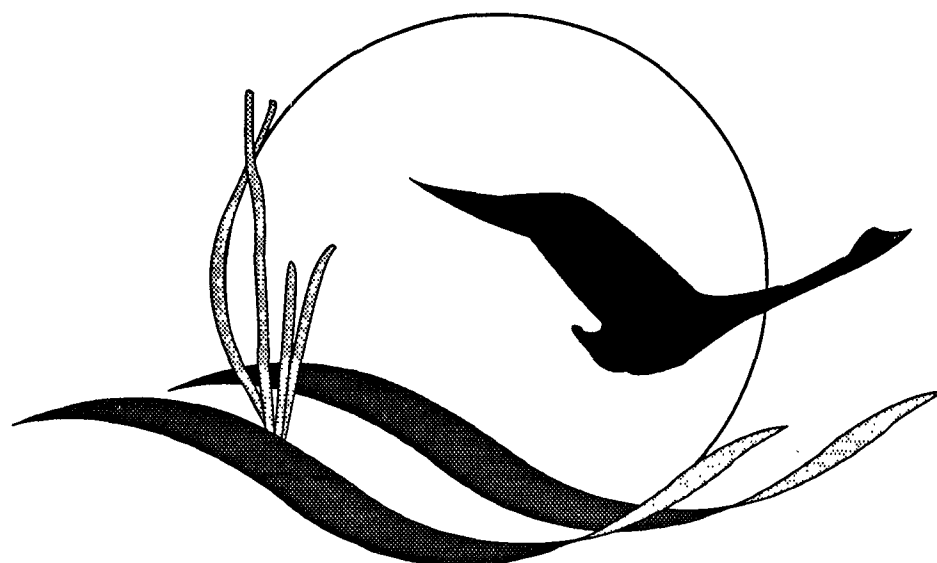


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# Chesapeake Bay Fall Line Toxics Monitoring Program 1992 Final Report



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## Chesapeake Bay Program

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# Chesapeake Bay Fall Line Toxics Monitoring Program 1992 Final Report

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U.S. Environmental Protection Agency  
Office of Research and Development  
Washington, D.C. 20460  
Philadelphia, PA 19107





## **ACKNOWLEDGEMENTS**

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**Maryland Department of the Environment**

**United States Geological Survey**

**George Mason University, Department of Chemistry**

**Occoquan Watershed Management Laboratory**

**Metropolitan Washington Council of Governments**

**US Environmental Protection Agency, Chesapeake Bay Program Office**



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## **EXECUTIVE SUMMARY**

### **Introduction**

A critical step in understanding the effects of toxic substances on the Chesapeake Bay's ecosystems is knowing the types and quantities of substances being delivered to the estuary. The Chesapeake Bay Fall Line Toxics Monitoring Program was established in April, 1990 as a pilot study to define the magnitude and timing of toxic substances entering the Chesapeake Bay from the area above the fall line of the Susquehanna and James rivers. Sampling for metals for the Potomac River was incorporated into the Fall Line Toxics Monitoring Program in May, 1991. In March, 1992, the program was expanded to include organic constituents. The Fall Line Toxics Monitoring Program can now provide preliminary information on toxic substances originating from combined point and nonpoint sources above the fall line.

### **Objectives**

This report focused on samples collected between March 1992 and March 1993. The purpose of this study was to:

- (1) determine the ambient concentrations, nature, and transport of selected metals and organic contaminants over a range of hydrologic conditions in three major tributaries to the Chesapeake Bay;
- (2) improve monthly and annual load estimates of metals and organic contaminants entering the estuary at three major tributaries to the Chesapeake Bay by employing ultra clean sampling techniques and lowering analytical quantitation levels; and
- (3) upgrade the quality assurance program by increasing the number of quality-control samples in order to ensure the adequacy of sampling procedures and sample analysis.

### **Sampling Stations**

Samples were collected from the fall lines of three major tributaries to the Chesapeake Bay. These stations are the Susquehanna River at Conowingo Dam, the James River near Cartersville and the Potomac River at Chain Bridge. The Susquehanna River is the largest tributary to the Chesapeake, draining approximately 27,100 square miles. The James River has a drainage area of 6,257 square miles and the Potomac River drains 11,560 square miles. Collectively, these three rivers provide approximately 79% of the total freshwater flow to the estuary (Table ES-1).

**Table ES-I. Drainage Characteristics of the Susquehanna, Potomac, and James Rivers.**

Location	Average Daily Flow		Drainage Area		Yield
	(cfs)	Pct. of Tot. Flow	(sq. miles)	Pct. of Tot. DA	(cfs/sq. miles)
Susquehanna @ Conowingo	36,370	51%	27,100	42%	1.34
Potomac @ Chain Bridge	10,340	16%	11,570	18%	0.89
James @ Cartersville	7,416	12%	6,257	10%	1.19

---

## Results

Results suggest that some constituents appear to be discharge dependent. Total-recoverable zinc and dissolved zinc concentrations showed similar patterns as river discharge at the James River station. At the Susquehanna River, dissolved copper appeared related to discharge, whereas at the Potomac River, total-recoverable chromium and zinc varied similarly with discharge. Particulate PAHs also appeared to be discharge dependent. These observations are based on visual inspection of the data. A longer record with more frequent sampling would be needed to establish a statistical relationship between discharge and concentration.

Temporal patterns may also exist for some constituents. Organonitrogen herbicides, primarily atrazine, peaked in May, for James River and June for Susquehanna and Potomac rivers. Organophosphorus compounds were rarely detected. Organochlorine pesticides, while detected often, did not show the same degree of temporal variability as organonitrogen pesticides.

A summary of metals concentrations at the three rivers for the period March 1992 through March 1993 is presented in Table ES-II. Organonitrogen and organophosphorus pesticides are presented in Table ES-III, Table ES-IV and organochlorine constituents are presented in Table ES-IV.

One of the program's objectives was to determine if the use of ultra clean sampling techniques and lowered constituent quantitation levels improved the quality of data. Ultra clean techniques were employed at the Susquehanna and James rivers. In general, the number of occurrences of detectable concentrations of metals was increased by employing these methods. At the Susquehanna, the new techniques improved results for total-recoverable copper, lead, and zinc and for dissolved copper, lead and zinc. The James River had

**Table ES-II.** Summary of Metals Concentrations, Frequency of Detection and Range, for the period March 1992 through March 1993.

Metal	Potomac		James		Susquehanna	
	Freq. Det.	Range ug/l	Freq. Det.	Range ug/l	Freq. Det.	Range ug/l
Aluminum, D			24/25	10-660	21/28	20-230
Arsenic, TR	0/20		0/26		1/28	<1-1
Arsenic, D					3/24	<.6-1.6
Cadmium, TR	0/21		0/28		0/28	
Cadmium, D					2/24	<1-1.24
Chromium, TR	8/21	<1-13.2	19/28	<1-20	17/27	<1-6
Chromium, D			0/5		19/27	0.5-5.4
Copper, TR	17/21	<2-16	26/28	<1-13	24/28	<1-5
Copper, D			5/5	<1-3	27/27	0.36-3.1
Iron, TR					9/9	3000
Iron, D			25/25	43-1100	23/24	<3-810
Lead, TR	6/21	<4-14	15/28	<1-15	22/28	<1-10
Lead, D			2/5	<1-2	12/27	<0.06-2.2
Lithium, TR					0/3	
Manganese, TR					3/3	25/170
Mercury, TR					2/28	<.1-0.5
Mercury, D					0/11	
Nickel, TR	2/21	<8-40	5/6	<1-13	10/10	5-12
Nickel, D			2/8	<1-7	13/13	2-9
Selenium, TR	0/20		0/2		0/3	
Silver, TR					0/3	
Strontium, TR					10/10	50-130
Zinc, TR	15/21	<15-63	1/28	<10-60	18/28	<10-30
Zinc, D			0/5		24/27	1.1-21.6

D=Dissolved  
TR= Total-Recoverable

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**Table ES-III. Organonitrogen and Organophosphorus Pesticide Concentrations in Dissolved Phase, March 1992 through February 1993.**

Pesticide	Potomac		James		Susquehanna	
	Freq. Det.	Range	Freq. Det.	Range	Freq. Det.	Range
Alachlor	5/15	9 - 20.9	7/23	4.2 - 20.2	7/19	2.5 - 23.1
Atrazine	14/15	9.6 - 579	15/23	3.9 - 476.3	17/19	7.7 - 293.7
Cyanazine	6/15	9.8 - 212.4	9/23	2.4 - 24.9	9/19	4.1 - 108
Diazinon	1/15	10	6/23	2.8 - 11.6	2/19	5.8 - 17.1
Hexazinone	3/15	1.8 - 19.7	10/23	1.3 - 16.8	8/19	1.0 - 16.3
Malathion	1/15	11.5	2/23	3.1 - 11.6	3/19	4.3 - 7.7
Metolachlor	13/15	9.1 - 358	12/23	1.4 - 210.3	19/19	1.4 - 139.6
Prometon	9/15	8.2 - 17.0	6/23	1.7 - 18.1	8/19	2.4 - 18.9
Simazine	12/15	5.7 - 142.8	12/23	2.6 - 369.6	11/19	2.3 - 91.3

Table ES-IV. Organochlorine Pesticide Concentrations in Dissolved and Particulate Phase, March 1992 through February 1993.

Pesticide	Potomac- Diss.		James- Diss.		Susquehanna- Diss.		Potomac- Part.		James- Part.		Susquehanna- Part.	
	Freq. Det.	Range ng/l	Freq. Det.	Range ng/l	Freq. Det.	Range ng/l	Freq. Det.	Range ng/l	Freq. Det.	Range ng/l	Freq. Det.	Range ng/l
Aldrin	5/10	0.3-0.5	6/19	0.2-1.6	10/16	0.2-1.6	1/10	2.3	1/20	2.4	1/15	0.1
Dieldrin	8/10	0.4-4.1	9/19	0.2-2.4	6/16	0.2-5.5	5/10	0.2-3.6	6/20	0.1-0.5	7/15	0.1-1.9
4,4'-DDT	1/10	1.7	0/19		2/16	0.3-0.5	2/10	1.1-1.2	2/20	0.4-1.4	3/15	0.3-1.4
Oxychlordane	2/10	0.2-31.8	7/19	0.1-12.1	8/16	0.3-11.1	3/10	0.1-3.6	6/20	0.1-1.4	6/15	0.2-1.2
α-Chlordane	4/10	0.8-5.3	15/19	0.1-17.2	11/16	0.1-3.1	5/10	0.3-3.2	9/20	0.1-1.2	5/15	0.1-0.6
γ-Chlordane	5/10	0.2-3.5	10/19	0.2-8.5	8/16	0.2-3.6	3/10	0.2-0.4	9/20	0.1-1.8	6/15	0.1-0.6
Permethrin	0/10		0/19		1/16	7.1	1/10	15.1	0/20		1/15	2.8
Fenvalerate	0/10		1/19	4.0	2/16	2.3-3.8	1/10	3.5	1/20	2.6	0/15	
PCBs (112 Congeners)	7/10	0.5-3.6	16/19	0.4-6.7	14/16	0.3-9.6	8/10	0.9-39.0	13/20	0.4-13.6	13/15	0.4-12.7

improved results for total-recoverable arsenic, copper and zinc and for dissolved arsenic, copper, lead and zinc. The higher quantitation levels employed for Potomac samples was adequate for total-recoverable copper and zinc.

Contamination was of concern for certain constituents. At the Susquehanna River, contamination was a problem with total-recoverable chromium and dissolved chromium and mercury. At the James River, dissolved chromium and lead exhibited contamination problems.

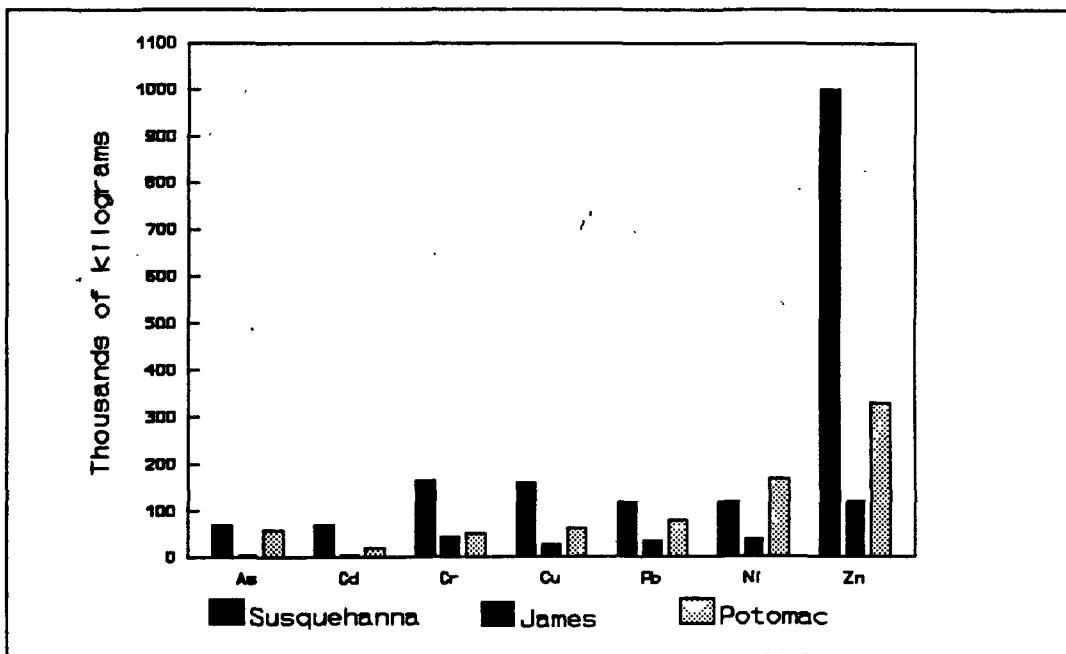
## **Loading Estimates**

Monthly and annual loads were prepared for the sampled constituents for each of the three tributaries. The loadings presented in this report represent the principal investigators' best estimates of monthly and annual loads based on a very limited data set. The loads provided in this report represent a range of potential loads. Minimum loads were calculated by assigning constituent concentration a value of zero when the concentration was below quantitation level. Maximum loads were calculated by assigning sample concentrations that were below the quantitation level to the quantitation level. It should be noted that there exists a high degree of uncertainty in the loading estimates for substances that had a large number of observations below quantitation level. These loads should be used only for "order of magnitude" comparisons between fluvial sources and other sources (atmospheric, point sources) of toxic substances entering Chesapeake Bay.

Figure ES-1 compares annual loading estimates of selected total-recoverable metals using maximum loading estimates for each river. In general, water discharge had a significant effect on load estimates of metals. For the Susquehanna and James rivers, the lowered quantitation levels in 1992-1993 significantly improved the load estimates for certain metals when compared with loads estimated during 1990-1991. At the Susquehanna River, load estimates were improved in 1992-1993 for total-recoverable copper, lead and zinc, and dissolved arsenic, cadmium, copper, lead and zinc. Load estimates for the James River were improved in 1992-1993 for total-recoverable arsenic, copper and zinc and for dissolved arsenic, chromium, copper, lead and zinc. At the Potomac river, the best load estimate was for total-recoverable copper, which had only two observations below quantitation level.

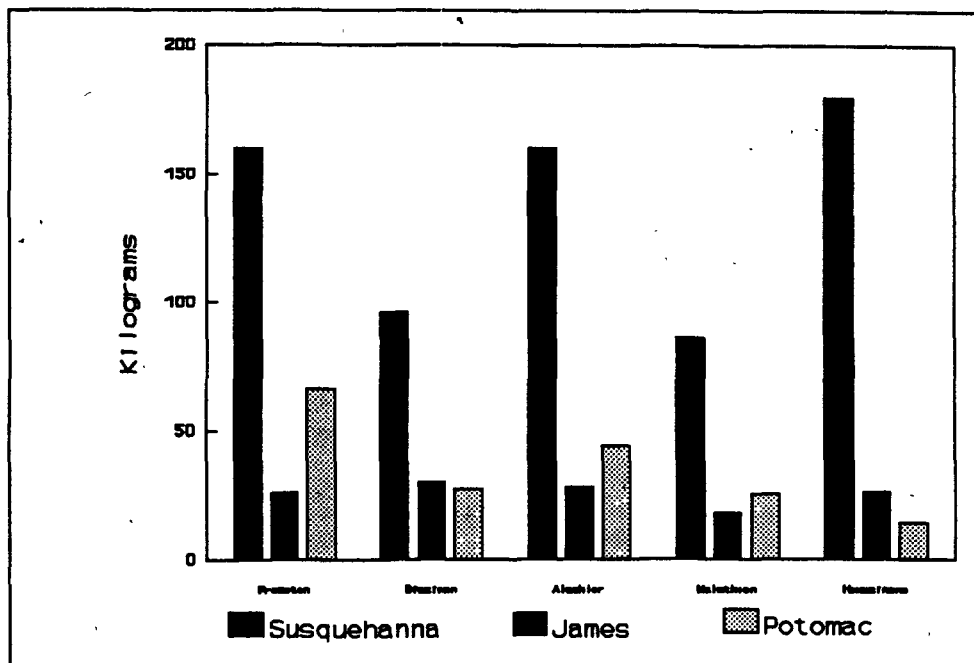
Figure ES-2 and Figure ES-3 present maximum annual load estimates for organonitrogen and organophosphorus pesticides, dissolved and particulate phases combined. Maximum annual load estimates for organochlorine compounds are presented in Figure ES-4. In general, annual load estimates of pesticides were highest for the Susquehanna River, followed by the Potomac and James rivers. However, loads were not always in direct proportion to river discharge. Organonitrogen and organophosphorus loads were disproportionately higher in the Potomac in comparison with the Susquehanna. Chlordane was disproportionately higher in the James River.

**Figure ES-1.** Maximum annual loads of selected metals for Susquehanna, James, and Potomac rivers.

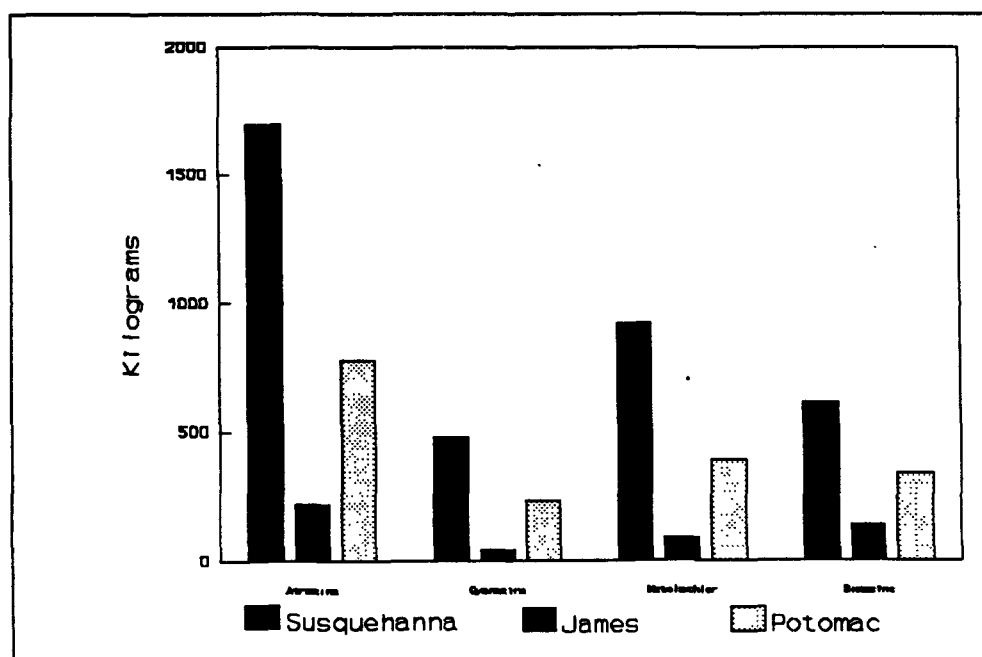




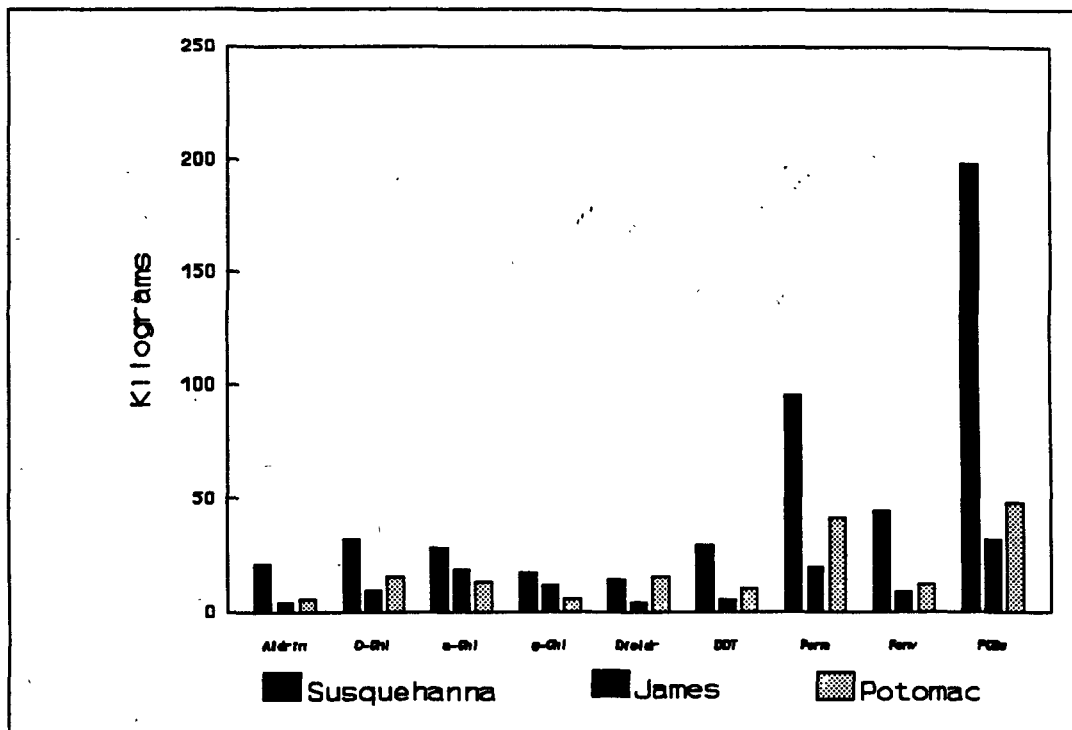
**Figure ES-2.** Maximum annual loads of organonitrogen and organophosphorus compounds for the Susquehanna, James and Potomac rivers.



**Figure ES-3.** Maximum annual loads of organonitrogen and organophosphorus pesticides for the Susquehanna, James and Potomac rivers.



**Figure ES-4.** Maximum annual loads of organochlorine compounds for the Susquehanna, James and Potomac rivers.





## **PROGRAM OVERVIEW**

Chesapeake Bay is a collection of delicate ecosystems, many of which have been greatly perturbed, both by mismanagement of the resources within the Bay, as well as by continued and excessive pollution from the surrounding watershed. Only within the last ten to fifteen years have state and local governments recognized the imminent danger of pollutants to this rich natural and economic resource. Since the early 1980's there has been a growing commitment by all the states in the watershed of Chesapeake Bay, with backing from federal environmental agencies, to study this problem and begin clean-up measures. The emphasis in clean-up efforts has been directed toward the reduction of nutrient inputs to the Bay, particularly nitrogen and phosphorus. There is now a need to identify and quantify the toxic substances, such as insecticides, herbicides, and certain metals, which are also entering the Bay.

This report focuses on a project conducted to quantify the magnitude and timing of toxic substance loadings from several of the major tributary sources of Chesapeake Bay. As such, the study assesses the combined input of toxics from point and non-point sources within the watershed from fluvial sources, but does not address other issues, such as atmospheric deposition to the Bay proper, groundwater inputs, or the fate of toxic substances once they enter the estuary.

The present study will (1) quantify the concentrations and fluxes of toxic substances entering the Bay from the watershed, (2) provide a baseline for future comparisons, an important aspect for assessment of clean-up efforts and toxic reduction strategies, (3) allow determinations of surface water quality to be made, and (4) provide essential information for calibration of the Chesapeake Bay mass-balance models presently being developed.

## **Metal and Organic Contaminants Introduction**

In 1990 and 1991, a pilot study was conducted by the U.S. Geological Survey (USGS) in cooperation with the Maryland Department of the Environment (MDE) and the U.S. Environmental Protection Agency, Chesapeake Bay Program Office (EPA), to enhance the understanding of the nature and transport of toxic substances entering Chesapeake Bay from its major tributaries. The purpose of the 1990-91 Chesapeake Bay Fall Line Toxics Monitoring Program was to identify and quantify toxic substances entering the Chesapeake Bay from above the fall lines of two major tributaries, the Susquehanna and James Rivers. Combined, these rivers represent 65 percent of the total freshwater flow to the Chesapeake Bay from fluvial sources. The study was continued through 1992, incorporating refinements from the pilot study.

The specific objectives of the 1990-91 pilot study were: (1) to identify types and quantities of toxic substances in fluvial transport; (2) to characterize constituent concentration with respect to seasonality, water discharge, and time; and (3) to estimate monthly and annual constituent loads from two major tributaries to the Chesapeake Bay, the Susquehanna and James rivers. Results of the study are documented in the report *Chesapeake Bay Fall Line Toxics Monitoring Program: 1990-91 Loadings*, (1993) on file in the EPA Chesapeake Bay Program Office, Annapolis, Maryland.

During this two-year period, many of the metals and organic contaminants analyzed were detected in fluvial transport. However, due to a limited occurrence of storm events during the

1990-91 sampling period, sample collection was restricted primarily to baseflow conditions and many constituent measurements were below analytical quantitation levels. In addition, the analytical quantitation levels were not commensurate with the levels being used in other research efforts, such as the atmospheric deposition study, within the Chesapeake Bay Program. The decision, therefore, was made to revise the project during 1992-93 to include (1) ultra clean sampling techniques for the collection of water samples; (2) lowered analytical quantitation levels for metal and organic contaminant analyses; and (3) continued monitoring during baseflow and stormflow conditions to better represent toxic substances in transport. During this period, the Potomac River was added to the fall line toxics monitoring network.

In 1992, samples were collected throughout the year to estimate loads of toxic substances from the Susquehanna River at Conowingo, Maryland, the James River at Cartersville, Virginia, and the Potomac River at Chain Bridge, Washington, D.C., during periods of varying flow. Figure 1 shows the drainage area of Chesapeake Bay, and the locations of the sampling sites.

The specific objectives of the 1992 Chesapeake Bay Fall Line Toxics Monitoring Program were:

- (1) Determine the ambient concentrations, nature, and transport of selected metals and organic contaminants over a range in flow conditions at the major tributaries to the Chesapeake Bay. These data will be used for comparison to water quality standards and in calculating load estimates.
- (2) Improve the monthly and annual calculations of total-recoverable metal and organic contaminant load estimates entering the Chesapeake Bay at the major tributaries to the Bay. Load estimates were to be improved by: a) adopting ultra clean sampling methods b) lowering the analytical quantitation level, thereby increasing the number of values above the reporting limits; and c) obtaining additional high flow samples over a longer period of record.
- (3) Upgrade the quality-assurance program by increasing the number of quality-control samples in order to ensure the adequacy of sampling procedures and sample analysis.

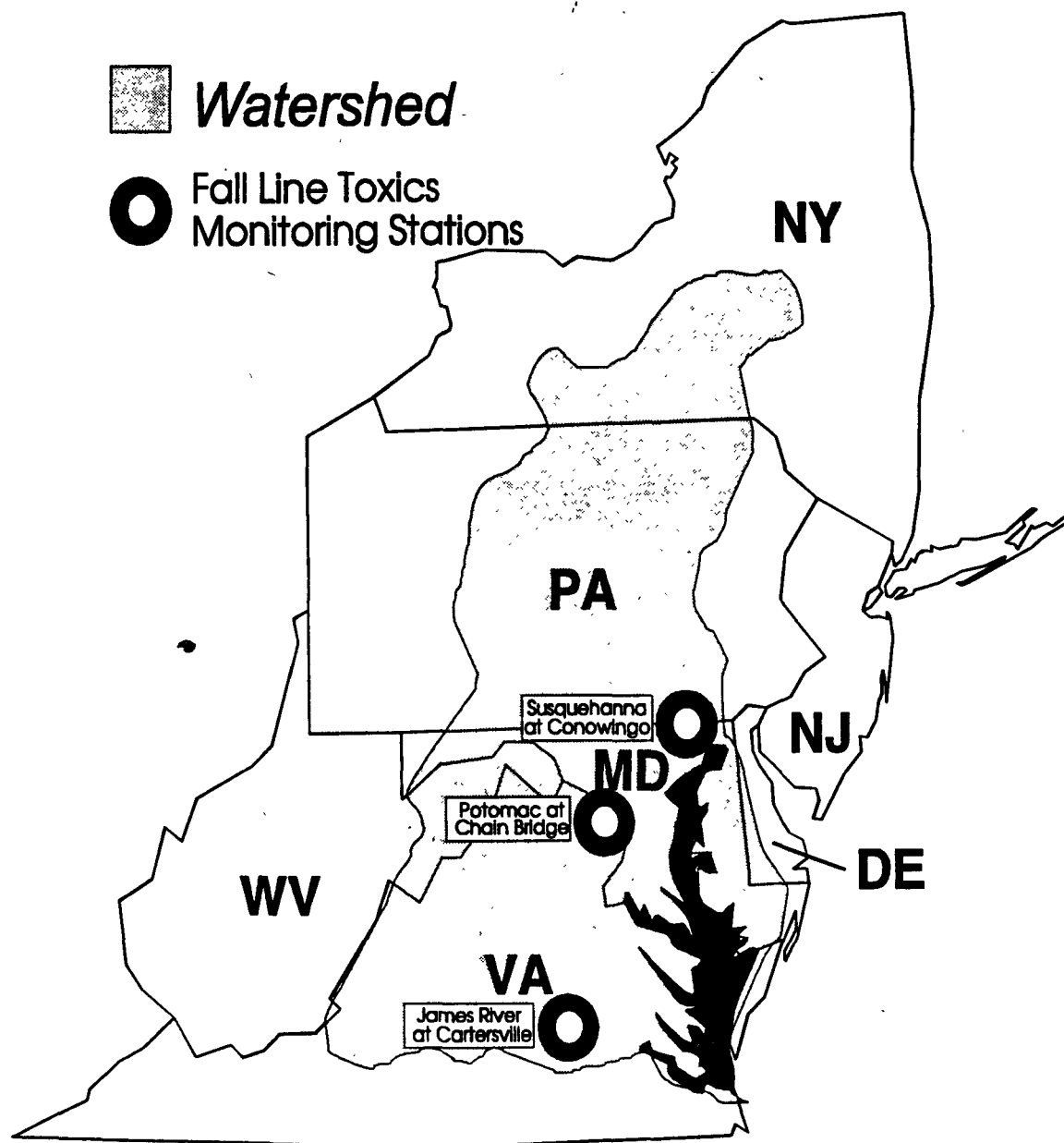
## **Sampling Station Descriptions**

Each sampling location has unique physical characteristics, sampling methodologies and sampling histories. The following sections describe the characteristics of each sampling location.

### *Susquehanna River at Conowingo Dam, Maryland*

The Susquehanna River was selected for the Fall Line Toxics Monitoring Program because it is the Chesapeake Bay's largest tributary, draining approximately 27,100 square miles above the fall line, and contributing an average of 51 percent of the freshwater flow to the Chesapeake Bay annually. The monitoring station, located at Conowingo, Maryland, is the southern-most downstream site of three dams on the Susquehanna River, which include Safe Harbor, Holtwood, and Conowingo Dams. The Conowingo Dam is a hydroelectric powerplant and is located ten miles up the tidally-influenced portion of the Susquehanna River known as Susquehanna Flats.

**Figure 1.** Location of the Chesapeake Bay fall line toxics monitoring stations.



Baseflow and stormflow nutrient and suspended sediment data have been collected as part of the Chesapeake Bay River Input Monitoring Program since late 1984. Data have also been collected for the same set of parameters through the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) since 1979, and from a USGS water quality study conducted during 1978-1981 for selected metals and pesticides. The specific location of the monitoring site is latitude 39°39'31", longitude 76°10'28", in Harford County, Maryland; the hydrologic unit is 02050306.

#### *James River at Cartersville, Virginia*

The James River at Cartersville, Virginia, with a drainage area of 6,257 square miles, was selected for the Fall Line Toxics Monitoring Program as another major tributary to the Chesapeake Bay. It contributes an average of 12 percent of the freshwater flow to the Chesapeake Bay. The James River is less affected by dams and other manmade structures than the Susquehanna River, and so may be more representative of a natural river system. Historical data at this station include nutrients and suspended solids collected during base flow and stormflow events as part of the Fall Line River Input Project begun in late 1988. Also, as part of the U.S. Geological Survey National Stream Quality Accounting Network (NASQAN) since 1979, samples have been collected for a number of water quality constituents, so that an extensive water chemistry data base exists. The specific location of this monitoring site is latitude 37°40'15", longitude 78°05'10", located on State Highway 45 in Goochland County, Virginia; the hydrologic unit is 02080205.

The sample-collection methods at the Susquehanna and James Rivers for both the 1990-91 period and the 1992 period were designed to ensure that samples were representative of river conditions. The methods were adapted from procedures that are documented in two USGS published reports: *Field Methods for Measurement of Fluvial Sediment* (Edwards and Glysson, 1988) and *Methods for Collection and Processing of Surface-Water and Bed-Material Samples for Physical and Chemical Analyses* (Ward and Harr, 1990).

Samples for the entire sampling period (1990-92) were analyzed for concentrations of selected dissolved and total-recoverable metals. For 1992, specific parameters were selected based on the results of the 1990-91 study and included all metals on the Chesapeake Bay Program's Chesapeake Bay Toxics of Concern List (Chesapeake Bay Program, 1991).

Because concentrations of total-recoverable metals are usually related to the amount and nature of suspended sediment, a sand-fine suspended-sediment analysis was also performed during the entire sampling period of 1990-92. This analysis provides the breakdown of the particle size distribution of suspended sediments transported in river flow (sands, greater than 0.062  $\mu\text{m}$  in diameter; silts, less than 0.062  $\mu\text{m}$ ). The relationship between the particle size and concentrations of total-recoverable metals may be key in the development of load estimations for metals.

#### *Potomac River at Chain Bridge, Washington, D.C.*

The Occoquan Watershed Monitoring Laboratory (OWML) established a Potomac Fall Line Pollutant Input Monitoring Station in the early spring of 1983 for the Washington Metropolitan Area Coordinated Potomac River Monitoring Program. Since the original installation, the station

has been included in the Fall Line River Input Monitoring Program established as a part of Maryland's Chesapeake Bay Water Quality Monitoring Program. The station operations cost is currently shared by funding from the Metropolitan Washington Council of Governments (MWCOG) and the Maryland Department of the Environment. Under normal operations, the station is used to collect data on conventional pollutants (nutrients, *etc.*). During the period March 1992 to March 1993, the station was also used to collect baseflow and stormflow samples for selected metals and organic contaminants.

The Potomac River fall line is located upstream of the northwestern border of Washington, D.C. The fall line water quality monitoring operations conducted by MWCOG/OWML are located at two separate points on the river just downstream of the fall line.

The Little Falls Dam is located on the Potomac River just below the fall line near Washington, D.C. The river drains 11,560 square miles at the dam location. The dam, which creates a pool for the major raw water intake for the Washington Aqueduct Authority, is located at a natural bifurcation in the stream, and provides control section for the maintenance of a stage-discharge relationship (Prugh *et al.*, 1986). A USGS stream gage has maintained a continuous hydrologic record at the site since 1930. From a sampling standpoint, a well-mixed cross section is key to the successful characterization of river flow with a point sample. The wide cross section (approximately 1700 ft.), and the natural bifurcation created by a mid-stream island ensure that the river cross section is poorly mixed at the Little Falls Dam, and therefore unsuitable for the extraction of a point sample representative of the entire flow of the River.

One and a half miles downstream of the Little Falls Dam, the Potomac River passes through a very narrow (approximately 200 feet) constriction in the vicinity of the Virginia Route 123 crossing at Chain Bridge, latitude 38°55'46" and longitude 77°07'02". This location, because of its well-mixed cross section, was found to be suitable for the withdrawal of both baseflow and storm runoff samples. However, because the location is subject to backwater influences from tidal cycles in the upper estuary, it was found to be unsuitable for the establishment of a stage-discharge relationship that could be used to pace automatic sampling equipment.

Because the deficiencies at each location disqualified both for the joint role of gaging and sampling station, each site was instrumented to accomplish the function for which it was best suited, and to rely upon telecommunications hardware and software to coordinate station operation. The Little Falls station, therefore, was instrumented for flow measurement, and the Chain Bridge station was equipped for automatic sample retrieval. Because there is only a minor increase in total drainage area between the two locations (two minor first-order tributaries), it was determined that the two stations could be operated as a single gaging and sampling system. The link was accomplished via telephone with an OWML-designed and constructed computerized gaging system placed at the two locations. The operation of this station is described later in this report.



## **SAMPLING PROGRAM**

### **Metal and Organic Contaminant Sampling Program - Susquehanna River**

Water quality samples were collected at the Susquehanna River at Conowingo Dam using an equal-discharge increment method, meaning that the samples were collected along the river cross section at the midpoint of equal increments of discharge. Samples were collected during periods of baseflow and stormflow. Storms on the Susquehanna River, for the purpose of this study, were operationally defined as occurring when water passed over the spillway. This represents a discharge exceeding 80,000 cubic feet per second (ft<sup>3</sup>/s), which is the maximum turbine capacity.

Sample collection methods and equipment used during the 1990-91 and the 1992 study are presented in the following text. Equipment and methods used in 1992 reflect the adoption of ultra clean sampling techniques.

#### *Sample collection methods for the 1990-91 period*

The field-collection equipment used at this site included a Nalgene (metals) or glass (organic contaminants) collection bottle, an epoxy-coated weighted bottle holder, and a polyethylene churn splitter. For separation of the "dissolved" fraction of a sample, an aliquot of water collected with this equipment was processed through a 0.45  $\mu$ m cellulose membrane filter, that was mounted in a 142 millimeter plastic filter stand. The collection bottle, churn splitter, and filter stand were cleaned with a 10% hydrochloric acid solution and rinsed with deionized water prior to each sampling event. All equipment was rinsed with sample water prior to collection.

Water quality samples for metal analysis were collected at several sections along the upper and lower catwalks of the dam, located directly over the turbine outflow. At each section, the sample bottle, placed in the weighted sampler, was lowered into the river and allowed to fill, but not overflow. The water quality sample was then poured into the churn splitter. A churn splitter is a sample consolidation device that is designed to produce homogeneous samples that are representative of the entire river cross section. Once water had been collected from all sections, the composite sample was mixed in the churn splitter.

Subsamples were then poured from the churn splitter into precleaned sample bottles. At each section, a suspended-sediment sample was also collected in a precleaned glass bottle placed in the weighted sampler. Samples for organic analysis were collected directly into sample bottles at the midpoint of the river cross section.

Samples for total-recoverable metal analyses were preserved with nitric acid (1 mL per 250 mL of sample). Samples for dissolved metals analysis were filtered on-site, placed in pre-cleaned bottles, and preserved with nitric acid. Total-recoverable and dissolved mercury (Hg) samples were preserved with 10 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. No preservative was added to the samples for organic contaminant or suspended sediment analysis.

All of the sample bottles were labeled with the station number, date, time, and analysis to be

conducted. Information was also recorded on field sheets. Metal and organic contaminant samples were packed in ice-filled coolers and sent to the NWQL for analysis. The suspended sediment samples were analyzed at the USGS Sediment Laboratory in Harrisburg, Pennsylvania.

*Sample collection methods for the 1992 period*

Standard operating procedures for collection and processing of water quality samples are given in the 1992 project Quality Assurance Project Plan (QAPP). Some of the techniques are presented or expanded on in the following text.

Water quality samples were collected according to ultra clean sampling protocol developed by Dr. Howard Taylor of the National Research Program of the U.S. Geological Survey, Boulder, Colorado, for metals, and Dr. Gregory D. Foster, George Mason University, for organic contaminants. These methods include the use of sample collection and processing equipment which are non-contaminating and analyte-inert.

Specifically, the term "ultra clean" indicates:

1. Stringent precleaning of all containers, sampling equipment, filtration equipment, and filters;
2. Use of very high-quality water and acids for preparatory washing, blanks, preservation, and analysis;
3. Avoidance of contact between sample water and either metal or plastic surfaces, depending on the class of analyte;
4. Special precaution in the field handling of samples, including:
  - a. Avoidance of all metal or plastic surfaces,
  - b. Use of non-contaminating gloves and forceps,
  - c. Avoidance of car exhaust and atmospheric deposition; and
5. Use of a class 100 clean hood for laboratory processing and analyses of metals samples.

Project-dedicated sampling equipment included: a Teflon-coated stainless steel churn splitter, Teflon dosing bottles and bags for storing and transporting equipment; a double-check-ball 2 liter Teflon bailer, normally used for groundwater sample collection; and a 100 foot length of 7/32 inch diameter nylon or polyester rope wound on a plastic "Cordwheel" to lower and raise the bailer to and from the point of sample collection. Project-dedicated laboratory equipment included a Teflon filter apparatus, Teflon-coated tweezers, and Teflon bags for storage of equipment.

The equipment, including the bailer and nozzle, filter apparatus, Teflon bags, bins, and churn splitter were washed with a soapy water wash, thoroughly rinsed with tap water, rinsed with a flush of lab-grade methanol, two flushes with high-quality organic-free water, a flush with 10% nitric acid solution, and two flushes of high-quality inorganic-free water, before and after each sampling trip. The bailer was then stored in clean Teflon bags which slipped into a 3 inch PVC tube. Other equipment was stored in clean Teflon bags in clean high-density-polyethylene bins.

All equipment coming into contact with the sample was thoroughly rinsed initially with river water. This rinsing included collecting two bailer volumes (approximately one gallon) and pouring each through the nozzle of the bailer into the churn splitter. The churn splitter was thoroughly washed with river water, ensuring that all surfaces came into contact with the water. The river-water rinse was discarded and the rinse step repeated.

Samples for metal analysis were collected in bottles provided by the USGS NWQL; the prescribed 250 mL polyethylene, acid-rinsed bottles were prepared for the ultra clean program by two initial rinses of high-quality inorganic-free water, a 24-hour soak in 10% Ultrex nitric acid, and two 24 hour soaks with high-quality inorganic-free water. The bottles were then refilled 1/2 to 3/4 full with fresh high-quality inorganic-free water and stored for use as needed.

Samples for organic contaminant analysis were collected in 37.5L stainless steel milk cans or 4L amber glass bottles with Teflon-lined lids. Water samples collected in the Teflon bailer were placed directly in the milk cans. The lids to the milk cans remained tightly fitted except during sample transfer from the bailer to prevent contamination.

Water quality samples were collected at five sections of equal discharge along the turbine outflow. At each section, the sample was poured directly into the churn splitter via a Teflon nozzle inserted into the bailer just before the moment of sample transfer. In order to minimize potential contamination, the collection process involved a minimum of two people, a designated "clean" person and a designated "dirty" person. The clean person, with a change of surgical gloves at each sample collection point along the cross-section was responsible for handling the sample-collection device only and avoiding contact with metal objects or anything else that could contaminate the sample. The dirty person, also with a clean pair of gloves at each section, handled all other equipment involved in the sample collection process. This process was continued at each of the five sampling points along the cross section.

Field measurements were performed for water and air temperature, pH, specific conductance, dissolved oxygen, alkalinity, and barometric pressure. All field information was recorded on both the laboratory analytical services request form and on the field sheet.

Processing of the samples was conducted in a designated van set up specifically for ultra clean water quality sample processing. Inside the van, the composited sample was churned and poured from the churn-splitter into the designated sample and holding bottles.

Water quality samples designated for total-recoverable analysis were preserved on site with Ultrex nitric acid (1 mL per 250 mL of sample), dispensed from a Teflon dosing-bottle outside the van, and transported back to the office lab to be processed for shipment to the NWQL laboratory, Denver, Colorado. Samples for dissolved analysis were transported in 500 mL Teflon-holding bottles to the office lab and filtered using a non-contaminating and analyte-inert filter apparatus and 0.4  $\mu$ m polycarbonate-membrane-filters that were initially rinsed with 0.1% Ultrex nitric acid and then rinsed with high-quality inorganic-free water. Filtration was conducted in a Class 100 laminar flow hood. A filter blank was performed with each filtration using high-quality inorganic-free water. All metals samples were preserved with Ultrex nitric acid dispensed from a 300 mL Teflon-dosing bottle delivering a 1 mL dose. A list of sample bottles used and the preservation methods are given in Table 1. Specific sample process

procedures are given in detail in the project QAPP.

Samples for organic analysis were processed on-site immediately after collection or were shipped on ice to George Mason University. Because travel times were relatively short (<2 hours), no preservatives were added to the samples for organic contaminant analysis.

## **Metal and Organic Contaminant Sampling Program - James River**

Water quality samples at the James River at Cartersville, Virginia, were also collected using an equal-discharge increment method, meaning that samples were collected along the river cross section at the midpoint of equal increments of discharge. Water-quality samples were collected using a depth-integrated sampler. As at the Susquehanna, samples were collected during periods of both baseflow and stormflow. For the purpose of this study, at the James River samples were considered stormflow samples if the maximum discharge after a precipitation event was greater than 12,000 cubic feet per second (cfs).

Sample collection methods and equipment used during the 1990-91 and the 1992 study are presented in the following text. Equipment and methods used in 1992 reflect the adoption of ultra clean sampling techniques. Although there is some overlap with the procedures used on the Susquehanna River, there are a number of differences also. Therefore, the entire procedure is given.

### *Sample collection methods for 1990-1991 period*

The field-collection equipment used at this site differed depending on the flow conditions. At those times when the mean cross-sectional velocity at the James River was greater than 1.5 feet per second (ft/s), corresponding to a discharge of approximately 4,200 cfs, a depth-integrating sampler was used. At a velocity less than 1.5 ft/s, the depth-integrating sampler is ineffective so a point sampler was used.

The equipment used at this site included an epoxy-coated weighted-bottle sampler or an epoxy-coated depth-integrating sampler, depending on the flow velocity. Within each sampler was a glass collection bottle, from which the sample was poured into a polyethylene churn splitter. An aliquot of water collected with this equipment was processed through a 0.45  $\mu\text{m}$  cellulose membrane filter, which was mounted on a 142 millimeter plastic filter stand, for separation of the "total" and "dissolved" fractions of a sample. All equipment was rinsed with sample water prior to sample collection. Samples for the determination of suspended sediment were collected directly into a glass bottle placed in the depth-integrating sampler. These bottles had been pre-cleaned at the USGS Sediment Laboratory in Harrisburg, Pennsylvania.

Water quality samples for the analysis of metals and organic contaminants were collected at the midpoint of five sections of equal discharge. At each section, the sample bottle was placed either in the weighted-bottle sampler or the depth integrating sampler, then was lowered into the river and allowed to fill, but not overflow. The water-quality sample was then poured into the churn splitter. Once water had been collected from all five sections, the composite sample was mixed in the churn. Subsamples were then poured into precleaned sample bottles. At each section, a suspended-sediment sample was collected using a glass bottle placed in either the

**Table 1.** James River sample bottles and preservation techniques.

TOTAL RECOVERABLE METALS - NATIONAL WATER QUALITY LABORATORY		
Bottle Designation	Bottle Size and Prep.	Preservation
RAH	8 oz. acid-rinsed	Add 1 ml ultrex nitric acid.
RA	8 oz. acid-rinsed	Add 1 ml ultrex nitric acid.
FA	8 oz. acid-rinsed	Add 1 ml ultrex nitric acid.
RAM	8 oz. glass	Add 5 ml KCr2.
FU	8 oz. regular	None.
RU	8 oz. regular	None.
TOC	4 oz. amber glass	Ice sample.
DISSOLVED METALS - NATIONAL RESEARCH PROGRAM		
Bottle Designation	Bottle Size and Prep.	Preservation
MERCURY HOLDING-BOTTLE	500 ml Teflon	Ice sample.
METALS HOLDING-BOTTLE	500 ml Teflon	None.
FA/FU HOLDING-BOTTLE	500 ml Teflon	None.
pH CHECK BOTTLE	8 oz. regular	None.
FA BLANK	8 oz. acid-rinsed	Add 1 ml ultrex nitric acid.
FA RINSE	8 oz. acid-rinsed	None.
FA	8 oz. acid-rinsed	Add 1 ml ultrex nitric acid.
FA BLANK FILTER	50 mm petri-dish	None.
FA FILTER	50 mm petri-dish	None.
FAM BLANK	4 oz. glass	Add 5 ml K2CrO4. Chill.
FAM RINSE	4 oz. glass	None.
FAM	4 oz. glass	Add 5 ml K2CrO4. Chill.
ORGANIC COMPOUNDS - GEORGE MASON UNIVERSITY		
Bottle Designation	Bottle Size and Prep.	Preservation
ORGANICS SAMPLE	4-liter amber glass	Chill.
EQUIPMENT BLANK	4-liter amber glass	Chill.

depth-integrating sampler or the weighted-bottle sampler. Samples for total-recoverable metal analyses were preserved with nitric acid (1 mL per 250 mL of sample). Samples for dissolved metals analysis were filtered on-site, placed in precleaned bottles, and preserved with nitric acid. Total-recoverable and dissolved Hg samples were preserved with 10 mL of a nitric acid/potassium dichromate solution. No preservation was needed for the suspended-sediment samples. The bottle type, volume, and preservation for each sample are listed in the 1990-91 QAPP on file at the EPA Chesapeake Bay Program Office.

All of the sample bottles were labeled with the station number, date, time, and analysis to be conducted. Information was also recorded on field sheets. Metal samples were packed in ice-filled coolers and sent to the NWQL for analysis. The suspended-sediment samples were sent to the USGS Sediment Laboratory in Harrisburg, Pennsylvania.

#### *Sample collection methods for 1992 period*

Standard operating procedures for collection and processing of water quality samples are given in the 1992 project QAPP. Some of the techniques are presented or expanded on in the following text.

Water quality samples collected in 1992 were collected according to the ultra clean sampling protocol developed by Dr. Howard Taylor of the National Research Program of the U.S. Geological Survey, Boulder, Colorado. These methods include the use of sample collection and processing equipment which are non-contaminating and analyte-inert.

Specifically, the term ultra clean indicates:

1. Stringent precleaning of all containers, sampling equipment, filtration equipment, and filters;
2. Use of very high-quality water, organic solvents, and acids for preparatory washing, blanks, preservation, and analysis;
3. Avoidance of contact between sample water and metal or plastic surfaces;
4. Special precaution in the field handling of samples, including:
  - a. avoidance of all metal and/or plastic surfaces,
  - b. use of non-contaminating gloves and forceps,
  - c. avoidance of car exhaust and atmospheric deposition; and
5. Use of a plexiglass glove box for laboratory processing and analysis of metals samples.

At the James River at Cartersville, special equipment was utilized to collect and process a contaminant-free representative sample. Project-dedicated field equipment included: a 3 liter Teflon sampling bottle fitted with Teflon cap, nozzles, and bottle-to-cap adapter, a Teflon-coated stainless steel churn splitter, Teflon dosing bottles and bags for storing and transporting equipment. A modified D-77 depth-integrating sampler fitted with the Teflon sampling bottle was used for sample collection. The weight of the D-77 sampler requires that a 4-wheel boom fitted with an electric motor and a B-reel be used to lower and raise the sampler at the point of sample collection. Project-dedicated laboratory equipment included a Teflon filter apparatus, Teflon-coated tweezers and Teflon bags for storage of equipment.

The equipment, including the Teflon bottle, cap, and nozzle, filter apparatus, Teflon bags, bins, and churn-splitter, was washed with a liquinox soapy water wash, thoroughly rinsed with tap water, rinsed with a flush of lab-grade methanol, two flushes with high-quality inorganic-free water, a flush with 10% nitric acid solution, and two flushes of high-quality inorganic-free water after each sampling trip. The Teflon bottle, nozzles and other equipment were stored in clean Teflon bags in clean high-density-polyethylene bins.

All equipment coming in contact with sample water was thoroughly rinsed with river water before sampling began. This rinsing included collecting one sampler volume (approximately three liters each time), thoroughly rinsing the sampler bottle, then pouring the water into the churn splitter. The churn-splitter was thoroughly washed with river water, ensuring that all surfaces came in contact with the water. The river water rinse was discarded and the step repeated.

Samples were collected in bottles provided by the USGS NWQL; the prescribed 250 mL polyethylene, acid-rinsed bottles were prepared for the ultra clean program by 2 initial rinses of high-quality inorganic-free water, a 24-hour soak in 10% nitric acid (made with Ultrex nitric acid and high-quality inorganic-free water), and two 24-hour soaks with high-quality inorganic-free water. The bottles were then refilled 1/2 to 3/4 full with fresh high-quality inorganic-free water (to be used as a filter rinse) and stored for use as needed.

Samples were collected at the midpoint of five sections of equal discharge along the bridge. At each section, the sample was poured directly into the churn splitter. The sampling process involved a minimum of two people, a designated "clean hands" person and a designated "dirty hands" person. The clean hands person, with a change of surgical gloves at each sample collection point along the cross-section, was responsible for handling the sample bottle and nozzle only. The dirty hands person handled all other equipment, particularly any equipment with metal surfaces. This process was continued at each of the five sampling points along the cross-section.

Samples for organic contaminant analysis were collected in 37.5 L stainless steel milk cans or 4-L amber glass bottles with Teflon lined caps. Precleaned milk cans were prepared for the fluvial samples by rinsing the can twice with 2 L of surface water. The rinses were discarded prior to the placement of the surface water samples in the containers. Amber glass bottles were prepared using a similar technique, but were further heated to 350 °C twelve hours and prerinsed with methanol.

Measurements of water and air temperature, pH, specific conductance, dissolved oxygen, and barometric pressure were conducted in the field. All field information was recorded on both the laboratory analytical services request form and on the field sheet.

Initial processing of the samples was conducted in a designated van, set up specifically for water-quality sample processing. Inside the van, the sample composite was churned and transferred from the churn-splitter into the designated sample bottles and holding bottles.

Sample water designated for total-recoverable metals analysis was preserved on site with Ultrex nitric acid (1 mL per 250 mL of sample), dispensed from a Teflon dosing bottle, then was transported back to the office lab to be processed for shipment to the NWQL. Dissolved metals

samples were transported in 500 mL Teflon holding bottles to the office lab and filtered using a Teflon filter apparatus and 0.4  $\mu$ m polycarbonate membrane filters that were initially rinsed with 0.1% Ultrex nitric acid wash and then rinsed with high-quality inorganic-free water. A filter blank was processed with each filtered sample using high-quality inorganic-free water.

All metals samples were preserved with Ultrex nitric acid dispensed from a Teflon dosing bottle delivering a 1 mL dose. Filtration was conducted in a plexiglass glovebox lined with Teflon. A list of sample bottles used and the preservation methods are given in Table 1. Specific sample processing procedures are given in detail in the QAPP.

Samples for organic contaminant analysis were processed on-site immediately after collection or were shipped on ice to George Mason University. Because travel times were relatively short (e.g., <2 hrs), no preservatives were added to samples for organic contaminant analysis.

### **Metal and Organic Contaminant Sampling Program - Potomac River**

As mentioned earlier in this report, the OWML-operated monitoring station at Chain Bridge on the Potomac River is paced from the USGS gage at Little Falls, where the flow measurement is performed.

The flow measuring equipment located at the Little Falls Dam station includes a microcomputer with an internal modem, an analog-to-digital (A/D) converter, and a contact pressure transducer submerged in the river. The transducer is oriented in the river flow in such a way as to assure that only static head is sensed. The pressure transducer creates an output voltage corresponding to river stage which is sent to the A/D converter, which then transforms the signal to a computer-readable digital form. The microcomputer is equipped with a program which reads the signal from the A/D converter, calculates water surface height above the datum, and determines discharge from a rating curve file stored in random access memory (RAM). The rating curve for the Little Falls Dam was developed, and is currently maintained, by the USGS.

When the pressure transducer senses an increase in stage, the computer program enters a storm computation subroutine, and begins calculating the total river flow volume passing the gage. During a storm, at pre-set increments of flow volume, the computer contacts the Chain Bridge station via telephone, and instructs the equipment to withdraw a sample.

The microcomputer located at the Little Falls station stores flow data in RAM files. Stage, flow, and sample collection data may be retrieved over the telephone link using a third computer located at OWML. Data are stored hourly during baseflow conditions and every 15 minutes during storms.

The major consideration in siting the sample intake for the station was the requirement to extract a truly representative sample of the river flow at a variety of stages, ranging from baseflow to extreme storm peaks. In order to accomplish this objective at Little Falls, the site of the gage, it would have been necessary to install multiple sample intakes across the river cross section in order to adequately represent the various bifurcations and velocities observed. Indeed, the river cross section at Little Falls was deemed to be so poorly mixed that it was impractical to obtain representative samples of the river flow at that point.



As noted previously, however, at Chain Bridge the river has been observed to be well-mixed. The flow is constricted into a single channel near the Virginia shore, making the retrieval of samples convenient. A room is located inside the bridge abutment on the Virginia side, providing a convenient location to house sampling equipment. This location was also previously used by the USGS to house a continuous monitor prior to 1983. Significant modifications to the abutment room were undertaken, however, following the resurfacing of the Chain Bridge deck.

Because of the high suction lift from the water surface to the sampling room, it was necessary to install a submersible pump at the sample intake point. The pump was attached to a flexible intake line which was fixed to the downstream side of the bridge abutment. In the sampling room, the pump discharge was routed to a constant head tank designed to allow complete mixing of the discharge flow, minimize sedimentation, and allow rapid sample turnover. With the submersible pump operating at 10 gpm, the constant head tank was designed to allow a turnover time of less than one minute. The sampler is a Sigmamotor Refrigerated Automatic Sampler (Sigmamotor, Inc.). A peristaltic pump is employed to transport samples from the constant head tank into the sample containers. Because the constant head tank maintains a fixed water surface elevation, the pump maintains a constant intake velocity, which is greater than 3 ft/s, thereby avoiding loss of sediment in the sample stream. The unit may be programmed to collect discrete or composite samples. Samples are kept at 4°C in the refrigerated compartment located in the sampler base.

Samples for organic contaminant analysis were acquired from the head tank and placed in 37.5 L stainless steel milk cans. The milk cans were then sealed and transported to George Mason University for immediate processing.

Activation of the automatic sampling equipment at the Chain Bridge station is accomplished by a microcomputer paced by the equipment located at the Little Falls gaging station. When the microcomputer receives a call from the Little Falls station, it activates the submersible pump through an electrical relay. After allowing the constant head tank to fill, the computer triggers the sampler to withdraw an aliquot from the tank.

Because of the large drainage area of the Potomac River at Chain Bridge, storm events may continue over a number of days. For this reason, during storm events samples are retrieved daily in order to avoid exceeding established holding times in the field. All installed equipment is housed in the sampling room enclosed in the bridge abutment. A site log of the performance, calibration, and maintenance of all instrumentation is kept as a part of the permanent station record.

The automated sampling system described above allows flow-weighted composite samples to be collected automatically through the duration of a storm event. This method eliminates most of the common problems associated with attempting to occupy sampling sites with personnel during a storm in order to collect grab samples. Further, the method allows multiple samples to be collected at equally spaced flow volume increments throughout a storm which may last several days. During baseflow periods manual grab samples were collected.

The only on-site measurements conducted as a part of the fall line monitoring program were dissolved oxygen, pH, temperature, alkalinity, and conductivity. All the foregoing analyses are

conducted in accordance with accepted practice as detailed in *Methods for Chemical Analyses of Water and Wastes* (EPA, 1979), the applicable edition of *Standard Methods for the Examination of Water and Wastewater* (APHA, 1992), and manufacturer's literature, as appropriate. In the strictest sense, the measurement of time and stage at the Little Falls Gage may also be considered to be on-site analyses. These are conducted as described above, and are recorded on-site upon collection of baseflow samples.

The station at Chain Bridge is operated in such a way as to establish a well-defined estimate of both base- and stormflow loads of conventional pollutants entering the estuary. To this end, the station operates automatically, and attempts to sample all storm events occurring throughout the year. The addition of toxics monitoring to the station analytical schedule did not significantly alter the operating protocol.

## **QUALITY ASSURANCE PROGRAM**

A Quality Assurance Project Plan (QAPP) for the Maryland and Virginia Fall Line Toxics Monitoring Program was prepared by the USGS and MDE for the 1990-91 period. This original QAPP was revised in 1992 to reflect changes to the program including an updated list of the constituents sampled, lowered analytical quantitation levels, and ultra clean water quality sampling techniques. The 1990-91 and 1992 QAPP are available for review at the EPA Chesapeake Bay Program Office, Annapolis, Maryland. Some of the material included in the 1992 QAPP is presented or expanded on in this report.

For the Susquehanna and James Rivers, the transition to ultra clean sampling and analysis techniques was designed to minimize possible contamination of water quality samples and to ensure that samples could be collected and analyzed for metals at lower quantitation levels. Quality assurance was emphasized at the beginning of the sampling period in order to assess as quickly as possible the new, ultra clean methods in use.

### **Metals Quality Assurance Program - Susquehanna River**

The following quality-control samples were collected for metals at the Susquehanna River station:

- (1) Five sets of samples were collected to compare the 1990-91 sample collection and analysis methods (known as "old" methods) to the 1992 sample collection and analysis methods (known as "new" or ultra clean methods) for both total-recoverable and dissolved metals.
- (2) Six equipment-blank samples were collected using 1992 ultra clean methods for both total-recoverable and dissolved metal analyses, in order to identify any potential sources of contamination to the water quality sample from sample collection and/or field processing techniques. An equipment-blank sample was collected by passing high-quality, inorganic-free water through all sample collection apparatus as well as filter apparatus, using 1992 analytical methods.
- (3) Nine filter-blank samples were collected using 1992 ultra clean methods for the dissolved metals analyses, in order to identify any potential sources of contamination to the water quality sample from the filter apparatus. A filter-blank sample is collected by passing high-quality, inorganic-free water through the filter step only, and analyzed using the 1992 methods.
- (4) Two sets of replicate water quality samples were collected using 1992 ultra clean methods for both total-recoverable and dissolved metal analyses, in order to assess the precision of the laboratory methods.

The laboratories providing water analyses and data for this program were the USGS National Water Quality Laboratory for total-recoverable metal analyses, the USGS National Research Program Laboratory for dissolved metal analyses, and the USGS Sediment Laboratory for suspended sediment analyses.

## **Metals Quality Assurance Program - James River**

The following quality-control samples were collected for metals at the James River station:

- (1) Five sets of samples were collected to compare the 1990-91 sample collection and analysis methods (known as "old" methods) with the 1992 sample collection and analysis methods (known as "new" or ultra clean methods) for both total-recoverable and dissolved metals.
- (2) Four equipment-blank samples were collected using the 1992 ultra clean methods for total-recoverable metal analyses, in order to identify any potential sources of contamination to the water quality sample from sample collection techniques. An equipment-blank sample was collected by passing high-quality inorganic-free water through all sample collection apparatus then analyzed using the 1992 analytical methods.
- (3) Sixteen filter-blank samples were collected using ultra clean methods for the dissolved metals analyses, in order to identify any potential sources of contamination to the water quality sample from the filter apparatus. A filter-blank sample is collected by passing high-quality, inorganic-free water through the filter step only, and analyzed using the 1992 analytical methods.
- (4) Two sets of replicate water quality samples were collected using 1992 ultra clean methods for total-recoverable metals, and one for dissolved metal analyses, in order to assess the precision of the laboratory methods.

The laboratories providing water analyses and data for this program were the same as for the Susquehanna River.

## **Metals Quality Assurance Program - Potomac**

The quality assurance program for the Potomac River was limited to only the laboratory component. Therefore, no equipment blanks were collected. Because analysis was performed for total recoverable metals only, a filter blank was not necessary. The laboratory quality assurance program consisted of blanks, duplicates and spiked samples that were part of the normal operating procedures. Samples to be tested as duplicates, or those to be spiked for a recovery analysis, were chosen from the entire sample set that was to be analyzed at any particular time.

## **Organic Contaminant Quality Assurance Program - Susquehanna, James and Potomac Rivers**

The reliability of analytical data was determined through quality assurance procedures conducted throughout this field study. The following quality assurance samples were collected and processed for the Chesapeake Bay Fall Line Toxics Monitoring Program:

- (1) **Field Blanks.** Dissolved phase and filter blanks were acquired by rinsing all water

sampling equipment with contaminant-free distilled water (double distilled water with further removal of trace organic impurities by extraction using a 10-g C-18 bonded phase silica cartridges) on-site prior to sample collection. The distilled water rinse was collected in a stainless steel milk can for further processing. Blank water was subsequently filtered through a stacked arrangement of 15.0-cm (diameter) Whatman GF/D and GF/F filters housed in the Millipore filtration apparatus. The filtered water was extracted as a sample in the usual fashion. The filter was removed from the filter holder, wrapped in aluminum foil, and stored in an ice chest until its return to the analytical laboratory. The filter was then put in long term storage at -20 °C until analysis. Field blanks indicated the presence of contamination in the analysis introduced during sample collection in the field. Precautions, described above for ultraclean sampling, were adopted to minimize sample contamination. Suspected "analytes" detected in the field blanks were used to screen sample concentrations. Field blank concentrations which were detected and quantified at levels >0.5 times the dissolved phase or particulate phase sample concentrations were used to flag sample concentrations in the fall line data base. Flagged concentrations are those which have questionable quality. Field blank results also provided feedback on the effort being placed into cleaning field equipment, etc., and corrective measures were undertaken when possible if this occurred. Ten dissolved phase and filter phase field blanks were analyzed in the Susquehanna River fall line study, and twelve dissolved phase and filter phase field blanks were analyzed in the James River fall line study.

- (2) **Laboratory Blanks.** Seven laboratory blanks were processed between March 1992 and February 1993, and were performed periodically throughout the entire Chesapeake Bay Fall Line Toxics Monitoring Program. Laboratory blanks consisted of two components: a dissolved phase component and filter phase component. Contaminant-free distilled water was filtered in the laboratory and the filtrate was extracted in the normal fashion. Suspected analytes in the laboratory blanks were used as a means of correcting sample concentrations. Average suspected analyte concentrations from the seven laboratory blanks (for both dissolved and filter phases) were averaged and subtracted (i.e., as a background subtraction) from individual sample concentrations to provide net sample concentrations for each analyte.
- (3) **Matrix Spikes.** Nine matrix spikes were performed for Susquehanna, Potomac, and James river fall line samples. Matrix spikes were used to determine the magnitude of determinant and indeterminant errors present in the analysis. A total of five matrix spike experiments were carried out with Carbopack B sorbents (including three Susquehanna River sub-samples and two James River sub-samples) between March and July 1992, and a total of four matrix spike evaluations were performed on Potomac River sub-samples using C-18 bonded phase silicas. Matrix spikes provided information regarding the accuracy and precision of the reported results, and matrix spikes accounted for 10% of all samples processed. A percent mass recovery (%Rec) value and its uncertainty (%RSD) were computed for the matrix spikes according to the equations below:

$$\% \text{Rec} = \frac{\text{Mass}_{\text{recovered}}}{\text{Mass}_{\text{spiked}}} \times 100 \quad (1)$$

$$\% \text{RSD} = \frac{\text{Standard Deviation}_{\text{Rec}}}{\text{Mean } \% \text{Rec}} \times 100 \quad (2)$$

- (4) **Extraction Mass Balance.** Approximately 30% of the number of extractions initially included both front and back sorbent cartridges (in the stacked configuration) to determine analyte breakthrough occurring during the extraction of dissolved phase analytes. Breakthrough was evaluated according to the calculation of collection efficiency ( $C_E$ ) shown below (%B is the percent of analyte measured on the back sorbent cartridge, and %F is the percent of analyte measured on the front sorbent cartridge):

$$C_E = (1 - \frac{\%B}{\%F}) \times 100$$

A solvent rinse of milk cans or glass bottles was performed during the collection of fall line samples to determine detectable levels of analysis of associated with container surfaces.

- (5) **Duplicate Analysis.** Method precision was further evaluated through the analysis of the organonitrogen and organophosphorus pesticides in duplicate samples. Several of the fall line samples were analyzed in duplicate for these pesticides. Duplicate analyses were conducted for thirteen river fall line samples including all three tributaries.
- (6) **Enrichment Factors.** The LSE sorbent cartridges employed in this study act to preconcentrate the target analytes from water on solid sorbents. The degree of preconcentration used in this study was necessary to achieve the desired QL values. Preconcentration is defined in this study by the enrichment factor ( $E_f$ ), which is calculated from the sample volume (ca. 10 L in this study), the final volume of the sample extract subjected to GC/MS or GC-ECD analysis (ca. 0.2 mL), and the efficiency of extraction from the sample, determined from the percent mass recovery (%Rec) values of the matrix spike data. The enrichment factor was calculated by using the relation:

$$E_f = \frac{\text{Volume}_{\text{sample}}}{\text{Volume}_{\text{sample extract}}} \times \frac{\% \text{Rec}}{100} \quad (4)$$

- (7) **Error Evaluation.** Determinate errors in the reported fluvial sample concentrations provided in this report can be derived from the %Rec values determined from the matrix spike experiments. Dividing the reported fluvial sample concentrations by %Rec/100 would, theoretically, provide the actual ambient analyte concentration in the fluvial sample at the time of collection. Although this correction procedure was not adopted in this study, it does give a perspective on the accuracy of the reported fluvial concentrations and insight on the level of potential biases in the data.

Indeterminate (random) errors associated with GC/MS and GC-ECD analyses are derived from a consideration of errors arising from the following sources: (a)

measurement of the amount of internal standard added to each sample extract in the analysis ( $\% \alpha_1$ ), (b) variations in relative response factors computed from instrument calibration data from the analysis of at least 10 calibrations ( $\% \alpha_2$ ), and (c) the measurement of each fluvial sample volume via a 2.0 L graduated cylinder -- or the measurement of particulates collected on GF/F filters by using analytical balances -- ( $\% \alpha_3$ ). Each of the random error terms in internal standard quantitation relation can be expressed in terms of percent relative error ( $\% \alpha$ ) according to the equation

$$C(\pm \% \alpha_4)_{\text{sample}} = \text{RF} \times \frac{\text{Mass}(\pm \% \alpha_1)_{\text{std}}}{\text{RRF}(\pm \% \alpha_2) \times V(\pm \% \alpha_3)_{\text{sample}}} \quad (5)$$

which is the same equation described above for internal standard quantitation but in this case errors are factored into it. The RF term in equation 5 is the response factor (area of analyte peak divided by area of internal standard peak in GC analysis) which has no assigned indeterminate error. Because RF is a ratio of GC peak areas, it is assumed that the indeterminate error terms cancel. Therefore, the error associated with any single reported concentration ( $\% \alpha_4$ ) can be expressed as propagated random error by the relation:

$$\% \alpha_4 = (\% \alpha_1^2 + \% \alpha_2^2 + \% \alpha_3^2)^{\frac{1}{2}} \quad (6)$$

It is assumed that random errors in the dissolved phase and particle phase measurements are equal. That is, the random error in measuring the volume of a dissolved phase sample is equal in magnitude to the error in measuring the mass of particulates isolated on the filters. In fact, measuring the mass of particulates has a smaller random error contribution than measuring sample volume, and, therefore, would tend to overestimate error slightly for the particulate phase measurements.

## **LABORATORY ANALYSIS METHODS**

### **Metals Laboratory Analysis Methods - Susquehanna and James Rivers**

The USGS National Water Quality Laboratory (NWQL) in Denver, Colorado performed analyses of all constituents during the 1990-91 period, and performed analyses for total-recoverable metals during the 1992 period. The analytical procedures used by the laboratory are standard procedures used in water quality studies, and are documented in the publication entitled, *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments* (Fishman and Friedman, 1985). The NWQL quality assurance program provides an ongoing measure of the quality of data reported, and documentation is available on request. The USGS National Research Program (NRP) in Boulder, Colorado, performed all analyses of dissolved metals collected during 1992. In order to achieve the lower quantitation levels necessary for the program, new techniques were developed for the analysis of dissolved metals that did not follow EPA analytical guidelines.

Metals monitored for the ultra clean study, and their analytical methods and quantitation levels are summarized in Table 2.

### **Metals Laboratory Analysis Methods - Potomac River**

Water samples that have been collected and preserved for analysis are often digested or extracted to solubilize trace elements associated with particulates in the sample. There are several types of digestion procedures. These vary primarily in the type and concentration of acid used, and the temperature at which the digestion is performed. The decision to use a particular digestion method is dependant upon the extent of sediment breakdown desired. For geological purposes a strong digestion, referred to as a "total digestion", is often needed to break down particulates into their elemental components. For environmental purposes a "total recoverable" digestion is generally preferred to extract elements sorbed onto the particulates. A total recoverable digestion is often chosen for environmental work because the interest is in trace metals that are labile and may become available to an ecosystem. OWML uses a total-recoverable digestion method as described in the 18th Edition of *Standard Methods for the Examination of Water and Wastewater* (APHA, 1992). It is listed in section 3030 and titled Preliminary Treatment for Acid-Extractable Metals. The extraction is done with 6N hydrochloric acid with the sample heated until the boiling point is reached (approximately an hour).

OWML purchased new instrumentation for metals analysis in the spring of 1992 (Perkin-Elmer 5100 system from Perkin-Elmer Corporation). Samples collected at the Chain Bridge station on the Potomac River were analyzed using the new instrumentation. The new instrumentation has the capability of measuring metals by either flame or furnace atomization followed by light absorption spectrophotometry. All metals were analyzed using furnace analyses, except for zinc, which was analyzed using flame atomic absorption. The analyses were performed in accordance with the manufacturer's guidelines and using a stabilized platform furnace atomization method. This method of furnace atomization is recommended in EPA Method Number 200.9 (EPA, 1991). The EPA method was written for drinking water analysis but is also applicable for



**Table 2.** Monitored metals and scheduled methods of analysis at the Susquehanna and James River stations.

Constituent	Analytical Technique	Quantitation Level( $\mu\text{g/L}$ )
Al (aluminum, Dis)	AA, DCP	10
As (arsenic, TR)	AA, gaseous hydride	1.0
As (arsenic, Dis)	ICP-MS	0.6
Ba (barium, TR)	AA, direct aspiration	100
Cd (cadmium, TR)	AA, graphite furnace	1.0
Cd (cadmium, Dis)	ICP-MS	0.1
Cr (chromium, TR)	AA, DCP	1.0
Cr (chromium, Dis)	ICP-MS	0.2
Cu (copper, TR)	AA, graphite furnace	1.0
Cu (copper, Dis)	ICP-MS	0.02
Fe (iron, TR)	AA, direct aspiration	10
Fe (iron, Dis)	AA, direct	10
Pb (lead, TR)	AA, graphite furnace	1.0
Pb (lead, Dis)	ICP-MS	0.06
Li (lithium, TR)	AA, direct aspiration	10
Mn (manganese, TR)	AA, direct aspiration	10
Hg (mercury, TR)	AA, cold vapor	0.1
Hg (mercury, Dis)	Cold vapor fluorescence	0.003
Ni (nickel, TR)	AA, graphite furnace	1.0
Ni (nickel, Dis)	AA, graphite furnace	1.0
Se (selenium, TR)	AA, gaseous hydride	1.0
Ag (silver, TR)	AA, graphite furnace	1.0
Sr (strontium, TR)	AA, direct aspiration	1.0
Zn (zinc, TR)	AA, direct aspiration	10
Zn (zinc, Dis)	ICP-MS	0.08

$\mu\text{g/L}$  = micrograms per liter; AA = Atomic Absorption; ICP-MS = Inductively coupled plasma, mass spectrometer; DCP = Direct current plasma; Dis = dissolved; TR = total-recoverable

non-potable freshwater samples.

### *Detection and Quantitation Levels for Metals*

As part of the procedure of bringing the new instrumentation on-line, OWML performed a detection limit study. Method detection (MDL) and quantitation levels (QL) were determined for each of the two atomization techniques—flame and furnace.

***Metals Analyzed by Flame Atomic Absorption Spectrophotometry.*** A commonly-used method for determining detection limits in the environmental field is outlined in the *Federal Register* (Vol. 49, No. 209, Appendix B to Part 136, October 26, 1984). A similar method for the calculation of the detection limit is listed in *Standard Methods for the Examination of Water and Wastewater* (APHA, 1992). That document also provides methods for calculation of quantitation levels. Quantitation levels are determined by multiplying the detection limit by a factor to represent concentrations that can be consistently measured as reliable. A key factor in the determination of detection and subsequent quantitation levels is the concentration chosen to be analyzed. Guidelines refer to trying to estimate the detection limit and using a concentration for analysis that is 1-10 times the estimated detection limit.

Rather than using a single concentration, it has been suggested that it may be more valid to measure a range of concentrations. Taylor (1987) is a proponent of the concept of using multiple concentrations. Taylor also states that the uncertainty of a value close to the determined method detection limit can be as much as 100%. Quantitation levels may be as high as 5-10 times the method detection limit and are valuable when increased validity of results is desired.

OWML chose to determine a quantitation level that could provide a 20-30% mean absolute difference in precision when measuring seven replicates of a standard. The percent mean absolute difference is defined as:

$$\text{Percent Mean Absolute Difference} = \frac{\sum_n | (C_{\text{obs}} - C_{\text{actual}}) |}{\frac{n}{C_{\text{actual}}}} \times 100 \quad (7)$$

A few of the elements that were analyzed had quantitation levels that provided a mean absolute difference in precision of less than 20%; these elements, therefore, will be measured with less error. A 20-30% difference was considered optimal: less than 20% may be overly conservative while greater than 30% may not be considered conservative enough. The common method of computing detection limits was employed. This involved analyzing seven replicates of a single concentration. However, in accordance with Taylor's recommendation for using multiple concentrations, six concentrations were chosen. This resulted in a total of 42 analyses, as opposed to 7, for computing the detection limit. The six chosen concentrations ranged from below the estimated detection limit to above ten times the estimated detection limit, depending upon the element. In most cases, a factor of 1.0-2.7 provided a mean absolute difference in precision of 20-30%, and this was used to determine the quantitation levels. Lead and nickel were difficult to measure at trace concentrations and only two of the six concentrations chosen were found to be in the detectable range.

*Metals Analyzed by Furnace Atomic Absorption Spectrophotometry*

The number of samples analyzed using a furnace atomic absorption spectrophotometer is of concern because these analyses require a long analysis time and higher expense per sample analyzed. When determining furnace detection limits the number of samples analyzed was decreased to seven replicates of a single carefully selected concentration for each element. The quantitation levels were conservatively estimated by either multiplying the detection limit by a factor of two or by choosing the standard concentration used in the detection limit study. The simplified approach of multiplication by a factor is fairly standard in reference texts and articles on quantitation limits (APHA, 1992; *Federal Register*, 1984; Keith, *et al.*, 1983; Taylor, 1987). The use of the standard concentration as the quantitation level was chosen when the standard deviation was so low that the resulting detection and quantitation levels were also calculated to be very low. Although extremely low detection limits are a positive attribute in laboratory analysis, OWML is also concerned with reporting limits that are achievable and not simply an artifact of statistics. Because of this, in the case of cadmium and chromium, the lowest standard measurable was considered a more valid measure than the MDL calculation.

OWML is reporting QLs for the case of all metals. Also, because of the analysis procedure employed (specifically, analysis by flame AA, and, if the concentration were below the QL for flame AA, then analysis by furnace AA), the effective QLs for all values reported are those for furnace AA. The QL for Zinc is for the flame AA method. This is because this element could not be resolved at a lower QL using furnace AA.

**Organics Laboratory Analysis Methods - Susquehanna, James and Potomac Rivers**

The fluvial samples collected from the fall line study were analyzed for the presence of nine organonitrogen and organophosphorus pesticides, eight organochlorine pesticides, 112 polychlorinated biphenyl (PCB) congeners, and four polycyclic aromatic hydrocarbons (PAH). The names of the analytes, the fluvial phase analyzed, and quantitation levels for each analyte are listed in Table 3.

*Filtration of Suspended Particulate Matter*

Suspended particulate matter  $\geq 0.7 \mu\text{m}$  in nominal diameter was isolated from water in all of the fall line samples via filtration through pre-cleaned glass fiber filters. River water placed in the milk cans from collection was pumped via a positive displacement pump at a rate of ca. 1 L/min. (Model QB-1, Fluid Metering Inc., Oyster Bay, NY) through a stacked configuration of a 15-cm Whatman GF/D glass fiber filter (25  $\mu\text{m}$  nominal pore diameter) overlaying a 15-cm Whatman GF/F glass fiber filter (0.7  $\mu\text{m}$  nominal pore size) housed in a Millipore stainless steel filtration apparatus. (The filter holder had been customized by the addition of a PTFE Teflon O-ring in place of the original Viton O-ring to minimize sample contamination and analyte reaction.) The filtered water was collected in another precleaned 37.5-L stainless steel milk can for subsequent extraction. Convuluted TFE Teflon tubing was used for sample transfer lines, the only type of surface apart from the metering pump that was allowed to come in contact with the water during sample filtration.

**Table 3.** Monitored organic contaminants and scheduled methods of analysis. The fluvial phase analyzed, dissolved and particulate, is indicated along with the method of analysis and quantitation levels (QLs).

Analyte	method	QL, diss. ng/L	QL, part. ng/g
(organonitrogen & organophosphorus group)			
simazine	gc/ms	2.0	na
prometon	gc/ms	1.6	na
atrazine	gc/ms	1.3	na
diazinon	gc/ms	2.5	na
alachlor	gc/ms	2.5	na
malathion	gc/ms	2.3	na
metolachlor	gc/ms	0.7	na
cyanazine	gc/ms	2.4	na
hexazinone	gc/ms	0.8	na
(organochlorine group)			
aldrin	gc-eed	0.2	2.2
oxychlordane	gc-eed	0.1	1.8
<u>gamma</u> -chlordane	gc-eed	0.1	1.7
<u>alpha</u> -chlordane	gc-eed	0.1	1.7
dieldrin	gc-eed	0.2	2.1
4,4'-DDT	gc-eed	0.5	6.0
<u>cis</u> - & <u>trans</u> (c/t)-permethrin	gc-eed	1.7	21.6
<u>cis</u> - & <u>trans</u> (c/t)-fenvalerate	gc-eed	0.6	7.3
ΣPCBs (112 congeners)	gc-eed	0.5	6.0
(polycyclic aromatic hydrocarbon group)			
naphthalene	gc/ms	0.1	1.0
fluoranthene	gc/ms	0.3	1.0
benz(a)anthracene	gc/ms	1.0	1.4
benzo(a)pyrene	gc/ms	2.0	2.7

gc/ms=gas chromatography/mass spectrometry; gc-eed=gas chromatography-electron capture detection.

GF/D and GF/F filters were folded into quarters together and placed in precleaned aluminum foil envelopes as soon as filtration was completed. The envelopes were sealed, labeled, added to Zip-lock plastic bags, and placed in an ice chest until they were returned to the GMU analytical laboratory. The filters were stored in a freezer at -20 °C until chemical analysis was performed.

#### *Analyte Isolation and Preconcentration from Water*

The monitored organic contaminants (Table 3) were extracted from the filtered fall line samples by using liquid-solid extraction (LSE) according to procedures previously described by Foreman and Foster (1991). Eight to twelve liters of filtered surface water was passed through LSE sorbent cartridges configured in a stacked front and back arrangement. For the extraction of Susquehanna and James River filtered water, the front sorbent cartridge contained 4 g of Carboxpack B graphitized carbon (120/400 mesh; Supelco, Inc., Bellefonte, PA) and the back cartridge contained 2 g of the same sorbent. For the extraction of filtered Potomac River water, cartridges containing 10-g of octadecylsilyl-bonded silica (C18) (Varian Assoc., Inc., Harbor City, CA) were used similarly in a stacked front and back arrangement.

Filtered water was pumped through the LSE cartridges using a Model QRHB-1CKC (Fluid Metering) pump at a flow rate of 50-75 mL/min. Upon completion of the extraction step the sorbent cartridges were rinsed with 10 mL of distilled water, and the cartridges were wrapped in aluminum foil, labeled, placed in Zip-lock plastic bags, and immediately placed in an ice chest. Upon return to the GMU laboratory, the LSE cartridges were placed in storage at 3 °C and they were subsequently eluted within 24 hours of returning to the laboratory.

On-site LSE was performed at the Susquehanna River and James River stations during base flow sampling for as many samplings as scheduling would allow. Extractions were performed in a USGS Chevrolet van at the Susquehanna River site, and in a volunteer firehouse in Cartersville, VA, located within one mile of the James River sampling location. Potomac River samples were extracted at the GMU analytical laboratory immediately upon arrival. All of the storm samples from each of the three fall line sites were extracted in the GMU analytical laboratory by using exactly the same approach described above for the 4-L surface water samples.

#### *Field and Laboratory Blanks*

Field blanks were performed on-site during each Susquehanna and James River base flow sampling event. Field blanks consisted of a distilled water (Burdick and Jackson, Muskegon, MI) rinse of all of the surface water sampling equipment (contacting all of the surfaces a normal sample would contact during sampling, filtration, and LSE) which was collected in a precleaned stainless steel milk can. The blank was subsequently filtered and extracted as was a normal sample. Four to eight liters of distilled water rinse was typically used as the field blank. A single blank was processed prior to the filtration and extraction of surface water samples. During storm sampling, all of the surface water sampling equipment was rinsed with distilled water on-site in the normal manner, but in this case the blanks were shipped on ice to the GMU analytical laboratory and processed according to the usual procedure.

Laboratory blanks were performed intermittently to check for equipment and reagent contamination. Laboratory blanks were performed in exactly the same fashion as described for

field blanks except they were conducted without the distilled water rinse of the surface water sampling equipment.

### *Matrix Spikes*

A matrix spike as defined in this study was the addition of each target analyte to eight to twelve liters of a filtered sub-sample of the composited surface water sample collected at each of the river fall lines. In this procedure, the filtered sub-sample was transferred to a precleaned 37.5-L milk can and the target analytes were added to the water as a methanol solution (5 mL) to give a final concentration of ca. 100 ng/L for each component (for PCBs, the amount corresponded to 300 ng/L of total PCBs). The amended water was mixed thoroughly by agitation, and was subsequently extracted in the normal manner. Results from the matrix spikes were used to calculate the mass percentages of the amended target analytes recovered from the surface water samples.

### *Sample Container Rinse*

Hydrophobic organic compounds dissolved in water are known to undergo sorption reactions with the walls of sample containers. The degree of sorption depends on the physicochemical properties and reactivity of the analytes and the surface composition of the container. Sorption from water to the surface would reduce the dissolved phase concentrations of the organic contaminants underbiasing the data. Milk cans and glass bottles which came in contact with the sample were solvent rinsed with 50 mL of cyclohexane:isopropanol (7:3) after filtration and extraction had been completed. The solvent rinses were analyzed by using the procedures described below.

### *Equipment and Glassware Cleaning and Preparation*

All non-volumetric glassware was scrupulously cleaned with Alconox detergent in hot tap water, rinsed with distilled water, and baked in a muffle furnace at 450 °C for 15 hours. Baked glassware was stored wrapped in aluminum foil (all aluminum foil used for wrapping and storage in this study was fired at 450 °C prior to use), and was repeatedly rinsed with *n*-hexane and methanol before use. Volumetric glassware was initially soaked in 15% aqueous nitric acid, washed in Alconox detergent, rinsed with distilled water, and hexane rinsed repeatedly prior to use. Volumetric (i.e., precisely calibrated) glassware was also stored wrapped in aluminum foil.

Stainless steel milk cans were washed in the same manner as glassware but were not baked. The cans were repeatedly rinsed with methanol prior to use and were stored with their lids securely fastened to prevent the entry of organics into clean cans from ambient air.

Positive displacement pumps and associated Teflon tubing were thoroughly washed with methanol and distilled water between extractions. This was often accomplished in the field as well as the laboratory depending on the sampling schedule. All exposed ends of Teflon tubing were kept wrapped with aluminum foil when not in use to prevent contamination.

### *LSE Cartridge Elution*

LSE cartridges were eluted according to the procedures described by Foreman and Foster (1991). The LSE cartridges were initially dewatered by purging with nitrogen for 30 minutes followed by vacuum aspiration for an additional 5 minutes. Each cartridge was subsequently eluted with 60 mL of cyclohexane:isopropanol (7:3, v/v) solvent (both Carbo-pack B and C18 sorbents) into a 250 mL boiling flask with the aid of nitrogen gas head pressure: 20 mL of solvent was quickly purged through the cartridge to wet the sorbent with the elution solvent and then 40 mL of solvent was allowed to saturate the sorbent for 15 minutes in static mode; the remaining solvent was purged through the cartridge in dynamic mode at a rate of 2 drops/sec (ca. 15 mL/min) until the sorbent bed was dry.

When a visible water layer was present in the eluent, approximately 5 mL of isopropanol was added to the boiling flask, then the eluent volume was reduced to approximately 10 mL by using rotary-flash evaporation. As the solvent volume was reduced to ca. 10 mL, 5 mL of cyclohexane was added to the flask to check for the presence of water, which, if present, would produce a cloudy emulsion. When needed, subsequent 5 mL additions of the cyclohexane-isopropanol mixture were added and solvent volume reduction continued until the eluent was clear when mixed with cyclohexane. The eluent was further reduced to approximately 5 mL and transferred to centrifuge tube by a pasteur pipet, rinsing the sides of the flask twice with 2 mL of cyclohexane:isopropanol solvent. The volume was further reduced to 0.2 mL by using nitrogen gas evaporation, occasionally rinsing the centrifuge tube with solvent to release any analytes adhering to the sides of the tube. The concentrated eluents were centrifuged for 15 minutes at 3000 rpm, and then the samples were transferred to sample vials by using a 500 µL syringe.

### *Glass Fiber Filter Extraction*

Filters were thawed to room temperature, placed in glass Soxhlet extraction thimbles, and extracted for 24 hours in a Soxhlet extractors with cyclohexane:isopropanol (7:3). Both GF/D and GF/F filters were combined for each sample in the Soxhlet apparatus during the extraction (i.e., no attempt was made to measure particle size differences in sorption and fluvial transport).

### *Alumina/Silica Fractionation*

The organochlorine compounds (PCBs, aldrin, oxychlordane, alpha- & gamma-chlordane, dieldrin, 4,4'-DDT, cis- & trans-permethrin, and cis- & trans-fenvaterate) were analyzed by using a gas chromatograph equipped with an electron capture detector (i.e., GC-ECD). Because of the limited selectivity of the instrument for the target analytes and the number of interfering organochlorine compounds that may also be present in the samples, extracts from the LSE cartridges and filters needed to be fractionated via column chromatography prior to GC-ECD analysis to isolate the PCBs (plus aldrin) and the remaining organochlorines in separate fractions. Fractionation columns consisted of 25 mL medical grade polypropylene syringe barrels that were fitted with 25 mm ANOTOP filters (0.2 µm pore size; Alltech Associates, Inc.), which in turn were fitted with PTFE (Teflon) flow valves to regulate solvent flow through the cartridge. The cartridges were packed, in order of filling from bottom to top, with 2 g of granular anhydrous sodium sulfate (J.T. Baker Chemical Co.), 3 g of fully activated silica gel (60/200 mesh, Fisher Chemical Co.; previously activated at 135 °C), 6 g of 2% (wt/wt) water deactivated neutral

alumina (80/200 mesh, Fisher Chemical Co.; previously activated at 500 °C), and 4 g of anhydrous sodium sulfate. The sorbent cartridges were connected through polypropylene adapters to 25 mL polypropylene reservoirs, and the tops of the reservoirs were connected to a nitrogen evaporator manifold through 1/8 in. (od) Teflon tubing.

The fractionation columns were first washed with 50 mL of *n*-hexane, which was discarded, and the extracts were loaded into the sorbent cartridges and were eluted with 45 mL of *n*-hexane (PCBs plus aldrin) followed by 45 mL of dichloromethane (chlordanes, dieldrin, DDT, permethrins, and fenvalerates). Details of the eluent compositions in this fractionation sequence are described by Shan (1991). Each eluent was collected separately and both eluents are concentrated to a final volume of 0.2 mL by using rotary flash evaporation and nitrogen gas blowdown and analyzed by using GC-ECD.

PAHs associated with fluvial particulates eluted in the DCM fraction in column chromatography. The DCM fraction was further analyzed by using GC/MS for PAHs.

#### *Instrument Parameters*

The fall line target analytes have instrument analysis designations along with their quantitation levels (QLs) as shown in Table 3. QL values for each analyte were calculated according to analytical procedures previously described by Foster et al. (1993). A Hewlett-Packard (HP) 5890 Series II gas chromatograph (GC) equipped with an electron capture detector (ECD) was used to measure all of the organochlorine compounds. The GC-ECD output was transferred from an HP 3396A recording integrator to an HP Vectra QS/20 microcomputer through HP 3396A file server software (ver. 1.2). Hard copies of each chromatogram obtained from GC-ECD analysis were labeled and stored, according to sample name, in a filing cabinet. The report files uploaded to the Vectra computer were imported into Quattro Pro (ver. 2) spreadsheet software (Borland Associates, Scotts Valley, CA), evaluated as needed, and stored both on floppy disks and the Vectra QS/20 hard drive. Periodically, data on the Vectra QS/20 hard drive was backed up on 40 megabyte streamer tapes for long term storage.

The GC/MS analyses were performed on a HP 5890A GC coupled to a Finnigan INCOS 50 mass spectrometer. The system is controlled and operated through INCOS 50 software. The mass spectrometer was tuned and calibrated daily with perfluorotributyl amine. Data files produced by the INCOS 50 system were archived and converted to PCDS (ver. 3.0; Finnigan) format for auto-quantitation. Archived data files on the INCOS 50 GC/MS were electronically transmitted via ethernet to the HP Vectra QS/20 microcomputer for processing and storage. The GC/MS data files, quantitation files, and calibration files were stored on floppy disks and on the hard drive of the Vectra computer. Streamer tape backup copies were made periodically. Specific instrument operational parameters used for both GC-ECD and GC/MS have been described in the fall line survey QA document (Foster 1992).

#### *Instrument Calibration and Quantitation*

All instruments were calibrated daily prior to the analysis of the fluvial samples. Primary standards were prepared either from neat compounds (Chem Service Inc., West Chester, PA) or were obtained as preprepared solutions with known analyte concentrations and accompanying



QA/QC information (Chem Service). Secondary calibration standards were prepared from the primary standards using the appropriate mixtures and dilutions. The PCB calibration standard was prepared from a 1:1:1 (wt/wt/wt) mixture of Arochlors 1242:1254:1260, and the relative abundance of each congener was determined by using the composition data of Schulz et al. (1989) for the same Arochlor mixtures. One-hundred and twelve PCB congeners were quantitated in each dissolved phase and suspended particle sample extract. A single calibration standard for GC-ECD and GC/MS was used to calculate relative response factors (RRF's) by manipulating the fundamental internal standard quantitation formula shown below:

$$\frac{A_{\text{analyte}}}{C_{\text{analyte}}} = \text{RRF} \times \frac{A_{\text{std}}}{C_{\text{std}}} \quad (8)$$

During calibration, the analyte and internal standard concentrations were known to four significant figures and all integrated GC peak areas (instrument analog to digital count output) were obtained from the GC. Peak identifications were made by using relative retention time data (retention time of analyte/retention time of internal standard). Relative response factors were calculated from calibration procedures and the internal standard quantitation equation above. Calibration rrf data was recorded and a hard copy was saved on file daily to query instrument variability and drift through time. Quantitation levels were calculated from a signal-to-noise ratio of three in instrumental analysis.

In GC/MS analysis, confirmation of the monitored organic contaminants was determined by the presence of 2 characteristic electron impact-ionization mass peaks that were present at the correct retention time and had the correct relative abundance relative to the primary quantitation ion. At least one of the confirmatory ions needed to be present for the detection of an organic contaminant.

Organic contaminants detected and quantitated by using GC-ECD were confirmed when possible by combining several sample extracts and reducing the extract volumes to <100 µL. The combined and volume-reduced extracts were analyzed by GC/MS to confirm the presence of organochlorine compounds detected via GC-ECD.

## LOAD ESTIMATION METHOD

Load estimates were calculated for the 1990-91 period using one of two load estimation techniques: a log linear regression model termed the "Adjusted Maximum Likelihood Estimator" (AMLE) (Cohn, 1988), or the Interpolation-Integration model (II). A discussion of the AMLE technique and resulting load estimates is provided in the report *Chesapeake Bay Fall Line Toxics Program: 1990-1991 Loadings* (1993). Annual estimates for this period are presented in the following text for comparative purposes.

Annual load estimates for 1992 were calculated using the AMLE model, when applicable. Otherwise, the load estimates were made with the Interpolation-Integration model (II), which is a consistent method between all members of the Chesapeake Bay Fall Line Toxics Program. Monthly load estimates using the Interpolation-Integration method are also provided for the 1992 sampling period.

Load estimates calculated using the Interpolation-Integration model were made by first calculating daily loads and then summing these values over each monthly period. Daily loads were calculated using the following formula:

$$\text{Load}_{t,i} = Q_t \times C_{t,i} \times K \quad (9)$$

$\text{Load}_{t,i}$  = calculated load for constituent i on day t in pounds per day  
 $Q$  = mean daily discharge for day t, in cubic feet per second  
 $C_{ti}$  = concentration of constituent i for day t in micrograms per liter  
 $K$  = conversion factor (2.4485 secs x L x kg/ft<sup>3</sup> x  $\mu$ g x days)

Mean discharge was calculated daily using flow values electronically measured every 15 minutes. Metal and organic contaminant concentrations were measured less frequently and, therefore, daily values were interpolated from the existing data set. Interpolated data points were assigned the value of the nearest measured concentration.

The load estimates were calculated twice to determine a range in values. Censored data were assigned a value of zero for the calculation of a lower boundary, or "minimum" load, and were assigned the values of the quantitation level for each constituent in order to calculate an upper boundary, or "maximum" load.

The AMLE model is still considered the loading estimate method of choice because it incorporates long-term trends, has improved handling of censored data (values below quantitation level), and provides an estimate of model and prediction error. A range in load estimates was calculated using the AMLE based on statistical variance observed in the data as determined by the model.

Samples for the Potomac River were integrated over storm events; therefore the following adjustments to the II Model were made. To compute baseflow loads, the first step was to divide the time interval between each pair of successive baseflow samples at the midway point. The

first half of this interval was then associated with the concentrations of trace metals in the first sample of the pair, while the second half was associated with the concentration of the second sample of the pair. The time before the very first baseflow sample (*i.e.*, at the start of the sampling period) was associated with the very first baseflow sample, and, similarly, the time interval after the last baseflow sample was associated with that sample. Daily baseflow values were obtained from MWCOG. These daily flow values were multiplied by the concentration associated for that day and the time for which the flow and concentration were valid. Normally, the time would be one day (86,400 seconds), unless the beginning or end of a storm event or the dividing point of the interval between two successive baseflow samples occurred that day. All the daily baseflow loads and all the stormflow loads for each month were then summed to obtain the total load for the month.

For the organic constituents, baseflow loads were estimated separately from storm flow loads. Loads estimated from storm flow were assumed to be contributed entirely from runoff. No attempt was made to estimate baseflow loads separately during storm events.

## **HYDROLOGIC CONDITIONS**

### **Susquehanna River**

The USGS stream-gaging data values for daily water discharge were used in calculating toxic substances loadings at the Susquehanna River fall line monitoring stations. The calendar year long-term average water discharge for the Susquehanna River at Conowingo Dam is 40,956 cubic feet per second (ft<sup>3</sup>/s). The average water discharge in 1990, 1991, and 1992 at this station was 48,535, 29,748, and 35,495 ft<sup>3</sup>/s, respectively. Calendar year 1990 was the only year that flow exceeded the long-term mean. Water discharge for the three-year period is illustrated in Figure 2.

### **James River**

USGS stream-gaging data values for daily water discharge were used in calculating toxic substance loadings at the James River fall line monitoring station. Figure 3 shows the long-term monthly discharge at the James River station, overlain by the 1990-92 calendar year hydrograph. The calendar year long-term average water discharge for the James River at Cartersville is 7,113 cfs. Average water discharge in calendar years 1990, 1991, and 1992 at the James River was 8,397, 6,930, and 7,173 cfs, respectively. For these periods, water discharge in 1990 exceeded the long-term average, 1991 was below average, and 1992 was close to the long term average.

### **Potomac River**

The flows in the Potomac River at Little Falls during the period of this study (March, 1992, to March, 1993) were either below or at the 60-year average reported by the USGS (1991) for all months except June and July of 1992, and March of 1993. Flows in September, 1992, were near the average, and those in January, 1993, were slightly above average. Flows in October, 1992, and February, 1993, were approximately one-half the average, whereas those in November, 1992, were less than one-half the average. March, 1993, had flows that were more than twice the average. The annual flow for the 12 month period of April 1992, to March 1993, was 10% higher than the 60-year average. Figure 4 shows the 1990 to 1993 hydrograph and long-term mean monthly discharge for the Potomac River.

Figure 2. Hydrograph showing mean monthly and long-term mean monthly discharge for the Susquehanna River fall line at Conowingo, Maryland.

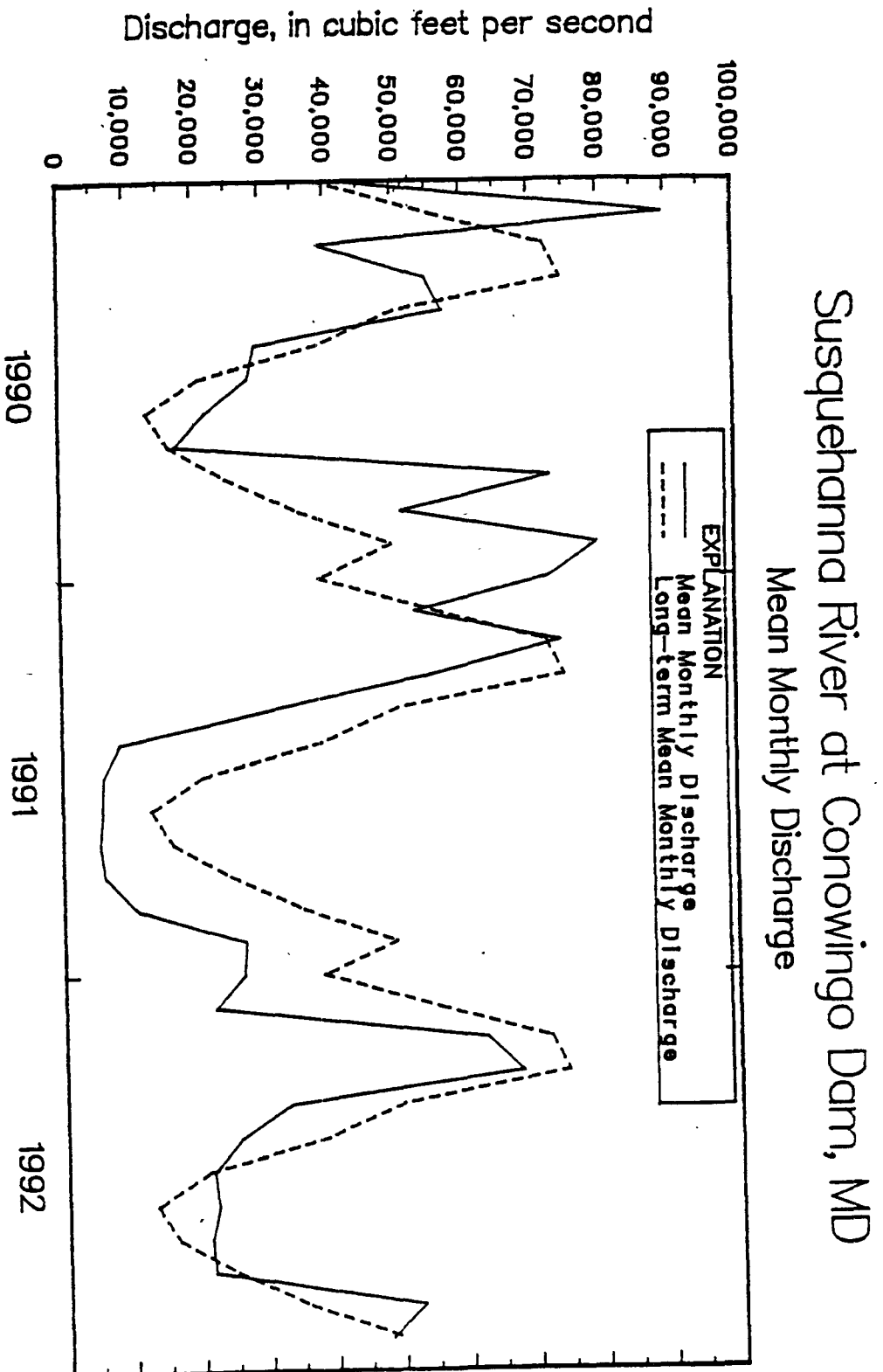


Figure 3. Hydrograph showing mean monthly and long-term mean monthly discharge for the James River fall line at Cartersville, Virginia.

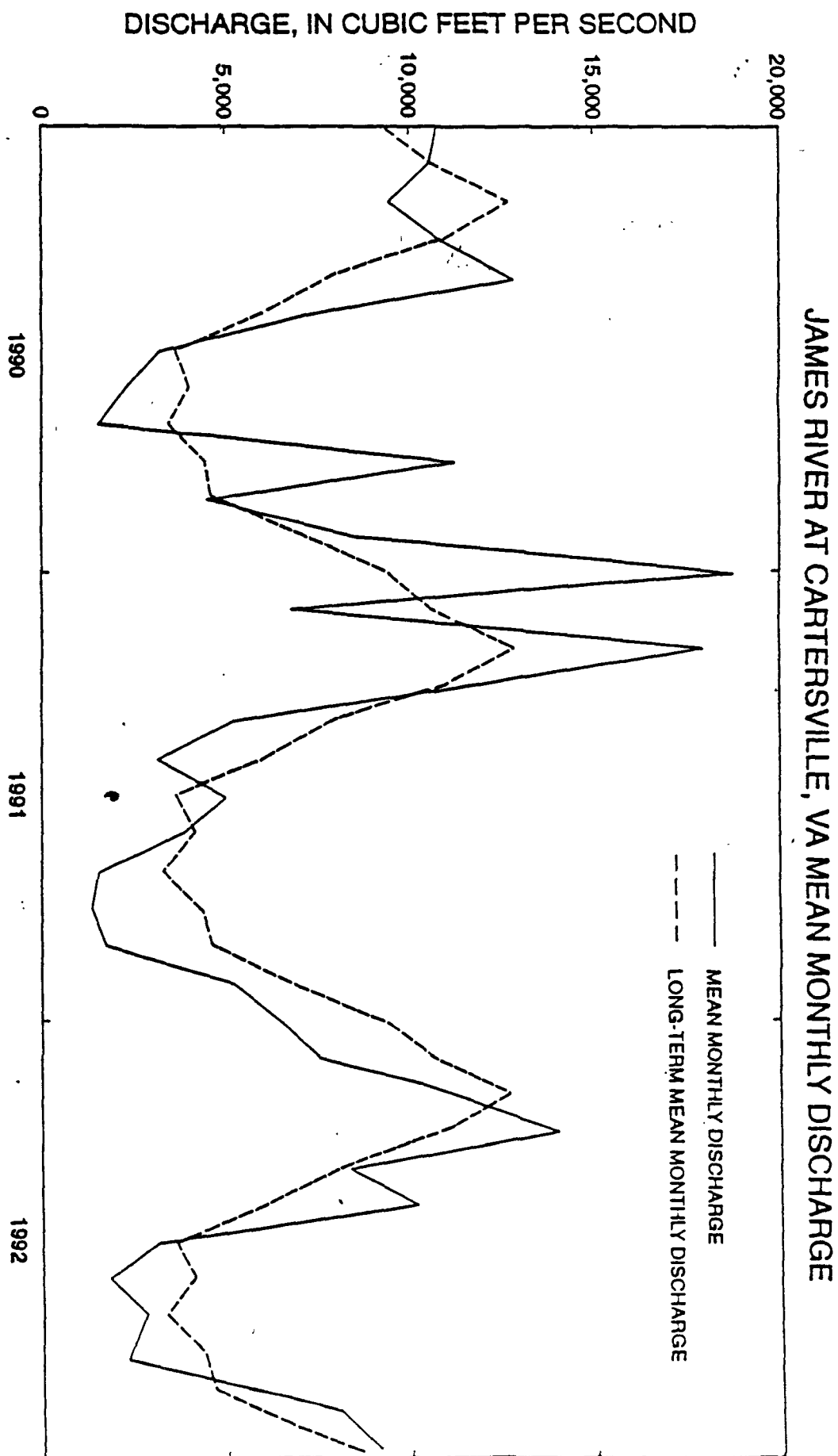
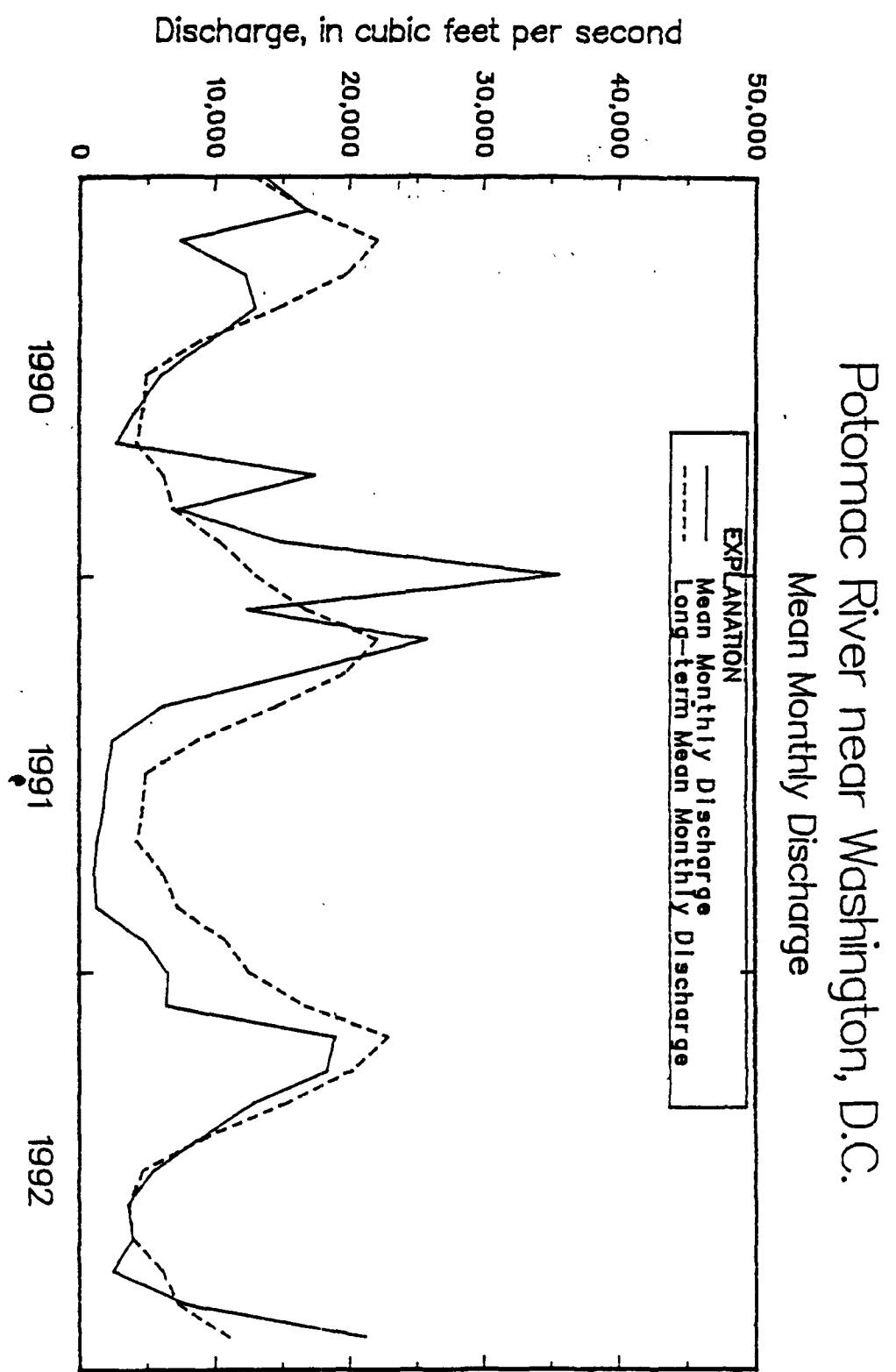


Figure 4. Hydrograph showing mean monthly and long-term mean monthly discharge for the Potomac River fall line at Chain Bridge, District of Columbia.



## **QUALITY ASSURANCE RESULTS**

### **Metals Quality Assurance Results - Susquehanna River**

The quality-assurance program included collection of quality-control samples to meet the QA objectives of the project. Results of these analyses for metals are listed in Table 4 and Table 5. Five sets of samples were collected to compare the "old" 1990-91 sample collection and analysis methods to the "new" 1992 ultra clean sample collection and analysis methods (Table 4). Results indicate that for total-recoverable concentrations of As, Cd, and Zn there was no difference in values between the two collection techniques. Concentrations of total-recoverable Cr, Cu, Hg, and Pb were lower in samples collected using the ultra clean techniques. Results of the dissolved analyses indicate that generally concentrations of Pb and Zn were lower using the ultra clean techniques, while concentrations of Cr and Cu were higher.

Equipment blanks were performed prior to sample collection at the midpoint of the sample-collection cross section using high-quality inorganic-free water provided by the USGS Ocala, Florida laboratory. Blank samples were collected to monitor the efficiency of the new ultra clean techniques. Results for the equipment and filter blanks initially indicated that clean samples were being collected. After the first two months, however, a ubiquitous contamination problem developed for most of the dissolved metal constituents. The source of the contamination is still under investigation. The two sampling periods are discussed separately.

In order to provide a preliminary assessment of new sampling procedures, four equipment blank samples were collected using ultra clean methods during March and April 1992 for both total-recoverable and dissolved metal analyses (Table 5, Figure 20-Figure 23). Specifically, we wished to identify any potential sources of contamination to the water-quality sample from the ultra clean sample collection and/or field processing techniques. Results indicate that equipment blank samples did not contain detectable concentrations of total-recoverable As, Cd, Cu, or Zn. One occurrence each of total-recoverable Cr (1 µg/L) and total-recoverable Pb (2 µg/L) was detected, and total-recoverable Hg was present in all but one equipment-blank sample at a range of 0.2 µg/L or less during this initial two-month period. Results of the equipment blank samples collected during this period for the dissolved metal analysis indicate that no detectable concentrations of dissolved As, Cd, and Pb were present. One occurrence each of dissolved Cr (0.9 µg/L) and dissolved Cu (0.2 µg/L) was detected, two occurrences of dissolved Zn (0.4 and 1.2 µg/L) were detected, and dissolved Hg was consistently present in all equipment-blank samples at 0.032 µg/L or less during this initial two-month period.

In addition to the equipment-blank samples, which identify potential sources of contamination to the water quality sample from the entire sample collection procedure, four filter-blank samples were collected during March and April, 1992 to identify potential sources of contamination to the sample from the filter step only (Table 5). Results from the first two months of sampling indicate that dissolved As, Cd, Cr, and Pb were not present in detectable concentrations. Only one occurrence each of dissolved Cu (0.1 µg/L) and dissolved Zn (0.9 µg/L) was reported. Dissolved Hg was present in all of the blanks at about 0.035 µg/L or less during the initial two-month period.



**Table 4.** Quality assurance data collected at the Susquehanna River fall line at Conowingo, Maryland, to compare old and new sample collection techniques for total-recoverable and dissolved trace metals.

Total Recoverable Metals							
Date	Discharge (ft <sup>3</sup> /s)	Sediment (% finer)	Suspended Sediment (mg/l)	<u>Arsenic</u>		<u>Cadmium</u>	
				old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)
03-30-92	169,000	100	49	<1	<1	<1	<1
04-03-92	88,500	99	22	<1	<1	<1	<1
04-22-92	87,700	98	15	<1	<1	<1	<1
05-12-92	66,300	100	13	<1	<1	<1	<1
07-15-92	12,300	--	2	<1	<1	<1	<1

Date	<u>Chromium</u>		<u>Copper</u>		<u>Lead</u>		<u>Mercury</u>		<u>Zinc</u>	
	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)
03-30-92	26	1	4	2	3	3	2.9	0.50	20	20
04-03-92	<1	<1	3	1	2	1	0.20	<0.10	10	10
04-22-92	72	3	5	2	4	1	0.20	<0.10	<10	<10
05-12-92	22	<1	2	1	1	<1	<0.10	<0.10	<10	<10
07-15-92	8	3	2	1	<1	<1	--	<0.10	<10	<10

Dissolved Metals								
Date	<u>Chromium</u>		<u>Copper</u>		<u>Lead</u>		<u>Zinc</u>	
	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)
03-30-92	<1	1.1	1	3.1	<1	2.2	<10	21.6
04-22-92	<1	5.4	3	1.9	<1	0.6	20	5.9
05-12-92	<1	3.52	1	1.7	<1	0.76	<10	5.02
07-15-92	<1	3.46	1	1.53	<1	0.19	<10	2.93

Table 5. Results of field equipment blank and filter blank samples collected at the Susquehanna River at Conowingo, Maryland, for trace metals using ultraclean techniques.

DATE	BLANK TYPE	Total-Recoverable							Dissolved						
		As (1)	Cd (1)	Cr (1)	Cu (1)	Hg (1.0)	Pb (1)	Zn (10)	As (.6)	Cd (.1)	Cr (.2)	Cu (.02)	Hg (.020)	Pb (.06)	Zn (.08)
Initial two-month assessment period (March and April 1992)															
19920315	Equipment	<1	<1	1	<1	0.10	<1	<10	..	..	..	..	..	..	..
19920329	Equipment	<1	<1	..	<1	0.15	<1	<10	<0.6	<0.1	<0.2	<0.02	0.032	<0.06	<0.08
	Filter	..	..	..	..	..	..	..	..	..	..	..	0.035	..	..
19920330	Equipment	<1	<1	<1	<1	<0.10	2	<10	<0.6	<0.1	<0.2	0.2	0.027	<0.06	0.4
19920331	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	<0.02	0.029	<0.06	<0.08
19920403	Equipment	<1	<1	<1	<1	0.20	<1	<10	<0.6	<0.1	0.9	<0.02	0.027	<0.06	1.2
19920422	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	0.1	0.020	<0.06	0.9
19920424	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	<0.02	0.026	<0.06	<0.08
-----															
19920512	Equipment	<1	<1	0	<1	<0.10	<1	<10	<0.6	<0.1	6.32	0.35	..	<0.06	..
	Filter	..	..	..	..	..	..	..	<0.6	<0.1	1.76	<0.02	..	<0.06	2.22
19920519	Filter	..	..	..	..	..	..	..	<0.6	0.66	1.56	0.16	..	0.45	0.80
19920619	Filter	..	..	..	..	..	..	..	<0.6	<0.1	0.29	<0.02	..	<0.06	2.73
19920715	Equipment	<1	<1	4	<1	<0.10	<1	<10	<0.6	1.10	4.27	0.51	..	0.37	2.63
	Filter	..	..	..	..	..	..	..	<0.6	1.23	2.03	0.32	..	0.49	1.70
19920902	Filter	..	..	..	..	..	..	..	<0.6	<0.1	0.43	<0.02	..	<0.06	1.59
19921118	Filter	..	..	..	..	..	..	..	<0.6	<0.1	0.40	0.16	..	<0.06	1.21
19921125	Filter	..	..	..	..	..	..	..	<0.6	<0.1	0.46	0.16	..	<0.06	1.20
19921130	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	0.07	..	<0.06	1.28
19930105	Equipment	..	..	..	..	..	..	..	<0.6	0.22	3.65	0.10	..	0.22	1.86
	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	<0.02	..	<0.06	2.29
19930108	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	<0.02	..	<0.06	0.11
19930311	Equipment	..	..	..	..	..	..	..	<0.6	<0.1	0.17	<0.02	..	<0.06	1.14
	Filter	..	..	..	..	..	..	..	<0.6	<0.1	0.26	<0.02	..	<0.06	1.15
19930325	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	0.22	..	0.10	9.46
19930327	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	0.73	..	0.16	7.52
19930328	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	<0.02	..	<0.06	2.51
19930330	Equipment	<1	<1	<1	<1	<0.10	<1	<10	<0.6	<0.1	<0.2	<0.02	..	<0.06	1.36
	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	<0.02	..	<0.06	0.22
19930331	Filter	..	..	..	..	..	..	..	<0.6	<0.1	<0.2	<0.02	..	<0.06	1.99

[Equipment blank = high-quality inorganic-free water through boiler, churn, holding bottles, and filter apparatus (for dissolved constituents only); Filter blank = high-quality inorganic-free water through filter apparatus, for dissolved constituents only;  
 .. = a constituent was not analyzed; \* = date pending; < = value is less than the analytical reporting limit].

During the period from May to September 1992, two equipment-blank samples were collected for the analysis of both total-recoverable and dissolved metals, and five filter-blank samples were collected for the analysis of the dissolved metals. Results of equipment-blank samples for total-recoverable analyses for this period indicate that no detectable concentrations of total-recoverable As, Cd, Cu, Hg, Pb, or Zn were present. Total-recoverable Cr, however, was present in both equipment-blank samples at 8 µg/L or less. These results are consistent with the March to April 1992 period with the exceptions of total-recoverable Pb and total-recoverable Hg, which were detected during the March to April 1992 period but not during the May to September 1992 period.

Results of equipment-blank samples for dissolved analyses for the May to September period indicate that all dissolved constituents were detected with the exception of dissolved As. Dissolved Cd was detected once at 1.10 µg/L, dissolved Cr at 4.27 and 6.32 µg/L, dissolved Cu at 0.35 and 0.51 µg/L, dissolved Pb once at 0.37 µg/L, and dissolved Zn once at 2.63 µg/L. These results are inconsistent with the earlier March to April 1992 period for dissolved Cd and Pb, when they were not detected. Moreover, the concentrations of dissolved Cr, Cu, and Zn were much higher during the May to September 1992 period than during the March to April 1992 period. Data for dissolved Hg are pending.

Results of the filter blanks paralleled the results of the equipment blanks in that they were consistently higher during the latter part of the sampling period. In the March-April sampling period, environmental concentrations were two to five times higher than blank concentrations for the four constituents. This indicates sufficient sensitivity in our methods for detection of these elements above ambient background contamination. From March to September, 1992, elevated concentrations of total-recoverable Cr, and dissolved Cr, Cu, Pb, and Zn occurred in the blank samples. Dissolved Cu was the only constituent that continued to show significantly higher values for river water samples. Quality-control checks were continued after the September period to determine the source of contamination occurring in the blank samples.

Two sets of replicate samples were collected to assess the precision of the laboratory methods. Estimates of precision were made by dividing the range in replicates by the average of the replicate values. Precision was poor, primarily because concentration values occurred at or near the quantitation levels, and only two sets of replicates were used in the calculation.

### **Metals Quality Assurance Results - James River**

The quality-assurance program for the James River also consisted of the collection of quality-control samples to meet the quality assurance objectives of the project. Results of these analyses for metals are listed in Table 7 and Table 7.

As at the Susquehanna, equipment blank samples were collected prior to sample collection and analyzed to 1) compare the old and new sampling techniques, and 2) to identify any potential sources of contamination from the ultra clean sampling protocols and/or field techniques (Table 7). Results indicate that the equipment blank samples for both old and new techniques did not contain detectable quantities of total-recoverable As or Cd. Random occurrences of total-recoverable Cr, Cu, Pb, and Zn were, however, reported in two of the four blank samples. With one exception (Cr on 9/3/92), the concentrations of all constituents found in the blanks that

**Table 6.** Quality assurance data collected at the James River fall line at Cartersville, Virginia, to compare old and new sample collection techniques for total-recoverable metals.

Total Recoverable Metals							
Date	Discharge (ft <sup>3</sup> /s)	Sediment (% finer)	Suspended Sediment (mg/l)	<u>Arsenic</u>		<u>Cadmium</u>	
				old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)
04-10-92	4750	89	4	<1	<1	<1	<1
04-24-92	80100	73	454	<1	<1	<1	<1
04-28-92	14700	69	62	<1	<1	<1	<1
05-20-92	10900	88	31	<1	<1	<1	<1
06-24-92	5600	88	6	<1	<1	<1	<1

Date	<u>Chromium</u>		<u>Copper</u>		<u>Lead</u>		<u>Zinc</u>	
	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)
04-10-92	2	<1	8	1	<1	<1	20	<10
04-24-92	6	4	10	6	15	10	60	60
04-28-92	3	1	2	2	2	2	10	<10
05-20-92	<1	<1	3	<1	2	1	<10	<10
06-24-92	2	10	2	2	<1	<1	<10	<10

Dissolved Metals								
Date	<u>Chromium</u>		<u>Copper</u>		<u>Lead</u>		<u>Zinc</u>	
	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)	old (ug/l)	new (ug/l)
04-10-92	<1	0.6	<1	1.17	<1	0.09	<10	2.42
04-24-92	<1	<0.2	3	3.10	<1	2.83	<10	11.65
04-28-92	<1	<0.2	2	1.20	2	0.55	<10	3.72
05-20-92	<1	1.12	3	0.99	1	0.40	<10	1.50
06-24-92	<1	11.60	2	1.77	<1	0.20	<10	2.08

# Chesapeake Bay Fall Line Toxics Monitoring Program: 1992 Final Report

**Table 7.** Results of field equipment blank and filter blank samples collected at James River at Cartersville, Virginia, for trace metals using ultraclean techniques.

Date	Discharge (ft/s)	Sediment (% finer)	Sus. Sed. (mg/l)	As		Cd	
				OLD TR	NEW TR	NEW DIS	NEW TR
04-10-92	4750	89	4			<0.6	--
04-23-92	111000	90	888			<0.6	--
04-24-92	80100	73	454			<0.6	--
04-26-92	21800	85	106			<0.6	--
04-27-92	17500	80	74			<0.6	--
04-28-92	14700	69	62			<0.6	--
05-20-92	10900	88	31	<1	<1	<0.6	<1
06-24-92	5600	88	6		<1	<0.6	<1
07-22-92	1980	85	3		<1	<0.6	<1
09-03-92	1580	83	2	<1	<1	<0.6	<1
09-03-92	1580	83	2			<0.6	--
10-28-92	1750	84	1			<0.6	--
11-23-92	5340	86	14			<0.6	--
11-25-92	23000	79	165			<0.6	--
12-11-92	32800	73	485			<0.6	--
12-12-92	18200	91	167			<0.6	--
01-28-93	9180	92	8			<0.6	--
02-23-93	20300	66	98			<0.6	--
02-24-93	25500	53	193			<0.6	--
02-25-93	20000	54	105			<0.6	--

[ft/s= feet per second; %finer= percentage of sample finer than sand size (0.62 microns); mg/l= milligrams per liter; OLD= old technique; NEW= ultraclean technique; TR= total recoverable; DIS= dissolved; blanks collected for dissolved constituents using the new techniques are filter blanks only, and are therefore not considered full equipment blanks.]

**Table 7 (cont.).** Results of field equipment blank and filter blank samples collected at James River at Cartersville, Virginia, for trace metals using ultraclean techniques.

Date	Cr			Cu			Pb			Zn		
	OLD TR	NEW TR	NEW DIS	OLD TR	NEW TR	NEW DIS	OLD TR	NEW TR	NEW DIS	OLD TR	NEW TR	NEW DIS
04-10-92			<2			<.30			<.06			<.08
04-23-92			<2			.40			<.06			4.30
04-24-92			.6			1.70			.60			2.30
04-26-92			<2			.20			<.06			.40
04-27-92			<2			<.02			<.06			.30
04-28-92			<2			.40			<.06			4.90
05-20-92	<1	<1	2.7	<1	<1	<.02	<1	<1	<.06	<10	<10	<.08
06-24-92		<1	6.9		<1	1.30		<1	.89		<10	2.88
07-22-92		<1	<2		4	.11		4	<.06		<10	.45
09-03-92	2	20	3.1	4	2	1.05	4	2	1.08	50	20	3.86
09-03-92			3.7			1.33			1.16			4.37
10-28-92			<2			1.07			.67			2.02
11-23-92			<2			.28			.09			1.83
11-25-92			<2			.28			.23			2.51
12-11-92			3.36			1.9			1.96			3.34
12-12-92			<2			.24			<.06			1.91
01-28-93			<2			.1			.08			.35
02-23-93			<2			.12			<.06			.26
02-25-93			.2			.37			<.06			.91

[ft/s= feet per second; %finer= percentage of sample finer than sand size (0.62 microns); mg/l= milligrams per liter; OLD= old technique; NEW= ultraclean technique; TR= total recoverable; DIS= dissolved; blanks collected for dissolved constituents using the new techniques are filter blanks only, and are therefore not considered full equipment blanks.]

were collected using the new technique were consistently lower than those using the old technique.

In addition to the equipment blanks, which assess potential sources of contamination to the water quality sample from the entire sample collection procedure, filter blank samples were collected with each dissolved metal analysis sent to the USGS National Research Program. Results from the filter blank samples indicate that, with the exception of dissolved As, all dissolved constituents were detected in the blank samples to varying degrees. Dissolved Cd was detected only within a period between June and September 1992. Within that same time interval Cr, Cu, Pb and Zn were detected consistently in the sample blanks. From September 1992 through March 1993 Cr, Cu, Pb and Zn continued to be detected periodically, but generally at lower levels than for the June-September period. Low levels of Hg contamination were present in all of the blanks at about 0.03 µg/L or less during the sampling period (Terry Brinton, personal commun, 1993).

Five sets of environmental samples were collected during 1992 to compare the "old" 1990-91 sample collection and analysis methods with the "new" ultra clean collection and analysis methods used in 1992 (Table 7). Results indicate that for total-recoverable As and Cd, there were no differences in the concentrations between the two collection techniques, with both methods resulting in non-detectable values for those constituents. Concentrations of total-recoverable Cr, Cu, Pb, and Zn using the new technique were lower than or equal to concentrations generated using the old technique with one exception; a sample collected on 6/24/92 had a greater Cr value using the ultra clean technique than the old technique. For dissolved As and Cd, again there was no difference between results from the old and new technique, with both methods resulting in non-detectable concentrations of these constituents. For Cr, Cu, Pb and Zn, most samples resulted in concentrations that, for the new technique, were lower than or effectively equal to concentrations resulting from the old technique. A set of samples collected on 6/24/92, however, displayed differences in concentrations between the two techniques, with the sample from the new technique resulting in greater values.

Two sets of replicate samples were collected to evaluate laboratory precision. Estimates of precision for each constituent were made by dividing the range in duplicates by the average between the duplicate values. Precision was generally good for total-recoverable metals. Only one set of duplicates was available for dissolved metals (9/3/92); the precision for dissolved metals was poorer than for total-recoverable metals, possibly because the concentration levels were lower and therefore subject to greater variability.

## **Metals Quality Assurance Results - Potomac**

As mentioned earlier, there was no special field quality assurance program for the Potomac River metals monitoring, and laboratory quality assurance was performed in conjunction with other samples from other projects. Therefore, there are no results that are specific to the Potomac. Instead, all data that have been reported are those that have passed all laboratory quality assurance and quality control procedures. These include, but are not limited to, blanks, duplicates and spiked samples.

## **Organics Quality Assurance Results - Susquehanna, James and Potomac Rivers**

### *Field Blanks*

Concentrations of the organic contaminants detected in the field blanks are shown in Figure 5- Figure 19 for each of the three fall line sampling programs. The average QL for each compound class of contaminants is shown by the dotted line in all of the figures.

Organonitrogen and Organophosphorus Pesticides. Field blank concentrations were used for two purposes: (1) as a check of the quality of the low detection limit method; and (2) to flag fall line sample concentrations when field blank concentrations were  $>0.5$  times the magnitude of the fall line sample concentrations. Flagged sample concentrations denote that the particular concentration value is suspected of having a sizable, but unknown, determinate error associated with it. The field blank that was used to compare with a particular fall line sample was the one that was performed the same day as the fall line sample analysis. If a field blank was not performed the same day as the fall sample analysis, then the preceding field blank was used for comparison purposes.

The concentrations of the organonitrogen and phosphorus pesticides in the Susquehanna River field blanks were below QL concentrations for most of the samples. Exceptions included atrazine on the 7/15/92 sampling date, alachlor on 3/6/92 and 9/2/92, prometon on 9/2/92, hexazinone on 3/6/92 and 7/15/92, cyanazine on 9/2/92, and malathion in all blanks after 4/3/92. With the exception of malathion, the occurrence of these pesticides in the field blanks were random and dropped below QL concentrations at the next sampling period. In addition, the field blank concentrations of these pesticides were low, often much lower than measured concentrations in the fall line samples. It is of interest to note that this elevated blank concentration of malathion coincides with the commencement of malathion application in residential areas for mosquito control, but the exact reason for this phenomenon is not clear. The only flagged sample concentrations for this group of pesticide for the Susquehanna River database include only metolachlor in the 25 November and 30 November storm samples.

The organonitrogen and phosphorus pesticide field blanks for the James River fall line samples show a pattern similar to that seen for the Susquehanna River: most field blank concentrations were  $<QL$  values. However, a few random detectable concentrations of the monitored compounds were found in the field blanks, particularly metolachlor and malathion. The field blank concentrations were well below fall line sample concentrations in all but two instances. The only flagged concentrations in the James River database for the organonitrogen and organophosphorus pesticides are for malathion in a 22 July baseflow sample and hexazinone in a 3 September baseflow sample.

Laboratory blanks were conducted to determine the amounts of organonitrogen and phosphorus pesticides that were introduced into the samples during laboratory analysis, and they were nearly free of any interfering organonitrogen and organophosphorus pesticides. On-site filtration and LSE was not performed for the Potomac River fall line sampling, and because of this the laboratory blanks corresponding to the Potomac River fall line sampling were used in the same fashion as field blanks for the Susquehanna and James Rivers. There are no flagged



**Figure 5.** Field blank concentrations of the organonitrogen and organophosphorus pesticides in the dissolved phase for samples processed at the Susquehanna River fall line.

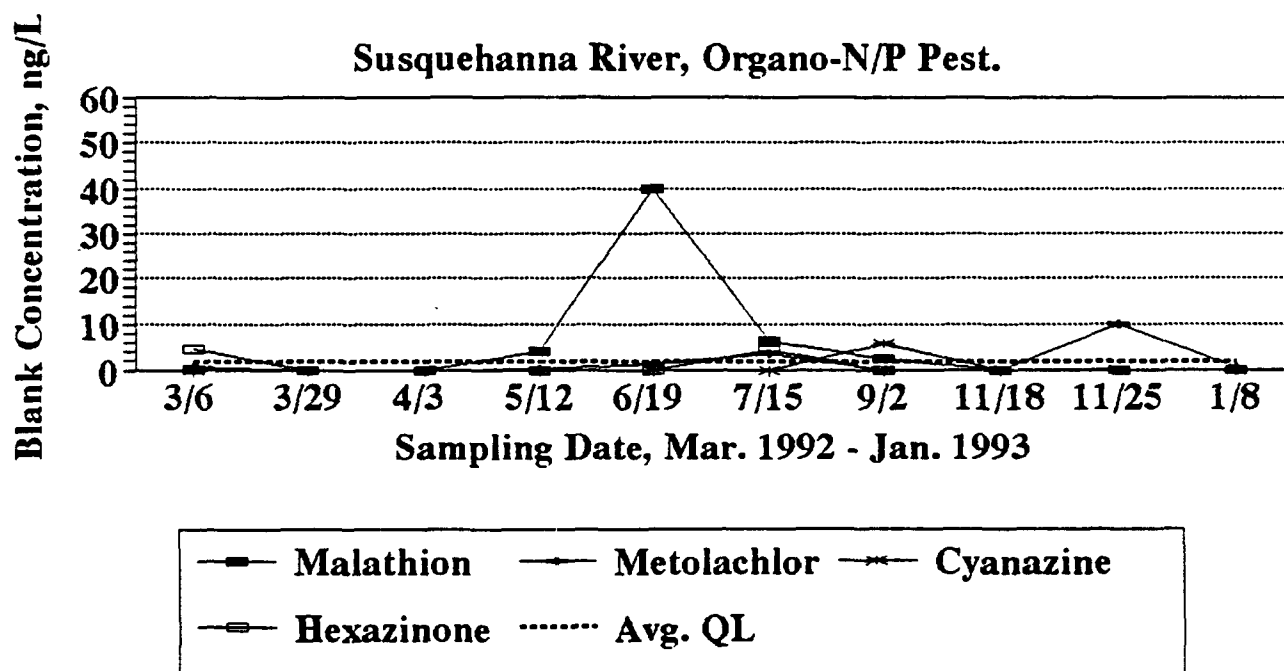
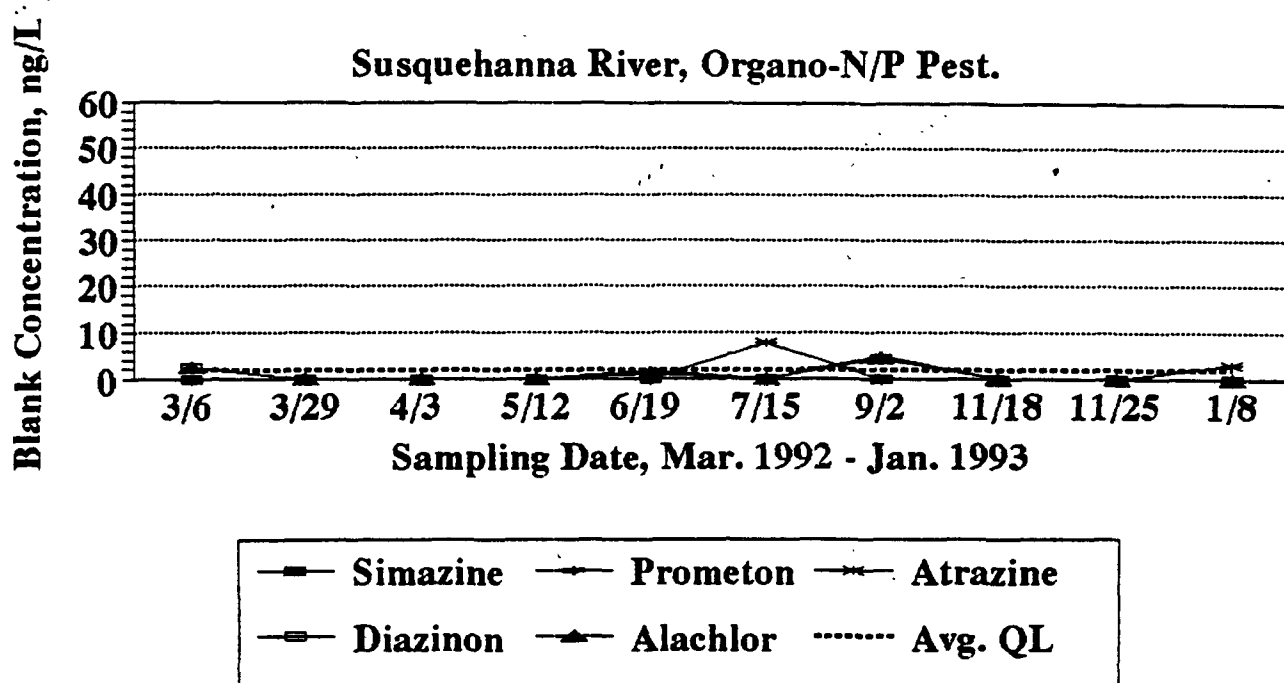


Figure 6. Field blank concentrations of the organochlorines in the dissolved phase for the samples processed at Susquehanna River fall line.

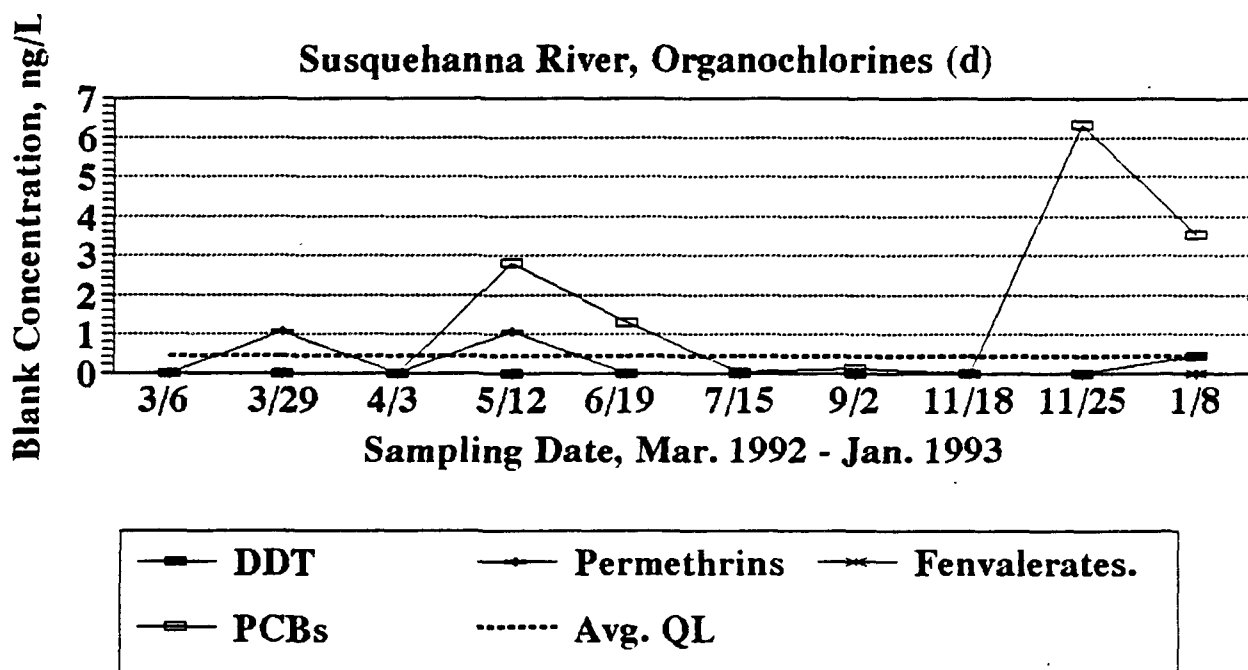
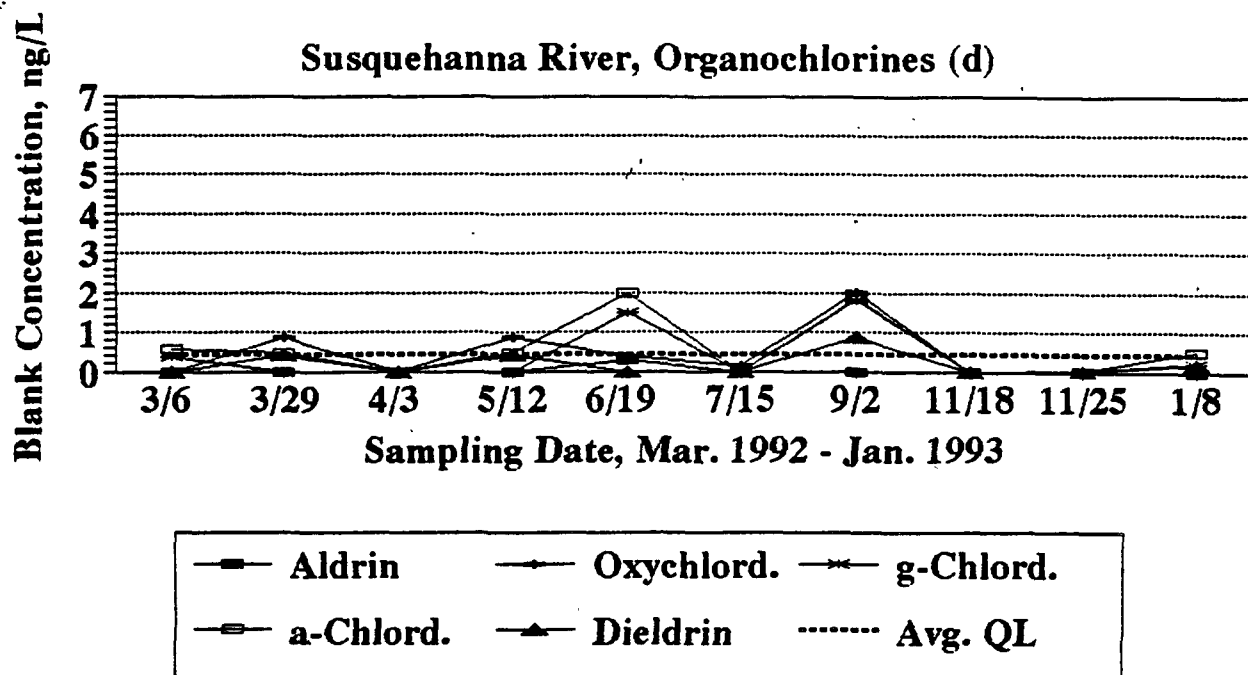


Figure 7. Field blank concentrations of the organochlorines in GF/D and GF/F filters for samples processed at the Susquehanna River fall line.

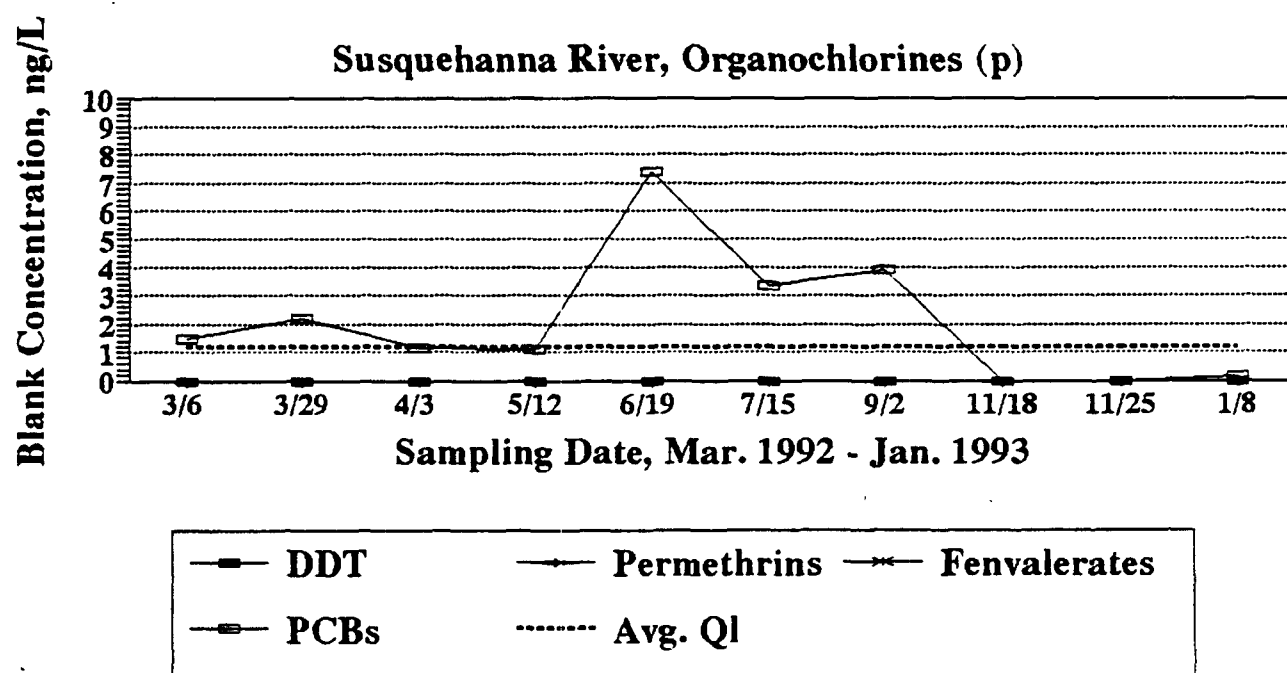
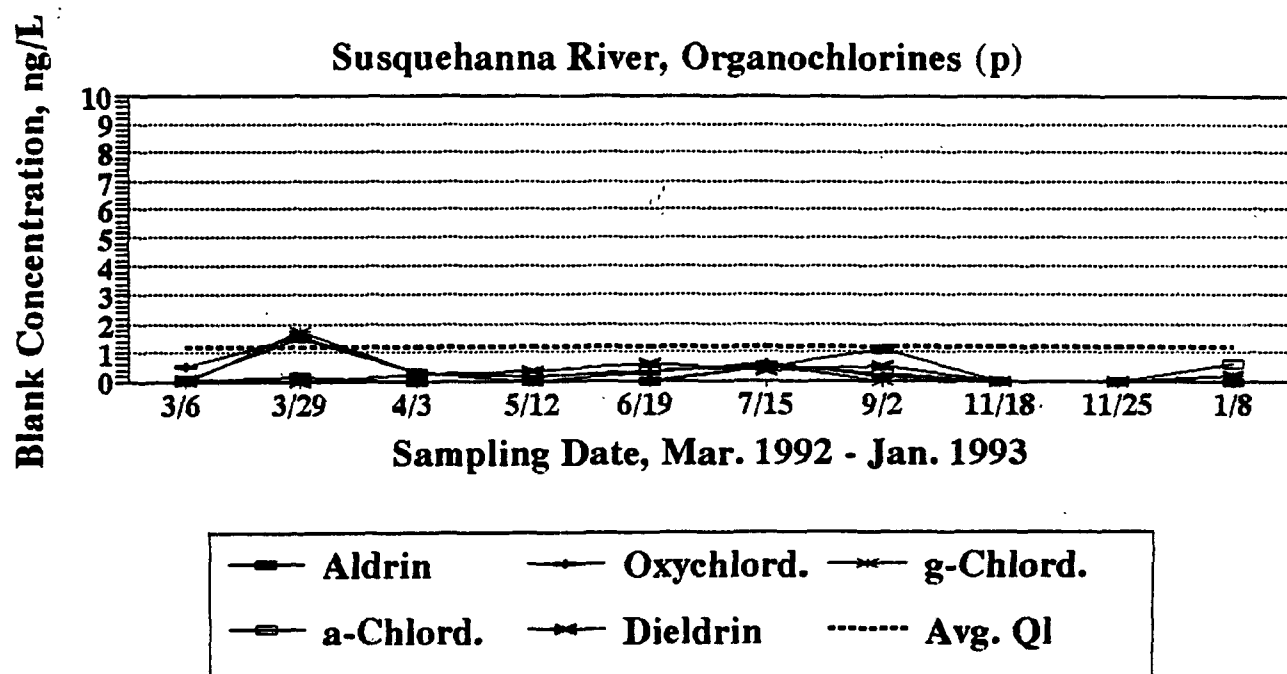
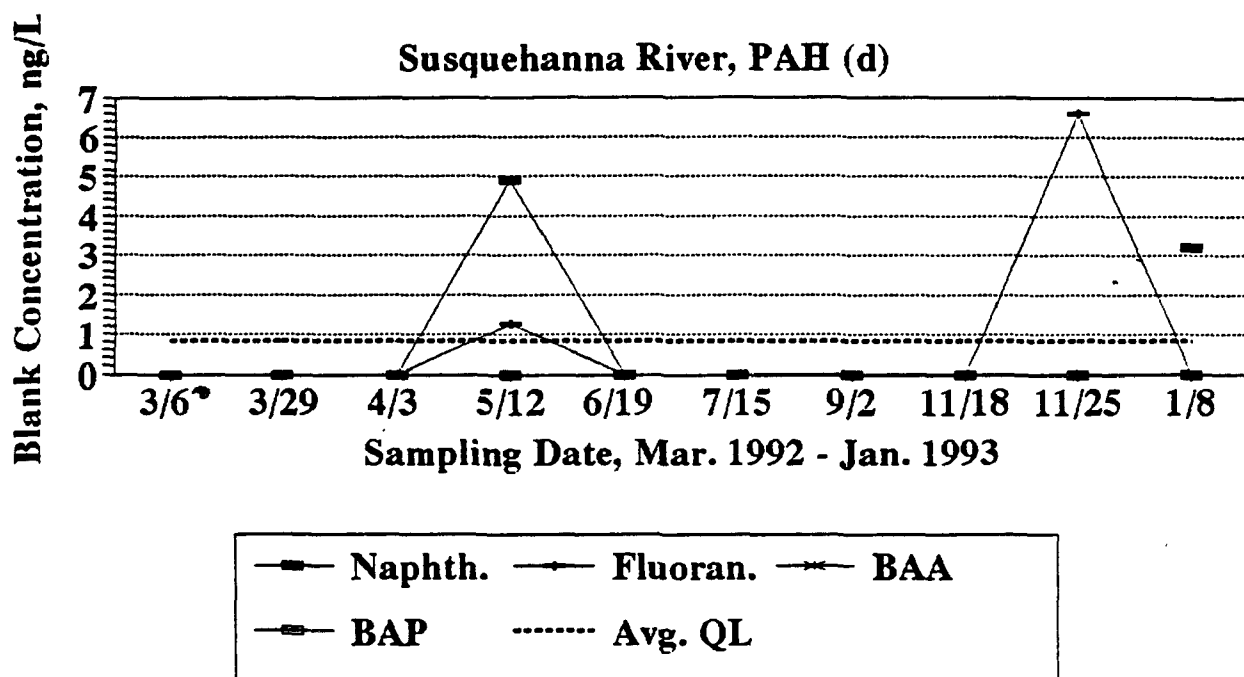
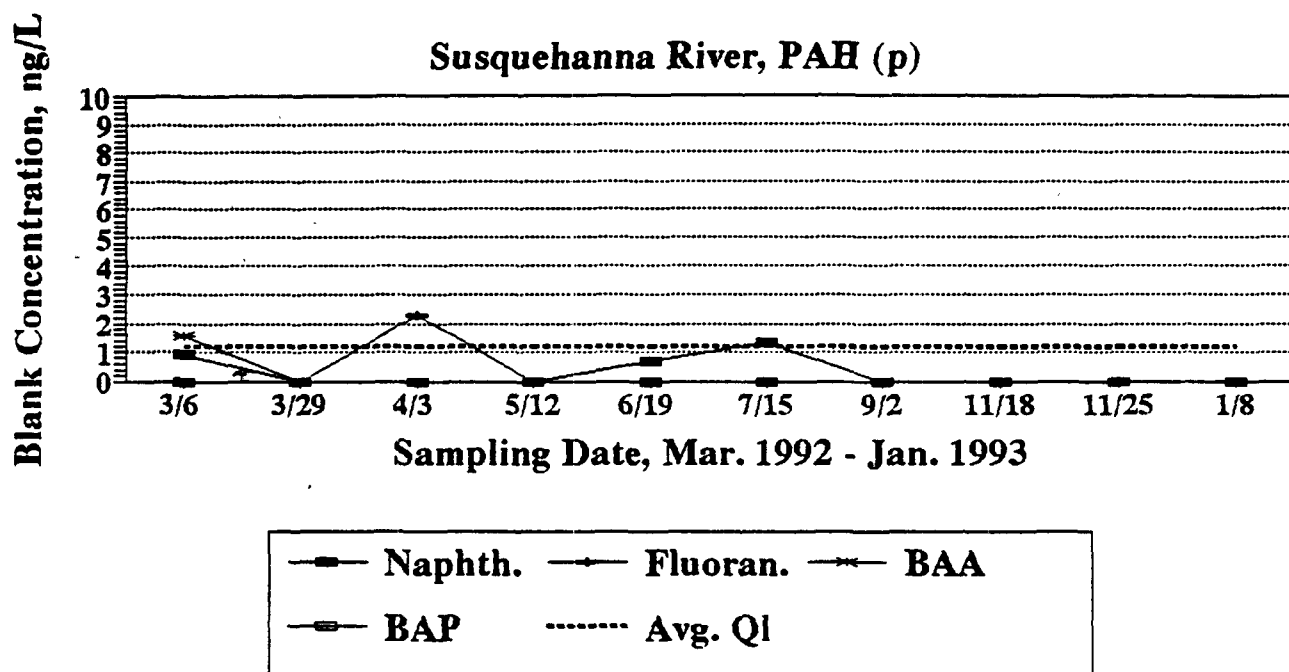


Figure 8. Field blank concentrations of the polynuclear aromatic hydrocarbons in the dissolved phase for the samples processed at Susquehanna River fall line.



**Figure 9.** Field blank concentrations of the polynuclear aromatic hydrocarbons in GF/D and GF/F filters for samples processed at the Susquehanna River fall line.



**Figure 10.** Field blank concentrations of the organonitrogen and organophosphorus pesticides in the dissolved phase for samples processed at the James River fall line.

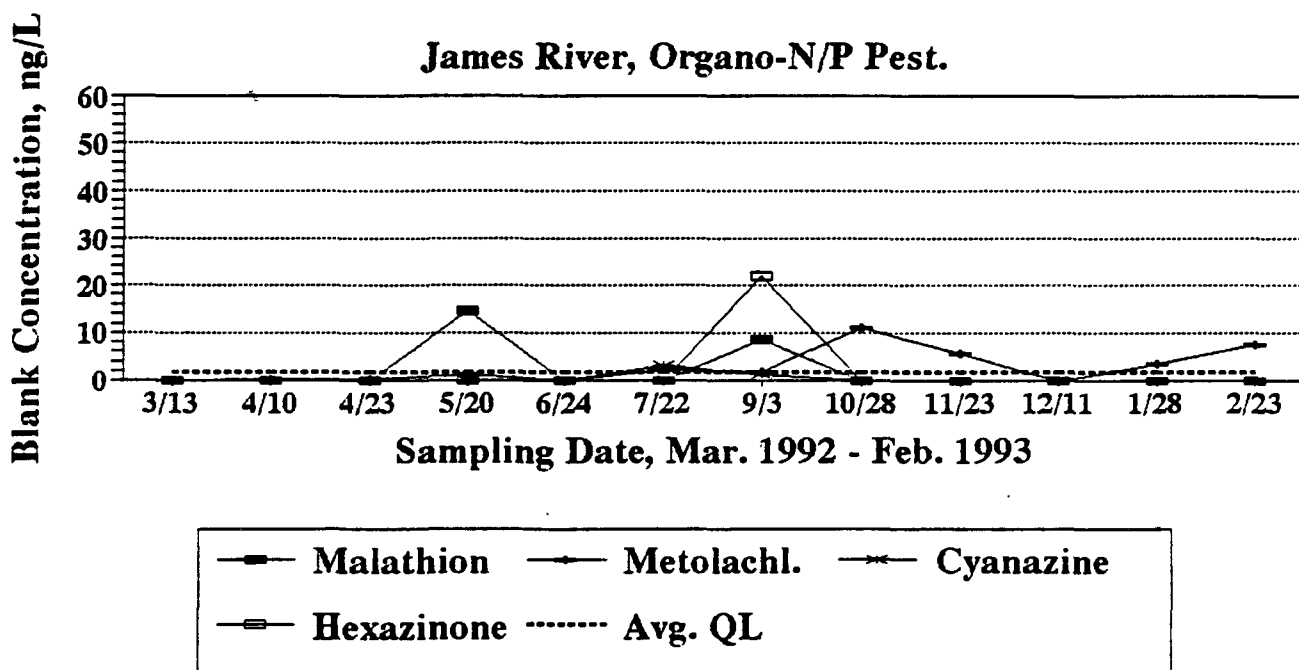
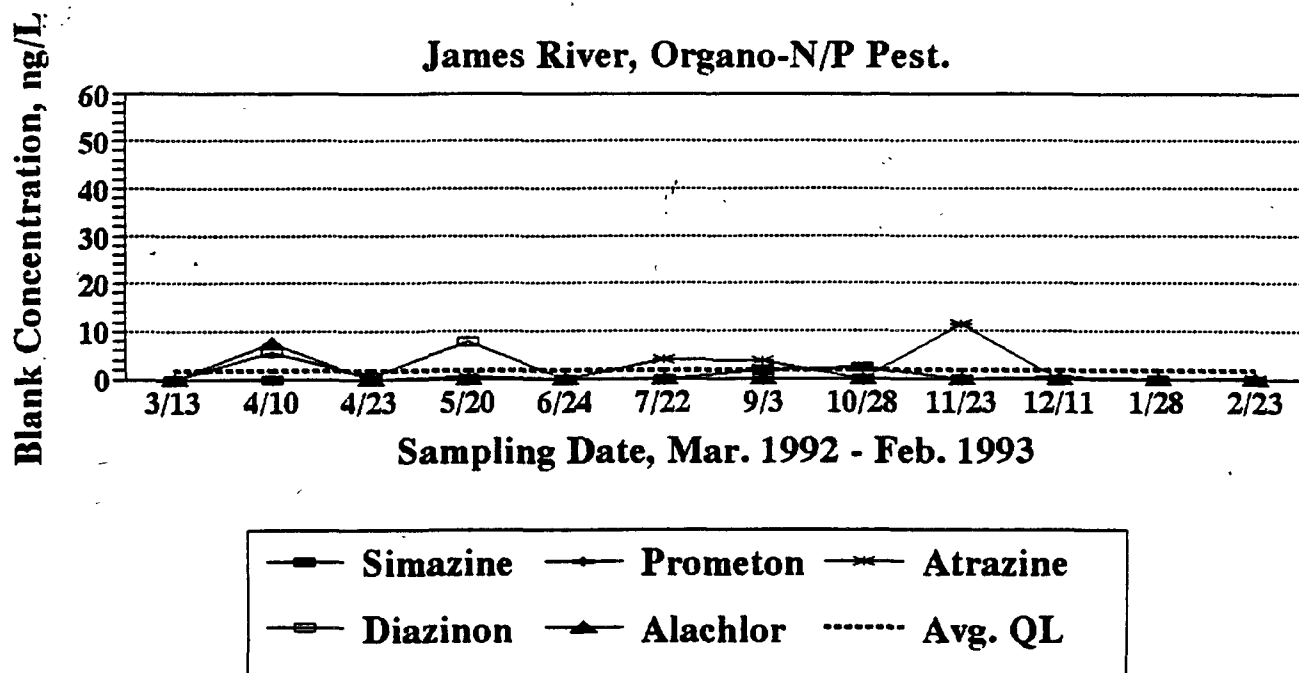


Figure 11. Field blank concentrations of the organochlorines in the dissolved phase for the samples processed at James River fall line.

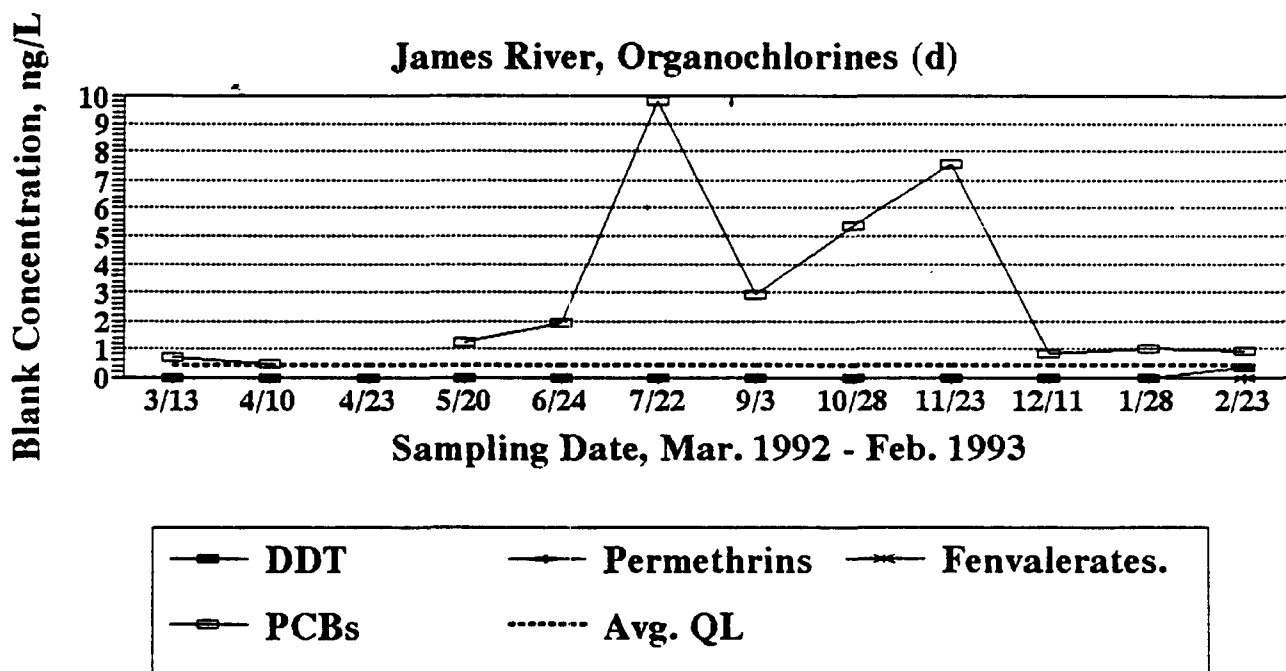
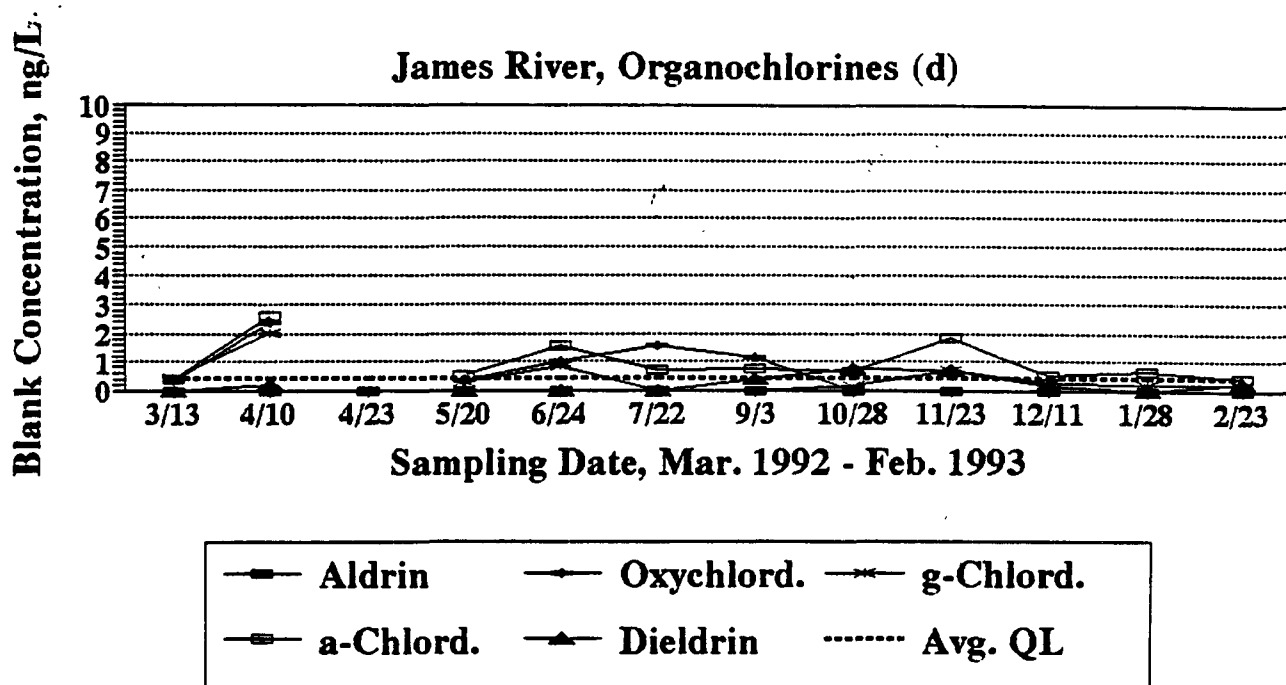
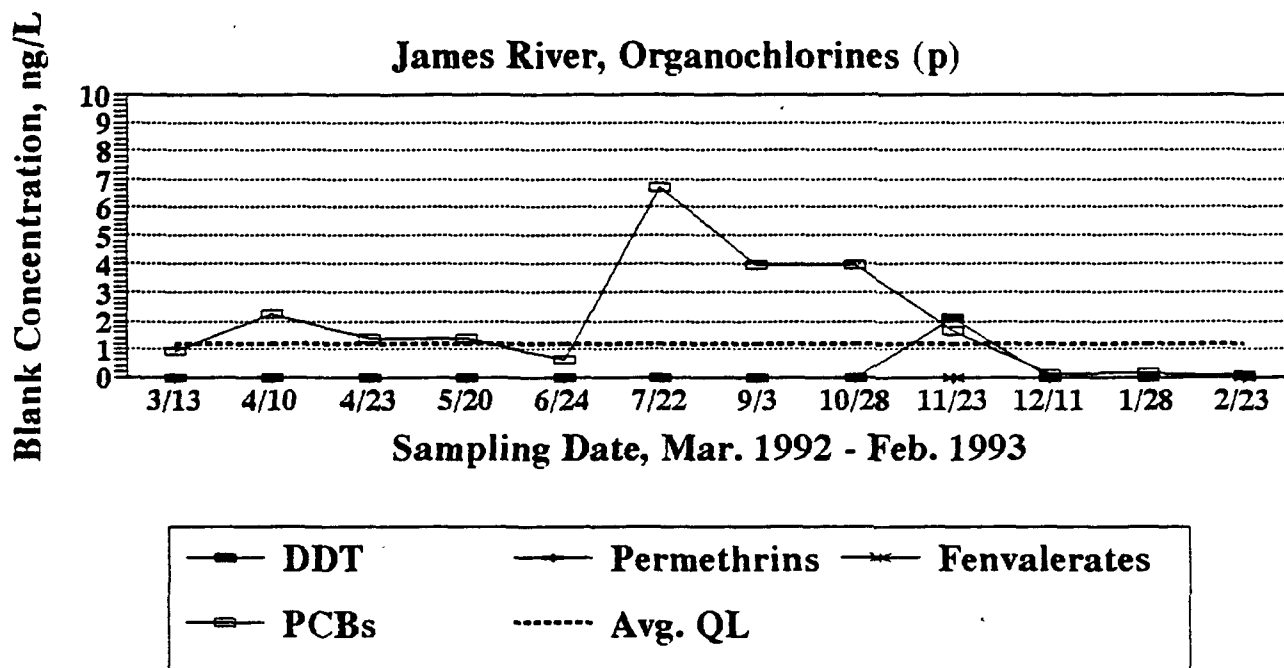
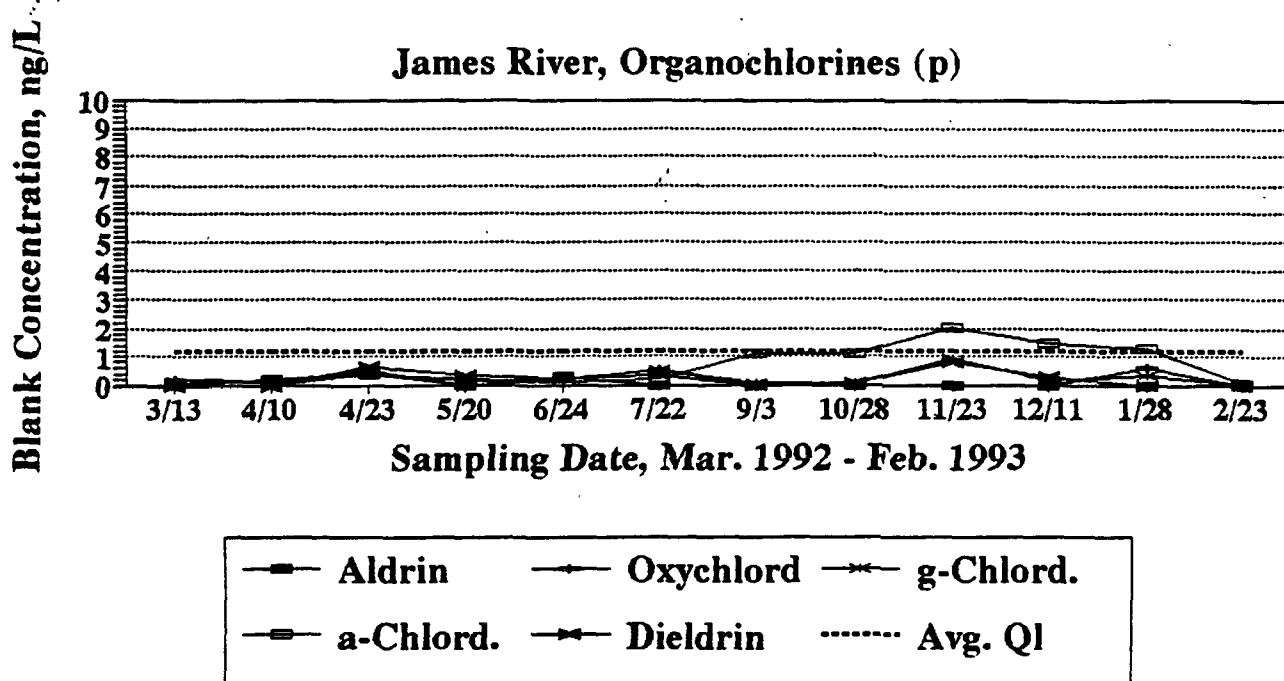
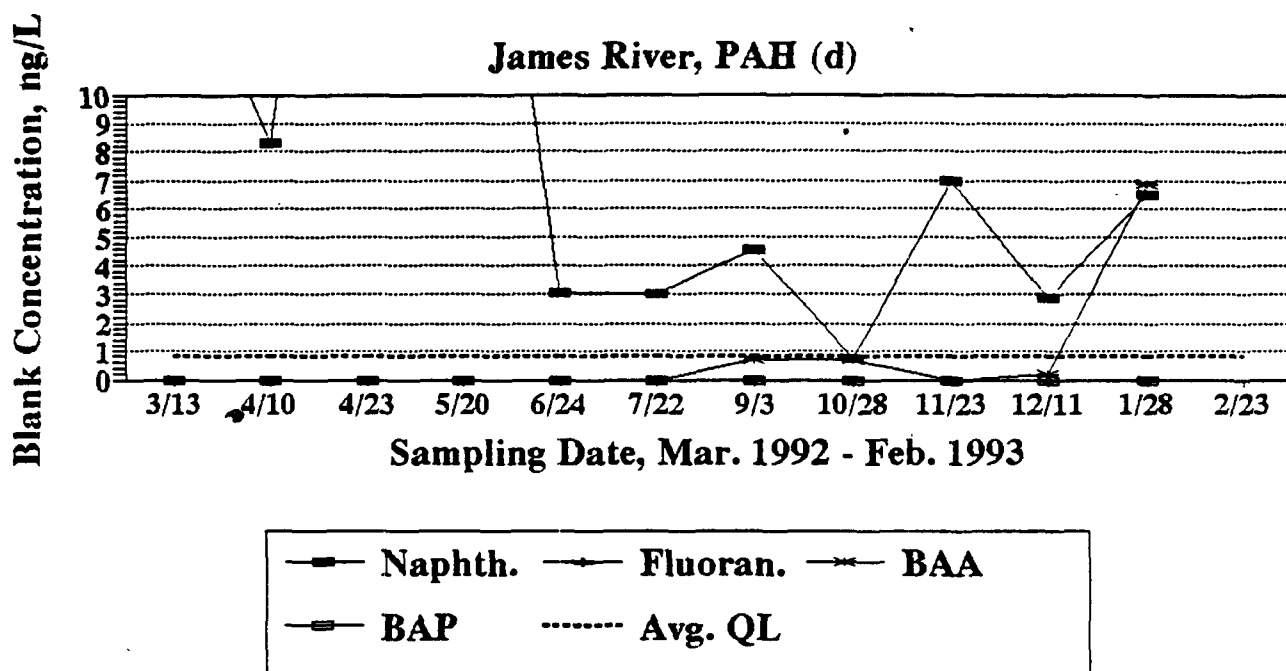


Figure 12. Field blank concentrations of the organochlorines in GF/D and GF/F filters for samples processed at the James River fall line.





**Figure 13.** Field blank concentrations of the polynuclear aromatic hydrocarbons in the dissolved phase for the samples processed at James River fall line.



**Figure 14.** Field blank concentrations of the polynuclear aromatic hydrocarbons in GF/D and GF/F filters for samples processed at the James River fall line.

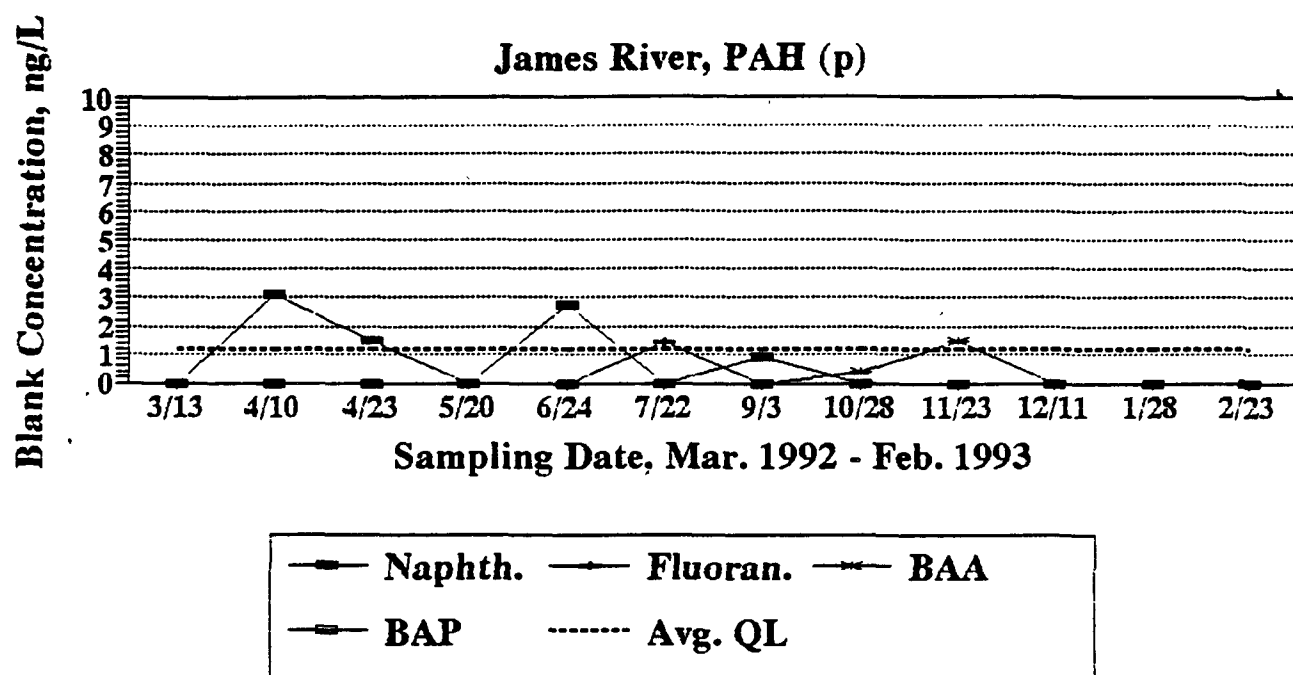


Figure 15. Laboratory blank concentrations of the organonitrogen and organophosphorus pesticides in the dissolved phase.

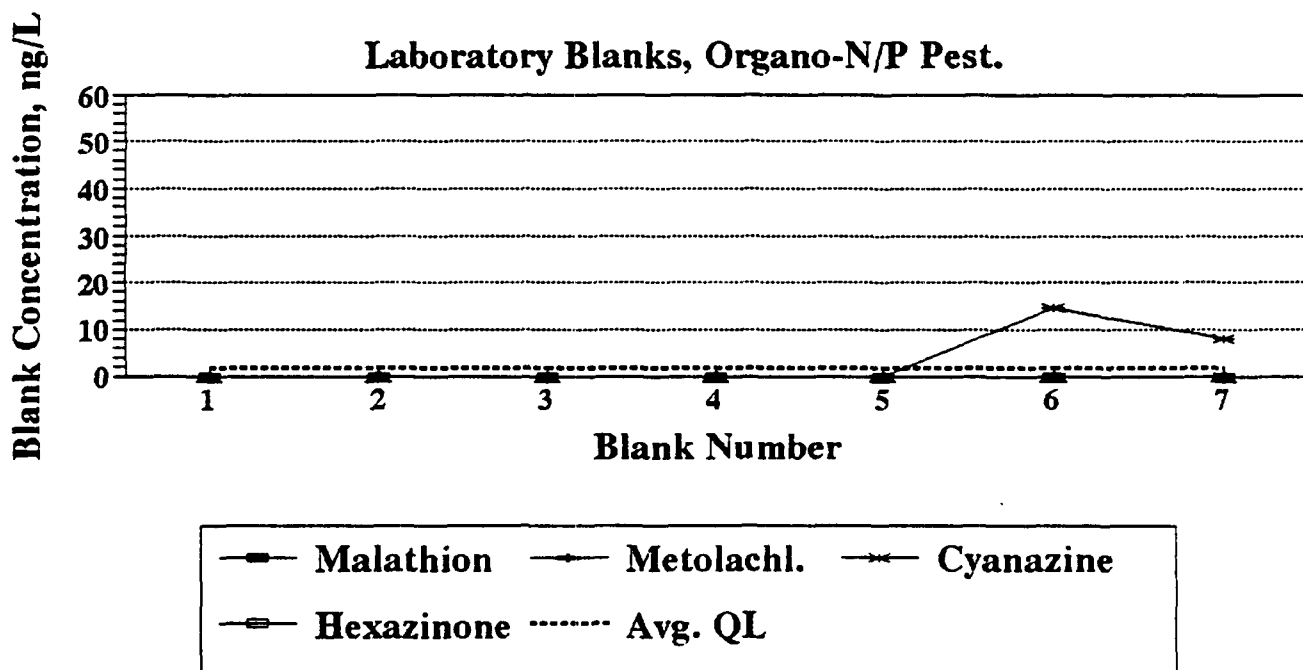
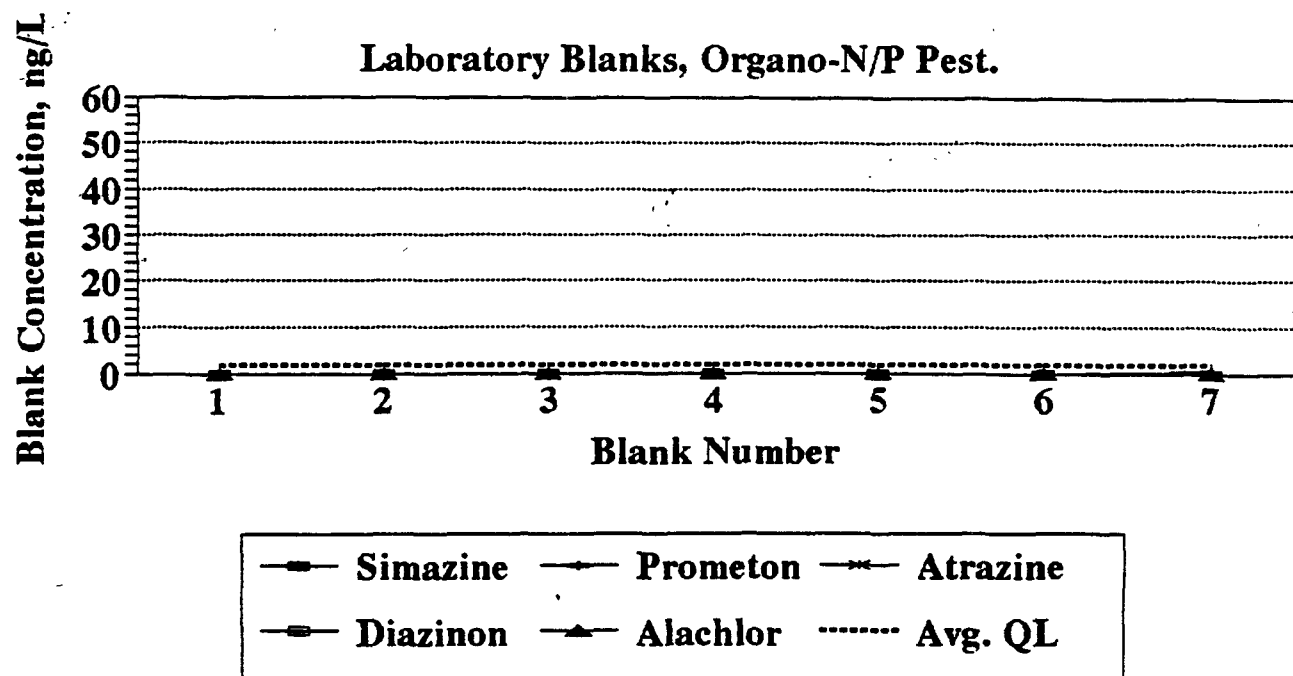


Figure 16. Laboratory blank concentrations of the organochlorines in the dissolved phase.

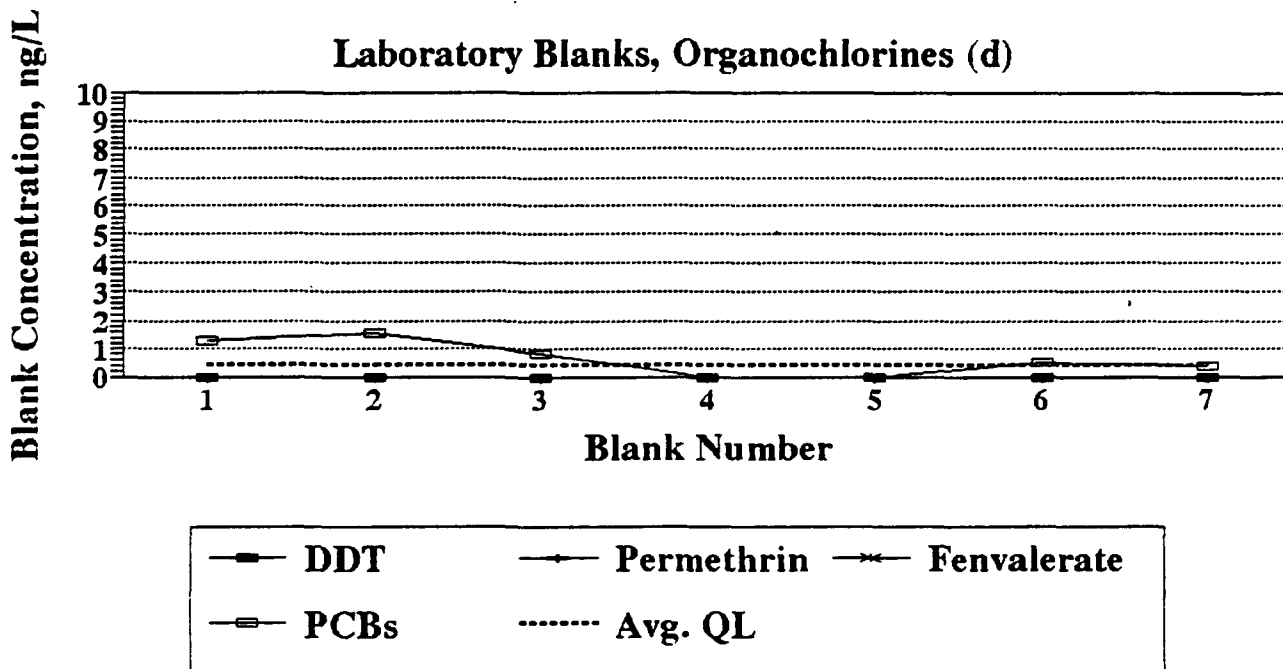
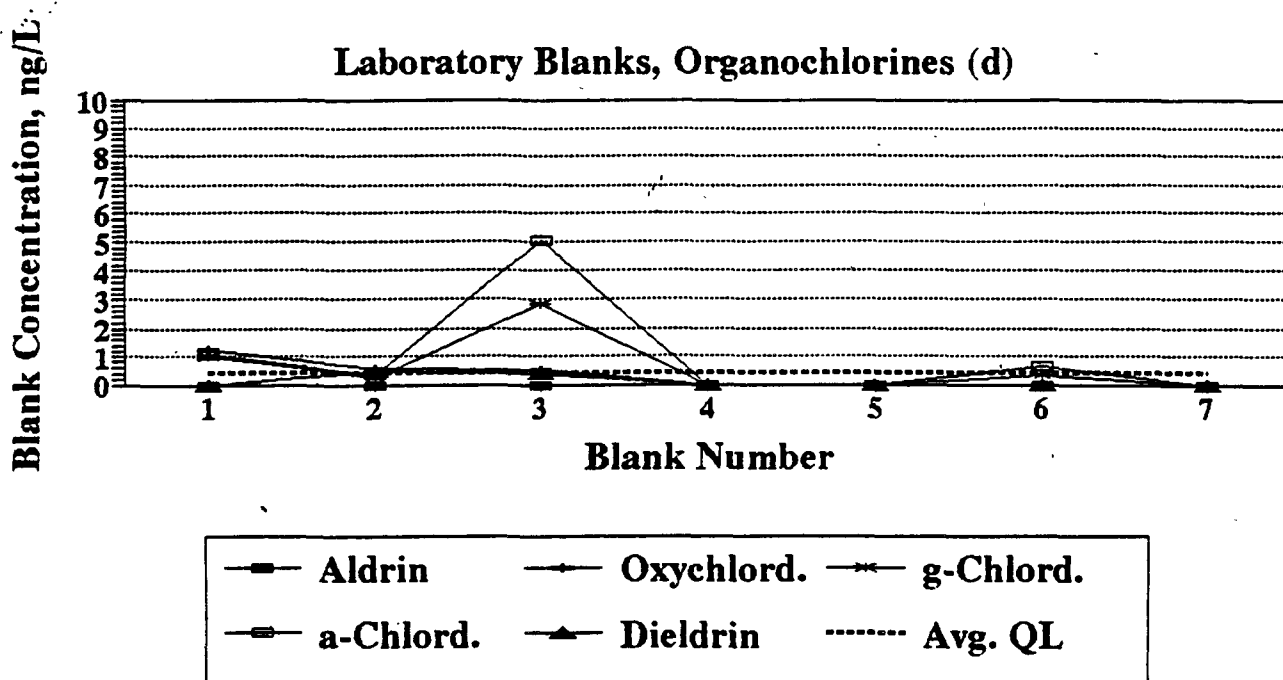


Figure 17. Laboratory blank concentrations of the organochlorines in GF/D and GF/F filters.

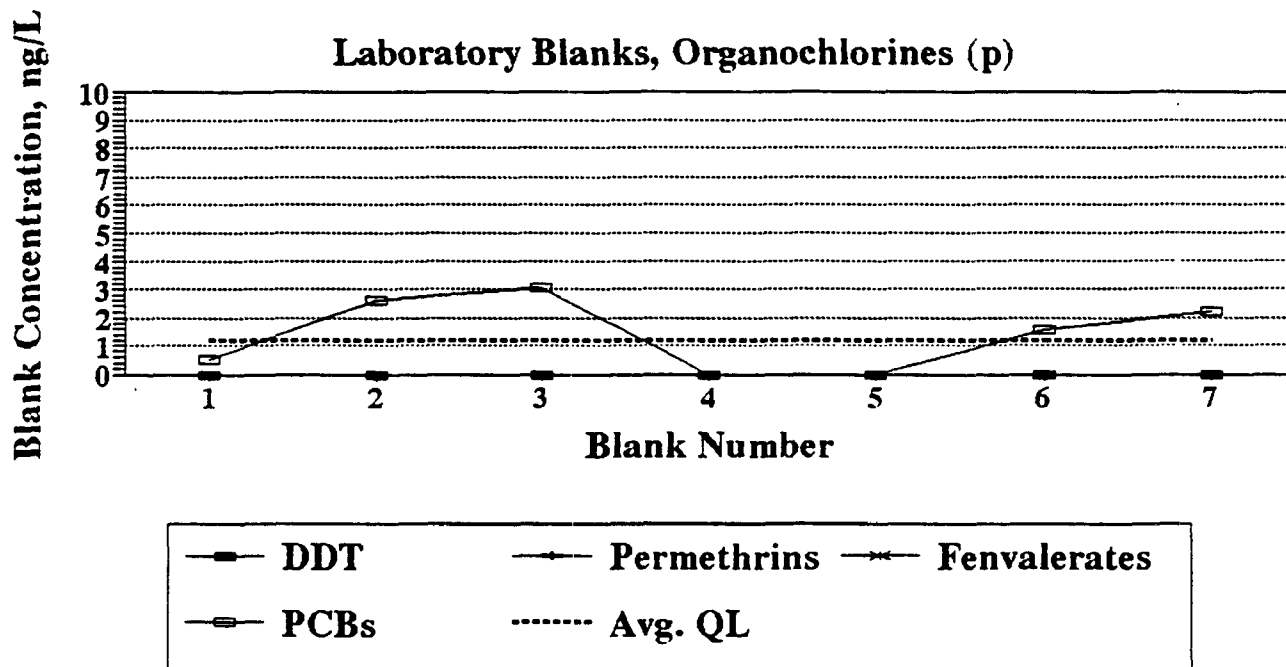
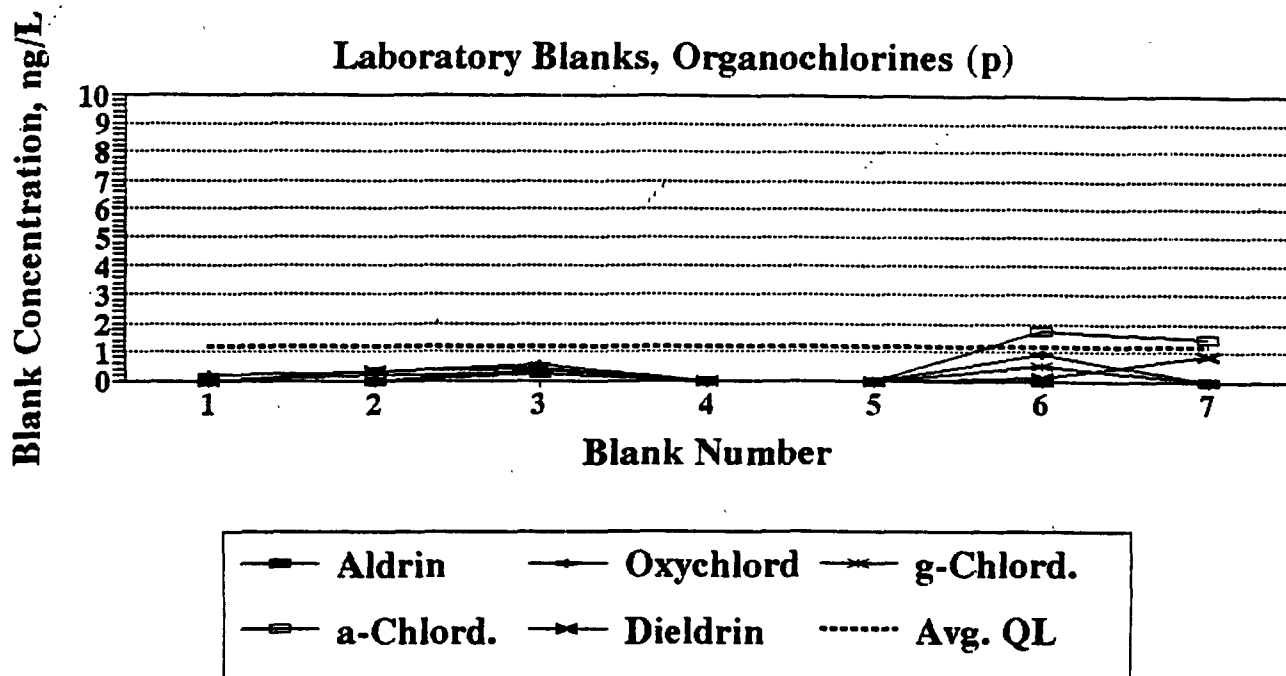


Figure 18. Laboratory blank concentrations of the polynuclear aromatic hydrocarbons in the dissolved phase.

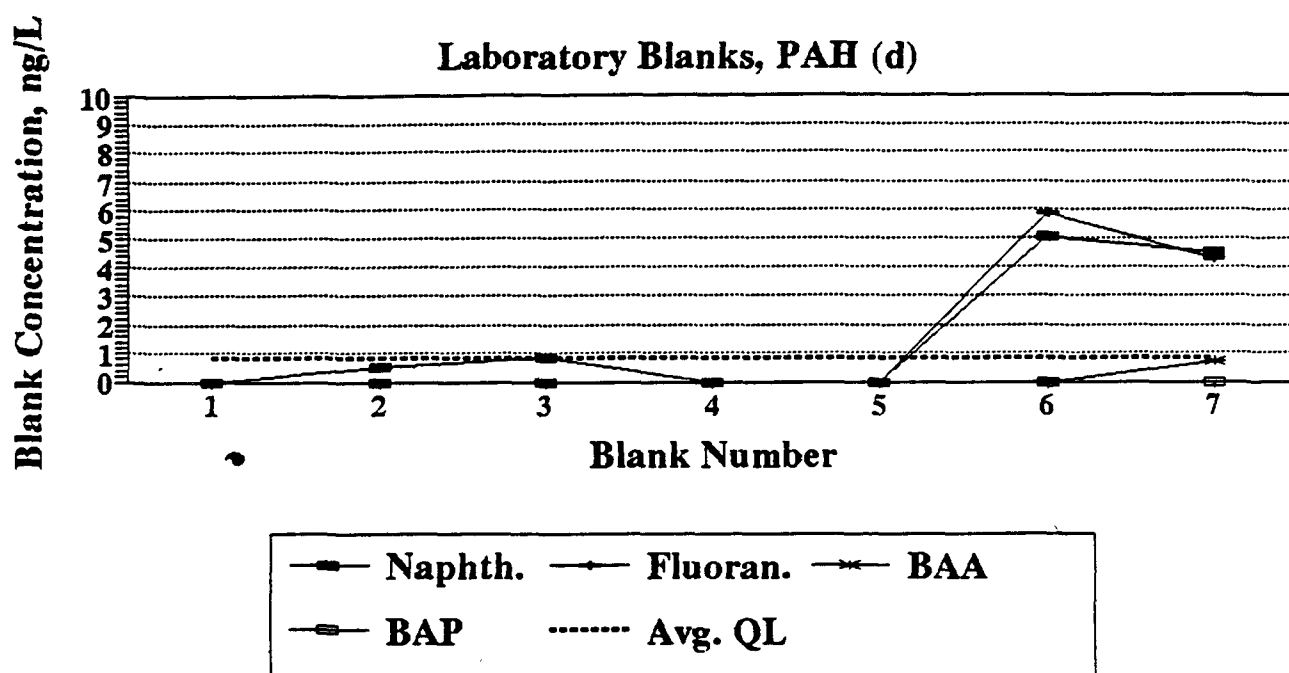
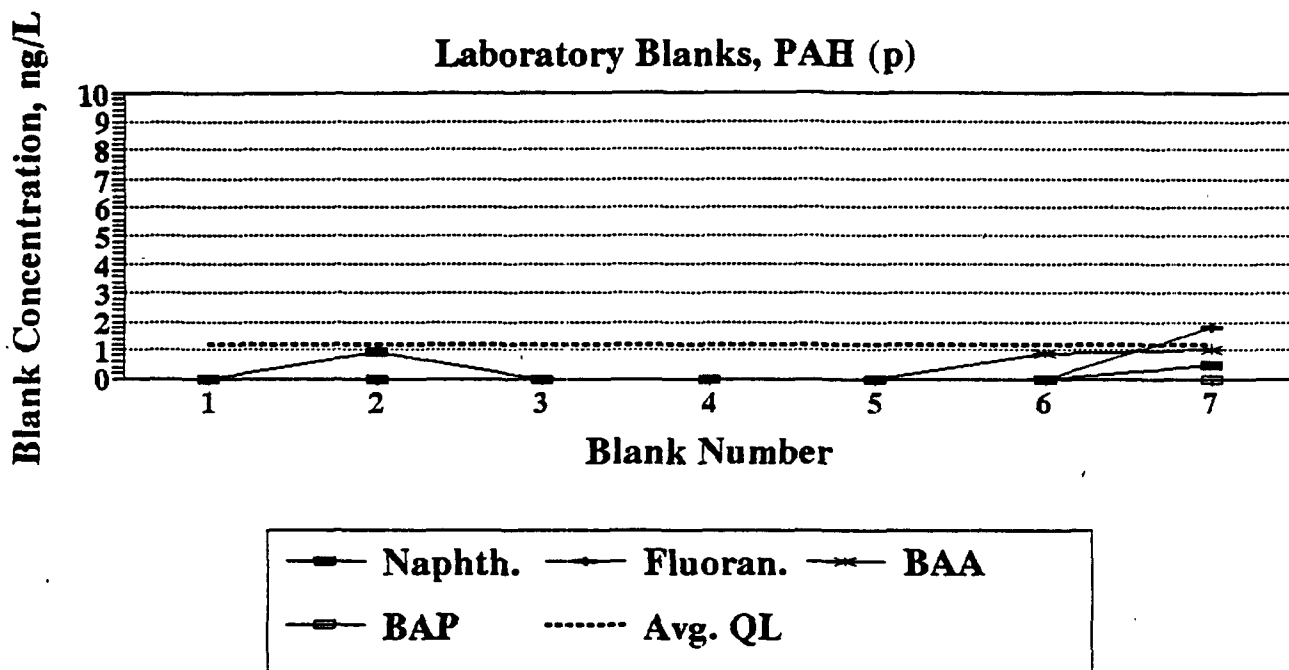


Figure 19. Laboratory blank concentrations of the polynuclear aromatic hydrocarbons in GF/D and GF/F filters.



concentrations of the organonitrogen and organophosphorus pesticides in the Potomac River database.

**Organochlorine Compounds.** Field blank concentrations of the organochlorine compounds in both the dissolved and particulate phases exceeded QL values more often than any other group of contaminants. This is due primarily to lack of specificity in the GC-ECD analysis compared with GC/MS, and the further lack of spectrometric data (i.e., confirmatory ions) in GC-ECD analysis. However, excluding the PCBs, the concentrations of the monitored contaminants detected in the field blanks were relatively small and oscillated around the QL values. There was no apparent relation in field blank concentration and type of fluvial sample (i.e., baseflow or storm flow).

Susquehanna River field blanks showed that PCBs were often detected at concentrations >QL values in both phases. However, the PCB blanks were not actually as high as related to the fall line samples, with the exception of the 11 November 1992 field blank. The PCBs are presented in the figures as total PCBs and represent the summed quantity of 112 individual congeners ( $\Sigma$ PCB). The corrections that were made to the fluvial sample PCB concentrations were done by subtracting out individual congener concentrations, and it was found that many of the PCB congeners detected in the blanks were not present in the samples. The blank concentrations were a smear of very low levels of interfering substances at extremely low concentrations that when summed over 112 peaks often gave rise to >QL concentrations, and in some cases substantially above because of the unusual occurrence of uncommon PCB congeners. It must be emphasized that the sample PCB congener profiles reflected the dominant congeners in the secondary Arochlor 1:1:1 standard and not the congener profiles present in the blanks. The net effect of this would be to substantially lower the PCB blank concentrations if the blanks were normalized for those congeners present in the samples. However, the 3/6/92 Susquehanna River dissolved phase PCB blank was contaminated to such an extent that quantitation of natural levels was not possible. There are nine flagged concentrations of the organochlorine compounds in the dissolved phase and eight in the particulate phase database.

Organochlorine concentrations in the James River field blanks were typically at or below the QL concentrations. The exception, as noted above for the Susquehanna River field blanks, is with the PCBs, which showed relatively high concentrations in several summer and autumn periods, although the PCB congeners in the blanks did show the same patterns as observed in the fall line samples.

Concentrations of the organochlorine compounds in the laboratory blanks were normally below QL concentrations, with a few exceptions notably alpha- and gamma- chlordane in dissolved phase and PCBs in particulate phase. As was observed with the organonitrogen and organophosphorus pesticides, the organochlorine compound concentrations were frequently lower in the laboratory blanks relative to the field blanks. This demonstrates that collection of large volumes of surface water in the field does increase contamination. Whether this increased contamination during sampling in the field is due to inadequate cleaning and preparation of sampling equipment or is inherent in the sampling process, such as the sorption of atmospheric-derived vapors to container surfaces, has not been determined.

**Polynuclear Aromatic Hydrocarbons.** PAH concentrations in the field blanks were generally low in each of the fall line samples with the exception of naphthalene, especially in the dissolved



phase. In the Susquehanna River field blanks, naphthalene was detected at concentrations >QL values for the 5/12/92 and 1/8/93 field blanks, and fluoranthene in the 5/12/92 and 11/25/92 field blanks for dissolved phase analysis. In the particulate phase, only fluoranthene was substantially above the QL value for the 4/3/92 field blank. Three dissolved phase and three particulate phase PAH concentrations were flagged in the Susquehanna River database.

Naphthalene was detected at high concentrations in the dissolved phase field blanks conducted at the James River fall line. The source of this interference has not been determined. The only other PAH detected in the James River dissolved field blanks was benz(a)anthracene at 1/28/93. Naphthalene was detected in three of the particulate phase James River field blanks above QL concentrations, showing that the particulate phase field blanks were relatively free of interfering PAH. As a result, seven dissolved phase sample concentrations and three particulate phase sample concentrations were flagged in the James River database.

Laboratory blanks were free of PAH interferences with two exceptions where naphthalene and fluoranthene were detected in dissolved phase blanks substantially above QL values.

#### *Matrix Spikes*

Distilled water and matrix spike recoveries fall line dissolved phase and particulate phase sub-samples are summarized in Table 8, Table 9, and Table 10. Recoveries for Carbopack B and C18 sorbents have been reported separately because the measured recoveries for the two sorbents were different, with generally higher recoveries being observed using C18 for the Potomac River fall line samples.

There were no apparent differences between recoveries using Carbopack B sorbent cartridges for the Susquehanna and James River fall line samples, therefore, the %rec values were combined for extractions performed on these two fluvial sources. A total of five matrix spike experiments were carried out with Carbopack B (including three Susquehanna River sub-samples and two James River sub-samples) between March 1992 and February 1993, and a total of four matrix spike evaluations were performed on Potomac River sub-samples.

#### *Extraction Mass Balance*

The mass distribution of analytes between front and back LSE traps is shown in Table 8 and Table 9. Collection efficiency values indicate that analyte breakthrough from the front cartridges during LSE was not a major problem in this study. Typically, greater than 90% of the analytes were collected on the front traps for both Carbopack B and C18 sorbents. As a result of these findings, LSE performed on all baseflow samples now incorporates only front traps. However, filtered fall line samples from storm sample collection are extracted with the tandem trap configuration because of the high turbidity observed in these samples. Some breakthrough has been observed for native analytes during the processing of storm samples.

**Table 8.** Summary of matrix spike recoveries using Carbopack B sorbent cartridges for Susquehanna and James River fall line samples.<sup>a</sup>

Analyte	Distilled Water		Surface Water	
	Front Cartridge %Rec(RSD)	C <sub>E</sub>	Front Cartridge %Rec(RSD)	C <sub>E</sub>
<b>Organonitrogen &amp; Organophosphorus Pesticides</b>				
Simazine	53 ( 5)	99%	61 (33)	96%
Prometon	83 (16)	99%	57 (21)	94%
Atrazine	104 (12)	98%	65 (39)	95%
Diazinon	109 (15)	96%	93 (35)	98%
Alachlor	98 (17)	98%	80 (56)	97%
Malathion	91 ( 8)	99%	79 (n=2)	98%
Metolachlor	109 (26)	97%	92 (38)	95%
Cyanazine	98 (42)	99%	57 (33)	96%
Hexazinone	102 ( 7)	96%	137 (50)	86%
<b>Organochlorines</b>				
Aldrin	58 ( 7)	94%	46 ( 8)	96%
Oxychlordane	46 (22)	98%	40 (23)	92%
<u>gamma</u> -Chlordane	59 (14)	87%	46 (23)	92%
<u>alpha</u> -Chlordane	61 (13)	92%	48 (24)	94%
Dieldrin	71 (3)	97%	65 (22)	93%
4,4'-DDT	na	-	105 (24)	99%
c/t-Permethrin	62 ( 5)	82%	56 (78)	74%
c/t-Fenvalerate	33 ( 6)	77%	34 (50)	85%
ΣPCBs	na	-	65 (n=1)	-
<b>Polycyclic Aromatic Hydrocarbons</b>				
Naphthalene	na	na	na	na
Fluoranthene	na	na	na	na
Benz(a)anthracene	na	na	na	na
Benzo(a)pyrene	na	na	na	na

<sup>a</sup>Three distilled water and five surface water replicates were performed unless otherwise specified by the number in parenthesis; C<sub>E</sub> = collection efficiency; na = not available.

**Table 9.** Summary of matrix spike recoveries using C18 sorbent cartridges for the Potomac River fall line samples.<sup>a</sup>

Analyte	Distilled Water <sup>b</sup>		Surface Water	
	Front Cartridge %Rec(RSD)	C <sub>E</sub>	Front Cartridge %Rec(RSD)	C <sub>E</sub>
<b>Organonitrogen &amp; Organophosphorus Pesticides</b>				
Simazine	92 ( 3)	100%	44 ( 7)	96%
Prometon	78 (12)	100%	56 (10)	94%
Atrazine	93 ( 3)	100%	87 (24)	94%
Diazinon	95 ( 1)	98%	119 (24)	99%
Alachlor	95 ( 3)	100%	109 (21)	96%
Malathion	102 ( 1)	100%	114 (n=1)	97%
Metolachlor	93 ( 4)	99%	109 (28)	95%
Cyanazine	86 ( 3)	97%	105 (33)	97%
Hexazinone	na	-	151 (56)	85%
<b>Organochlorines</b>				
Aldrin	48 (n=2)	98%	40 (24)	99%
Oxychlordan	56 (n=2)	99%	65 ( 5)	92%
gamma-Chlordane	70 (n=2)	98%	74 ( 6)	92%
alpha-Chlordane	75 (n=2)	97%	80 ( 8)	93%
Dieldrin	92 (n=2)	98%	105 ( 8)	93%
4,4'-DDT	91 (n=2)	97%	93 (22)	99%
c/t-Permethrin	90 (n=2)	83%	85 (13)	84%
c/t-Fenvalerate	79 (n=2)	86%	91 (19)	86%
ΣPCBs	64 (n=2)	96%	57 (12)	84%
<b>Polycyclic Aromatic Hydrocarbons</b>				
Naphthalene	na	-	35 (n=1)	na
Fluoranthene	na	-	105 (n=1)	na
Benz(a)anthracene	na	-	110 (n=1)	na
Benzo(a)pyrene	na	-	80 (n=1)	na

<sup>a</sup>Three distilled water and five surface water replicates were performed unless otherwise specified by the number in parenthesis; <sup>b</sup>Data from Foreman and Foster (1991) and this study; C<sub>E</sub> = collection efficiency; na = not available.

**Table 10.** Summary of spike recoveries of monitored organic contaminants from filtered particulates.

Analyte	%Rec(RSD) <sup>a</sup>
<b>Organochlorines</b>	
Aldrin	105 ( 3)
Oxychlordan	84 (22)
<u>gamma</u> -Chlordane	68 (18)
<u>alpha</u> -Chlordane	64 (27)
Dieldrin	106 (11)
4,4'-DDT	45 (20)
c/t-Permethrin	na
c/t-Fenvalerate	na
ΣPCBs	86 ( 5)
<b>Polycyclic Aromatic Hydrocarbons</b>	
Naphthalene	83 (11)
Fluoranthene	98 ( 4)
Benz(a)anthracene	101 ( 3)
Benzo(a)pyrene	98 (16)

<sup>a</sup>Spike concentration at 20 µg/kg; na = not available.

Results from the analysis of solvent rinses of both milk can containers and glass bottles used during the collection of fluvial samples has revealed no detectable levels of the target analytes associated with container surfaces. Only the containers from the first three months of sampling have been analyzed, but it is assumed that since the same sampling protocol is used for every fluvial sampling that the results can be applied universally.

#### *Enrichment Factors*

The enrichment factors for each of the fall line target analytes, for the fluvial samples only, are listed in Table 11. The matrix spike %Rec values used to calculate enrichment factors were those listed in Table 8 and Table 9 for river water.

#### *Error Evaluation*

The magnitudes of the percent relative uncertainty terms calculated for each analyte are listed in Table 12, where it can be seen that the major source of indeterminate error in the analysis is in gc/ms and gc-ecd analysis, given the variations in relative response factors from instrument calibration data (RF,  $\% \alpha_2$ ).

**Table 11.** Enrichment factors for the monitored organic contaminants in filtered surface water samples for both sorbents used in this study.

Analyte	E <sub>f</sub> -Carbopack B	E <sub>f</sub> -C18
<b>Organonitrogen &amp; Organophosphorus Pesticides</b>		
Simazine	30500	22000
Prometon	28500	28000
atrazine	32500	43500
Diazinon	46500	59500
Alachlor	40000	54500
Malathion	39500	57000
Metolachlor	46000	54500
Cyanazine	28500	52500
Hexazinone	68500	75500
<b>Organochlorines</b>		
Aldrin	23000	20000
Oxychlordane	20000	32500
<u>gamma</u> -Chlordane	23000	37000
<u>alpha</u> -Chlordane	24000	40000
Dieldrin	32500	52500
4,4'-DDT	52500	46500
c/t-Permethrin	28000	42500
c/t-Fenvalerate	17000	45500
ΣPCBs	na	28500
<b>Polycyclic Aromatic Hydrocarbons</b>		
Naphthalene	na	25000
Fluoranthene	na	52500
Benz(a)anthracene	na	55000
Benzo(a)pyrene	na	40000

E<sub>f</sub> = enrichment factor; na = not available.

**Table 12.** Indeterminate errors associated with the concentrations of the monitored organic contaminants in the fall line samples.

Analyte	IS % $\alpha_1$	RRF % $\alpha_2$	Vol % $\alpha_3$	Conc % $\alpha_4$
<b>Organonitrogen &amp; Organophosphorus Pesticides</b>				
Simazine	2	11	1	11
Prometon	2	26	1	26
Atrazine	2	10	1	10
Diazinon	2	21	1	21
Alachlor	2	19	1	19
Malathion	2	27	1	27
Metolachlor	2	22	1	22
Cyanazine	2	41	1	41
Hexazinone	2	38	1	38
<b>Organochlorines</b>				
Aldrin	2	8	1	8
Oxychlordane	2	18	1	18
<u>gamma</u> -Chlordane	2	10	1	10
<u>alpha</u> -Chlordane	2	8	1	8
Dieldrin	2	8	1	8
4,4'-DDT	2	31	1	31
c/t-Permethrin	2	13	1	13
c/t-Fenvalerate	2	27	1	27
$\Sigma$ PCBs	2	10	1	10
<b>Polycyclic Aromatic Hydrocarbons</b>				
Naphthalene	2	12	1	12
Fluoranthene	2	28	1	28
Benz(a)anthracene	2	27	1	27
Benzo(a)pyrene	2	32	1	32

IS = error propagated from addition of internal standard; RRF = error propagated from instrument response factors in quantitation; Vol = error propagated from measuring the sample volume; Conc = propagated error associated measured concentrations of the monitored organic contaminants in the samples.

na=not available.

## **WATER QUALITY DATA RESULTS**

### **Metals Water Quality Data - Susquehanna River**

Following are the results of water quality data collected for metals and suspended sediment during the 1992 ultra clean study for the Susquehanna River. Results of the 1990-91 study may be found in a report written for EPA Chesapeake Bay Program Office entitled *Chesapeake Bay Toxics Monitoring Program: 1990-1991 Loading Results* available in the Annapolis, Maryland office. A listing of instantaneous discharge and concentration data collected during the entire 1990-92 sampling period for the Susquehanna River are presented in Appendix A.

Samples were collected in 1992 under baseflow conditions during March, May, June, July, September, and November. Two storm events were sampled, one each during March and April. Discrete samples were collected daily throughout the storm events.

An assessment of 1992 data quality was made based on results of the quality-assurance program. Through a comparative analyses of quality-control (QC) equipment-blank sample concentrations and concurrently collected environmental concentrations, constituent data were given a grade of excellent, good, fair, poor, or invalid. Data quality for a constituent collected in 1992 was considered excellent if no detectable concentrations of the constituent were found in the blank samples; good, if detectable concentrations of the constituent were found in the blank samples yet none of them exceeded environmental concentrations; fair, if detectable concentrations of the constituent were found in the blank samples and less than half of them exceeded environmental concentrations; poor, if detectable concentrations of the constituent were found in the blank samples and more than half of them exceeded environmental concentrations; and invalid, if detectable concentrations of the constituent were found in the blank samples, all of which exceeded environmental concentrations. Based upon this criteria, excellent data were collected for total-recoverable As, Cd, Cu, Zn, and dissolved As. Good data were collected for total-recoverable Pb and dissolved Cu. Fair data were collected for total-recoverable Hg and dissolved Cd, Cr, Pb, and Zn, and poor data, considered suspect, were collected for total-recoverable Cr and dissolved Hg. Dissolved Cr values, although considered of fair quality, are suspect due to the significant increase observed in concentration data during 1992. This criteria is more rigorous than the previous data quality assessment conducted for the *Chesapeake Bay Fall Line Toxics Monitoring Program 1992 Interim Report*, as it will be used to determine the effect that ultra clean sampling techniques and lowered reporting limits had on load estimates.

Instantaneous discharge and concentration data collected in 1992 for the Susquehanna River station are listed in Table 13 and are discussed in this text. Analysis for total-recoverable trace metals and suspended sediment is complete. However, dissolved metal analysis for samples collected after June, 1992 are pending. Concentration data associated with a less-than (<) sign indicates that the constituent concentration is less than the quantitation limit. A dash (--) indicates that the constituent was not analyzed. Asterisks (\*\*) denote pending data. Figure 20-Figure 23 show the concentrations for selected dissolved and total-recoverable metals for the 1992 data collection period with the concentrations for blanks collected during the sampling period.



Table 13. Metal water-quality data for the Susquehanna River fall line at Conowingo, Maryland, for the period March 1992 through March 1993.

Date/Time	Discharge (CFS)	Suspended Sediment (mg/L)	Suspended Sediment % finer than 0.62 mm	Aluminum Diss (ug/L)	Arsenic Diss (ug/L)	Arsenic TR (ug/L)	Barium TR (ug/L)	Cadmium Diss (ug/L)	Cadmium TR (ug/L)	Chromium Diss (ug/L)	Chromium TR (ug/L)
19920315/1315	77,900	24	99	20	--	< 1	<100	--	< 1	< 1	2
19920316/1300	80,100	17	91	30	--	< 1	--	--	< 1	< 1	1
19920329/1700	165,600	90	99	70	< 0.6	< 1	<100	< 0.1	< 1	0.5	1
19920330/1330	169,400	49	100	50	< 0.6	< 1	--	< 0.1	< 1	1.1	1
19920331/1400	120,200	75	100	30	< 0.6	< 1	--	< 0.1	< 1	1.97	3
19920403/1145	88,500	22	99	20	< 0.6	< 1	--	< 0.1	< 1	1.4	< 1
19920422/1230	87,700	15	98	110	< 0.6	< 1	--	< 0.1	< 1	5.4	3
19920424/1100	88,700	23	98	230	< 0.6	< 1	--	< 0.1	< 1	2.7	< 1
19920512/1130	66,300	13	100	20	< 0.6	< 1	--	< 0.1	< 1	4.40	< 1
19920512/1145	66,300	--	--	150	--	--	--	1.24	< 1	2.12	< 1
19920519/1000	9,160	10	99	80	< 0.6	< 1	--	--	< 1	--	--
19920619/1345	22,800	5	98	70	< 0.6	< 1	--	< 0.1	< 1	1.27	< 1
19920715/1300	12,300	2	--	20	< 0.6	< 1	--	< 0.1	< 1	2.97	3
19920715/1305	12,300	--	--	50	1.61	< 1	--	< 0.1	< 1	2.67	1
19920902/1030	36,400	8	98	40	1.15	< 1	--	< 0.1	< 1	1.18	2
19920902/1035	36,400	--	--	40	< 0.6	< 1	--	< 0.1	< 1	1.86	6
19921118/1100	54,700	10	--	<10	< 0.6	< 1	--	< 0.1	< 1	< 0.20	< 1
19921125/1330	70,400	38	--	<10	< 0.6	< 1	--	< 0.1	< 1	0.44	5
19921130/1400	70,400	13	--	<10	< 0.6	< 1	--	< 0.1	< 1	0.77	5
19930105/1430	95,900	25	99	30	< 0.6	< 1	--	0.16	< 1	1.90	5
19930108/1300	114,000	18	96	20	< 0.6	< 1	--	< 0.1	< 1	0.63	--
19930311/1400	70,900	14	99	30	--	< 1	--	--	< 1	--	< 1
19930325/1130	145,000	21	96	<10	< 0.6	< 1	--	< 0.1	< 1	< 0.20	< 1
19930327/1245	162,000	32	96	<10	< 0.6	< 1	--	< 0.1	< 1	0.36	1
19930328/1330	184,000	28	98	20	< 0.6	< 1	--	< 0.1	< 1	0.59	1
19930330/1645	314,000	79	99	<10	< 0.6	< 1	--	< 0.1	< 1	< 0.20	3
19930331/0145	321,000	67	99	<10	0.65	< 1	--	< 0.1	< 1	< 0.20	< 1
19930331/1400	415,000	97	98	<10	< 0.6	< 1	--	< 0.1	< 1	< 0.20	5

[CFS = cubic feet per second; mg/L = milligrams per liter; ug/L = micrograms per liter; Dupl = Duplicate sample; Diss = dissolved (filtered with 0.45 micron filter); TR = Total recoverability; < = value is less than the analytical reporting limit; -- = constituent was not analyzed; \*\* = data pending].

Table 13. (cont.)

Date/Time	Copper, Diss (ug/L)	Copper, IR (ug/L)	Iron, Diss (ug/L)	Iron, IR (ug/L)	Lead, Diss (ug/L)	Lead, IR (ug/L)	Lithium, IR (ug/L)	Manganese, IR (ug/L)	Mercury, Diss (ug/L)	Mercury, IR (ug/L)	Nickel, Diss (ug/L)	Nickel, IR (ug/L)	Selenium, IR (ug/L)
19920315/1315	2	< 1	--	900	< 1	1	< 10	170	--	< 0.10	4	7	< 1
19920316/1300	2	< 1	--	640	< 1	2	< 10	140	--	< 0.10	4	7	< 1
19920329/1700	1.5	3	480	--	< 0.06	4	--	--	**	< 0.10	--	--	--
19920330/1330	3.1	2	55	--	2.2	3	--	--	0.035	0.50	--	--	--
19920331/1400	1.63	2	810	--	0.84	3	--	--	0.026	0.20	--	--	--
19920403/1145	2.0	1	410	--	0.9	1	--	--	0.021	< 0.10	--	--	--
19920422/1230	1.9	2	290	--	0.6	2	--	--	0.024	< 0.10	--	--	--
19920424/1100	2.2	2	430	--	0.8	2	--	--	--	< 0.10	--	--	--
19920512/1130	1.45	1	42	--	0.45	< 1	--	--	**	< 0.10	8	--	--
19920512/1145	--	--	--	--	--	--	--	--	--	--	--	--	--
19920519/1000	1.18	2	300	--	0.69	< 1	--	--	**	< 0.10	--	--	--
19920619/1345	1.19	1	120	--	< 0.06	< 1	--	--	**	< 0.10	--	--	--
19920715/1300	1.12	1	4	--	0.13	< 1	--	--	**	< 0.10	--	--	--
19920715/1305	1.07	1	91	--	0.12	< 1	--	--	**	< 0.10	--	--	--
19920902/1030	0.97	< 1	6	--	< 0.06	1	--	--	**	< 0.10	7	--	--
19920902/1035	0.95	5	18	--	< 0.06	2	--	--	**	< 0.10	--	--	--
19921118/1100	1.18	2	21	--	< 0.06	< 1	--	--	**	< 0.10	9	--	--
19921125/1330	1.55	2	540	--	< 0.06	3	--	--	**	< 0.10	--	--	--
19921130/1400	0.97	2	< 3	--	< 0.06	1	--	--	**	< 0.10	--	--	--
19930105/1430	1.47	2	12	--	0.92	2	--	--	--	< 0.10	--	--	--
19930108/1300	0.69	5	14	--	< 0.06	1	--	--	--	< 0.10	--	--	--
19930311/1400	--	2	13	--	--	1	--	--	--	< 0.10	4	5	--
19930325/1130	0.74	< 1	17	650	< 0.06	1	--	--	--	< 0.10	4	5	--
19930327/1245	1.49	2	11	800	0.28	1	--	--	--	< 0.10	2	5	--
19930328/1330	0.79	2	12	830	< 0.06	1	--	--	--	< 0.10	2	5	--
19930330/1645	1.24	4	17	2400	1.03	4	--	--	--	< 0.10	3	9	--
19930331/0145	0.36	4	22	3000	< 0.06	5	--	--	--	< 0.10	3	12	--
19930331/1400	0.39	3	--	3000	< 0.06	5	--	--	--	< 0.10	3	12	--

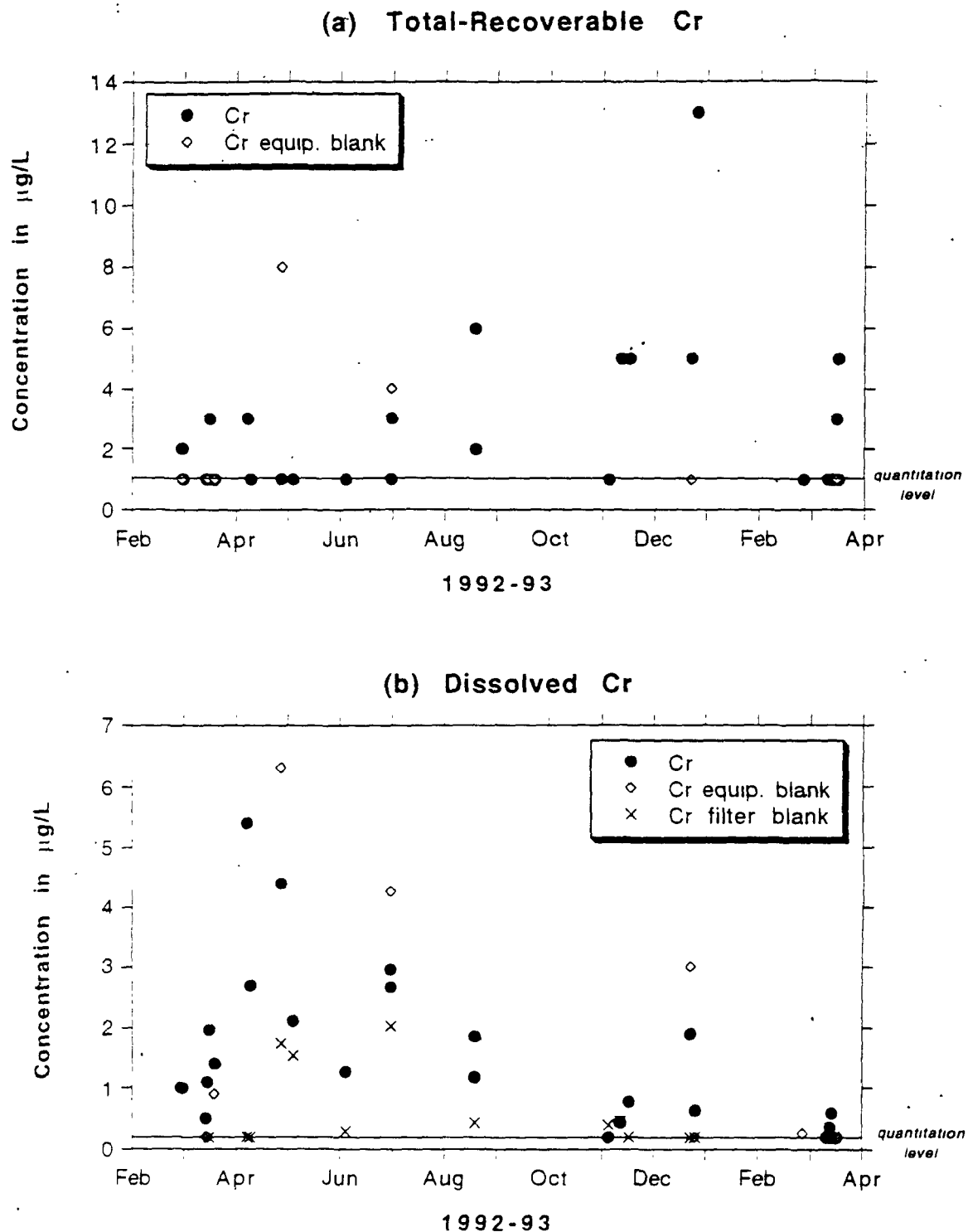
[CFS = cubic feet per second; mg/L = milligrams per liter; ug/L = micrograms per liter; Dupl = Duplicate sample; Diss = dissolved (filtered with 0.45 micron filter); IR = total recoverable; < = value is less than the analytical reporting limit; -- = constituent was not analyzed; \*\* = data pending].

Table 13. (cont.)

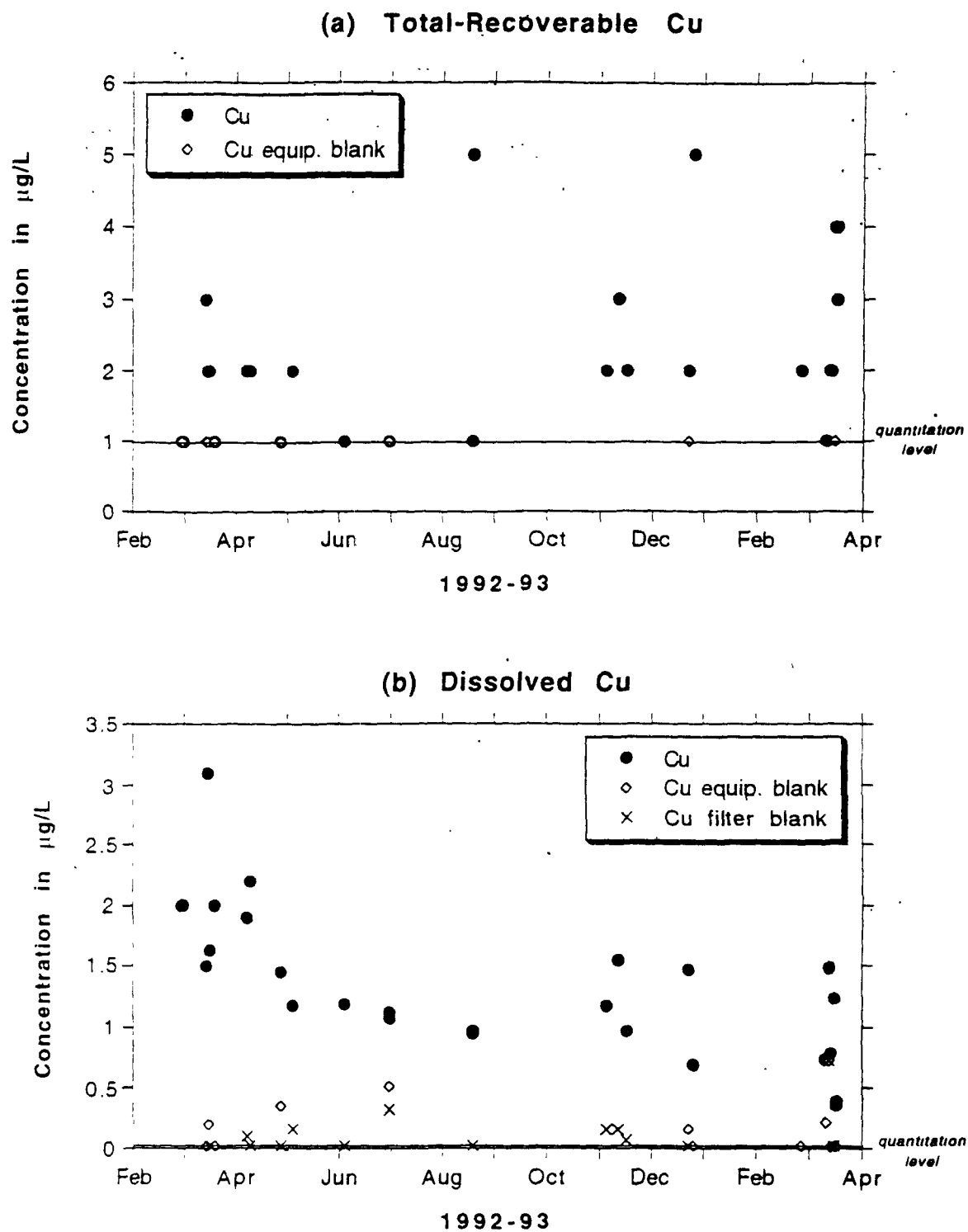
Date/Time	Silver TR (ug/L)	Strontium TR (ug/L)	Zinc Diss (ug/L)	Zinc TR (ug/L)
19920315/1315	< 1	70	<10	10
19920316/1300	< 1	50	<10	10
19920329/1700	--	--	2.0	30
19920330/1330	--	--	21.6	20
19920331/1400	--	--	6.74	30
19920403/1145	--	--	9.7	10
19920422/1230	--	--	5.9	<10
19920424/1100	--	--	7.4	<10
19920512/1130	--	--	3.65	<10
19920512/1145	--	--	--	--
19920519/1000	--	--	1.92	<10
19920619/1345	--	--	5.19	<10
19920715/1300	--	--	3.07	<10
19920715/1305	--	--	2.37	<10
19920902/1030	--	--	1.10	30
19920902/1035	--	--	1.18	<10
19921118/1100	--	--	3.86	30
19921125/1330	--	--	3.27	30
19921130/1400	--	--	2.64	10
19930105/1430	--	--	9.83	30
19930108/1300	--	--	4.45	30
19930311/1400	--	130	--	10
19930325/1130	--	100	2.59	<10
19930327/1245	--	100	15.06	<10
19930328/1330	--	80	8.06	10
19930330/1645	--	70	4.00	20
19930331/0145	--	60	1.72	30
19930331/1400	--	60	1.55	30

(CFS = cubic feet per second; mg/L = milligrams per liter; ug/L = micrograms per liter; Dupl = Duplicate sample; Diss = dissolved (filtered with 0.45 micron filter); TR = total recoverable; < = value is less than the analytical reporting limit; -- = constituent was not analyzed; \*\* = data pending).

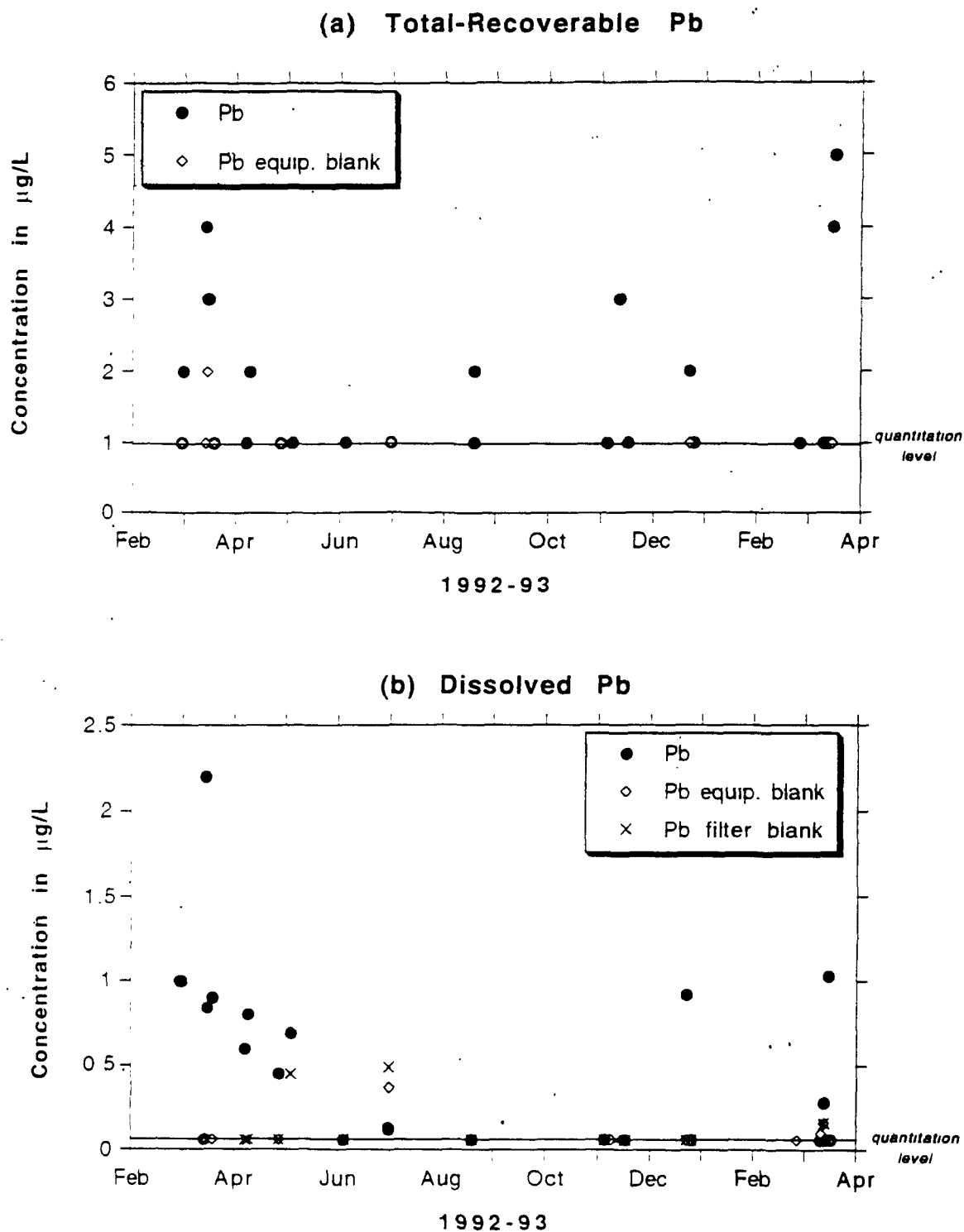
**Figure 20.** Concentrations of (a) total recoverable and (b) dissolved chromium for 1992 for the Susquehanna River fall line at Conowingo, Maryland. Included on the graphs are analyses of equipment (total) and filter (dissolved) blanks.



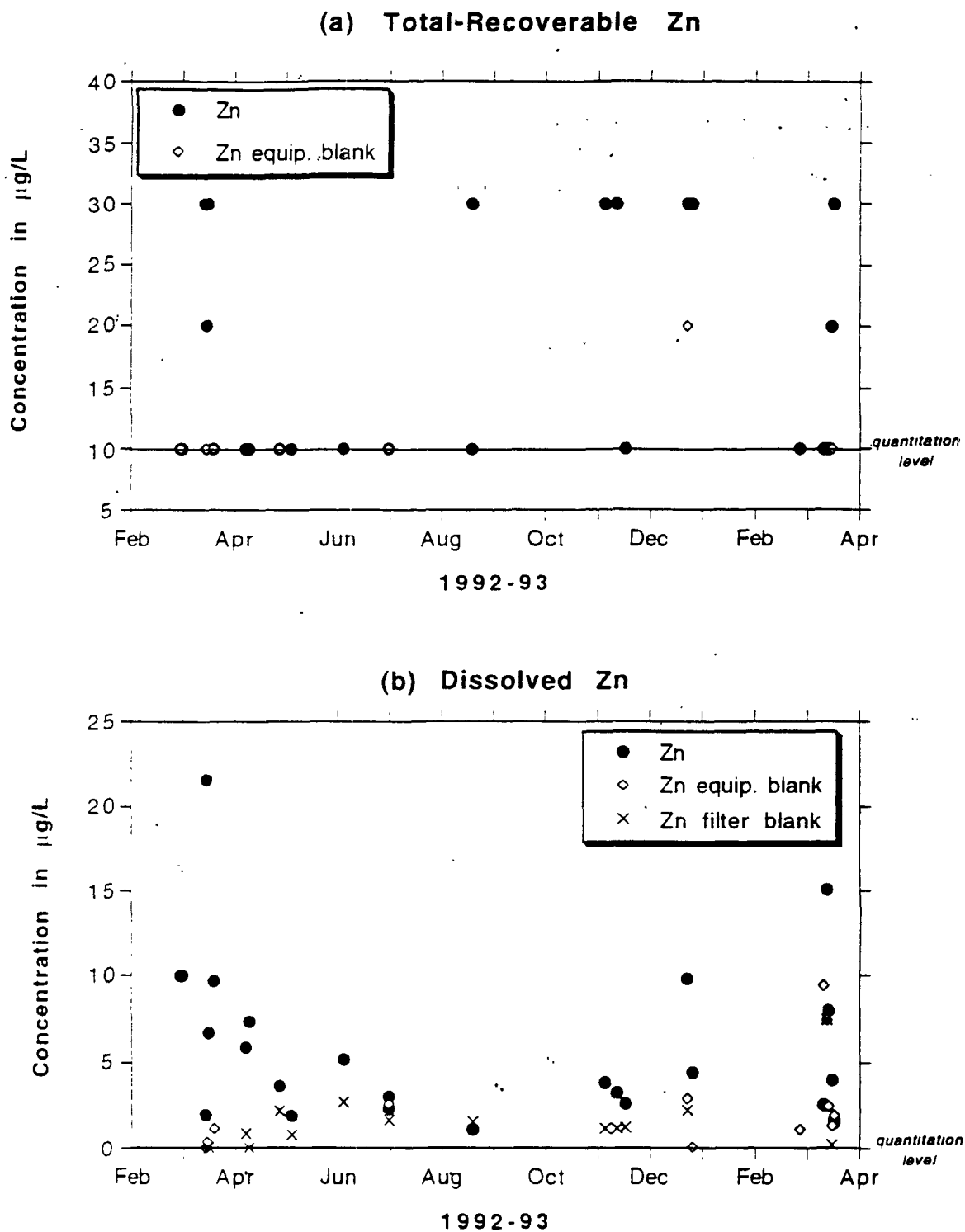
**Figure 21.** Concentrations of (a) total recoverable and (b) dissolved copper for 1992 for the Susquehanna River fall line at Conowingo, Maryland. Included on the graphs are analyses of equipment (total) and filter (dissolved) blanks.



**Figure 22.** Concentrations of (a) total recoverable and (b) dissolved lead for 1992 for the Susquehanna River fall line at Conowingo, Maryland.



**Figure 23.** Concentrations of (a) total recoverable and (b) dissolved zinc for 1992 for the Susquehanna River fall line at Conowingo, Maryland. Included on the graphs are analyses of equipment (total) and filter (dissolved) blanks.



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The majority of metals monitored during the report period March 1992 through March 1993 were detected in fluvial transport (Table 13, Figure 20-Figure 23). Metals detected included dissolved Al, As, Cd, Cr, Cu, Fe, Pb, Hg, Ni, Zn, and total-recoverable Cr, Cu, Fe, Pb, Hg, Mn, Ni, Sr, and Zn. Cadmium, Cr, Cu and Pb, all of which are regarded as "Toxics of Concern" in the USEPA Chesapeake Bay Program, were evident in transport. Metals that were not detected above quantitation levels throughout the 1992 monitoring period included total-recoverable As, Ba, Cd, Li, Ag, and Se.

Concentrations of total-recoverable Hg and Pb exceeded the EPA chronic freshwater aquatic life criteria at the Susquehanna River station during 1992. Exceedances of water quality criteria for Hg occurred on 3/30/92 and 3/31/92. Exceedance of water quality criteria for Pb occurred on 3/29/92. All exceedances were detected during stormflow conditions.

Regression statistics indicate that discharge is important in describing the variability in concentration data for dissolved Al, total-recoverable Cu, and suspended sediment. Seasonality is important in describing the variability in concentration data for dissolved Ni, total-recoverable Cu, Ni, Zn, and suspended sediment.

### **Metals Water Quality Data - James River**

This portion of the report presents results of water quality data collected for metals and suspended sediment during the 1992 ultra clean study for the James River. A listing of instantaneous discharge and concentration data collected during the entire 1990-1992 sampling period for the James River is presented in Appendix B.

Samples were collected in 1992 under baseflow conditions during March, May, June, July, September, and October. Three storm events were sampled, a week-long event in April, and two shorter events, one each in November and December. Discrete samples were collected during baseflow and each storm event.

For the James River, as for the Susquehanna River, an assessment of 1992 data quality was made based on results of the quality-assurance program. Through a comparative analysis of quality-control equipment-blank sample concentrations and concurrently collected environmental concentrations, constituent data were given a grade of excellent, good, fair, poor, or invalid, using the same criteria as for the Susquehanna River. This comparative analysis should, however, be looked at with the realization that for dissolved constituents there were blanks available for each dissolved analysis while for total-recoverable constituents, only four blanks were collected. This means that if any values were detected in the blanks for total-recoverable metals, the entire total-recoverable data set would be rated as fair, and if two values were detected, the data would be rated as poor.

Based on the criteria, excellent data were collected for total-recoverable As and Cd and dissolved Cu. Good data were collected for dissolved Cu. Fair data were collected for total-recoverable Cu, Cr, Pb and Zn, and dissolved Pb and Zn. Poor data, considered suspect, were collected for dissolved Cd and Cr. These criteria are more rigorous than the previous data quality assessment conducted for the *Chesapeake Bay Fall Line Toxics Monitoring Program 1992 Interim Report*, they will be used to determine the effect ultra clean sampling techniques and lower reporting



limits had on load estimates.

Instantaneous discharge and concentration data collected during 1992 for the James River are presented in Table 14. Concentration data associated with a "less than" sign (<) indicate that the constituent concentration is less than the quantitation level. A dash (--) indicates that the constituent was not analyzed. Asterisks (\*\*) denote pending data. Figure 24-Figure 27 show the concentrations for selected dissolved and total-recoverable metals for the 1992 data collection period with the concentrations for blanks collected during that same period.

Most metals monitored during the report period, March 1992 through February 1993, were detected in fluvial transport (Table 14, Figure 24-Figure 27). Metals detected include dissolved Al, As, Cr, Cu, Fe, Pb, and Zn, and total-recoverable Cd, Cr, Cu, Pb, Zn, and Hg. Cadmium, Cr, Cu, and Pb, all of which are regarded as "Toxics of Concern" in the USEPA Chesapeake Bay Program, were evident in transport. Metals that were not detected above quantitation levels throughout the 1992 monitoring period included dissolved As, and total-recoverable As and Cd.

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**Table 14** Metal water-quality data for the James River fall line at Cartersville, Virginia, for the period March 1992 through March 1993.

Date	Time	Discharge, Inst. (ft <sup>3</sup> /s)	Sediment, Suspended (mg/l)	Sed. Sus		Al, DIS (ug/l)	As, DIS (mg/l)	As, TR (ug/l)	Cd, DIS (ug/l)	Cd, TR (ug/l)
				Sieve Dia	% Finer than .062 mm					
04-10-92	1000	4570	4	89		20	<6	<1	<1	<1
04-23-92	1200	111000	888	90		60	<6	<1	<1	<1
04-24-92	1000	80100	454	73		120	<6	<1	<1	<1
04-26-92	1200	21800	106	85		210	<6	<1	<1	<1
04-27-92	1030	17500	74	80		170	<6	<1	<1	<1
04-28-92	1000	14700	62	69		140	<6	<1	<1	<1
05-20-92	1100	10900	31	88		120	<6	<1	<1	<1
06-24-92	802	5600	6	88		80	<6	<1	<1	<1
07-22-92	902	1980	3	85		50	<6	<1	<1	<1
07-22-92 (DUP)	915	1980	3	85		50	--	<1	<1	<1
09-03-92	1200	1580	2	83		80	<6	<1	<1	<1
09-03-92 (DUP)	1215	1580	2	83		60	<6	<1	3.4	<1
10-28-92	1100	1750	1	84		<10	<6	<1	<1	<1
11-23-92	930	5340	14	86		110	<6	<1	<1	<1
11-25-92*	900	23000	165	79		660	<6	<1	<1	<1
12-11-92*	1000	32800	485	73		390	<6	<1	<1	<1
12-12-92	1100	18200	167	91		320	<6	<1	<1	<1
01-28-93	915	9180	8	92		100	<6	<1	<1	<1
02-23-93	1000	20300	98	66		450	<6	<1	<1	<1
02-24-93	1100	25500	193	53		380	<6	<1	<1	<1
02-25-93	845	20000	105	54		260	<6	<1	<1	<1
02-23-93	1000	20300	98	66		450	<6	<1	<1	<1
02-24-93	1100	25500	193	53		380	<6	<1	<1	<1
02-25-93	845	20000	105	54		260	<6	<1	<1	<1

[INST= instantaneous, mg/l= milligrams per liter, ug/l= micrograms per liter, \* = dissolved analysis questionable; -- = analysis not requested]

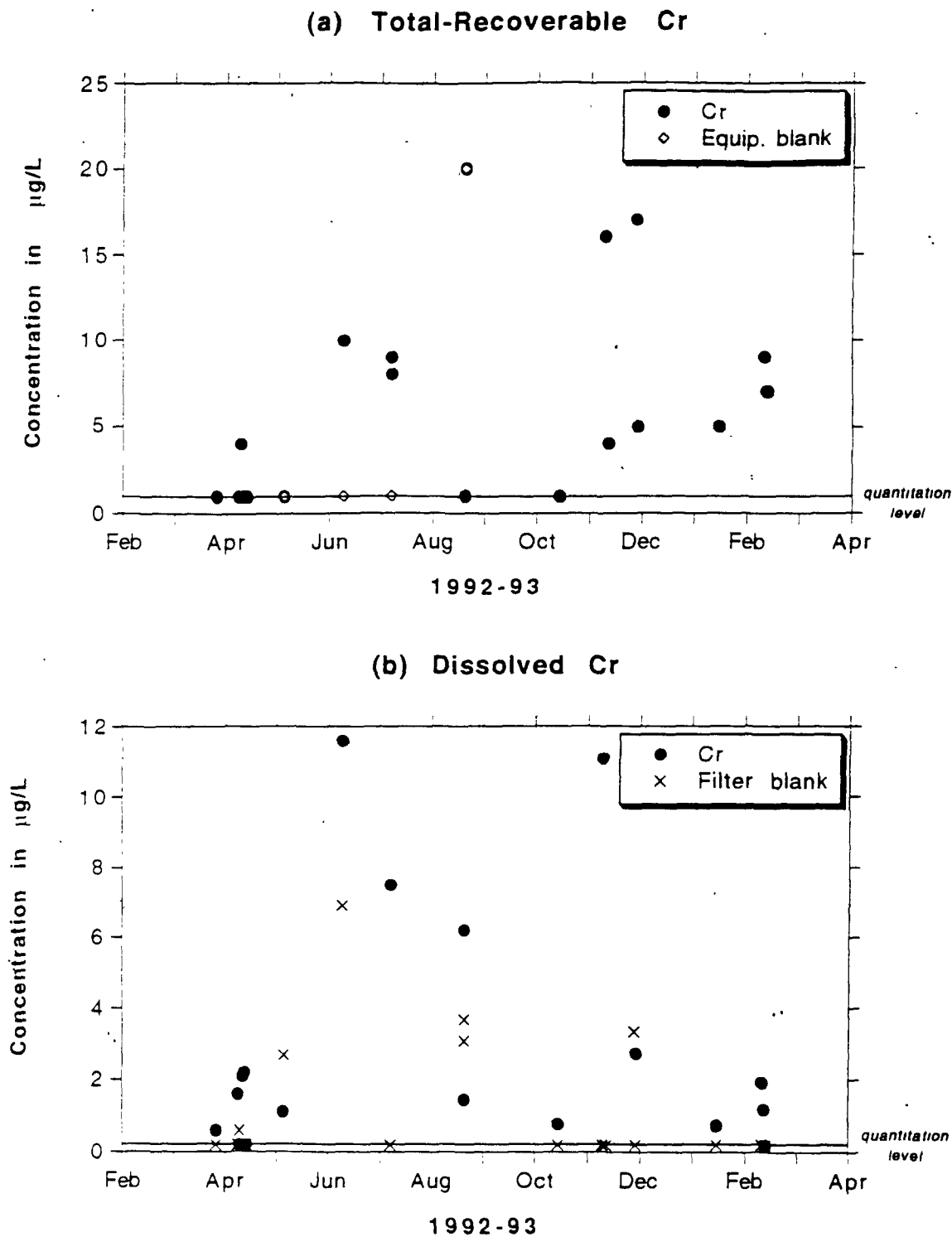
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Table 14. (cont.)

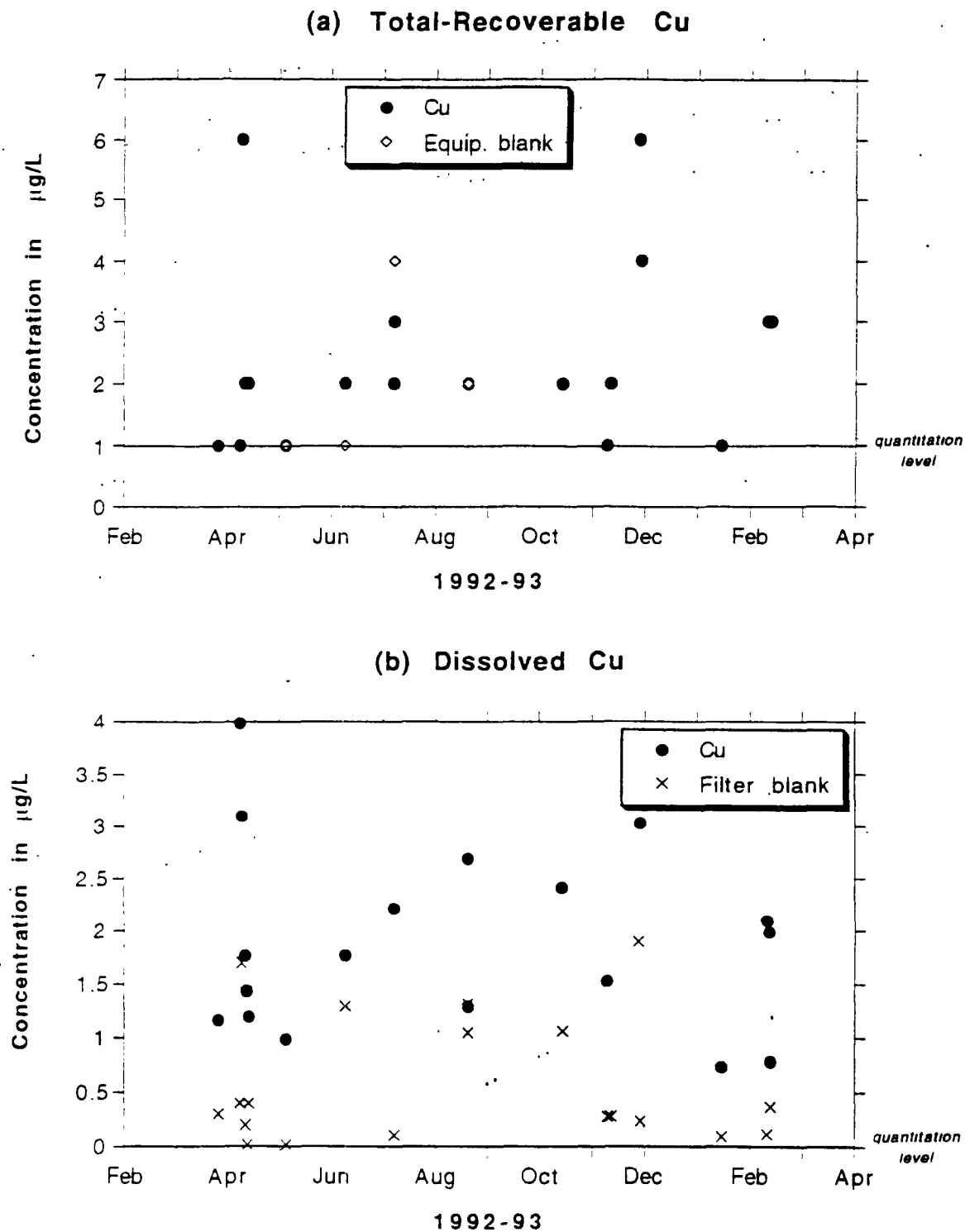
Date	Cr, DIS (ug/l) (01030)	Cr, TR (ug/l) (01034)	Cu, DIS (ug/l) (01040)	Cu, TR (ug/l) (01042)	Fe, DIS (ug/l) (01046)	Pb, DIS (ug/l) (01049)	Pb, TR (ug/l) (01051)	Zn, DIS (ug/l) (01090)	Zn, TR (ug/l) (01092)	Hg, TR (ug/l) (71900)
04-10-92	0.6	<1	1.17	1	110	09	<1	2.42	<10	<0.10
04-23-92	1.6	<1	3.99	1	200	4.06	<1	15.26	<10	<0.10
04-24-92	<2	4	3.10	6	140	2.83	10	11.65	60	0.10
04-26-92	2.1	1	1.77	2	380	1.10	3	8.51	<10	<0.10
04-27-92	2.2	1	1.44	2	310	83	2	7.66	<10	<0.10
04-28-92	<2	1	1.20	2	270	55	2	3.72	<10	<0.10
05-20-92	1.12	<1	99	<1	200	40	1	1.50	<10	<0.10
06-24-92	11.60	10	1.77	2	170	20	<1	2.08	<10	<0.10
07-22-92	7.5	8	2.22	2	120	<06	<1	1.09	<10	<0.10
07-22-92 (DUP)	--	9	--	3	100	--	<1	--	<10	<0.10
09-03-92	1.45	20	1.30	2	92	1.60	<1	1.20	<10	<0.10
09-03-92 (DUP)	6.2	1	2.69	2	88	1.44	<1	4.91	<10	<0.10
10-28-92	78	<1	2.42	2	140	41	<1	4.73	<10	<0.10
11-23-92	11.09	16	1.53	1	380	57	<1	4.7	<10	<0.10
11-25-92*	2.61	4	2.77	2	890	3.01	4	12.72	30	<0.10
12-11-92*	5.83	17	4.22	6	1100	3.15	8	16.51	50	<0.10
12-12-92	2.74	5	3.03	4	800	1.97	4	11.68	30	<0.10
01-28-93	74	5	0.74	<1	320	25	<1	2.02	<10	<0.10
02-23-93	1.92	9	2.10	3	840	80	2	6.12	10	<0.10
02-24-93	1.19	7	1.99	3	450	1.53	3	8.47	30	<0.10
02-25-93	<20	7	79	3	400	18	2	2.53	20	<0.10

[INST= instantaneous, mg/l= milligrams per liter, ug/l= micrograms per liter. \* = dissolved analysis questionable; --= analysis not requested]

**Figure 24.** Concentrations of (a) total recoverable and (b) dissolved chromium for 1992 for the James River fall line at Cartersville, Virginia. Included on the graphs are analyses of equipment (total) and filter (dissolved) blanks.



**Figure 25.** Concentrations of (a) total recoverable and (b) dissolved copper for 1992 for the James River fall line at Cartersville, Virginia. Included on the graphs are analyses of equipment (total) and filter (dissolved) blanks.



**Figure 26.** Concentrations of (a) total recoverable and (b) dissolved lead for 1992 for the James River fall line at Cartersville, Virginia. Included on the graphs are analyses of equipment (total) and filter (dissolved) blanks.

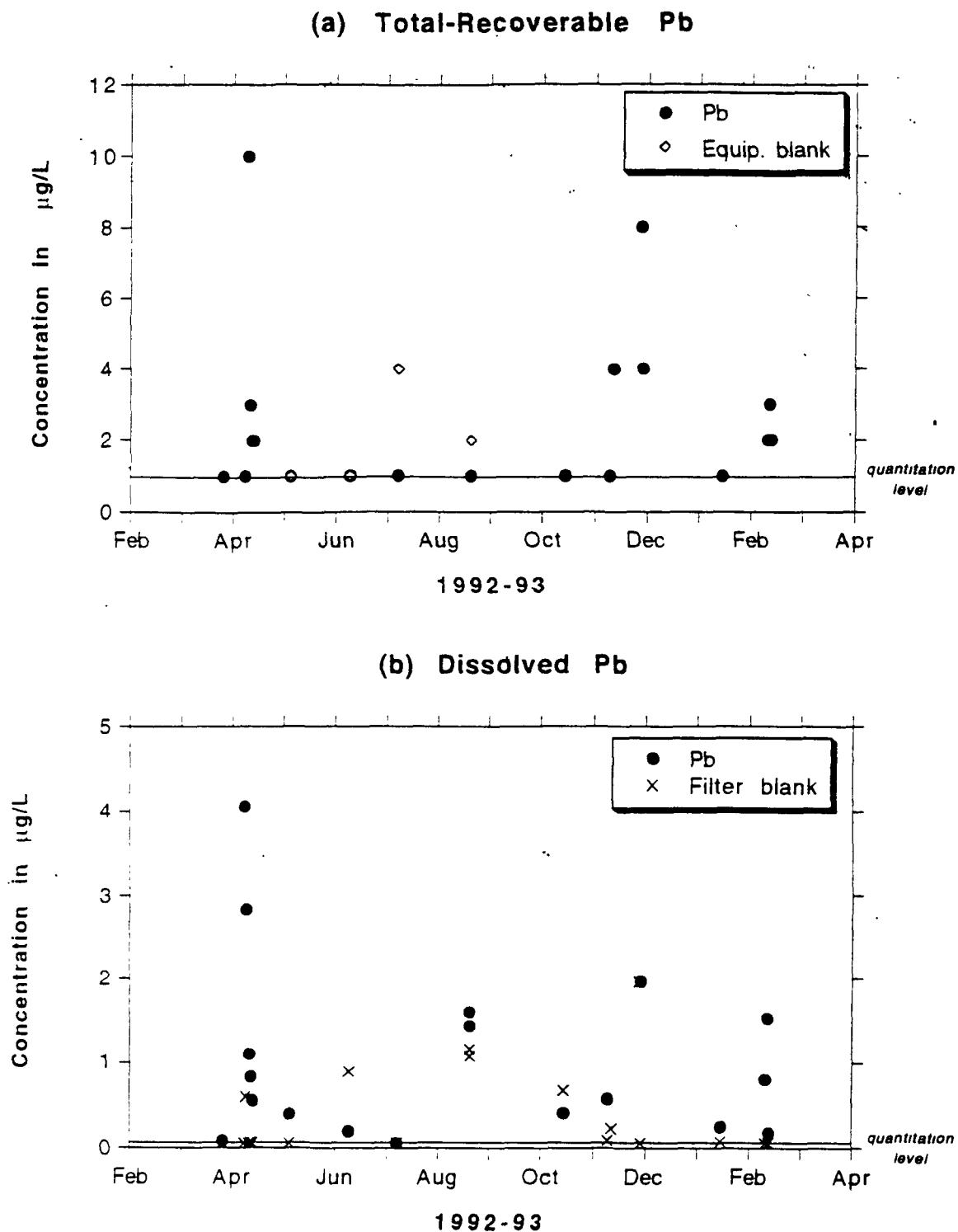
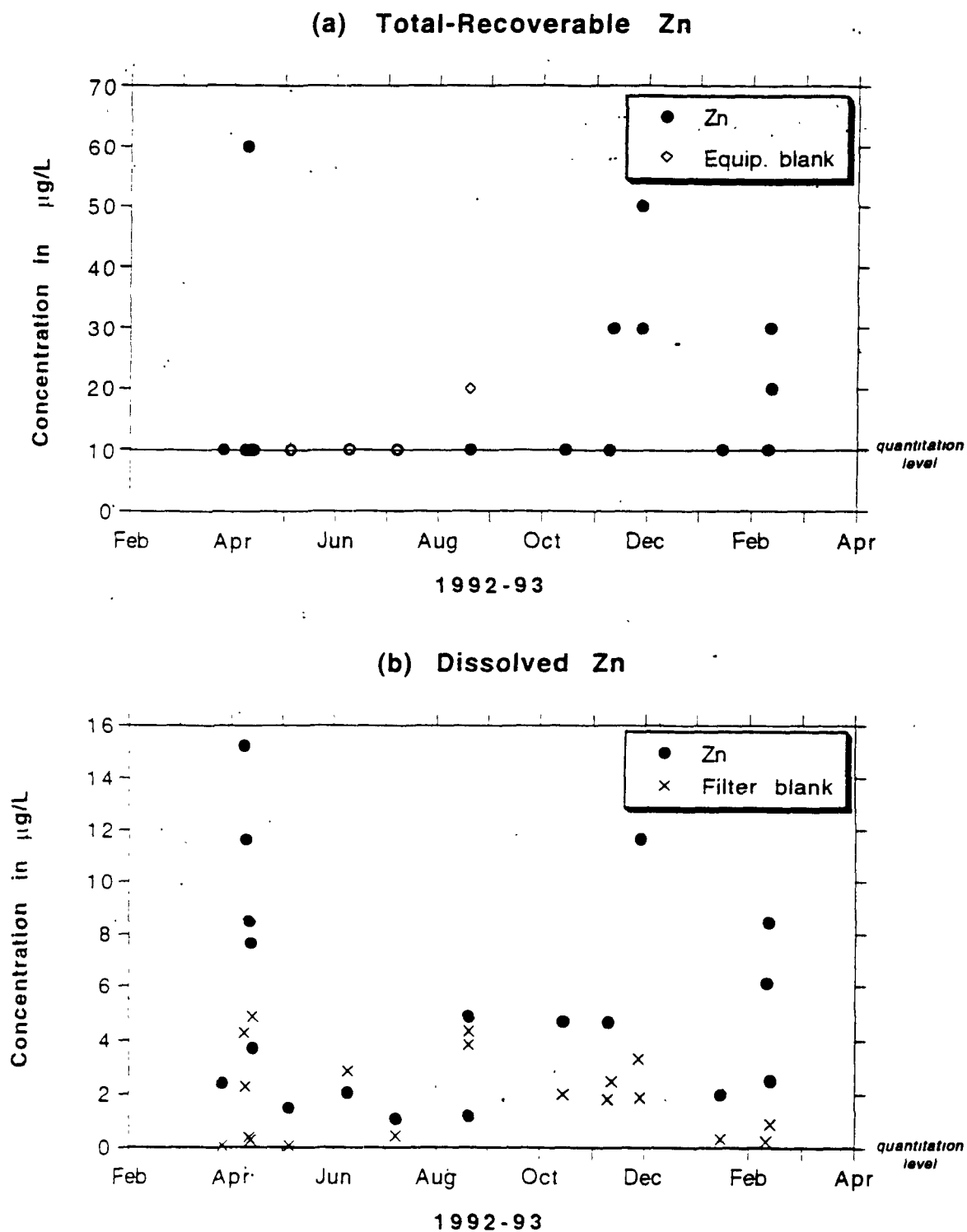


Figure 27. Concentrations of (a) total recoverable and (b) dissolved zinc for 1992 for the James River fall line at Cartersville, Virginia. Included on the graphs are analyses of equipment (total) and filter (dissolved) blanks.



## **Metals Water Quality Data - Potomac River**

During the thirteen month monitoring period of March, 1992, to March, 1993, twelve baseflow and nine stormflow samples were collected. Baseflow samples were collected once each month. OWML attempted to collect a sample for every storm event. There were few storms of sufficient flow and duration that resulted in adequate sample volume collected to enable analysis for the constituents of concern. One storm in March, 1992, at the beginning of the sampling period was missed. The earliest sample (a baseflow sample) was collected on March 17, 1992, and the last sample (a stormflow sample) was composited for March 27-April 1, 1993. The last two stormflow samples (LabID numbers 24158 and 24180) for the period of March 21-March 27 and March 27-April 1, 1993, were collected while the river was entirely in stormflow. Due to holding-time limitations, two samples had to be collected for this long event. Also due to the fact that the storm lasted until the end of the month, the last baseflow sample, scheduled to be collected then, could not be collected. Baseflow loads for March, 1993, were, therefore, estimated based on the baseflow concentrations of February, 1993.

A summary of the concentration data is given in Table 15. The samples are arranged chronologically. Stormflow samples have a beginning and ending date/time combination (*i.e.*, Date1/Time1 and Date2/Time2). These samples also have a total flow value reported. In those cases, the flow reported in the 'Flow' column is the average flow during the storm (*i.e.*, total flow divided by the duration of the storm). The stage and flows are as measured at Little Falls. As noted earlier, however, there is very little added flow between Little Falls and Chain Bridge. pH values are not given for stormflow samples, because these were composite samples. Figure 28 is a plot of the total monthly flows at Chain Bridge; the data are given in Table 16.



Table 15. Summary of metals data gathered at Chain Bridge on the Potomac River, March, 1992-March, 1993

Station	LabID	Date1	Time1	Date2	Time2	Type of Flow <sup>1</sup>	Stage <sup>2</sup> (feet)	Flow <sup>3</sup> (m <sup>3</sup> /s)	Total Flow (cubic meters)	pH	Total Susp. Solids (mg/L)	All metals concentrations in µg/L							
												As	Cd	Cr	Cu	Ni	Pb	Se	Zn
PR01	22254	03/17/92	11 49			B	4 50	444 9		7 4	12 8	na	<2 0	<2 5	<5 0	<12	<4 0	na	19
PR01	22455	04/21/92	09 10			B	3 46	152 5		7 8	3 6	<5 0	<2 0	<2 5	3 9	<12	<4 0	<7 0	<15
PR01	22536	04/21/92	18 00	04/29/92	09 31	S		1189 3	7 6×10 <sup>8</sup>		na	<5 0	<2 0	13 1	16 0	40	10 5	<7 0	63
PR01	22723	05/17/92	17 00	05/18/92	18 57	S		314 0	2 9×10 <sup>7</sup>		93	<5 0	<2 0	3 6	4 7	<12	<4 0	<7 0	20
PR01	22711	05/19/92	10 05			B	4 67	502 4		7 8	30	<5 0	<2 0	<2 5	2 4	<12	6 6	<7 0	19
PR01	22865	06/05/92	23 00	06/11/92	03 50	S		583 2	2 6×10 <sup>8</sup>		107	<5 0	<2 0	<2 5	5 9	<12	5 8	<7 0	37
PR01	22887	06/16/92	09 00			B	3 64	194 5		8 1	8 4	<5 0	<2 0	<2 5	4 2	<12	<4 0	<7 0	<15
PR01	22991	07/06/92	10 02			B	3 84	247 4		8 0	12 0	<5 0	<2 0	<2 5	4 5	<12	<4 0	<7 0	<15
PR01	23195	08/11/92	09 14			B	3 11	86 2		8 0	3 6	<5 0	<2 0	<2 5	<2 0	<12	10 9	<7 0	<15
PR01	23347	09/09/92	09 30			B	3 60	184 7		8 0	14 4	<5 0	<2 0	<2 5	3 3	<12	<4 0	<7 0	25

<sup>1</sup> B = baseflow, S = stormflow<sup>2</sup> Measured at USGS gage at Little Falls<sup>3</sup> Computed from stage. For stormflow, this number is the average flow during the storm; i.e., the total flow divided by the duration of the storm.

na Not analyzed

Table 15. (cont.)

Station	LabID	Date1	Time1	Date2	Time2	Type of Flow <sup>1</sup>	Stage <sup>2</sup> (feet)	Flow <sup>3</sup> (m <sup>3</sup> /s)	Total Flow (cubic meters)	pH	Total Susp. Solids (mg/L)	All metals concentrations in µg/L							
												As	Cd	Cr	Cu	Ni	Pb	Se	Zn
PR01	23495	10/06/92	09 10			B	3.01	70.8		8.5	5.2	<5.0	<2.0	2.0	<12	<4.0	<7.0	18	
PR01	23737	11/18/92	10 30			B	3.56	175.2		8.2	7.2	<5.0	<2.0	3.6	<12	<4.0	<7.0	<15	
PR01	23776	11/23/92	02 45	11/28/92	16 31	S		573.0	2.7×10 <sup>8</sup>		210	<5.0	<2.0	6.0	<12	7.7	<7.0	36	
PR01	23786	12/08/92	10 20			B	3.38	135.7		8.0	2.8	<5.0	<2.0	<2.0	<12	<4.0	<7.0	<15	
PR01	23845	12/18/92	06 15	12/22/92	21 12	S		598.0	3.7×10 <sup>8</sup>		na	<5.0	<2.0	2.5	<12	<4.0	<7.0	18	
PR01	23860	01/01/93	13 00	01/04/93	03 27	S		808.8	1.8×10 <sup>8</sup>		91	<4.0	<1.0	2.0	<8.0	<4.0	<5.0	26	
PR01	23876	01/05/93	10 02			B	4.89	581.4		7.8	51	<4.0	<1.0	<1.0	<8.0	<4.0	<5.0	20	
PR01	23997	02/08/93	10 48			B	3.66	199.5		8.3	<1.0	<4.0	<1.0	<2.0	<8.0	<4.0	<5.0	16	
PR01	24128	03/05/93	10 16	03/11/93	13 56	S		2506.5	1.3×10 <sup>9</sup>		285	<4.0	<1.0	13.2	10.0	14	<5	56	
PR01	24158	03/21/93	10 54	03/27/93	13 46	S		2455.9	1.3×10 <sup>9</sup>		83	<4.0	<1.0	3.2	4.2	<8.0	<4.0	<5	22
PR01	24180	03/27/93	13 47	04/01/93	10 36	S		2691.2	1.1×10 <sup>9</sup>		64	<4.0	<1.0	1.3	3.8	<8.0	<4.0	<5	17

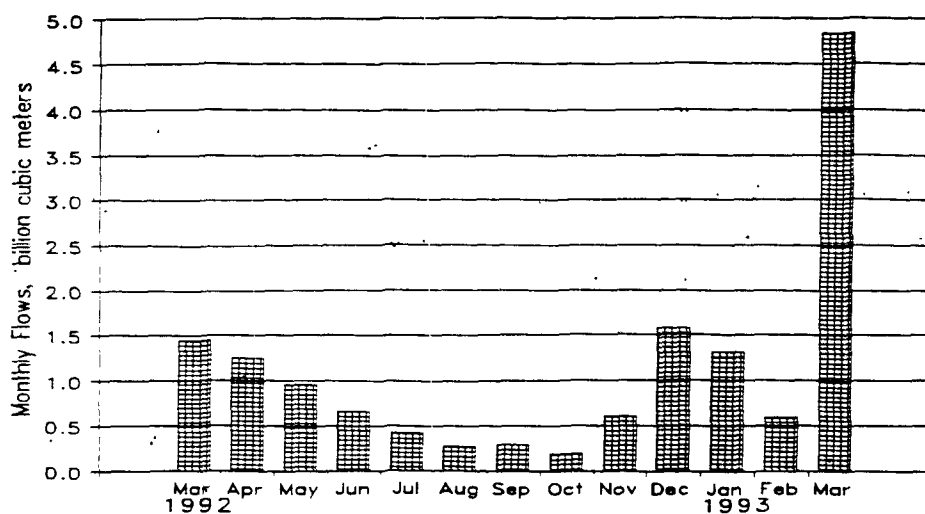
B = baseflow, S = stormflow.

Measured at USGS gage at Little Falls

Computed from stage For stormflow, this number is the average flow during the storm, i.e., the total flow divided by the duration of the storm

na Not analyzed

**Figure 28.** Total Monthly Flows at Chain Bridge on the Potomac River: March, 1992, to March, 1993



**Table 16.** Monthly flows at Chain Bridge on the Potomac River: March, 1992, to March, 1993

Month	Flow, $\times 10^9 \text{ m}^3$
March, 1992	1.44
April	1.25
May	0.96
June	0.66
July	0.42
August	0.27
September	0.29
October	0.19
November	0.60
December	1.57
January, 1993	1.31
February	0.59
March	4.83
<b>Total</b>	<b>12.95</b>

## **Organics Water Quality Data - Susquehanna, James and Potomac Rivers**

The concentrations of all of the monitored organic contaminants are listed in Appendix C for each of the three rivers. The lists in Appendix C include concentrations measured during both baseflow and storm flow hydrologic conditions, the numbers of which type of sample can be obtained from the database. Flagged concentrations in the database are indicated by a measured concentration value bound by parenthesis.

### *Organonitrogen and Organophosphorus Pesticides*

The organonitrogen and organophosphorus pesticides were analyzed in the filtered river fall line samples only. The fractional composition of organic compounds in the suspended particulate phase in aquatic systems is governed by several variables, including the magnitude of particle/water partition coefficients, the amount of organic carbon associated with the particle phase, and the concentration of suspended particulates. Because the partition coefficients of the organonitrogen and organophosphorous pesticides are near or less than 1,000, the fractional composition of these pesticides in the particle phase is predicted to be less than 5% even for total suspended particulate concentrations as large as 1,000 mg/l (Samiullah 1990). The particle phase is not important in the fluvial transport of the organonitrogen and organophosphorous pesticides analyzed in this study. Summaries of the maximum, minimum, and average concentrations of the organonitrogen and organophosphorus pesticides are provided in Table 17 through Table 19.

Peak concentrations of the organonitrogen and organophosphorus pesticides occurred during the months of agricultural field application, from approximately April 1992 through June 1992. These pesticides are highly mobile and are readily washed from soils during precipitation, and are transported from field sites in surface runoff. However, only 1-2% of the total amount of the applied pesticides in this category, e.g., atrazine, are typically accounted for in surface runoff from the results of field studies of this type. Concentrations of the organonitrogen and organophosphorous pesticides in the river fall line samples dropped dramatically after June 1992 to below quantitation levels during the winter months. During the winter months, the concentrations of these pesticides were slightly elevated in storm flow relative to baseflow samples.

The trend in pesticide occurrence was similar for each of the three river fall lines. Atrazine was the most frequently detected pesticide and was present at the highest concentration, followed by metolachlor, simazine, and cyanazine. The organophosphate pesticides were not often detected in the river fall line samples, and were present at concentrations <20 ng/L.

### *Organochlorine Compounds*

The concentrations of the organochlorine compounds in the river fall line samples are summarized in Table 17 through Table 19. Concentrations of the organochlorines in the fall line samples were much lower relative to the organonitrogen pesticides, as is expected because organochlorine pesticides have been banned from widespread agricultural use since the early 1970's or have had restricted use over the past 20 years (e.g., chlordane).

The most frequently detected organochlorines were the chlordanes (alpha- and gamma-), dieldrin, and PCBs. The organochlorines were also often detected in both dissolved and particulate phases. Particulate phase concentrations were dependent on river discharge, especially during summer and autumn when baseflow suspended sediment concentrations are low. The concentrations of hydrophobic organic compounds in the particulate phase depends on dissolved phase concentrations, sediment-water distribution constants (i.e.,  $K_d$ ), and particulate phase concentrations (i.e., TSP in this study), and fractional composition of organic carbon in the particulate phase. During low flow when particulate concentrations are low, particulate phase organochlorine concentrations are also very low because there is very little sediment in fluvial transport. Storms which occur during low flow dramatically increase particulate phase concentrations, and, thereby, enhance particulate associated organic contaminant concentrations.

The organochlorines have the greatest number of flagged concentrations relative to any of the other classes of organic contaminants monitored in this study. This can be partly explained by the way the analysis is performed for organochlorine analysis: the GC-ECD is not as selective as GC/MS. There exists a greater likelihood of achieving a false positive identification in GC-ECD relative to GC/MS because in GC-ECD analysis only chromatographic peaks are identified without chemical or spectral information provided. GC-ECD chromatograms contain many background peaks, many of which are near the analyte retention times. GC-ECD analysis is followed by GC/MS confirmation, but the concentrations of the organochlorines are below detection limits when even several sample extracts are combined for a single GC/MS analysis.

Unlike the organonitrogen and organophosphorus pesticides which differed in concentration between the three river fall line samples, the organochlorine concentrations were much similar in magnitude.

#### *Polynuclear Aromatic Hydrocarbons*

Concentrations of the four polynuclear aromatic hydrocarbons in the river fall line samples are summarized in Table 17 through Figure 28 (Appendix C contains all of the database concentrations). Naphthalene concentrations were higher in the dissolved phase relative to the particulate phase, which is dependent on the limited partitioning of naphthalene to suspended particulates in transport. Conversely, nearly all of the benzo(a)pyrene detected was associated with particulate material, reflecting its low water solubility and large sediment-water distribution constant ( $>\log 5$ ). PAH concentrations differed between the river fall line samples, with the highest concentrations detected in the James River suspended particulates.

Naphthalene was the only PAH that has a substantial number of flagged concentrations in the database.

**Table 17.** Summary of organic contaminant concentrations in surface water samples collected from the Susquehanna River fall line.

Susquehanna River, March 1992 - February 1993													
Concentration units are in ng/L													
	Dissolved Phase				Particulate Phase				Combined Dissolved + Particulate Phases				
Constituent	Max	Min	Avg	Freq	Max	Min	Avg	Freq	Max	Min	Avg	Freq	Total
Simazine	91.3	2.3	24.2	11	na	na	na	0	91.3	2.3	24.2	11	19
Prometon	18.9	2.4	8.8	8	na	na	na	0	18.9	2.4	8.8	8	19
Atrazine	293.7	7.7	56.3	17	na	na	na	0	293.7	7.7	56.3	17	19
Diazinon	17.7	5.8	11.8	2	na	na	na	0	17.7	5.8	11.8	2	19
Alachlor	23.1	2.5	11.8	7	na	na	na	0	23.1	2.5	11.8	7	19
Malathion	7.7	4.3	5.6	3	na	na	na	0	7.7	4.3	5.6	3	19
Metolachlor	139.6	1.4	31.3	17	na	na	na	0	139.6	1.4	31.3	17	19
Cynazine	108.0	4.1	35.7	9	na	na	na	0	108.0	4.1	35.7	9	19
Hexazinone	16.3	1.0	4.9	8	na	na	na	0	16.3	1.0	4.9	8	19
Aldrin	1.6	0.2	0.8	10	0.1	0.1	0.1	1	3.0	0.1	0.8	10	15
Oxychlordane	11.1	0.3	2.7	6	1.2	0.2	0.5	4	11.1	0.3	2.1	7	15
gamma-Chlordane	9.5	0.2	2.3	7	0.2	0.1	0.1	5	45.6	0.1	6.1	11	15
alpha-Chlordane	17.0	0.1	3.3	9	0.3	0.2	0.2	2	17.0	0.1	2.9	11	15
Dieldrin	5.5	0.2	1.6	5	1.9	0.1	0.8	7	21.4	0.1	4.1	9	15
4,4'-DDT	0.3	0.3	0.3	1	1.4	0.3	0.7	3	1.4	0.3	0.6	4	15
c/t-Permethrins	7.1	7.1	7.1	1	2.8	2.8	2.8	1	47.7	2.8	18.6	4	15
c/t-Fenvalerates	3.8	2.3	3.0	2	0.0	0.0	0.0	0	40.5	1.1	15.2	3	15
ΣPCBs	9.6	0.3	4.4	11	12.7	0.4	4.4	11	16.0	0.4	6.1	13	15
Naphthalene	39.5	1.0	6.6	12	3.8	0.5	1.6	8	12.0	0.5	3.2	13	15
Fluoranthene	7.2	0.5	2.3	5	18.9	2.5	10.0	10	24.9	0.4	9.1	12	15
Benz(a)anthracene	3.9	1.3	2.6	2	21.9	0.7	8.0	9	21.9	0.7	9.0	9	15
Benz(a)pyrene	0.0	0.0	0.0	0	55.1	9.6	30.6	3	55.1	4.7	24.2	4	15

Max = maximum measured concentration, Min = minimum measured concentration, Avg = average measured concentration, Freq = frequency of detection, Total = total number of samples analyzed, na = not analyzed

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**Table 18.** Summary of organic contaminant concentrations in surface water samples collected from the James River fall line.

James River, March 1992 - February 1993													
Concentration units are in ng/L													
	Dissolved Phase				Particulate Phase				Combined Dissolved + Particulate Phases				
Constituent	Max	Min	Avg	Freq	Max	Min	Avg	Freq	Max	Min	Avg	Freq	Total
Simazine	369.6	2.6	50.1	12	na	na	na	0	369.6	2.6	50.1	12	24
Prometon	18.1	1.7	5.5	6	na	na	na	0	18.1	1.7	5.5	6	24
Atrazine	476.3	3.9	60.7	15	na	na	na	0	476.3	3.9	60.7	15	24
Diazinon	11.6	2.8	6.8	6	na	na	na	0	11.6	2.8	6.8	6	24
Alachlor	20.2	4.2	9.9	7	na	na	na	0	20.2	4.2	9.9	7	24
Malathion	11.6	3.1	7.3	2	na	na	na	0	11.6	3.1	7.3	2	24
Metolachlor	210.3	1.4	31.3	12	na	na	na	0	210.3	2.1	34.1	11	24
Cynazine	24.9	2.4	11.6	9	na	na	na	0	24.9	2.4	11.6	9	24
Hexazinone	16.8	1.3	8.0	10	na	na	na	0	16.8	1.3	7.5	9	24
Aldrin	1.6	0.2	0.6	6	2.4	2.4	2.4	1	2.7	0.2	1.0	6	20
Oxychlorane	12.1	0.1	4.4	7	1.4	0.3	0.9	4	12.9	0.3	5.1	6	20
gamma-Chlordane	8.5	0.2	2.9	10	1.8	0.2	0.5	6	8.5	0.2	2.7	11	20
alpha-Chlordane	17.2	0.1	3.9	15	1.2	0.1	0.4	5	17.2	0.1	5.1	11	20
Dieldrin	2.4	0.2	0.7	9	0.1	0.1	0.1	3	2.4	0.1	0.6	10	20
4,4'-DDT	0.0	0.0	0.0	0	1.4	0.4	0.9	2	1.4	0.4	0.9	2	20
c/t-Permethrins	0.0	0.0	0.0	0	0.0	0.0	0.0	0	0.0	0.0	0.0	0	20
c/t-Fenvalerates	4.0	4.0	4.0	1	2.6	2.6	2.6	1	4.0	2.6	3.3	2	20
ΣPCBs	16.7	0.4	1.8	16	13.6	0.4	5.3	11	18.3	0.4	5.5	15	20
Naphthalene	34.8	0.2	7.3	16	14.8	0.1	3.2	8	34.8	0.2	8.1	13	20
Fluoranthene	2.9	0.3	1.1	9	196.8	0.2	35.6	15	198.7	0.5	32.0	17	20
Benz(a)anthracene	8.8	1.7	5.7	4	27.2	2.1	13.2	13	29.4	1.7	12.9	15	20
Benzo(a)pyrene	9.1	9.1	9.1	1	137.2	9.4	39.1	9	137.2	9.4	40.1	9	20

Max = maximum measured concentration. Min = minimum measured concentration. Avg = average measured concentration. Freq = frequency of detection. Total = total number of samples analyzed. na = not analyzed

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**Table 19.** Summary of organic contaminant concentrations in surface water samples collected from the Potomac River fall line.

Potomac River, March 1992 - February 1993													
Concentration units are ng/L													
	Dissolved Phase				Particulate Phase				Combined Dissolved + Particulate Phases				
Constituent	Max	Min	Avg	Freq	Max	Min	Avg	Freq	Max	Min	Avg	Freq	TOTAL
Simazine	142.8	5.7	62.5	12	na	na	na	0	142.8	5.7	62.5	12	15
Prometon	17.0	8.2	13.5	9	na	na	na	0	17.0	8.2	13.5	9	15
Atrazine	579.0	9.6	158.5	14	na	na	na	0	579.0	9.6	158.5	14	15
Diazinon	10.0	10.0	10.0	1	na	na	na	0	10.0	10.0	10.0	1	15
Alachlor	20.9	9.0	12.3	5	na	na	na	0	20.9	9.0	12.3	5	15
Malathion	11.5	11.5	11.5	1	na	na	na	0	11.5	11.5	11.5	1	15
Metolachlor	358.0	9.1	95.7	13	na	na	na	0	358.0	9.1	95.7	13	15
Cynazine	212.4	9.8	114.4	6	na	na	na	0	212.4	9.8	114.4	6	15
Hexazinone	19.7	1.8	8.6	3	na	na	na	0	19.7	1.8	8.6	3	15
Aldrin	0.5	0.3	0.5	3	2.3	2.3	2.3	1	2.3	0.3	0.9	4	10
Oxychlorane	31.8	31.8	31.8	1	3.6	1.8	2.7	2	31.8	1.8	12.4	3	10
gamma-Chlordane	3.5	0.2	1.5	4	0.4	0.2	0.3	3	3.5	0.2	1.4	5	10
alpha-Chlordane	5.3	0.8	3.5	3	3.2	0.3	1.5	4	8.5	0.3	2.7	6	10
Dieldrin	4.1	0.4	1.5	6	3.6	0.2	1.7	5	6.1	0.2	2.2	8	10
4,4'-DDT	1.7	1.7	1.7	1	1.2	1.1	1.1	2	2.8	1.1	2.0	2	10
cis-Permethrin	0.0	0.0	0.0	0	15.1	15.1	15.1	1	15.1	15.1	15.1	1	10
cis-Fenvalerate	0.0	0.0	0.0	0	3.5	3.5	3.5	1	3.5	3.5	3.5	1	10
ΣPCBs	3.6	0.5	2.2	5	39.0	1.1	14.4	3	42.6	1.1	10.8	5	10
Naphthalene	19.8	3.7	9.4	8	5.3	0.7	2.8	5	25.1	4.4	11.1	8	10
Fluoranthene	1.4	1.4	1.4	1	10.5	0.6	4.8	8	10.5	0.6	4.4	9	10
Benzo(a)anthracene	3.5	3.5	3.5	1	12.4	7.7	9.3	3	12.4	3.5	7.9	4	10
Benzo(a)pyrene	0.0	0.0	0.0	0	11.4	3.5	7.5	2	11.4	3.5	7.5	2	10

Max = maximum measured concentration, Min = minimum measured concentration, Avg = average measured concentration, Freq = frequency of detection, Total = total number of samples analyzed, na = not analyzed



## **LOAD RESULTS**

### **Metal Loads - Susquehanna River**

Susquehanna River load estimates for the 1992 sampling period are given in Table 20. Bar graph summaries of the maximum monthly load estimates for April, 1992 through March, 1993 are presented in Figure 29 for total-recoverable and dissolved Cr, Cu, Pb, and Zn. The loads presented have been calculated with the II model.

The accuracy of load estimates is, to a large extent, determined by the quality of data used to calculate them. Based on the 1992 data quality assessment, discussed previously in this report, load estimates for total-recoverable As, Cd, Cu, Pb, Hg, Zn and dissolved As, Cd, Cu, Pb, and Zn are considered fair to excellent in terms of data quality. Loads calculated for dissolved and total-recoverable Cr and dissolved Hg are considered suspect in terms of data quality.

Figure 29 provides a graphical representation of 1992 monthly loads calculated using the Interpolation Integration method. The Susquehanna River produces the highest loads in metals during the spring freshets, when discharges are greatest. Loading estimates are therefore highly correlated to discharge. Suspended sediments are also increased during periods of high flow and it is likely that much of the toxic metal loads are carried on suspended particles. Constituent loadings of suspended sediment averaged over 2.5 billion kilograms(2,559,248,986) in 1992. Of the metals monitored, dissolved Fe had the greatest load, followed by dissolved Al and total-recoverable Zn.

**Table 20.** Monthly load estimates in kg for the Susquehanna River fall line at Conowingo, Maryland, for the period March 1992 through March 1993.

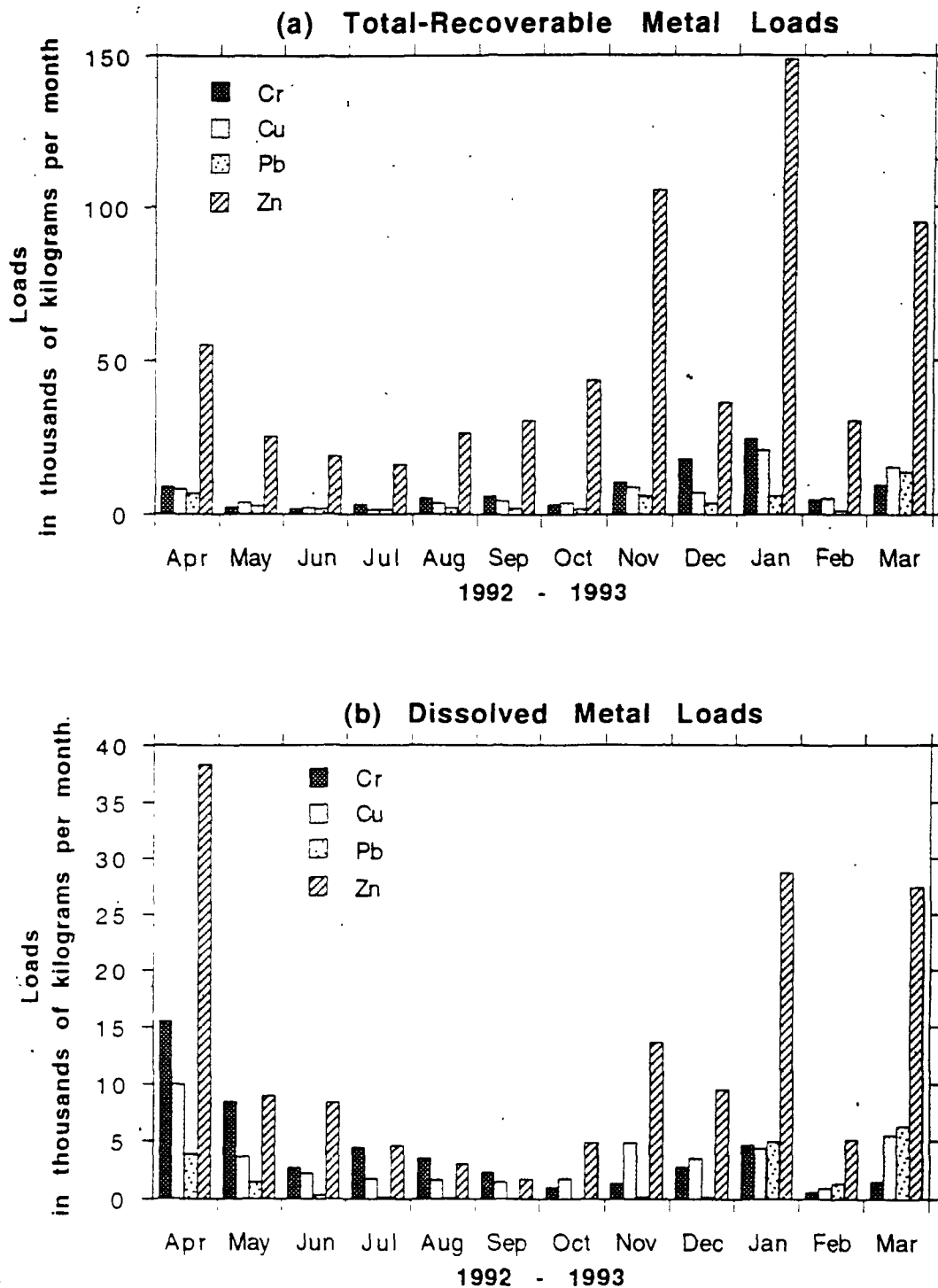
Constituent	April 1992		May 1992		June 1992		July 1992		August 1992		September 1992	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Aluminum (dis)	535.6	535.6	262.8	262.8	136.1	136.1	59.42	59.42	63.89	63.89	61.77	61.77
Arsenic (dis)	0	3.001	0	1.519	0	1.130	1.734	1.770	1.645	1.645	1.359	1.359
Arsenic (TR)	0	5.002	0	2.532	0	1.884	0	1.637	0	1.688	0	1.544
Cadmium (dis)	0	0.500	1.088	1.254	0.522	0.668	0	0.164	0	0.169	0	0.154
Cadmium (TR)	0	5.002	0	2.532	0	1.884	0	1.637	0	1.688	0	1.544
Chromium (dis)	15.52	15.52	8.530	8.530	2.750	2.750	4.522	4.522	3.509	3.509	2.347	2.347
Chromium (TR)	5.777	8.853	0	2.532	0	1.884	3.152	3.213	5.300	5.300	6.177	6.177
Copper (dis)	10.01	10.01	3.703	3.703	2.238	2.238	1.798	1.798	1.718	1.718	1.483	1.483
Copper (TR)	8.282	8.282	3.768	3.768	2.305	2.305	1.637	1.637	3.613	3.613	4.633	4.633
Iron (dis)	1.991	1.991	471.8	471.8	301.8	301.8	82.16	82.16	46.01	46.01	18.53	18.53
Lead (dis)	3.855	3.855	1.475	1.475	0.290	0.378	0.197	0.201	0.091	0.148	0	0.093
Lead (TR)	6.910	6.910	0.716	2.890	0	1.884	0	1.637	1.444	2.169	2.316	2.316
Mercury (dis)	0.110	0.110	0.061	0.061	0.045	0.045	0.039	0.039	0.041	0.041	0.037	0.037
Mercury (TR)	0.055	0.528	0	0.253	0	0.188	0	0.164	0	0.169	0	0.154
Nickel (dis)	32.02	32.02	20.26	20.26	15.07	15.07	11.52	11.52	11.82	11.82	10.81	10.81
Nickel (TR)	35.01	35.01	17.72	17.72	13.19	13.19	11.46	11.46	11.82	11.82	10.81	10.81
Zinc (dis)	38.32	38.32	9.067	9.067	8.403	8.403	4.602	4.602	3.070	3.070	1.760	1.760
Zinc (TR)	25.52	55.55	0	25.32	0	18.84	0	16.37	19.25	26.50	30.89	30.89
Sus Sediment	114.521	114.521	33.865	33.865	11.523	11.523	3.456	3.456	9.150	9.150	12.354	12.354

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Table 20. (cont.)

Constituent	October 1992		November 1992		December 1992		January 1993		February 1993		March 1993	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Aluminum (dis)	21.27	32.34	0	38.91	0	36.33	136.3	136.3	41.17	41.17	98.02	127.1
Arsenic (dis)	0.468	1.132	0	2.334	0	2.180	0	2.975	0	0.823	0.565	3.816
Arsenic (TR)	0	1.638	0	3.891	0	3.633	0	4.958	0	1.372	0.896	6.315
Cadmium (dis)	0	0.164	0	0.389	0	0.363	0.198	0.570	0	0.137	0	0.631
Cadmium (TR)	0	1.638	0	3.891	0	3.633	0	4.958	0	1.372	0	6.315
Chromium (dis)	0.808	1.070	0.915	1.359	2.797	2.797	4.697	4.697	0.539	0.642	0.469	1.525
Chromium (TR)	2.177	3.234	8.341	10.56	18.16	18.16	24.79	24.79	4.275	4.792	7.003	9.993
Copper (dis)	1.816	1.816	4.890	4.890	3.524	3.524	4.387	4.387	0.973	0.973	5.529	5.529
Copper (TR)	3.808	3.808	8.901	8.901	7.265	7.265	21.08	21.08	5.310	5.310	14.71	15.73
Iron (dis)	29.62	29.62	651.3	653.0	0	10.90	66.94	66.94	18.69	18.69	98.16	98.16
Lead (dis)	0	0.098	0	0.233	0	0.218	0	4.958	0	1.372	0	6.315
Lead (TR)	0.798	1.904	3.908	6.130	3.633	3.633	6.197	6.197	1.372	1.372	14.07	14.07
Mercury (dis)	0.039	0.039	0.093	0.093	0.087	0.087	NM	NM	NM	NM	NM	NM
Mercury (TR)	0	0.164	0	0.389	0	0.363	NM	NM	NM	NM	NM	NM
Nickel (dis)	11.68	13.68	35.02	35.02	32.69	32.69	19.83	19.83	5.489	5.489	20.90	20.90
Nickel (TR)	11.47	11.47	27.24	27.24	25.43	25.43	24.79	24.79	6.861	6.861	43.41	43.41
Zinc (dis)	4.877	4.877	13.69	13.69	9.590	9.590	28.73	28.73	5.144	5.144	27.49	27.49
Zinc (TR)	43.83	43.83	105.8	105.8	36.33	36.33	148.7	148.7	30.82	30.82	78.52	94.98
Sus. Sediment	15.319	15.319	71.904	71.904	47.224	47.224	74.013	74.013	13.227	13.227	263.936	263.936

**Figure 29.** Monthly loading estimates (upper limit) of (a) total recoverable and (b) dissolved chromium, copper, lead, and zinc for the Susquehanna River fall line at Conowingo Dam, Maryland, for the period March 1992 through March 1993.



### **Metal Loads - James River**

Monthly load estimates for the 1992 sampling period are given in Table 21. Bar graphs of the maximum monthly load estimates for 1992 are presented in Figure 30 for total-recoverable and dissolved Cr, Cu, Pb, and Zn.

The quality of load estimates is determined by the quality of the data used to calculate them. Based on the data quality assessment discussed previously in this report, load estimates for total-recoverable As, Cd, Cu, Cr, Pb, and Zn and dissolved As, Cu, Pb, and Zn are considered fair to excellent in terms of data quality. Loads calculated for dissolved Cr and Cd are considered suspect in terms of data quality.

**Table 21** Monthly load estimates in kg for the James River fall line at Cartersville, Virginia, for the period March 1992 through March 1993.

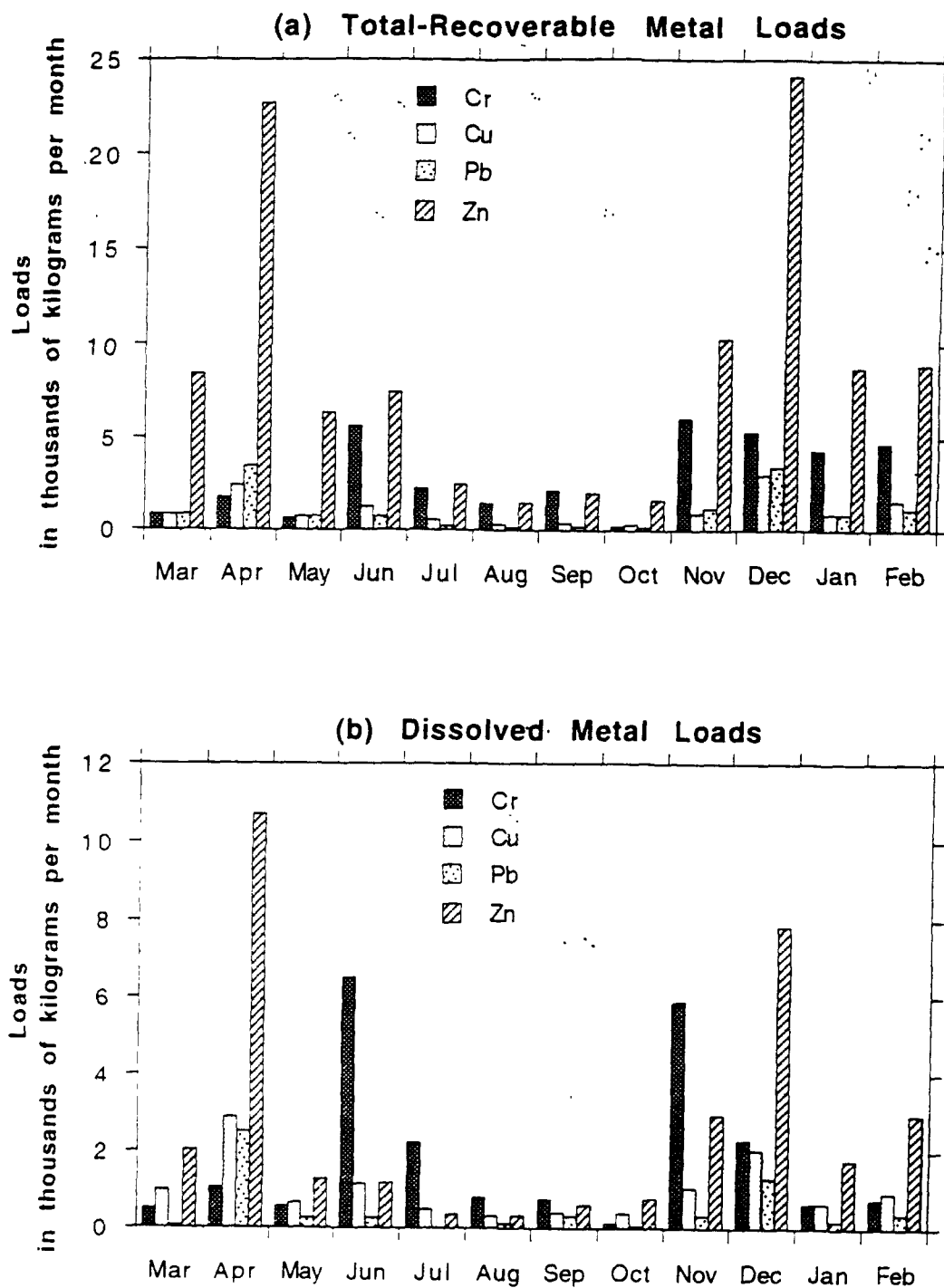
Constituent	March 1992		April 1992		May 1992		June 1992		July 1992		August 1992	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Aluminum (dis)	16,944	16,944	88,863	88,863	79,480	79,480	68,280	68,280	15,311	15,311	9,226	9,226
Arsenic (dis)	0	508	0	628	0	382	0	450	0	150	0	90
Arsenic (TR)	0	847	0	1,047	0	637	0	750	0	249	0	150
Cadmium (dis)	0	85	0	105	0	64	0	75	0	25	150	156
Cadmium (TR)	0	847	0	1,047	0	637	0	750	0	249	0	150
Chromium (dis)	508	508	987	1,054	547	578	6,537	6,537	2,259	2,259	814	814
Chromium (TR)	0	847	1,162	1,781	150	637	5,436	5,643	2,262	2,262	1,449	1,449
Copper (dis)	991	991	2,903	2,903	662	662	1,167	1,167	511	511	315	315
Copper (TR)	847	847	2,454	2,454	300	787	1,087	1,294	576	576	333	333
Iron (dis)	93,193	93,193	196,451	196,451	137,963	137,963	133,731	133,731	33,116	33,116	14,828	14,828
Lead (dis)	76	76	2,522	2,522	263	263	271	271	19	28	134	138
Lead (TR)	0	847	2,866	3,486	787	787	207	750	0	249	0	150
Mercury (TR)	0	85	24	105	0	64	0	75	0	25	0	15
Zinc (dis)	2,050	2,050	10,730	10,730	1,289	1,289	1,201	1,201	366	366	331	331
Zinc (TR)	0	8,472	14,676	22,703	0	6,373	0	7,502	0	2,494	0	1,503
Sus Sediment	19,432,471	19,432,471	491,130,659	491,130,659	24,405,252	24,405,252	9,666,286	9,666,286	1,032,337	1,032,337	365,561	365,561

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Table 21. (cont.)

Constituent	September 1992		October 1992		November 1992		December 1992		January 1993		February 1993	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Aluminum (dis)	14,274	14,274	2,121	2,121	58,709	58,709	214,439	214,439	87,970	87,970	186,402	186,402
Arsenic (dis)	0	122	0	101	0	378	0	420	0	528	0	381
Arsenic (TR)	0	204	0	168	0	631	0	701	0	880	0	634
Cadmium (dis)	357	357	13	29	0	63	0	70	0	88	0	63
Cadmium (TR)	0	204	0	168	0	631	0	701	0	880	0	634
Chromium (dis)	781	781	153	153	5,895	5,895	2,307	2,307	651	651	768	768
Chromium (TR)	2,141	2,141	77	238	5,953	6,060	5,338	5,338	4,389	4,398	4,751	4,751
Copper (dis)	408	408	404	404	1,060	1,060	2,053	2,053	651	651	953	953
Copper (TR)	408	408	336	336	940	940	3,023	3,023	880	880	1,626	1,626
Iron (dis)	18,352	18,352	23,155	23,155	214,052	214,052	540,965	540,965	281,503	281,503	375,104	375,104
Lead (dis)	320	320	77	77	342	342	1,315	1,315	220	220	389	389
Lead (TR)	0	204	0	168	0	1,238	3,429	3,429	880	880	1,192	1,192
Mercury (TR)	0	20	0	17	0	63	0	70	0	0	0	0
Zinc (dis)	622	622	782	782	2,967	2,967	7,859	7,859	1,777	1,777	2,956	2,956
Zinc (TR)	2,039	2,039	0	1,680	6,078	10,358	24,152	24,152	8,797	8,797	8,976	8,976
Sus. Sediment	407,822	407,822	175,362	175,362	38,037,594	38,037,594	166,752,766	166,752,766	7,037,577	7,037,577	56,543,896	56,543,896

**Figure 30.** Monthly loading estimates (upper limit) of (a) total recoverable and (b) dissolved chromium, copper, lead, and zinc for the James River fall line at Cartersville, Virginia, for the period March 1992 through March 1993.



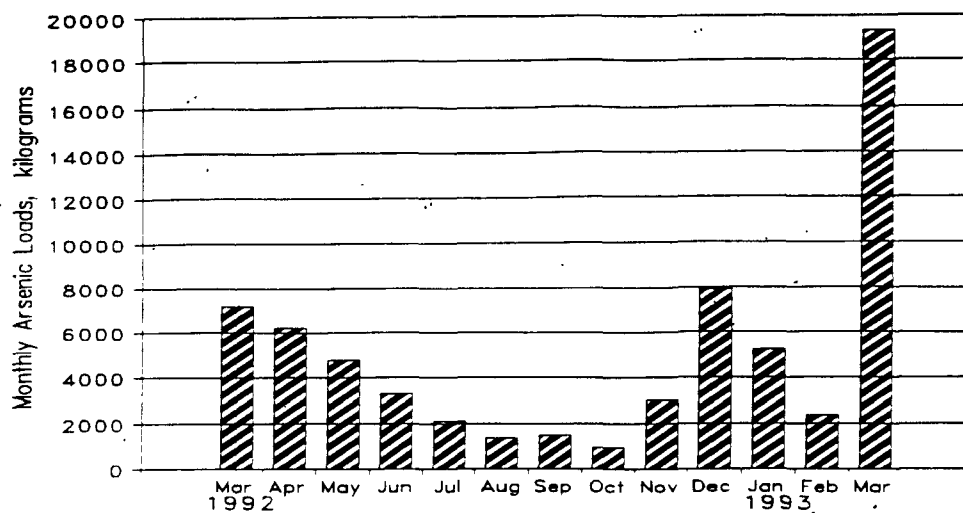


## **Metal Loads - Potomac River**

Figure 31-Figure 38 are plots of the computed monthly loads for the metals and Table 22-Table 29 are the data tables associated with these plots. As discussed earlier, load estimates were performed using two different substitutions for censored data. A minimum estimate was obtained by replacing all values below the QL by zero, and a maximum estimate was obtained by replacing all values below the QL by the QL. In this manner, two loading estimates were obtained for each month. If all data for that month was above the QL, then both estimates resulted in the same load value. The heavily-shaded region of the plot, thus, represents the range between the two estimates.

Figure 39 and Table 30 give the total loads for the eight metals during the April, 1992, to March, 1993, period. (The month of March, 1992, was not included in order to obtain a load for one year.) The minimum and maximum load estimates are the sums of the monthly load estimates for each individual metal.

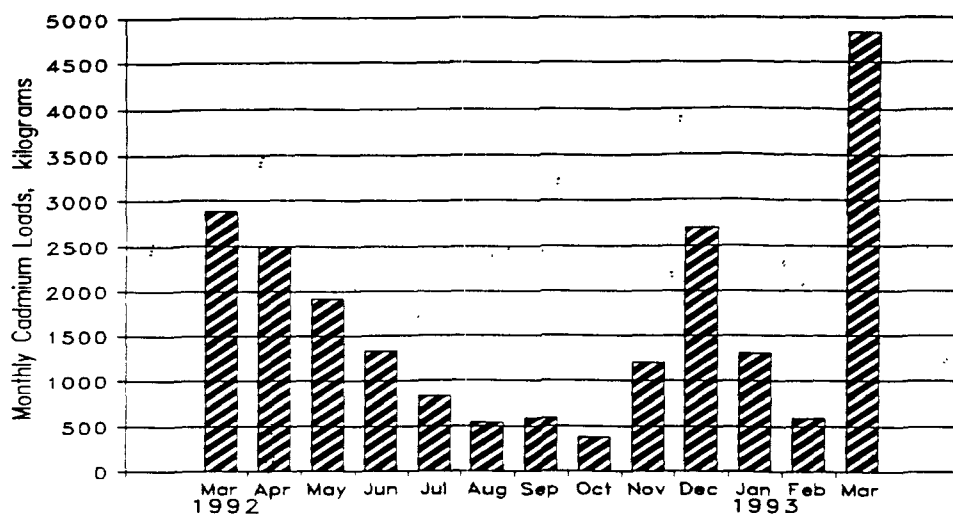
**Figure 31.** Arsenic Loads at Chain Bridge on the Potomac River: March 1992 to March 1993.



**Table 22.** Estimated monthly arsenic loads at Chain Bridge on the Potomac River: March, 1992, to March, 1993

Estimated Monthly Arsenic Loads, kilograms		
Month	Minimum	Maximum
March, 1992	0	7211
April	0	6258
May	0	4791
June	0	3318
July	0	2085
August	0	1357
September	0	1468
October	0	943
November	0	3010
December	0	7875
January, 1993	0	5267
February	0	2342
March	0	19322
<b>Total</b>	<b>0</b>	<b>65247</b>

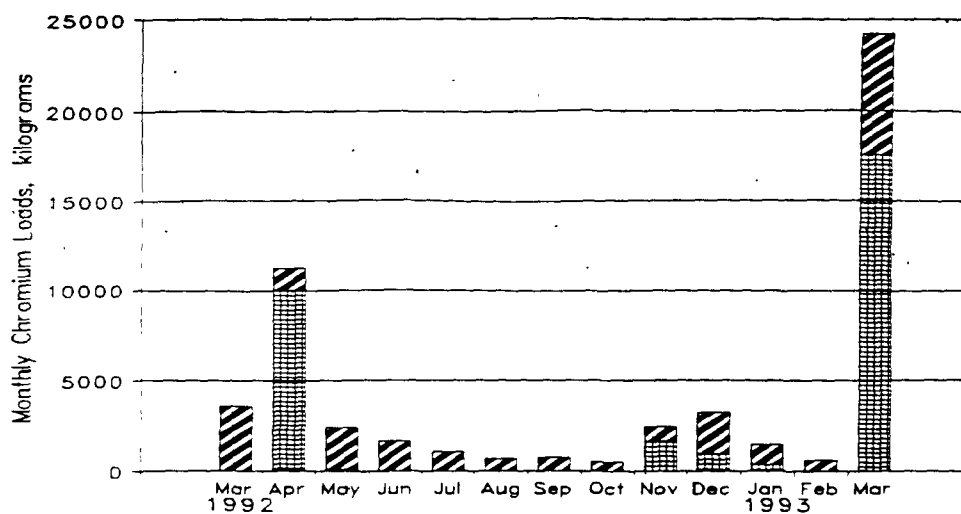
**Figure 32.** Cadmium Loads at Chain Bridge on the Potomac River: March 1992 to March 1993.



**Table 23.** Estimated monthly cadmium loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

Estimated Monthly Cadmium Loads, kilograms		
Month	Minimum	Maximum
March, 1992	0	2885
April	0	2503
May	0	1916
June	0	1327
July	0	834
August	0	543
September	0	587
October	0	377
November	0	1204
December	0	2697
January, 1993	0	1310
February	0	586
March	0	4830
<b>Total</b>	<b>0</b>	<b>21600</b>

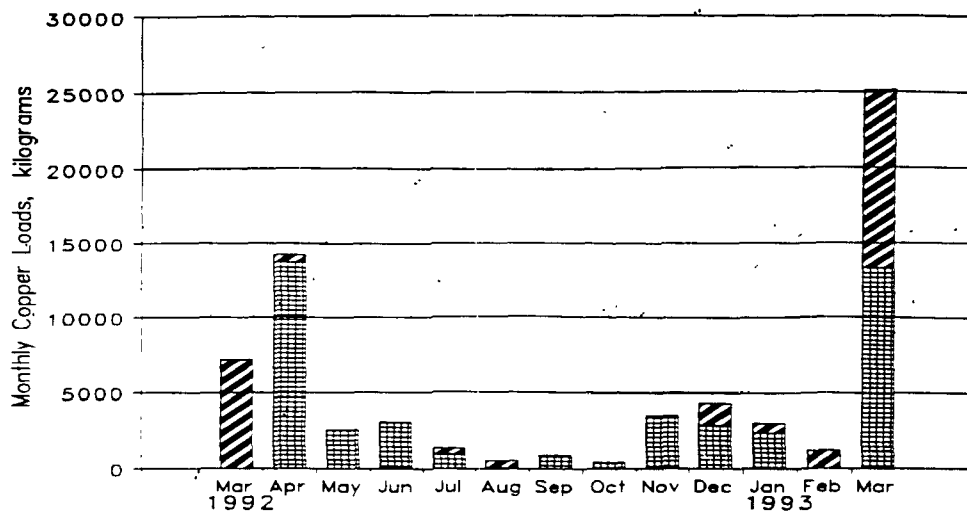
**Figure 33.** Chromium Loads at Chain Bridge on the Potomac River: March 1992 to March 1993.



**Table 24.** Estimated monthly chromium loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

Estimated Monthly Chromium Loads, kilograms		
Month	Minimum	Maximum
March, 1992	0	3606
April	10017	11234
May	106	2428
June	0	1659
July	0	1043
August	0	678
September	0	734
October	0	472
November	1631	2457
December	920	3258
January, 1993	362	1492
February	0	586
March	17570	24204
<b>Total</b>	<b>30606</b>	<b>53849</b>

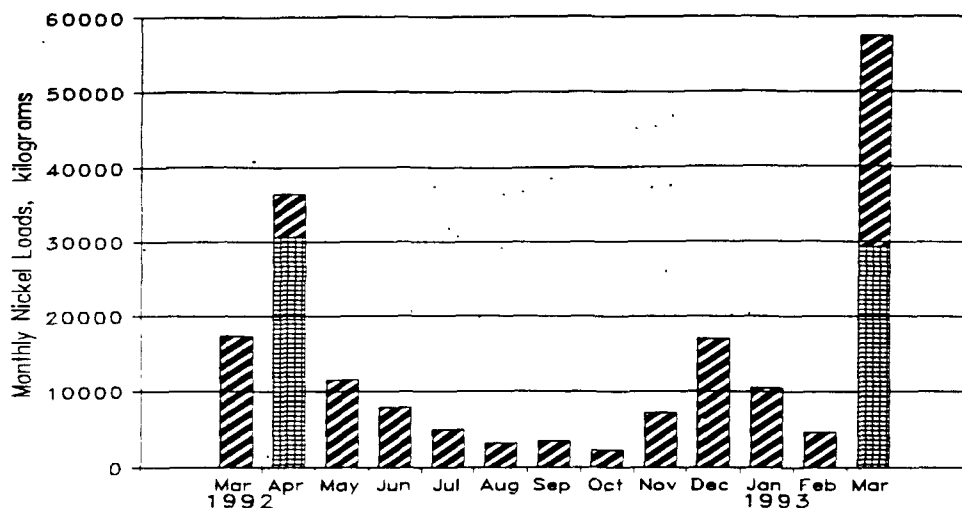
**Figure 34.** Copper Loads at Chain Bridge on the Potomac River: March 1992 to March 1993.



**Table 25.** Estimated monthly copper loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

Estimated Monthly Copper Loads, kilograms		
Month	Minimum	Maximum
March, 1992	0	7211
April	13713	14251
May	2551	2551
June	3069	3069
July	952	1363
August	86	577
September	867	867
October	404	404
November	3370	3487
December	2854	4362
January, 1993	2355	3013
February	0	1171
March	13310	25101
<b>Total</b>	<b>43534</b>	<b>67429</b>

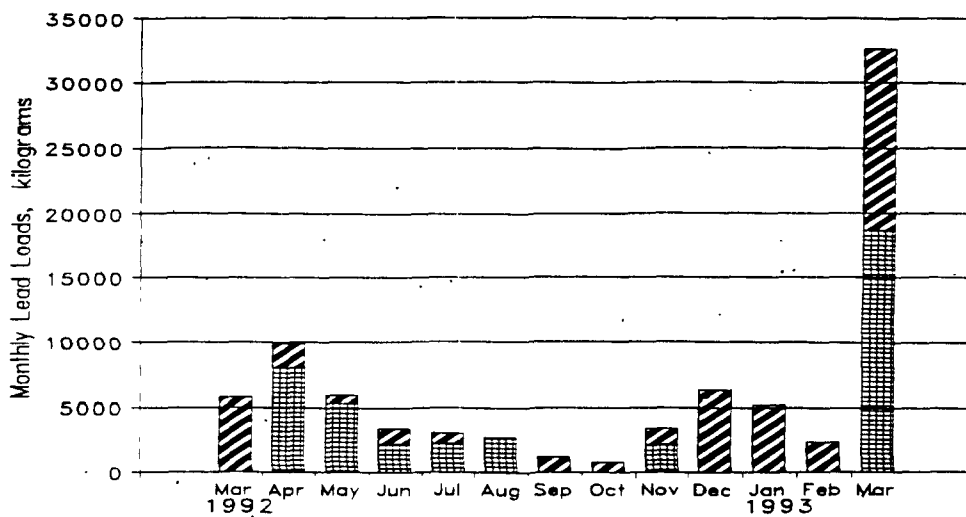
**Figure 35.** Nickel Loads at Chain Bridge on the Potomac River: March 1992 to March 1993.



**Table 26.** Estimated monthly nickel loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

Estimated Monthly Nickel Loads, kilograms		
Month	Minimum	Maximum
March, 1992	0	17308
April	30586	36428
May	0	11498
June	0	7963
July	0	5005
August	0	3256
September	0	3523
October	0	2263
November	0	7224
December	0	17089
January, 1993	0	10484
February	0	4684
March	29283	57278
<b>Total</b>	<b>59868</b>	<b>184002</b>

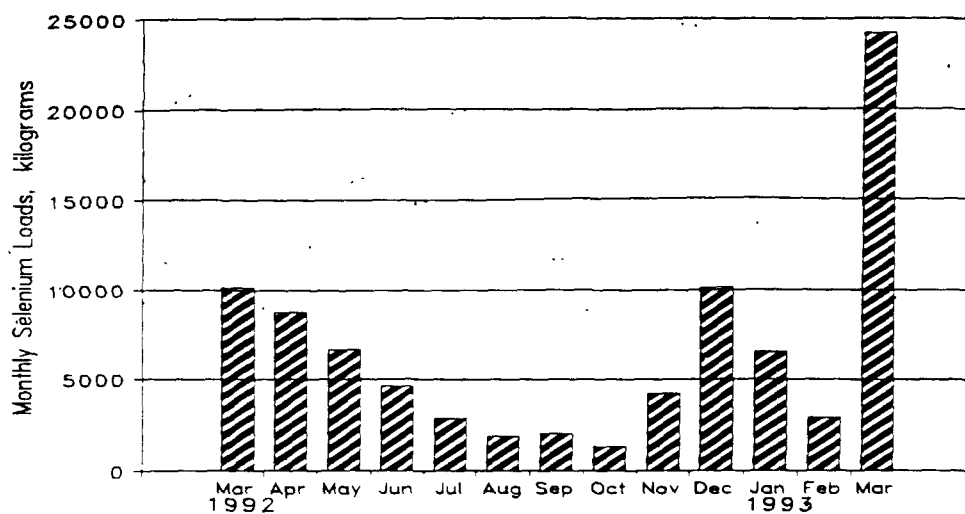
**Figure 36.** Lead Loads at Chain Bridge on the Potomac River: March 1992 to March 1993.



**Table 27.** Estimated monthly lead loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

Estimated Monthly Lead Loads, kilograms		
Month	Minimum	Maximum
March, 1992	0	5769
April	8029	9976
May	5320	5928
June	2156	3377
July	2240	3086
August	2672	2777
September	0	1174
October	0	754
November	2093	3414
December	0	6300
January, 1993	0	5242
February	0	2342
March	18635	32632
<b>Total</b>	<b>41144</b>	<b>82772</b>

**Figure 37.** Selenium Loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

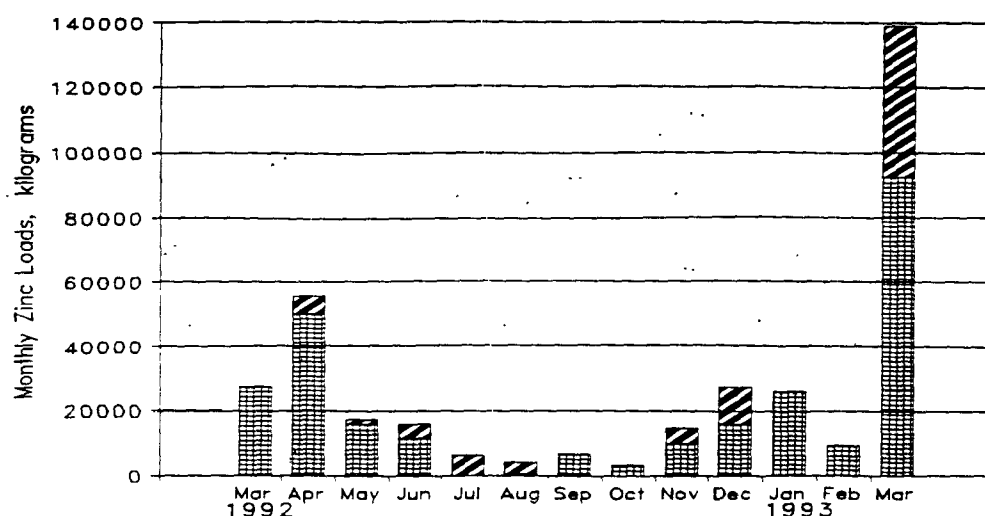


**Table 28.** Estimated monthly selenium loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

Estimated Monthly Selenium Loads, kilograms		
Month	Minimum	Maximum
March, 1992	0	10096
April	0	8761
May	0	6707
June	0	4645
July	0	2919
August	0	1899
September	0	2055
October	0	1320
November	0	4214
December	0	10119
January, 1993	0	6552
February	0	2928
March	0	24152
<b>Total</b>	<b>0</b>	<b>86368</b>



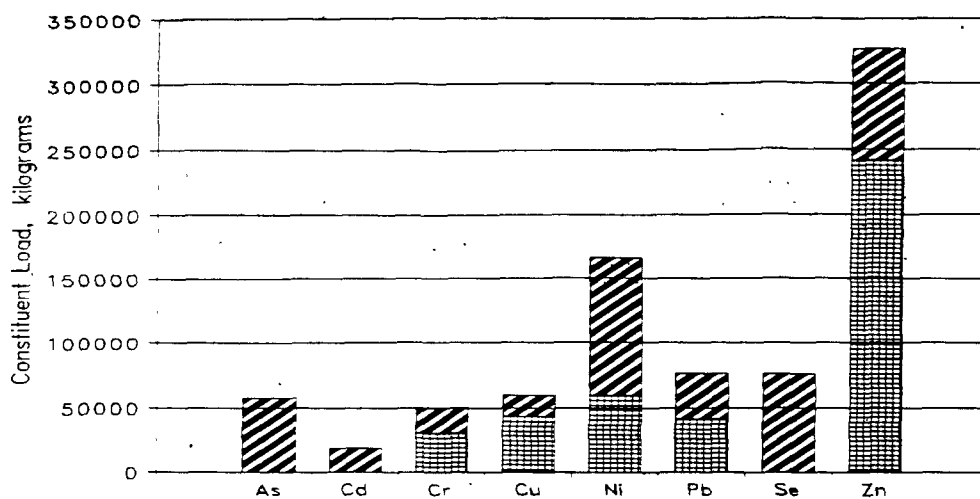
**Figure 38.** Zinc Loads at Chain Bridge on the Potomac River: March, 1992, to March, 1993



**Table 29.** Estimated monthly zinc loads at Chain Bridge on the Potomac River: March 1992 to March 1993.

Estimated Monthly Zinc Loads, kilograms		
Month	Minimum	Maximum
March, 1992	27404	27404
April	50217	55906
May	15902	17743
June	11496	16077
July	0	6256
August	655	4332
September	6793	6793
October	3093	3345
November	9787	14739
December	15684	26994
January, 1993	25981	25981
February	9368	9368
March	92466	139279
<b>Total</b>	<b>268847</b>	<b>354216</b>

**Figure 39.** Load Estimates for the Period of April, 1992, to March, 1993, for the Metal Species Monitored at Chain Bridge on the Potomac River



**Table 30.** Range of load estimates for monitored metals for the period of April 1992 to March 1993 at Chain Bridge on the Potomac River.

Constituent	Range of Load Estimates (kilograms)	
	with Values Below the Quantitation Limit (QL) Set to	
	Zero	the QL
Arsenic (As)	0	58035
Cadmium (Cd)	0	18715
Chromium (Cr)	30606	50243
Copper (Cu)	43534	60218
Nickel (Ni)	59868	166694
Lead (Pb)	41144	77003
Selenium (Se)	0	76272
Zinc (Zn)	241443	326812

## **Organics Loads - Susquehanna, James and Potomac Rivers**

Estimates of monthly pesticide and PCB loads for each tributary in the fall line study are listed in Table 31-Table 39. The monthly loads were estimated separately for the dissolved and particulate phases. Estimated loads in these tables were calculated from both the maximum and minimum daily fluxes summed for each month providing maximum and minimum load estimates. Zero loads represent minimum values that were calculated assuming that there was no existing level (i.e., 0 ng/L) of contaminant in the fluvial sample when the measured value was <QL values, and this approach probably provides underestimates the actual amount in fluvial transport. Conversely, the maximum loads were calculated using the QL value when the fluvial constituent concentrations were below quantitation levels, likely providing an overestimate of the monthly loads. Therefore, the actual load probably lies somewhere between these two estimates. The most accurate load estimates exist when the maximum and minimum loads are identical or are very close in magnitude, because this indicates that the particular constituent was detected in nearly every fluvial sample analyzed.

**Table 31.** Fluvial loads for the organonitrogen and organophosphorus pesticides at the Susquehanna River fall line during the period of March 1992 to February 1993.

Susquehanna River, March 1992-February 1993 Organonitrogen & Organophosphorus Pesticides																		
Load (kg)																		
	Simazine		Prometon		Atrazine		Diazinon		Alachlor		Malathion		Metolachlor		Cyanazine		Hexazinone	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Month																		
Mar	10	1	8	0	69	69	19	8	22	17	14	6	93	93	34	27	7	5
Apr	151	142	37	30	179	179	15	0	28	17	15	2	154	154	93	93	13	13
May	218	218	45	45	170	170	6	0	25	25	5	0	94	94	93	93	13	13
June	92	92	23	23	481	481	5	0	37	37	4	0	228	228	187	187	2	0
July	45	45	7	7	120	120	4	0	5	1	4	0	51	51	21	21	1	0
Aug.	21	21	4	3	89	89	4	0	4	0	4	0	31	31	9	7	2	1
Sept.	4	4	2	0	67	67	4	0	4	0	4	0	19	19	4	0	2	1
Oct.	6	5	3	0	60	60	4	0	4	0	4	0	25	25	4	0	12	12
Nov.	18	15	10	6	106	106	10	0	10	0	9	0	55	55	9	0	29	28
Dec.	16	13	6	0	120	120	9	0	9	0	8	0	62	62	9	0	37	37
Jan.	22	17	8	0	158	158	12	0	12	0	11	0	81	81	12	0	49	49
Feb.	6	5	2	0	45	45	3	0	3	0	3	0	23	23	3	0	14	14
Totals	610	580	160	110	1700	1700	96	8	160	97	86	8	920	920	480	430	180	170

**Table 32** Combined fluvial loads (sum of dissolved and particulate phase contributions) for the organochlorines at the Susquehanna River fall line during the period of March 1992 to February 1993.

Susquehanna River, March 1992-February 1993 Organochlorine Compounds Combined Loads (kg)																			
Month	Aldrin		Oxy-chlordane		gamma-Chlordane		alpha-Chlordane		Dieldrin		4,4'-DDT		cis-&trans-Permethrin		cis-&trans-Fenvalerate		ΣPCBs		
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	
Mar	2.4	0.0	3.1	0.0	3.5	0.0	7.0	0.0	2.5	0.0	3.8	0.0	13.1	0.0	4.5	0.0	23.2	0.0	
Apr	3.8	1.5	4.2	1.7	4.7	2.9	11.0	5.9	2.7	1.0	4.6	0.0	16.8	0.0	6.0	0.0	28.4	15.0	
May	0.9	3.2	1.0	3.7	1.0	4.3	0.6	10.5	0.6	1.0	1.7	0.0	5.7	0.9	2.0	0.5	10.8	27.5	
June	2.7	0.7	5.4	0.7	1.9	1.0	2.7	0.4	2.2	0.0	1.4	0.0	4.8	0.0	1.7	0.0	11.2	9.3	
July	2.6	2.5	0.4	5.2	0.3	0.0	0.3	0.0	0.5	2.1	1.0	0.0	3.6	0.0	1.3	0.0	15.7	10.7	
Aug.	1.4	2.5	0.3	0.2	0.3	0.0	0.2	0.1	0.4	0.1	1.1	0.0	4.0	0.0	1.4	0.0	10.0	15.5	
Sept.	0.5	1.3	0.3	0.0	0.3	0.1	0.2	0.1	0.4	0.0	1.1	0.0	3.8	0.0	1.3	0.0	5.1	9.2	
Oct.	0.7	0.4	1.4	0.0	0.5	0.2	0.5	0.0	0.5	0.0	1.3	0.0	4.2	0.0	2.4	0.0	8.4	4.0	
Nov.	1.7	0.4	3.9	1.2	1.1	0.3	1.5	0.3	1.1	0.2	4.5	0.4	12.3	0.0	5.9	1.2	25.5	8.0	
Dec.	1.7	1.0	4.6	3.6	1.1	0.7	1.4	1.2	1.1	0.6	3.2	2.6	9.6	3.0	6.4	3.1	22.2	19.4	
Jan	2.3	1.0	6.0	4.2	1.6	0.8	2.1	1.1	1.5	0.7	4.3	1.4	13.0	0.0	8.5	4.1	29.3	22.2	
Feb.	0.7	1.3	1.7	5.5	0.4	1.1	0.5	1.6	0.4	1.0	1.2	1.8	3.6	0.0	2.4	5.4	8.4	29.2	
Totals	21	16	32	26	17	11	28	21	14	7	29	6	95	4	44	14	198	170	

**Table 33.** Combined fluvial loads (sum of dissolved and particulate phase) for the polynuclear aromatic hydrocarbons at the Susquehanna River fall line during the period of March 1992 to February 1993.

Susquehanna River, March 1992-February 1993 Polynuclear Aromatic Hydrocarbons										
Combined Load (kg)										
Month	Naphthalene		Fluoranthene		Benz(a)anthracene		Benzo(a)pyrene			
	Max	Min	Max	Min	Max	Min	Max	Min		
Mar.	126	126	25	22	18	11	16	0		
Apr.	53	53	26	19	23	15	32	13		
May	2	2	29	28	17	17	7	0		
June	7	7	1	0	3	0	6	0		
July	2	2	1	0	2	0	4	0		
Aug.	6	6	3	2	3	0	5	0		
Sept	9	9	4	4	2	0	5	0		
Oct.	10	10	5	4	3	1	5	0		
Nov.	21	21	21	19	9	4	13	1		
Dec.	24	24	10	9	6	2	12	0		
Jan.	32	32	14	12	9	4	16	0		
Feb	9	9	4	3	2	1	4	0		
Totals	300	300	140	120	98	55	120	14		

**Table 34.** Fluvial loads for the organonitrogen and organophosphorus pesticides at the Potomac River fall line during the period from March 1992 to February 1993.

Potomac River, March 1992-February 1993 Organonitrogen & Organophosphorus Pesticides Monthly Load (kg)																		
Month	Simazine		Prometon		Atrazine		Diazinon		Alachlor		Malathion		Metolachlor		Cynazine		Hexazinone	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Mar.	23	23	12	11	50	50	4	0	9	7	3	0	19	19	4	0	1	0
Apr	56	56	3	1	48	48	3	0	4	1	3	0	30	30	3	0	1	0
May	98	98	8	8	157	157	2	0	7	6	2	0	66	66	65	64	1	0
June	88	88	8	8	296	296	4	3	8	8	4	3	150	150	104	104	6	6
July	31	31	5	5	107	107	1	0	3	3	1	0	72	72	35	35	1	1
Aug.	10	10	3	3	16	16	1	0	1	0	1	0	14	14	1	0	0	0
Sept.	3	2	7	7	23	23	1	0	1	0	1	0	12	12	5	5	0	0
Oct.	1	1	3	3	9	9	0	0	0	0	0	0	5	5	2	2	0	0
Nov.	2	2	9	9	28	28	1	0	1	0	1	0	15	15	6	6	0	0
Dec.	28	27	3	0	27	27	4	0	4	0	4	0	10	10	4	0	1	0
Jan.	3	0	2	0	13	13	3	0	3	0	3	0	1	0	3	0	1	0
Feb.	1	0	1	0	4	4	1	0	1	0	1	0	0	0	1	0	0	0
Totals	340	340	66	56	780	780	27	3	44	25	25	3	390	390	230	220	14	6

**Table 35** Combined fluvial loads (sum of dissolved and particulate phase contributions) for the organochlorines at the Potomac River fall line during the period of March 1992 to February 1993.

Potomac River, March 1992-February 1993 Organochlorine Compounds Combined Load (kg)																		
	Aldrin		Oxy- chlordane		gamma- Chlordane		alpha- Chlordane		Dieldrin		4,4'-DDT		cis-&trans- Permethrin		cis-&trans- Fenvalerate		ΣPCBs	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Month																		
Mar	0.9	0.8	0.2	0.0	0.5	0.3	0.6	0.5	0.6	0.3	0.9	0.0	3.2	0.0	1.1	0.0	14.5	1.6
Apr	0.8	0.7	0.2	0.0	0.2	0.0	0.2	0.0	0.4	0.0	0.9	0.0	3.1	0.0	1.1	0.0	3.2	0.1
May	0.4	0.3	2.8	2.8	0.1	0.0	1.6	1.5	3.3	3.3	0.6	0.0	2.1	0.0	0.7	0.0	4.2	0.0
June	0.9	0.7	9.2	9.1	1.2	1.0	1.7	1.6	2.7	1.8	0.8	0.0	2.9	0.0	1.0	0.0	13.5	11.9
July	0.5	0.5	0.1	0.0	0.1	0.1	0.1	0.0	0.3	0.0	0.3	0.0	0.9	0.0	0.3	0.0	1.7	0.6
Aug	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.2	0.0	0.6	0.0	0.2	0.0	0.7	0.0
Sept	0.1	0.0	0.1	0.0	0.1	0.0	0.2	0.2	0.3	0.3	0.3	0.0	1.0	0.0	0.4	0.0	0.8	0.7
Oct.	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.4	0.0	0.1	0.0	0.3	0.3
Nov.	0.1	0.0	0.1	0.0	0.1	0.0	0.3	0.3	0.4	0.4	0.4	0.0	1.3	0.0	0.5	0.0	0.9	0.9
Dec.	1.0	0.0	2.1	1.9	2.6	2.3	8.6	9.2	5.6	5.6	3.4	2.9	19.1	15.4	4.9	3.6	5.9	5.3
Jan	0.5	0.0	0.3	0.0	0.6	0.0	0.0	1.4	1.0	0.8	1.3	0.0	4.4	0.0	1.5	0.0	1.3	0.0
Feb.	0.2	0.0	0.1	0.0	0.3	0.1	0.1	0.7	0.5	0.4	0.7	0.2	1.9	0.0	0.7	0.0	0.6	0.0
Totals	5.6	3.0	15	14	5.9	3.8	13	15	15	13	9.9	3.1	41	15	12	3.6	48	22



**Table 36.** Combined fluvial loads (sum of dissolved and particulate phase contributions) for the polynuclear aromatic hydrocarbons at the Potomac River fall line during the period of March 1992 to February 1993.

Potomac River, March 1992-February 1993 Polynuclear Aromatic Hydrocarbons									
Combined Load (kg)									
	Naphthalene		Fluoranthene		Benz(a)anthracene		Benzo(a)pyrene		
Month	Max	Min	Max	Min	Max	Min	Max	Min	Min
Mar	14.2	14.2	1.3	0.8	20.0	18.4	3.9	0.0	0.0
Apr	7.4	7.4	1.9	1.7	3.8	1.8	3.8	0.0	0.0
May	7.2	7.2	1.6	1.4	1.4	0.0	10.3	8.2	8.2
June	13.5	13.5	4.4	4.2	1.9	0.0	5.7	2.2	2.2
July	5.7	5.7	2.2	2.1	2.4	1.9	1.1	0.0	0.0
Aug	1.5	1.5	0.8	0.7	2.4	2.1	0.7	0.0	0.0
Sept	2.1	2.1	0.5	0.4	0.9	0.2	1.3	0.0	0.0
Oct	0.8	0.8	0.2	0.1	0.3	0.0	0.5	0.0	0.0
Nov.	2.6	2.6	0.6	0.4	0.9	0.0	1.6	0.0	0.0
Dec	8.9	5.6	6.4	5.8	8.9	3.5	12.0	0.0	0.0
Jan	7.5	0.0	0.8	0.0	2.9	0.0	5.4	0.0	0.0
Feb.	3.3	0.0	2.1	1.8	2.4	1.3	2.7	0.6	0.6
Totals	75	60	23	19	48	29	49	11	11

**Table 37.** Fluvial loads for the organonitrogen and organophosphorus pesticides at the James River fall line during the period of March 1992 to February 1993.

James River, March 1992-February 1993 Organonitrogen & Organophosphorus Pesticides																		
Load (kg)																		
Month	Simazine		Prometon		Atrazine		Diazinon		Alachlor		Malathion		Metolachlor		Cynazine		Hexazinone	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Mar	2	0	1	0	1	0	2	0	3	1	2	0	1	0	3	1	2	2
Apr	99	98	2	0	128	127	4	2	12	12	4	2	55	55	10	9	10	9
May	20	20	1	0	36	36	2	0	2	1	1	0	18	18	15	15	3	3
June	10	10	1	1	29	29	2	0	2	0	2	1	11	11	7	7	3	3
July	1	1	1	1	4	4	1	1	1	0	1	0	1	1	1	0	1	0
Aug.	1	1	0	0	1	1	1	0	0	0	0	0	1	1	0	0	1	0
Sept	1	1	0	0	1	1	1	0	1	0	0	0	2	2	0	0	3	0
Oct	<1	0	3	3	3	3	2	2	0	0	0	0	0	0	0	0	0	0
Nov.	2	1	10	10	13	13	6	6	2	0	2	0	0	0	2	0	1	1
Dec.	1	0	4	3	5	4	4	4	2	0	2	0	0	0	2	0	1	0
Jan.	2	0	1	0	1	0	4	4	2	0	2	0	1	0	2	0	1	0
Feb	1	0	1	0	2	1	2	2	2	0	1	0	1	0	1	0	1	0
Totals	140	130	26	18	220	220	30	20	28	15	18	3	92	89	43	32	26	18

**Table 38.** Combined fluvial loads (sum of dissolved and particulate phase contributions) for the organochlorines at the James River fall line during the period of March 1992 to February 1993.

James River, March 1992-February 1993 Organochlorine Compounds																		
Combined Load (kg)																		
Month	Aldrin		Oxy-chlordane		gamma-Chlordane		alpha-Chlordane		Dieldrin		4,4'-DDT		cis-&trans-Permethrin		cis-&trans-Fenvalerate		ΣPCBs	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Mar	0.2	0.0	1.0	0.0	1.5	0.9	2.5	2.5	0.5	0.4	0.6	0.0	2.1	0.0	0.7	0.0	8.8	0.0
Apr	0.7	0.5	5.5	3.5	5.9	5.8	12.5	12.4	0.5	0.2	0.8	0.0	2.6	0.0	1.0	0.1	7.6	7.3
May	0.1	0.1	1.6	1.6	2.0	2.0	1.3	0.7	0.9	0.5	0.4	0.0	1.4	0.0	2.0	1.6	3.6	2.6
June	1.5	1.5	0.6	0.6	0.8	0.7	0.6	0.3	0.5	0.4	0.5	0.0	1.7	0.0	1.1	0.5	2.2	0.9
July	0.3	0.3	0.0	0.0	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.0	0.6	0.0	0.2	0.0	0.3	0.0
Aug	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.0	0.5	0.0	0.2	0.0	0.2	0.1
Sept	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.2	0.0	0.7	0.0	0.2	0.0	0.2	0.1
Oct.	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.6	0.0	0.2	0.0	1.0	0.9
Nov.	0.3	0.0	0.3	0.2	0.2	0.0	0.2	0.0	0.2	0.0	0.7	0.0	2.3	0.0	0.8	0.5	4.1	3.8
Dec.	0.3	0.0	0.2	0.0	0.4	0.3	0.6	0.0	0.4	0.3	0.7	0.1	2.3	0.0	0.8	0.0	2.0	1.5
Jan.	0.3	0.0	0.2	0.0	0.7	0.6	1.0	0.0	0.7	0.5	0.8	0.0	2.7	0.0	0.9	0.0	0.9	0.0
Feb.	0.2	0.0	0.1	0.0	0.5	0.4	0.6	0.0	0.4	0.3	0.6	0.0	2.0	0.0	0.7	0.0	0.8	0.3
Totals	4.1	2.3	9.6	5.8	12	11	19	16	4.4	2.7	5.6	0.1	20	0.0	8.8	2.7	32	18

**Table 39.** Combined fluvial loads (sum of dissolved and particulate phase contributions) for the polynuclear aromatic hydrocarbons at the James River fall line during the period of March 1992 to February 1993.

James River March 1992-February 1993 Polynuclear Aromatic Hydrocarbons									
Combined Load (kg)									
	Naphthalene		Fluoranthene		Benz(a)anthracene		Benzo(a)pyrene		
	Max	Min	Max	Min	Max	Min	Max	Min	
Month									
Mar	17	17	56	56	2.7	1.8	2.6	0.0	
Apr	26	25	52	52	14	13	44	41	
May	9.5	0.0	14	14	2.3	1.6	12	11	
June	9.2	0.0	5.1	4.9	3.6	3.2	5.5	3.6	
July	1.5	0.0	0.1	0.0	0.8	0.5	0.8	0.0	
Aug	0.5	0.0	0.3	0.3	0.3	0.0	0.6	0.0	
Sept	0.9	0.0	0.7	0.6	0.5	0.0	0.8	0.0	
Oct.	0.2	0.0	0.2	0.1	0.4	0.0	0.7	0.0	
Nov.	0.5	0.5	2.3	1.9	4.5	3.3	5.4	3.0	
Dec	0.5	0.1	3.0	2.8	2.5	1.1	4.2	1.6	
Jan.	0.6	0.0	0.7	0.5	1.8	0.0	3.3	0.0	
Feb.	0.6	0.1	2.8	2.7	2.2	1.1	3.1	0.8	
Totals	67	43	140	140	35	26	82	61	

## **WATER QUALITY DATA DISCUSSION**

### **Water Quality Metal Data - Susquehanna River**

The 1992 study resulted in the development of ultra clean sampling procedures, adoption of lowered quantitation levels, an extensive quality-assurance program, identification of metals in fluvial transport, and estimates of toxic loadings entering the Chesapeake Bay. Additionally, results from the 1992 quality assurance program were used to assess the quality of 1992 concentration data and load estimates, and to make inferences as to the validity of 1990-91 fall line results when ultra clean techniques were not used.

Concentration data collected throughout the period 1990-93 for the Susquehanna station are presented in Appendix A. Results are reported for dissolved and total-recoverable metals. Ranges in constituent concentration provide year to year comparisons for river samples. Boxplots of concentration data collected over the three year period are shown in Figure 40.

Figure 41-Figure 44 show the concentrations of total-recoverable and dissolved Cr, Cu, Pb, and Zn for the entire three-year sampling period. The old quantitation levels for 1990-91 and new levels for 1992 are indicated on each graph for the dissolved species. The quantitation levels did not change over the sampling period for total-recoverable metals. Where duplicate measurements were made, the average of the two data points was used for the time series.

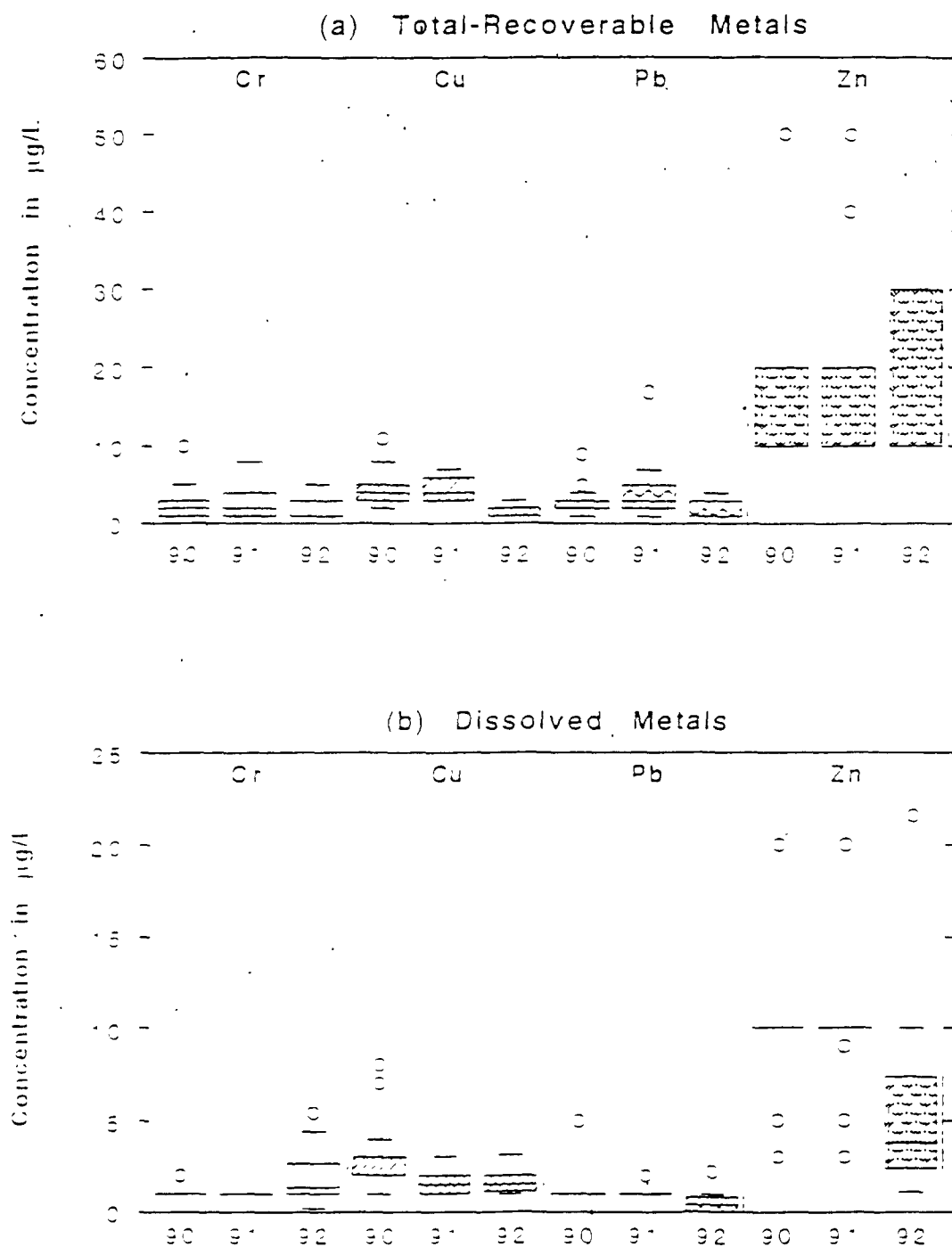
The ultra clean sampling procedures as well as the lowered quantitation levels for 1992 significantly improved concentration data for some constituents. Concentration data for a particular constituent were considered improved in 1992 if one or more of the following criteria were met: (1) if more ambient concentration data were detected; (2) if the range in concentration data decreased in 1992 or the precision increased; and (3) if concentration data exhibited a better relation with discharge.

Based on these criteria, water quality data were improved in 1992 for total-recoverable Cu, Pb, Zn, and dissolved Cu, Pb, and Zn. Although dissolved Cr and Hg met one or more of the criteria, they were not considered improved in 1992 due to their suspect data quality.

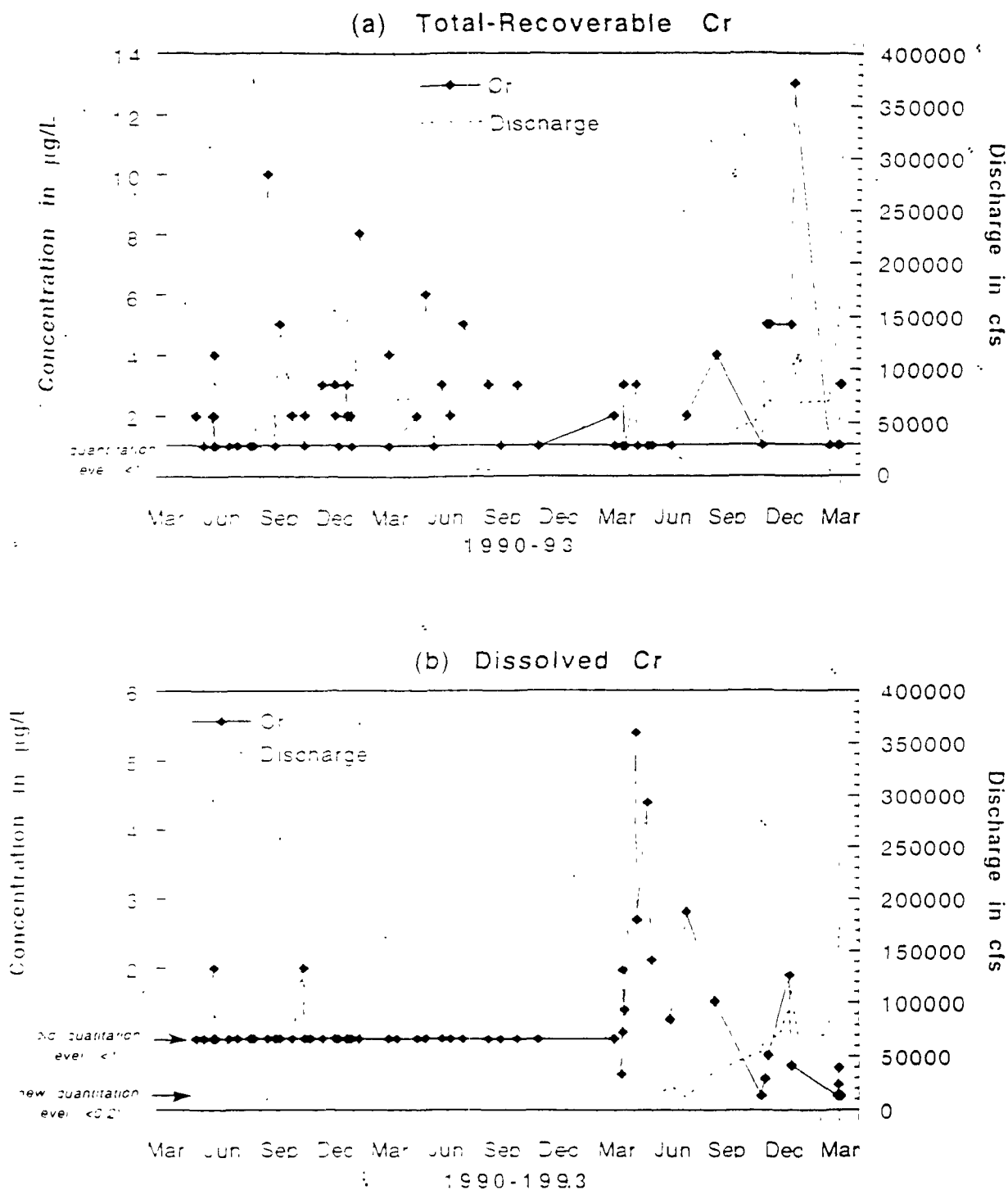
Generally, results indicate that there was a greater percentage of detections in 1992 compared to the 1990-91 period for dissolved Cr, Pb, Hg, and Zn, a result of lowered quantitation levels in 1992. Total-recoverable Cu, Pb, and Zn were detected less frequently and at lower concentrations in 1992, which may be attributed to the cleaner sample-collection methods used during that period. Precision in concentration data increased in 1992 for dissolved Cr and Cu, while concentration data exhibited a better relation with discharge in 1992 for total-recoverable Cu, Pb, and dissolved Cr, Cu, Pb, and Zn. High censoring (values below quantitation levels) in 1990-91 masked the concentration/discharge relation that later became evident with lower quantitation levels.

Because data were improved for a number of constituents in 1992, the validity of previously collected data for the fall line program was assessed. A general assessment of the validity of 1990-91 concentration data was made from observing the range in 1990-93 concentration data

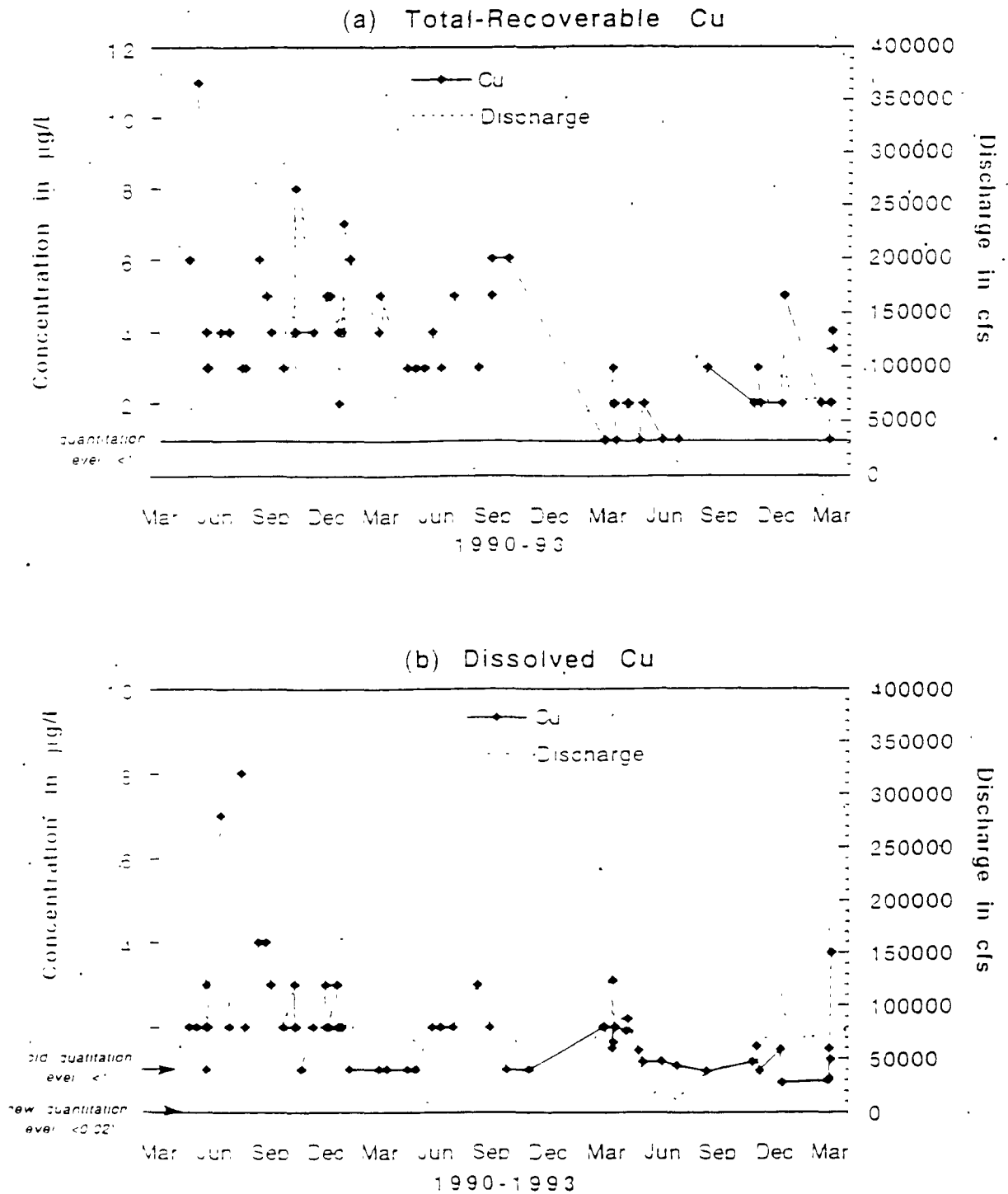
**Figure 40.** Boxplots showing (a) total recoverable and (b) dissolved chromium, copper, lead, and zinc concentrations during 1990-1992 at the Susquehanna River fall line station.



**Figure 41.** Concentration of (a) total recoverable and (b) dissolved chromium and instantaneous discharge for the Susquehanna River fall line station for the 1990-1992 sampling period.

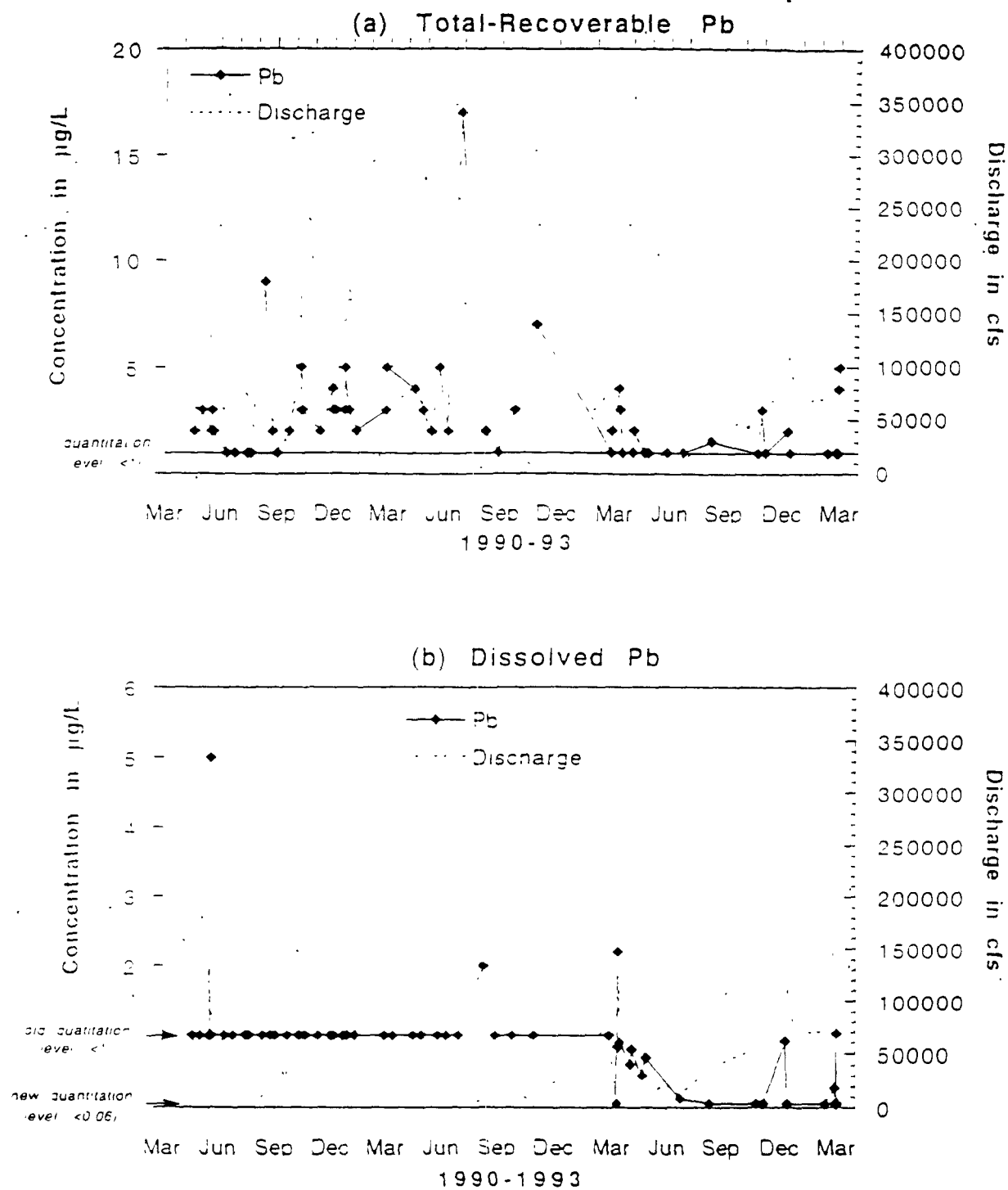


**Figure 42.** Concentration of (a) total recoverable and (b) dissolved copper and instantaneous discharge for the Susquehanna River fall line station for the 1990-1992 sampling period.

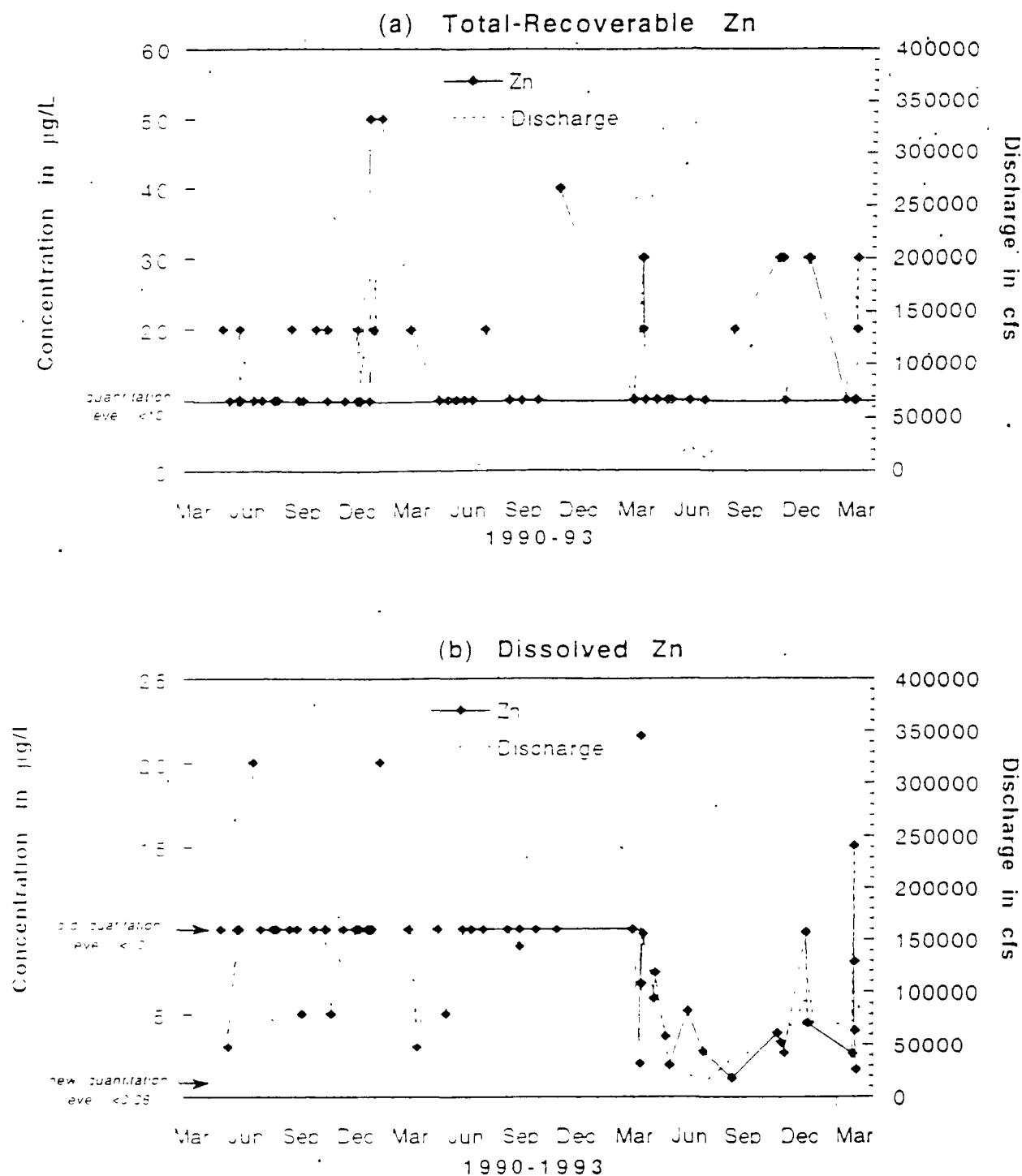




**Figure 43.** Concentration of (a) total recoverable and (b) dissolved lead and instantaneous discharge for the Susquehanna River fall line station for the 1990-1992 sampling period.



**Figure 44.** Concentration of (a) total recoverable and (b) dissolved zinc and instantaneous discharge for the Susquehanna River fall line station for the 1990-1992 sampling period.



(Figure 41-Figure 44). If the range in concentration data for a given constituent remained approximately the same throughout the three-year period and the 1992 data for that constituent was considered valid, data collected during 1990-91 was also considered valid. Additionally, if data collected during the 1990-91 period were all at or below quantitation levels, the data was considered valid. If, however, the range in concentration data for a given constituent exhibited a significant decrease in 1992, when ultra clean techniques were implemented, and the 1992 data for that constituent was considered valid, the quality of data collected in 1990-91 was considered suspect. Applying this criteria to constituents monitored throughout the 1990-91 period at the Susquehanna River station, valid concentration data was collected during 1990-91 for total-recoverable As, Cd, Cr, Pb, Hg, and dissolved As, Cd, Cr, Cu, Pb, Hg, and Zn are valid. Water quality data collected for total-recoverable Cu and Zn during the 1990-91 period is considered suspect.

Colloids and dissolved organic matter are expected to strongly influence metal concentration in the fluvial environment. Ratios of dissolved to total-recoverable metal concentration were higher than expected for many of the constituents monitored at the Susquehanna River station, including Cr, Cu, Pb, and Zn. Significance of the dissolved fraction may be related to the chemical or biotic conditions that exist within the reservoir (pH,  $E_H$ , dissolved oxygen, bacterial action). Reducing conditions, which exist at the bottom of the reservoir, where water is drawn by the turbines, affects sediment-bound metals by increasing their solubility in the water column. Limitations on the separation of colloiddally-sized particles, which are inherent to the filtration procedure, may also be a factor.

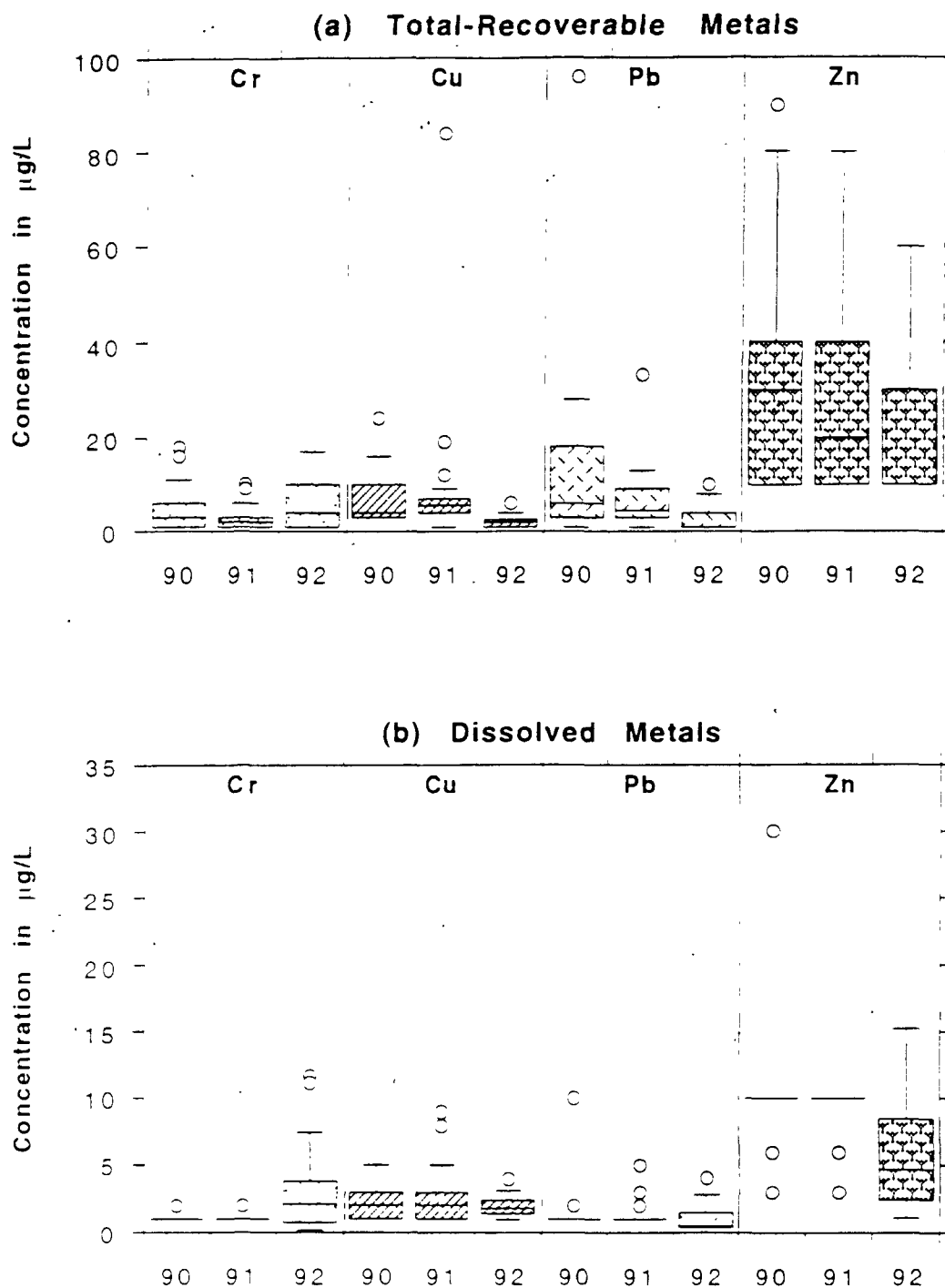
### **Water Quality Metal Data - James River**

Concentration data collected throughout the period 1990-92 are presented in Appendix B for the James River. Ranges of constituent concentration shown provide year to year comparisons for river samples. Figure 45 shows boxplots of selected constituent concentrations over the three-year period.

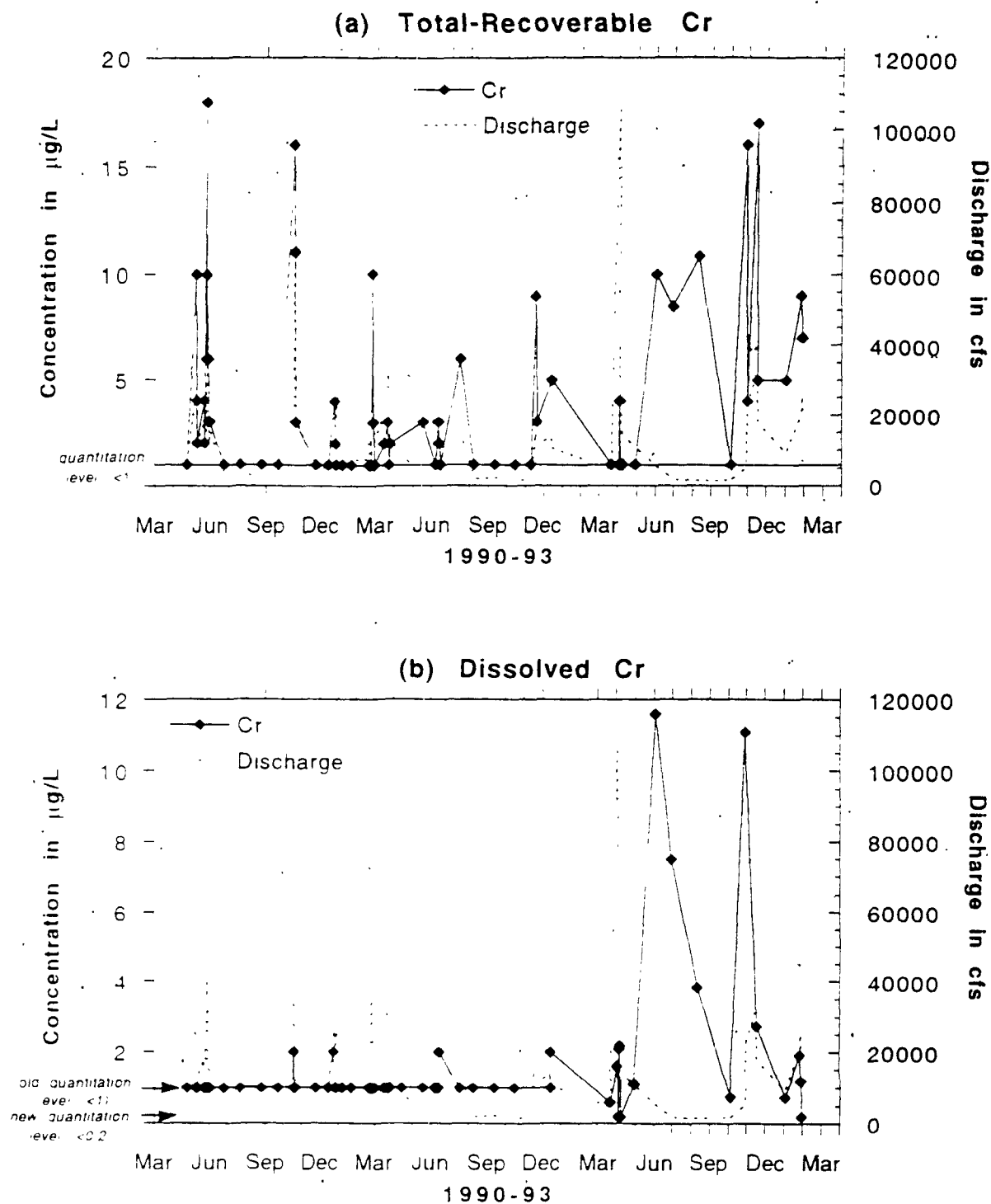
Figure 46-Figure 49 show the concentrations of selected metals in environmental samples over the three-year data collection period. The quantitation levels for 1990-91 and the new levels for 1992 are indicated on each graph for the dissolved species. The quantitation levels for total-recoverable metals did not change over the sampling period. The ultra clean sampling procedures and the lowered quantitation levels for 1992 significantly improved concentration data for some constituents. Concentration data were considered improved in 1992 if one or more of the following criteria were met: (1) if there were a greater number of detections of ambient concentration data, (2) if the range in concentration data decreased in 1992 or the precision was increased; and (3) if concentration data exhibited a better relation with discharge.

Based on these criteria, water quality data were improved in 1992 for total-recoverable As and and dissolved As, Cu, Pb, and Zn. Although dissolved Cr and Cd met one or more of these criteria, they were not considered improved in 1992 due to the suspect data quality. Also, although total-recoverable Pb and Zn did not meet the specific criteria above, plots of the data clearly show that for these constituents, improved quality of the data is shown by fewer detections of ambient concentration data as compared to previous data.

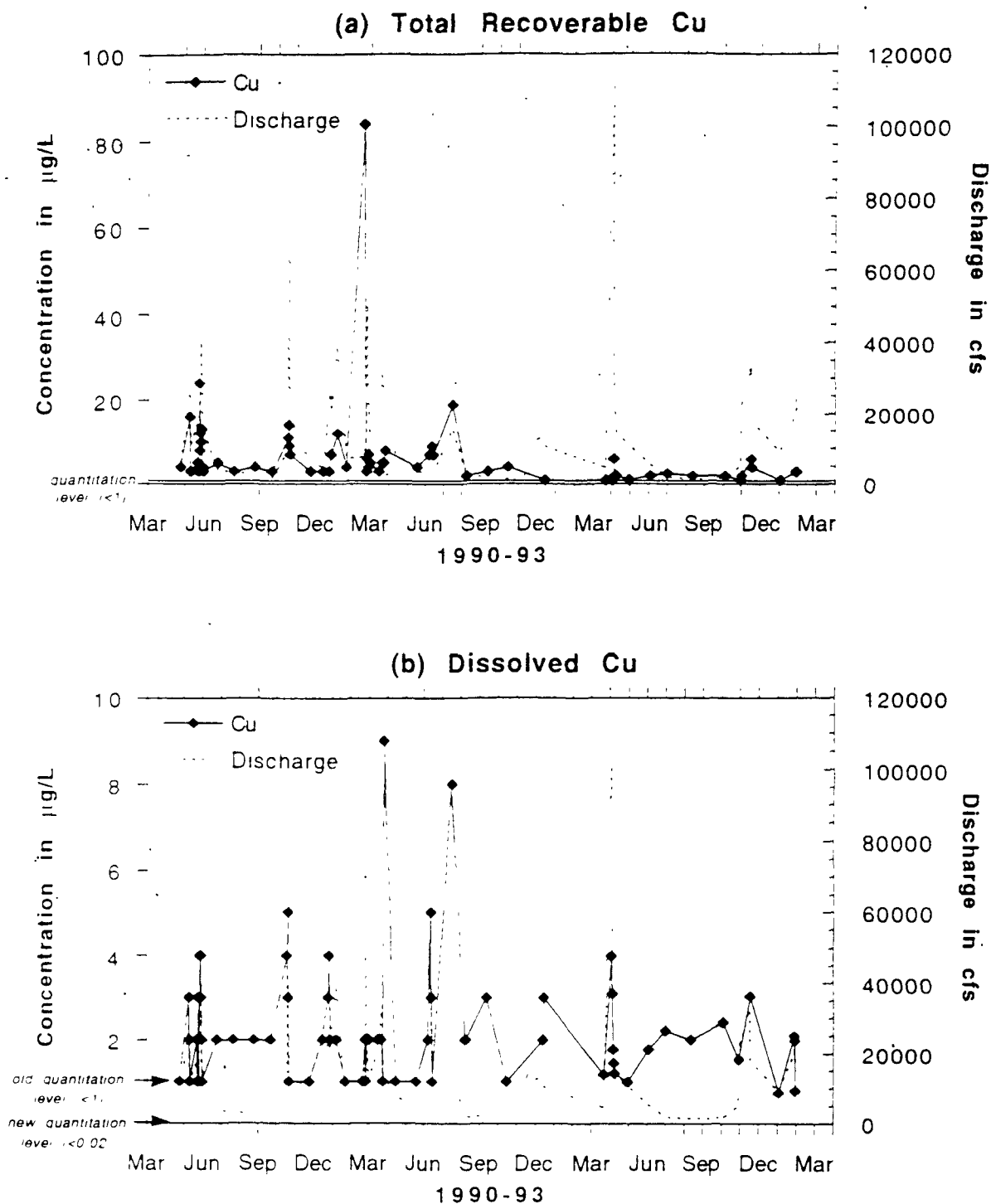
**Figure 45.** Boxplots showing (a) total recoverable and (b) dissolved chromium, copper, lead, and zinc concentrations during 1990-1992 at the James River fall line station.



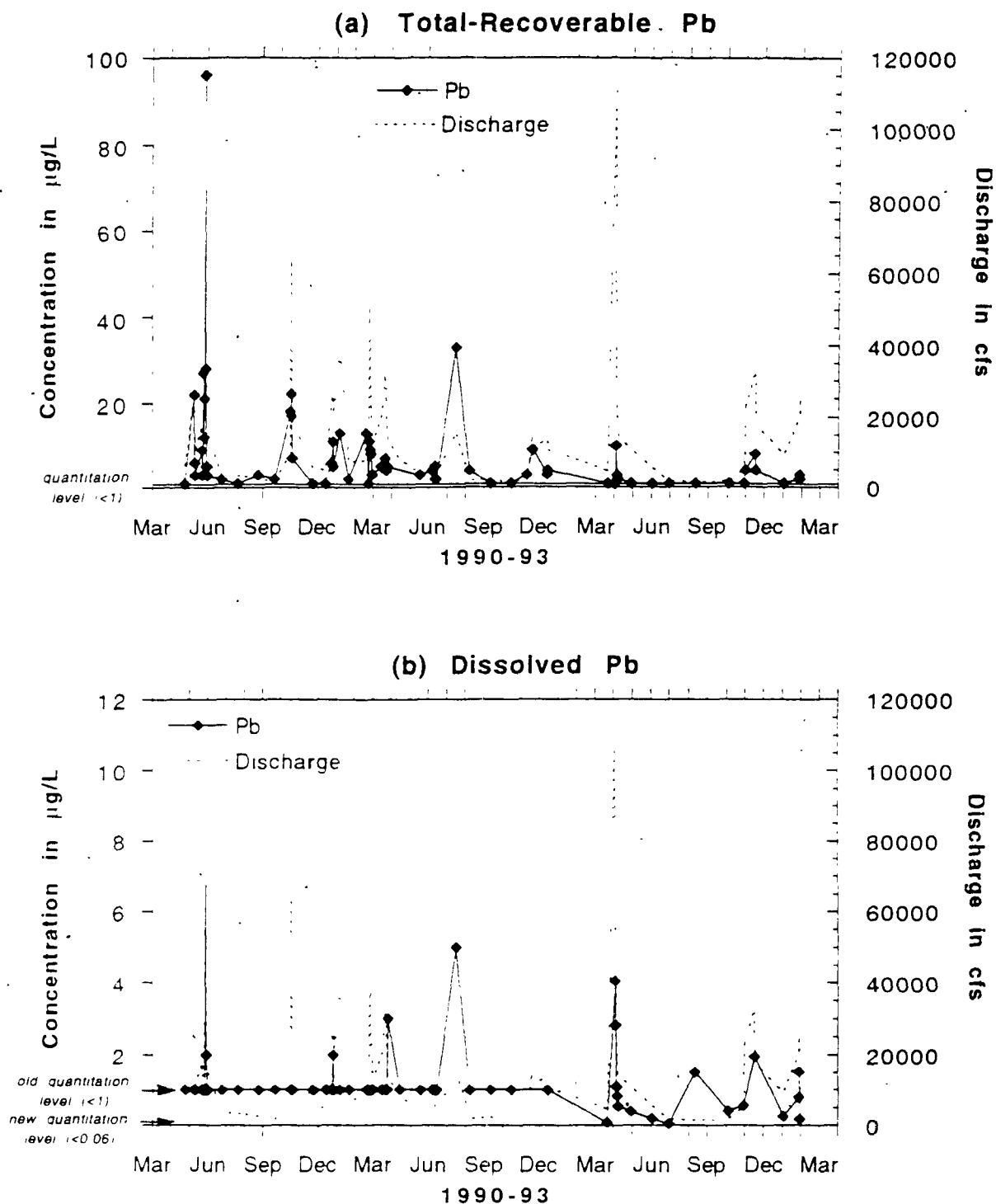
**Figure 46.** Concentration of (a) total recoverable and (b) dissolved chromium and instantaneous discharge for the James River fall line station for the 1990-1992 sampling period.



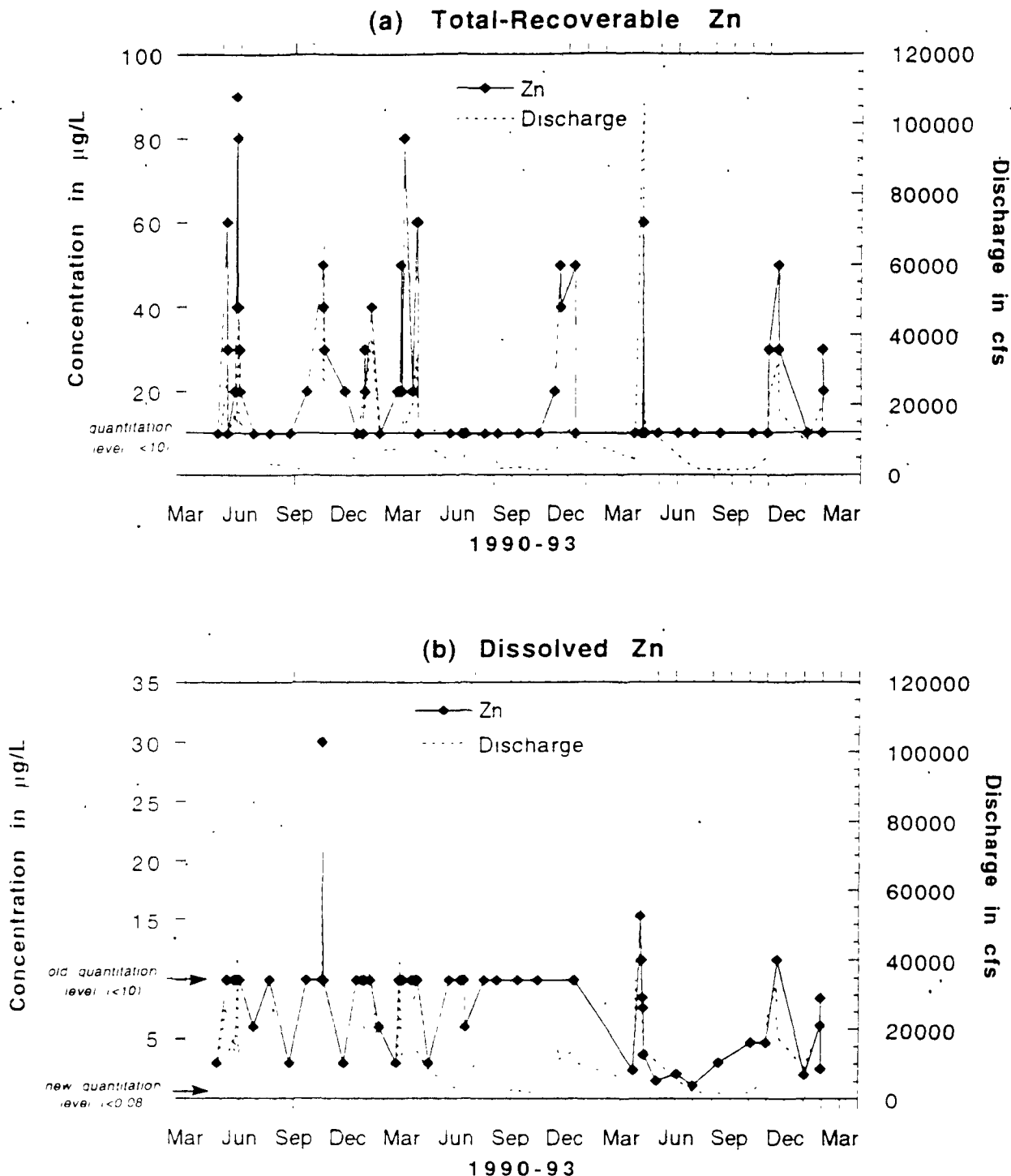
**Figure 47.** Concentration of (a) total recoverable and (b) dissolved copper and instantaneous discharge for the James River fall line station for the 1990-1992 sampling period.



**Figure 48.** Concentration of (a) total recoverable and (b) dissolved lead and instantaneous discharge for the James River fall line station for the 1990-1992 sampling period.



**Figure 49.** Concentration of (a) total recoverable and (b) dissolved zinc and instantaneous discharge for the James River fall line station for the 1990-1992 sampling period.





Generally, there was an increased percentage of detections in 1992 compared to the 1990-91 period for dissolved Cd, Cr, Cu, Pb, and Zn, due to the lowered quantitation levels in 1992. Total-recoverable Ar, Cu, Pb and Zn, were detected less frequently and at lower concentrations in 1992, which may be attributed to the cleaner sample-collection methods used during that period. Precision in concentration data increased in 1992 for dissolved As, Cr and Cu, and concentration data showed an improved relation with discharge in 1992 for dissolved Pb and Zn.

Because data were improved for a number of constituents in 1992, the validity of previously collected data for the Fall Line program was also assessed. A general assessment of the validity of 1990-91 data can be made by observing the changes in 1990-92 concentration data (Figure 46-Figure 49). If the range in concentration data for a given constituent remained approximately the same throughout the three-year period, and the 1992 data for that constituent are considered valid, it can be assumed that the data collected during 1990-91 is also valid. Additionally, if data collected during the 1990-91 period were all at or below quantitation levels, the data can be considered valid. If, however, the range in concentration data for a given constituent exhibits a significant decrease in 1992, and the 1992 data for that constituent are considered valid, the quality of the data collected in 1990-91 may be considered suspect. Applying these criteria to constituents monitored throughout the 1990-91 period at the James River station, it appears that concentration data collected during 1990-91 for total-recoverable As, Cd, Cr, Cu, and Zn, and dissolved As, Cd, Cu, Pb, and Zn are valid. Water quality data collected for total-recoverable Pb and dissolved Cr during 1991 are considered suspect.

### **Water Quality Metal Data - Potomac River**

While some preliminary conclusions can be drawn from the data, it should be recognized that these are based on a fairly limited dataset. Over the thirteen month sampling period, a total of twelve baseflow and nine stormflow samples were collected. Observations based on the data will therefore be subject to the caveat that the data may be extended in reaching certain conclusions, and that these may be invalidated after more data have been gathered.

#### *Relationships Between Discharge and Suspended Sediments and the Constituent Concentration*

As can be seen in Figure 28, the total flow in March 1993, was more than three times the total flow for the next highest months—March and December 1992. The Potomac River was in stormflow for 18 days during that month. The concentrations of most metals and total suspended solids rose substantially during stormflow (see Table 15). Although there was no general correlation between the magnitude of the stormflow and the concentration of the measured constituent, Cr and Zn concentrations rose during storms. The two storms of March 1993, March 5-11 and March 21-April 1, had average flows that were more than double the average flow of the April 21-29, 1992 storm. However, metal concentrations were higher for the April 21-29, 1992, storm than they were for the March 1993 storms.

It is also interesting to note that the storm of May 17-18, 1992, which had an average storm discharge of 314.0 m<sup>3</sup>/s, had similar concentrations of metals as had the baseflow samples collected when the baseflow was in the same range (baseflow samples of March 17, May 19, and June 16, all in 1992). This can be most clearly seen in the case of zinc. The average concentration of Zn during the storm of May 1992 was 20 µg/L, whereas that for the baseflow

sample of March 17, 1992 (flow of 444.9 m<sup>3</sup>/s) was 19 µg/L. and for the baseflow sample of May 19, 1992, (flow of 502.4 m<sup>3</sup>/s) was 19 µg/L. Such trends are also discernible when the storm of December 18-22, 1992 (average flow of 598.0 m<sup>3</sup>/s) is compared to the baseflow samples which were taken when the flow was in the same range (baseflow samples of May 19, 1992, and January 5, 1993). The storm of November 23-28, 1992 had significantly higher concentrations of Cr, Cu and Zn, even though the flow was in the same range (573.0 m<sup>3</sup>/s). Also, lower flows can result in higher concentrations—such as the Zn concentration of 25 µg/L observed for the baseflow sample of September 9, 1992, when the flow was 184.7 m<sup>3</sup>/s. Similar aspects are seen with respect to the other metals. It would, therefore, be premature to draw any conclusion regarding any relationship between the discharge and the constituent concentration. A statement can be made that it appears that the expected rise in constituent concentrations with a rise in flow is seen if the average flow during storms is significantly higher than the prevailing baseflow. With the limited data at hand, the basis for such a statement is quite tenuous. The relationship between higher flows and higher TSS values appears to be better supported.

## **Water Quality Organic Data - Susquehanna, James and Potomac Rivers**

### *Organonitrogen and Organophosphorus Pesticides*

All three rivers showed similar temporal patterns in the relative concentrations of the organonitrogen and organophosphorus pesticides measured during the March 1992 to February 1993 sampling period. The dominant pesticide in this group in fluvial transport was atrazine, followed by, in roughly descending abundance, metolachlor, cyanazine, simazine, prometon, alachlor, diazinon, and malathion. The magnitude of the fluvial sample concentrations varied with the source of water. Peak concentrations of atrazine, for example, varied from 255 ng/L in the Susquehanna River to 540 ng/L in the Potomac River to 58 ng/L in the James River (Appendix C).

Concentrations peaked in May (James River) or June (Susquehanna and Potomac Rivers), and the largest measured concentrations of the organonitrogen herbicides directly coincided with their period of field application which has been reported to occur from April to July (Pait et al. 1992). It appears that these pesticides are subject to maximal runoff during the spring flush from heavy rainfall. In addition, the peak concentrations of the organonitrogen herbicides in the fall line study correspond to a similar temporal trend observed for the fluvial transport of related herbicides in the Cedar River basin, Iowa, where peak concentrations were observed during June and early July (Squillace and Thurman 1992). The triazine herbicides, especially atrazine, simazine, and cyanazine, and chloracetanilide herbicides, especially metolachlor and alachlor, were the most commonly detected pesticides in this group.

The organophosphorus pesticides were rarely detected, and when present in the fluvial samples their concentrations were near the QL values. Organophosphorus pesticides typically have short half-lives in aquatic systems (Tinsley 1979, Lyman et al. 1990) are not expected to have extremely elevated concentrations in non-point source runoff especially if sampling occurs at locations remote from the area of field application.

Percent deviation values (calculated from replicate measurements as  $(rep_1 - rep_2)/[(rep_1 + rep_2)/2] \times 100$ ) from duplicate measurements of the organonitrogen and organophosphorus pesticides in

the same water source were quite high when measured concentrations were near the QLs (e.g., 200% for alachlor in the Potomac River), but were much lower when concentrations were above ca. 20 ng/L. Reproducibility appeared to be much better at the largest measured concentrations, especially when the measured concentrations were one to two orders of magnitude larger than the QL values. In fact, at concentrations above ca. 20 ng/L the %deviation values for the duplicate samples compared quite favorably with the indeterminate error values shown in Table 12.

The organonitrogen and organophosphorus pesticides were not analyzed in the particulate phase of the fluvial samples. The fractional composition of organic compounds in the suspended particulate phase in aquatic systems is governed by several variables, including the magnitude of particle/water partition coefficients, the amount of organic carbon associated with the particle phase, and the concentration of suspended particulates. Because the partition coefficients of the organonitrogen and organophosphorus pesticides are near or less than 1,000, the fractional composition of these pesticides in the particle phase is predicted to be less than 5% even for TSPs as large as 1,000 mg/L (Samiullah 1990). The particle phase is not important in the fluvial transport of monitored organonitrogen and organophosphorus pesticides.

#### *Organochlorine Compounds*

The organochlorine pesticide and PCB concentrations in both dissolved and particulate phase fluvial samples are shown for each river in Appendix C. Two storms were sampled in the Susquehanna River during the sampling period, and one each in the James and Potomac Rivers (although more storms occurred at the Potomac River). The concentrations of the organochlorine compounds were much lower than were the organonitrogen and organophosphorus pesticides in the same samples. Typical organochlorine concentrations in the fluvial samples, including dissolved and particulate phases, were in the 1-20 ng/L range. The organochlorine pesticides detected most often included aldrin, the chlordane isomers, and dieldrin.

The organochlorine pesticides did not appear to show the degree of temporal variability that was evident with the organonitrogen pesticides (e.g., atrazine). A determination of concentration dependency on river discharge for these analytes has not been made but correlations between flow and concentration are in progress. The concentrations of the organochlorine pesticides in the fluvial samples seemed to vary in a rather random way and no obvious pattern was evident, with the exception that for the James and Potomac Rivers the organochlorine pesticide concentrations were slightly larger in storm samples relative to baseflow samples. Most of the measured concentrations were within 2 to 10 times the respective QL values. More comprehensive determinations of the organochlorine pesticides in the fluvial samples will likely require the development of a method with QL's in the range of 0.01 ng/L, a full order of magnitude lower than those inherent in the present method.

Closer evaluation of the chlordane isomers, alpha- and gamma- isomers, showed that, generally, the alpha isomer tended to be the predominant form in the dissolved phase of the fluvial samples. There was no apparent trend of this kind in the particulate phase samples, although the concentrations of the two isomers appeared to be more similar in magnitude. The permethrins and fenvalerates were only detected in one sample, which was fenvalerate in the 20 May particulate phase for the James River (2.6 ng/L).

The PCB concentrations for both dissolved and particulate phases are also listed for the three rivers in dissolved and particulate phases in Appendix C. (The individual congener concentrations can be obtained from G.D. Foster at the Chemistry Department at George Mason University upon request.) Total PCB concentrations ( $\Sigma$ PCBs) typically ranged from 1-20 ng/L in both dissolved and particulate phases, but higher levels were observed throughout the sampling period in the Susquehanna River fluvial samples. The PCBs were observed commonly in both the dissolved and particulate phases, with larger concentrations appearing often in the particulate phase. This large fraction of the PCBs in the particulate phase reflects the large partition coefficients these contaminants have in freshwater systems.

#### *Polynuclear Aromatic Hydrocarbons*

The PAH concentrations in the fluvial samples are listed in Appendix C. The dissolved phase PAH concentrations showed no definite trend in concentrations throughout the March to September period, a pattern similar to the OC compounds. However, the particulate phase PAH concentrations were dramatically elevated during storm events for the three rivers. One explanation for this observation is that substantially more sediment was collected on filters during storm flow, thereby allowing lower quantitation levels in this matrix.

Naphthalene was the most prominent PAH detected in the dissolved phase samples, which correlates with the fact this compound has the highest water solubility of the PAH group. Furthermore, the prominence of all four PAH in the dissolved phase indirectly correlated with water solubilities; for example, benzo(a)pyrene was rarely detected in the dissolved phase and it has the lowest water solubility. In contrast, fluoranthene and benz(a)anthracene were frequently detected in the particulate phase of the fluvial samples. These two PAH have large enough octanol-water partition coefficients to thermodynamically favor partition into sediment materials with appreciable organic matter content. Interestingly, the highest concentrations of PAH detected in all of the collected fluvial samples occurred in James River March storm samples.

## **METAL AND ORGANIC LOADS DISCUSSION**

### **Metal Loads Discussion - Susquehanna River**

Water discharge has a significant effect on resulting load estimates for metals. Although the concentration of metals carried by suspended sediment may theoretically decrease during period of high discharge due to dilution by larger grain size sediments, the transport, or load, of metals will significantly increase. This is due to the large increase in water volume that occurs during storm events, which is capable of carrying a greater mass of sediment.

Susquehanna River load estimates for the 1990-92 sampling period are given in Table 40. Bar graph summaries of the maximum annual load estimates for 1990-92 are presented in Figure 50 for total-recoverable and dissolved Cr, Cu, Pb, and Zn.

The adoption of ultra clean sampling procedures and lowered quantitation levels in 1992 significantly improved load estimates for some constituents. Two criteria used to determine if load estimates for a particular constituent were improved included: (1) if concentration data for the constituent was improved in 1992 as a result of the ultra clean study; and/or (2) if the upper-bound load estimate for the constituent was minimized due to lower quantitation level in 1992. Based on these criteria, load estimates were improved in 1992 for total-recoverable Cu, Pb, Zn and dissolved As, Cd, Cu, Pb, and Zn. Load estimates were improved for total-recoverable Cu, Pb, and Zn, and dissolved Cu, Pb, and Zn based on improved data quality. Loads were improved for dissolved As, Cd, Pb, and Zn based on lower quantitation levels used in 1992. Although dissolved Cr and Hg met the above criteria, they were not considered improved in 1992 due to their suspect data quality.

Generally, the improvements in 1992 either lowered the quantitation level, thereby increasing the number of detections, and/or improved the analytical accuracy for a specific metal. Therefore, for these constituents, the ranges on the load estimates for 1992 are generally smaller and the estimates are presumed to be closer to the true values, than for the 1990-91 period. For example, loads for dissolved Zn in the 1990-91 period were based primarily on values determined as equal to or less than the quantitation level ( $<10 \mu\text{g/L}$ ) (Figure 50). The load estimates (Table 40) have a considerable range in values (216,000 to 912,000 and 225,600 to 601,400 kg/year) for 1990 and 1991, respectively, in comparison to 1992 when almost all of the measured concentrations for dissolved Zn were greater than the quantitation level and the range in load was reduced (234,000 to 373,000 kg/year).

Load estimates were improved for a number of constituents in 1992. The validity of 1990-91 load estimates was determined based on an assessment of the 1990-91 water quality data, discussed previously. Generally, results suggest that 1990-91 load estimates are considered valid for total-recoverable As, Cd, Cr, Pb, Hg and dissolved As, Cd, Cr, Cu, Pb, Hg, and Zn. Load estimates which may be considered suspect due to data quality include total-recoverable Cu and Zn. Load estimates for these constituents should be considered, at best, upward biased estimates of the true load.

**Table 40.** Range in Susquehanna River fall line load estimates for 1990 to 1992. Units are in thousands of kilograms per year. The modeling technique used to calculate each set of estimates is indicated.

Constituent	1990		1991		1992		Model
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	
Aluminum (DIS)	1,245	1,434	673.2	792.5	827.8	993.8	AMLE
Arsenic (DIS)	0	42.93	0	26.51	5.206	21.09	II
Arsenic (TR)	0	42.93	0	26.51	0	31.81	II
Cadmium (DIS)	0.193	42.93	18.96	26.51	1.610	4.661	II
Cadmium (TR)	0	42.93	0	26.51	0	31.81	II
Chromium (DIS)	5.994	44.25	4.589	26.51	43.41*	50.39*	II
Chromium (TR)	86.14	91.35	73.37	82.63	63.55*	74.43*	II
Copper (DIS)	101.7	119.9	45.27	54.38	43.07	49.94	AMLE
Copper (TR)	184.7*	224.2*	85.24*	105.4*	60.31	71.35	AMLE
Iron (DIS)	1,291	1,291	1,156	1,167	7,541*	7,553*	II
Iron (TR)	18,844	38,706	12,247	18,886	17,100	28,919	AMLE
Lead (DIS)	10.76	43.79	10.96	26.95	7.037	14.22	II
Lead (TR)	127.3	167.6	64.81	86.79	41.66	52.90	AMLE
Mercury (DIS)	0	4.293	1.238	3.270	0.843	0.843	II
Mercury (TR)	0.215	4.293	2.061	4.039	0.315	3.397	II
Nickel (DIS)	122.2	122.2	90.53	90.53	216.3	216.3	II
Nickel (TR)	223.3	277.9	139.0	170.6	146.7	190.4	AMLE
Zinc (DIS)	98.3	415.1	102.7	273.7	106.7	169.8	II
Zinc (TR)	580.13	775.9*	345.3*	473.2*	348.6	452.9	AMLE
Sus. Sediment	803,644	900,626	394,073	453,861	418,390	476,767	AMLE

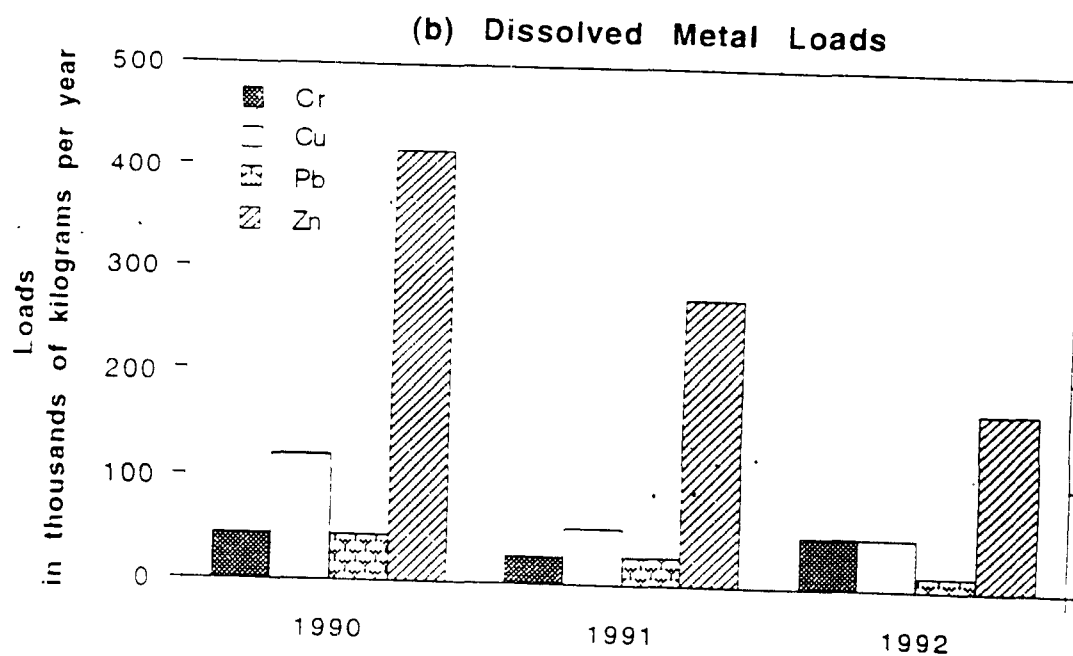
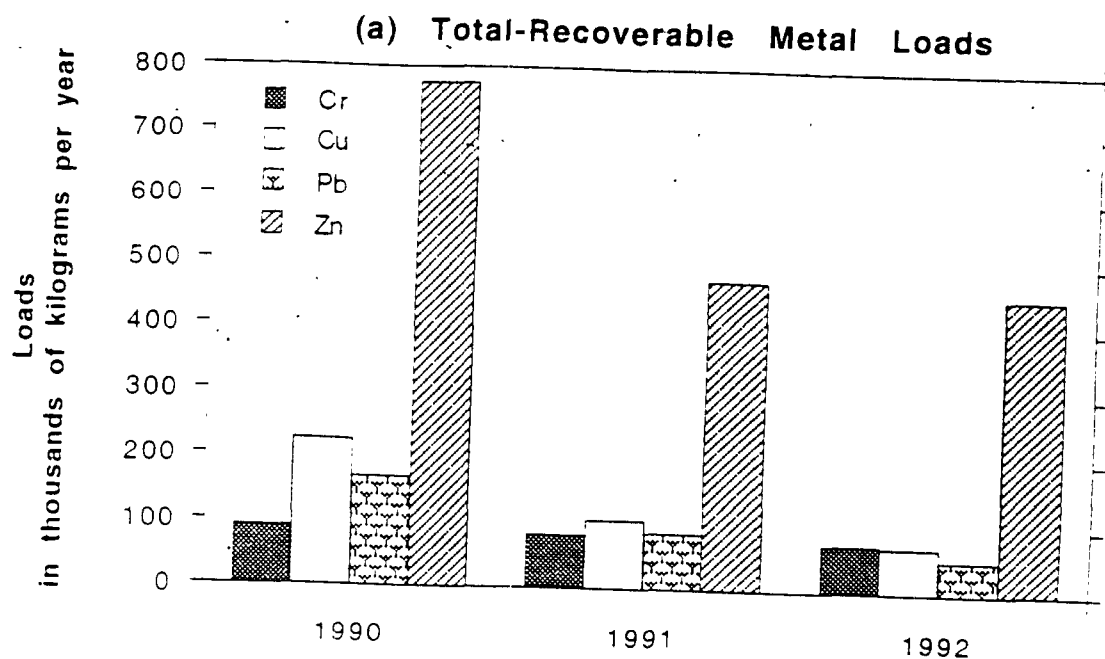
Notes: DIS = dissolved load

TR = total recoverable load

II = Interpolation - Integration model

\* = loads are suspect, based on quality assurance results

Figure 50. Annual loading estimates of (a) total recoverable and (b) dissolved chromium, copper, lead, and zinc during 1990-1992 at the Susquehanna River fall line station.



Greatest loads over the three-year period were observed in 1990, corresponding to the year of greatest discharge. Dissolved Cr, Ni, and Fe were the only exceptions, with their greatest transport occurring in 1992. Load estimates calculated for dissolved Cr and Fe were not considered valid, however, due to the suspect water quality data that was used to estimate them.

There are several limitations associated with estimating toxic constituent loads. First, calculating loads for metals is always difficult due to high censoring and multiple reporting limits within the data base. Second, due to high censoring, modeling of these constituents in terms of hydrologic variables such as discharge, or seasonality, is often impossible. Third, it is difficult to collect representative river samples for metals with concentrations in the parts per trillion range. As a result of the ultra clean study in 1992, error associated with these limitations has been significantly reduced, and load estimates have been improved.

### **Metal Loads Discussion - James River**

Load estimates for the James River for the 1990-92 sampling period are given in Table 41. Bar graph summaries of the maximum annual load estimates for 1990-92 are presented in Figure 51 for total-recoverable and dissolved Cr, Cu, Pb, and Zn.

The adoption of ultra clean sampling procedures and lowered quantitation levels in 1992 improved load estimates for some constituents. Two criteria used to determine if load estimates for a particular constituent were improved included: (1) whether concentration data for the constituent were improved in 1992 as a result of the ultra clean study; and/or (2) if the upper-bound load estimate for the constituent was minimized due to lower quantitation levels in 1992. Based on these criteria, load estimates were improved in 1992 for total-recoverable As, Cu, Pb and Zn, and dissolved As, Cd, Cr, Cu, Pb, and Zn. Although the quality of dissolved Cr and Cd data is considered suspect, based on the lower ranges of concentration values in 1992, the loads for these constituents were also improved.

Generally, the program changes in 1992 served to either lower the level of quantitation and/or improve the analytical accuracy for a specific constituent. Therefore, for these constituents, the ranges of load estimates for 1992 are generally smaller and the estimates are presumed to be closer to the true values than those for the 1990-91 period.

Because the load estimates were improved for a number of constituents in 1992, the validity of the 1990-91 load estimates must be determined. The validity of 1990-91 load estimates is based on an assessment of the 1990-91 water quality data discussed previously. Results suggest that 1990-91 load estimates are considered valid for total-recoverable As, Cd, Cu, Cr, Pb and Zn, and dissolved As, Cu, Pb, and Zn. Load estimates which may be considered suspect due to data quality include dissolved Cr and Cd. Load estimates for these constituents should be considered upwardly biased estimates of the true load.

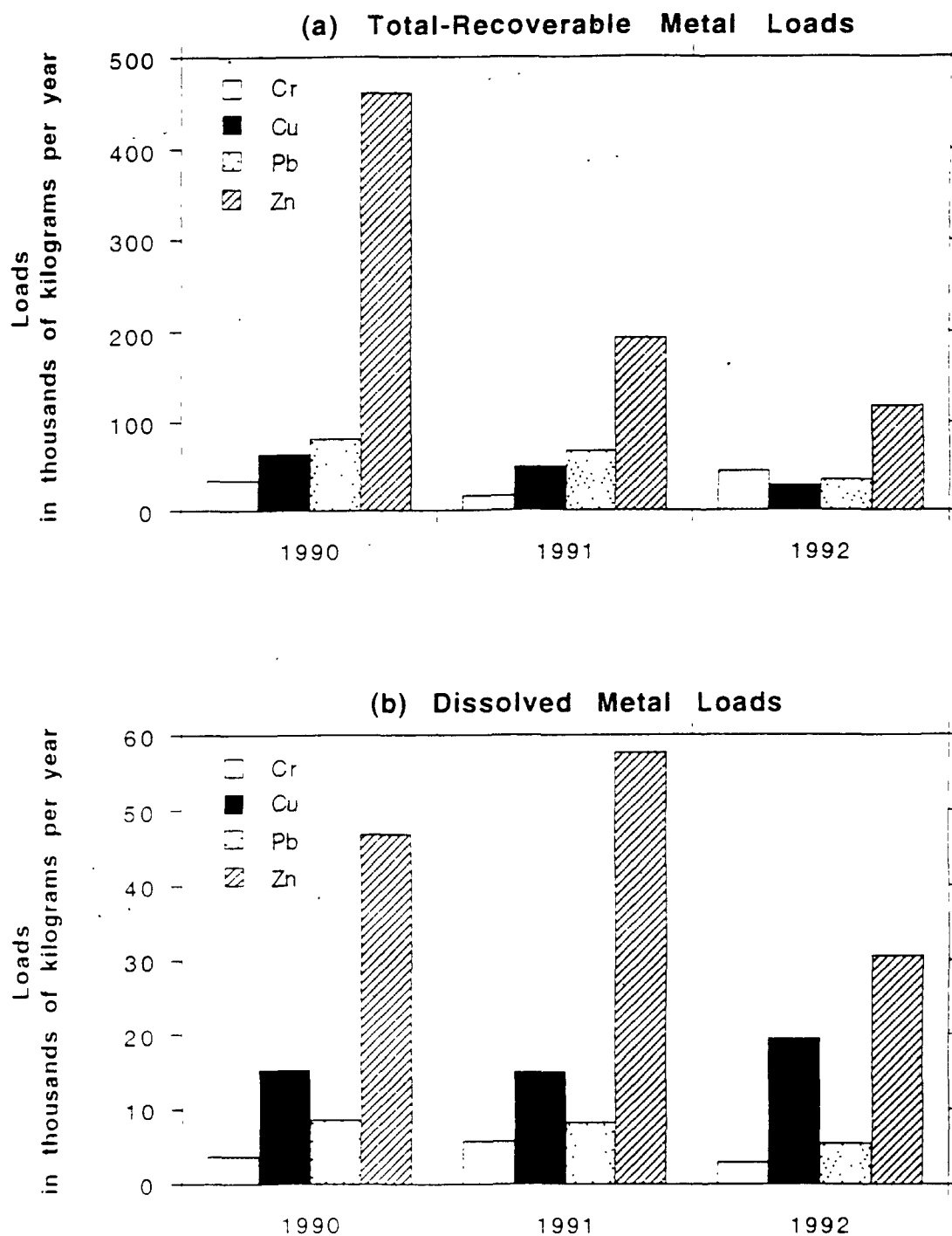


**Table 41.** Range in James River fall line load estimates for 1990 to 1992. Units are in thousands of kilograms per year. The modeling technique used to calculate each set of estimates is indicated.

Constituent	1990		1991		1992		Model
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	
Aluminum (DIS)	392	530	378	424	729	949	AMLE
Arsenic (DIS)	NM	NM	NM	NM	0	3.85	II
Arsenic (TR)	0	6.22	0	7.49	0	6.43	II
Cadmium (DIS)	NM	NM	NM	NM	.519	1.13	II
Cadmium (TR)	0	7.49	0	6.22	0	6.43	II
Chromium (DIS)	2.09	3.72	3.98	5.74	.84	3.04	AMLE
Chromium (TR)	22.3	34.2	12.6	16.5	30.7	44.2	AMLE
Copper (DIS)	11.8	15.4	12.5	15.2	11.8	19.6	AMLE
Copper (TR)	44.8	64.4	38.9	49.1	22.4	28.2	AMLE
Iron (DIS)	683	1290	868	1340	1490	1940	AMLE
Lead (DIS)	3.77	8.66	5.44	8.25	11.8	5.45	II
Lead (TR)	53.6	81.9	48.9	67.2	24.5	34.5	AMLE
Mercury	.008	.749	.006	.622	.024	.643	II
Nickel (DIS)	6.98	11.1	5.70	7.37	4.80	6.87	AMLE
Nickel (TR)	21.0	28.9	18.7	23.0	25.0	37.5	AMLE
Zinc (DIS)	6.63	46.9	6.09	57.7	30.7	30.7	II
Zinc (TR)	245	461	150	193	93.4	118	AMLE
Sus. Sediment:	576,000	700,000	465,000	554,000	669,000	892,000	AMLE

Notes: DIS = dissolved load  
 TR = total recoverable load  
 II = Interpolation - Integration model

**Figure 51.** Annual loading estimates of (a) total recoverable and (b) dissolved chromium, copper, lead, and zinc during 1990-1992 at the James River fall line station.



## **Metal Loads Discussion - Potomac River**

A general statement can be made about the metals loads and censored data. The greater the number of observations below the QL value for any metal, the larger the range of possible loads. However, the fact that in some cases there is only one value for the load does not imply that that value is a highly accurate estimate of the load. One should keep in mind that, although the loadings during storms can be estimated fairly accurately from the average flow-weighted storm concentration and the total stormflow (as has been done for this report), the loadings for baseflow are based on one baseflow sample analysis per month. The collection of fewer samples leads to a higher level of uncertainty associated with load computations. These limitations can be overcome by more frequent baseflow sampling, and/or a longer-term sampling effort wherein the average loadings over a period of years may give a better approximation of the true baseflow loadings.

*Arsenic:* As can be seen in Figure 31 and Table 22, the range of loads estimated for Arsenic is large. This is due to the fact that As was never detected above the QL in any of the samples (see Table 15). The uncertainty associated with the value of the constituent concentration, therefore, leads to larger ranges of possible loads. The low loading estimates are all zero, because to obtain these all values below the QL were set to zero. The high As loads expected varied between about 950 and 19300 kilograms (Kg) during the monitoring period. The total estimated load for As during the thirteen month period of the study ranged between 0 and 65200 Kg, with the lowest load occurring in October, 1992. Because As was never detected above the QL, the high loads reflect the flows for the months—small flows resulted in smaller loads, and the largest flow of March, 1993, resulted in the largest load.

*Cadmium:* Cadmium monthly loads (see Figure 32 and Table 23) have characteristics similar to those for As, because Cd, too, was not found above the QL in any sample. Because the QL for Cd is lower than that for As (initially 2 µg/L and later 1 µg/L, as opposed to 5 µg/L and 4 µg/L), the computed estimated loads were similarly lower. The lowest estimated high load occurred in October, 1992, and was 377 Kg, while the highest load of 4830 Kg was obtained in March, 1993. The total estimated load for the duration of the study ranged between 0 and 21600 Kg.

*Chromium:* For the most part, chromium estimated monthly loads ranged between 0 and 3600 Kg, except for the month of April, 1992, and March, 1993, where the estimated loads were 11234 and 24204 Kg, respectively (see Figure 33 and Table 24). Although the range bars appear shorter for Cr than they do for As and Cd, this is actually not the case and is due to the scale of the y-axes being different. In reality, the ranges (between the low and the high estimate) are comparable. The high April, 1992, load is due to a Cr concentration of 13.1 µg/L observed for an eight-day storm (April 21-29, 1992). The high March, 1993, load is due to two causes—a concentration of 13.2 µg/L for the storm of March 5-11, 1993, combined with high flows for both that storm and the one from March 21-April 1, 1993. The latter storm, even though it had Cr concentrations in the range of 1-3 µg/L, contributed a large load because of the total stormflow of  $2.4 \times 10^9$  m<sup>3</sup>. The month with the lowest load was, again, October, 1992. The months of April, 1992, and March, 1993, accounted for 66% of the total estimated high load. The total Cr load was in the range of 30600 to 53800 Kg.

*Copper:* The estimated load values for copper show the result of having most values above the

QL (see Figure 34 and Table 25). The estimated ranges show very small deviations between the low and high estimates, except for both the months of March. The high loads range from 400 to 7200 Kg, except for April, 1992, and March, 1993, when the loads were about 14300 and 25100 Kg, respectively. These loads accounted for 58% of the total load. The total copper load was in the range of 43500 to 67400 Kg.

*Nickel:* The estimated loads observed for nickel ranged from 0 to 17300 Kg (see Figure 35 and Table 26). Again, the months with high flows due to storms—April, 1992, and March, 1993—had much higher loads at 36400 and 57300 Kg, respectively. It should be noted that all observed values for Ni were below the QL, except for the value associated with the storm in April, 1992, which was 40 µg/L, and that for the storm of March 5-11, 1993, which was 22 µg/L. This was in spite of the fact that the QL for Ni was lowered from 12 to 8 µg/L in January, 1993. The April, 1992, estimated load was about 2.1 times higher than the highest estimated load for any other month, and the March, 1993, load was, similarly, about 3.3 times higher. It is clear that, just as for the other constituents, the April, 1992, and March, 1993, storms were responsible for a large part of the Ni loading to the Potomac during the course of the study. In fact, these two months accounted for 51% of the total load. The total estimated Ni loads ranged from 59900 to 184000 Kg.

*Lead.* Similar to the results seen with copper, the estimated loads for lead (Figure 36 and Table 27) had a narrower range for each month—except for March, 1992, and the December, 1992, to March, 1993, period—due to the greater number of values above the QL. The variability is greater than that for copper because there were more values below the QL than for copper. Again, the loads for April, 1992 (ranging between 8000 and 10000 Kg), and March, 1993 (ranging between 18600 and 32600 Kg), were greater than those for the other months. These loads constitute 51% of the total load. The estimated loads for September, 1992, are lower than those for August, 1992, although the average September flow was twice that of August. October, 1992, was again the month with the lowest load. The total estimated loads for lead ranged between 41100 and 82800 Kg.

*Selenium.* Selenium was not detected above the QL, and this is reflected in the low load estimates of zero for each month (see Figure 37 and Table 28). In fact, apart from the numerical value of the load estimates, the characteristics of the monthly loadings are similar to those for As and Cd, which were also not detected above the QL. The total loads ranged between 0 and 86400 Kg.

*Zinc* Along with copper and lead, zinc was detected most frequently (Table 15). For most months, with the exception of April, 1992 and March, 1993, the estimated loads ranged between 0 and 27400 Kg (see Figure 38 and Table 29). April, 1992, estimated loads were in the range of 55900 Kg, and March, 1993, loads were in the range of 139300 Kg. The total loads for Zn were from 268900 to 354200 Kg. The months of April, 1992, and March, 1993, contributed 55% of the total load during the period. A large portion of this was due to the storm average concentrations of 63 µg/L (April 21-29, 1992) and 56 µg/L (March 5-11, 1993).

### *Total Load Estimates*

Figure 39 and Table 30 present the total load estimates for the metals monitored. These load estimates are for the 12-month period of April, 1992, to March, 1993. It can be seen that the load for Zn was the highest, followed by that of Ni. The loading values for most of the other metals were relatively close to each other in the 50000 to 75000 Kg range. Cd had the lowest estimated load of 19000 Kg, and this was due to the fact that it was never detected; even when the QL was lowered from 2.0 to 1.0  $\mu\text{g/L}$ . Although the load for Ni was quite high, the uncertainty associated with the estimates was also the highest inasmuch as all observed concentrations, except two, were below the QL. The uncertainty in the estimate for Zn was somewhat less. The best estimate was obtained for copper, because only four measured concentrations, all baseflow, were below the QL (see Table 15). In most cases, except when all measured concentrations were below the QL (i.e., for As, Cd and Se), the storms of April 21-29, 1992, and those of March 5-11 and March 21-April 1, 1993, contributed a large fraction of the total load for the metal. This fraction ranged from 51 to 66%. This may perhaps indicate that, although it is important to perform more frequent baseflow sampling, the greater degree of accuracy obtained in estimating the loads may not have much effect on the total loads because of the overwhelming nature of the loads that occur during large storms.

### **Organic Loads Discussion - Susquehanna, James and Potomac Rivers**

Estimates of monthly pesticide, PCB and PAH loads for each tributary in the fall line study are listed in Table 31-Table 39. The monthly loads were estimated separately for the dissolved and particulate phases. Estimated loads in these tables were calculated from both the maximum and minimum daily fluxes summed for each month providing maximum and minimum load estimates. Zero loads represent minimum values that were calculated assuming that there was no existing level (i.e., 0 ng/L) of contaminant in the fluvial sample when the measured value was <QL values, and this approach probably provides underestimates the actual amount in fluvial transport. Conversely, the maximum loads were calculated using the QL value when the fluvial constituent concentrations were below QLs, likely providing an overestimate of the monthly loads. Therefore, the actual load probably lies somewhere between these two estimates. The most accurate load estimates exist when the maximum and minimum loads are identical or are very close in magnitude, because this indicates that the particular constituent was detected in nearly every fluvial sample analyzed.

For the organonitrogen and organophosphorus pesticides, maximum and minimum loads were nearly identical for atrazine, metolachlor, cyanazine, and simazine for each month, while prometon, hexazinone, alachlor, diazinon, malathion monthly maximum and minimum loads varied more substantially. For the organochlorine group, the PCBs, aldrin, the chlordanes, and dieldrin provided the most accurate load estimates as shown in Table 31-Table 39. DDT, the permethrins, and the fenvalerates alternatively nearly always had zero minimum estimated monthly loads, indicating that the greatest errors in load estimations exist for these compounds. The DDT, permethrin, and fenvalerate concentrations in river water are quite low.

The temporal variations in monthly loads of the organonitrogen and organophosphorus pesticides were different for the three rivers. For example, the greatest monthly loads occurred during June for the Susquehanna and Potomac Rivers, while in contrast the greatest monthly loads of the

same compounds occurred in April for the James River. James River loads appeared to be more discharge dominated than the other rivers, possibly because lesser amounts of these pesticides are used in the basin relative to the other river basins. The concentrations of these pesticides were the lowest in the James River fluvial samples. The maximum monthly loads for the Susquehanna and Potomac Rivers occurred during the period of heaviest pesticide application.

The organochlorine compound loads had a different temporal profile than the organonitrogen and organophosphorus compounds in some instances. In the Susquehanna River, the greatest loads occurred in April for both the dissolved and particulate phases showing dominance to flow and are contrasted to the organonitrogen and organophosphorus loads in this river. The organochlorine compounds are not intentionally applied in basin and loads appeared to be discharge dominated. However, in contrast to this trend the PCB loads were the greatest during June, July, and August. In the Potomac River, the organochlorine loads were the greatest during June, similar to the pattern shown for the organonitrogen and organophosphorus pesticides. Discharge in the Potomac River was as high in June as it was during the spring months of March and April. In the James River, the organochlorine and organonitrogen loads were both at the highest levels during April due to the coincidence of the highest discharge in the river.

Loadings of the organochlorine pesticides were seldom greater than 1 kg/month, with the exception May and June loadings. Both the particulate and dissolved phases are important in the fluvial transport of the organochlorine pesticides. The permethrins, fenvalerates, and 4,4'-DDT were not detected in any of the fluvial samples from the fall line study, and consequently there was no estimated loading for each. Zero monthly loads were much more common for the organochlorine compounds than for the organonitrogen and phosphorus pesticides.

PCB loadings in the Potomac River were higher in the spring and early summer than in late summer. Unlike the organonitrogen and organochlorine pesticides, PCB loadings were the largest in March, especially in the particulate phase of the fluvial samples.

PAH loadings were the highest during the spring months and during storm events. Naphthalene was the predominant PAH in the dissolved phase load while fluoranthene and benz(a)anthracene were the predominant PAHs in the particulate phase load for all of the fall line locations.

## **RECOMMENDATIONS**

### **Metals Program**

Several pieces of information must still be obtained to further understand the nature and transport of toxic substances entering the Chesapeake Bay from its major tributaries. Future fall line toxics monitoring programs must include: (1) improved Susquehanna River Potomac and James load estimates, given their potential impact on Bay water quality; (2) determination of the impact that "total", "total-recoverable" and "dissolved" concentration has on load estimates; (3) determination of the concentration of toxic chemicals in Susquehanna River bed sediments, behind Conowingo Dam, that will be transported during major storm events, and; (4) determination of the toxic loadings from Bay watersheds with different land uses.

Load estimates calculated for the Susquehanna River must continue to be improved given their potential impact on Bay water quality. The Susquehanna River contributes an average of 50 percent of the freshwater inflow to the Chesapeake Bay annually. A long-term record of water quality data is needed to continue to refine the load estimates. The information may also prove useful in the future for calibration of the Chesapeake Bay Watershed Model and, hence, for prediction of the future environment of the Bay.

An initial comparison of total versus total-recoverable metal concentration was made in 1992 at the Susquehanna River station. "Total" refers to the complete dissolution of metals associated with sediment in a water sample. "Total-recoverable" concentration refers to the acid-extractable fraction of metals associated with sediment in a water sample. This initial study revealed that constituents previously undetected using total-recoverable analysis can be detected in ambient concentration using total analysis. These results suggest that monitoring of the total concentration of metals would provide a means of estimating loads for previously undetected toxic constituents and that load estimates could be compared to varying sources (atmospheric, point source). However, the value of assessing non-labile fractions may be questionable. As well as assessing the impact that total versus total-recoverable concentration has on load estimates, the impact dissolved concentration has on load estimates must also be assessed. The dissolved fraction represents a large portion of the total metal in a water sample for many constituents at the Susquehanna River station. Because the dissolved fraction is readily available to the biota, it poses great concern with regard to loading estimates.

Continued monitoring of the Susquehanna River should include analysis of metals from bottom sediment. Bottom sediments can act as a reservoir for many metals and must, therefore, be given serious consideration. High flow conditions during large storm events (>400,000 cubic feet per second) at the Susquehanna River station cause scour behind Conowingo Dam, thereby transporting toxic-laden sediments to the Bay. As well as providing an historical record of chemical conditions, the concentration of metals in the bottom sediments can provide essential information on the transport of suspended sediment during major storm events.

The Potomac River at Chain Bridge offers some unique characteristics (well-mixed, narrow channel) that allow for effective automated sampling of the flow in a cost-efficient manner.

The initial phase of monitoring at Chain Bridge on the Potomac has been beneficial in allowing for the estimation of loadings. However, the question of annual loadings, complicated by variabilities from year to year, cannot yet be answered satisfactorily. It is recommended that baseflow monitoring continue, perhaps on a more-frequent basis (say, twice to four times per month), for another one to two years (for a total of two to three years). Following that, the baseflow can be monitored less frequently. However, an effort should be made to monitor all storm events, especially the larger ones, because a disproportionate fraction of the total load in any time period is due to large storms. It is felt that this recommendation will make more prudent use of limited funds.

The 1990-1992 study has provided information needed to refine the network design for future fall line toxic monitoring studies, including adoption of ultra clean sample-collection techniques and development of the toxics-loading model. Results suggest that a minimum of two years of water quality monitoring (60 water quality samples) throughout a range of flow conditions is necessary to characterize constituent concentration and to estimate toxic constituent loads. This implies that fall line toxics monitoring can be extended to other Bay tributaries, with varying landuse, for a two-year period. Upon completion of the monitoring period, characterization of constituent concentration and calculation of toxic loadings to the Bay can be provided. Additionally, if future needs include the assessment of trends that may have developed in response to toxic-reduction strategies established within the Bay basin, a second term of two-year monitoring can be conducted to subsequently assess trends.

A tributary that would provide valuable information regarding toxic inputs from Bay basins of varying land use would be the Patuxent River. Land use in the Patuxent River is rapidly becoming urbanized. Additionally, the basin is contained entirely within Maryland so the impact of controls imposed by the state can be directly assessed. The Patuxent River has an extensive historical data base which includes water quality data for nutrients, dissolved metals, and suspended sediment.

### **Organics Program**

Annual loadings of selected organic contaminants from the fall lines of major tributaries of Chesapeake Bay have been determined, and comparisons can be made among the pathways of contaminant fluxes in Chesapeake Bay. However, the present loading estimates from fluvial transport are burdened by sizable uncertainties. Individual recommendations are listed below:

(1) Include all tributaries of the Bay (approximately nine) in the fall line toxics monitoring program. Although fluxes have been determined for three of the Bay's largest tributaries, differences in land use could substantially impact flux estimates (in kg/yr/km<sup>2</sup>), providing systematic errors in the determination of annual budgets. All of the tributaries could be incorporated through a rotational basis, focusing on one or two tributaries per year. The present synoptic approach, which includes all the tributaries, does not use the same load estimation techniques, therefore systematic variations in the estimation of annual loads will be inherent.

(2) Streamline sampling and analysis. To help lower the cost of conducting low detection limit analyses, fewer samples will need to be collected for organics analysis. Detection limits continue to decrease, and the feasibility of collecting 60 samples per year for analysis is diminishing.



Streamlining can be accomplished in several ways:

- (a) continuous sampling devices should be tested such as the automated sampler at Chain Bridge on the Potomac River,
- (b) semipermeable membrane devices which are deployable in situ to sample dissolved phase constituents, and
- (c) continuous samples could provide time integrated composite samples, minimizing short-term variability in constituent concentrations.

(3) Determine temporal variability in constituent concentrations. Sampling is conducted twice per month, and temporal variability has never been defined. Temporal variability could be factored into loading computations to provide more accurate load estimates.

(4) Invest efforts to determine linear free energy relationships that exist between dissolved and particulate phase constituent concentrations. This predictive tool could be used to minimize the number of phases that need to be subjected to analysis, because, for example, particulate phase concentrations could be estimated given dissolved phase concentrations. This would be extremely valuable in conjunction with number 2(b) above.

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## **APPENDICES**

Appendix A: Susquehanna River water quality data: January 1990-March 1993

Appendix B: James River water quality data: January 1990-December 1993

Appendix C: Susquehanna, James, and Potomac Rivers concentration data for monitored organic contaminants

## APPENDIX A

## SUSQUEHANNA R AT CONOWINGO, MD

## WATER QUALITY DATA, CALENDAR YEAR JANUARY 1990 TO DECEMBER 1990

DATE	TIME	DIS- CHARGE, INST CUBIC FEET PER SECOND	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- ITY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE LAB (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER WHOLE FIELD (STAND- ARD UNITS)
APR 20...	1200	62200	12.0	17.0	775	--	173	160	11.2	7.2
* 20...	1205	62200	12.0	17.0	775	--	173	--	11.2	7.2
MAY 03...	1330	61100	17.0	14.0	--	8.1	--	220	7.9	7.3
08...	1330	133000	18.0	24.0	759	--	185	179	9.2	7.0
19...	1230	89600	24.0	24.0	--	--	169	156	6.5	6.1
20...	1530	89000	20.5	22.0	--	--	--	149	--	6.4
21...	1230	87900	17.0	19.0	760	--	157	152	9.3	6.8
23...	1200	88600	18.5	20.0	--	--	170	168	9.6	7.1
JUN 13...	1230	52600	23.0	25.0	769	--	237	232	7.7	6.7
27...	1125	48300	25.0	28.0	764	7.2	265	265	6.7	7.2
JUL 18...	1135	79000	24.0	28.0	770	--	250	246	7.3	6.9
25...	1200	52800	27.0	28.0	768	--	186	189	6.6	7.0
AUG 16...	1130	6400	27.5	28.0	--	--	270	268	6.7	7.1
29...	1200	53000	25.0	28.0	758	--	283	282	7.6	6.9
SEP 06...	1100	41000	26.0	28.0	764	2.2	267	250	6.9	7.0
26...	0945	28000	18.0	28.0	760	--	283	277	6.9	7.1
* 26...	0950	26000	18.0	19.0	760	--	283	--	6.9	7.1
OCT 15...	1300	174000	22.0	23.0	--	--	153	168	--	--
16...	1400	125000	19.0	19.0	771	--	162	164	8.4	6.8
26...	1300	128300	19.0	19.0	772	--	185	186	6.9	6.8
26...	1330	257000	19.0	19.0	760	38	136	128	6.9	6.5
NOV 15...	1210	97600	7.0	7.0	773	--	175	164	13.5	6.9
DEC 06...	1135	164000	7.0	17.0	765	--	220	208	14.0	6.8
07...	1140	131000	6.0	14.0	768	--	155	156	13.6	6.7
12...	1130	79400	6.0	16.0	768	--	175	163	13.6	6.9
26...	1200	147000	6.0	13.0	778	--	163	156	13.6	6.9
27...	1200	143000	5.0	2.0	786	--	148	146	13.6	6.9

DATE	PH WATER WHOLE LAB (STAND- ARD UNITS)	ALKA- LITY WAT WH TOT FE MG/L AS CACO3	ALKA- LITY WAT DIS TOT FE MG/L AS CACO3	ALKA- LITY LAB (MG/L AS CACO3)	SEDI- MENT. DIS- CHARGE, SUS- PENDED (MG/L)	SEDI- MENT. DIS- CHARGE, SUS- PENDED (T/DAY)	SED. SUSP. SIEVE DIAM. % FINER 0.062 MM	ALUM- INUM. DIS- SOLVED (UG/L AS AL)	ARSENIC DIS- SOLVED (UG/L AS AS)	ARSENIC TOTAL (UG/L AS AS)
APR 20	7.9	30	--	29	15	2520	--	30	--	<1
20	--	30	--	--	--	--	--	40	--	<1
MAY 03	7.4	7	47	42	13	2150	79	40	<1	--
08	7.4	36	--	35	15	5370	98	50	--	--
19	7.1	51	--	32	18	4360	87	20	--	<1
20	7.1	--	--	30	37	8890	100	40	--	<1
21	7.0	27	--	27	23	5460	--	30	--	<1
24	7.8	31	--	29	15	3590	98	20	--	<1
JUN 13	7.9	50	--	50	10	1420	100	60	--	<1
27	7.8	51	--	49	11	1430	97	30	--	<1
JUL 18	7.7	40	--	38	12	2560	100	30	--	<1
25	7.5	34	--	32	10	1430	92	30	--	<1
AUG 16	7.3	46	--	47	3	138	92	40	--	<1
29	7.5	44	--	51	3	1140	96	30	--	<1
SEP 06	7.3	45	--	43	5	553	98	20	<1	<1
26	7.3	45	--	45	20	1510	86	30	--	<1
26	--	45	--	--	--	--	--	20	--	<1
OCT 15	7.5	--	--	30	47	22100	99	50	--	<1
16	7.5	28	--	28	39	13100	99	30	--	<1
17	7.3	35	--	36	33	4860	98	20	--	<1
26	7.4	31	29	28	76	52700	99	50	1	--
NOV 15	7.5	37	--	34	34	8960	98	50	--	<1
DEC 06	7.7	47	--	44	33	14600	97	50	--	<1
07	7.5	33	--	30	39	13700	99	30	--	<1
12	7.5	35	--	31	12	2570	98	30	--	<1
26	7.7	38	--	33	40	15900	98	70	--	<1
27	8.0	32	--	30	30	11600	98	60	--	<1

\* Duplicate samples collected for quality-assurance purposes.

## APPENDIX A...Continued

## SUSQUEHANNA R AT CONOWINGO, MD

## WATER QUALITY DATA, CALENDAR YEAR JANUARY 1990 TO DECEMBER 1990

DATE	CADMIUM DIS- SOLVED (UG/L AS CD)	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD)	CHRO- MIUM, DIS- SOLVED (UG/L AS CR)	CHRO- MIUM, TOTAL RECOV- ERABLE (UG/L AS CR)	COPPER, DIS- SOLVED (UG/L AS CU)	COPPER, TOTAL RECOV- ERABLE (UG/L AS CU)	IRON, DIS- SOLVED (UG/L AS FE)	LEAD, DIS- SOLVED (UG/L AS PB)	LEAD, TOTAL RECOV- ERABLE (UG/L AS PB)
APR 20	--	<1	<1	2	2	6	--	<1	2
20	--	<1	<1	2	2	6	--	<1	2
MAY 03	<1.0	<1	1	2	2	11	11	<1	2
18	--	<1	<1	2	2	6	--	<1	2
19	--	<1	<1	1	2	6	--	<1	2
20	--	<1	<1	4	2	6	--	<1	2
21	--	<1	<1	2	2	6	--	<1	2
23	--	<1	<1	<1	2	6	--	<1	2
JUN 13	--	<1	<1	2	2	6	--	<1	2
27	--	<1	<1	<1	2	6	--	<1	2
JUL 18	--	<1	<1	<1	2	6	--	<1	2
25	--	<1	<1	<1	2	6	--	<1	2
AUG 16	--	<1	<1	10	2	6	--	<1	2
29	--	<1	<1	<1	2	6	--	<1	2
SEP 06	<1.0	<1	<1	5	2	6	5	<1	2
26	--	<1	<1	2	2	6	--	<1	2
26	--	<1	<1	2	2	6	--	<1	2
OCT 15	--	<1	<1	--	2	6	--	<1	2
15	--	<1	<1	--	2	6	--	<1	2
19	--	<1	<1	--	2	6	--	<1	2
26	<1.0	--	<1	--	2	6	67	<1	2
NOV 15	--	<1	<1	2	2	6	--	<1	2
DEC 06	--	<1	<1	2	2	6	--	<1	2
07	--	<1	<1	2	2	6	--	<1	2
12	--	<1	<1	2	2	6	--	<1	2
26	--	<1	<1	2	2	6	--	<1	2
27	--	<1	<1	2	2	6	--	<1	2

DATE	MERCURY DIS- SOLVED (UG/L AS HG)	MERCURY TOTAL RECOV- ERABLE (UG/L AS HG)	NICKEL, DIS- SOLVED (UG/L AS NI)	NICKEL, TOTAL RECOV- ERABLE (UG/L AS NI)	SELE- NIUM, TOTAL (UG/L AS SE)	SILVER, TOTAL RECOV- ERABLE (UG/L AS AG)	ZINC, DIS- SOLVED (UG/L AS ZN)	ZINC, TOTAL RECOV- ERABLE (UG/L AS ZN)
APR 20	--	<0.10	3	5	<1	<1	<10	20
20	--	<0.10	3	5	<1	<1	<10	20
MAY 03	<0.1	<0.10	3	5	--	<1	<10	20
18	--	<0.10	3	5	<1	<1	<10	20
19	--	<0.10	3	5	<1	<1	<10	20
20	--	<0.10	3	5	<1	<1	<10	20
21	--	<0.10	3	5	<1	<1	<10	20
23	--	<0.10	3	5	<1	<1	<10	20
JUN 13	--	<0.10	2	3	<1	<1	<10	20
27	--	<0.10	2	3	<1	<1	<10	20
JUL 18	--	<0.10	3	5	<1	<1	<10	20
25	--	<0.10	3	5	<1	<1	<10	20
AUG 16	--	<0.10	3	5	<1	<1	<10	20
29	--	<0.10	3	5	<1	<1	<10	20
SEP 06	--	<0.10	3	7	<1	<1	<10	20
26	--	<0.10	3	7	<1	<1	<10	20
26	--	<0.10	3	7	<1	<1	<10	20
OCT 15	--	<0.10	5	--	<1	<1	<10	--
15	--	<0.10	5	--	<1	<1	<10	--
19	--	<0.10	3	7	<1	<1	<10	20
26	<0.1	--	3	7	--	<1	<10	20
NOV 15	--	<0.10	4	6	<1	<1	<10	<10
DEC 06	--	<0.10	4	7	<1	<1	<10	20
07	--	<0.10	4	7	<1	<1	<10	20
12	--	<0.10	4	7	<1	<1	<10	20
26	--	<0.10	4	8	<1	<1	<10	20
27	--	<0.10	4	8	<1	<1	<10	20

## APPENDIX A...Continued

## SUSQUEHANNA R AT CONOWINGO, MD

## WATER QUALITY DATA, CALENDAR YEAR JANUARY 1991 TO DECEMBER 1991

DATE	TIME	DIS-CHARGE, INST. CUBIC FEET PER SECOND	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- ITY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE LAB (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER WHOLE FIELD (STAND- ARD UNITS)	PH WATER WHOLE LAB (STAND- ARD UNITS)
JAN											
02...	1230	169000	4.0	10.0	773	--	192	178	14.3	7.4	8.2
03...	1110	181000	4.0	12.0	774	--	161	153	14.2	6.8	7.4
15...	1100	55300	3.0	12.0	771	3.6	260	247	14.0	6.9	8.3
MAR											
06...	1200	233000	8.0	18.0	756	--	215	201	12.2	7.1	8.1
07...	1130	201000	8.0	15.0	752	--	150	141	12.0	--	7.9
21...	1100	72500	8.0	15.0	766	8.0	205	205	12.8	6.7	7.9
APR											
24...	1030	73500	12.0	15.0	758	--	234	219	12.5	7.2	7.7
MAY											
08...	1000	66300	18.0	23.0	773	3.2	194	187	12.0	--	7.9
22...	1120	9700	23.0	25.0	768	--	210	210	9.3	7.2	7.4
JUN											
05...	1010	9900	28.0	28.0	765	--	254	249	4.1	7.5	7.6
19...	1015	5400	27.0	22.0	766	--	260	--	3.4	7.3	7.9
* 19...	1020	5400	27.0	22.0	766	--	260	274	3.4	7.3	7.5
JUL											
10...	1025	6200	29.0	28.0	762	2.0	332	334	7.2	6.9	7.5
AUG											
11...	1035	6500	28.0	26.0	763	--	395	418	5.5	7.4	7.5
SEP											
11...	1030	4400	27.0	27.0	763	0.60	390	389	5.5	7.2	7.5
* 11...	1035	4400	27.0	27.0	763	--	390	--	5.6	7.4	--
OCT											
09...	1030	4300	20.0	15.0	774	--	400	402	9.1	7.3	7.6
30...	1030	10600	16.0	17.0	771	3.1	410	419	9.0	7.8	7.8
NOV											
13...	1035	4700	11.0	16.0	766	--	420	--	9.5	7.8	--

DATE	ALKA- LITY WATER TOTAL FIELD MG/L AS CACO3	ALKA- LITY WATER TOTAL FIELD MG/L AS CACO3	ALKA- LITY LAB (MG/L AS CACO3)	SEDI- MENT, SUS- PENDED (MG/L)	SEDI- MENT, DIS- CHARGE, SUS- PENDED (T/DAY)	SED SUSP SIEVE DIAM * FINER THAN .062 MM	ALUM- NUM, DIS- SOLVED (UG/L AS AL)	ARSENIC DIS- SOLVED (UG/L AS AS)	ARSENIC TOTAL (UG/L AS AS)	BARIUM, TOTAL RECOV- ERABLE (UG/L AS BA)	CADMIUM DIS- SOLVED (UG/L AS CD)
JAN											
02...	51	--	33	37	16900	95	20	--	<1	--	--
03...	103	--	20	37	13100	95	40	--	<1	--	--
15...	47	47	46	3	1190	90	20	--	<1	--	--
MAR											
06...	45	--	39	33	20800	100	40	--	<1	--	--
07...	--	--	26	56	30400	99	20	--	<1	--	--
21...	44	43	39	13	2540	99	20	<1	--	--	1.0
APR											
24...	49	--	44	24	4760	78	30	--	<1	<100	--
MAY											
08...	--	--	38	14	2510	98	70	<1	<1	<100	<1.0
22...	42	--	41	6	157	98	--	<1	<1	<100	--
JUN											
05...	54	--	43	8	214	99	20	--	<1	<100	--
19...	49	--	46	7	102	83	<10	--	<1	100	--
* 19...	49	--	46	5	73	92	<10	--	<1	<100	--
JUL											
10...	51	34	49	4	67	93	<10	--	<1	<100	--
AUG											
11...	60	--	60	6	105	92	20	--	<1	100	--
SEP											
11...	58	51	59	6	71	90	<10	<1	<1	100	<1.0
* 11...	59	--	--	--	--	--	<10	--	<1	<100	--
OCT											
09...	63	--	62	9	104	94	20	--	<1	<100	--
30...	67	67	66	5	143	94	10	--	--	--	--
NOV											
13...	75	--	--	6	76	93	<10	--	1	<100	--

\* Duplicate samples collected for quality-assurance purposes



## APPENDIX A...Continued

## SUSQUEHANNA R AT CONOWINGO, MD

## WATER QUALITY DATA, CALENDAR YEAR JANUARY 1991 TO DECEMBER 1991

DATE	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD)	CHRO- MIUM, DIS- SOLVED (UG/L AS CR)	CHRO- MIUM, TOTAL RECOV- ERABLE (UG/L AS CR)	COPPER, DIS- SOLVED (UG/L AS CU)	COPPER, TOTAL RECOV- ERABLE (UG/L AS CU)	IRON, DIS- SOLVED (UG/L AS FE)	IRON, TOTAL RECOV- ERABLE (UG/L AS FE)	LEAD, DIS- SOLVED (UG/L AS PB)	LEAD, TOTAL RECOV- ERABLE (UG/L AS PB)	LITHIUM TOTAL RECOV- ERABLE (UG/L AS LI)	MANGA- NESE, TOTAL RECOV- ERABLE (UG/L AS MN)
JAN 02...	<1	1	2	2	4	--	--	1	3	--	--
JAN 03...	<1	<1	1	2	7	--	--	<1	3	--	--
JAN 15...	<1	<1	8	1	6	--	--	1	2	--	--
MAR 06...	<1	1	4	1	4	--	--	<1	3	--	--
MAR 07...	<1	<1	<1	1	5	--	--	1	5	--	--
MAR 21...	--	<1	--	1	--	60	--	<1	--	--	--
APR 24...	<1	<1	2	1	3	--	690	1	4	<10	150
MAY 08...	<1	<1	6	1	3	33	530	<1	3	<10	180
MAY 22...	<1	--	<1	--	3	--	220	--	2	<10	130
JUN 05...	<1	<1	3	2	4	--	290	<1	5	<10	190
JUN 19...	<1	<1	2	2	3	--	180	<1	2	<10	120
JUN 19...	<1	<1	3	2	6	--	210	<1	13	<10	130
JUL 10...	<1	<1	5	2	5	--	260	<1	17	<10	110
AUG 21...	<1	<1	3	3	3	--	320	2	2	<10	100
SEP 11...	<1	<1	1	2	5	11	160	<1	<1	<10	110
SEP 11...	<1	<1	<1	2	6	--	180	<1	<1	<10	110
OCT 09...	<1	<1	3	1	6	--	380	<1	3	<10	90
OCT 30...	--	--	--	--	--	<3	--	--	--	--	--
NOV 13	<1	<1	<1	<1	--	--	250	<1	7	<10	120

DATE	MERCURY DIS- SOLVED (UG/L AS HG)	MERCURY TOTAL RECOV- ERABLE (UG/L AS HG)	NICKEL, DIS- SOLVED (UG/L AS NI)	NICKEL, TOTAL RECOV- ERABLE (UG/L AS NI)	SELE- NIUM, TOTAL (UG/L AS SE)	SILVER, TOTAL RECOV- ERABLE (UG/L AS AG)	STRON- TIUM, TOTAL RECOV- ERABLE (UG/L AS SR)	ZINC, DIS- SOLVED (UG/L AS ZN)	ZINC, TOTAL RECOV- ERABLE (UG/L AS ZN)
JAN 02	--	<0.10	5	7	<1	<1	--	<10	20
JAN 03	--	<0.10	5	12	<1	<1	--	<10	20
JAN 15	--	0.10	5	--	<1	<1	--	20	50
MAR 06...	--	<0.10	4	8	<1	<1	--	<10	20
MAR 07...	--	<0.10	3	3	<1	<1	--	<10	20
MAR 21...	<0.1	--	3	--	--	--	--	3	--
APR 24...	--	<0.10	2	6	<1	<1	120	<10	<10
MAY 08...	0.2	<0.10	2	3	<1	<1	100	5	<10
MAY 22...	--	<0.10	--	4	<1	<1	120	--	<10
JUN 05...	--	<0.10	1	4	<1	<1	150	<10	<10
JUN 19...	--	<0.10	1	2	<1	<1	140	<10	<10
JUN 19...	--	<0.10	1	3	<1	<1	140	<10	<10
JUL 10...	--	<0.10	<1	10	<1	<1	190	<10	20
AUG 21...	--	0.20	2	3	<1	<1	220	<10	<10
SEP 11...	<0.1	<0.10	2	3	<1	<1	220	9	<10
SEP 11...	--	<0.10	2	3	<1	<1	240	<10	<10
OCT 09...	--	<0.10	2	4	<1	<1	240	<10	<10
OCT 30...	--	--	4	--	--	--	--	--	--
NOV 13	--	<0.10	3	4	<1	<1	210	<10	40

## APPENDIX A...Continued

## SUSQUEHANNA R AT CONOWINGO, MD

## WATER QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	TIME	DIS- CHARGE, INST CUBIC FEET PER SECOND	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- ITY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER WHOLE FIELD (STAND- ARD UNITS)	PH WATER WHOLE LAB (STAND- ARD UNITS)
MAR											
14...	1400	87900	6.0	8.0	762	--	188	169	12.8	6.9	7.3
15...	1315	77900	6.0	8.0	764	--	173	186	13.0	7.7	7.7
16...	1300	80100	7.0	4.0	771	--	172	162	13.0	7.7	7.7
29...	1700	166000	7.0	17.0	764	--	223	179	12.8	7.7	7.7
30...	1330	169000	8.0	17.0	762	--	208	174	12.8	7.7	7.7
31...	1400	120000	7.0	16.0	759	--	174	155	12.7	7.7	7.7
APR											
03...	1145	88500	7.0	8.0	758	--	176	169	12.3	7.6	7.9
22...	1230	87700	13.0	22.0	764	--	188	187	10.8	7.9	7.9
24...	1100	88700	13.0	21.0	759	--	178	168	10.8	7.9	7.9
MAY											
12...	1130	66300	16.0	20.0	768	4.2	218	200	10.1	7.6	8.1
19...	1000	9160	19.5	17.0	--	--	208	205	--	7.8	7.9
JUN											
19...	1345	22800	26.0	23.0	--	--	205	195	5.9	7.4	7.5
JUL											
15...	1300	12300	28.0	33.0	758	--	310	289	5.2	7.4	7.5
* 5...	1305	12300	28.0	33.0	758	--	310	286	5.2	7.4	7.5
SEP											
* 02...	1030	36400	26.0	21.0	770	3.0	272	257	6.6	7.9	7.9
* 02...	1035	36400	26.0	21.0	770	--	272	258	6.6	7.9	7.9
NOV											
18	1100	54700	6.0	8.0	776	1	197	171	15.1	7.5	7.5
20	1330	70400	10.0	14.0	764	--	181	184	15.0	7.5	7.5
30	1400	70400	8.0	7.5	759	--	148	158	11.8	7.9	7.9

DATE	ALKA- LITY WATER WHOLE FIELD (MG/L AS CACO3)	ALKA- LITY WATER WHOLE LAB (MG/L AS CACO3)	ALKA- LITY LAB (MG/L AS CACO3)	SEDI- MENT, SUS- PENDED (MG/L)	SEDI- MENT, CHARGE, SUS- PENDED (T/DAY)	SED SUSP. SOLVE DIAM. FINER THAN 062 MM	ALUM- NUM, SOLVE (UG/L AS AL)	ARSENIC DIS- SOLVED (UG/L AS AS)	ARSENIC TOTAL (UG/L AS AS)	BARIUM, TOTAL RECOV- ERABLE (UG/L AS BA)	CADMIUM DIS- SOLVED (UG/L AS CD)
MAR											
14...	33	--	30	28	6650	97	30	--	<1	<100	--
15...	26	--	28	28	3050	49	20	--	<1	<100	--
16...	--	--	28	28	3680	91	30	--	<1	<100	--
29...	--	32	30	26	20200	46	70	<0.60	<1	--	<0.1
30...	--	30	26	75	24300	100	30	<0.60	<1	--	<0.1
APR											
03...	--	28	28	22	5260	99	20	<0.60	<1	--	<0.1
22...	--	27	35	22	3550	98	110	<0.60	<1	--	<0.1
24...	--	34	31	23	5510	98	230	<0.60	<1	--	<0.1
MAY											
12...	--	46	43	13	2330	100	20	<0.60	<1	--	<0.1
19...	--	--	--	10	247	99	80	<0.60	<1	--	1.24
JUN											
19...	41	--	--	5	308	98	70	<0.60	<1	--	<0.1
JUL											
15...	--	59	57	2	66	--	20	<0.60	<1	--	<0.1
SEP											
02...	--	53	54	--	8	786	50	1.61	<1	--	<0.1
NOV											
18	--	43	33	10	1480	99	40	1.15	<1	--	<0.1
20	--	40	33	18	2220	100	40	<0.60	<1	--	<0.1
30	--	32	33	13	2470	97	40	<0.60	<1	--	<0.1

\* Duplicate samples collected for quality-assurance purposes

## APPENDIX A...Continued

## SUSQUEHANNA R AT CONOWINGO, MD

## WATER QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD)	CHRO- MIUM, DIS- SOLVED (UG/L AS CR)	CHRO- MIUM, TOTAL RECOV- ERABLE (UG/L AS CR)	COPPER, DIS- SOLVED (UG/L AS CU)	COPPER, TOTAL RECOV- ERABLE (UG/L AS CU)	IRON, DIS- SOLVED (UG/L AS FE)	IRON, TOTAL RECOV- ERABLE (UG/L AS FE)	LEAD, DIS- SOLVED (UG/L AS PB)	LEAD, TOTAL RECOV- ERABLE (UG/L AS PB)	LITHIUM TOTAL RECOV- ERABLE (UG/L AS LI)	MANGA- NESE, TOTAL RECOV- ERABLE (UG/L AS MN)
MAR											
14...	<1	<1.00	<1	2.00	3	--	1100	<1.0	10	<10	25
15...	<1	<1.00	2	2.00	<1	--	900	<1.0	--	<10	170
16...	<1	<1.00	1	2.00	<1	--	640	<1.0	2	<10	140
29...	<1	0.50	1	1.50	3	480	--	<0.06	3	--	--
30...	<1	1.10	1	3.10	55	--	--	2.20	3	--	--
31...	<1	1.97	3	1.63	200	810	--	0.24	3	--	--
APR											
03...	<1	1.40	<1	2.00	1	410	--	0.90	1	--	--
22...	<1	2.40	3	2.90	2	290	--	0.60	1	--	--
24...	<1	2.70	<1	2.20	2	430	--	0.30	2	--	--
MAY											
12...	<1	4.40	<1	1.45	1	42	--	0.45	<1	--	--
19...	<1	2.12	<1	1.18	1	300	--	0.69	<1	--	--
JUN											
19...	<1	1.27	<1	1.19	1	120	--	<0.06	<1	--	--
JUL											
15...	<1	2.97	3	1.12	1	4	--	0.13	<1	--	--
15...	<1	2.67	1	1.07	1	91	--	0.12	<1	--	--
SEP											
02...	<1	1.18	2	0.97	<1	5	--	<0.06	1	--	--
02...	<1	1.36	5	0.95	5	18	--	<0.06	2	--	--
NOV											
18...	<1	<0.10	<1	1.16	2	21	--	<0.06	<1	--	--
25...	<1	1.11	2	1.65	3	540	--	<0.06	1	--	--
30...	<1	1.77	2	1.97	3	<3	--	<0.06	1	--	--

DATE	MERCURY DIS- SOLVED (UG/L AS HG)	MERCURY TOTAL RECOV- ERABLE (UG/L AS HG)	NICKEL, DIS- SOLVED (UG/L AS NI)	NICKEL, TOTAL RECOV- ERABLE (UG/L AS NI)	SILVER, TOTAL RECOV- ERABLE (UG/L AS SE)	SILVER, TOTAL RECOV- ERABLE (UG/L AS AG)	STRON- TIUM, TOTAL RECOV- ERABLE (UG/L AS SR)	ZINC, DIS- SOLVED (UG/L AS ZN)	ZINC, TOTAL RECOV- ERABLE (UG/L AS ZN)
MAR									
14...	--	<0.10	4	6	<1	<1	110	<10.0	30
15...	--	<0.10	5	7	<1	<1	70	<10.0	10
16...	--	<0.10	--	--	<1	<1	50	<10.0	10
29...	**	<0.10	--	--	--	--	--	2.30	30
30...	0.035	0.50	--	--	--	--	--	21.60	20
31...	0.026	0.20	--	--	--	--	--	9.74	30
APR									
03...	0.021	<0.10	--	--	--	--	--	9.70	10
22...	0.021	<0.10	--	--	--	--	--	5.90	<10
24...	0.024	<0.10	--	--	--	--	--	1.40	<10
MAY									
12...	**	<0.10	8	--	--	--	--	3.65	<10
19...	**	<0.10	--	--	--	--	--	1.92	<10
JUN									
19...	**	<0.10	--	--	--	--	--	5.19	<10
JUL									
15...	**	<0.10	--	--	--	--	--	3.07	<10
15...	**	<0.10	--	--	--	--	--	2.37	<10
SEP									
02...	**	<0.10	7	--	--	--	--	1.10	30
02...	**	<0.10	--	--	--	--	--	1.18	<10
NOV									
18...	**	<0.10	9	--	--	--	--	3.86	30
25...	**	<0.10	--	--	--	--	--	3.27	30
30...	**	<0.10	--	--	--	--	--	2.84	10

\*\* Data pending.

## APPENDIX A...Continued

## SUSQUEHANNA R AT CONOWINGO, MD

## WATER QUALITY DATA, CALENDAR YEAR JANUARY 1993 TO MARCH 1993

DATE	TIME	DIS-CHARGE, INST CUBIC FEET PER SECOND	TEMPER-ATURE WATER (DEG C)	TEMPER-ATURE AIR (DEG C)	BARO-METRIC PRES-SURE (MM OF HG)	TUR-BID-ITY (NTU)	SPE-CIFIC CON-DUCT-ANCE (US/CM)	SPE-CIFIC CON-DUCT-ANCE LAB (US/CM)	OXYGEN, DIS-SOLVED (MG/L)	PH WATER WHOLE FIELD (STAND-ARD UNITS)	PH WATER WHOLE LAB (STAND-ARD UNITS)	ALKA-LINITY WAT DIS TOT IT FIELD MG/L AS CACO3
JAN 05...	1430	95900	5.0	18.0	742	--	138	155	13.0	--	7.2	26
08...	1300	114000	6.0	9.0	766	--	163	154	12.9	7.9	7.3	28
MAR 11...	1400	70900	4.0	10.0	763	8.0	290	255	12.5	7.3	7.6	--
25...	1130	145000	5.0	9.0	771	--	270	258	13.0	7.3	7.7	45
27...	1245	162000	6.0	11.0	766	--	225	207	13.2	7.5	7.4	25
28...	1230	184000	7.0	15.0	759	--	220	202	12.7	7.3	7.4	31
30...	1330	314000	7.0	16.0	757	--	160	154	12.5	7.3	7.0	17
31...	0145	321000	7.0	8.0	761	--	165	149	12.5	7.2	7.0	25
31...	1400	415000	8.0	15.0	759	--	146	132	12.3	7.2	7.1	20

DATE	ALKA-LINITY LAB (MG/L AS CACO3)	SEDI-MENT, SUS-PENDED (MG/L)	SEDI-MENT, DIS-CHARGE, SUS-PENDED (T/DAY)	SED-SUSP, STEVE DIAM, FINER TRAN 062 MM	ALUM-INUM, DIS-SOLVED (UG/L AS AL)	ARSENIC, DIS-SOLVED (UG/L AS AS)	ARSENIC, TOTAL (UG/L AS AS)	CADMIUM, DIS-SOLVED (UG/L AS CD)	CADMIUM, TOTAL RECOV-ERABLE (UG/L AS CD)	CHRO-MIUM, DIS-SOLVED (UG/L AS CR)	CHRO-MIUM, TOTAL RECOV-ERABLE (UG/L AS CR)	COPPER, DIS-SOLVED (UG/L AS CU)
JAN 05...	--	25	6470	99	30	<0.60	<1	0.16	<1	1.90	5	1.47
08...	28	18	5540	96	20	<0.60	<1	<0.10	<1	0.63	--	0.69
MAR 11...	46	14	2680	99	30	--	<1	--	<1	--	<1	--
25...	--	21	8220	96	30	<0.60	<1	<0.10	<1	<0.20	<1	0.74
27...	39	32	14000	96	<10	<0.60	<1	<0.10	<1	0.36	1	0.49
28...	40	28	13900	98	20	<0.60	<1	<0.10	<1	0.59	1	0.79
30...	27	79	67000	94	<10	<0.60	<1	<0.10	<1	<0.20	3	1.24
31...	35	67	58100	94	<10	0.65	1	<0.10	<1	<0.20	<1	0.36
31...	23	97	109000	98	<10	<0.60	<1	<0.10	<1	<0.20	5	0.39

DATE	COPPER, TOTAL RECOV-ERABLE (UG/L AS CU)	IRON, DIS-SOLVED (UG/L AS FE)	IRON, TOTAL RECOV-ERABLE (UG/L AS FE)	LEAD, DIS-SOLVED (UG/L AS PB)	LEAD, TOTAL RECOV-ERABLE (UG/L AS PB)	MERCURY, TOTAL RECOV-ERABLE (UG/L AS HG)	NICKEL, DIS-SOLVED (UG/L AS NI)	NICKEL, TOTAL RECOV-ERABLE (UG/L AS NI)	STRON-TIUM, TOTAL RECOV-ERABLE (UG/L AS SR)	ZINC, DIS-SOLVED (UG/L AS ZN)	ZINC, TOTAL RECOV-ERABLE (UG/L AS ZN)
JAN 05...	2	12	--	0.92	2	<0.10	--	--	--	9.83	30
08...	5	14	--	<0.06	1	<0.10	--	--	--	4.45	30
MAR 11...	2	13	--	--	1	<0.10	4	5	130	--	10
25...	<1	17	650	<0.06	1	<0.10	4	5	100	2.59	<10
27...	2	11	800	0.28	1	<0.10	2	5	100	15.06	<10
28...	2	12	830	<0.06	1	<0.10	2	5	80	8.06	10
30...	4	17	2400	1.03	4	<0.10	3	9	70	4.00	20
31...	4	22	3000	<0.06	5	<0.10	3	12	60	1.72	30
31...	3	--	3000	<0.06	5	<0.10	3	12	60	1.55	30



## APPENDIX B

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1990 TO DECEMBER 1990

DATE	DIS- CHARGE, INST. CUBIC FEET PER SECOND	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- ITY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE LAB (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER WHOLE FIELD (STAND- ARD UNITS)	ALKA- LITY WAT DIS TOT IT FIELD MG/L AS CACO3	SEDI- MENT, SUS- PENDE (MG/L)
APR											
25...	6390	19.0	21.5	752	2.7	129	135	8.7	7.7	47	11
MAY											
11...	27800	18.0	18.5	755	--	65	--	7.9	7.0	--	472
12...	16100	17.5	9.0	758	--	120	--	8.6	7.0	--	159
13...	11400	17.0	22.0	745	--	110	--	8.9	7.4	--	56
24...	17800	18.5	22.5	750	--	165	--	8.4	7.5	--	146
25...	13800	18.0	21.0	765	--	220	--	7.0	7.6	--	89
27...	22700	19.0	20.0	752	--	98	--	9.3	7.2	--	748
28...	15300	18.0	18.0	760	--	97	--	9.3	7.4	--	142
29...	37100	16.5	18.0	746	--	86	--	9.6	7.4	--	246
30...	44700	17.0	23.0	747	--	105	--	9.2	7.0	--	182
31...	39700	17.0	19.0	757	--	127	--	9.1	7.2	--	197
JUN											
01...	24100	17.5	20.5	757	--	123	--	9.4	6.8	--	--
01...	24100	17.5	20.5	757	--	123	--	9.4	6.8	--	133
02...	18800	18.5	20.0	757	--	108	--	9.5	7.0	--	83
03...	15600	19.5	20.5	752	--	115	--	8.9	6.9	--	87
27...	3620	26.0	30.0	760	2.8	162	156	7.9	8.2	50	7
JUL											
25...	3430	28.0	26.5	752	--	153	--	7.4	7.5	--	7
AUG											
29...	2600	29.0	33.0	744	1.4	260	260	7.2	8.3	73	5
SEP											
26...	1560	18.5	18.5	745	--	275	--	8.9	8.3	--	1
OCT											
23...	42900	15.5	24.0	750	--	80	--	9.0	7.3	--	--
24...	66500	16.5	19.0	749	--	80	--	8.5	6.3	--	230
25...	35800	15.5	16.0	752	--	105	--	9.0	7.5	--	272
26...	19400	14.0	13.0	753	--	88	--	9.8	7.4	--	115
NOV											
29...	5760	11.0	11.5	753	3.4	220	220	10.6	7.6	71	6
DEC											
21...	4950	7.5	9.0	765	--	143	--	11.7	7.7	--	6
31...	26100	9.0	15.0	--	--	92	--	11.8	6.5	--	89

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1990 TO DECEMBER 1990

DATE	SED. SUSP. SIEVE DIAM. % FINER THAN .062 MM	ALUM- INUM, DIS- SOLVED (UG/L AS AL)	ARSENIC DIS- SOLVED (UG/L AS AS)	ARSENIC TOTAL (UG/L AS AS)	BARIUM, DIS- SOLVED (UG/L AS BA)	CADMIUM DIS- SOLVED (UG/L AS CD)	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD)	CHRO- MIUM, DIS- SOLVED (UG/L AS CR)	CHRO- MIUM, TOTAL RECOV- ERABLE (UG/L AS CR)	COPPER, DIS- SOLVED (UG/L AS CU)
APR										
25...	97	30	<1	<1	25	<1.0	<1	<1	<1	1
MAY										
11...	87	120	--	<1	--	--	<1	<1	10	3
12...	94	60	--	<1	--	--	<1	<1	4	2
13...	97	40	--	<1	--	--	<1	<1	2	1
24...	92	40	--	<1	--	--	<1	<1	4	2
25...	98	70	--	<1	--	--	<1	<1	2	1
27...	90	190	--	<1	--	--	<1	1	18	3
28...	94	70	--	<1	--	--	<1	<1	6	<1
29...	97	170	--	<1	--	--	<1	<1	10	3
30...	99	190	--	<1	--	--	<1	<1	6	4
31...	85	70	--	<1	--	--	<1	<1	6	3
JUN										
01...	--	40	--	<1	--	--	<1	<1	3	1
01...	92	50	--	<1	--	--	<1	<1	3	4
02...	83	40	--	<1	--	--	<1	<1	3	2
03...	77	50	--	<1	--	--	<1	<1	3	<1
27...	96	60	--	<1	--	--	<1	<1	1	2
JUL										
25...	96	20	--	<1	--	--	<1	<1	<1	2
AUG										
29...	91	30	<1	1	39	<1.0	1	<1	<1	2
SEP										
26...	83	20	--	<1	--	--	<1	<1	<1	2
OCT										
23...	--	90	--	<1	--	--	<1	<1	16	4
24...	97	260	--	<1	--	--	<1	2	11	5
25...	92	80	--	<1	--	--	<1	2	11	3
26...	91	90	--	<1	--	--	<1	<1	3	<1
NOV										
29...	98	10	<1	<1	33	<1.0	<1	<1	<1	1
DEC										
21...	95	<10	--	<1	--	--	<1	<1	<1	2
31...	52	100	--	<1	--	--	<1	2	4	3

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1990 TO DECEMBER 1990

DATE	COPPER, TOTAL RECOV- ERABLE (UG/L AS CU)	IRON, DIS- SOLVED (UG/L AS FE)	LEAD, DIS- SOLVED (UG/L AS PB)	LEAD, TOTAL RECOV- ERABLE (UG/L AS PB)	MERCURY DIS- SOLVED (UG/L AS HG)	NICKEL, DIS- SOLVED (UG/L AS NI)	NICKEL, TOTAL RECOV- ERABLE (UG/L AS NI)	SELE- NIUM, TOTAL (UG/L AS SE)	ZINC, DIS- SOLVED (UG/L AS ZN)	ZINC, TOTAL RECOV- ERABLE (UG/L AS ZN)
APR										
25...	4	99	<1	1	<0.1	<1	<1	<1	<3	<10
MAY										
11...	16	--	1	22	--	<1	6	<1	<10	60
12...	3	--	<1	6	--	1	4	<1	<10	30
13...	3	--	<1	3	--	<1	1	<1	<10	10
24...	5	--	1	9	--	<1	3	<1	<10	20
25...	3	--	<1	3	--	<1	2	<1	<10	20
27...	24	--	1	27	--	5	18	<2	<10	90
28...	8	--	<1	12	--	1	6	<1	<10	40
29...	12	--	<1	21	--	1	7	<1	<10	80
30...	10	--	10	96	--	1	4	<1	<10	40
31...	13	--	2	28	--	1	5	<1	<10	40
JUN										
01...	4	--	1	4	--	1	4	<1	<10	30
01...	4	--	2	5	--	<1	4	<1	<10	30
02...	4	--	1	5	--	<1	4	<1	<10	30
03...	3	--	<1	3	--	<1	3	<1	<10	20
27...	5	--	<1	2	--	<1	2	<1	6	<10
JUL										
25...	3	--	1	1	--	2	1	<1	<10	<10
AUG										
29...	4	50	<1	3	<0.1	1	1	<1	<3	<10
SEP										
26...	3	--	1	2	--	2	3	<1	<10	20
OCT										
23...	11	--	1	18	--	2	9	<1	<10	50
24...	14	--	1	22	--	2	7	<1	<10	40
25...	9	--	1	17	--	1	10	<1	30	40
26...	7	--	<1	7	--	1	4	<1	<10	30
NOV										
29...	3	70	1	1	<0.1	1	2	<1	<3	20
DEC										
21...	3	--	1	1	--	1	1	<1	<10	<10
31...	3	--	1	6	--	<1	2	<1	10	<10



## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1991 TO DECEMBER 1991

DATE	DIS- CHARGE, INST. CUBIC FEET PER SECOND	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- ITY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE LAB (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER FIELD (STAND- ARD UNITS)	ALKA- LINITY WAT DIS TOT IT FIELD MG/L AS CACO3	SEDI- MENT, SUS- PENDED (MG/L)
JAN											
02...	25100	7.0	10.0	762	--	94	--	14.4	7.5	--	187
03...	19500	8.0	9.5	758	--	95	--	11.5	7.4	--	76
14...	39500	6.0	11.0	757	--	88	--	10.4	7.1	--	204
29...	7280	5.0	13.0	753	4.1	140	145	12.2	7.6	53	6
FEB											
28...	7750	6.0	13.0	755	4.3	121	127	12.6	7.6	41	6
MAR											
04...	15600	12.5	11.0	734	--	145	--	10.1	7.3	--	53
05...	51100	11.5	18.0	746	--	150	--	9.8	6.8	--	439
07...	25000	15.0	12.5	750	--	135	--	11.4	6.7	--	121
08...	21200	9.5	9.0	750	--	118	--	11.0	6.9	--	82
10...	12600	8.0	10.0	748	--	130	--	11.6	7.0	--	34
26...	20700	11.5	13.0	755	--	119	--	10.1	7.6	--	90
APR											
01...	33500	11.5	12.5	753	--	115	--	--	6.9	--	137
03...	19700	10.0	12.0	763	--	109	--	10.7	7.5	--	31
05...	13800	12.5	19.0	768	--	120	--	10.9	7.6	--	--
25...	8170	14.0	19.0	752	4.5	159	135	9.6	7.6	46	9
MAY											
30...	4110	29.0	28.5	760	--	169	--	7.2	7.8	--	4
JUN											
19...	2280	26.0	22.0	764	--	171	--	7.3	7.4	--	5
24...	5970	25.0	23.0	768	--	185	--	7.2	7.3	--	40
25...	5840	25.0	22.0	769	--	170	--	7.4	8.0	--	28
27...	3780	25.5	24.0	768	1.5	204	206	7.8	7.6	59	10
JUL											
30...	15900	23.0	21.5	749	--	131	--	6.8	7.1	--	167
AUG											
22...	2080	26.5	24.0	765	1.9	205	204	7.7	8.1	61	3
SEP											
26...	2340	21.0	19.0	749	--	225	--	8.2	7.8	--	7
OCT											
30...	1500	15.5	18.0	762	--	305	--	9.9	8.1	--	1
30...	1500	--	18.0	762	--	--	--	--	--	--	--
NOV											
26...	2000	7.0	4.0	767	1.1	260	272	13.2	7.6	70	2
DEC											
04...	15000	10.5	6.0	751	--	168	--	9.5	7.2	--	249
06...	11500	8.0	5.0	758	--	211	--	11.6	7.6	--	--
30...	13900	5.0	10.0	758	--	120	--	12.0	7.2	--	141
31...	10700	5.5	1.0	770	--	120	--	12.0	7.0	--	66

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1991 TO DECEMBER 1991

DATE	SED. SUSP. SIEVE DIAM. % FINER THAN .062 MM	ALUM- INUM, DIS- SOLVED (UG/L AS AL)	ARSENIC DIS- SOLVED (UG/L AS AS)	ARSENIC TOTAL (UG/L AS AS)	BARIUM, DIS- SOLVED (UG/L AS BA)	CADMIUM DIS- SOLVED (UG/L AS CD)	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD)	CHRO- MIUM, DIS- SOLVED (UG/L AS CR)	CHRO- MIUM, TOTAL RECOV- ERABLE (UG/L AS CR)	COPPER, DIS- SOLVED (UG/L AS CU)
JAN										
02...	84	90	--	<1	--	--	<1	1	2	4
03...	65	50	--	<1	--	--	<1	<1	<1	2
14...	89	90	--	<1	--	--	<1	<1	1	2
29...	85	30	--	<1	--	--	<1	<1	<1	1
FEB										
28...	94	<10	<1	<1	23	<1.0	<1	<1	<1	1
MAR										
04...	61	20	--	<1	--	--	<1	<1	<1	2
05...	71	170	--	<1	--	--	<1	<1	10	1
07...	91	30	--	<1	--	--	<1	<1	3	2
08...	70	100	--	<1	--	--	<1	<1	3	2
10...	85	20	--	<1	--	--	<1	<1	<1	2
26...	93	30	--	<1	--	--	<1	<1	2	2
APR										
01...	72	50	--	<1	--	--	<1	<1	3	2
03...	93	30	--	<1	--	--	<1	<1	<1	1
05...	--	210	--	<1	--	--	<1	<1	2	9
25...	79	30	<1	--	25	<1.0	--	<1	--	1
MAY										
30...	91	40	--	<1	--	--	<1	1	3	<1
JUN										
19...	92	20	--	<1	--	--	<1	<1	<1	2
24...	97	70	--	<1	--	--	<1	<1	3	5
25...	97	60	--	<1	--	--	<1	<1	2	3
27...	97	30	--	<1	--	--	<1	2	1	<1
JUL										
30...	90	220	--	<1	--	--	<1	<1	6	8
AUG										
22...	95	<50	<1	<1	30	<1.0	<1	<1	1	2
SEP										
26...	96	20	--	<1	--	--	<1	<1	1	3
OCT										
30...	91	<10	--	<1	--	--	<1	<1	<1	<1
30...	--	10	--	3	--	--	<1	<1	<1	1
NOV										
26...	100	20	--	<1	36	--	<1	--	1	--
DEC										
04...	84	--	--	<1	--	--	<1	--	9	--
06...	--	--	--	<1	--	--	<1	--	3	--
30...	91	190	--	<1	--	--	<1	<1	5	2
31...	87	200	--	<1	--	--	<1	2	5	3

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1991 TO DECEMBER 1991

DATE	COPPER,			LEAD,		NICKEL,			ZINC,	
	TOTAL RECOVERABLE (UG/L AS CU)	IRON, DIS- SOLVED (UG/L AS FE)	LEAD, DIS- SOLVED (UG/L AS PB)	TOTAL RECOVERABLE (UG/L AS PB)	MERCURY DIS- SOLVED (UG/L AS HG)	NICKEL, DIS- SOLVED (UG/L AS NI)	TOTAL RECOVERABLE (UG/L AS NI)	SELE- NIUM, TOTAL (UG/L AS SE)	ZINC, DIS- SOLVED (UG/L AS ZN)	TOTAL RECOVERABLE (UG/L AS ZN)
JAN										
02...	7	--	2	11	--	1	4	<1	<10	30
03...	7	--	1	5	--	<1	6	<1	<10	20
14...	12	--	<1	13	--	2	8	<1	<10	40
29...	4	--	<1	2	--	1	2	<1	6	<10
FEB										
28...	84	75	1	13	<0.1	6	2	<1	3	20
MAR										
04...	3	--	<1	1	--	1	2	<1	<10	20
05...	6	--	<1	11	--	1	6	<1	<10	50
07...	4	--	1	9	--	<1	6	<1	<10	20
08...	7	--	<1	3	--	<1	3	<1	10	20
10...	5	--	1	3	--	<1	2	<1	<10	80
26...	3	--	1	5	--	1	3	<1	<10	20
APR										
01...	5	--	1	7	--	<1	4	<1	<10	60
03...	5	--	1	1	--	<1	1	<1	<10	60
05...	8	--	3	5	--	1	1	<1	<10	<10
25...	--	80	1	--	<0.1	1	--	--	<3	--
MAY										
30...	4	--	1	3	--	1	4	<1	<10	<10
JUN										
19...	7	--	1	4	--	1	7	<1	<10	10
24...	9	--	<1	5	--	2	2	<1	<10	<10
25...	7	--	1	2	--	1	1	<1	<10	<10
27...	7	--	<1	2	--	1	<1	<1	6	<10
JUL										
30...	19	--	5	33	--	<1	5	<1	<10	10
AUG										
22...	2	150	<1	4	<0.1	<1	2	<1	<10	<10
SEP										
26...	3	--	<1	.	--	<1	1	<1	<10	<10
OCT										
30...	7	--	<1	2	--	<1	1	<1	<10	<10
30...	4	--	<1	.	--	2	<1	<1	<10	<10
NOV										
26...	--	140	--	3	--	1	2	<1	--	20
DEC										
04...	--	--	--	9	--	--	8	<1	--	50
06...	--	--	--	9	--	--	4	<1	--	40
30...	--	--	<1	3	--	<1	4	<1	<10	50
31...	<1	--	<1	4	--	--	4	<1	<10	10

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	DIS- CHARGE, INST. CUBIC FEET PER SECOND	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- ITY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE LAB (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER FIELD (STAND- ARD UNITS)	ALKA- LINITY WAT DIS TOT IT FIELD MG/L AS CACO3
JAN										
05...	17600	8.5	12.0	751	--	101	--	10.9	7.1	--
06...	23100	8.0	11.0	750	--	165	--	11.1	7.4	--
07...	13900	7.0	13.0	755	--	120	--	11.2	7.2	--
08...	10500	7.0	11.0	760	--	110	--	11.6	7.1	--
29...	3760	4.0	0.0	763	4.0	167	176	13.0	7.4	52
FEB										
18...	8640	5.5	4.0	757	--	237	--	11.9	7.2	--
19...	8050	6.0	9.0	752	--	235	--	11.8	7.6	--
26...	12900	8.0	6.0	744	28	117	110	13.8	7.1	31
27...	36200	7.0	9.0	751	--	110	--	12.0	7.0	--
28...	36200	7.0	15.0	748	--	102	--	12.0	7.0	--
29...	21300	9.0	8.0	752	--	93	--	10.8	7.2	--
MAR										
02...	12600	9.0	17.0	759	--	115	--	11.3	7.3	--
04...	9140	10.5	7.0	763	--	121	--	10.6	7.4	--
APR										
10...	4750	15.0	18.0	757	--	162	--	10.8	7.7	--
10...	4750	15.0	18.0	757	--	162	159	10.8	7.7	--
23...	111000	16.0	27.0	760	--	138	144	10.6	7.0	--
24...	80100	15.5	19.0	753	--	85	--	8.5	7.0	--
24...	80100	15.5	19.0	753	--	85	92	8.5	7.0	--
25...	21800	17.0	17.0	750	--	118	122	8.7	7.3	--
27...	17500	14.0	16.5	754	--	155	131	11.0	6.9	--
28...	14700	13.5	14.5	755	--	135	136	9.8	6.9	--
28...	14700	13.5	14.5	755	--	135	--	9.8	6.9	--
30...	9730	14.0	19.0	752	8.5	155	150	9.9	7.5	52
MAY										
20...	11000	19.0	18.0	766	--	135	--	8.6	7.3	--
20...	10900	19.0	18.0	766	--	135	134	8.6	7.3	--
JUN										
24...	5600	22.0	24.0	749	--	178	172	8.4	7.8	--
24...	5600	22.0	24.0	749	--	178	--	8.4	7.8	--

## APPENDIX 8...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	SED. SUSP.				BARIUM, DIS- SOLVED (UG/L AS BA)	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD)	CHRO- MIUM, DIS- SOLVED (UG/L AS CR)	CHRO- MIUM, TOTAL RECOV- ERABLE (UG/L AS CR)	COPPER, DIS- SOLVED (UG/L AS CU)
	SEDI- MENT, SUS- PENDE (MG/L)	SIEVE DIAM. % FINER THAN .062 MM	ALUM- INUM, DIS- SOLVED (UG/L AS AL)	ARSENIC TOTAL (UG/L AS AS)					
JAN									
05...	98	78	170	<1	--	<1	<1	3	4
06...	133	77	100	<1	--	<1	<1	4	4
07...	75	81	90	<1	--	<1	<1	3	3
08...	39	87	--	<1	--	<1	--	7	--
29...	2	95	--	<1	--	<1	--	<1	--
FEB									
18...	49	81	--	--	--	<1	--	<1	--
19...	34	82	--	<1	--	<1	--	<1	--
26...	114	78	80	<1	19	<1	--	4	--
27...	345	74	--	--	--	<1	--	12	--
28...	381	88	--	<1	--	<1	--	8	--
29...	145	81	--	--	--	<1	--	4	--
MAR									
02...	36	85	--	--	--	<1	--	1	--
04...	20	86	--	--	--	<1	--	2	--
APR									
10...	--	--	--	<1	--	<1	<1	2	<1
10...	4	89	20	<1	--	<1	--	<1	--
23...	888	90	60	<1	--	<1	--	<1	--
24...	--	--	--	<1	--	<1	<1	6	3
24...	454	73	120	<1	--	<1	--	4	--
26...	106	85	210	<1	--	<1	--	1	--
27...	74	80	170	<1	--	<1	--	1	--
28...	62	69	140	<1	--	<1	--	1	--
28...	--	--	--	<1	--	<1	<1	3	2
30...	30	85	20	--	29	--	--	--	--
MAY									
20...	--	--	--	<1	--	<1	<1	<1	3
20...	31	88	120	<1	--	<1	--	<1	--
JUN									
24...	--	--	80	<1	--	<1	--	10	--
24...	--	--	--	<1	--	<1	<1	2	2

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	COPPER,	IRON,	LEAD,	LEAD,	NICKEL,	NICKEL,	SELE-	ZINC,	ZINC,
	TOTAL	DIS-	DIS-	TOTAL	DIS-	TOTAL	NIUM,	DIS-	TOTAL
	RECOV-	SOLVED	SOLVED	RECOV-	SOLVED	RECOV-	TOTAL	SOLVED	RECOV-
	ERABLE	(UG/L	(UG/L	ERABLE	(UG/L	ERABLE	(UG/L	(UG/L	ERABLE
	(UG/L	AS FE)	AS PB)	(UG/L	AS NI)	(UG/L	AS SE)	AS ZN)	(UG/L
	AS CU)			AS PB)		AS NI)			AS ZN)
JAN									
05...	12	--	1	9	<1	1	<1	<10	20
06...	6	--	--	9	<1	2	<1	<10	20
07...	9	--	2	14	<1	2	6	<10	10
08...	--	--	--	--	--	6	<1	--	30
29...	3	--	--	2	--	2	<1	--	20
FEB									
18...	4	--	--	6	--	2	<1	--	20
19...	3	--	--	16	--	2	<1	--	20
26...	2	200	--	8	<1	4	<1	--	30
27...	10	--	--	27	--	8	<1	--	40
28...	4	--	--	37	--	13	<1	--	70
29...	7	--	--	22	--	5	<1	--	30
MAR									
02...	13	--	--	7	--	2	<1	--	10
04...	3	--	--	<1	--	<1	<1	--	<10
APR									
10...	8	--	<1	<1	--	--	--	<10	20
10...	1	110	--	<1	--	--	--	--	<10
23...	1	200	--	<1	--	--	--	--	<10
24...	10	--	<1	15	--	--	--	<10	60
24...	6	140	--	10	--	--	--	--	60
26...	2	380	--	3	--	--	--	--	<10
27...	2	310	--	2	--	--	--	--	<10
28...	2	270	--	2	--	--	--	--	<10
28...	2	--	2	2	--	--	--	<10	10
30...	--	56	--	--	<1	--	--	--	--
MAY									
20...	3	--	1	2	--	--	--	<10	<10
20...	<1	200	--	1	--	--	--	--	<10
JUN									
24...	2	170	--	<1	--	--	--	--	<10
24...	2	--	<1	<1	--	--	--	<10	<10

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA.

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	DIS- CHARGE, INST. CUBIC FEET PER SECOND	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- ITY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE LAB (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER WHOLE FIELD (STAND- ARD UNITS)	ALKA- LITY WAT DIS TOT IT FIELD MG/L AS CaCO3
JUL										
22...	1980	29.0	25.5	760	--	205	218	6.3	6.5	--
22...	1980	29.0	25.5	760	--	205	217	6.3	6.5	--
SEP										
03...	1680	25.0	24.5	758	1.0	295	291	7.7	8.3	77
03...	1580	25.0	24.5	758	--	295	288	7.7	8.3	--
03...	--	25.0	24.5	758	--	295	291	7.7	8.3	--
OCT										
28...	1750	12.0	15.0	753	--	250	253	10.4	8.0	--
NOV										
23...	5340	11.0	20.0	750	--	165	170	10.2	7.8	--
23...	5450	11.0	20.0	750	5.7	165	160	10.2	7.8	39
25...	23000	12.0	15.5	760	--	145	141	10.2	7.4	--
DEC										
11...	32800	3.0	8.0	738	--	88	84	12.7	7.2	--
12...	18200	4.0	7.0	751	--	95	89	12.4	7.2	--

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	SEDIMENT, SUSPENDED (MG/L)	SED. SUSP. SIEVE DIAM. % FINER THAN .062 MM	ALUMINUM, DIS-SOLVED (UG/L AS AL)	ARSENIC TOTAL (UG/L AS AS)	BARIUM, DIS-SOLVED (UG/L AS BA)	CADMIUM TOTAL RECOVERABLE (UG/L AS CD)	CHROMIUM, DIS-SOLVED (UG/L AS CR)	CHROMIUM, TOTAL RECOVERABLE (UG/L AS CR)	COPPER, DIS-SOLVED (UG/L AS CU)
JUL									
22...	3	85	50	<1	--	<1	--	8	--
22...	--	--	50	<1	--	<1	--	9	--
SEP									
03...	2	83	40	--	40	--	--	--	--
03...	--	--	80	<1	--	<1	--	20	--
03...	--	--	60	<1	--	<1	--	1	--
OCT									
28...	1	84	<10	<1	--	<1	--	<1	--
NOV									
23...	14	86	110	<1	--	<1	--	16	--
23...	14	86	20	--	25	--	--	--	--
25...	165	79	660	<1	--	<1	--	4	--
DEC									
11...	485	73	390	<1	--	<1	--	17	--
12...	167	91	320	<1	--	<1	--	5	--



## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1992 TO DECEMBER 1992

DATE	COPPER, TOTAL RECOV- ERABLE (UG/L AS CU)	IRON, DIS- SOLVED (UG/L AS FE)	LEAD, DIS- SOLVED (UG/L AS PB)	LEAD, TOTAL RECOV- ERABLE (UG/L AS PB)	NICKEL, DIS- SOLVED (UG/L AS NI)	NICKEL, TOTAL RECOV- ERABLE (UG/L AS NI)	SELE- NIUM, TOTAL (UG/L AS SE)	ZINC, DIS- SOLVED (UG/L AS ZN)	ZINC, TOTAL RECOV- ERABLE (UG/L AS ZN)
JUL									
22...	2	120	--	<1	--	--	--	--	<10
22...	3	100	--	<1	--	--	--	--	<10
SEP									
03...	--	43	--	--	<1	--	--	--	--
03...	2	92	--	<1	--	--	--	--	<10
03...	2	88	--	<1	--	--	--	--	<10
OCT									
28...	2	140	--	<1	--	--	--	--	<10
NOV									
23...	1	380	--	<1	--	--	--	--	<10
23...	--	120	--	--	1	--	--	--	--
25...	2	890	--	4	--	--	--	--	30
DEC									
11...	6	1100	--	8	--	--	--	--	50
12...	4	800	--	4	--	--	--	--	30

## APPENDIX B...Continued

## JAMES RIVER AT CARTERSVILLE, VA

## WATER-QUALITY DATA, CALENDAR YEAR JANUARY 1993 TO DECEMBER 1993

DATE	DIS- CHARGE, INST.	TEMPER- ATURE WATER (DEG C)	TEMPER- ATURE AIR (DEG C)	BARO- METRIC PRES- SURE (MM OF HG)	TUR- BID- IDY (NTU)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	SPE- CIFIC CON- DUCT- ANCE (US/CM)	OXYGEN, DIS- SOLVED (MG/L)	PH WATER WHOLE FIELD (STAND- ARD UNITS)	ALKA- LITY WAT DIS TOT IT FIELD MG/L AS CACO3	SED- SUSP. SIEVE DIAM. % FINER THAN .062 MM		
	CUBIC FEET PER SECOND												
JAN													
28...	9180	3.5	2.0	757	--	155	160	13.4	6.8	--	8	92	
FEB													
23...	20300	5.0	3.0	751	--	125	129	10.4	6.6	--	98	66	
24...	25500	4.0	1.0	759	--	140	155	12.6	6.6	--	193	53	
25...	20000	3.5	-2.0	767	16	138	145	12.8	6.5	39	105	54	
25...	20000	3.5	-2.0	767	--	138	147	12.8	6.5	--	105	54	
DATE	ALUM- INUM, DIS- SOLVED (UG/L AS AL)	ARSENIC TOTAL (UG/L AS AS)	BARIUM, DIS- SOLVED (UG/L AS BA)	CADMIUM TOTAL RECOV- ERABLE (UG/L AS CD)	CHRO- MIUM, TOTAL RECOV- ERABLE (UG/L AS CR)	COPPER, TOTAL RECOV- ERABLE (UG/L AS CU)	IRON, DIS- SOLVED (UG/L AS FE)	LEAD, TOTAL RECOV- ERABLE (UG/L AS PB)	NICKEL, DIS- SOLVED (UG/L AS NI)	NICKEL, TOTAL RECOV- ERABLE (UG/L AS NI)	ZINC, TOTAL RECOV- ERABLE (UG/L AS ZN)		
JAN													
28...	100	<1	--	<1	5	<1	320	<1	<1	2	<10		
FEB													
23...	450	<1	--	<1	9	3	840	2	7	13	10		
24...	380	<1	--	<1	7	3	450	3	<1	3	30		
25...	60	--	23	--	--	--	100	--	<1	--	--		
25...	260	<1	--	<1	7	3	400	2	<1	4	20		



[illegible]



## DISSOLVED PHASE CONSTITUENTS

[illegible]

# PARTICULATE PHASE CONSTITUENTS

SAMPLE	TSP	Simazine	Prometon	Atrazine	Diazinon	Alachlor	Malathion	Metolachlor	Cymazine	Hexazin	Aldrin	Oxychlor	Chlordane	(biorda	Dieldrin	4,4'-DD	Permethrin	Fenvalerate	PCBs	cis- & tra cis- & trans-	gamma- alpha-	Naphthyl	Fluorant	Benz(a)ant	Benz(a)
VOLUM	mg																								
Liters																									
SAMPLE																									
Concentration in ng/l, QI less than quantitation level, na not analyzed																									
11 March - 31 October 1992																									
20 March Base Flow	35	260	451	na	na	na	na	na	na	na	na	QI	QI	0.2	0.3	0.2	QI	QI	QI	QI	QI	QI	0.6	12.4	QI
22 April Base Flow	25	945	93	na	na	na	na	na	na	na	na	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI
29 May Base Flow	34	425	550	na	na	na	na	na	na	na	na	QI	QI	2.1	3.6	3.6	QI	QI	QI	QI	QI	QI	1.4	QI	11.4
11 June Storm Flow	2	720	291	na	na	na	na	na	na	na	na	QI	QI	QI	3.5	3.5	QI	QI	QI	QI	QI	3.3	8.3	QI	QI
30 June Base Flow	33	420	110	na	na	na	na	na	na	na	na	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	5.3	8.3	QI	QI
4 August Base Flow	30	485	390	na	na	na	na	na	na	na	na	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	1.9	1.4	2.7	7.7
6 October Base Flow	29	820	155	na	na	na	na	na	na	na	na	QI	QI	QI	0.5	0.2	QI	QI	QI	QI	QI	0.7	0.7	QI	QI
19 December Storm	2	740	249	na	na	na	na	na	na	na	na	QI	QI	0.3	3.2	1.0	1.2	15.1	3.5	3.0	1.2	5.7	QI	QI	QI
26 January Base Flo	9	825	55	na	na	na	na	na	na	na	na	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI	QI
22 March Base Flow	11	320	940	na	na	na	na	na	na	na	na	QI	QI	0.4	(0.5)	QI	1.1	QI	QI	QI	QI	10.5	7.8	3.5	

US Federal Reserve

1913

1914

1915

Philadelphia, Pa. 1917