments, as well as comparison of results to studies in other estuaries. They also found that on the basis of several toxicity tests, sediments at their sampling stations were “very or extremely toxic,” that toxicity decreased with depth into the sediment, and that total chlorine and metals were the primary causes of the toxicity.

The Maryland Department of Natural Resources (MdDNR) is currently conducting several studies in the upper reaches of the Pocomoke River Basin to collect baseline data for nutrients in agricultural watersheds, to document the effects of best management practices, and to determine the cause of lesions on fish. The USGS Chesapeake Bay Ecosystem Project and the USGS Maryland-Delaware-D.C. District are collaborating with MdDNR to quantify the surface- and ground-water components of the nutrient loads from these basins and to collect stormwater samples.

The Maryland Department of the Environment (MDE) also has been collecting surface-water and bed-sediment nutrient data at selected stations in the lower tidal parts of the Pocomoke River (Eskin and others, 1997), and is sending additional surface-water samples to the University of Maryland Chesapeake Biological Laboratory (CBL) for analysis of pesticides and trace metals.

Helz and others (1985) established baseline values for selected trace metals in Coastal Plain deposits and used these to infer anthropogenic enrichments in some areas of Chesapeake



Explanation	
★	Fishkill sites in the lower eastern shore of the Chesapeake Bay (1997)
▲	Surface Water Sampling Sites
01485705	Site Identifier

Figure 1. Location of water-quality sampling sites in the Pocomoke River and tributaries in Maryland

Bay sediments. Other recent studies to measure contaminants in Chesapeake Bay sediments include: Velinsky and others (1994), for organic compounds in the Potomac and Anacostia Rivers; Wade and others (1994), for trace metals in the Potomac and Anacostia Rivers; and Owens and Cornwell (1995), for trace metals in the central mainstem of the Bay. Eskin and others (1996) provided a comprehensive summary of recent information on contaminants in Chesapeake Bay sediments. Except for the more contaminated areas such as the Baltimore Harbor, and the Anacostia and Elizabeth Rivers (the Chesapeake Bay Program's three major "Regions of Concern"), reliable data on trace metals and organic compounds in Chesapeake Bay surface water are very sparse due to limitations in the techniques used to measure low ambient concentrations. The report of the Fall Line Toxics Monitoring Program for 1994 contains the most accurate measurements for dissolved and particulate trace-element and organic-compound data in the Chesapeake Bay (Chesapeake Bay Program, 1996).

Description of Study Area

The Pocomoke River is a tributary in Maryland on the lower Eastern Shore of the Chesapeake Bay estuary (fig. 1). The Pocomoke watershed is within the Atlantic Coastal Plain and is underlain by an extensive unconfined surficial aquifer composed of fluvial sands and silts. This aquifer is under shallow water-table conditions, and supplies much of the groundwater flow to the local tributaries. Most of the homes within the Pocomoke River drainage area use wells completed in the surficial aquifer for household water supply, and have individual septic systems.

Ditching is very common in the Pocomoke River Basin due to poor drainage and the shallow water table. The topography is flat and the relief is low, and because of the extensive ditching, many of the river segments are unprotected by significant riparian zones. Most of the watersheds are small and have only first- and second-order streams that may be subject to tidal incursions. Agriculture is the dominant land use in the Pocomoke River Basin (Shedlock and others, 1999) and concentrated poultry operations with adjacent corn fields dominate the landscape.

The lower part of the Pocomoke River is tidally influenced and has brackish water with salinities ranging up to 14 ppt (parts per thousand). The river and tributaries are organic-rich, with characteristic tea-colored water and high levels of total organic carbon (TOC) in bed sediment.

Acknowledgments

This study was done under the aegis of the Chesapeake Bay Program's Fall-Line Toxics Project. The authors would like to thank Captain Jack Howard for providing transportation to stations on the mainstem of the Pocomoke River, and the Maryland Departments of the Environment and Natural Resources for coordination on sampling stations and assistance with the collection of organic samples. Brenda Feit-Majedi and David Brower of the USGS provided invaluable service in collecting these samples under difficult field conditions. Arthur Horowitz

and Kent Elrick, also of the USGS, provided excellent technical assistance in analyzing trace-element samples, as did Kimberly Lauer at George Mason University in analyzing and evaluating the sterol compounds in sediment and chicken-manure samples. The authors also appreciate the thoughtful technical reviews by Gary Fisher, Rosanna Kroll, James Gerhart, and Tracy Hancock, as well as thorough editing by Valerie Gaine and Chester Zenone.

SAMPLE COLLECTION AND HANDLING

Results presented in this paper are based on analyses of samples of water and sediment collected in the Pocomoke River and its tributaries under baseflow conditions (table 1). Streamwater at five stations was sampled on September 29-30, 1997. Samples were collected at two stations on the mainstem of the Pocomoke River: one at the mouth near Fair Island (station 01485730) and one several miles upstream near Rehoboth Branch (01485705). Both of these stations had major fish kills in August and September of 1997 that were potentially related to *Pfiesteria piscicida* blooms. The tide was flowing out strongly when these two stations were sampled in 1997. Three other stations in small freshwater streams or ditches that drain to the Pocomoke River or Marumsco Creek also were sampled. Two of the streams directly drain agricultural areas with a high density of chicken houses (stations 01485700 and 01485720), and the Marumsco Creek station (01485750) was selected as a control station with tree farms and black-water forest as the dominant apparent land cover in the contributing watershed. The water at stations 01485720 and 01485750 did not appear to be flowing during any of the sampling times. Follow-up samples (December 1997) of riverbed sediment at station 01485705 and chicken manure from a storage shed near Shelltown, Md., were collected in December, 1997, for further investigation of sterol compounds.

Table 1. Locations and station descriptions of Pocomoke River sampling stations

Field ID ¹	Station Name	USGS Station Number	Station Description	Lat/Long	
NP-B	Pocomoke River near Kingston, Md.	01485705	Mainstem of the Pocomoke River off the Rehoboth Boat Ramp, several miles upstream from the mouth.	38°02'19" 75°39'42"	Mainstem Stations
NP-A	Fair Island Canal near Kingston, Md.	01485725	Just east of Fair Island Canal in the mainstem of the Pocomoke River.	37°57'48" 75°39'16"	
NP-A1	Pocomoke Sound near Kingston, Md.	01485730	By Fair Island at the mouth of the Pocomoke River.	37°57'02" 75°39'14"	
NP-1	Rehoboth Branch near Kingston, Md.	01485700	A small stream draining agricultural areas, north of Shelltown, Md.	38°03'31" 75°39'38"	Tributary Stations
NP-5	Pocomoke River trib near Kingston, Md.	01485720	A ditch draining directly from a farm field and chicken house, south of Shelltown, Md.	37°58'16" 75°38'06"	
NP-6	Unnamed Ditch near Kingston, Md.	01485722	A tidally influenced ditch draining directly from a farm field.	37°58'33" 75°39'09"	
NP-7	Marumsco Creek trib near Kingston, Md.	01485750	A ditch draining to Marumsco Creek; "Control Station."	37°59'34" 75°41'18"	

¹ Field IDs correspond to Maryland Department of the Environment designated station locations

In February 1999, a comparison study was conducted to resolve discrepancies in data collected by USGS and analyses by the CBL. The same five locations were sampled with a slight shift in location for two of the stations for logistical reasons – stations 01485730 and 01485720 were moved to stations 01485725 and 01485722, respectively. It is assumed that results for these stations would not differ significantly for spatial reasons, because the surrounding environments are very similar. At stations 01485725 and 01485700, duplicate samples were collected by USGS and CBL personnel and exchanged for analysis to determine if there were artifacts from sampling techniques or analytical methods. Results analyzed by CBL are published in a separate report (Baker and others, 1999).

Trace elements and organic compounds (dissolved and particulate phases) were analyzed in surface water, and trace elements were analyzed in bed sediments from all five sampling stations in 1997. Samples were collected for surface water only in 1999. All samples were collected at the center of flow. Samples for dissolved trace metals were collected with a peristaltic pump using an in-line 0.45 µm polycarbonate capsule filter. All field processing for dissolved metals was conducted inside a portable isolation chamber to avoid atmospheric contamination. Dissolved-metal samples were fixed within 24 hours with 5 mL of Optima HNO₃ per liter of sample, double bagged in acid-washed zip-lock plastic bags and shipped overnight on ice to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. Samples of whole water for the analysis of particulate trace-elements were collected by dipping two high-density polyethylene carboys (total volume -- 30 liters) directly into the stream. Bed sediments were collected by dipping clean glass jars directly into the sediments or from the center of an Eckman dredge sample. The carboys were shipped with bed-sediment samples overnight (without ice) to the USGS Georgia District Laboratory. Samples for organic analysis were collected into 4-liter, brown, baked-glass bottles, transported directly to the Shared Research Instrumentation Facility (SRIF) at George Mason University, and kept at 4 °C (degrees Celsius) until extraction. Ultra-clean sampling techniques were used for the collection of all surface-water samples and are documented in more detail in the 1994 final report of the Chesapeake Bay Fall Line Toxics Monitoring Program (Chesapeake Bay Program, 1996).

On December 13, 1997, a single bed-sediment sample was collected near the shore at Station 01485705, and a sample of 4-week-old chicken manure was collected from a nearby farm storage shed. These two samples were shipped overnight (without ice) to the SRIF, where they were stored at 4°C for subsequent analysis for selected steroid compounds.

A hydrolab maintained and operated by MdDNR was used to measure field parameters at the mainstem river stations in both 1997 and 1999. For other stations, field measurements were made by USGS personnel. Dissolved oxygen was measured using the Winkler method, and pH was measured using an Orion pH meter with a solid-gel combined electrode. Suspended-sediment samples were collected in a 500-mL (milliliter) dip bottle and analyzed by gravimetric methods at the USGS Kentucky District Laboratory in 1997, and at the USGS Georgia District Laboratory in 1999.

ANALYSIS OF SAMPLES

Concentrations of dissolved trace elements were determined by several methods at the NWQL. Samples for dissolved trace elements collected in 1997 were all analyzed by direct-injection, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using pneumatic nebulization sample introduction. Samples from stations 01485705 and 01485730 were diluted by 500x and 1,000x, respectively, to reduce physical interferences associated with the saline matrices, and arsenic and selenium determinations were corrected for chloride interference. Such dilutions have significantly reduced the precision; therefore, trace-element data from these two stations in 1997 should be viewed as qualitative. Reporting limits for each element measured in these two samples were determined by taking the standard deviation of three separate readings and multiplying this number by two. In a subsequent review of this method, it was determined that other interfering artifacts were present in the sample matrix, particularly for dissolved arsenic and selenium. The presence of relatively high concentration of bromide from seawater caused a large positive interference on the measurement of arsenic and selenium by ICP-MS. Additionally, the effects of relatively high inorganic and organic carbon concentrations positively biased dissolved chromium determinations. Details of corrections used for these interferences can be found in Garbarino (1999). When samples were collected in February 1999, several analytical methods were used to compare and better quantify the trace-element concentrations: (1) ICP-MS analysis was used for all trace elements as in 1997. Dilutions of 5x were used for samples from stations 01485722 and 01485750, and a 10x dilution was used for samples from station 01485725; (2) arsenic and selenium concentrations were also determined by Graphite Furnace – Atomic Absorption Spectroscopy (GF-AAS) using direct-injection and no dilution; and (3) a chelation-extraction procedure was used with ICP-MS to measure dissolved vanadium, chromium, manganese, cobalt, nickel, copper, zinc, molybdenum, cadmium, and lead. The extraction procedure is similar to the method used by the U.S. Environmental Protection Agency (Long and Martin, 1991); however, the major differences were that the trace elements were not concentrated after the removal of the matrix elements and the trace elements were not determined in real time by ICP-MS. Ten milliliters (mL) of sample was passed through a column packed with macroporous iminodiacetate chelating resin. Dissolved trace metals were preferentially sequestered by the resin relative to the alkaline and alkaline-earth elements. In general, the greater the cationic charge of the elemental ion, the more strongly the ion is bound to the resin. Consequently, elements that can exist in an anionic form, such as chromium, are not retained by the resin, leading to negatively biased results. After the alkaline and alkaline-earth elements were washed from the resin with an acetate buffer, trace elements were eluted from the resin with 10 mL of 1 molar nitric acid and analyzed by ICP-MS. All laboratory methods at NWQL are documented and verified for bias, accuracy, and precision with standard-reference materials and through participation in the USGS Office of Water Quality sample-testing program (Maloney and others, 1994; Pritt and Raese, 1995). Documentation of the ICP-MS method for low-level trace-element analysis is given in Garbarino and Taylor (1994) and Garbarino (1999). Documentation of the GF-AAS method for arsenic and selenium is given in Jones and Garbarino (1999). Quality-control results for analyses of dissolved trace elements in blanks, field samples, and for standard-reference materials are presented in tables 2 through 4. Quality-assurance results for some of the elements using the chelation-extraction procedure were not as good as those determined by other methods (tables 4a and 4b). Recoveries for chromium and zinc from standard-reference materials were

Table 2a. Dissolved trace-element concentrations measured in field blanks and replicate field samples by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

[Field-blank samples were collected at the Pocomoke River station 01485720 on September 30, 1997, at Pocomoke River station 01485705 on February 12, 1999, and at a Fall Line Toxics Monitoring Program station on the Chester River (01493112) on August 11, 1998. One set of triplicate field samples was collected at station 01493112 on May 28, 1998, and one set of duplicate field samples was collected at station 01485750 on February 12, 1999. Concentration values and standard deviations (for triplicate values) are given for the replicates. All units are in micrograms per liter. INT, not reported due to interference; S.D., standard deviation]

ICP-MS	Field Blank (9/30/97)	Field Blank (8/11/98)	Field Blank (2/12/99)	Field Blank (2/12/99)	Triplicate Concentration Values (S.D.) (5/28/98)	Duplicate Concentration Values (2/12/99)
Aluminum	0.13	<0.04	0.136	0.427	2.25/2.42/2.55 (0.15)	2620/2420
Silver	0.006	0.02	0.031	<0.02	.011/.014/.037 (0.014)	0.078/0.045
Arsenic	0.03	0.02	0.02	0.01	.42/.435/.43 (0.0076)	INT
Barium	0.06	0.004	0.065	0.016	99/99/97.1 (1.10)	143/142
Beryllium	0.03	<0.008	<0.03	<0.03	.023.028/.02 (0.004)	1.7/1.74
Boron	ND	0.30	4.58	4.88	8.4/8.6/8.8 (0.20)	319/327
Cadmium	<0.04	<0.004	0.005	0.005	.015/.021/.028 (0.0065)	0.367/0.38
Cobalt	0.03	<0.002	0.001	0.003	.303/.302/.305 (0.0015)	10.6/10.7
Chromium	0.1	0.028	0.399	0.777	2.08/2.3/2.16 (0.111)	3.14/2.58
Copper	<0.1	0.014	0.093	0.117	.47/.481/.475 (0.0055)	2.76/2.46
Lithium	0.016	0.024	0.041	0.027	.65/.70/.71 (0.032)	10.6/11.2
Manganese	0.02	0.002	0.047	0.074	175.3/178/175 (1.65)	210/219
Molybdenum	0.07	0.022	0.031	<0.01	.172/.174/.182 (0.0053)	0.396/0.34
Nickel	<0.02	0.007	0.031	0.038	1.77/1.73/1.75 (0.02)	15.5/15.9
Lead	0.04	0.005	0.008	0.023	.013.016/.021 (0.004)	0.985/0.98
Antimony	0.004	0.064	<0.08	<0.08	.097/.100/.118 (0.011)	0.179/<0.08
Selenium	0.04	<0.16	0.185	0.132	.26/.28/.29 (0.015)	INT
Strontium	0.04	0.005	0.042	0.134	85.3/86.2/84.76 (0.727)	960/947
Uranium	0.004	0.001	<0.002	<0.002	.012/.013/.012 (0.0006)	0.116/0.123
Vanadium	0.066	0.014	0.04	0.06	.74/.78/.75 (0.021)	<0.08/<0.08
Zinc	0.2	<0.006	0.504	0.199	1.985/2.08/2.055 (0.049)	102/104

Table 2b. Dissolved trace elements determined for USGS standard reference water samples by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) [All units are in micrograms per liter. ICP-MS results correspond to analyses of standard-reference water sample T145 performed at the beginning, middle, and end of the batch of samples. Data for T145 are published in Farrar and Long (1997).]

	ICP-MS Results	T145 Most Probable Value
Aluminum	59 ± 1	68 ± 11
Silver	7.9 ± 0.1	7.6 ± 9
Arsenic	9.68 ± 0.08	10 ± 1
Barium	38.9 ± 0.6	37 ± 2
Beryllium	9.6 ± 0.3	9.0 ± 0.7
Boron	46.2 ± 0.6	46 ± 6
Cadmium	9.6 ± 0.2	9.3 ± 0.8
Cobalt	10.0 ± 0.1	10 ± 0.9
Chromium	15.5 ± 0.2	15 ± 1
Copper	11.53 ± 0.06	11 ± 1
Lithium	26.87 ± 0.06	27 ± 2
Manganese	20.7 ± 0.1	21 ± 2
Molybdenum	9.4 ± 0.2	9 ± 1
Nickel	11.7 ± 0.2	11 ± 1
Lead	13.0 ± 0.2	13 ± 1
Antimony	9.2 ± 0.1	9 ± 1
Selenium	9.7 ± 0.1	10 ± 1
Strontium	204 ± 6	203 ± 9
Uranium	1.20 ± 0.02	1.1 ± 0.1
Vanadium	11.2 ± 0.06	12 ± 2
Zinc	9.8 ± 0.2	10 ± 2

Table 3a. Dissolved arsenic and selenium concentrations measured in field blanks by Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS)
 [Samples were collected at the Pocomoke River station 01485705 on February 12, 1999. Laboratory reporting limits for both elements were 0.9 micrograms per liter, so all values are presented only as estimates. All units are in micrograms per liter.]

GF-AAS	Field Blank (2/12/99)	Field Blank (2/12/99)	Duplicate Concentration Values (2/12/99)
Arsenic	0.3	0.1	0.6/0.3
Selenium	0.5	0.5	0.1/0.1

Table 3b. Dissolved trace elements determined in USGS standard reference water samples – analyses by Graphite Furnace-Atomic Absorbtion Spectroscopy (GF-AAS)
 [All units are in micrograms per liter. Standard reference water samples T133, T139, T143, and T149 Most probably value (MPV) data are published in open -file reports by Long and Farrar (1995), Farrar and Long (1996), Farrar and Long (1997), and Farrar (1997), respectively.]

GF-AAS	Arsenic	Selenium
T133	27.4	22.3
MPV	27 ± 3	21 ± 4
T139	5.8	4.1
MPV	6 ± 1	5 ± 1
T143	16.3	10.1
MPV	15 ± 1	10 ± 2
T149	0.8	1.8
MPV	1 ± 0.6	2.1 ± 0.8

Table 4a. Quality-assurance blank-subtracted results for dissolved trace-element measurements in chelation extracts using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

[The undiluted sample from station 01485725 was used for spike recovery and duplicate determinations. A sample was also collected by personnel from the Chesapeake Biological Laboratory (CBL) to rule out sampling artifacts. The sample was spiked with 10 micrograms per liter of each element. All units are in micrograms per liter (µg/L).]

Chelation-Extraction ICP-MS	Lab Blank	Field Blank	Spike Recovery (in percent)	Duplicate Concentration Values	Duplicate sample collected by CBL
Cadmium	2.8	0.4	81	0.5/0.7	0.7
Cobalt	0.002	0.006	97	0.21/0.20	0.18
Chromium	0.45	0.23	95	0.06/0.02	0.01
Copper	0.20	0.02	90	1.1/0.9	0.9
Manganese	0.27	0.34	78	41/42	40
Molybdenum	0.096	0.02	94	2.4/2.4	2.3
Nickel	0.40	0.08	92	0.50/0.55	0.51
Lead	0.046	0.01	90	0.01/0	0.003
Vanadium	0.13	0.06	100	0.42/0.39	0.39
Zinc	1.8	0.4	90	2.9/3.1	2.3

Table 4b. Blank-subtracted results for dissolved trace elements determined in chelation extracts of USGS standard-reference water sample T145 by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

[A 1:10 dilution of the standard-reference material was also analyzed to detect matrix and background effects. All units are in micrograms per liter. Most probable value (MPV) data for T145 are published in Farrar and Long (1997)].

	Extraction Results	Extraction Results 1:10 dilution	T145 MPV
Cadmium	7.8	1.0	9±1
Cobalt	9.9	1	10±1
Chromium	6.9	1.0	15±1
Copper	9.8	1.1	11±1
Manganese	21	2.1	21±2
Molybdenum	8.5	1.2	9±1
Nickel	9.7	0.82	11±1
Lead	12	1.2	13±1
Vanadium	11	1.2	12±2
Zinc	6.6	1.1	10±2

poor, and blanks for these elements as well as for cadmium and nickel were close to the ranges of ambient concentrations. Therefore, concentrations that are reported from the chelation-extraction method should be viewed as qualitative and used primarily for comparison to other techniques.

Samples for analysis of major ions were collected in 1999 and shipped on ice to the NWQL. The analytical methods for major ions are documented in Fishman and Friedman (1989).

For particulate trace-element analysis, samples of approximately 30 L (liters) were collected in high-density polyethylene carboys and shipped to the USGS Sediment-Partitioning Project Laboratory in Atlanta, Ga. At the laboratory, suspended sediment was separated from whole water by continuous tangential-flow centrifugation in a Westfalia centrifuge. Samples were processed at 4 liters per minute. The sediment was then freeze-dried and digested with inverse Lefort aquaregia (2 mL hydrofluoric acid / 6 mL nitric acid / 4 mL perchloric acid) in open vessels under a laminar-flow hood. Acid digestates were analyzed by ICP except for silver, cadmium, and lead, which were analyzed by flame atomic-absorption spectroscopy. Arsenic, selenium, and antimony were extracted and analyzed separately as the hydrides. Mercury was also analyzed separately using a cold-vapor method. Total carbon and total sulfur were determined on a Leco SE444 DR carbon/sulfur analyzer. The analytical methods are slightly modified from those used by Horowitz and others (1989). Precision for particulate trace elements was estimated from two sets of field triplicates (table 5a). Results for standard reference materials are presented in table 5b and in Horowitz and others (1989).

Methods and quality assurance for the analysis of pesticides and other organic compounds in surface water are documented in the 1994 Final Report of the Chesapeake Bay Fall Line Toxics Program (Chesapeake Bay Program, 1996). In brief, the streamwater samples were concentrated using a Goulden continuous-flow extractor, dried with anhydrous sodium sulfate, and reduced to approximately 1 mL by flash rotary evaporation and nitrogen-gas blowdown. The samples were then analyzed by GC-MS for target pesticides and polyaromatic hydrocarbons (PAHs), and then by broad GC scans with MS library searches for selected peaks to screen for unknown compounds.

Steroids were extracted from sediment samples and from the sample of chicken manure by column chromatography and analyzed by use of GC-MS. The samples were initially weighed (3 to 8 grams per sample), dried with anhydrous sodium sulfate, extracted three times into a 2:1 mixture of dichloromethane and methanol, saponified with 2-molar-methanolic potassium hydroxide, and extracted into dichloromethane (DCM), followed by flash rotary evaporation for a final sample volume of 5 mL. The extracts were then fractionated by column chromatography to isolate the steroids using a modified procedure from Shan and others (1994). The fractionation columns contained sodium sulfate, silica gel, and 4-percent water-deactivated alumina. The columns were eluted with 40 mL each of n-hexane, 1:1 DCM/hexane, 1:1 DCM/methanol (MeOH), and finally MeOH. Prior to analysis of the samples, a steroid spike was eluted to determine the elution order. After column fractionation, the sample was concentrated using a Savant speed-vac and nitrogen-gas blowdown to reduce the volume to 0.5 mL. Samples were then analyzed using a Hewlett Packard (HP) bench-top GC-MS and

Table 5a. Precision of particulate-trace-element, total-organic-carbon, and total-sulfur measurements in water samples collected on September 30, 1997 (Pocomoke Sound near Kingston, Md., USGS station 01485730) and on April 10, 1998 (Chesterville Branch, USGS station 01493112).

[Concentration values and standard deviations are given for each set of replicates. Except where noted, units are in milligrams per kilogram. Where all three measurements were less than the reporting limit, no standard deviation was determined. wt%, weight percent on a dry weight basis.]

	<u>September 30, 1997</u>		<u>April 10, 1998</u>	
	<u>Concentration Values</u>	<u>Standard Deviation</u>	<u>Concentration Values</u>	<u>Standard Deviation</u>
Aluminum ¹	6.2/6.2/6.2	0	11.2/11.1/11.3	0.100
Silver	<0.5/<0.5/<0.5	--	<0.5/<0.5/<0.5	--
Arsenic	14/14/14	0	19/20/20	0.6
Barium	280/260/290	15	870/790/960	85
Beryllium	1.8/1.8/1.8	0	4.0/3.9/4.2	0.20
Cadmium	0.3/0.3/0.3	0	0.3/0.2/0.3	0.058
Cobalt	12/12/11	0.58	20/22/18	2.0
Chromium	63/63/62	0.58	100/100/100	0
Copper	16/15/16	0.58	31/31/31	0
Iron ¹	3.6/3.6/3.6	0	6.0/6.0/6.0	0
Lithium	69/69/68	0.58	84/74/95	10
Manganese	1100/1100/1100	0	1300/1300/1300	0
Mercury	0.05/0.05/0.05	0	0.06/0.05/0.06	0.0058
Molybdenum	<5/<5/<5	--	<5/<5/<5	--
Nickel	28/29/26	1.5	51/50/52	1.0
Phosphorus	1300/1300/1300	0	2800/2700/2900	100
Lead	31/30/31	0.58	47/50/44	3.0
Antimony	0.8/0.8/0.7	0.058	1.0/0.8/1.1	0.15
Selenium	0.6/0.6/0.6	0	0.8/0.8/0.8	0
Strontium	620/610/630	10	77/76/78	1.0
Titanium ¹	0.44/0.44/0.43	0.0058	0.59/0.55/0.63	0.040
Thallium	<50/<50/<50	--	<50/<50/<50	--
Uranium	<50/<50/<50	--	<50/<50/<50	--
Vanadium	89/89/88	0.58	150/150/160	5.8
Zinc	180/180/180	0	170/170/170	0
Total Organic Carbon ¹	4.3/4.2/4.3	0.058	2.4/2.4/2.4	0
Total Sulfur ¹	2.3/2.2/2.4	0.12	0.1/0.1/0.1	0

¹Units are in weight percent on a dry weight basis

Table 5b. Results of analyses for particulate trace elements in selected standard reference materials [Reference materials were obtained from the National Institute of Standards and Technology (NIST 2709 and NIST 2711) and the U.S. Geological Survey (SDO - 1, SGR-2, and SCO-1). Except where noted, units are in milligrams per kilogram. ND, not determined; MPV, most probable value reported for the standard reference material.]

	USGS Results	NIST 2709 MPV	USGS Results	NIST 2711 MPV	USGS Results	USGS SDO-1 MPV	USGS Results	USGS SGR-2 MPV	USGS Results	USGS SCO-1 MPV
Aluminum ¹	7.4	7.5 ± 0.1	6.5	6.5 ± 0.1	6.6	6.5 ± 0.1	3.5	3.5 ± 0.1	7.4	7.2 ± 0.1
Silver	0.9	<0.5	4.2	4.6 ± 0.4	<0.5	0.2	<0.5	0.2	<0.5	0.1
Arsenic	19	18 ± 1	120	105 ± 8	78	69 ± 9	76	67 ± 5	13	12.4 ± 1.4
Barium	950	970 ± 40	690	730 ± 40	--	400 ± 40	260	290 ± 40	600	570 ± 30
Beryllium	4.7	ND	1.9	ND	2.6	3.3 ± 0.6	0.9	1.1 ± 0.2	1.5	1.9 ± 0.1
Cadmium	0.2	0.4 ± 0.01	41	41.7 ± 0.3	0.1	<2 - <10	0.8	0.9 ± 0.1	<0.1	0.2 ± 0.1
Cobalt	14	13 ± 1	11	(10)	55	47 ± 6	13	12 ± 2	13	11 ± 1
Chromium	110	130 ± 4	40	(47)	67	66 ± 8	31	32 ± 3	69	68 ± 5
Copper	32	35 ± 1	110	114 ± 2	58	60 ± 10	60	66 ± 9	27	29 ± 2
Iron ¹	3.5	3.5 ± 0.1	2.9	2.9 ± 0.1	6.6	6.5 ± 0.2	2.0	2.1 ± 0.1	3.6	3.6 ± 0.1
Lithium	54	ND	28	ND	27	29 ± 6	120	150 ± 30	38	45 ± 3
Manganese	550	540 ± 20	660	640 ± 30	320	320 ± 40	240	270 ± 30	400	410 ± 30
Mercury	1.4	1.40 ± 0.08	6.0	6.25 ± 0.19	0.19	0.19 ± 0.08	0.29	0.31	0.07	0.05
Molybdenum	<5	(2)	<5	(2)	170	130 ± 20	36	35 ± 1	<5	1
Nickel	130	88 ± 5	20	21 ± 1	100	100 ± 10	22	29 ± 5	19	27 ± 4
Phosphorus	670	620 ± 50	870	860 ± 70	520	480 ± 30	1500	1400 ± 300	1100	900 ± 90
Lead	19	19 ± 1	1100	1162 ± 30	26	28 ± 5	43	38 ± 4	33	31 ± 4
Antimony	6.5	7.9 ± 0.6	17	19 ± 2	4.1	4.1 - 4.8	2.8	3.4 ± 0.5	2.4	2.5 ± 0.1
Selenium	1.6	1.6 ± 0.1	1.3	1.5 ± 0.1	1.8	1.9 - 6.8	3.7	3.5 ± 0.3	0.9	0.9 ± 0.1
Strontium	220	230 ± 2.0	230	245 ± 1	75	75 ± 11	360	420 ± 20	160	170 ± 20
Titanium ¹	0.34	0.34 ± 0.02	0.30	0.31 ± 0.02	0.42	0.43 ± 0.02	0.15	0.15 ± 0.02	0.36	0.38 ± 0.04
Vanadium	110	112 ± 5	81	82 ± 3	160	160 ± 20	130	128 ± 6	130	130 ± 10
Zinc	110	106 ± 3.0	350	350 ± 5	72	64 ± 7	84	74 ± 9	120	100 ± 10
Total Organic Carbon ¹	1.1	1.2	1.8	2.0	9.8	10 ± 0.4	26.0	26.0	1.1	0.8 ± 0.1
Total Carbon	1.1	1.2	1.8	2.0	9.3	10 ± 0.4	26.0	26.0	1.0	0.8 ± 0.1
Total Sulfur ¹	0.1	0.1	<0.1	0.0	4.9	5.4 ± 0.4	0.7	1.5 ± 0.1	<0.1	0.1

¹ Units are in weight percent on a dry weight basis

Table 6. Gas Chromatograph – Mass Spectrograph (GC-MS) parameters used in the analysis of steroids in samples of sediment and chicken manure from the Pocomoke River Basin

[All temperatures are in degrees Celsius (°C); mL/min, milliliters per minute; V, volts; mm, millimeters; EI, electron ionization; eV, electron volts.]

Parameters	Instrument Settings
Inlet Configuration	Splitless
Purge Delay	1.0 minute
Injection Volume	1 microliter
Injector Temperature	200 °C
Carrier Gas	Helium, 1.00 mL/min (constant flow)
GC Columns	HP-50 (30 meter by 0.25 mm id with a 0.25 film thickness)
Column Programs	100° (2 min); 100°-200°@ 10°/min; 200° (0.1 min); 200°-260°@ 5°/min; 260° (10 min); 260°-270°@ 5°/min; 270° (20 min)
Detector Temperature	260 °C
Transfer Line	290 °C
MS Mode	EI, 70eV
MS Source Temp./ Voltage	200°/1150-1300 V
MS Acquisition Rate	Selective Ion Mode

cholestane as the internal standard. The Gas Chromatograph (GC) component is an HP-5890 GC with an HP 50 Capillary column. The column is 30 meters long with a 0.25-mm internal diameter, has a 0.25 film thickness, and is 50 percent diphenyl- and 50 percent dimethyl-siloxane copolymer. The GC was operated in a splitless mode with a 1-minute purge time and inlet temperature of 200 °C (table 6). The MS component utilized electron-impact ionization and was operated in a selective ion-monitoring mode. Detection limits for sample compounds were determined by running the same concentration of a dilution of these compounds with integration of five replicates. The variability associated with these integrations was then multiplied by a Student's t-test critical value of 2.571. Calibration curves were generated to find exact concentrations of the quantified steroids. All four-point calibration curves generated were within a linear range with an R² value between 1 and 0.98.

FIELD CONDITIONS AT TIME OF SAMPLING

For sampling in the fall of 1997, the first two sampling stations, 01485705 and 01485730, had brackish conditions, with salinities of up to 14.4 parts per thousand at the mouth of the river (table 7a). Suspended-sediment concentrations and sediment-size fractionation were variable between stations, but differences did not reflect any obvious variations in geographic or hydrologic conditions.

There were some differences in field measurements from 1999 compared to those from 1997 (table 7b). Most notably, the conductivity as estimated by salinity or specific conductance at station 01485705 was much lower in 1999, most likely due to differences in tidal conditions. The high specific conductance as well as the concentrations of the major ions indicate saltwater intrusion at two of the other tributary stations in 1999 -- 01485722 and 01485750 (tables 7b and 8).

RESULTS OF TRACE-ELEMENT ANALYSIS

The results of trace-element analyses on the dissolved and particulate fractions of surface water and bed sediment are presented in tables 9, 10, and 11. Concentrations of dissolved arsenic and selenium for some of the 1997 samples are not reported because of interference from bromide. Both ICP-MS and GF-AAS methods were used in 1999 to determine dissolved trace elements and to identify potential artifacts associated with each method. Samples with high salinity were analyzed by ICP-MS following two different sample treatments: (1) Dilution of the sample to an acceptable salinity level, and (2) extraction of selected trace elements from the saline matrix. All the samples also were analyzed for dissolved arsenic and selenium directly, without dilution by GF-AAS. The reporting limits for GF-AAS (0.9 µg/L) are higher than the ambient concentrations of arsenic and selenium, so these data are considered estimates only. Concentrations of arsenic and selenium detected in the split samples that were analyzed at CBL and Frontier Geosciences were lower than those measured by USGS, but the former laboratories use hydride-generation atomic fluorescence spectrometry (HG-AFS), a method that has detection limits at single-digit nanograms per liter. It is uncertain if the HG-AFS method can measure organic forms of arsenic and selenium as those assumed to be in the Pocomoke River Basin. The accuracy of the concentrations of other dissolved trace elements in the two samples collected in 1997 from the mainstem Pocomoke River was reduced due to

Table 7a. Field-measured parameters and suspended-sediment concentrations for sampling stations in the Pocomoke River Basin on September 30, 1997
 [Suspended sediment concentrations and the percentage of fine sediments were analyzed at the USGS Kentucky District Laboratory. $\mu\text{S}/\text{cm}$, microsiemens per centimeter; ppt, parts per thousand; mg/L, milligrams per liter; mm, millimeters; $^{\circ}\text{C}$, degrees Celsius; -- data not available]

	Pocomoke River near Kingston, Md. 01485705	Pocomoke Sound near Kingston, Md. 01485730	Rehoboth Branch near Kingston, Md. 01485700	Pocomoke River tributary near Kingston, Md. 01485720	Marumsco Creek tributary near Kingston, Md. 01485750
Salinity (ppt)	7.5	14.4	--	--	--
pH	7.1	7.7	6.3	7.3	7.0
Dissolved Oxygen (mg/L)	7.0	7.6	--	8.6	--
Water Temp. ($^{\circ}\text{C}$)	21.7	21.0	18.7	25.0	22.0
Suspended Sediment (mg/L)	15	78	8	47	6
Fine Sediment (% finer than 0.062 mm)	94.6	77.5	28.1	70.9	75.0

Table 7b. Field-measured parameters and suspended-sediment concentrations for sampling stations in the Pocomoke River Basin on February 12, 1999
 [Suspended sediment was analyzed at the USGS Georgia District Laboratory. $\mu\text{S}/\text{cm}$, microSiemens per centimeter; mg/L, milligrams per liter; $^{\circ}\text{C}$, degrees Celsius; ND, not determined]

	Pocomoke River near Kingston, Md. 01485705	Fair Island Canal near Kingston, Md. 01485725	Rehoboth Branch near Kingston, Md. 01485700	Unnamed Ditch near Kingston, Md. 01485722	Marumsco Creek tributary near Kingston, Md. 01485750
Specific Conductance ($\mu\text{S}/\text{cm}$)	353	13,300	ND	ND	ND
pH	6.5	7.3	ND	ND	ND
Dissolved Oxygen (mg/L)	9.1	10.1	8.9	11.8	ND
Water Temp. ($^{\circ}\text{C}$)	8.0	8.8	12.0	16.0	ND
Suspended Sediment (mg/L)	37	139	5	49	36

Table 8. Laboratory determinations for major-ion concentrations, specific conductance, and pH for samples collected in the Pocomoke River Basin on February 12, 1999
 [All concentration units are in milligrams per liter (mg/L). Sulfate, bicarbonate, and silica are presented as mg/L of SO_4^{2-} , HCO_3^- , and SiO_2 , respectively. Specific conductance (Sp. Cond.) was measured in microSiemens per centimeter ($\mu\text{S}/\text{cm}$). Ca^{2+} , calcium; Mg^{2+} , magnesium; Na^+ , sodium; K^+ , potassium; HCO_3^- , bicarbonate; Cl^- , chloride; SO_4^{2-} , sulfate; F⁻, fluoride; SiO_2 , silicate]

	Pocomoke River near Kingston, Md. 01485705	Fair Island Canal near Kingston, Md. 01485725	Rehoboth Branch near Kingston, Md. 01485700	Unnamed Ditch near Kingston, Md. 01485722	Marumsco Creek tributary near Kingston, Md. 01485750
pH	6.6	6.7	6.1	6.0	4.7
Sp. Cond.	380	13,100	261	5,190	7,260
Ca^{2+}	9.2	110	16	70	63
Mg^{2+}	8.2	328	7.6	112	171
Na^+	45	2796	17	898	1350
K^+	6.2	100	4.8	32	38
HCO_3^-	16	56	9.9	13	3.7
Cl^-	83	4,500	27	1,600	2,300
SO_4^{2-}	32	630	50	250	290
F ⁻	<0.10	0.21	<0.10	0.30	0.22
SiO_2	14	7.0	15	7.3	11

interference from salinity. Samples were diluted and analytical results were corrected for excess chloride, but the final results showed high reporting limits with many values reported as less than these limits (table 9a). Samples with high salinities collected in 1999 also were diluted but at a much smaller ratio than those in 1997, or extracted to remove salinity interferences, thus allowing for less censoring of the data. Arsenic and selenium results were corrected for interferences from chloride and bromide, and chromium results were corrected for interferences from carbon. Evaluation of the blanks and standard-reference-material concentrations measured by ICP-MS indicates that the values for the concentrations of dissolved trace elements are accurate.

On the basis of the values from the freshwater stations, where interference from bromide was not an issue, the concentrations of dissolved arsenic and selenium in the Pocomoke River were typically within or above the range of concentrations measured at other Chesapeake Bay Fall Line stations (table 9b; and unpublished data on file at the Maryland-Delaware-D.C. District office of the USGS). The concentrations of particulate selenium did not appear to be abnormally high when compared to data from other sources (tables 10a, 10b, and 11). Concentrations of arsenic in suspended sediment at the Pocomoke stations ranged from 9.5 to 21 mg/kg (milligrams per kilogram). These values are in the upper range of concentrations when compared to sediment data from other national studies. Samples of fine-grained sediment collected at USGS National Stream-Quality Assessment Network (NASQAN) stations had a median arsenic concentration of 4.4 mg/kg, and a range of 0.3 to 48 mg/kg (Horowitz and others, 1989). Rice (1999) reported a median concentration of 6.3 mg/kg for arsenic in bed sediment of the conterminous United States, with an interquartile concentration range of 4.6 to 9.2 mg/kg. Particulate and bed-sediment concentrations of arsenic and selenium at all of the Pocomoke stations also were much higher than background crustal abundances (1.8 and 0.05

Table 9a. Dissolved trace-element concentrations for direct-injection Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analysis on water-column samples collected in the Pocomoke River Basin on September 30, 1997
 [Ranges of concentrations from nine major Chesapeake Bay tributary Fall Line stations in 1994 are included for comparison (Chesapeake Bay Program, 1996). All units are in micrograms per liter. <, less than; INT, no values reported because of bromide interference; --, no data available.]

Station	Pocomoke River near Kingston, Md. 01485705 ¹	Pocomoke Sound near Kingston, Md. 01485730 ¹	Rehoboth Branch near Kingston, Md. 01485700	Pocomoke River tributary near Kingston, Md. 01485720	Marumsco Creek tributary near Kingston, Md. 01485750	Range of concentrations at Fall Line stations
Aluminum	280	260	21.8	9.6	24	8.4 – 115
Silver	<11	<40	0.005	0.05	0.03	--
Arsenic	INT	INT	0.68	INT	INT	0.09 – 0.47
Barium	110	120	63	117	89	--
Beryllium	< 11	< 120	0.04	< 0.1	< 0.2	--
Cadmium	< 22	< 1	0.02	0.13	< 0.2	0.03 – 0.24
Cobalt	< 60	< 80	1.06	1.2	0.61	--
Chromium	< 80	< 200	1.7	2.1	3.5	0.03 – 0.28
Copper	< 400	< 400	6.1	10	4	0.11 – 2.3
Lithium	48	79	1.41	54	54	--
Manganese	66	< 60	40.8	92	59.7	1.4 – 135
Molybdenum	< 50	150	0.26	4.4	4.2	--
Nickel	< 300	< 200	5.6	11	4	<0.1 – 3.2
Lead	< 50	< 50	0.02	0.04	0.16	<0.03 – 0.34
Antimony	<30	< 20	0.09	0.34	0.3	--
Selenium	INT	INT	0.66	INT	INT	--
Strontium	2,140	3,480	183	2,930	3,690	--
Uranium	< 1	< 1	0.024	0.38	0.76	--
Vanadium	< 20	< 20	0.85	< 0.1	< 0.1	--
Zinc	420	83	14.2	14.4	3.7	0.3 - 19

¹Stations with brackish water in the tidal part of the Pocomoke River High salinities have greatly reduced the precision of measurements at these stations, which are shown in italics. Reporting limits have been adjusted to more accurately reflect this loss of information.

Table 9b. Dissolved trace-element concentrations for direct-injection Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analysis on water-column samples collected in the Pocomoke River Basin on February 12, 1999

[Ranges of concentrations for samples that were collected and analyzed by personnel from Chesapeake Biological Laboratories and Frontier Geosciences as well as historical values from nine major Chesapeake Bay tributary Fall Line stations (1994) are included for comparison (Chesapeake Bay Program, 1996). [All units are in micrograms per liter. <, less than; --, no data available; CBL, Chesapeake Biological Laboratory; FG, Frontier Geosciences.]

Station	Pocomoke River near Kingston, MD 01485705	¹ Fair Island Canal near Kingston, Md. 01485725	Rehoboth Branch near Kingston, Md. 01485700	¹ Unnamed Ditch near Kingston, Md. 01485722	¹ Marumscocreek tributary near Kingston, Md. 01485750	Range of concentrations analyzed by CBL	Range of concentrations analyzed by FG	Range of concentrations at Fall Line stations
Aluminum	87.0	14.5	131.3	263	2620	--	--	8.4 – 115
Silver	<0.02	<0.2	<0.02	<0.1	<0.1	--	--	--
Arsenic	0.84	<1	0.44	<0.5	<0.5	0.10 – 0.39	0.014 – 0.22	0.09 – 0.47
Barium	33.0	40.2	72.7	151	143	--	--	--
Beryllium	0.033	<0.3	0.39	0.84	1.71	--	--	--
Boron	37.0	865	21.5	244	319	--	--	--
Cadmium	0.007	<0.05	0.20	0.52	0.37	0.009 – 0.42	0.01 – 0.44	0.03 – 0.24
Cobalt	0.417	0.92	4.92	5.80	10.6	--	--	--
Chromium	0.535	2.29	0.517	1.85	3.14	0.81 – 1.61	0.64 – 1.12	0.03 – 0.28
Copper	2.24	5.1	2.07	2.6	2.8	2.18 – 6.83	1.10 – 2.52	0.11 – 2.3
Iron	260	<100	98	58	210	--	--	--
Lithium	1.89	33.0	3.89	5.79	10.6	--	--	--
Manganese	46.9	41.9	109	185	210	--	--	1.4 – 135
Molybdenum	0.133	3.2	0.081	0.469	0.40	--	--	--
Nickel	1.29	3.7	6.2	9.35	15.5	1.32 – 13.4	1.1 – 24.7	<0.1 – 3.2
Lead	0.164	<0.2	0.090	0.325	0.99	0.13 – 0.69	0.15 – 0.82	<0.03 – 0.34
Antimony	<0.08	<0.8	<0.08	<0.4	<0.4	--	--	--
Selenium	1.0	<5	0.5	<2	<2	0.12 – 0.60	0.092 – 0.25	--
Strontium	100	1,680	127	713	960	--	--	--
Uranium	0.059	0.668	0.049	0.061	0.116	--	--	--
Vanadium	0.84	<0.8	0.83	<0.4	<0.4	--	--	--
Zinc	6.0	6.1	45.9	62.7	102	8.44 – 79.7	5.59 - 106	0.3 - 19

¹Samples from brackish water are indicated by an asterisk. Higher salinities have reduced the precision of these measurements. Reporting limits have been adjusted to more accurately reflect this loss of information

Table 9c. Dissolved arsenic and selenium concentrations determined by Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS)

[Samples were undiluted for this analysis. All units are in µg/L (micrograms per liter), and all values are considered estimates because they are below the method reporting limits of 0.9 µg/L.]

	Pocomoke River near Kingston, Md.	Fair Island Canal near Kingston, Md.	Rehoboth Branch near Kingston, Md.	Unnamed Ditch near Kingston, Md.	Marumsco Creek tributary near Kingston, Md.
Station	01485705	01485725	01485700	01485722	01485750
Arsenic	0.1	0.1	0.6	0.5	0.6
Selenium	0.3	0.4	0.5	0.5	0.1

Table 9d. Blank-subtracted dissolved trace-element concentrations determined in chelation-extracts by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

[All units are in µg/L (micrograms per liter). Values should be considered in context of the associated quality-control data (tables 4a and 4b) and the fact that chelation results can be negatively biased because the method's accuracy is dependent on the charge of the trace-element ion in the sample.]

	Fair Island Canal near Kingston, Md.	Unnamed Ditch near Kingston, Md.	Marumsco Creek tributary near Kingston, Md.
Station	01485725	01485722	01485750
Cadmium	0.5	0.8	0.6
Cobalt	0.21	6.7	12
Chromium	0.06	0.27	0.75
Copper	1.1	1.6	1.1
Manganese	41	213	246
Molybdenum	2.4	0.25	0.26
Nickel	0.5	9.2	17
Lead	0.01	0.31	1.0
Vanadium	0.42	0.71	0.18
Zinc	2.9	60	99

Table 10a. Particulate trace-element, total organic-carbon, and total sulfur concentrations from water-column samples collected in the Pocomoke River Basin on September 30, 1997

[Ranges of concentrations from nine major Chesapeake Bay tributary Fall-Line stations in 1994 are included for comparison (Chesapeake Bay Program, 1996). Except where noted, units are in milligrams per kilogram (mg/kg). TOC, Total Organic Carbon; TS, Total Sulfur; <, less than; --, no values are available.]

	Pocomoke River near Kingston, Md.	Pocomoke Sound near Kingston, Md.	Rehoboth Branch near Kingston, Md.	Pocomoke River tributary near Kingston, Md.	Marumsco Creek tributary near Kingston, Md.	Range of concentrations at Fall Line stations
Station	01485705	01485730	01485700	01485720	01485750	
Aluminum ¹	5.1	6.2	2.3	5.9	4.5	0.9 – 29
Silver	<1.0	<0.5	<1.5	<1	<1	--
Arsenic	15	14	9.5	12	21	--
Barium	300	280	200	290	240	--
Beryllium	1.7	1.8	2.5	1.4	2.5	--
Cadmium	0.8	0.3	1.0	0.4	0.8	0.52 – 33.1
Cobalt	19	12	31	21	6	--
Chromium	190	63	36	110	52	20 – 320
Copper	19	16	18	24	23	2.6 - 281
Iron ¹	4.5	3.6	2.3	3.4	12.8	--
Lithium	52	69	19	49	49	0.02 - 184
Manganese	2,100	1,100	1,300	1,600	390	10 – 16,830
Mercury	--	0.05	--	0.08	0.07	--
Molybdenum	16	<5	<15	<10	<10	--
Nickel	110	28	32	58	26	0.7 – 331
Phosphorus	2,400	1,300	4,800	3,800	1,800	--
Lead	110	31	33	50	48	<3.0 – 130
Antimony	1.0	0.8	0.6	0.8	1.1	--
Selenium	0.6	0.6	0.6	0.9	1.4	--
Strontium	170	620	180	210	430	--
Titanium ¹	0.35	0.44	0.11	0.36	0.24	--
Thallium	<100	<50	<150	<100	<100	--
Uranium	<100	<50	<150	<100	<100	--
Vanadium	85	89	33	84	94	--
Zinc	170	180	190	210	250	<3.0 - 1095
TOC ¹	--	4.3	--	7.8	--	--
TS ¹	--	2.3	--	0.6	--	--

¹ Units are in weight percent on a dry weight basis

Table 10b. Particulate trace-element, total organic-carbon, and total sulfur concentrations from water-column samples collected in the Pocomoke River Basin on February 12, 1999

[Ranges of concentrations from nine major Chesapeake Bay tributary Fall-Line stations in 1994 are included for comparison (Chesapeake Bay Program, 1996). Except where noted, units are in milligrams per kilogram (mg/kg). TOC, Total Organic Carbon; TC, Total Carbon; TS, Total Sulfur; <, less than; --, no values are available; ND, not determined.]

Station	Pocomoke River near Kingston, Md.	Fair Island Canal near Kingston, Md.	Rehoboth Branch near Kingston, Md.	Unnamed Ditch near Kingston, Md.	Marumsco Creek tributary near Kingston, Md.	Range of concentrations at Fall Line stations
	01485705	01485725	01485700	01485722	01485750	
Aluminum ¹	1.4	6.3	0.6	1.5	4.5	0.9 – 29
Silver	<0.5	<0.5	<0.5	<0.5	<1.5	--
Arsenic	2.3	11	0.8	1.4	8.3	--
Barium	53	370	28	67	360	--
Beryllium	0.4	1.8	0.6	2.9	6.1	--
Cadmium	<0.1	0.1	0.1	0.1	1.7	0.52 – 33.1
Cobalt	3	17	2	2	39	--
Chromium	16	71	11	14	86	20 – 320
Copper	3	14	3	6	25	2.6 - 281
Iron ¹	0.8	3.9	0.5	0.6	2.2	--
Lithium	16	45	3	8	30	0.02 - 184
Manganese	230	750	62	58	770	10 – 16,830
Mercury	0.02	0.10	0.02	0.05	ND	--
Molybdenum	<5	<5	<5	<5	<15	--
Nickel	<1	24	<1	<1	44	0.7 – 331
Phosphorus	390	2,200	130	460	3,300	--
Lead	11	35	12	11	54	<3.0 – 130
Antimony	<0.1	0.4	0.1	0.2	0.9	--
Selenium	0.1	0.7	0.1	0.3	1.0	--
Strontium	160	110	150	170	230	--
Titanium ¹	0.07	0.40	0.01	0.05	0.21	--
Vanadium	19	84	4	18	60	--
Zinc	65	170	57	68	400	<3.0 - 1095
TOC ¹	1.4	6.9	4.2	4.5	ND	--
TC ¹	1.3	7.0	4.0	4.5	ND	--
TS ¹	2.0	0.5	2.4	2.6	ND	--

¹ Units are in weight percent on a dry weight basis

Table 11. Bed-sediment trace-element, total organic-carbon, and total sulfur concentrations from samples collected in the Pocomoke River Basin on September 30, 1997

[Medians and ranges of concentrations from recent USGS National Stream Quality Assessment Network (NASQAN) data are included for comparison (Horowitz and others, 1989). Except where noted, units are in milligrams per kilogram. TOC, Total Organic Carbon; TS, Total Sulfur; <, less than; --, no values are available.]

Station	Pocomoke River near Kingston, Md. 01485705	Pocomoke Sound near Kingston, Md. 01485730	Rehoboth Branch near Kingston, Md. 01485700	Pocomoke River tributary near Kingston, Md. 01485720	Marumsco Creek tributary near Kingston, Md. 01485750	USGS NASQAN Data (Median/Range)
Aluminum ¹	5.6	4.7	5.0	2.3	3.2	4.0 / 0.1–8.7
Silver	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	--
Arsenic	10.9	10.4	7.2	1.3	4.6	4.4 / 0.3–48
Barium	300	300	400	470	200	--
Beryllium	1.7	1.4	4.1	0.4	1.3	--
Cadmium	0.7	0.5	1.2	0.2	0.3	--
Cobalt	10	9	24	2	3	9 / <1–107
Chromium	54	44	37	9	19	29 / 1–135
Copper	13	10	25	4	16	11 / <1–43
Iron ¹	3.7	2.8	2.6	0.8	2.5	2.0 / 0.1–11.6
Lithium	50	39	31	8	26	--
Manganese	400	380	220	110	88	600/<100–4,200
Mercury	0.08	0.05	0.07	0.01	0.04	0.03/<0.01–0.47
Molybdenum	<5	<5	<5	<5	<5	--
Nickel	22	16	30	3	8	14 / <1–110
Phosphorus	1,300	780	2,600	260	350	--
Lead	24	20	25	10	21	15 / <1–121
Antimony	0.4	0.5	0.3	0.1	0.3	0.4 / <0.1–2.2
Selenium	0.6	0.4	1.0	0.1	0.4	0.2 / <0.1–2.3
Strontium	120	110	83	95	90	--
Titanium ¹	0.42	0.51	0.33	0.33	0.27	0.28 / 0.06–0.83
Thallium	<50	<50	<50	<50	<50	--
Uranium	<50	<50	<50	<50	<50	--
Vanadium	73	62	58	19	35	--
Zinc	140	130	210	16	55	47 / 1–200
TOC ¹	6.7	3.1	9.0	0.4	2.7	0.5 / 0.1–11.3
TS ¹	0.8	0.5	0.2	0.1	1.4	--

¹ Units are in weight percent on a dry weight basis

mg/kg, respectively; Greenwood and Earnshaw, 1984). Data from two other Delmarva tributaries, which are farther north on the peninsula and have watersheds with fewer poultry operations than the Pocomoke River Basin, also had concentrations of suspended particulate arsenic that were within the ranges found in the Pocomoke River samples (unpublished data on file at the Maryland-Delaware-D.C. District office of the USGS), indicating the need for more study on the sources and sinks of arsenic in this region.

Concentrations of dissolved zinc in samples collected at the five Pocomoke River stations in 1997 ranged from 3.7 to 420 $\mu\text{g/L}$, with the highest values occurring in the mainstem of the river. The range of dissolved zinc concentrations in 1999 was similar to those in 1997, although the spatial distribution of the samples shifted, possibly due to differences in tidal fluctuations. Higher values may be associated with higher salinities, but there are exceptions to this pattern and the sources of zinc are not yet identified. The elevated concentrations of dissolved zinc also were verified by the chelation-extraction-ICP-MS method. Particulate and bed-sediment zinc concentrations also appeared to be above the normal ranges of concentrations at some of the stations (tables 10a, 10b, and 11), but there was no consistent pattern nor repetition of any pattern between 1997 and 1999 data. Sources for zinc in the Pocomoke River Basin are not currently documented, and the concentrations in the freshwater samples are within the ranges of those found at several other Fall Line stations (Chesapeake Bay Program, 1996).

Concentrations of copper did not appear to be elevated in any of the phases analyzed during this study. Results of the ICP-MS method on the chelation extracts show that the true values are lower than those determined by direct injection, with concentrations for dissolved copper ranging from 1.1 to 2.07 $\mu\text{g/l}$ in 1999. Particulate and bed-sediment copper concentrations were in the low range when compared to other Chesapeake Bay Fall Line stations and to national NASQAN data (tables 10 a and b; 11). Additionally, there is no evidence from this study that either lead or cadmium are anthropogenically enriched at any of the Pocomoke River stations.

Concentrations of strontium and lithium were elevated in a number of the samples. Using the specific conductance values from 1999, it was possible to back calculate the expected concentrations of strontium and lithium for that year given that the samples had a predominantly seawater source. These theoretical numbers closely matched the observed values, suggesting a plausible source for these elements.

Concentrations of total organic carbon (TOC) and phosphorus were high in both bed-sediment and suspended-sediment samples. Concentrations of phosphorus were typically above 1,000 mg/kg and TOC ranged from 0.4 to 9.0 percent by dry weight. The highest concentrations for both TOC and phosphorus were measured in the samples collected at the Rehoboth Branch station (01485700), and this pattern was repeated in both 1997 and 1999. This tributary drains a very active agricultural area within the Pocomoke River Basin, thus providing a reasonable explanation for the higher levels of organic carbon and phosphorus.

RESULTS OF ORGANIC-COMPOUND ANALYSIS

Concentrations of selected pesticides, pesticide metabolites, and polyaromatic hydrocarbons in samples collected in September 1997 are presented in tables 12 and 13 . With the exceptions of a few detections of low levels of the common triazine and acetanilide herbicides, most of these compounds either were not detected or were detected at less than the reporting limits. When compared to data from other stations within the Chesapeake Bay watershed, the herbicides with measurable concentrations were well within the low to normal range of concentrations of these compounds for mixed-agricultural watersheds. (Chesapeake Bay Program, 1996).

The broad GC-MS scans of surface-water samples displayed many peaks in the lower end of the chromatogram, which were tentatively identified as fatty-acid methyl esters and steroids. Most of the peaks could not be definitively identified on the basis of library searches, although at least one major peak had a 99-percent probability of being cholesterol, and there were significant amounts of sitosterol, stigmasterol, and ergosterol. Animals are the primary source for cholesterol, whereas sitosterol, stigmasterol, and ergosterol may be derived from either plants or animals (Hassett and Lee, 1977). A primarily human source for the cholesterol was unlikely because of only small amounts of coprostanol, a human-generated metabolite of cholesterol (Venkatesan and Kaplan, 1990). Some compounds found in the GC-MS scans also were tentatively classified in the class of estradiol-hormone compounds, but no specific identifications were made and further study is needed to more accurately identify these compounds.

Area counts (integrations of the areas under the peaks) were made for each of the cholesterol peaks on the gas chromatograms at the various stations (table 14). Although area counts from broad GC scans are semi-quantitative and do not provide true concentrations, they do allow comparison of cholesterol concentrations at each station relative to those at other stations. The highest observed concentration of cholesterol was at station 01485720, which is in a ditch near a chicken house. The mainstem station (01485705) had the next highest value, a ditch near another farm field had an intermediate value (station 01485700), and values at the control station (01485750) and the station at the mouth of the Pocomoke River (01485730) were lowest and nearly identical. These data indicate a trend, with the highest concentrations occurring in the source areas near the poultry houses, more moderate concentrations in the mainstem of the Pocomoke River, and the lowest concentrations near the mouth of the river, where the greatest dilution and mixing would probably take place.

Results of quantitative analysis of selected sterol compounds in samples of bed sediment and chicken manure collected from the Pocomoke River Basin in December 1997 are presented in table 15. Results of similar analyses of sediments from Baltimore Harbor (G.D. Foster, George Mason University, unpublished data, 1998) are presented for comparison. These data are currently being reviewed to identify any unique combinations and/or ratios of these compounds that can be used as indicators of the sources of the organic matter. To date, no unique markers have been found. Writer and others (1995) have suggested that ratios of coprostanol to (cholestanol + cholesterol) above 0.06 indicate large organic point sources such as those found in effluent discharges in municipal areas.

Table 12. Selected pesticide and pesticide-metabolite concentrations for samples collected in the Pocomoke River Basin on September 29, 1997

[Ranges of dissolved concentrations from nine major Chesapeake Bay tributary Fall Line stations are included for comparison (Chesapeake Bay Program, 1996). All units are in nanograms per liter. ND, compound was not detected; < RL – compound was detected, but was at a level less than the reporting limit; --, no values are available]

	Pocomoke River near Kingston, Md.	Pocomoke Sound near Kingston, Md.	Rehoboth Branch near Kingston, Md.	Pocomoke River tributary near Kingston, Md.	Marumscoc Creek tributary near Kingston, Md.	Method Reporting Limits	Range of concentrations at Fall Line stations
	01485705	01485730	01485700	01485720	01485750		
2,6 Diethylalanine	<RL	<RL	<RL	<RL	<RL	0.3	--
EPTC	ND	ND	<RL	<RL	<RL	0.4	--
Butylate	<RL	<RL	<RL	<RL	<RL	0.4	--
Pebulate	<RL	ND	<RL	<RL	<RL	0.6	--
Tebuthiuron	<RL	<RL	<RL	<RL	<RL	2.0	--
Propachlor	ND	ND	ND	ND	ND	0.6	--
Ethoprop	ND	<RL	<RL	ND	<RL	1.2	--
Desethylatrazine	<RL	<RL	<RL	<RL	<RL	1.0	--
Ethalfuralin	ND	ND	ND	ND	ND	0.8	--
Phorate	ND	ND	ND	ND	ND	1.3	--
Trifluralin	ND	ND	ND	ND	ND	1.0	--
Benfluralin	ND	ND	ND	ND	ND	1.3	--
Dimethoate	<RL	<RL	ND	ND	ND	1.4	--
Simazine	12.4	12.0	5.9	9.2	7.0	0.5	ND – 171
Carbofuran	<RL	ND	<RL	<RL	ND	0.6	--
Prometon	7.4	ND	6.6	3.3	<RL	1.0	<RL – 37.2
Atrazine	40.0	51.9	60.7	34.6	23.7	0.4	<RL – 631
Fonofos	ND	ND	ND	ND	ND	0.7	--
Terbufos	ND	ND	ND	<RL	ND	1.1	--
Pronamide	1.8	10.0	ND	ND	ND	0.5	--
Disulfoton	<RL	ND	<RL	ND	ND	0.9	--
Diazinon	ND	ND	ND	ND	<RL	0.7	ND – 24.2
Terbacil	<RL	ND	ND	2.9	ND	0.4	--
Triallate	ND	ND	ND	ND	<RL	0.4	--
Propanil	ND	ND	ND	ND	ND	0.4	--
Metribuzin	ND	<RL	9.7	<RL	<RL	0.7	--
Parathion, methyl-	ND	ND	10.7	10.8	ND	0.6	--
Carbaryl	ND	ND	ND	ND	ND	0.5	--
Acetachlor	<RL	ND	<RL	2.2	2.3	0.5	--
Alachlor	ND	ND	6.7	ND	ND	0.3	<RL – 177
Linuron	5.9	ND	6.3	4.5	5.2	0.6	--
Metolachlor	1.1	ND	150.9	<RL	ND	0.3	<RL – 452
Malathion	ND	ND	<RL	ND	ND	0.6	ND – 23.8
Chlorpyrifos	ND	ND	4.2	ND	ND	0.7	--
Parathion	ND	ND	ND	ND	ND	0.3	--
Dacthal	ND	ND	ND	ND	ND	0.2	--
Cyanazine	2.9	4.0	ND	ND	2.6	0.4	ND - 239
Pendimethalin	ND	ND	ND	ND	ND	0.9	--
Napropamide	1.0	0.6	ND	2.8	<RL	0.3	--
Propargite	ND	ND	ND	ND	ND	0.4	--
Azimphos, methyl-	ND	ND	ND	ND	ND	0.3	--

Table 13. Selected Polyaromatic Hydrocarbon (PAH) concentrations from samples collected in the Pocomoke River Basin on September 29, 1997 [Ranges of dissolved concentrations from nine major Chesapeake Bay tributary Fall Line stations are included for comparison (Chesapeake Bay Program, 1996). All units are in nanograms per liter. ND , compound was not detected; <RL – compound was detected, but at a level less than the reporting limit; INT, compound not determined due to interference; --, no values are available]

	Pocomoke River near Kingston, Md.	Pocomoke Sound near Kingston, Md.	Rehoboth Branch near Kingston, Md.	Pocomoke River tributary near Kingston, Md.	Marumsco Creek tributary near Kingston, Md.	Method Reporting Limits	Range of concentrations at Fall Line stations
	01485705	01485730	01485700	01485720	01485750		
Naphthalene	<RL	<RL	<RL	<RL	<RL	0.7	--
Acenaphthylene	<RL	<RL	<RL	<RL	<RL	0.7	<RL – 2.22
Acenaphthene	<RL	<RL	<RL	<RL	<RL	0.8	ND – 2.27
Fluorene	<RL	<RL	ND	<RL	<RL	0.7	<RL – 2.15
Phenanthrene	<RL	<RL	<RL	<RL	<RL	0.8	<RL – 4.77
Anthracene	ND	ND	<RL	ND	ND	0.7	--
1-Methylphenanthrene	ND	<RL	ND	ND	<RL	0.3	--
Fluoranthene	<RL	<RL	<RL	<RL	<RL	0.6	ND – 2.77
Pyrene	INT	INT	INT	INT	INT	0.5	ND – 2.82
2-Methylfluoranthene	ND	ND	ND	ND	ND	0.8	--
1-Methylpyrene	ND	ND	ND	ND	ND	0.7	--
Benz[a]anthracene	ND	ND	ND	ND	ND	0.9	ND – 0.35
Chrysene	ND	ND	ND	ND	ND	0.3	ND – 2.61
4-Methylchrysene	ND	ND	ND	ND	ND	0.4	--
Benzo[b]fluoranthene	ND	ND	ND	ND	ND	0.9	--
Benzo[k]fluoranthene	ND	ND	ND	ND	ND	0.9	--
Benzo[a]pyrene	ND	ND	ND	ND	ND	1.2	ND - <RL
Perylene	ND	ND	ND	ND	ND	1.4	ND – 8.59
Indeno[1,2,3-cd]pyrene	<RL	<RL	<RL	<RL	<RL	2.4	--
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	2.3	--
Benzo[ghi]perylene	ND	ND	ND	ND	ND	1.6	--

Table 14. Gas chromatogram peak area counts for cholesterol peaks from water samples collected in the Pocomoke River Basin in 1997

[Area counts are used as a qualitative measurement of relative concentrations.]

Station No.	Location	Cholesterol (area counts)
01485700	Ditch from agricultural watershed	36,633
01485705	Pocomoke River mainstem	54,839
01485720	Ditch by a chicken house	68,153
01485730	Mouth of the Pocomoke River	18,963
01485750	Ditch in undeveloped basin	18,915

Table 15. – Mean concentrations of steroidal lipids in Pocomoke River bed sediment collected near the shoreline at station 01485705 on December 13, 1997

[Similar measurements from Baltimore Harbor (G.D. Foster, George Mason University, unpublished data, 1998) and chicken manure collected at a storage shed near station 01485705 are presented for comparison. [All units are in nanograms per kilogram as dry weight; <RL, Below reporting limits; ND, not detected]

Organic Fatty-Acid Compound	Pocomoke River Bed Sediment	Baltimore Harbor Bed Sediment	Chicken Manure	Method Reporting Limit
Coprostanol	103	174	29,400	27.6
Epicoprostanol	183	307	38,000	21.0
Coprostanone	91.3	126	<RL	52.2
Cholestanol	362	604	20,400	29.0
Cholesterol	882	1,190	314,000	41.8
Cholestanone	54.8	70.9	<RL	43.3
Campesterol	491	602	71,200	55.9
Stigmasterol	741	528	40,500	39.3
Stigmastanol	483	591	35,000	53.3
β -Sitosterol	1,820	762	210,000	52.5
Fucosterol	127	223	ND	44.0

Pocomoke River and Baltimore Harbor sediments had ratios of 0.083 and 0.097 for these compounds.

SUMMARY AND IMPLICATIONS

This report presents evidence of the presence of significant quantities of contaminants other than nutrients in the Pocomoke River and tributaries within its watershed, but the implications of these findings are still speculative. The results of laboratory analyses of samples of bed sediment confirm that there is a large load of organic waste in the river -- total organic carbon in the sediments ranged from 0.4 to 9 percent. Many of the organic compounds found in the water column and sediments are in the classes of steroids and fatty-acid methyl esters, and some have been identified as animal-waste products. For example, coprostanol has been used in the past as an indicator of sewage sludge that was being dumped in large amounts into coastal waters (Grimalt and others, 1990; Hatcher and others, 1977, 1979; Pierce and Brown, 1984). Many of the compounds found in the Pocomoke River sediments have not yet been identified, but at least several are in the class of estradiol-hormone compounds and have the potential to promote endocrine-disrupting effects in aquatic life. Estradiols are produced naturally in animals and elevated levels would not be unexpected in areas of concentrated poultry operations due to the high density of animals in the watershed.

The importance of identifying organic compounds in the Pocomoke River sediments becomes more apparent when the following information is considered: (1) dinoflagellates are heterotrophic organisms that consume fixed organic carbon for growth; (2) *Pfiesteria piscicida* spends a large part of its life cycle in sediments living on detrital organic carbon; and (3) the high levels of total organic carbon that were documented in the sediments must provide a significant source of energy and carbon to these microorganisms. It is vital to understand the nature of the organic-carbon compounds that are supporting *Pfiesteria piscicida* during these stages of its life cycle, and it is unknown how various steroid compounds may affect the growth of this microorganism.

Water-column and sediment samples from most of the sampling stations contained concentrations of some trace elements that were within or above the high range of what could be expected for natural waters of the Chesapeake Bay Basin and other streams of the United States. The idea that some of these trace elements, such as arsenic, selenium, and zinc, may be coming from animal manure residues is not new (Gupta and Karuppiah, 1996a and b; Jackson and Miller, 1999), but there is still no direct evidence that links the occurrence of these elements in rivers to agricultural sources in the watersheds. Arsenic is contained in a known poultry-feed additive called Roxarsone (3-nitro-4-hydroxyphenylarsonic acid). Roxarsone is currently the most commonly used arsenical compound in poultry feed in the United States, with 23 to 45 grams of arsenic per ton fed to most broiler chickens for increased weight gain, feed efficiency, and improved pigmentation (Animal Health Institute, 1996). Most of this compound is directly excreted by the chickens, and poultry litter from commercial broilers can contain from 15 to 35 parts per million of total arsenic (Morrison, 1969; Jackson and Miller, 1999). No specific information is

currently available on the amount of arsenic that is fed to poultry in the Pocomoke River Basin, but the U. S. Department of Agriculture's 1997 Census of Agriculture estimated that approximately 600 million broiler chickens were produced on the Delmarva Peninsula in that year, suggesting the potential for large loads of this trace element, particularly in areas with a high density of poultry-feeding operations. Evidence from the current study indicates that arsenic is present in the Pocomoke River, but more study is necessary to differentiate natural versus anthropogenic sources, and to determine the fate and transport of trace elements that are used as feed additives.

It should also be noted that Station 01485750, located on Marumsc Creek, was selected as a control station because no obvious sources of poultry waste were observed in the surrounding watershed. Results of sampling, however, indicate that this station is chemically similar to the others in this study. Water chemistry measured in 1999 indicates that this station is strongly influenced by tidal waters, that some hydrologic exchange between basins is likely. The entire lower Eastern Shore area of the Chesapeake Bay has very low relief, is extensively ditched, and has a high water table, so that inter-basin transport of contaminants must be considered. Hydrologic flow regimes can be very complicated under these conditions. It is also possible that an undocumented source of contaminants exists in the basin, since no detailed reconnaissance has been conducted of the source areas. Source areas for future sampling stations in the Pocomoke River Basin will need to be carefully documented and delineated.

At present, it is not known how the presence of any of the trace elements or organic compounds detected in the Pocomoke River Basin may affect either fish health or the growth of *Pfiesteria piscicida*. Evidence from fish-health studies currently being conducted by the U. S. Geological Survey strongly indicates that most of the lesions observed in menhaden captured in the Pocomoke River during 1997 and 1998 were related to a fungal pathogen, although *Pfiesteria piscicida* may have killed fish later on in the events (Blazer and others, 1999). Massive necroses, possibly due to the toxins, were found by Blazer and others on top of the chronic inflammatory lesions formed in response to the fungus. These findings show that the fungal infections were present prior to the fish kill, however, and potentially prior to exposure to *Pfiesteria piscicida*. The presence of high levels of contaminants in the water column supports this conclusion, because of the probable detrimental effects some of these chemicals may have on fish health, vigor, and susceptibility to fungal infections.

Finally, the data presented in this report support the hypothesis that poultry manure is a source of organic-compound contaminants found in the Pocomoke River and its tributaries. This conclusion is based on the analyses of only a few samples collected under similar hydrologic conditions, however, and should therefore be viewed with caution. There is also evidence that some trace elements -- arsenic and zinc -- are elevated above normal levels for streams in natural waters, but the elevations are not large and the sources for these elements are still undetermined. It would be helpful to the discussion presented here to expand sampling for toxic contaminants to other Eastern Shore tributaries with high levels of animal agriculture, and to sample more frequently and during other flow regimes, such as storms, during the seasons of high manure applications. The data collected for this study

document only two base-flow sampling events. More data are needed to establish potential correlations between the occurrence and concentrations of toxic contaminants, fish health, land use and agricultural practices, and the occurrence of pathogens.

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