Effects of Dredging on the Water Quality of the Anacostia River

Final Report

Submitted by:

David J. Velinsky
Interstate Commission on the Potomac River Basin

Jeffery Cornwell
Horn Point Environmental Laboratory
University of Maryland, and

Gregory Foster
Department of Chemistry
George Mason University

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EXECUTIVE SUMMARY

The objectives of this study were to assess the potential impact of dredging operations at the Bladensburg Marina on the Anacostia River in the District of Columbia and Prince George's County, Maryland. Specifically, this investigation determined 1) the background concentrations of dissolved and particulate trace metals (e.g., Cu, Co, Fe, Mn, Ni, Pb, and Zn) and organics (e.g., congener specific polychlorinated biphenyls, polycyclic aromatic hydrocarbons, $\alpha+\gamma$ chlordane, and selected pesticides) in the upper tidal Anacostia River; 2) if dredging operations increase the concentrations of these contaminants to the surface waters of the local area (i.e., $\leq$ 100 m); and 3) if these contaminants, if increased, are transported to the waters of the District of Columbia.

To address these objectives, a total of 25 water samples were collected from the areas above and below the Bladensburg Marina (refer to Figure 1). In conjunction, five sediment samples were obtained from within the marina area. Water samples were filtered and analyzed for dissolved and particulate metals and organics, as well as for various forms of nitrogen, phosphorus, and carbon. By comparing upstream, marina, and downstream concentrations an estimate of the impact of dredging to the water quality of the upper Anacostia River was obtained.

Total suspended matter (TSM) ranged from approximately 3 to 50 mg/L for the three transects. Generally, lower concentrations of TSM were found upstream of the dredge, both above and below the confluence of the NE and NW Branches of the Anacostia River. Concentrations increased downstream of the confluence to the boundary of the District of Columbia. Within the marina, concentrations did not increase in relationship to the location of the dredge, except for one sample. Below this sample, TSM concentrations decreased, indicating only local resuspension from the dredge.

Most nutrient concentrations did not appear to be correlated with distance from the dredge. Dissolved phosphate, ammonium, and nitrate+nitrite concentrations ranged from 0.05 to 0.2 μmol P/L, 0.9 to 2.3 μmol N/L, and 20 to 40 μmol N/L, respectively. Ammonium concentrations did increase downstream of the marina and this increase may be related to a benthic flux of ammonium within the tidal Anacostia River.

This study indicates that the dredging in the Bladensburg Marina does not effect the surface water quality of the upper tidal Anacostia River. Within the marina, dissolved and particulate concentrations of most trace metals and organic compounds did not substantially increase at or just below the dredge. In a few instances however, concentrations of both dissolved and particulate contaminants were slightly higher just at the dredge head (e.g., transect 3). This increase was very localized with concentrations decreasing just downstream of the dredge (i.e., tens of meters). Below the dredge, but still within the marina area, concentrations were fairly constant, while downstream of the marina concentrations of most organic compounds and trace metals increased or were variable. Concentrations of trace metals and organic compounds were generally lowest in the area above the marina between the confluence of the NE and NW Branches and the Rt. 450 bridge.

In all cases, concentrations of dissolved trace metals, the more bio-available fraction, were substantially lower than published water quality standards using both the District of Columbia and the State of Maryland's criteria. Concentrations of total metals (i.e., dissolved+particulate) are also below these criteria and are similar to other areas in Chesapeake Bay. Dissolved concentrations of PCBs were above the PCB standards (DC and MD) for two samples in transect 2. Concentrations of dissolved $\alpha+\gamma$ chlordane were above standards for five samples in transects 1 and 2. Total PCBs and total chlordane (i.e., dissolved and particulate) exceeded standards in at least 15 more cases. Dissolved concentrations of chlordane and PCBs in all samples were higher than those stated for human health effects (i.e., risk level of 10^{-6})

Future studies should focus on the source of the elevated levels of chlordane and PCBs in the Maryland portion of the Anacostia River. Samples should be obtained from both the NE and NW Branches during storm and base flows to determine the magnitude of water and sediment transport of contaminants to the Anacostia River. Current work at the fall-line of the Potomac River indicates that storm flows are more important in the transport of material than base flows and that the transport phase may be different (Foster and Lippa, 1993). This may be just as important for the Anacostia River. Also, samples should be obtained in the other smaller creeks and runs that flow into the Anacostia River. These smaller creeks account for approximately a quarter of the total flow to the Anacostia River. Results from this study also

indicate that benthic processes may influence the water column chemistry of nutrients and trace metals. Additional work should be undertaken to investigate the importance of the bottom sediments in retaining and recycling both nitrogen and sediment-bound contaminants like trace metals.

INTRODUCTION

The dredging of navigation channels and marinas is necessary in many areas because of continual sediment runoff and related deposition. This is a result of many factors including land use changes in many watersheds. Due to the particle-reactive nature of many organic and inorganic contaminants, the increase in sediment deposition has also increased the deposition of many anthropogenic chemicals. These chemicals result from industrial and municipal sewer discharges, as well as non-point source discharges such as runoff from streets and roadways (i.e., urban runoff). As a result of dredging operations, sediments and associated-contaminants may be re-mobilized back into the water column. Chemicals that are sorbed to sediment particles may desorb into the water column and potentially effect the local biota (i.e., toxicity and bio-accumulation) as well as be transported to other less contaminated areas of the river.

The mechanisms for the desorption of chemicals are complex, especially for metals that are loosely-bound to particulates. In natural waters, clay minerals, calcium carbonate, iron and manganese oxides, and organic carbon particles can act as carrier phases for many trace metals (Stumm and Morgan, 1981). The dissolved concentration of metals can control, in large extent, the surface sorption rate onto one or more of these phases. Other processes such as flocculation, precipitation reactions, redox transformation to more insoluble species, biological uptake, and abiotic and biotic degradation also can affect the distribution between dissolved and particulate forms of metals and organics. During dredging operations, bottom sediments can be resuspended, potentially resulting in the destruction of specific carrier phases that contain trace metals (i.e., oxidation of sulfide phases) and organics (i.e., oxidation of organic carbon). As a result of the disruption of the bed sediment, reduced forms of iron and manganese can be released to the oxygenated water column forming new carrier phases once oxidized (i.e., iron and manganese oxides). When a carrier phase is destroyed, the complexed metal can be released back into the water or re-adsorbed onto another carrier phase present in the water.

The objectives of this study were to assess the potential impact of dredging operations at the Bladensburg Marina on the Anacostia River in the District of Columbia and Prince

George's County, Maryland. Specifically, this investigation determined 1) the background concentrations of dissolved and particulate trace metals (e.g., Cu, Co, Fe, Mn, Ni, Pb, and Zn) and organics (e.g., congener specific polychlorinated biphenyls, polycyclic aromatic hydrocarbons, $\alpha + \gamma$ chlordane, and selected pesticides) in the upper tidal Anacostia River; 2) if dredging operations increase the concentrations of these contaminants to the surface waters of the local area (i.e., $\leq$ 200 m); and 3) if these contaminants, if increased, are transported to the waters of the District of Columbia.

Past studies reveal no general trend in the overall effect of dredging on rivers or estuaries. The effects of dredging on the water quality of a system likely must be considered on a case by case basis. Changes in water quality cannot be predicted from the examination of the sediment prior to dredging. Dependent on many factors including the oxidation state of the sediment (i.e., oxic or anoxic), pH, salinity, particle types, and the mixing zone of the river, the partitioning of trace metals could be affected as a result of dredging. For example, after the initial resuspension of material, trace metals could adsorb onto the particles and settle to the bottom therefore lowering the concentration of metals in the water column. Once buried in the sediments, diagenetic processes could remobilize the metals back into the water increasing the water column concentrations of specific metals.

To best assess the impact of dredging, both laboratory and field studies should be undertaken to determine the impact of dredging to the water column of an area. Biggs (1968) and Cronin et al. (1970) measured increased levels of dissolved nitrate, ammonium and phosphate around dredging operations. Dissolved trace metals, such as iron (Fe), copper (Cu), and zinc (Zn), did not increase in concentration due to dredging in the studies by Windom (1975) and May (1973). Tramontano and Bohlen (1984) determined that dredge-induced injection of dissolved and particulate materials is a near-field effect producing only minor increases in trace metals and nutrients. Concentrations of dissolved copper decreased to background levels within 50 m of the dredging operations, while dissolved ammonium concentrations reached background levels within 200 m. Variability in the concentration and flux of sediment-associated contaminants due to fluvial transport and storm events were of the same order as variability associated with dredging. Similar conclusions were presented by Eadie et al. (1980) in their study of the Grand River, MI.

The effect of dredging on the concentrations of organics such as polychlorinated biphenyls (PCBs) and hydrocarbons (i.e., polycyclic aromatic hydrocarbons, PAHs) have not been well studied. Depending on a number of factors such as particle concentration, size, and composition (i.e., organic carbon content and composition), as well as the salinity, dissolved organic carbon (both concentration and type), and the octanol-water partition coefficient (K_{ow}) of the compound, dredging operations could re-introduce contaminants into the water thus enabling them to be transported downstream. As a related example, Huggett and Bender (1980) showed that tidal resuspension of bottom sediments (i.e., a proxy for dredging) released kepone back into the water column, enabling the re-introduced kepone to be transported down the James River and remain as a potential source for finfish and benthic filter feeders.

The U.S. Army Corp of Engineers (COE) Environmental Laboratory has studied the potential release of sediment-associated contaminants in numerous laboratory studies (see COE, 1992 for a review). These studies have been directed more toward the evaluation of leachate quality in confined disposal facilities for dredged material than toward potential release at the point of dredging. The COE uses an elutriate test to predict, within an **order of magnitude**, the release of sediment-bound contaminants to the water column (COE, 1988). Elutriate tests predicted a greater release of contaminants than observed during dredging, indicating that this test provides a conservative estimate of the effects of dredging.

Presently, the long-term dredging operations in the Anacostia River are centered around the Bladensburg Marina (Figure 1). This dredging is performed year round as part of the Anacostia Watershed Restoration Project. The Maryland National Capital Park and Planning Commission (MNCPPC) is currently using a hydraulic cutterhead suction-type dredge to increase channel depths of the marina area. This type of dredge uses a rotating cutter apparatus surrounding the intake end of the suction pipe and can dig and pump all types of alluvial and compacted sediments. Resuspension by a cutterhead is related to cutter rotation speed, ladder swing rate, and depth of cut into the sediment. In a study of resuspension by a cutterhead dredge in the Savannah River, increased levels of suspended particulates (up to 90 mg/L) were observed up to 30 m downstream of the dredge in the upper and middle depths of the water column (COE, 1986). Higher concentrations (e.g., 100-200 mg/L) were observed nearer the bottom of the river.

OBJECTIVES

The purpose of this study was to investigate the effect of dredging in the Bladensburg marina to the surface waters of the Anacostia River. Field sampling in the Anacostia River was performed on September 9th and 22nd, 1992 (Table 1). Subsequent sampling for turbidity, dissolved oxygen, and conductivity was accomplished in October, 1992. All sampling was performed on a falling tide up to approximately 0.5 hour after the tide had turned to flood.

Table 1. Sampling Dates and General Information for Bladensburg Marina Study.

Date/1992	Dredge Operating	Transects	# of Samples	Parameters
September 9	No	1	5	All
September 22	Yes	2 and 3	22	All
October 14	No	4 and 5	21	Turbidity
October 23	No	6 and 7	22	Turbidity

Note: Standard hydrographic data collected for all dates.

Below are listed the three specific objectives, and the number and type of water samples that were taken to address each objective:

Objective 1: *Determine background concentrations of dissolved and particulate trace metals (e.g., Cu, Co, Fe, Mn, Ni, Pb, and Zn), organics (total PCBs, total PAHs, and $\alpha + \gamma$ chlordane), and nutrients (nitrogen and phosphorus species) in the Anacostia River.*

To accomplish this objective, five water samples were taken after dredging operations had been stopped for three days (Table 1). These samples were collected on September 9, 1992 (transect 1). Also, water samples were taken above the dredge at the same time as the sampling below the dredge on September 22, 1992 (transects 2 and 3). These stations were sampled twice during the day to assess short term temporal variability in river water quality. (Note that the dredge was in operation on September 22nd.) In addition, certain stations were sampled in duplicate to assess sampling and analytical variability. A total of 12 water samples were analyzed for the parameters listed in Table 2 to assess background concentrations.

Table 2. List of Measured Parameters.

PARAMETER

Organics:
D-Chlordane
P-Chlordane
D-PCBs
P-PCBs
D-PAHs
P-PAHs

Ancillary Parameters:
Total Suspended Matter (TSM)
Nephelometric Turbidity (NTU)
D-Organic Carbon (DOC)
D-NH_4^+, NO_3^-+NO_2^-,
HPO_4^{3-}, and $HSiO_4^{2-}$
D-Chloride (Cl^-)

D-Sulfate (SO_4^{2-})
P-Organic C, N,& P

Metals:
D-Lead (Pb)
P-Pb
D-Copper (Cu)
P-Cu
D-Iron (Fe)
P-Fe
D-Cobolt (Co)
P- Co

D-Zinc (Zn)
P-Zn
D-Manganese (Mn)
P-Mn

D - Dissolved; P - Particulate; Chlordane, PCBs, and PAHs, include 2 ($\alpha + \gamma$), 90, and 16 individual compounds, respectively; see below.

Objective 2: ***Determine if dredging operations at the Bladensburg Marina increase the concentrations of these contaminants and nutrients in the dissolved and particulate phases of the river water.***

To accomplish this objective, eight water samples were taken on September 22, 1992 around or below the dredge (transects 2 and 3) while the dredge was in operation. These stations were sampled twice during the day to assess short-term temporal variability. Certain stations were sampled in duplicate to assess sampling and analytical variability. A total of 18 samples were obtained to assess the impact from the dredging operations.

Objective 3: ***If the contaminants are increased in concentration below the dredging operation, assess the relative magnitude of this increase to background and storm transport to the waters of the District of Columbia.***

To accomplish this objective, two samples were taken close to the District's border with Prince George's County. By analyzing the trends in background, close to the dredge, and downstream concentration data, an assessment of the possible impact to the Anacostia River in the District of Columbia will be made. Also, water quality calculations may be used to assess the relative contribution of dissolved and particulate matter from the dredging operations compared to baseline and storm runoff events. In addition to the collection of water samples, three sediment samples were obtained, one sample at the Rt. 450 bridge while the other two were collected below the dredging operation in the marina.

STUDY AREA AND SAMPLE COLLECTION

Study Area

The study area for this investigation was the Bladensburg Marina in Prince George's County Maryland (Figure 1). The marina is located approximately 13 km upstream from the mouth of the Anacostia River, just downstream from the head of tide. The drainage area of the Anacostia Basin is approximately 440 km^2 and is comprised of three distinct regions: the tidal river from its confluence with the Potomac to the marina, and the Northeast and Northwest Branches located in Prince George's and Montgomery Counties (MD). The watershed drains two geologic and physiographic provinces: the Piedmont Plateau (approximately 30% of the area) and the Coastal Plain (approximately 70% of the area).

The climate of the watershed is temperate and humid, with an average annual rainfall of 105 cm/yr that is distributed evenly over the year. The rainfall and groundwater runoff produce high velocity waters from the Piedmont into the Coastal Plain area starting at the Rt. 450 Bridge and Bladensburg Marina. Once the flow reaches the tidal portion of the Anacostia, water movement is slowed with typical flushing times from 20 to 40 days. Under drought conditions, the flushing time increases to approximately 100 days.

Bladensburg, founded in 1742, was an important trading seaport until the mid-1800's. The Anacostia channel, which accommodated ocean-going ships to Bladensburg during this time period, was reported to have been 12 m deep. The transformation of the watershed from forested to agricultural in the 1800's to the urbanized area at present (approximately 54% urban area) greatly increased sediment runoff and siltation. As a result, the maximum depth of the river and marina area today is approximately $<$ 1 to 2 m.

Recent projects along the Anacostia River (i.e., Anacostia Watershed Restoration

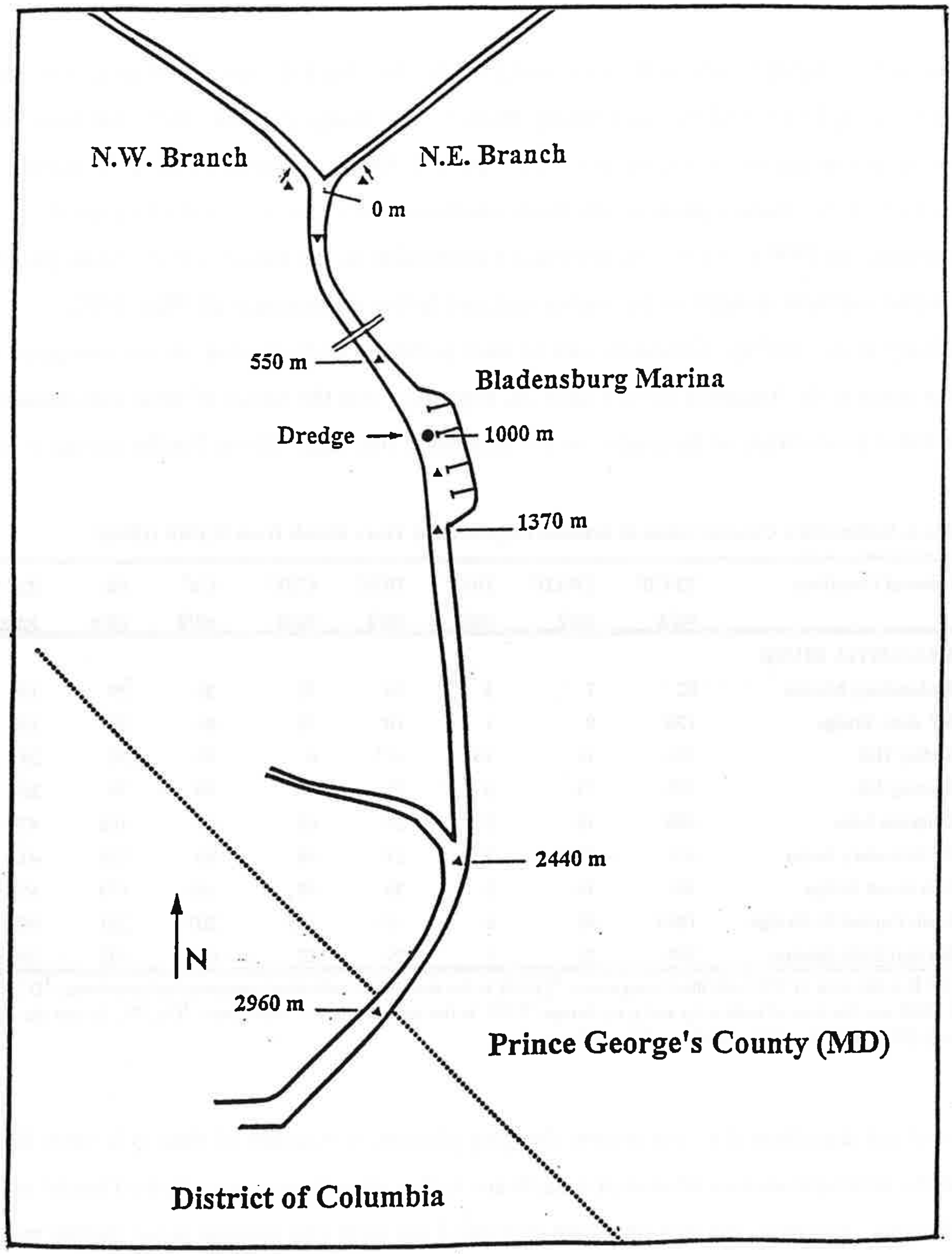

Figure 1. Study area indicating specific sample locations (▲) listed in Tables 4. The circle (●) in the marina indicates the location of the dredge during the project. Stations located near the dredge (-3, +3, +6, +12) are not shown on this map. Distances not to scale.

Program) are trying to restore the river and provide a boating and recreational area. One such project is the dredging of the Bladensburg Marina. The dredging of the marina and channel area has proceeded on a continual basis since the mid-1960's. Concerns have been raised as to the effect of the dredge operations on the downstream water quality, into the District of Columbia. In 1990 and 1991, the Interstate Commission on the Potomac River Basin (ICPRB) collected sediment samples in the marina area and farther downstream (ICPRB, 1990; Velinsky et al., 1992a). Concentrations of most pollutants in the marina are low compared to other areas in the Anacostia River (Table 3), suggesting that the source of these contaminants are either downstream of the marina or not retained in this area. Given that the marina is an area of net deposition (i.e., the current dredging program is evidence of this), it is more likely that the dominant sources of most pollutants are farther downstream towards the District of Columbia. However, the data presented in Table 3 are from one location in the marina and river, sampled once. Spatial and temporal variations may reveal areas and times of higher concentrations within the marina. Regardless, the resuspension of sediments due to the dredging process could enhance the bio-availability of sediment bound contaminants and transport to other areas of the river system.

Table 3. Sedimentary Concentrations of Selected Organics and Trace Metals from ICPRB (1990)* .

General Locations	∑PCB[1] ng/g	∑PAH[2] µg/g	DDT[3] ng/g	DDE[3] ng/g	CHL[4] ng/g	Cu[5] µg/g	Pb µg/g	Zn µg/g
ANACOSTIA RIVER								
Bladensburg Marina	82	7	5	10	32	35	29	159
NY Ave. Bridge	130	9	1	10	33	44	29	180
Hickey Hill	220	12	10	<1	6	50	50	241
Benning Rd.	320	11	3	15	50	50	79	265
Kingman Lake	480	16	2	35	65	95	168	479
NE Boundary Sewer	430	17	3	27	96	80	136	415
11th Street Bridge	380	16	3	35	48	103	179	452
South Capitol St. Bridge	1800	45	6	<1	105	207	351	587
Buzzard Point Marina	360	11	1	29	22	92	107	396

*[1]∑PCB is the sum of 209 individual congeners. [2]∑PAH is the sum of 15 individual aromatic hydrocarbons. [3]DDT and DDE are the sum of both o+p and p+p forms. [4]CHL is the sum of α and γ chlordane. [5]Cu, Pb, Zn are the strong (HCl) acid digestible fraction of the sediment.

Water Sampling

The District of Columbia's sampling boat (an 18 ft Boston Whaler) was used for most sampling, along with an all plastic canoe for collection of water and sediment from the NE and NW Branches of the Anacostia River. Station locations and distances from the confluence of the NE and NW Branches are given in Table 4. A Hydrolab Scout and Surveyor II were employed to determine *in situ* conditions of temperature, pH, dissolved oxygen (and %SAT), and conductivity. The meter was calibrated within 24 hours of sampling, along with a post-calibration test to check the drift of the meter. Water samples were hand collected by carefully lowering pre-cleaned 4 L bottles approximately 0.5 m below the surface of the water. The bottles were opened beneath the water's surface, rinsed three times, and allowed to fill. For organic samples, solvent-rinsed, pre-heated (450°C for 4 hours) glass bottles with Teflon lined-caps were used, while for trace metal and nutrient samples HCL and HNO_3 acid-soaked and deionized water rinsed high density polyethylene (HDPE) bottles were employed. The samples for chemical analysis were placed into coolers filled with blue ice (4°C). For further details concerning the specific chemical analyses, please see the QA/QC documentation

Table 4. Station Locations Relative to Confluence of NE and NW Branches.

Meters	Station Location
-122	Two stations, in NE and NW branches of the Anacostia River.
150	Between confluence and Rt. 450 bridge.
550	Below Rt 450 bridge; above marina (sediment sample).
1000	At dredge head, in marina.
1005	Just below dredge, in marina (sediment sample).
1015	Below dredge, in marina.
1030	Below dredge, in marina (sediment sample).
1060	Below dredge, in marina.
1370	Below dredge, in marina (sediment sample).
2440	Downstream of Colmar Manor and River Park in Anacostia River.
2960	In Anacostia River, just above Kenilworth Aquatic Garden.

Meters are taken from the confluence of the NE and NW Branches of the Anacostia River. For transects 1, 2, and 3 the dredge was located at 1000 m from the confluence.

(Velinsky et al., 1992b).

Samples for organics, trace metals, nutrients, and TSM were filtered upon return to the laboratory. All water samples were filtered through the appropriate filter (i.e., glass fiber, membrane, etc.) within a few hours of sample collection. Dissolved trace metals were acidified and stored at 4°C, while dissolved organic samples were extracted following filtration and stored at -20°C. Particulate samples were stored frozen until analysis. At all times, sample processing and preservation was geared to maintain sample integrity. All water samples were analyzed for the parameters listed in Table 2.

Field blanks consisted of a distilled water (Burdick and Jackson, Muskegon, MI) contained in a 4 L glass amber bottle that was brought to the field site and held under conditions similar to the samples. The blank was filtered and extracted in the normal fashion of a sample. Blanks were processed as the first samples prior to sample filtration and extraction. Trace metal and organic clean sampling procedures and storage of dissolved and particulate samples were used throughout the preparation and sampling (see QA/QC documentation). All materials coming in contact with the samplers were pre-cleaned for both organic and inorganic constituents.

Sediment Collection

Bottom sediments were collected with a KB corer (Wildco, Inc.) equipped with 2" polycarbonate core liners. This is a gravity coring device which takes relatively undisturbed cores in soft sediment deposits. The top 5 cm of sediment was extruded into a plastic bag which was kept refrigerated until the sample is dried (drying to commence within 24 hours). Additionally, in the shallow river area upstream of the dredge, a sediment sample was obtained by scooping the surface four centimeters of the sediment in a pre-heated glass jar.

Additional sediment samples were obtained in August of 1993 for organic analysis. For these samples, a petite-ponar grab sampler was used and approximately the top 3 to 5 cm of sediment was collected. The sampler was pre-cleaned with dilute-soap, ethanol, acetone, and methylene chloride, dried then rinsed with ambient river water prior to sample collection.

Additional Sampling

Due to the higher turbidity levels during transect 1 and the spacing of sample stations, it is unclear if the turbidity increase during transects 2 and 3 was due to the dredge.

There may be additional sources of suspended sediment between the upstream station and the dredge head, such as the sewer outfall near the boat ramp, or tidal resuspension of bottom sediment in the marina area. Therefore, additional samples for turbidity were taken in October, 1992.

MATERIALS AND METHODS

Organics

The complete description of the methods employed for the isolation, extraction, and quantitation of dissolved and particulate organic compounds is presented in Velinsky et al. (1992b). These methods will be briefly described below.

Suspended particulate matter (≥0.7 μm in diameter) was isolated from the water sample by filtration through glass fiber filters. Raw water was pumped via a positive displacement pump (Model QB-1, Fluid Metering Inc., Oyster Bay, NY) through a stacked arrangement of Whatman GFD (25 μm pore diameter) overlying Whatman GFF (0.7 μm pore size) 15 cm glass fiber filters housed in a Millipore stainless steel filtration apparatus. The filtered water was collected in a fresh 4 L glass amber bottle for further processing. Particle-laden filters were folded into quarters together (i.e., both the GFD and GFF filters) and placed in aluminum foil envelopes. The envelopes were sealed, labeled, and added to zip-lock plastic bags, then finally placed in freezer at -20°C until analysis.

The target analytes were extracted from filtered water with liquid-solid extraction (LSE). Four liters of water was passed through octadecylsilyl-bonded silia (C_{18}) containing LSE sorbent cartridges (Varian Assoc., Inc.) with procedures developed at the GMU laboratory (Foreman and Foster, 1991). The LSE cartridges were eluted within seven days of extraction.

LSE cartridges were eluted according to procedures previously developed by Foreman and Foster (1991). In brief, the LSE cartridges were initially de-watered by nitrogen gas purging for 30 minutes followed by vacuum aspiration for 5 minutes. Each cartridge was eluted with 60 mL of cyclohexane:isopropanol (7:3, v/v) solvent (both Carbopack B and C_{18} sorbents) into a 250 mL boiling flask with the aid of nitrogen head pressure. The eluent was reduced in volume to 0.2 mL by using rotary evaporator and nitrogen gas blowdown.

Filters were thawed to room temperature, placed in a Soxhlet extraction thimble, and extracted for 24 hours in a Soxhlet extraction apparatus using cyclohexane:isopropanol (7:3) as the solvent. Both GFD and GFF filters were combined for each sample in the Soxhlet apparatus during the extraction. Target analytes were spiked on filters prior to extraction.

Organohalogen contaminants (PCBs, aldrin, α- and γ-chlordane, dieldrin, and 4,4'-DDT) 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 organohalogens that may have also been present in the samples, extracts from the LSE cartridges and filters were fractionated via column chromatography prior to GC-ECD analysis to isolate PCBs + aldrin and the remaining pesticides as separate fractions (i.e., n-hexane for PCBs + aldrin and dichloromethane for chlordane, dieldrin, and DDT). Each eluent was collected separately and both eluents were concentrated to a final volume of 0.4 mL by using rotary flash evaporation and nitrogen blowdown and analyzed using GC-ECD.

Polynuclear aromatic hydrocarbons (PAH) associated with particulate matter were also fractionated using the same procedure described above after Soxhlet extraction. However, PAH were analyzed using GC/MS in both the hexane and dichloromethane fractions.

The complete target analyte list is shown in Table 5. A Hewlett-Packard (HP) 5890 Series II GC equipped with an electron capture detector was used to measure all organohalogen compounds. All GC separations were carried out by using high resolution capillary columns to attain the highest degree of efficiency and resolution in the analysis.

GC-ECD and GC/MS instruments were calibrated daily prior to the analysis of samples. Primary PAH and pesticide standards were prepared either from neat compounds (Chem Service Inc., West Chester, PA) or were obtained as pre-prepared solutions with known analyte concentrations (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. Approximately 112 PCB congeners were quantitated in each dissolved phase and suspended particle sample. A single calibration standard for GC-ECD and GC/MS was used to calculate relative response factors (RRFs) by manipulating the fundamental internal standard quantitation

TABLE 5. List of Organic Target Analytes for the Anacostia River Study.

ANALYTE	GC/MS	GC-ECD
PCBs (~ 90 congeners)		X
Organochlorine Pesticides		
Aldrin		X
α-Chlordane		X
γ-Chlordane		X
4,4'-DDT		X
Dieldrin		X
Polynuclear Aromatic Hydrocarbons		
Acenaphthene	X	
Acenaphthylene	X	
Anthracene	X	
Benz(a)anthracene	X	
Benzo(a)pyrene	X	
Benzo(b)fluoranthene	X	
Benzo(k)fluoranthene	X	
Benzo(ghi)perylene	X	
Chrysene	X	
Dibenz(ah)anthracene	X	
Fluoranthene	X	
Fluorene	X	
Indeno(123-cd)pyrene	X	
Naphthalene	X	
Phenanthrene	X	
Pyrene	X	

formula (Velinsky et al., 1992b).

GC peak identifications were made based upon retention time data, or if retention times had shifted, then retention times relative to the internal standards were used to identify individual constituents. RRFs were calculated from the calibration step. Calibration RRF data was recorded and a hard copy was saved on file daily to query instrument variability and drift through time. Method detection limits were determined for each analyte according to U.S. Environmental Protection Agency procedures previously described in detail in an earlier report (Grant et al., 1991).

The quality assurance checks and audits that were factored into this study involved a rigorous evaluation of the QA data provided through the procedures described above. Field blanks indicated the presence of contamination in the analysis, although procedures were scrupulously followed to minimize this problem for low level analysis. "Analyte" concentrations detected in the blanks were subtracted from the sample concentration to provide a more reliable estimate. Field blank results also provided feedback on the effort placed into cleaning field equipment, etc., and corrective measures were undertaken if this occurred. Matrix spikes provided information of the accuracy of the reported results. A percent mass recovery (%R) value was computed for each matrix spike which described quantitatively the accuracy of the method. Method precision could also be estimated through the analysis of duplicate samples and duplicate analyses were performed on 10% of the total number of samples analyzed.

Field blanks consisting of distilled water (Burdick and Jackson, Muskegon, MI) in 4L glass amber bottles were brought to the field site and held under conditions similar to the samples. The blanks were filtered and extracted as a regular sample. Duplicate field blanks were processed for each of the three Anacostia River sampling trips.

All non-volumetric glassware was scrupulously cleaned with Alconox detergent in hot tapwater, 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 solvent before use.

Trace Metals and Nutrients

Water Collection and Processing

Whole water samples were collected in 4 L HDPE jugs which were acid-soaked (1N HNO_3) and distilled deionized water rinsed (DDW) prior to use. A minimum of three rinses of the jugs were made with the actual sample water prior to sample storage. The samples were immediately filtered with acid-washed syringe filters (Sigma S 6261) for dissolved nutrients. The remaining sample was kept on ice until filtration (i.e., within 6 hours) for suspended matter, particulate nutrients, and particulate and dissolved trace metals.

The filtration for dissolved trace metals represented a potential source of artifact and contamination of the water sample. Samples were vacuum filtered through 47 mm diameter

0.4 μm Nuclepore filters held in acid-washed all plastic holders. The first 20 mL was used as a rinse of the filtration apparatus, and the remaining sample was retained in 60 mL acid-soaked Teflon bottles. Filtered water samples were acidified with Ultrex (J.T. Baker) nitric acid (75 μL in 50 mL sample) and kept refrigerated until analysis.

Nutrient samples were filtered using pre-heated (400°C for 2 hours) Whatman GFF glass fiber filters (0.7 μm pore size). After rinsing, samples were collected in three acid-washed 20 mL plastic vials for nutrient and anion (sulfate and chloride) analysis.

The analysis of anions and nutrient elements (water column dissolved and particulate, bottom sediment) followed the standard procedures for analysis in natural waters and sediments (Table 6). Similarly, the analysis of strong acid-extractable metals (i.e., hot (3:1 v/v) HCl-HNO_3) in solids is a relatively standard procedure which has been applied to a broad range of Chesapeake Bay projects, including those directly or indirectly sponsored by U.S. EPA (Chesapeake Bay Program, Joint NOAA and Toxics Subcommittee Toxics Research Program).

The analysis of dissolved trace metals was accomplished by chelation ion chromatography (CIC) (Siriraks et al., 1982; Long and Martin, 1992). This approach was more appropriate for this project than the conventional approach of graphite furnace atomic absorption spectrophotometry for several reasons: 1) minimal interferences from dissolved salts and organic matter, 2) the system is automated and there are few handling steps which could lead to contamination, 3) a single chromatographic run can analyze most trace metals simultaneously, and 4) the system is sensitive and can be used below 1 μg/L (ppb) for many metals. This system provided a rapid, accurate, and precise means of metal analysis for river water samples. Sirriraks et al. (1982) showed that this instrument provides data comparable to graphite furnace atomic absorption spectrometry (AAS), with comparisons made in a sea water matrix virtually identical.

Particulate trace metals were analyzed via AAS on acid-digested GFF glass fiber filters for Fe and Mn. The relatively large amount of material yielded sufficient metal for these analyses, but the filters had unacceptably high blanks for the other metals. For the other trace metals, the Nuclepore filters from the dissolved trace metal filtration were acid-digested and analyzed via chelation ion chromatography. Milligram amounts of NIST-certified estuarine sediment were analyzed with these sediment samples as part of the method validation

Table 6. Analytical Procedures Outline for Water Column and Sediment Samples.

Analysis	Description	Reference
Water Analyses		
Silicates, Nitrates	A Technicon Autoanalyzer II is used for colorimetric using standard procedures.	EPA equivalent procedures 370.1, 353.
Phosphates, Ammonium	Manual colorimetry, standard procedures.	Parsons et al. (1984)
TSM	Total suspended matter determined on glass fiber filters.	EPA 160.2
Chloride, Sulfate	Ion chromatography	EPA 300.0
Dissolved metals	Chelation ion chromatography	Sirriraks et al. (1990), EPA 200.10
Particulate metals	Filtration, aqua-regia digestion, analysis via chelation ion chromatography, (Mn and Fe via flame AAS)	Sirriraks et al. (1990), EPA 200.10
Particulate P	Aqua-regia extraction.	Aspila et al. (1976)
Particulate C,N	Combustion in Control Equipment CHN (glass fiber filters).	Manufacturer's Methods Book
Sediment Analyses		
Total C, N	High temperature combustion,TCD detection on a Control Instruments Elemental Analyzer	Manufacturer's Methods Book
Total P	A 1.0 N HCl extraction of ashed sediment, followed by standard colorimetry.	Aspila et al. (1976)
Percent water	Fresh sediment (> 1.0 g) is placed on pre-weighed Al pans, weighed, dried at 60°C and reweighed.	In-house method (UMD-CEES)
Trace metals	Aqua regia digestion to dryness, dissolved in 1N HCl, analysis via chelation ion chromatography or GF/Flame-AAS	Evans and Rigler (1980); Sirriraks et al. (1990), EPA 200.10

and QA/QC procedures. Particulate phosphorus was analyzed from the same digestion.

The CIC technique involved the pre-concentration of the metals in a 5-20 mL sample onto a concentrator column, the analytical separation of metals on a column and the postcolumn development of colored complexes. A UV/VIS spectrophotometer was used as a detector for this analysis. With 10 mL of sample, sub-ppb (< 1 μg/L) metal concentrations were obtained. All samples were run in duplicate on the CIC. In addition, five samples were analyzed for trace metals using the Zeeman-effect graphite furnace AAS equipment.

Turbidity

Sample Collection

Surface water samples (approximately 0.5 m below the surface) were obtained using 50 mL plastic bottles, held beneath the waters surface. Bottles were rinsed three times with ambient water prior to collection. Samples were kept in the dark at approximately 4°C until analysis (within 4 hours of collection).

Sample Analysis

Turbidity measurements were carried out by a nephelometric technique using a turbidimeter (HF Scientific, Inc. DRT Model 15C) following manufacturer's operating instructions and Standard Methods (1975) method 214A. Cuvettes used for this analyses are matched or indexed for accurate and precise measurements. For meter accuracy, a four point calibration (i.e., 0.02, 2, 18 and 180 NTU) was performed using a dilution series of Formazin (4000 NTU). The 0.02 NTU standard is a EPA reference standard provided by the manufacturer.

For each sample, the cuvette was rinsed with 0.2 μm filtered deionized water, rinsed three times with the sample, then filled. The cuvette was dried with Kimwipes and placed into the sample holder. The meter was read to within 1 NTU for the range 10 to 200 NTU. At one station (transect 4), triplicate water samples were collected to assess local variability along with meter precision.

Dissolved Organic Carbon (DOC)

Samples were collected along with the trace metal and nutrient samples (described above). Water samples were filtered using pre-heated glass fiber filters (e.g., 420°C for 2 hours; Whatman GFF 0.7 μm pore size) in an all glass filtration manifold. The filtration manifold and holder were pre-cleaned and pre-heated to oxidize and remove any background DOC. The manifold was cleaned between samples with DDW and ambient water. Filters were placed into the holder with all metal tweezers, and the filter and collection flask rinsed with approximately 50 mL of ambient water. Filtered water samples (5 mL) were acidified with 20 μl 6N HCl, quick frozen using liquid nitrogen, and stored until analysis (2 months).

DOC analyses were carried out by high temperature catalytic oxidation techniques using a Shimadzu TOC-5000 total carbon analyzer. This instrument is a commercially-available instrument based on that described by Suzuki et al. (1992).

Samples were thawed and bubbled with nitrogen for 10 minutes at 50 mL/min to remove inorganic carbon. The vials were then loaded onto the auto-analyzer tray for analysis. The manufacturers operating conditions were used and all samples were run in triplicate. Instrument calibration involved running a three point standard curve (1.2, 2.4, and 6 mg C/L) and a laboratory blank (DDW water), then fitting all data points (n=4) by least squares linear regression. The slope of this line was then taken as the response factor of the instrument and used to calibrate concentrations of unknowns. A calibration curve was run each day samples were run, and a log sheet was kept of these slopes and the blank (i.e., y-intercept) to check for long term drift in the instrument.

A field blank of DDW was brought to the field and treated as a sample. A large volume of water (100 mL) was placed into a cleaned bottle in the laboratory, and was analyzed before shipping to the field, and analyzed again upon return. Antipyrene, a refractory organic carbon compound, was also run daily as a check on the oxidation efficiency of the instrument. Samples which fell outside the range of the standard curve were automatically re-run by the instrument at either a smaller injection volume (100 μl is the standard injection volume) or at a higher instrument attenuation (x1 is the attenuation normally used).

All glassware used in these analyses, including the sample vials, were cleaned by washing in an Alconox solution, followed by rinsing in tap water, 10% HCl, and DDW. The glassware was then dried at 110°C in a conventional oven, and then baked clean of any residual organic matter in a muffle furnace at 550°C overnight. The filters were pre-heated at 420°C for 2 hours. Teflon-backed silicone septa were cleaned as above with the exception that they were dried in a conventional oven at 40°C and not placed in the muffle furnace.

RESULTS AND DISCUSSION

General Conditions During Sampling

Low tide in the Anacostia River was at approximately 1400 on September 9th. Sampling started at 1100 and lasted approximately one hour for the collection of five water samples. The dredge had not been in operation for the previous three days (due to equipment failure); however water clarity was poorer than expected due to an unexpected localized rain shower the previous evening. Turbidity levels ranged from 26 to 44 NTU, with no apparent trend downstream (Table 7). Due to a thundershower the previous evening, turbidity levels were higher during this sampling period than either of the two transects performed when dredging operations were underway (Table 7).

The second and third transects were accomplished on September 22nd; with low tide at approximately 1144. Dredging operations had been underway from approximately 0800 to 1000 at which point the dredge head became clogged and operations were suspended. After approximately 45 minutes the dredge was repaired and operations continued for the rest of the day. Sampling for transect 2 commenced 15 minutes after the dredge was operating. The second transect started at approximately 1100 and was completed at approximately 1145. Unfortunately, the one hour waiting period extended the third transect into a rising tide. The third transect started at approximately 1215 and was completed by 1330. At approximately 1230, the water level started to rise in the river as the tide changed from slack water to flood tide. Water clarity was much greater during both transects than during transect 1 as there was no runoff in the previous three to four days. Turbidity levels were similar for both transects (Table 7), and should allow for upstream/downstream comparisons for each transect.

Basic water quality parameters, including temperature, dissolved oxygen, conductivity, and pH, were taken at all stations. At stations downstream of the dredge, these parameters were measured at both the surface and near the bottom (Appendix I). This information was collected to help determine the degree to which the water column was mixed, and as basic geochemical parameters to help understand the distribution of trace metals within the water column.

Water temperatures during transects 1, 2 and 3 ranged from 22.8 to 26.1 °C. Temperatures were lower upstream compared to the marina area for transect 1, however this

Table 7*: Transect 1

STA ID	Distance (m)	Water Depth (m)	Temp. (oC)	pH	Cond (mmho/cm)	DO (mg/L)	Ox.Sat. (%)	Turb. (NTU)	Seechi Depth (cm)
T1- (-1200)NW	-122.0	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-1200)NE	-122.0	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-1100)	150.0	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-500)	550.0	<0.5	22.8	7.6	0.217	7.2	83.0	28.0	40.0
T1- (-3)	1000.0	3.0	22.9	7.4	0.223	6.7	78.0	37.8	41.0
T1- (+3)	1005.0	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+6)	1015.0	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+12)	1030.0	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+30)	1060.0	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+120)	1370.0	1.0	23.5	7.2	0.231	ND	ND	44.0	35.0
T1- (+800)	2440.0	2.6	24.3	7.0	0.224	ND	ND	26.1	60.0
T1- (+1300)	2960.0	1.2	23.6	6.8	0.225	ND	ND	26.8	58.0

						Dissolved --					Particulate -----------		
STA ID	Distance (m)	Seston (mg/L)	Seston (%C)	Seston (%N)	C/N (molar)	NH4 (uM)	NO2+3 (uM)	Si (uM)	PO4 (uM)	DOC (uM)	C (uM)	N (uM)	P (uM)
T1- (-1200)NW	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-1200)NE	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-1100)	150.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-500)	550.0	13.3	6.9	1.1	7.5	0.87	37.0	100.0	0.12	330.0	76.6	10.3	0.86
T1- (-3)	1000.0	24.6	5.9	0.9	7.5	1.56	38.6	100.0	0.09	318.0	121.6	16.2	1.18
T1- (+3)	1005.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+6)	1015.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+12)	1030.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+30)	1060.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+120)	1370.0	29.7	6.5	0.9	8.8	10.80	31.0	96.3	0.10	801.0	160.8	18.3	1.19
T1- (+800)	2440.0	19.9	7.1	0.9	8.8	18.90	27.0	98.5	0.21	383.0	118.0	13.4	0.85
T1- (+1300)	2960.0	22.8	6.6	0.8	10.1	17.40	26.0	101.0	0.20	366.0	124.9	12.4	0.71

* See note at end of tables.

Table 7: Transect 1 (continue)

STA ID	Distance (m)	Dissolved Metals Fe (ug/L)	Cu (ug/L)	Ni (ug/L)	Zn (ug/L)	Co (ug/L)	Mn (ug/L)	Particulate Metals Fe (ug/L)	Cu (ug/L)	Ni (ug/L)	Zn (ug/L)	Co (ug/L)	Mn (ug/L)
T1- (-1200)NW	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-1200)NE	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-1100)	150.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (-500)	550.0	16.1	0.56	0.74	2.3	0.17	7.3	595.0	0.92	0.73	8.91	0.39	33.3
T1- (-3)	1000.0	18.2	0.68	0.76	2.6	0.23	18.7	1250.0	1.60	0.40	5.33	0.29	48.4
T1- (+3)	1005.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+6)	1015.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+12)	1030.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+30)	1060.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T1- (+120)	1370.0	20.5	0.65	0.84	3.5	0.28	30.8	1190.0	1.44	0.47	6.40	0.40	67.6
T1- (+800)	2440.0	25.1	0.48	0.80	4.8	0.31	30.4	707.0	1.02	0.78	6.86	0.42	43.6
T1- (+1300)	2960.0	20.7	0.69	0.78	2.8	0.29	29.3	530.0	2.75	1.90	13.69	0.79	36.9

STA ID	Distance (m)	Dissolved PAHs (ng/L)	a+g Chlor (ng/L)	PCBs (ng/L)	Particulate PAHs (ng/L)	a+g Chlor (ng/L)	PCBs (ng/L)
T1- (-1200)NW	-122.0	ND	ND	ND	ND	ND	ND
T1- (-1200)NE	-122.0	ND	ND	ND	ND	ND	ND
T1- (-1100)	150.0	ND	ND	ND	ND	ND	ND
T1- (-500)	550.0	50.9	2.5	3.3	3.6	1.3	12.3
T1- (-3)	1000.0	72.2	4.6	2.3	88.4	1.5	11.3
T1- (+3)	1005.0	ND	ND	ND	ND	ND	ND
T1- (+6)	1015.0	ND	ND	ND	ND	ND	ND
T1- (+12)	1030.0	ND	ND	ND	ND	ND	ND
T1- (+30)	1060.0	ND	ND	ND	ND	ND	ND
T1- (+120)	1370.0	133.0	1.8	0.8	296.0	3.1	7.9
T1- (+800)	2440.0	176.5	8.6	3.9	119.6	4.1	16.7
T1- (+1300)	2960.0	123.2	1.8	2.2	26.3	2.6	10.5

Table 7: Transect 2

STA ID	Distance (m)	Water Depth (m)	Temp. (oC)	pH	Cond (mmho/cm)	DO (mg/L)	Ox.Sat. (%)	Turb. (NTU)	Seechi Depth (cm)
T2- (-1200)NW	-122.0	NS	NS	NS	NS	NS	NS	NS	NS
T2- (-1200)NE	-122.0	NS	NS	NS	NS	NS	NS	NS	NS
T2- (-1100)	150.0	0.3	24.8	8.6	0.264	11.2	134.9	3.4	>30
T2- (-500)	550.0	0.5	24.9	7.6	0.277	7.9	95.3	2.9	>50
T2- (-3)	1000.0	3.0	24.2	7.5	0.276	6.5	77.7	11.1	70.0
T2- (+3)	1005.0	2.3	23.0	7.4	0.211	6.0	70.4	8.5	78.0
T2- (+6)	1015.0	2.2	23.0	7.2	0.291	6.2	72.5	10.0	80.0
T2- (+12)	1030.0	2.0	23.7	7.1	0.240	6.3	74.3	9.9	85.0
T2- (+30)	1060.0	ND	23.3	7.2	0.289	6.2	72.2	9.5	72.0
T2- (+120)	1370.0	2.2	23.0	7.0	0.286	6.2	71.9	13.6	55.0
T2- (+800)	2440.0	2.2	23.3	6.9	0.293	5.0	58.4	13.5	55.0
T2- (+1300)	2960.0	2.6	23.1	6.9	0.295	4.2	48.6	12.5	58.0

						Dissolved					Particulate		
STA ID	Distance (m)	Seston (mg/L)	Seston (%C)	Seston (%N)	C/N (molar)	NH4 (uM)	NO2+3 (uM)	Si (uM)	PO4 (uM)	DOC (uM)	C (uM)	N (uM)	P (uM)
T2- (-1200)NW	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T2- (-1200)NE	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T2- (-1100)	150.0	3.2	17.1	2.1	9.6	1.32	34.5	45.3	0.11	634.0	45.0	4.7	0.33
T2- (-500)	550.0	6.6	13.4	1.9	8.3	1.66	38.9	47.5	0.08	187.0	73.4	8.9	0.20
T2- (-3)	1000.0	10.6	9.8	1.1	10.1	5.40	36.4	49.9	0.09	171.0	86.6	8.5	0.44
T2- (+3)	1005.0	11.3	9.7	1.4	8.3	8.16	36.0	49.8	0.09	182.0	91.3	11.0	0.26
T2- (+6)	1015.0	12.7	8.0	1.0	9.7	8.22	36.0	48.7	0.08	161.0	84.8	8.7	0.11
T2- (+12)	1030.0	13.0	6.5	0.7	10.4	7.25	37.0	48.6	0.15	200.0	70.9	6.8	0.07
T2- (+30)	1060.0	7.4	14.4	1.8	9.2	8.34	35.7	49.5	0.08	196.0	88.3	9.6	0.11
T2- (+120)	1370.0	11.7	10.5	1.1	11.1	24.10	27.6	54.8	0.10	207.0	102.3	9.2	0.06
T2- (+800)	2440.0	15.8	10.3	1.3	9.0	31.40	19.9	64.5	0.07	256.0	135.0	15.0	0.69
T2- (+1300)	2960.0	24.7	8.9	1.2	9.0	ND	ND	ND	ND	249.0	ND	ND	0.38

Table 7: Transect 2 (continue)

STA ID	Distance (m)	Dissolved Metals Fe (ug/L)	Cu (ug/L)	Ni (ug/L)	Zn (ug/L)	Co (ug/L)	Mn (ug/L)	Particulate Metals Fe (ug/L)	Cu (ug/L)	Ni (ug/L)	Zn (ug/L)	Co (ug/L)	Mn (ug/L)
T2- (-1200)NW	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T2- (-1200)NE	-122.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T2- (-1100)	150.0	31.2	0.73	1.34	2.24	0.13	3.3	95.6	0.06	0.19	1.72	0.03	9.70
T2- (-500)	550.0	24.7	0.61	0.91	1.09	0.14	3.5	179.0	0.44	0.39	4.03	0.12	17.29
T2- (-3)	1000.0	22.8	0.63	0.94	1.65	0.14	6.7	293.3	0.98	0.38	5.42	0.29	33.25
T2- (+3)	1005.0	22.5	0.90	0.90	1.32	0.19	8.4	355.6	0.91	0.54	1.62	0.17	33.92
T2- (+6)	1015.0	22.7	0.54	0.86	1.61	0.12	8.1	232.6	1.00	0.67	2.67	0.20	31.39
T2- (+12)	1030.0	23.4	0.55	0.77	0.70	0.11	7.1	234.4	1.01	0.58	1.98	0.18	30.49
T2- (+30)	1060.0	21.9	0.47	0.77	0.76	0.16	8.4	93.1	0.73	0.49	0.56	0.01	21.94
T2- (+120)	1370.0	22.3	0.44	0.77	0.65	0.18	15.7	168.9	0.56	0.75	2.42	0.18	34.60
T2- (+800)	2440.0	20.0	0.32	0.71	0.56	0.19	26.3	495.5	1.56	0.91	3.18	0.37	68.83
T2- (+1300)	2960.0	22.6	0.30	0.76	0.51	0.21	33.7	334.4	1.00	1.10	3.02	0.32	63.58

STA ID	Distance (m)	Dissolved PAHs (ng/L)	a+g Chlor (ng/L)	PCBs (ng/L)	Particulate PAHs (ng/L)	a+g Chlor (ng/L)	PCBs (ng/L)
T2- (-1200)NW	-122.0	ND	ND	ND	ND	ND	ND
T2- (-1200)NE	-122.0	ND	ND	ND	ND	ND	ND
T2- (-1100)	150.0	ND	ND	ND	ND	ND	ND
T2- (-500)	550.0	46.8	2.0	4.0	4.2	1.0	9.7
T2- (-3)	1000.0	171.6	5.1	9.5	2.0	1.1	10.5
T2- (+3)	1005.0	46.7	1.5	3.8	0.0	0.0	23.6
T2- (+6)	1015.0	55.6	2.0	4.5	8.1	0.0	8.2
T2- (+12)	1030.0	29.2	4.9	20.7	19.1	1.1	11.0
T2- (+30)	1060.0	130.6	2.4	3.0	1.1	0.0	21.9
T2- (+120)	1370.0	32.0	2.9	2.1	2.5	0.6	ND
T2- (+800)	2440.0	42.9	4.7	13.6	0.3	1.1	7.9
T2- (+1300)	2960.0	25.0	0.8	3.1	101.3	0.0	15.5

Table 7: Transect 3

STA ID	Distance (m)	Water Depth (m)	Temp. (oC)	pH	Cond (mmho/ cm)	DO (mg/L)	Ox.Sat. (%)	Turb. (NTU)	Seechi Depth (cm)
T3- (-1200)NW	-122.0	0.6	26.1	8.7	0.309	12.5	154.1	1.9	>60
T3- (-1200)NE	-122.0	0.9	27.2	9.6	0.248	14.4	181.5	2.7	>90
T3- (-1100)	150.0	NS	NS	NS	NS	NS	NS	NS	NS
T3- (-500)	550.0	0.6	24.6	8.0	0.273	9.4	112.8	5.5	>50
T3- (-3)	1000.0	1.8	25.8	7.3	0.268	5.5	67.9	13.5	ND
T3- (+3)	1005.0	0.8	24.0	7.0	0.290	6.2	73.7	15.1	66.0
T3- (+6)	1015.0	0.8	23.9	7.0	0.288	6.9	81.7	14.5	75.0
T3- (+12)	1030.0	0.7	23.6	7.0	0.290	6.7	79.0	15.5	70.0
T3- (+30)	1060.0	0.7	23.7	7.0	0.287	6.5	76.3	13.1	72.0
T3- (+120)	1370.0	0.5	23.6	7.0	0.290	6.4	74.9	15.1	58.0
T3- (+800)	2440.0	0.6	23.7	6.9	0.294	4.7	55.7	20.6	68.0
T3- (+1300)	2960.0	0.6	23.7	6.9	0.302	4.9	58.2	21.8	55.0

						Dissolved					Particulate		
STA ID	Distance (m)	Seston (mg/L)	Seston (%C)	Seston (%N)	C/N (molar)	NH4 (uM)	NO2+3 (uM)	Si (uM)	PO4 (uM)	DOC (uM)	C (uM)	N (uM)	P (uM)
T3- (-1200)NW	-122.0	3.3	20.4	2.0	12.1	1.07	19.5	51.4	0.13	168.0	56.7	4.7	0.42
T3- (-1200)NE	-122.0	5.9	10.8	1.1	11.7	0.88	39.5	56.7	0.08	Contam	53.1	4.5	0.39
T3- (-1100)	150.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T3- (-500)	550.0	4.8	11.3	1.4	9.3	2.33	35.7	43.9	0.08	235.0	45.5	4.9	0.51
T3- (-3)	1000.0	49.8	3.8	0.4	11.9	24.40	35.7	50.0	0.04	202.0	157.4	13.2	0.40
T3- (+3)	1005.0	11.3	8.6	1.0	9.9	16.40	35.7	50.0	0.04	209.0	81.2	8.2	0.34
T3- (+6)	1015.0	11.5	9.0	1.2	8.9	10.40	33.9	51.3	0.08	198.0	86.6	9.8	0.19
T3- (+12)	1030.0	14.5	10.1	1.0	11.3	10.10	35.5	48.2	0.04	202.0	122.4	10.8	0.56
T3- (+30)	1060.0	12.2	11.1	1.1	11.4	11.40	33.5	51.2	0.05	199.0	113.2	9.9	0.29
T3- (+120)	1370.0	13.8	11.6	1.4	9.9	23.00	25.8	56.7	0.07	209.0	133.5	13.4	0.89
T3- (+800)	2440.0	17.4	11.4	1.4	9.4	30.10	18.9	64.8	0.07	231.0	165.1	17.6	0.34
T3- (+1300)	2960.0	14.8	12.6	1.6	9.4	31.90	18.0	65.9	0.08	247.0	155.9	16.6	0.45

Table 7: Transect 3 (continue)

		Dissolved Metals						Particulate Metals					
STA ID	Distance (m)	Fe (ug/L)	Cu (ug/L)	Ni (ug/L)	Zn (ug/L)	Co (ug/L)	Mn (ug/L)	Fe (ug/L)	Cu (ug/L)	Ni (ug/L)	Zn (ug/L)	Co (ug/L)	Mn (ug/L)
T3- (-1200)NW	-122.0	32.6	0.56	0.69	0.86	0.14	2.4	26.4	0.20	0.09	2.15	0.02	5.9
T3- (-1200)NE	-122.0	26.3	0.66	0.64	0.80	0.16	1.5	67.9	0.42	0.21	3.54	0.08	9.8
T3- (-1100)	150.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
T3- (-500)	550.0	25.2	0.72	0.76	1.00	0.12	4.1	150.5	0.58	0.14	2.89	0.09	18.2
T3- (-3)	1000.0	18.0	0.40	0.88	0.71	0.22	14.0	990.7	2.48	1.69	13.57	0.86	86.9
T3- (+3)	1005.0	19.3	0.50	0.78	1.04	0.19	11.0	174.6	1.18	0.56	3.71	0.24	23.1
T3- (+6)	1015.0	21.4	0.50	0.69	0.70	0.19	9.2	136.1	0.79	0.21	2.97	0.18	27.6
T3- (+12)	1030.0	17.7	0.55	0.73	1.23	0.16	8.1	297.7	1.04	0.52	4.24	0.28	37.6
T3- (+30)	1060.0	19.0	0.55	0.77	0.71	0.18	10.5	163.7	0.93	0.39	3.10	0.21	44.0
T3- (+120)	1370.0	20.7	0.42	0.99	0.71	0.20	19.0	561.6	1.23	0.73	5.04	0.35	55.9
T3- (+800)	2440.0	19.4	0.34	0.84	0.81	0.21	28.9	203.8	1.18	0.65	2.35	0.33	51.1
T3- (+1300)	2960.0	20.4	0.32	0.85	1.20	0.21	31.2	239.9	1.22	0.72	2.35	0.40	65.5

		Dissolved			Particulate		
STA ID	Distance (m)	PAHs (ng/L)	a+g Chlor (ng/L)	PCBs (ng/L)	PAHs (ng/L)	a+g Chlor (ng/L)	PCBs (ng/L)
T3- (-1200)NW	-122.0	61.8	2.1	5.3	2.5	0.0	6.5
T3- (-1200)NE	-122.0	108.2	1.4	2.4	60.3	0.0	5.4
T3- (-1100)	150.0	ND	ND	ND	ND	ND	ND
T3- (-500)	550.0	18.0	1.4	1.8	32.7	1.0	11.0
T3- (-3)	1000.0	116.4	2.3	7.5	3939.0	3.2	17.8
T3- (+3)	1005.0	31.5	2.3	1.7	45.8	0.7	10.6
T3- (+6)	1015.0	3.6	1.6	1.7	11.1	2.1	13.7
T3- (+12)	1030.0	7.0	1.7	4.1	55.4	2.7	12.8
T3- (+30)	1060.0	16.4	2.6	5.2	5.5	1.0	14.5
T3- (+120)	1370.0	25.8	1.9	3.9	0.0	0.0	NA
T3- (+800)	2440.0	15.4	1.2	5.3	2.8	1.3	13.7
T3- (+1300)	2960.0	7.9	2.0	2.0	66.6	2.0	17.5

Table 7: Transect 4

STA ID	Distance (m)	Water Depth (m)	Temp. (oC)	pH	Cond (mmho/cm)	DO (mg/L)	Ox.Sat. (%)	Turb. (NTU)	Seechi Depth (cm)
T4 -1	150.0	0.2	18.4	8.3	0.209	10.7	113.0	7.8	ND
T4-1.5	155.0	ND	ND	ND	ND	ND	ND	ND	ND
T4 -2	550.0	0.5	18.0	8.2	0.211	11.2	117.0	7.5	ND
T4 -3	640.0	0.3	17.9	8.2	0.210	11.2	116.0	7.1	ND
T4 -4	760.0	ND	17.9	8.1	0.212	11.3	118.0	9.6	ND
T4 -5	790.0	0.5	17.7	8.0	0.246	10.7	107.0	25.0	ND
T4-11	795.0	ND	ND	ND	ND	ND	ND	ND	ND
T4 -6	880.0	0.6	17.9	8.1	0.210	11.2	117.0	11.3	ND
T4 -7	915.0	1.2	17.7	8.1	0.213	11.1	114.0	12.2	ND
T4 -8	1000.0	1.5	17.5	7.9	0.218	10.9	113.0	12.2	ND
T4 -9	1130.0	1.5	16.9	7.8	0.210	10.6	107.0	9.5	ND
T4-9.5	1222.0	ND	ND	ND	ND	ND	ND	ND	ND
T4 -10AVE	1370.0	1.5	16.0	7.5	0.214	10.1	101.6	ERR	ND

Transect 5

STA ID	Distance (m)	Water Depth (m)	Temp. (oC)	pH	Cond (mmho/cm)	DO (mg/L)	Ox.Sat. (%)	Turb. (NTU)	Seechi Depth (cm)
T5 -1	150.0	0.2	18.2	8.4	0.212	10.6	111.0	8.0	ND
T5-1.5	155.0	ND	ND	ND	ND	ND	ND	ND	ND
T5 -2	550.0	0.5	18.1	8.2	0.212	10.9	114.0	8.5	ND
T5 -3	640.0	0.3	18.1	8.2	0.213	11.2	117.0	7.9	ND
T5 -4	760.0	ND	ND	ND	ND	ND	ND	ND	ND
T5 -5	790.0	0.5	17.7	7.7	0.320	8.8	90.0	30.2	ND
T5 -11	795.0	0.3	17.6	7.7	0.280	9.6	98.0	28.0	ND
T5 -6	880.0	0.6	18.1	8.2	0.212	11.2	117.0	9.2	ND
T5 -7	915.0	1.2	17.9	8.1	0.214	11.3	117.5	9.1	ND
T5 -8	1000.0	1.5	17.6	8.0	0.216	11.2	116.0	12.8	ND
T5 -9	1130.0	1.5	16.9	7.8	0.216	10.9	110.0	14.1	ND
T5-9.5	1222.0	ND	ND	ND	ND	ND	ND	ND	ND
T5 -10	1370.0	1.5	16.0	7.5	0.214	10.1	101.6	15.0	ND

Table 7: Transect 6

STA ID	Distance (m)	Water Depth (m)	Temp. (oC)	pH	Cond (mmho/ cm)	DO (mg/L)	Ox.Sat. (%)	Turb. (NTU)	Seechi Depth (cm)
T6 -1	150.0	0.2	11.8	7.6	0.274	11.6	105.5	66.1	ND
T6 -2	155.0	0.2	10.9	8.4	0.276	13.4	119.3	8.6	ND
T6 -3	550.0	0.6	10.8	7.9	0.246	12.2	109.8	33.6	ND
T6 -4	640.0	0.9	10.6	7.9	0.243	12.3	109.8	32.6	ND
T6 -5	760.0	ND	10.8	7.9	0.246	12.2	109.2	34.1	ND
T6 -6	790.0	ND	12.3	7.5	0.370	8.0	72.7	17.3	ND
T6-6.5	795.0	ND	ND	ND	ND	ND	ND	ND	ND
T6 -7	880.0	ND	11.3	7.8	0.254	11.8	106.9	41.6	ND
T6-7.5	915.0	ND	ND	ND	ND	ND	ND	ND	ND
T6 -8	1000.0	ND	10.8	7.7	0.251	11.5	103.0	41.5	ND
T6 -9	1130.0	ND	10.9	7.3	0.255	10.6	95.1	10.5	ND
T6 -10	1220.0	1.1	11.2	7.6	0.251	9.9	89.3	11.2	ND
T6 -11	1370.0	1.1	12.7	7.6	0.258	9.3	88.3	22.1	ND

Transect 7

STA ID	Distance (m)	Water Depth (m)	Temp. (oC)	pH	Cond (mmho/ cm)	DO (mg/L)	Ox.Sat. (%)	Turb. (NTU)	Seechi Depth (cm)
T7 -1	150.0	ND	13.1	7.8	0.277	12.7	119.6	25.9	ND
T7 -2	155.0	ND	12.7	8.8	0.227	13.8	129.3	6.1	ND
T7 -3	550.0	ND	12.0	8.2	0.245	13.4	123.5	13.1	ND
T7 -4	640.0	ND	11.9	8.1	0.248	12.4	114.2	22.0	NS
T7 -5	760.0	ND	11.8	8.0	0.248	12.9	117.7	26.1	ND
T7 -6	790.0	ND	12.3	7.5	0.427	8.6	79.8	18.2	ND
T7 -6.5	795.0	ND	ND	ND	ND	ND	ND	ND	ND
T7 -7	880.0	ND	11.5	7.9	0.249	12.2	.111.4	32.4	ND
T7-7.5	915.0	ND	ND	ND	ND	ND	ND	ND	ND
T7 -8	1000.0	ND	11.1	7.7	0.251	11.4	103.0	38.2	ND
T7 -9	1130.0	ND	11.8	7.6	0.253	10.6	95.4	6.8	ND
T7 -10	1220.0	ND	11.1	7.6	0.253	10.2	92.5	10.8	ND
T7 -11	1370.0	ND	12.7	7.6	0.258	9.3	88.3	22.1	ND

Notes:

PAHs and PCBs are the sum of individual compounds, see Appendix II.

ND - Not determined

See text for description of parameters.

trend was reversed for transects 2 and 3. It is possible that the previous night's rain shower before transect 1 affected the temperature distribution in the upper portion of the river. Temperature differences between the near surface (approximately 0.5 m) and near bottom (generally around 2 to 3 m) were small for all transects and ranged from 0 to 0.8 °C with surface waters slightly warmer. There was no spatial trend in the temperature difference between near surface and bottom in the river of all three transects.

Dissolved oxygen concentrations ranged from 4.2 to 12.5 mg O_2/L for surface waters and from 3.3 to 6.3 mg O_2/L in near bottom waters. Dissolved oxygen concentrations were higher in the area above the marina and decreased downstream (Table 7, Appendix I). Oxygen concentration differences between near surface and near bottom waters were generally small in the upper marina area and increased downstream (Appendix I). The drop in oxygen concentration was not related to temperature changes as the temperatures were fairly uniform (Table 7, Appendix I). It is likely that as the water enters the tidal area of the marina, the residence time of the water increases allowing less exchange of oxygen between surface and near bottom waters. The decrease in oxygen concentrations downstream of the marina may be due to higher sediment (Sampou, 1990) and water column oxygen demand related to the fact that the sediments become more fine-grained and organic carbon rich farther downstream.

These data indicate that the water column was well-mixed or slightly-stratified during this sampling period. This is especially important because only near surface samples (i.e, 0.5 m) were collected to assess the impact of the dredge. Due to the shallowness of the area (2 to 3 m) and the lack of major stratification, the use of near surface samples should be sufficient to conservatively estimate the dredge's impact to the river.

Total Suspended Matter

Total suspended matter (TSM) ranged from approximately 3 to 50 mg/L for the three transects (Table 7; Figure 2). Generally, lower concentrations of TSM were found upstream of the dredge, both above and below the confluence of the NE and NW Branches of the Anacostia River (Figure 1). Concentrations increased downstream of the confluence to the boundary of the District of Columbia. Within the marina, concentrations did not increase in relationship to the location of the dredge (Figure 2), except for one sample. This sample (ID: T3 - (-3) at 1000 m downstream of the confluence; Table 7) was taken right at the dredge head

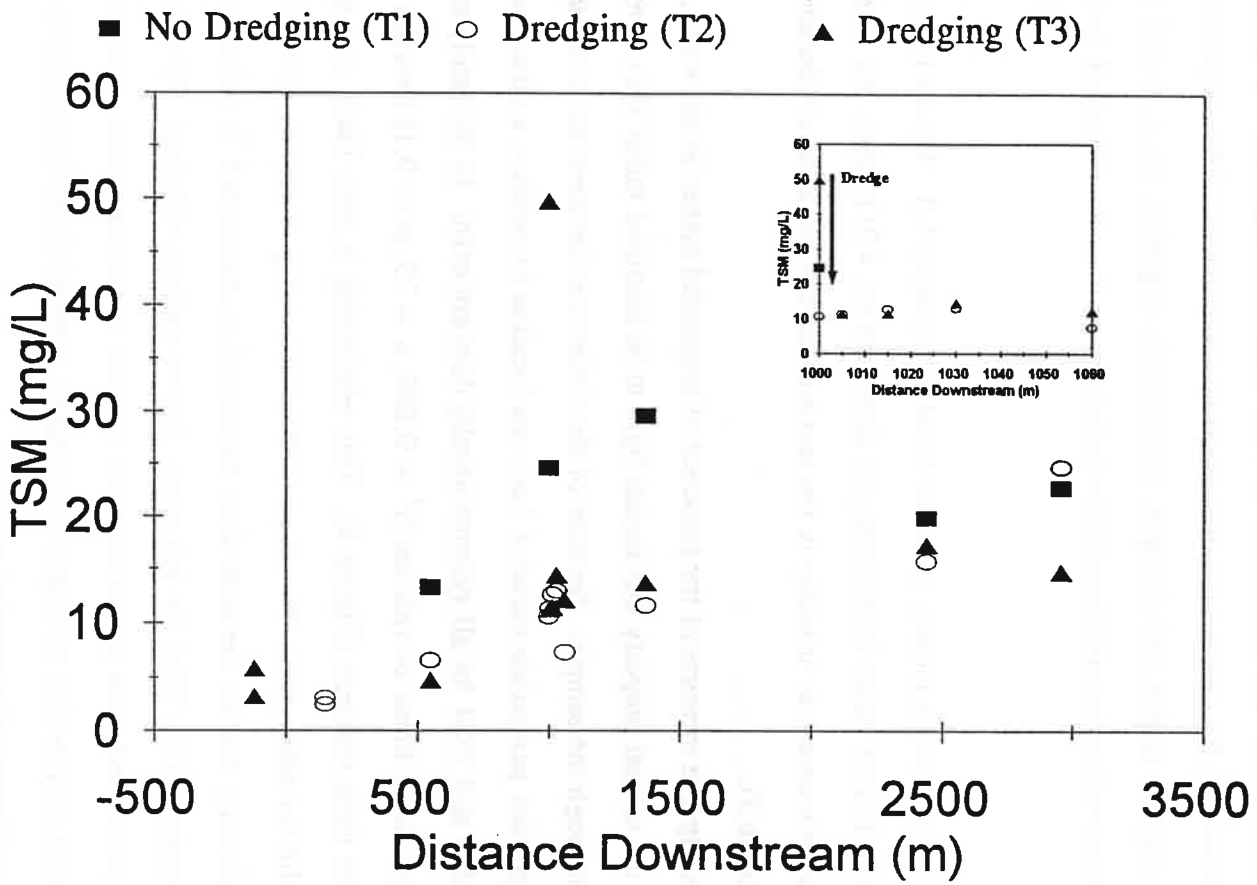

Figure 2. Distribution of total suspended matter (TSM) in the Anacostia River.

and had a TSM concentration of 50 mg/L. The high TSM may be an indication of "local" resuspension due to the cutterhead dredge. Below the dredge (>1000 m), TSM concentrations remained low and fairly constant for transects 2 and 3. Outside of the marina (i.e., at distances > 1370 m), concentrations increased, only slightly, to approximately 18 and 25 mg/L. The concentration and distribution of TSM suggest resuspension via dredging is not substantial. However, the distribution of the various components of the suspended particulate material (i.e., organic carbon and nitrogen, trace metals, organics, etc.), as well as dissolved material, may provide some additional information concerning the effects of dredging to the river system.

Turbidity

Levels of turbidity closely followed TSM in transects 1-3. Values ranged from <2 to 45 NTU, with lowest values in the area just above the Rt. 450 bridge. As with TSM, there was no noticeable increase in turbidity in the marina area that could be attributed to dredge operations (Figure 3).

Turbidity is a measure of the presence of suspended matter in the water, and is an expression of the optical property that causes light to be scattered rather than transmitted in straight lines through the sample. Because of the differences between the size, shape, and density of suspended particulate material from one location to another, a direct correlation between turbidity and TSM for all systems usually does not exist. In this study area however, there was a significant linear correlation ($r^2 = 0.865$, $n = 25$, $p > 0.1$) between TSM and turbidity for the three transects (Figure 4). This relationship is most likely area specific, and may not be valid for other sites. The slope of this relationship is slightly greater than unity (i.e., 1.5), indicating that for the other four transects (i.e.,transects 4-7) turbidity values are a close approximation of the TSM for this area. At two stations with high TSM, turbidity values were low (Figure 4) and these points were not included in the regression. Interestingly, the two outlier points may be due the input of suspended material from the operation of the dredge or other localized inputs of suspended material.

Additional water samples were taken for turbidity in mid-October 1992. These samples were obtained to assess the natural variability of suspended particulate material when the dredge was not in operation. Transects 4 and 5, as well as 6 and 7, were taken on the

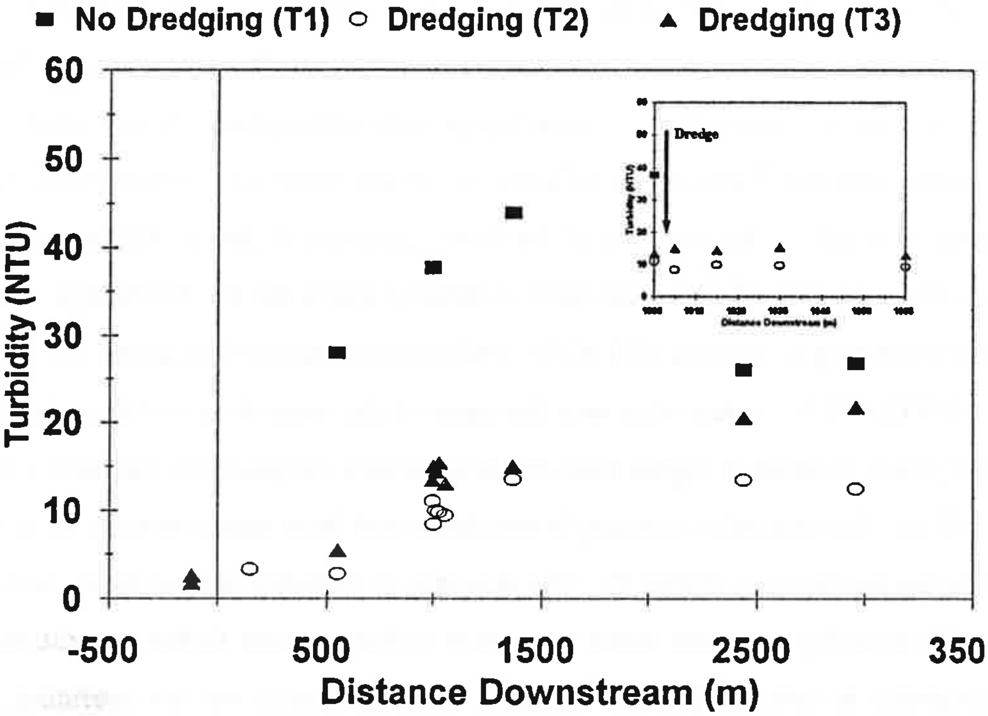

Figure 3. Distribution of turbidity in the Anacostia River.

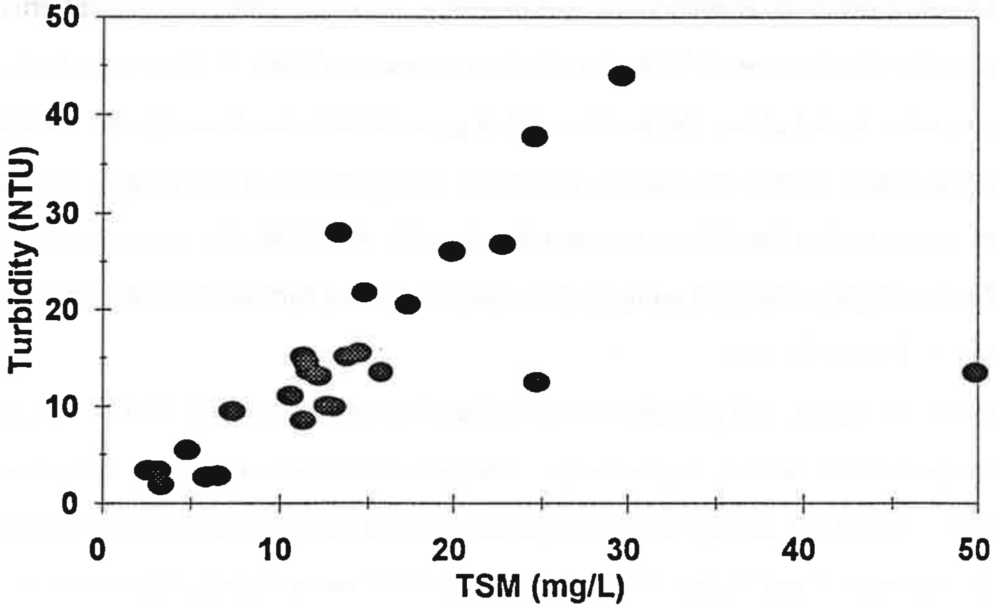

Figure 4. Concentrations of TSM and turbidity in the Anacostia River.

same day within 30 minutes of each other. Transects 4 exhibited fairly consistent turbidity (11.1 ± 2.9 NTU, mean ± 1σ), with no downstream trend within the marina area. There was substantial variability between the two sampling periods with turbidity levels substantially higher during transects 6 and 7 than 4 and 5 (Table 7). While there was no significant rain previous to transects 6 and 7, the turbidity of the river, upstream of the Rt. 450 bridge was elevated. Also, there was significant cross-river variability above the Rt. 450 bridge, with one side of the river exhibiting a turbidity of 8 NTU, while approximately 6 m across the river the turbidity was 65 NTU. It is unclear what was the cause of the cross-river variation during transect 6 and 7, but it resulted in higher turbidity downstream compared to transects 4 and 5 (25 versus 15 NTU). Interestingly, turbidity levels decreased from approximately 40 to 9 NTU just within the marina area (Table 7). The decrease in turbidity is most likely related to the mixing of high turbidity upstream water with lower turbidity water farther downstream. The overall variability in turbidity between transects when the dredge was not operating, along with the transects while the dredge was operating, indicates that there was no significant increase in turbidity and TSM as a result of dredging the marina area.

Particulate Carbon, Nitrogen, and Phosphorus

The concentrations of particulate carbon (PC), nitrogen (PN), and phosphorus (PP) were similar to the distribution of TSM for all three transects (Table 7, Figure 5a,b,c). Lower concentrations were found above the marina with a general increase downstream. There was no substantial increase, within the marina, related to the operation of the dredge, except for the sample taken at the dredge head from transect 3. As with the TSM, the concentrations of PC, PN, and PP were slightly elevated compared to concentrations further downstream in the marina (Table 7, Figure 5a,b,c).

Carbon, nitrogen, and phosphorus comprised between 4 to 20%, 0.4 to 4%, and 0.02 to 44% of the particulate matter, respectively. The percent carbon, nitrogen, and phosphorus during transect 1 (when the dredge was not operating) were fairly constant in the marina area (Table 7). In transects 2 and 3, the %PC, %PN, and %PP were slightly higher in the upstream section of the river (i.e., above the marina), decreasing to near constant levels below the Rt. 450 bridge in the river. The carbon to nitrogen ratio (molar) was fairly consistent within each transect, but increased slightly between transects. Transect 1 had significantly

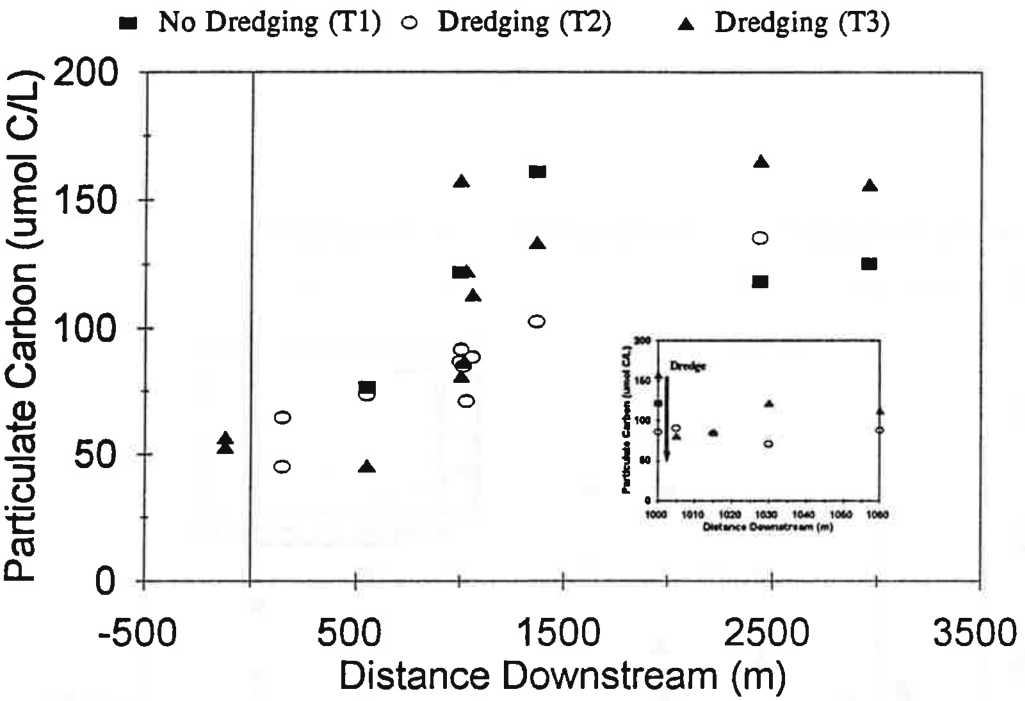

Figure 5a. Distribution of particulate carbon (PC) in the Anacostia River.

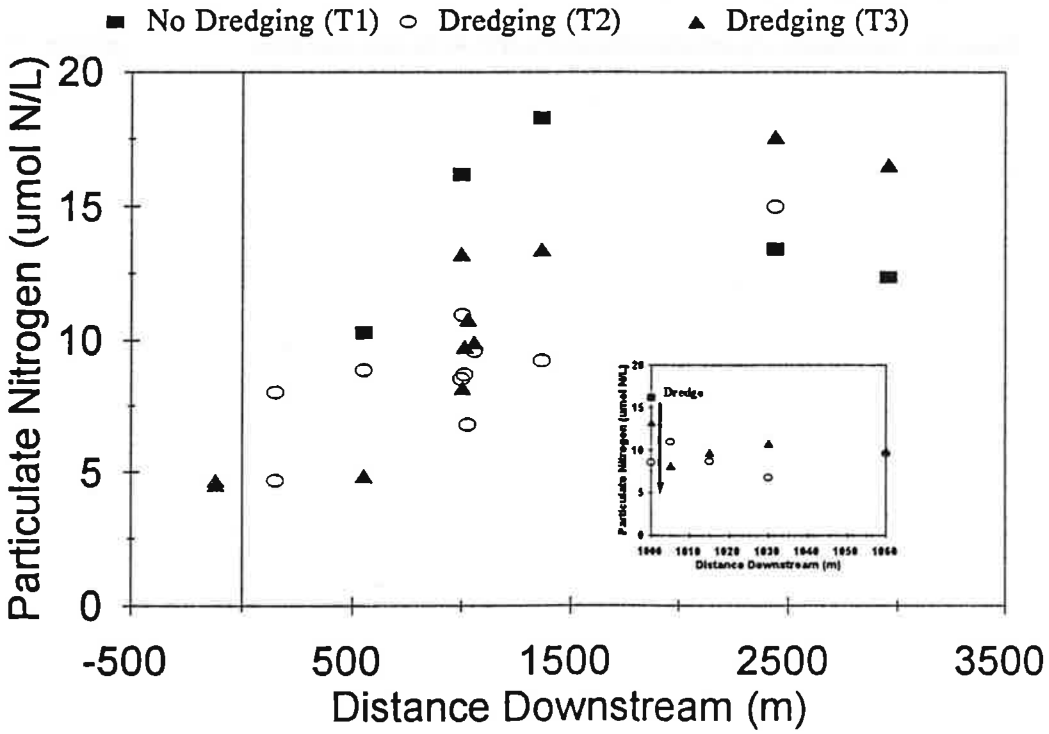

Figure 5b. Distribution of particulate nitrogen (PN) in the Anacostia River.

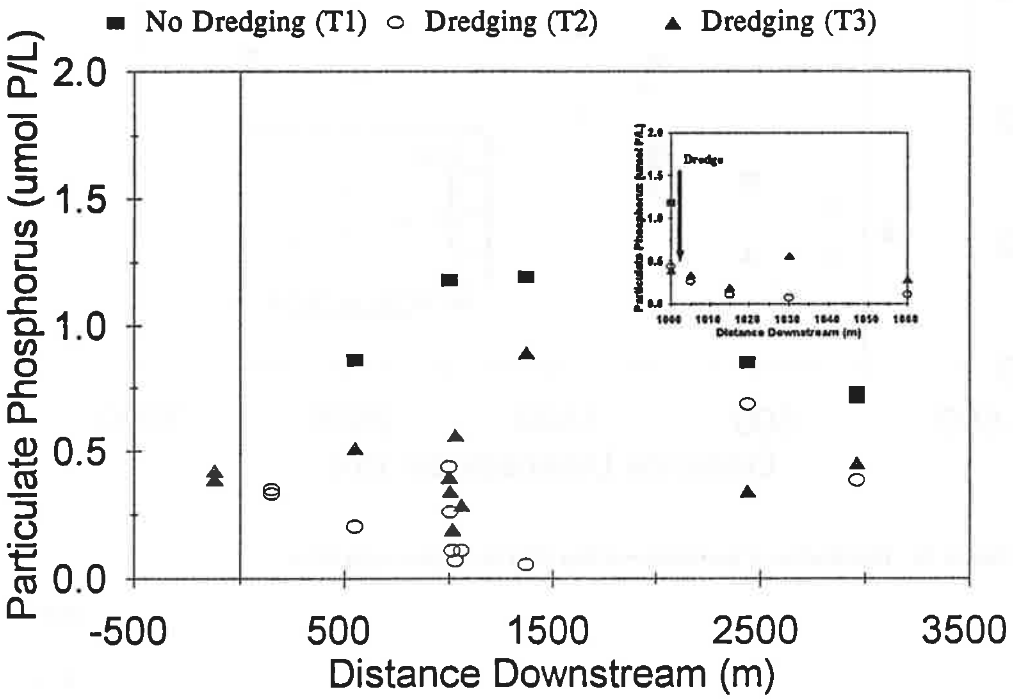

Figure 5c. Distribution of particulate phosphorus (PP) in the Anacostia River.

lower C/N (atomic) values (8.8 ± 1.3) compared to the three transects, and may be an indication of less degraded material present in the river after the rain event.

Dissolved Nutrients and Organic Carbon

As a result of the resuspension of sediment during dredging, dissolved nutrients that have accumulated in the pore waters of the sediments, can be released into the water column. The source of the dissolved nutrients in the pore waters of the sediments is the microbial breakdown of solid phase organic matter under both oxic and anoxic conditions. The products of organic matter decomposition are dissolved ammonium ($NH_4^+ + NH_3$) and ortho-phosphate, as well as dissolved organic carbon, nitrogen and phosphorus. In the presence of oxygen, ammonium can be oxidized to nitrate which could also accumulate in the pore waters or be reduced via denitrification.

Dissolved ammonium concentrations were lowest in the river above the marina, ranging from 0.9 to 2.3 μmol N/L for all transects (Table 7). Within the marina area, concentrations increased either at the dredge head or just downstream of the dredge (Figure 6). In transect 1, when the dredge was not operating, concentrations increased from approximately 2 μmol N/L in the marina to 19 μmol N/L further downstream in the Anacostia River. When the dredge was operating (i.e., transects 2 and 3), the increase in ammonium was greater. For example, during transect 2, ammonium concentrations increased to approximately 8 μmol N/L in the marina, increasing further (i.e., 31μmol N/L) at the New York Ave. Bridge. The concentration of ammonium at the dredge head during transect 3 (24 μmol N/L) was substantially higher compared to those above the marina (Figure 6). Just below the dredge within the marina, concentrations decreased to approximately 10 μmol N/L. Downstream of the marina concentrations increased to 30 μmol N/L at the New York Ave. Bridge. The increase in ammonium concentration at the dredge head during transect 3 was similar to the increase observed for TSM and PC, indicating that the resuspension of both dissolved and particulate material may be occurring in the area just around the dredge.

The increase in ammonium concentration downstream of the dredge could be due to a number of sources including: 1) dredging operations, 2) non-point sources including urban and grassland runoff, 3) point sources, and 4) benthic flux of ammonium. Only during transect 3 does there appear to be any localized increase in ammonium (and particulate matter)

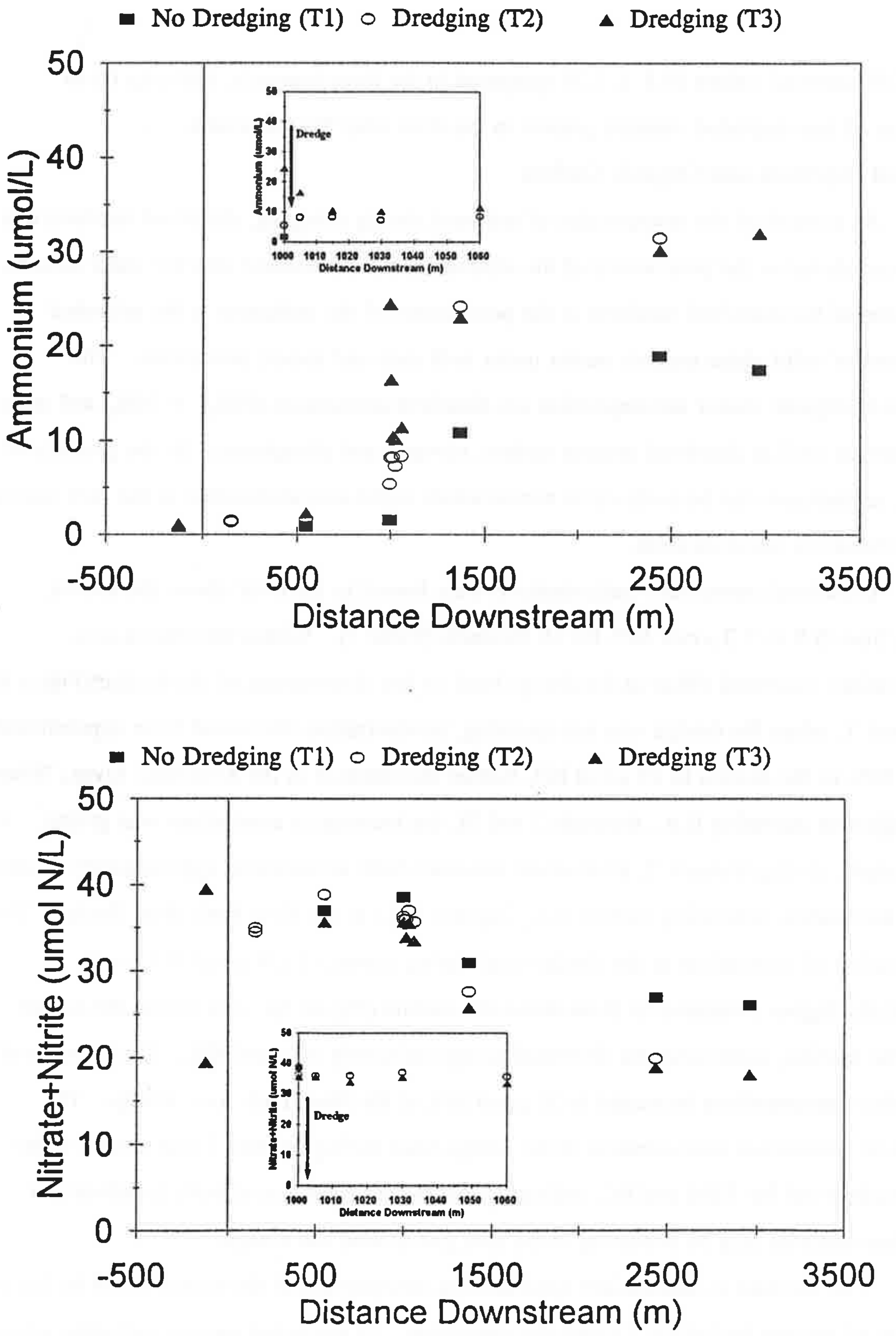

Figure 6. Distribution of dissolved ammonium and nitrate+nitrite in the Anacostia River.

occurring from the dredge. Below the dredge, however, concentrations rapidly decrease. Therefore, the increase in ammonium further downstream must be due to other sources. During transect 2 and 3, there was no precipitation or runoff in the three days prior to sampling. Also, there do not appear to be any discharge pipes within or below the marina area that would be a source of ammonium (or particulates). In an earlier study of the Anacostia River, Sampou (1990) determined that the benthic flux of ammonium to the water column of the Anacostia River was an important source of reduced nitrogen to the system. While the farthest upstream station in his study was at the New York Ave. Bridge (ANA-01), it is possible that this process could be affecting this upper area of the river as well. The summertime benthic flux of ammonium for all stations ranged from 300 to 1700 μmol N/m^2-hr (average 624 ± 130 μmol N/m^2-hr at ANA-01). As opposed to the more rapid flowing section of the river above the marina, the width and depth of the river increases at the marina, thereby increasing the residence time of the water and allowing ammonium to accumulate in the water column. As a rough estimate of the potential benthic source of water column dissolved ammonium, using a benthic flux of 600 μmol N/m^2-hr and a water residence time of 30 days, the concentration of ammonium in the water column of this portion of the river was calculated to be approximately 200 μmol N/L. This value is in good agreement with measured values considering that no loss mechanisms (i.e., nitrification and algal uptake) are accounted for which would tend to lower the concentrations. This result indicates that, for the warmer months of the year, a substantial amount of ammonium in the water column of the river is derived from the sediments and could help account for the distribution of ammonium in the marina and downstream river.

The distribution of dissolved nitrate ($NO_3^- + NO_2^-$) exhibited little variation between the upstream river and marina. Concentrations of nitrate in the upstream river section were approximately 34 μmol N/L and remained fairly constant in the marina (Table 7, Figure 6). Below the marina, concentrations for all transects decreased to approximately 22 μmol N/L at the New York Ave. Bridge. It appears that the operation of the dredge had no discernable effect on the concentration and distribution of dissolved nitrate in the river during this study.

Concentrations of dissolved phosphate varied from between approximately 0.05 to 0.2 μmol P/L for the three transects. Highest concentration were observed during transect 1 downstream of the marina (>2300 m) in the District's waters. Dissolved phosphate levels exhibited little variation during this study, especially in the marina where concentrations averaged 0.08 μmol P/L, with no spatial trend related to the location of the dredge (Figure 7).

The concentrations of dissolved organic carbon (DOC) were similar between transects 2&3 in the marina and further downstream (Figure 7). From the station just downstream of the Rt. 450 bridge to the New York Ave. bridge, concentrations of DOC averaged 208 ± 26 μmol C/L (n=18). There was no increase in concentrations at or just below the dredge during either transect. Concentrations of DOC averaged 349 ± 30 μmol C/L (n=4) for transect 1, except for one station in which the DOC was elevated (800 μmol C/L). Overall, there was little change in the distribution of DOC as a result of dredge operations.

Dissolved and Particulate Metals (Co, Cu, Ni, Fe, Mn, and Zn)

Concentrations of dissolved trace metals measured during this study were low and in many cases below 1 μg/L (Table 7). Concentrations of Co ranged from 0.15 to 0.3 μg/L, Zn from 0.50 to 4.8 μg/L, Cu from 0.29 to 0.98 μg/L, Ni from 0.64 to 1.33 μg/L, Fe from 16 to 33 μg/L, and Mn from 1.5 to 33 μg/L. Dissolved lead concentrations were all below the detection limit of 1 μg/L. These concentrations are comparable to other areas such as the Brazos River (Keeney-Kennicutt and Presley, 1986), St. Lawrence River (Yeats and Brewer, 1983), and world-average river concentrations presented in Martin and Whitfield (1983). Concentrations of some metals are lower than those determined from the Susquehanna River by Troup and Bricker (1975) and Zynjuk et al. (1993, unpublished data). In a survey of Chesapeake Bay rivers (i.e., Susquehanna, Potomac, James, and Rapponanock River), Windom et al. (1991 and unpublished data) determined the dissolved and particulate concentrations of various trace metals. For dissolved metals, Cu ranged from 0.76 to 1.8 μg/L, Zn from 0.05 to 2.5 μg/L, and Ni from 0.16 to 3.0 μg/L, comparable to those determined in the Anacostia River.

In transect 1, when the dredge was not operating, concentrations of dissolved Cu, Ni, and Zn remained constant downstream, while the concentrations of Fe and Co increased slightly (Figures 8-10). Dissolved Mn concentrations exhibited a substantial increase from 7.3 μg/L at the Rt. 450 bridge to 30 μg/L at the New York Avenue bridge within the District of Columbia (Figure 10). In transects 2 and 3, when the dredge was operating, there was no

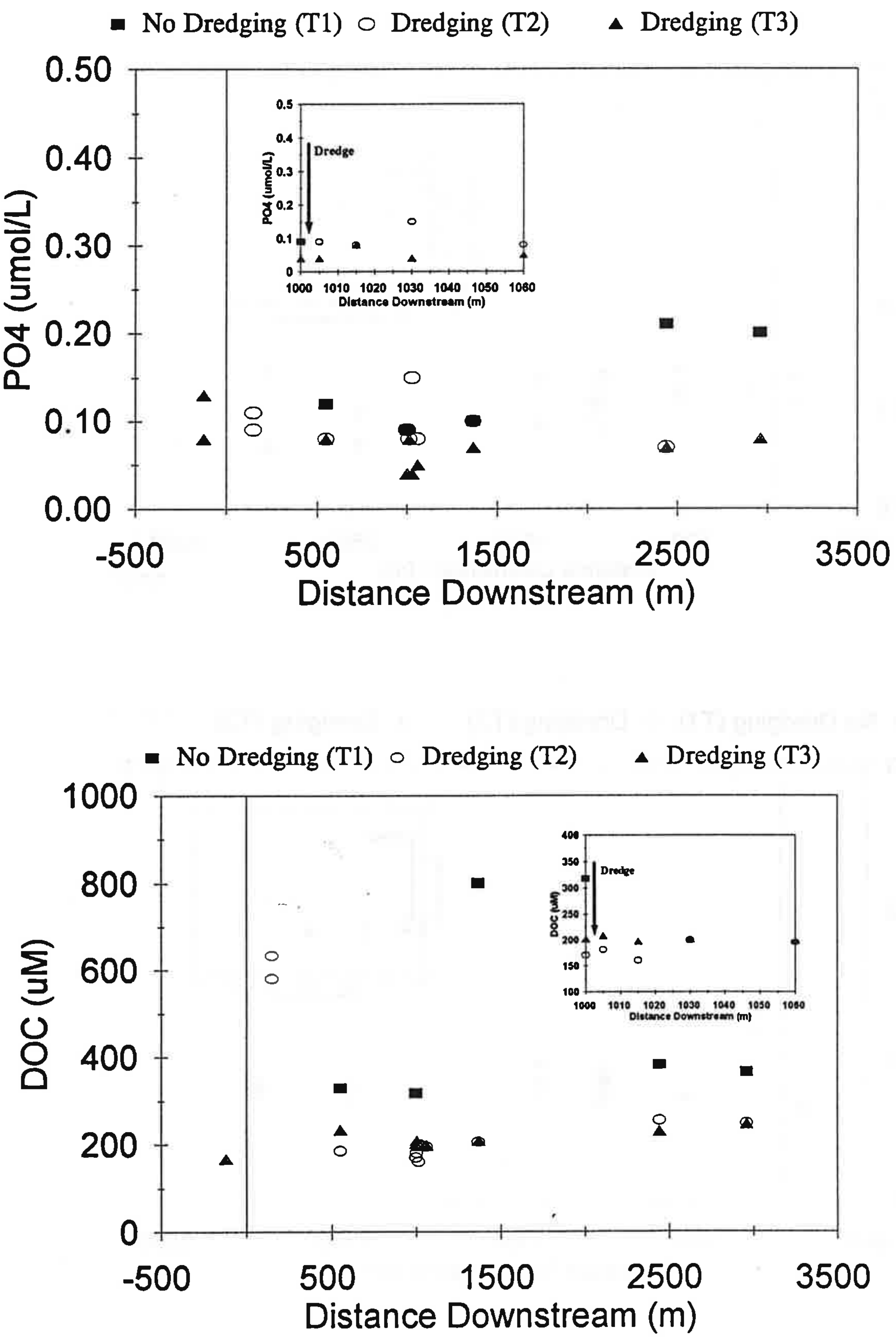

Figure 7. Distribution of dissolved phosphate and organic carbon (DOC) in the Anacostia River.

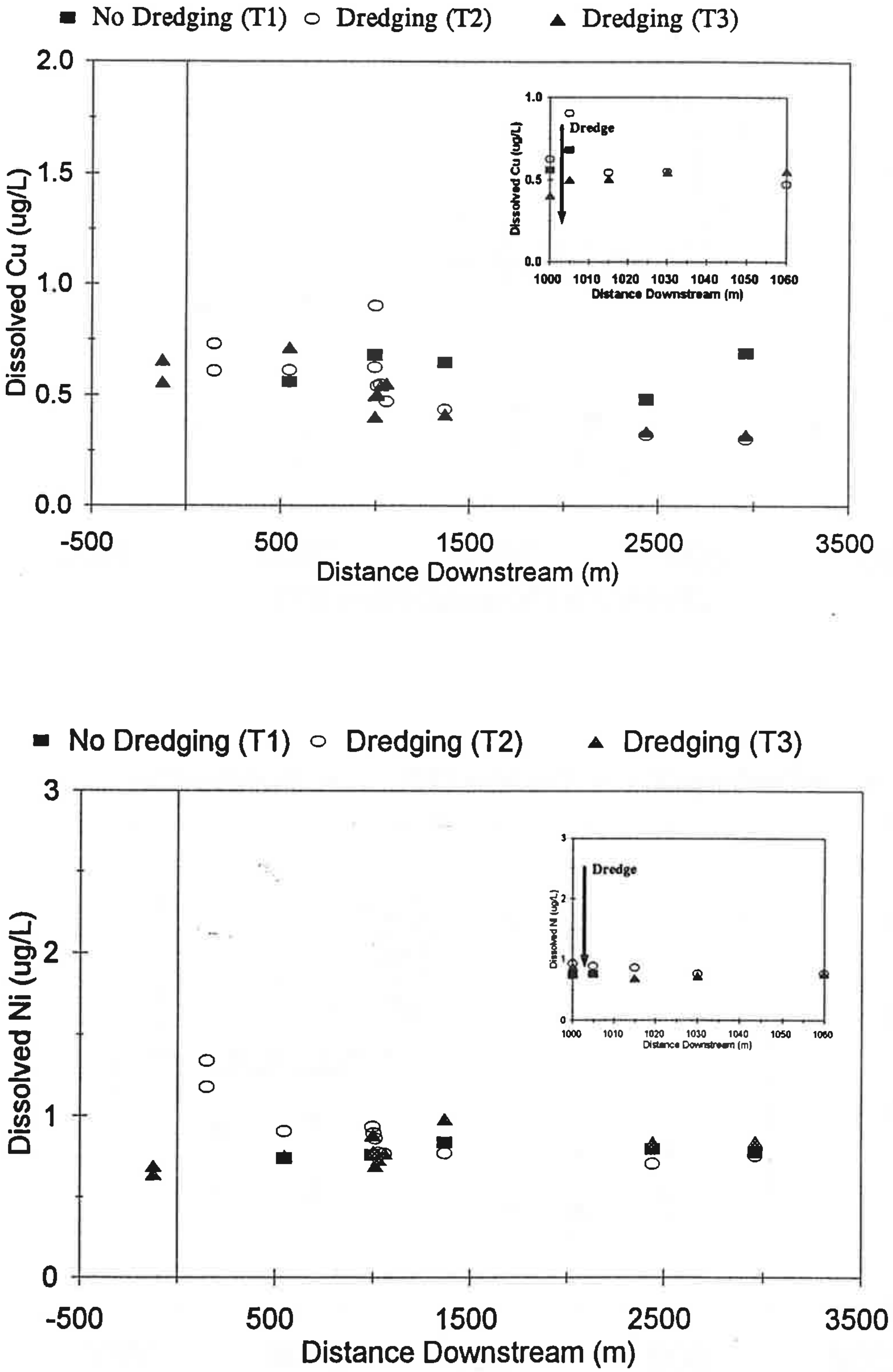

Figure 8. Distribution of dissolved copper and nickel in the Anacostia River.

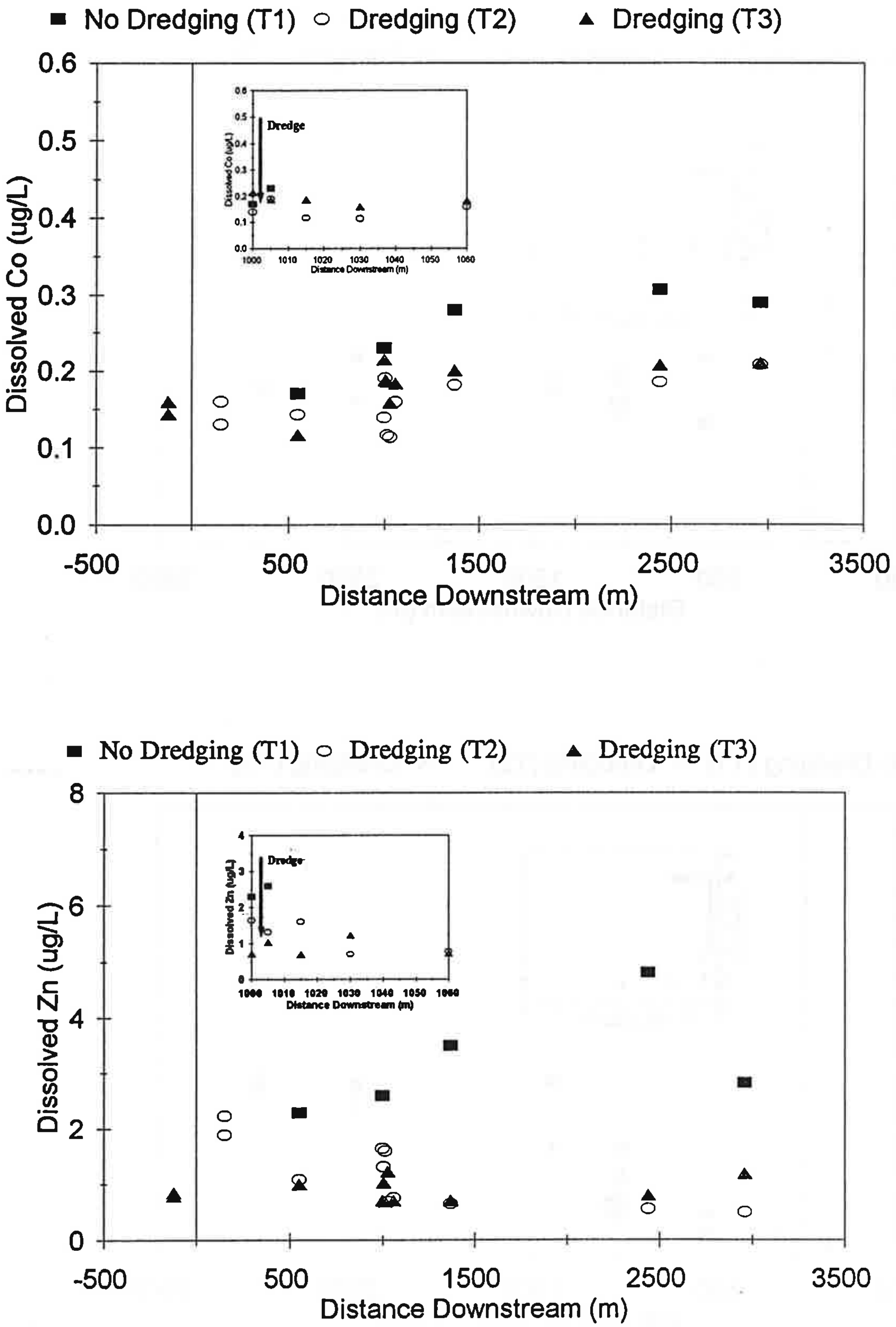

Figure 9. Distribution of dissolved cobalt and zinc in the Anacostia River.

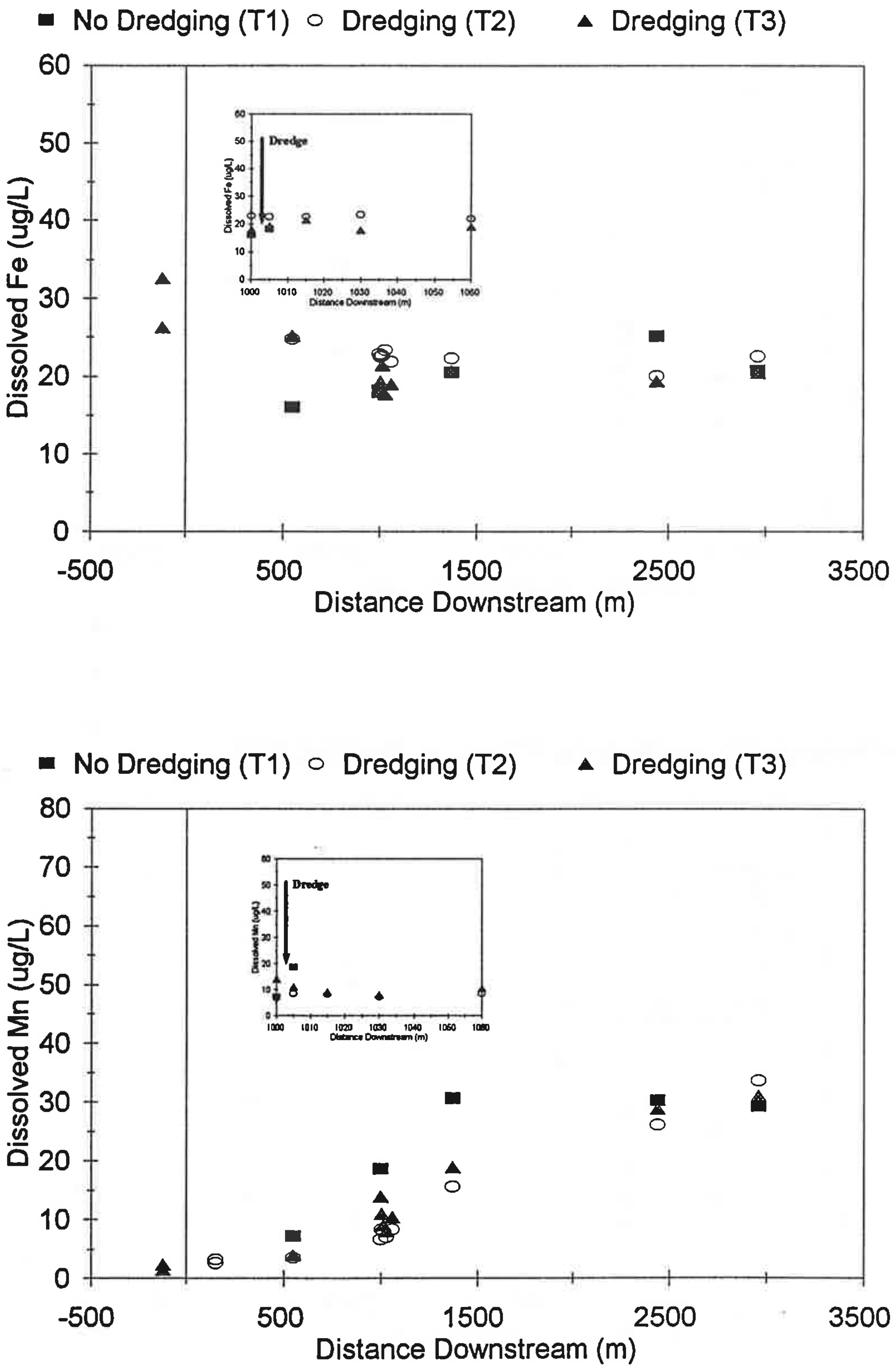

Figure 10. Distribution of dissolved iron and manganese in the Anacostia River.

significant change in the concentrations of dissolved metals near the dredge, with the exception of dissolved Mn and Fe. Concentrations of dissolved Cu, Ni, Zn, and Co varied by approximately ± 0.3 μg/L , while Mn and Fe exhibited changes of up to 10 μg/L during each transect. As in transect 1, dissolved Mn concentrations increased substantially from the confluence of the NE and NW branches to the most downstream station near the Kenilworth Aquatic Gardens (Figure 10). This increase starts at the Rt. 450 bridge, remains fairly constant within the marina, and increases to 33 μg/L at the New York Avenue bridge within the District of Columbia. A similar trend was observed in transect 3. Dissolved Fe concentrations decreased from above the Rt 450 bridge to the marina area, and remained fairly constant farther downstream for both transects (Figure 10). Concentrations of dissolved Fe averaged 22.2 ± 1.1 μg/L and 20.0 ± 1.3 μg/L ($n=7$) downstream of the dredge for transect 2 and 3, respectively.

These data indicated that there was no detectable concentration increase for dissolved metals related to the operation of the dredge during this sampling period. The increase in concentration of Mn from the marina area to the District of Columbia may be due to additional sources within the tidal river. When Mn oxides (e.g., MnO_2: birnessite, MnOOH: manganite, Mn_3O_4: hausmannite) in the sediments are reduced and solubilized during the microbial oxidation of organic matter, pore water Mn can increase in concentration relative to the overlying water. This creates a concentration gradient that may allow for the flux of pore water Mn into the overlying water. The longer residence time of water in the tidal portion of the river may allow for a benthic flux of dissolved Mn, as shown with ammonium (see above), to increase water column concentrations downstream of the marina area. If a benthic flux of Mn and ammonium was the cause of the increased concentrations downstream of the marina, then it would be expected that these two chemicals may be linearly-related in their distributions. This assumes that both chemicals have similar and constant source functions, and that removal processes, other than dilution, are constant for both chemicals. A significant linear relationship ($r = 0.764$, $n=26$, $p>0.001$) is observed between dissolved Mn and ammonium suggesting that these chemicals do have similar sources in the tidal Anacostia River which are most likely dominated by benthic processes.

Particulate trace metals were variable in concentration throughout this study.

Concentrations of Co ranged from 0.02 to 1.0 μg/L, Zn from 0.56 to 15 μg/L, Cu from 0.06 to 41 μg/L, Ni from 0.09 to 2.1 μg/L, Fe from 26 to 1300 μg/L, and Mn from 5.9 to 86 μg/L (Table 7). These concentrations are comparable or slightly higher than the ranges given by Windom et al. (1991, unpublished data) for Cu (0.4 - 1.8 μg/L), Zn (0.08 - 6.5 μg/L), and Ni (0.05 - 5.9 μg/L) for major rivers of Chesapeake Bay, including the Potomac River.

The distribution of the particulate trace metals generally reflected the TSM distribution with lower concentrations above the marina and increasing concentrations downstream (Figures 11-13). Just below the dredge, but still in the marina, there were no increases in particulate metal concentrations (see insets in Figures 11-13). Further downstream, particulate metal concentrations reached their highest levels of this study. These data indicated no substantial resuspension of bottom material to the near surface waters of the tidal river by the dredge during this time period.

To compare the relative importance of dissolved and particulate metal transport downriver, the partitioning of Cu, Co, Fe, Ni, Mn, and Zn between these phases were determined. To a large extent, the concentration of particulate metals depend on weathering reactions of the source rock within the drainage basin. These concentrations also may be influenced to some extent by anthropogenic sources as well as natural weathering processes. In urban rivers such as the Anacostia, other sources of metals (both dissolved and particulate) can also be important. These sources include, but are not limited to, industrial discharges (thought to minor in the Anacostia), atmospheric deposition, and street runoff. Once introduced into the river, particulate bound-metals can be released into the dissolved phase, while some dissolved metals can associate with particles and settle to the bottom or be transported out of the system. The partitioning between dissolved and particulate metals in an aquatic system is related to a series of complex processes including adsorption/desorption, precipitation/dissolution, and ion-exchange reactions (Troup and Bricker, 1975; Stumm and Morgan, 1981). In the upper Anacostia River, there was substantial variability between dissolved and particulate metals. On average, the relative importance of the dissolve forms are as follows: Ni (62%) > Co (50%) > Cu (40%) > Zn ≈ Mn (25%) > Fe (12%). On average, these data are consistent with the dissolved and particulate fractionation for the Susquehanna River provided by Troup and Bricker (1975). Therefore, riverine transport of Ni

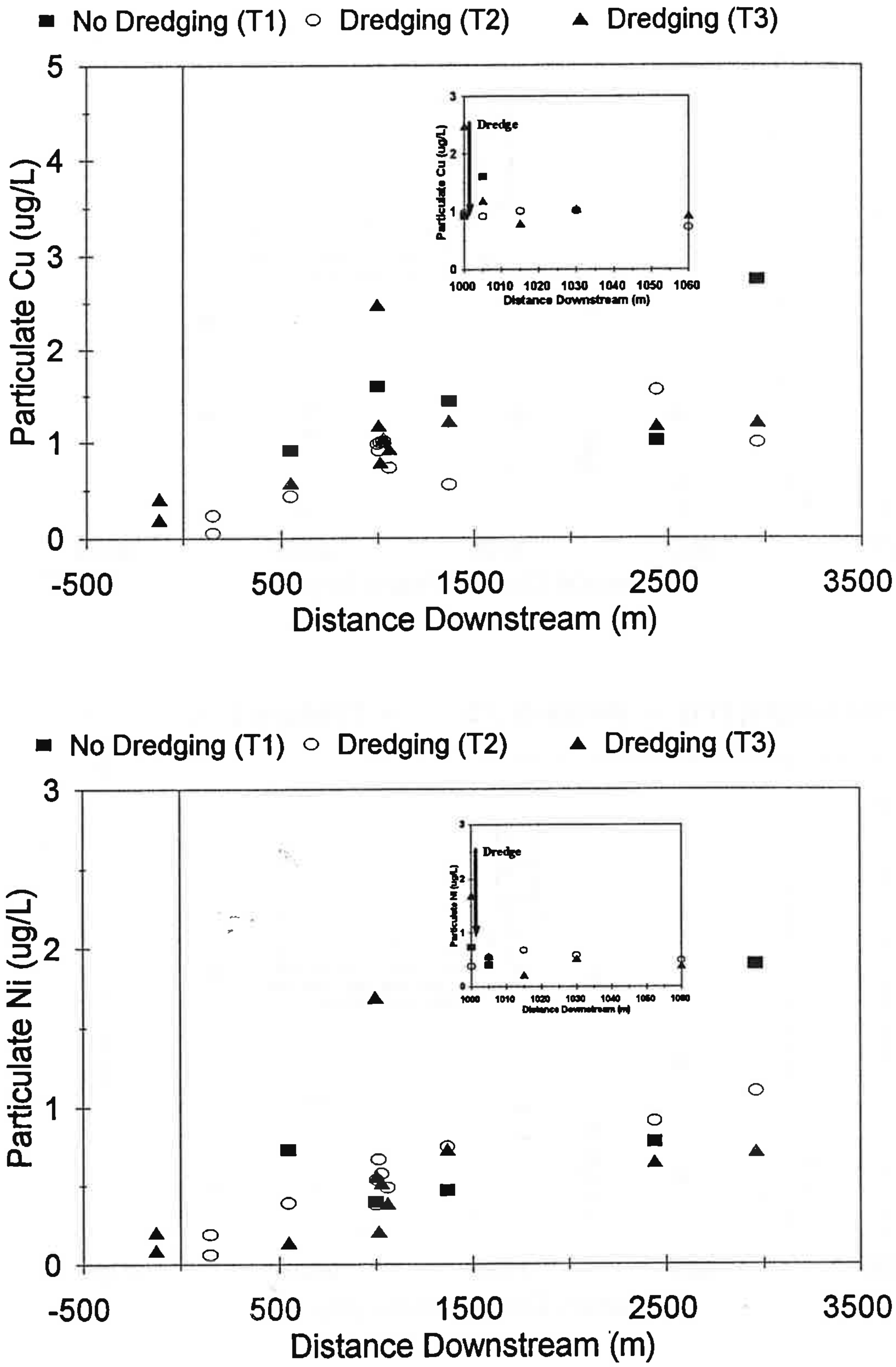

Figure 11. Distribution of particulate copper and nickel in the Anacostia River.

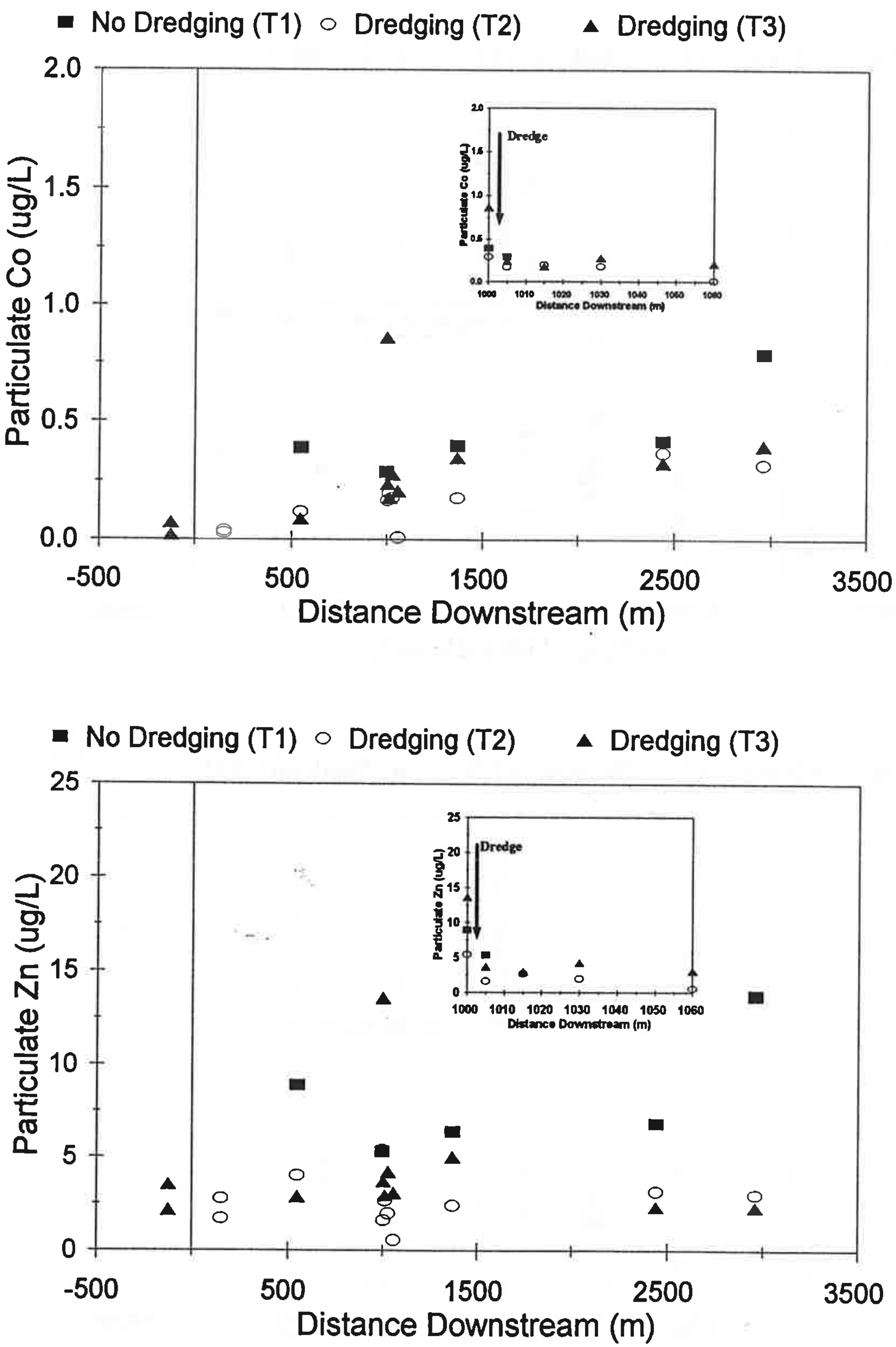

Figure 12. Distribution of particulate cobalt and zinc in the Anacostia River.

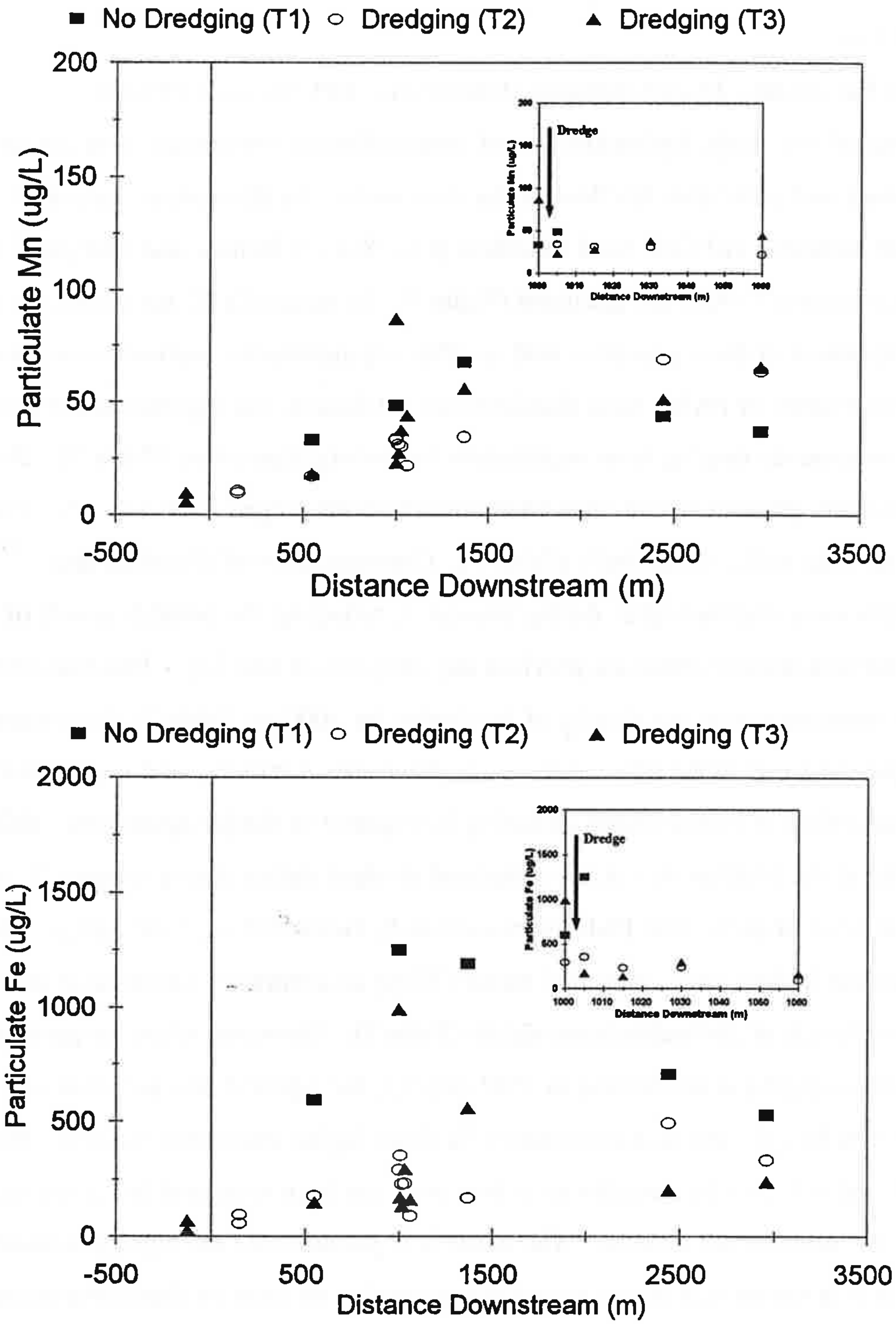

Figure 13. Distribution of particulate iron and manganese in the Anacostia River.

will be predominantly in the dissolved phase while Fe will be transported mainly in the particulate fraction.

Dissolved and Particulate Trace Organics (Chlordane, ΣPCBs, and ΣPAHs)

As part of this study, hydrocarbons and organochlorine compounds were measured in both the dissolved and particulate fractions of the river water. In this section, only total polychlorinated biphenyls (ΣPCB), total chlordane (i.e., Σ $\alpha+\gamma$ forms), and total polycyclic aromatic hydrocarbons (ΣPAH) are discussed (Table 7). In Appendix II, the results for the individual components of these groups as well as other organochlorine pesticides are presented.

Concentrations of PAHs, both dissolved and particulate, are reported as the sum of 16 individual compounds ranging from naphthalene to benzo(ghi)perylene (Table 7). During this study, dissolved, particulate and total PAH concentrations ranged from 4 to 177, <0.1 to 3900, and 15 to 4100 ng/L, respectively (Table 7). Concentrations of dissolved and particulate PAHs were slightly higher during transect 1, reflecting the possible runoff of PAHs as a result of the rain showers from the previous day (Figures 14 and 15). Dissolved PAH concentrations were highest in the vicinity of the dredge (at 1000 m; Table 7) along transects 2 and 3 in comparison to all of the other upstream or downstream stations, and may reflect a localized redistribution of hydrocarbons occurring in response to dredge operations. This was most evident for at the 1000 m (just at the cutterhead dredge) station during transect 3 in which concentrations of particulate PAHs were extremely elevated (i.e., 3900 ng/L). This sample also had the highest total suspended matter (TSM) concentration observed in this study, and had elevated levels of particulate trace metals (Table 7). However, when the particulate PAH concentration (ng/L) is normalized to TSM (mg/L), the adjusted concentration of particulate PAH is 80 μg/g and is approximately 10 times higher than other stations. The adjusted PAH is also higher by a similar ratio than what has been measured in the sediment (Table 3), the potential source material. Therefore, it is possible that the high particulate PAH concentration at this station was due to sample contamination or from an alternative source of sediment higher in PAH concentration.

Downstream of the dredge (> 10 m), concentrations of total PAHs were variable and decreased to an average of 62 and 37 ng/L for transects 2 and 3, respectively. Concentrations of both dissolved and particulate PAHs exhibited no discernable trend down the river. The

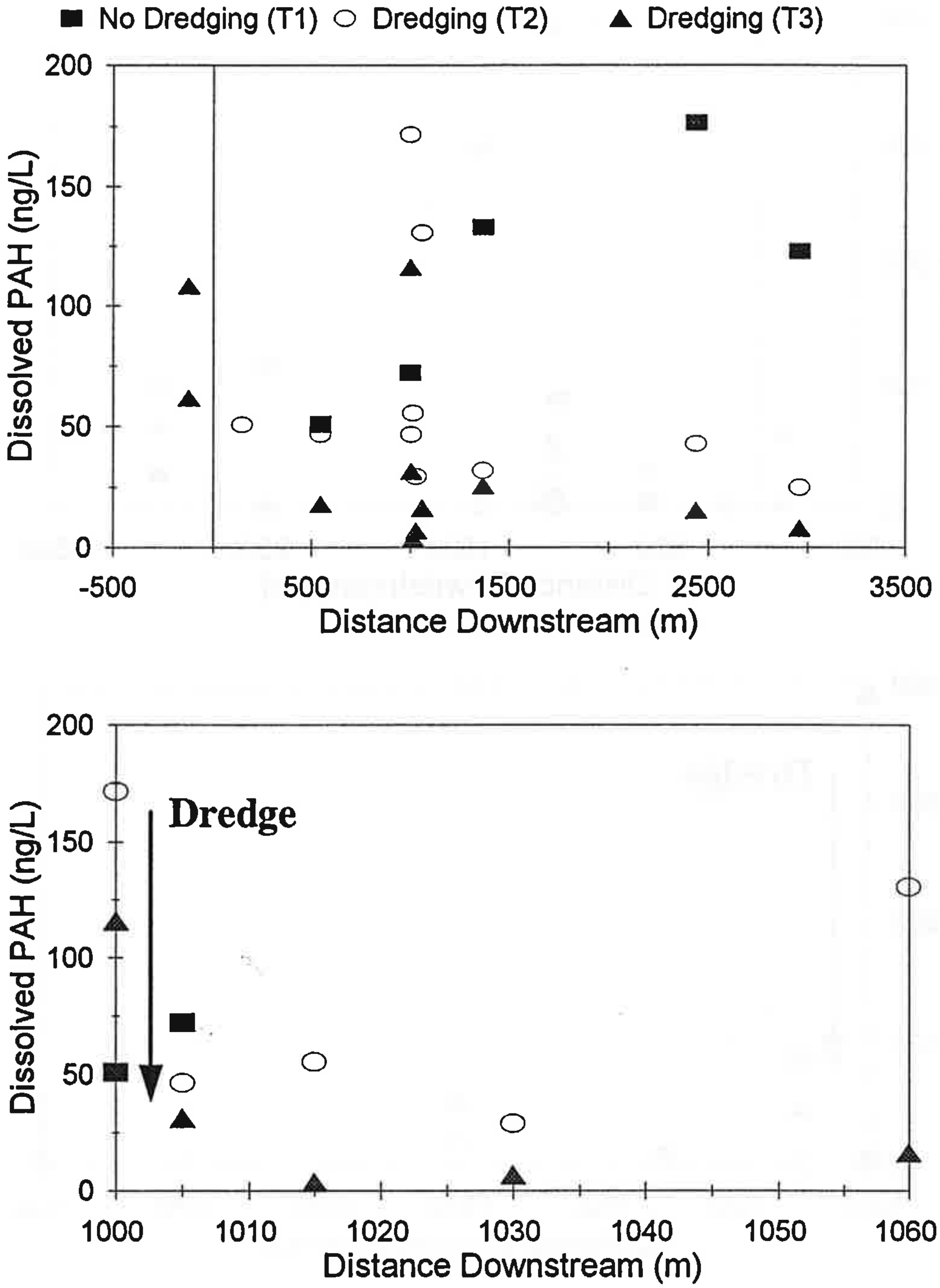

Figure 14. Distribution of dissolved polycyclic aromatic hydrocarbons (PAH) in the Anacostia River.

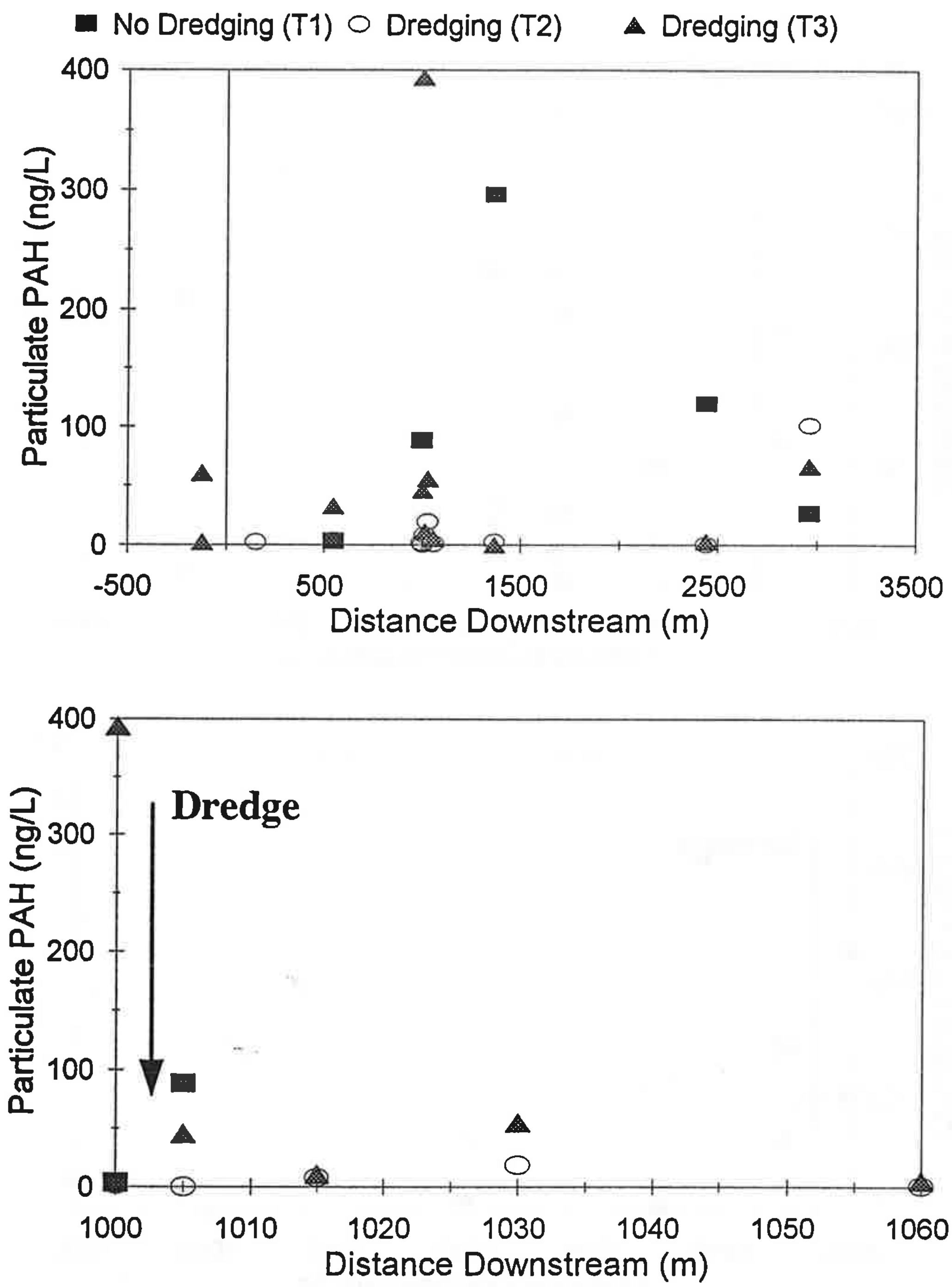

Figure 15. Distribution of particulate polycyclic aromatic hydrocarbons (PAH) in the Anacostia River.

variability in concentrations may be due to the low concentrations detected during this study and the increase in analytical variability at these low levels, as well as the limited number of samples taken during this study. Overall, these concentrations were substantially lower than those measured in the study by Pinkney et al. (1993). Concentrations of dissolved+particulate PAHs measured in their reference sites, near the East Capital and Bennings Road Bridges, for a similar set of aromatic compounds ranged from 830 to 900 ng/L (n=3). However, the sample locations for the Pinkney et al. (1993) study were farther downstream than the present study area and were most likely affected by runoff from Hickey Run, just above Kingman Lake.

Total chlordane is the sum of the alpha (α) and gamma (γ) forms of chlordane which are the dominant components of technical chlordane. Oxychlordane, a breakdown product of technical chlordane, was also detected in many samples and concentrations are reported in Appendix II. Dissolved, particulate, and total chlordane ranged from <0.3 to 8.6 ng/L, <0.3 to 4.1 ng/L, and <0.3 to 13 ng/L, respectively (Table 7), and concentrations were similar or slightly higher to those determined at the fall line of the Potomac River. Foster and Lippa (1993, unpublished data) reported ranges (n=7) for dissolved and particulate chlordane ($\alpha+\gamma$ forms) of <0.1 - 7.9 ng/L and <0.1 - 3.4 ng/L for the Potomac River at Chain Bridge, respectively.

Concentrations of total dissolved and particulate chlordane exhibited no apparent trend with regards to the location of the dredge or distance downstream from the marina (Figures 16 and 17). Concentrations of dissolved and particulate chlordane along transect 1 were similar or slightly higher than concentrations in transects 2 or 3. This is consistent with that observed for PAH concentrations. Qualitatively, concentrations of dissolved and particulate chlordane increased slightly between the upstream stations and the dredge [station ID = T# - (-3), at 1000 m] area. Downstream of the marina, concentrations of dissolved and particulate chlordane were variable and reached their highest level of approximately 9 and 4 ng/L, respectively (Figures 16 and 17).

Within the marina, concentrations of dissolved chlordane varied from 0.5 to 5 ng/L and did not appear to be affected when the dredge was in operation (Figure 16). Particulate chlordane concentrations varied from <0.1 to 3 ng/L and were slightly more variable than

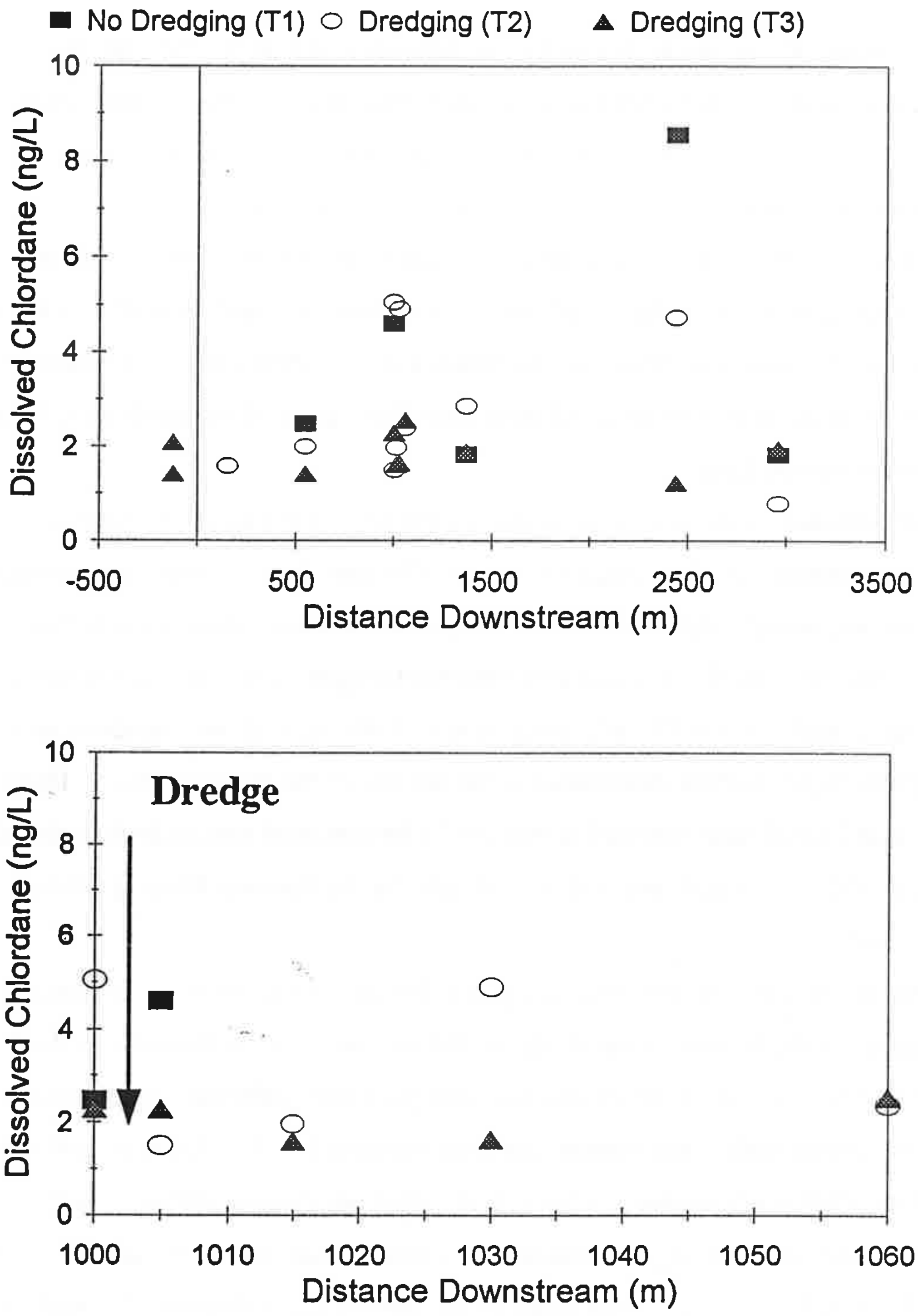

Figure 16. Distribution of dissolved (alpha+gamma) Chlordane in the Anacostia River.

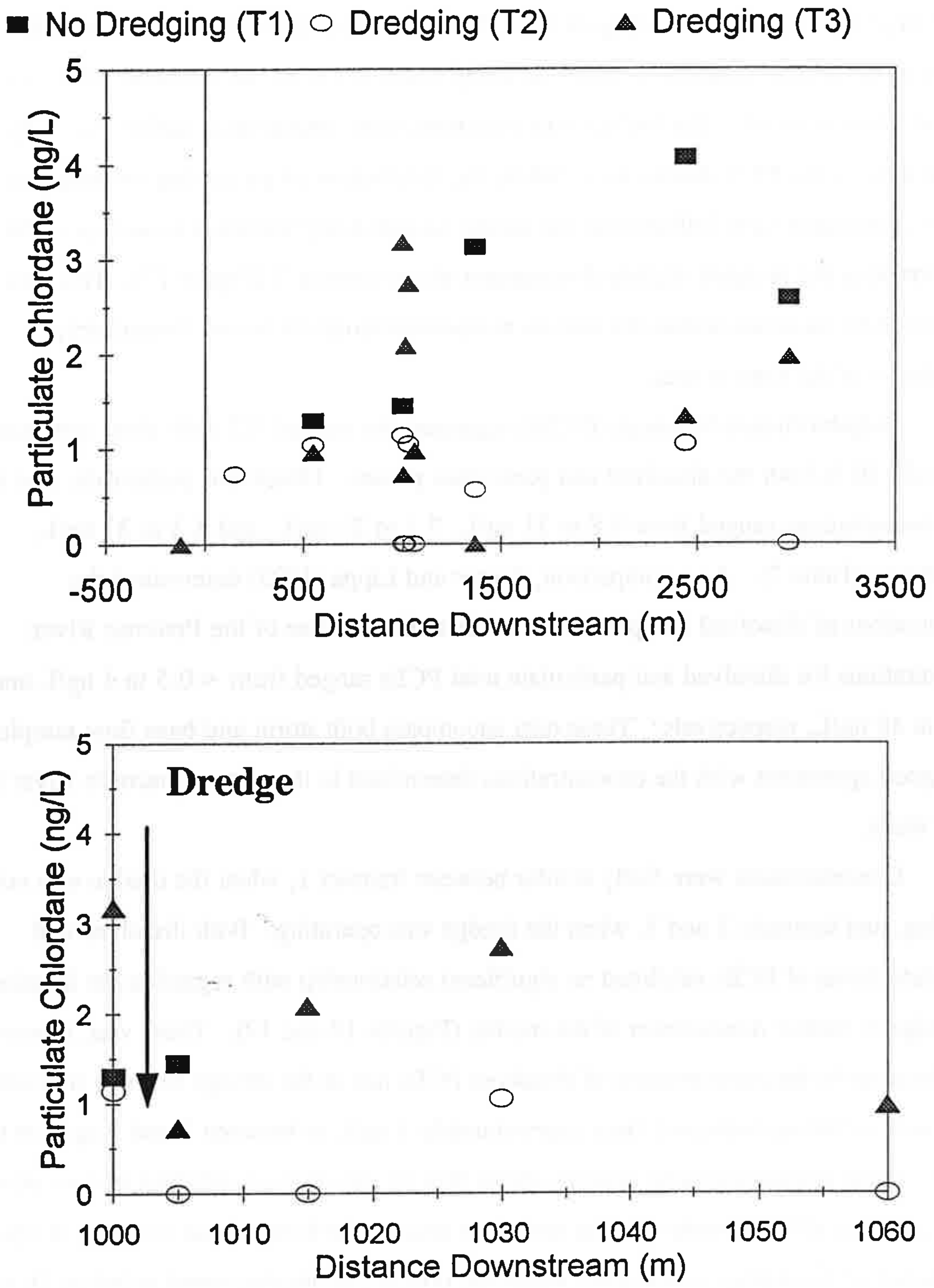

Figure 17. Distribution of particulate (alpha+gamma) Chlordane in the Anacostia River.

dissolved phase concentrations (Figure 17). This variability is most likely to due to the low amount of particulate material sampled, in many cases <100 mg of sediment, and the low concentrations detected. The highest concentrations were measured at station T3 - (-3), and were similar to the PAH distribution. While the distribution of particulate chlordane along transect 2 indicated little influence of the dredge in enhancing transport to surface waters, concentrations did increase slightly downstream along transect 3 (Figure 17). This increase appeared to be localized within the marina as concentrations decreased immediately downstream of the marina area.

Polychlorinated biphenyls (PCBs) represent the sum of 112 individual congeners (Appendix II) in both the dissolved and particulate phases. Dissolved, particulate, and total PCB concentrations ranged from 0.8 to 21 ng/L, 7.3 to 23 ng/L, and 8.3 to 31 ng/L, respectively (Table 7). As a comparison, Foster and Lippa (1993) determined the concentrations of dissolved and particulate PCBs at the fall-line of the Potomac River. Concentrations for dissolved and particulate total PCBs ranged from <0.5 to 4 ng/L and <0.5 to 40 ng/L, respectively. These data encompass both storm and base flow samples, and are in good agreement with the concentrations determined in the upper Anacostia River as part of this study.

Concentrations were fairly similar between transect 1, when the dredge was not operating, and transects 2 and 3, when the dredge was operating. Both dissolved and particulate forms of PCBs exhibited no significant relationship with regard to the location of the dredge or farther downstream of the marina (Figures 18 and 19). There was, however, a slight increase in the concentration of dissolved PCBs just at the dredge for both transects 2 and 3; concentrations increased from approximately 3 ng/L to between 7 and 9 ng/L at the dredge. These slightly elevated concentrations may be due to the operations of the cutterhead dredge, but this effect is limited to the area right around the dredge head itself (± 3 m); downstream of the dredge and marina, dissolved concentrations decreased to below 10 ng/L, except for one station in transect 2 (Figures 18 and 19). It is unclear as to the source of the high dissolved PCB concentration in the marina during transect 2 (i.e., 20 ng/L).

The partitioning of PCBs (and other organic compounds) between dissolved and particulate phases in the water is an important aspect in determining their fate, transport, and

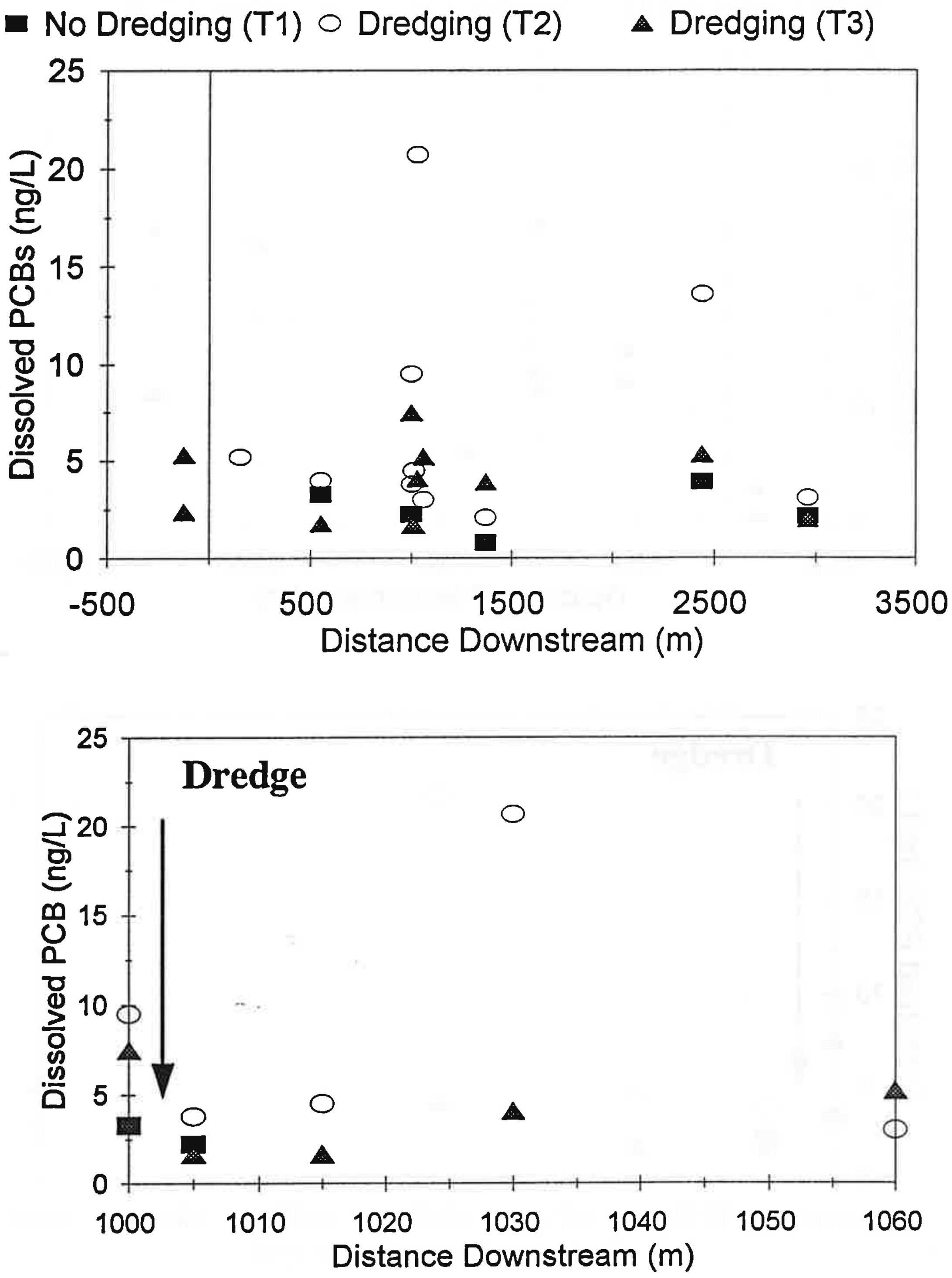

Figure 18. Distribution of dissolved polychlorinated biphenyls (PCB) in the Anacostia River.

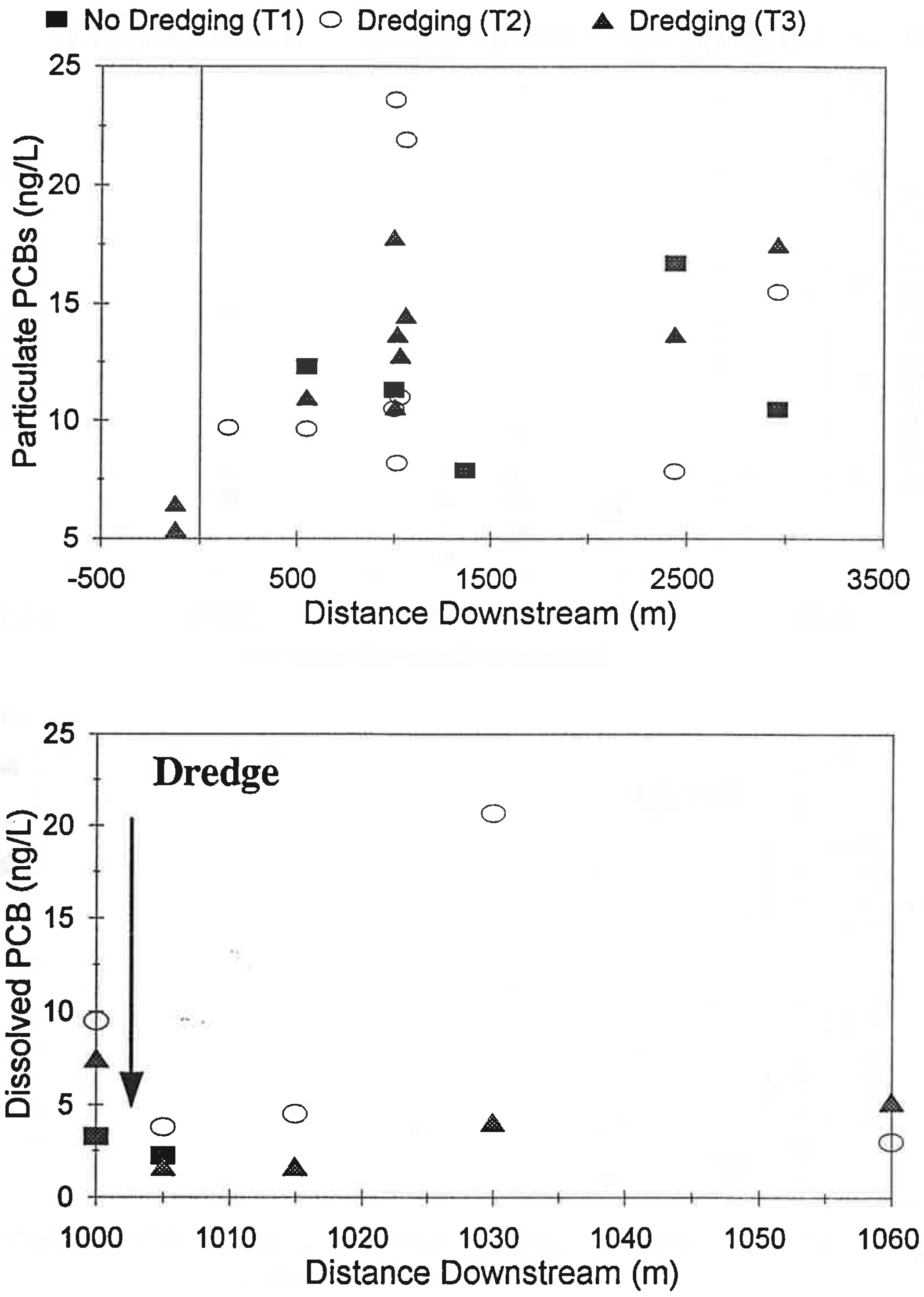

Figure 19. Distribution of particulate polychlorinated biphenyls (PCB) in the Anacostia River.

bioavailability in the Anacostia River. PCBs, due to their physical properties, are hydrophobic compounds with octanol-water (K_{ow}) partition coefficients ranging from 10^4 to 10^6 (Ericksen, 1991). This indicates that a majority of the PCBs may be in particulate phase. However, many factors determine the actual mass distribution or partitioning ($K_{p;}$; particulate /dissolved concentrations, L/Kg) between phases in surface waters such as the Anacostia River. Field K_p distributions may not always reflect those predicted using K_{ow} due to both physicochemical and geochemical variables such as: 1) the concentration and composition of particulate matter; 2) particle size; 3) concentration of dissolved organic carbon; and 4) the physico-chemical composition of the compound of interest (i.e., K_{ow}). Taking these factors into account the concentration of total PCBs can be expressed as

$$C_T = C_d + C_d\, K_{OC} f_{OC}[TSM]10^{-6} + C_d K_{DOC}[DOC]10^{-6}; \qquad (1)$$

where C_T is the total PCB concentration, C_d is the freely-dissolved concentration, K_{OC} is the K_{ow} corrected to organic carbon, f_{OC} is the fraction of organic carbon in the particulates, K_{DOC} is the dissolved organic partition coefficient, and [DOC] is the measured concentration of dissolved organic carbon. This equation states that the total concentration of PCB (or another hydrophobic organic compound) is the sum of the freely-dissolved form, the fraction sorbed to particulates, and the fraction bound to the dissolved organic carbon of the water (Eadie et al., 1992).

In the Anacostia River, approximately 75% (range of 25 to 90%) of the total PCBs are in the particulate fraction with the log K_p of the total PCBs ranging from 6 to approximately 4.5. At TSM concentrations < 17 mg/L, there was an inverse relationship between the log K_p and TSM, while at TSM concentrations > 17 mg/L, log K_p remained unchanged (average of 5.2). This indicates that the amount of particulate material may not be the only major factor controlling the partitioning of PCBs in the river. Also, it would be more appropriate to investigate the dissolved and particulate partitioning relationship using individual congeners opposed to total PCBs, taking into account the concentrations of dissolved and particulate organic carbon (Eadie et al., 1992; Bergan et al., 1993). This investigation, while out of the scope of this project, would help in the predication of the transport mode and bioavailability of PCBs in the Anacostia River.

Concentrations of Sediment-bound Contaminants

A limited number of sediment samples were collected as part of this study (Table 8). Samples for trace metal analysis were taken with a small diameter KB corer, while sediment samples for organic analysis were collected approximately a year later using a petite-ponar grab sampler. The two samples for trace metal analysis were taken within the marina area near the dredge, while samples for organic analysis were taken above and below the marina as well as near the dredge (Tables 4 and 8). Grain size (%silt+clay) and percent organic matter were measured on the samples taken for organic analysis only, and ranged from 11 to 76% and 1.4 to 7.6%, respectively (see Appendix II).

Sediment concentrations of trace metals are given in Table 9. These concentrations are similar to previous studies ICPRB (1990) as summarized in Table 3. Also, in a recent study of the trace metal distribution in the entire tidal Anacostia River, these concentrations are some of the lowest in the tidal Anacostia River (Velinsky et al., 1993). These results indicate no substantial accumulation of trace metals in the area, however sampling was limited (i.e., only two samples taken) and additional sampling needs to be accomplished to accurately address this issue.

Concentrations of sediment-bound organic contaminants are presented in Table 10. Generally, concentrations of these contaminants are similar or lower than those measured in ICPRB (1990) as summarized in Table 3. It should be noted that for DDT, PAHs, and PCBs, similar compounds may not be summed to give total concentrations thereby limiting this comparison. However, these concentrations are lower than previously reported concentrations in the tidal Anacostia River (Velinsky et al., 1992; Pinkney et al., 1993).

Comparison to Water Quality Standards

Water quality criteria for both the State of Maryland and the District of Columbia are presented in Table 11 (U.S. EPA Region III, 1993). For the State of Maryland, both acute and chronic concentrations are listed, while for the District of Columbia, concentrations are presented for Class C waters which are listed for "the protection and propagation of fish, shellfish and wildlife." Also, metal criteria for the District of Columbia are based on a relationship with the hardness of the ambient water which, for the District's water, generally range between 60 and 180 mg $CaCO_3$/ L (Karimi, personal communication). A value of 120

Table 8. Station Location and Collection Dates for Sediment Samples in the Marina Area.

ID #	Distance from Confluence (m)	Sample Description
Trace Metals:		
Collected: 9/22/92		
ANA #1	1005	Uniform brown silt and sand.
ANA #2	1030	Same as above, with green algae on surface.
Organics		
Collected: 7/19/93		
ANA #3	550	Black and clear sand, coarse grain.
ANA #4	1030	Brown/grey fine grain with sand.
ANA #5	1370	No description.

Note: samples for trace metal and organic analysis were collected on different dates.

Table 9. Concentrations of Trace Metals in Bed Sediments of the Marina.*

ID/ Depth	Fe	Cu	Ni	Zn	Co	Mn	Pb
ANA #1/ 0-1 cm	10.9	12.4	13.1	66.4	8.68	0.14	27.6
ANA #2/ 0-1 cm	13.2	14.9	17.7	101.0	10.4	0.19	30.6
ANA #2/ 2-4 cm	13.4	17.2	17.9	91.5	11.2	0.18	45.3
NBS-1 (ref. std.)	25.4	14.7	19.1	101.5	11.0	0.18	16.8
NBS-2 (ref. std.)	26.2	14.7	15.2	107.0	11.1	0.19	23.4
Certified Value	33.5	18.0	32.0	138.0	10.5	0.38	28.2
± 1σ	1.0	3.0	3.0	6.0	1.3	0.20	1.8

* Concentrations in μg/g dry weight, except Fe and Mn which are in mg/g.

Table 10. Concentrations of Organic Contaminants in Bed Sediments of the Marina.*

ID #	Aldrin	∑Chlor	Dieldrin	DDT	∑PAH	∑PCB
ANA #3	<0.01	0.92	<0.01	0.24	884.0	3.2
ANA #4	0.33	5.9	0.40	2.5	7700.0	28.0
ANA #5	0.60	12.0	0.71	1.5	14.0	11.0

* Concentrations in ng/g dry weight. ∑Chlor is the sum of cis and trans chlordane, DDT is 4,4'-DDT, and ∑PAH and ∑PCB are the sum of specific individual compounds (see Appendix II).

mg $CaCO_3$/ L was used for this study. The distinction between CCC and CMC for the District's criteria relate to the maximum value measured for a four day average (CCC) and a one hour average (CMC), respectively.

Concentrations of dissolved ammonium were converted to dissolved ammonia, at the *in-situ* pH and temperature, and in all cases concentrations were two orders of magnitude lower than published water quality criteria (U.S. EPA Region III, 1993). Dissolved trace metal concentrations of Cu, Fe, Ni, and Zn were below published criteria for both the State of Maryland and District of Columbia. Therefore, the potential impact to the water quality of the Anacostia River from dredging activities at the Bladensburg marina area is small with no significant increase in concentrations of dissolved metals to the river related to water quality standards.

Concentrations of organic components measured during this study indicate, in specific cases, dissolved ($\alpha + \gamma$) chlordane and PCBs higher than published water quality criteria for both the State of Maryland and District of Columbia (Table 11). The locations of these high concentrations were not related to the location of the dredge. Also, there does not appear any systematic spatial distribution with exceedances occurring only in Maryland waters, which would have suggested Maryland waters as a source. However, more samples were taken in Maryland waters than in the District during this study. Concentrations of dissolved chlordane were higher than water quality standards for specific locations in transects 1 and 2, but not for transect 3 (Table 7). Similarly, in transect 2 (for only two stations) were concentrations above the 0.014 μg/L criterion for PCBs. Concentrations of individual PAHs were lower than published criteria, where available, for all three transects of this study.

In almost all cases, concentrations of dissolved chlordane and PCBs were higher than published human health criteria based on a risk of 10^{-6} (Table 11). This indicates that, while concentrations did not appear to be influenced by the dredge, they were high enough to be a potential problem to human health via uptake and accumulation in fish of the river. Recent studies have shown that the concentration of PCBs and chlordane in fish tissue are elevated compared to the Potomac River (Velinsky and Cumins, unpublished data). The sources of these contaminants to this portion of the Anacostia River remain unclear at the present time.

Table 11. Water quality standards for the State of Maryland and District of Columbia.

	State of Maryland		District of Columbia Class C water (@120 mg/L hardness)		Human Health (10^-6 Risk)*	
	Acute	Chronic	CCC	CMC	Water+ Organisms	Organism only
Cd	3.9	1.1	1.3	4.8	ND	ND
Cu	18.0	12.0	13.8	21.0	ND	ND
Ni	1400.0	160.0	183.0	1650.0	610.0	4600.0
Zn	120.0	110.0	123.0	137.0	ND	ND
Co	ND	ND	ND	ND	ND	ND
Fe	ND	ND	1000.0	ND	ND	ND
Aldrin	3.0	ND	0.4	3.0	0.00013	0.00014
DDT	1.1	0.001	0.001	1.1	0.00059	0.00059
Dieldrin	2.5	0.002	0.0019	2.5	0.00014	0.00014
PCBs	2.0	0.014	0.014	ND	0.00004	0.00005
Chlordane	ND	ND	0.004	ND	0.00057	0.00059
Naphthalene	ND	ND	600.0	ND	ND	ND
Acenaphthene	ND	ND	50.0	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND	ND	ND

*Human health concentrations from U.S. EPA (40 CFR Part 131), December 22, 1992
ND - No Data
Units: ug/L or ppb

SUMMARY AND CONCLUSIONS

This study indicates that the dredging in the Bladensburg Marina does not effect the surface water quality of the upper tidal Anacostia River (Figures 8-19). Within the marina, dissolved and particulate concentrations of most trace metals and organic compounds did not substantially increase at or just below the dredge. In a few instances however, concentrations of both dissolved and particulate contaminants were slightly higher just at the dredge head (e.g., transect 3). This increase was very localized, with concentrations decreasing just downstream of the dredge (i.e., tens of meters). Below the dredge, but still within the marina area, concentrations were fairly constant, while downstream of the marina concentrations of most organic compounds and trace metals increased. Concentrations of trace metals and organic compounds were generally lowest in the area above the marina between the confluence of the NE and NW Branches and the Rt. 450 bridge.

It must be pointed out that the type of water sampling performed in this study may bias the conclusions concerning the effects of dredging on the river. At the time of sampling, water depths were approximately 1 to 2 m in the marina with water samples taken at approximately 0.5 m below the surface by submerging pre-cleaned bottles by hand. No samples were taken near the bottom of the river, either near the dredge or farther downstream. The sampling design employed during this study would not have detected any resuspension near the bottom. Although previous studies have shown that substantial resuspension can occur to the bottom waters near a dredge, this material quickly settles due to its larger grain size (see Introduction). Therefore, resuspension to bottom waters near the dredge is not expected to contribute significantly to downstream concentrations of organic compounds and trace metals.

In all cases, concentrations of dissolved trace metals were substantially lower than published water quality standards (WQS) using both the District of Columbia and the State of Maryland's criteria (Tables 11). These criteria are for dissolved concentrations which is considered the more bioavailable fraction. Concentrations of total metals (i.e., dissolved+particulate) are also below these criteria and are similar to other areas in Chesapeake Bay. In comparison to water quality standards (WQS) for both the District of Columbia and the State of Maryland (Table 11), dissolved concentrations of PCBs were above the PCB criterion for two samples in transect 2. Concentrations of dissolved $\alpha+\gamma$ chlordane were above WQS for five samples in transects 1 and 2. If total concentrations of both PCB and chlordane are used, concentrations would exceed WQS in many more cases (Table 11). Dissolved concentrations of chlordane and PCBs were all higher than those stated for human health effects to water+organisms at a risk level of 10^{-6} (Table 11).

Future studies should focus on the source of the elevated levels of chlordane and PCBs in the Maryland portion of the Anacostia River. Samples should be obtained from both the NE and NW Branches during storm and base flows to determine the magnitude of water and sediment transport of contaminants to the Anacostia River. Current work at the fall-line of the Potomac River indicates that storm flows are more important in the transport of material than base flows and that the transport phase may be different (Foster and Lippa, 1993). This may be just as important for the Anacostia River. Also, samples should be obtained in the other smaller creeks and runs that flow into the Anacostia River. These smaller creeks account for approximately a quarter of the total flow to the Anacostia River. Results from this study also indicate that benthic processes may have an influence on the water column chemistry of nutrients and trace metals. Additional work should be undertaken to investigate the importance of the bottom sediments in retaining and recycling both nitrogen and sediment-bound contaminants like trace metals.

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Appendix I: Dissolved and Particulate Trace Metals and Other Inorganics.

QUALITY ASSURANCE SUMMARY FOR THE ANACOSTIA RIVER TRACE METAL AND NUTRIENT STUDY

Report Submitted to:

Dr. David J. Velinsky
Interstate Commission on the Potomac River Basin
6110 Executive Boulevard, Suite 300
Rockville, MD

Report Submitted by:

Michael Owens and Jeffery Cornwell
University of Maryland CEES
Horn Point Environmental Laboratory
Cambridge, MD 21613-0775

10 January 1994

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Introduction

This report includes all the inorganic data collected on the Anacostia River Dredge Project. All data is arranged in tables according to the type sample analyzed. Samples analyzed in replicate are reported as averages in the following tables. All quality assurance and control data are also reported in tables at the end of this report. Methods used for this study are described in Velinsky et al. (1993; see main report)

Quality Assurance and Quality Control Information

Table E summarizes all duplicates measured for dissolved and particulate trace metals. These are duplicate samples which were collected on site and not replicate analyses of the same sample. The dissolved trace metals exhibit excellent agreement between replicates. The particulate trace metal replicates show good agreement with some expected scatter related to the increase in spatial variability of suspended material in river and tidal waters.

In order to check recoveries of the particulate trace metal analysis, a small amount of National Institute of Standard and Technology (N.I.S.T.) Estuarine Sediment was digested and analyzed along with the samples. The results are listed in Table F along with the N.I.S.T. certified analysis (i.e., means and standard deviations). Complete recovery of Fe, Cu, and P were achieved with this digestion procedure. Recoveries of the other metals were less than 100 percent but were similar to recoveries we observed with this digestion in the past.

Another QA/QC check used for this project was the analysis of a water reference standard (i.e., N.I.S.T. trace metal standard) which was analyzed by Chelation Ion Chromatography. Table E gives the results of this analysis along with the certified values. The reported values are in good agreement with the certified values with a slight under estimate of zinc and manganese.

Table G contains all replicate samples analyzed for particulate and dissolved nutrients. The replicates analyzed for nutrients are in good agreement.

Sediment trace metals were analyzed on three samples and the results are reported in

Table D. The N.I.S.T. estuarine sediment standard was digested along with these three sediment samples and these results are also listed in Table D. The recoveries of these trace metals are in accordance with the normal recoveries we see using this digestion. The replicate N.I.S.T. samples are in good agreement for all metals analyzed.

Anacostia River Dissolved and Particulate Nutrients

Table A

	Seston	Seston	Seston	Dissolved Nutrients (umol/L)				Particulate Nutrients (umol/L)	
ID	(mg/L)	% C	%N	NH4	NO3+NO2	Si	PO4	C	N
T1 -500	13.3	6.9	1.08	0.9	37.0	100.0	0.12	76.6	10.3
T1 - 3	24.6	5.9	0.92	1.6	38.6	100.0	0.09	121.6	16.2
T1 +120	29.7	6.5	0.86	10.8	31.0	96.3	0.10	160.8	18.3
T1 +800	19.9	7.1	0.94	18.9	27.0	98.5	0.21	118.0	13.4
T1 +1300	22.8	6.6	0.76	17.4	26.0	101.0	0.20	124.9	12.4
T2-1100	2.9	23.7	3.2	1.4	34.5	45.2	0.1	54.8	6.4
T2 -500	6.6	13.4	1.89	1.7	38.9	47.5	0.08	73.4	8.9
T2-3	10.6	9.8	1.13	5.4	36.4	49.9	0.09	86.6	8.5
T2 +3	11.3	9.7	1.35	8.2	36.0	49.8	0.09	91.3	11.0
T2 +6	12.7	8.0	0.96	8.2	36.0	48.7	0.08	84.8	8.7
T2 +12	13.0	6.5	0.73	7.3	37.0	48.6	0.15	70.9	6.8
T2 +30	7.4	14.4	1.82	8.3	35.7	49.5	0.08	88.3	9.6
T2 +120	11.7	10.5	1.11	20.1	27.6	54.8	0.10	102.3	9.2
T2 +800	15.8	10.3	1.33	31.4	19.9	64.5	0.07	135.0	15.0
T2 +1200	24.7	8.9	1.15	nd	nd	nd	nd	nd	nd
T3 -1200NE	3.3	20.4	1.98	1.1	19.5	51.4	0.13	56.7	4.7
T3 -1200NW	5.9	10.8	1.08	0.9	39.5	56.7	0.08	53.1	4.5
T3 -500	4.8	11.3	1.42	2.3	35.7	43.9	0.08	45.5	4.9
T3 -3	47.5	5.2	0.47	24.4	35.7	50.0	0.04	210.3	16.9
T3+3	11.3	8.6	1.01	16.4	35.7	50.0	0.04	81.2	8.2
T3 +6	11.5	9.0	1.19	10.4	33.9	51.3	0.08	86.6	9.8
T3 +12	14.5	10.1	1.04	10.1	35.5	48.2	0.04	122.4	10.8
T3 +30	12.2	11.1	1.14	11.4	33.5	51.2	0.05	113.2	9.9
T3 +120	13.8	11.6	1.36	23.0	25.8	56.7	0.07	133.5	13.4
T3 +800	17.4	11.4	1.42	30.1	18.9	64.8	0.07	165.1	17.6
T3 +1300	14.8	12.6	1.56	31.9	18.0	65.9	0.08	155.9	16.6

nd - no data

Anacostia River Dissolved Trace Metals

Table B

ID	Fe ppb	Cu ppb	Ni ppb	Zn ppb	Co ppb	Mn ppb
T1-500	16.1	0.558	0.739	2.29	0.166	7.28
T1-3	18.2	0.679	0.758	2.63	0.226	18.71
T1+120	20.5	0.649	0.839	3.48	0.278	30.89
T1+800	25.2	0.483	0.801	4.81	0.307	30.36
T1+1300	20.7	0.693	0.777	2.83	0.292	29.30
T2-1100	30.2	0.666	1.259	2.07	0.145	2.98
T2-500	24.7	0.614	0.909	1.09	0.143	3.53
T2-3	22.8	0.625	0.935	1.65	0.139	6.67
T2+3	23.0	0.903	0.896	1.31	0.190	8.45
T2+6	22.7	0.542	0.862	1.61	0.116	8.15
T2+12	23.4	0.550	0.774	0.70	0.113	7.07
T2+30	21.9	0.473	0.768	0.76	0.159	8.38
T2+120	22.3	0.435	0.772	0.65	0.181	15.66
T2+800	20.0	0.320	0.709	0.56	0.185	26.27
T2+1300	22.6	0.301	0.759	0.50	0.208	33.68
T3-1200NE	26.3	0.660	0.642	0.79	0.160	1.50
T3-1200NW	32.6	0.560	0.695	0.86	0.147	2.44
T3-500	25.2	0.716	0.756	1.00	0.166	4.08
T3-3	18.0	0.404	0.884	0.71	0.215	13.96
T3+3	19.3	0.500	0.782	1.04	0.187	11.04
T3+6	21.4	0.503	0.694	0.70	0.186	9.17
T3+12	17.7	0.546	0.734	1.23	0.158	8.13
T3+30	19.0	0.552	0.772	0.71	0.183	10.51
T3+120	20.7	0.415	0.986	0.71	0.200	19.00
T3+800	19.4	0.337	0.841	0.80	0.207	28.95
T3+1300	21.3	0.305	1.081	2.78	0.218	30.67

Anacostia River Particulate Trace Metals and Particulate P

Table C

	Fe	Mn	P	Cu	Ni	Zn	Co
ID	mg/g	mg/g	mg/g	ug/g	ug/g	ug/g	ug/g
T1 -500	44.6	2.50	2.07	69.2	55.0	668	29.1
T1 -3	50.8	1.97	1.54	65.1	16.2	217	11.8
T1 +120	40.1	2.28	1.29	48.5	16.0	216	13.4
T1 +800	35.5	2.19	1.37	51.3	39.1	344	21.0
T1 +1300	24.4	1.63	1.00	147.4	86.4	611	39.1
T2 -1100	27.8	3.62	3.86	49.9	47.0	779	11.8
T2 -500	27.2	2.62	0.99	66.2	58.8	612	18.2
T2 -3	27.6	3.13	1.32	92.0	36.2	510	27.2
T2 +3	31.4	2.99	0.73	79.9	47.9	143	15.4
T2 +6	18.3	2.47	0.28	78.7	52.9	210	15.8
T2 +12	18.0	2.34	0.17	77.2	44.3	152	13.7
T2 +30	12.7	2.98	0.47	99.1	66.9	76	0.0
T2 +120	14.4	2.96	0.15	48.2	64.6	208	15.8
T2 +800	31.4	4.35	1.39	98.4	57.6	201	23.7
T2 +1300	13.5	2.57	0.50	40.5	44.6	122	13.1
T3 -1200NE	20.2	3.52	4.19	125.5	61.4	1068	23.4
T3 -1200NW	20.4	2.93	3.74	33.2	14.9	364	3.7
T3 -500	31.2	3.78	3.42	120.0	28.6	600	19.0
T3 -3	19.9	1.75	0.26	49.9	34.0	280	17.3
T3 +3	15.4	2.04	0.97	104.4	49.5	327	21.3
T3 +6	11.8	2.42	0.53	68.2	18.4	258	15.7
T3 +12	20.6	2.59	1.24	71.5	35.8	293	19.6
T3 +30	13.4	3.61	0.75	76.6	32.3	255	17.1
T3 +120	40.7	4.06	2.07	89.1	53.2	366	25.2
T3 +800	11.7	2.94	0.63	67.9	37.3	135	19.1
T3 +1300	16.2	4.41	0.97	82.4	48.6	170	26.9

Anacostia River Sediment Trace Metals

Table D

ID	Pb ug/g	Cu ug/g	Zn ug/g	Co ug/g	Ni ug/g	Mn mg/g	Fe mg/g
ANA #1 0-1cm	27.6	12.4	66.4	8.7	13.1	0.139	10.9
ANA #2 0-1cm	30.9	14.9	101.0	10.4	17.7	0.192	13.2
ANA #2 2-4cm	45.3	17.2	91.5	11.2	17.9	0.180	13.4
NIST	16.8	14.7	101.5	11.0	19.1	0.183	25.4
NIST	23.4	14.7	107.0	11.1	15.2	0.186	26.2
NIST certified values							
Mean	28.20	18.00	138.00	10.50	32	0.375	33.5
Std	1.8	3	6	1.3	3	0.02	1.0

Table E

Replicate samples analyzed for dissolved trace metals in ppb

	Fe	Cu	Ni	Zn	Co	Mn
T2+3 A	23.582	0.976	0.969	1.218	0.209	8.352
T2+3 B	22.416	0.830	0.824	1.412	0.171	8.546
T2-1100 A	31.174	0.728	1.339	2.240	0.134	3.292
T2-1100 B	29.299	0.605	1.179	1.895	0.156	2.676
T3-1200NW A	32.964	0.581	0.698	0.858	0.145	2.502
T3-1200NW B	32.190	0.539	0.691	0.860	0.148	2.376
T3+1300 A	20.407	0.321	0.846	1.195	0.210	31.186
T3+1300 B	22.202	0.290	1.315	4.369	0.225	30.148

Standard reference material 1643c Trace Elements in Water

Chelation analysis		Cu	Ni	Zn	Co	Mn	Fe
NIST	ppb	18.9	49.8	63.6	20.5	25.3	122.4

NIST Certified values

	Cu	Ni	Zn	Co	Mn	Fe
Mean	22.3	60.6	73.9	23.5	35.1	106.9
Std	2.8	7.3	0.9	0.8	2.2	3.0

Table F

Replicate samples analyzed for particulate trace metals in ppb

	Cu	Ni	Zn	Co
T1 1300 A	120.76	83.45	601.22	34.57
T1 1300 B	173.96	89.27	601.22	43.67
T2 -1100 A	75.98	18.65	883.75	12.90
T2 -1100 B	23.82	75.44	673.45	10.72
T3 -1200NE A	156.95	60.95	1088.53	19.28
T3 -1200NE B	94.11	61.84	1047.87	27.62
T3 +30 A	82.42	45.80	250.84	26.08
T3 +30 B	84.39	40.62	331.46	33.12
T3 +30 C	76.58	32.33	254.54	17.10
T3 +3 A	104.42	49.47	327.15	21.32
T3 +3 C	85.03	34.01	289.07	16.16
NIST std.	14.38	22.22	83.28	4.09

Replicate samples analyzed for particulate Fe, Mn, and P in ppm

		Fe	Mn	P
T1 1300	A	23.28	1.62	1.00
T1 1300	B	25.57	1.64	1.00
T2 -1100	A	18.25	3.44	3.54
T2 -1100	B	37.38	3.79	4.17
T3 -1200	A	20.46	3.41	4.26
T3 -1200	B	19.96	3.64	4.13
NIST std.		26.65	0.21	0.57

NIST certifed values 1646 Estuarine Sediment

	Fe	Mn	Cu	Ni	Zn	Co	P
	ppm	ppb	ppb	ppb	ppb	ppb	ppm
Mean	33.5	375	18	32	138	10.5	0.54
Std	10	20	3	3	6	3	0.05

Table G

Replicate samples analyzed for dissolved and particulate nutrients

	Seston	Seston	Seston	Dissolved Nutrients (umol/L)				Particulate Nutrients (umol/L)	
ID	mg/L	% C	%N	NH4	NO3+NO2	Si	PO4	C	N
T1 +1300 A	22.8	6.6	0.76	17.4	26.0	101.0	0.20	124.9	12.4
T1 +1300 B	23.3	5.7	0.63	nd	nd	nd	nd	nd	
T2-1100 A	3.2	17.1	2.09	1.3	34.5	45.3	0.11	45.0	4.7
T2-1100 B	2.6	30.3	4.39	1.5	34.5	45.1	0.09	64.6	8.0
T3 -3 A	44.7	6.6	0.56	nd	nd	nd	nd	nd	
T3 -3 B	49.8	3.8	0.37	24.4	35.7	50.0	0.04	157.4	13.2
T3-3 C	nd	nd	nd	nd	nd	nd	nd	233.8	18.3
T3-3 D	nd	nd	nd	nd	nd	nd	nd	239.7	19.3
T3 +30A	nd	nd	nd	nd	nd	nd	nd	104.4	11.0
T3 +30B	nd	nd	nd	nd	nd	nd	nd	103.1	10.6
T3 +30C	nd	nd	nd	nd	nd	nd	nd	105.4	10.6
T3 +30D	nd	nd	nd	nd	nd	nd	nd	113.2	9.9
T3 -1200NE A	nd	nd	nd	nd	nd	nd	nd	56.7	4.7
T3-1200NE B	nd	nd	nd	nd	nd	nd	nd	59.6	5.1
T3-1200NE C	nd	nd	nd	nd	nd	nd	nd	49.2	5.2
T3-1200NE D	nd	nd	nd	nd	nd	nd	nd	51.5	5.1

Appendix II: Dissolved and Particulate Organic Compounds.

QUALITY ASSURANCE SUMMARY FOR THE ANACOSTIA RIVER STUDY

Report Submitted To

Dr. David J. Velinsky
Interstate Commission on the Potomac River Basin
6110 Executive Boulevard, Suite 300
Rockville, MD

Report Submitted By

Dr. Gregory D. Foster
Department of Chemistry
George Mason University
Fairfax, VA 22030

28 December 1993

Analytical Results

Concentrations of the organic contaminants detected in dissolved and particle phases of the Anacostia River samples are listed in Tables 1 and 2, respectively. The highest concentrations were observed for polychlorinated biphenyls (a total of 112 congeners) and polycyclic aromatic hydrocarbons (a total of 16 homologues) in both phases at most of the locations sampled, although many of the analytes were detected at low concentrations (i.e., < 1 ng/L). Most of the dissolved phase samples had detectable concentrations of organic contaminants (Table 1). In particle phase analysis, there existed a relatively greater number of measurements below analytical detection limits (Table 2) than was observed in the dissolved phase. This is because suspended particulate concentrations were relatively low, approximately 15 mg/L, and only four liters of sample was processed, ultimately providing a small amount of particle mass isolated on filters for the analysis. Based on the experiences of this analyst, the minimum amount of particle mass needed, under ideal conditions, for particle phase analysis is >100 mg. Most of the Anacostia River samples had total particle masses less than this amount; only samples TI-(-3), T1-(+120), T2-(+1300), and T3-(-3) met this criterion. The particle phase concentrations that were measured with less than 100 mg of total particle mass should be scrutinized. The 100 mg minimum is based on the fact that the adsorption of hydrophobic organics directly on filter surfaces in the absence of particulates can be important, and overbiased estimates of detection limits with very small particle masses isolated on filters are probable.

General QA Work Plan

Several laboratory blanks and one travel blank were processed during this study. Blank samples consisted of double glass distilled water that was further treated by extraction in C18 cartridges to remove trace organic impurities. Blank samples were 4 L in volume, and were processed as a typical sample in the analysis. Samples of filtered (0.7 μm Whatman GF/F) Potomac River water and distilled water ranging in volume from 1 to 10 L were spiked with each of the target analytes measured in the Anacostia River study at a concentration of ca. 100 ng/L.

Recoveries of the analytes from spiked water were determined for both river water and distilled water using procedures previously described by Foreman and Foster (1992). In the larger volume samples (6-10 L), an assessment was made regarding the breakthrough and retention of the analytes on the cartridges by (1) using tandem front and back LSE traps, and (2) eluting the front trap with methanol after the primary elution step (refer to description of methods in QA work plan). Glass fiber filters were also spiked with the target analytes and have been processed as described (refer to Foster 1992 QA work plan for Anacostia River study) but not completed.

The matrix spike results presented in this QA summary include only the dissolved phase recoveries. Bottom sediments are presently being analyzed for the full suite of analytes, and the final QA data for spiked filters is presently being compiled. Results for these analyses will be forwarded upon completion.

QA Results

Blank sample results are shown in Figure 1 for the Anacostia River study. A total of three laboratory blanks and one travel blank were processed and analyzed. Two additional travel blanks were prepared but were not processed completely after it was determined that an improper water source had been selected: the water source was single distilled water that was not acceptable for use as a blank sample. In this study, travel blanks were very similar to laboratory blanks because the water was sealed in bottles during transport to and from the laboratory, and was never allowed to contact any environment other than laboratory atmosphere. Therefore, two additional blanks served as surrogates for the two travel blanks discarded. Analyte concentrations in the dissolved phase blanks were low and usually below 0.5 ng/L except for travel blank number 1; the reason for this is described above. The particulate blanks show more variable analyte concentrations than the dissolved phase blanks, and the concentrations are slightly elevated although they were usually less than 1 ng/L. The results from the blank samples were used to correct the analyte concentrations in the river water samples. Blank corrections were performed according to procedures described by Keith (1988), wherein an average analyte concentration calculated from all of the blanks was subtracted from the sample concentrations to provide more accurate fluvial sample concentrations. All reported concentrations have been blank corrected for both dissolved and particulate phase analysis.

The recoveries of the target analytes spiked to the water samples are shown in Appendix 1 and Figure 2. Two water sources and two volume ranges, large (6-10 L) and small (1-4 L), were used to evaluate the performance of the dissolved phase analysis. Appendix 1 contains data for the large sample recoveries, showing the distribution of the analytes between front and back LSE cartridges and the amount of analyte collected from the elution with methanol. The majority of the analytes were collected on the front trap, and overall recoveries ranged from 56% for aldrin to 109% for dieldrin for the large volume Potomac River samples. One to 4 liter samples (1 replicate each) were processed to evaluate the effect of sample volume on recoveries, and there were no distinct differences in recoveries between the two volume regimes for Potomac River water (Figure 2).

Distilled water was used in the recovery evaluation to determine the significance of the natural water matrix on isolation and extraction performance. It has been observed that analyte recoveries are greater from distilled water than river water because distilled water is free of dissolved humic substances which can modify the surface of the C18 phase and reduce the retention of the analytes (Johnson et al. 1992). Some of the 1 to 4 L distilled water recoveries were slightly higher than the larger volumes (e.g., aldrin, oxychlordane, gamma-chlordane, alpha-chlordane, dieldrin, and DDT in Figure 2) but in large volume samples distilled water recoveries were not found to be enhanced relative to river water, and in fact were lower in several cases.

Further inspection of Appendix 1 reveals that less than 100 percent of the analyte spiked in water was detected. The mass balance does not add up to 100% As part of a thorough error evaluation conducted in our laboratory we have determined that up to 30 to 40% (worst case scenario) of the organochlorine and PAH analytes are subject to volatilization losses during sample work up. Exceptions to this include dieldrin and DDT which are not subject to volatilization losses, and the recoveries of these two analytes are near 100% (Appendix 1). To achieve very low detection limits, the C18 cartridge and filter extracts were reduced to a final volume of 0.2 mL. During volume reduction between 1 mL and 0.2 mL under nitrogen gas blowdown a substantial portion of the analytes can be lost from volume reduction. Factoring in the evaporative loss for each of the analytes would provide total recovery values approaching 100% for most of the analytes.

Variability was partially assessed in this study by collecting and processing duplicate fluvial samples for three sampling events. The results of the duplicate analyses were used to express percent deviations as an index of measurement variability. Percent deviation for duplicate analyses is defined by the following equation:

$$\% \text{ Deviation} = \left|(\text{Rep } 1 - \text{Rep } 2)/((\text{Rep } 1 + \text{Rep } 2)/2) \times 100\right|$$

The absolute value of the percent deviation result is determined to aid in averaging individual values, and no distinction is made regarding the sign of the deviation (i.e., positive or negative in magnitude). The average percent deviations for all of the duplicate analyses combined are plotted in Figure 3. Percent relative standard deviations were calculated by propagating uncertainties for each step in the analytical method and the values are also shown in Figure 3, and range from ca. 9% (alpha-chlordane) to 25% (PAH). Propagated analytical uncertainties are calculated from known tolerances of the volumetric and graduated glassware and from response variability determined from GC analysis. In all cases, analytical uncertainties were markedly below duplicate percent deviations for both dissolved and particulate phase analyses.

The ranges of the measured percent deviations combined for both dissolved and particulate phases were 17 to 118% for aldrin, 37 to 51% for oxychlordane (particle phase not included), 11 to 130% for gamma-chlordane, 3 to 130% for alpha-chlordane, 4 to 140% for dieldrin, 18 to 96% for total-PCBs, and 24 to 112% for total PAH. The overall average for the observed percent deviations was calculated to be 59%. Loosely interpreted, the overall average percent deviation can be used to indicate that the concentration data has a maximum variability of ca. 60%. The origin the this variability is not known exactly, but can be speculated to be due to the following reasons:

1. Sampling variability is important and is not accounted for in the analytical uncertainty calculations. Sampling variability and analytical variability are additive terms.

2. The percent deviations and analytical uncertainties are not directly comparable quantities because analytical uncertainties have been determined using the results of over 20 GC measurements. Given the large range of observed percent deviations, a larger sample size would likely result in lower uncertainties.

3. Relative analytical uncertainties are larger near detection limits and are smaller at higher concentrations. The concentrations measured in this study approached analytical detection limits. In addition, variability is much higher near detection limits with complex mixtures, where matrix-originated responses (peaks) in GC analysis can interfere with analyte quantitation. In this case, total error arises from both random error and systematic error (matrix effect). GC chromatograms for the organochlorine pesticides especially were quite complex.

References

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Johnson, WE, NJ Fendinger, and JR Plimmer, 1991. Solid-phase extraction of pesticides from water: possible interferences from dissolved organic material. Anal. Chem. 63, 1510-1513.

Keith, LH (ed.), 1988. Principles of Environmental Sampling. American Chemical Society, Washington, DC.

Table 1. Concentrations of dissolved phase organic contaminants in Anacostia River samples.

1. Dissovled phase organic contaminants in fluvial transport on 9/9/92 (first collection).

Concentrations are reported in ng/L concentration units and are valid to 2 significant figures

Analyte	AR1_S01 -500[R1]	AR1_S02 -500[R2]	AR1_S03 -3	AR1_S04 +120	AR1_S05 +800[1]	AR1_S06 +800[2]	AR1_S07 +1300
Aldrin	0.3	0.2	0.2	0.1	0.5	0.1	0.1
Oxychlordane	5.6	3.9	4.6	3.7	3.3	9.5	4.4
gamma-Chlordane	0.7	1.8	2.6	0.7	1.5	5.6	1.7
alpha-Chlordane	1.2	1.3	2.1	1.1	1.0	9.0	1.9
Dieldrin	1.3	1.3	1.7	1.4	1.7	2.9	1.8
4,4'-DDT	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl
total-PCB	4.4	3.3	2.3	0.8	4.2	3.5	2.2
total-PAH	59.5	42.3	72.9	133.0	272.0	87.3	123.2

2. Dissovled phase organic contaminants in fluvial transport on 9/22/92 (second collection).

Concentrations are reported in ng/L concentration units

Analyte	AR2_S01 -1100	AR2_S02 -500[1]	AR2_S03 -500[2]	AR2_S04 -3	AR2_S05 +3	AR2_SO6 +6	AR2_S07 +12	AR2_S08 +30	AR2_S09 +120	AR2_S10 +800[1]	AR2_S11 +800[2]	AR2_S12 +1300
Aldrin	0.4	0.1	0.1	0.2	0.2	0.4	4.3	0.1	<emdl	0.1	0.2	0.3
Oxychlordane	2.9	3.6	2.4	2.2	1.9	2.5	4.2	2.5	3.1	3.5	2.2	2.3
gamma-Chlordane	0.7	1.0	1.1	2.5	0.7	1.1	1.9	1.2	1.3	4.0	0.8	<emdl
alpha-Chlordane	0.9	1.0	1.0	2.6	0.8	0.9	3.0	1.2	1.5	3.8	0.8	0.8
Dieldrin	1.5	1.2	1.3	2.6	1.0	1.2	3.0	2.1	2.5	6.6	1.2	2.4
4,4'-DDT	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl
total-PCB	5.2	3.2	4.8	9.5	3.8	4.5	20.7	3.0	2.1	20.2	7.1	3.1
total-PAH	50.7	26.8	66.8	198.6	46.7	55.6	29.2	130.6	34.0	58.5	27.4	25.0

3. Dissovled phase organic contaminants in fluvial transport on 9/22/92 (third collection).

Concentrations are reported in ng/L concentration units

Analyte	AR3_S01 -1200NE	AR3_S02 -1200NW	AR3_S03 -500	AR3_S04 -3	AR3_S05 +3	AR3_S06 +6	AR3_S07 +12	AR3_S08 +30	AR3_S09 +120	AR3_S10 +800	AR3_S11 +1300
Aldrin	0.3	0.4	0.1	0.2	0.2	0.2	0.5	0.3	0.3	0.2	0.1
Oxychlordane	2.0	3.4	2.9	3.2	2.8	3.1	2.8	4.1	3.5	3.0	2.1
gamma-Chlordane	0.6	1.1	0.7	1.2	1.1	0.8	0.7	1.1	0.9	0.7	0.7
alpha-Chlordane	0.8	1.1	0.7	1.1	1.2	0.9	1.0	1.4	1.0	0.6	1.3
Dieldrin	1.0	<emdl	2.0	0.6	1.5	1.6	1.6	1.3	1.1	0.4	1.7
4,4'-DDT	<emdl	2.5	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl
total-PCB	2.4	5.3	1.8	7.5	1.7	1.7	4.1	5.2	3.9	5.3	2.0
total-PAH	108.2	61.8	24.7	185.9	43.6	19.2	13.3	16.6	25.8	16.8	7.9

<emdl = less than estimated method detection limit

Table 2. Concentrations of particulate phase organic contaminants in Anacostia River samples.

1. Particle phase organic contaminant concentrations in fluvial transport on 9/9/92 (first collection).

Concentrations are reported in ng/L concentration units and are valid to 2 significant figures

Analyte	AR1_S01 -500[R1]	AR1_S02 -500[R2]	AR1_S03 -3	AR1_S04 +120	AR1_S05 +800[1]	AR1_S06 +800[2]	AR1_S07 +1300
Aldrin	0.4	<emdl	0.3	0.3	0.6	0.4	0.3
gamma-Chlordane	0.6	0.7	0.8	1.8	1.5	1.8	1.4
alpha-Chlordane	0.5	0.9	0.7	1.4	2.1	2.7	1.2
Dieldrin	1.5	1.3	1.0	1.4	2.0	1.6	1.6
4,4'-DDT	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl
total-PCB	10.9	12.3	11.3	7.9	19.5	13.9	10.5
total-PAH	6.7	1.9	88.6	327.1	144.4	94.9	26.3

2. Particle phase organic contaminant concentrations in fluvial transport on 9/22/92 (second collection).

Concentrations are reported in ng/L concentration units

Analyte	AR2_SO1 -1100	AR2_S02 -500[1]	AR2_S03 -500[2]	AR2_S04 -3	AR2_S05 +3	AR2_SO6 +6	AR2_S07 +12	AR2_S08 +30	AR2_S09 +120	AR2_S10 +800[1]	AR2_S11 +800[2]	AR2_S12 +1300
Aldrin	0.3	0.3	0.1	<emdl	<emdl	0.4	0.4	<emdl	<emdl	0.3	0.6	0.2
gamma-Chlordane	0.4	0.8	0.5	0.6	0.3	0.3	0.4	<emdl	0.6	0.3	0.8	<emdl
alpha-Chlordane	0.3	0.8	0.3	0.5	<emdl	<emdl	0.6	0.1	<emdl	0.3	1.0	<emdl
Dieldrin	1.0	1.7	0.7	1.0	1.4	1.2	1.1	1.2	0.9	0.5	<emdl	<emdl
4,4'-DDT	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	19.1	<emdl	<emdl
total-PCB	9.7	8.8	10.5	10.5	23.6	8.2	11.0	21.9	<emdl	8.0	7.7	15.5
total-PAH	6.8	2.7	7.3	2.3	0.2	9.8	20.8	1.4	2.5	0.8	1.2	13.5

3. Particle phase organic contaminant concentrations in fluvial transport on 9/22/92 (third collection).

Concentrations are reported in ng/L concentration units

Analyte	AR3_S01 -1200NE	AR3_S02 -1200NW	AR3_S03 -500	AR3_S04 -3	AR3_S05 +3	AR3_S06 +6	AR3_S07 +12	AR3_S08 +30	AR3_S09 +120	AR3_S10 +800	ARS_S11 +1300
Aldrin	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl
gamma-Chlordane	<emdl	<emdl	<emdl	1.8	0.4	0.9	1.2	0.4	<emdl	0.3	<emdl
alpha-Chlordane	0.1	0.1	1.0	1.4	0.3	0.7	1.1	0.2	<emdl	0.5	<emdl
Dieldrin	0.4	0.5	1.2	1.2	0.7	0.6	1.3	0.9	<emdl	<emdl	<emdl
4,4'-DDT	<emdl	2.5	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl	<emdl
total-PCB	19.7	22.1	19.3	19.8	14.8	14.8	7.4	8.6	0.0	11.5	23.1
total-PAH	60.3	2.6	32.7	16175.8	46.1	11.3	56.9	6.6	0.0	3.8	66.7

<emdl = less than estimated method detection limit.

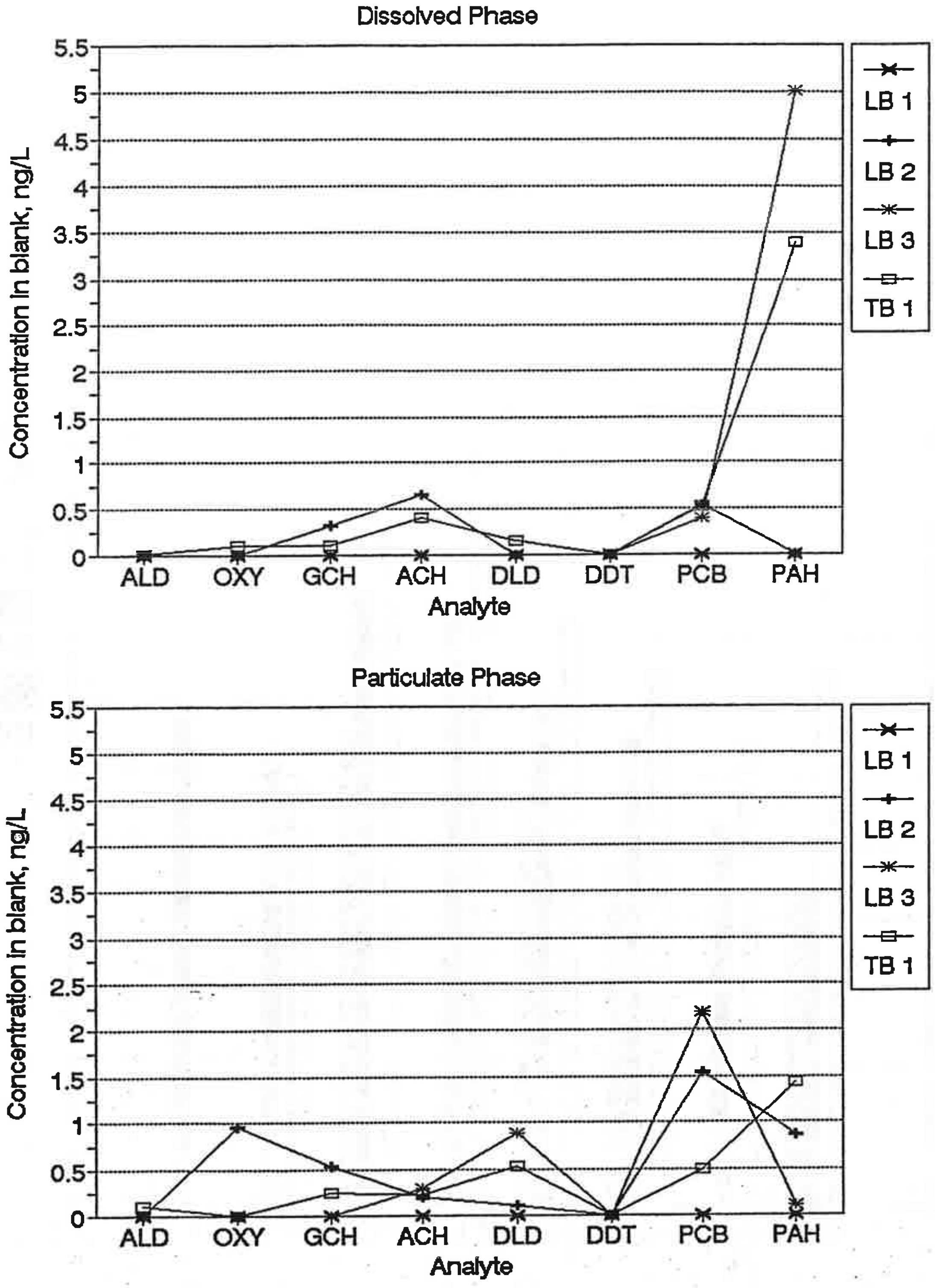

Figure 1. Analyte concentrations in dissolved and particulate phase laboratory and travel blanks: LB=laboratory blank; TB=travel blank.

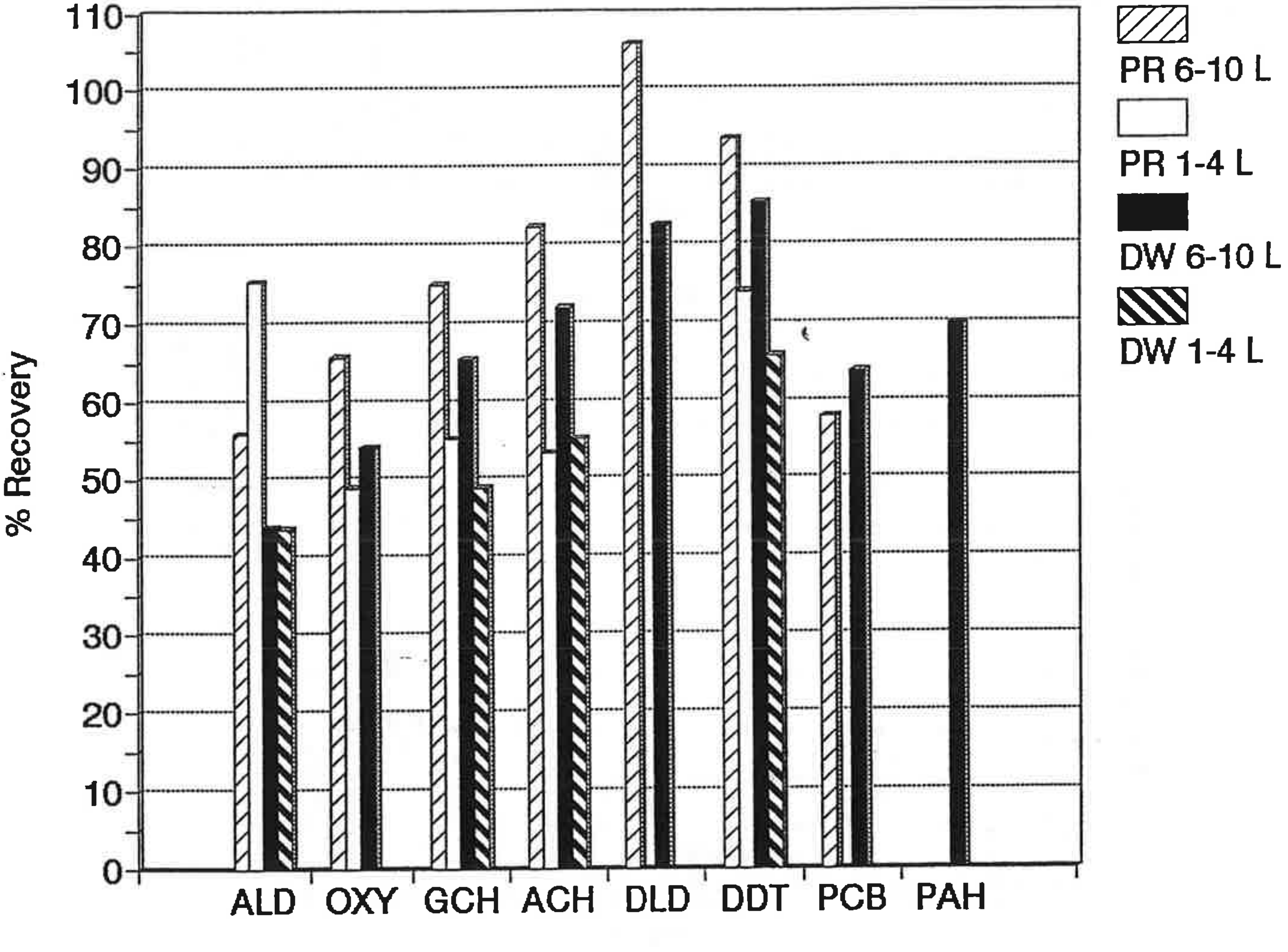

Figure 2. Matrix spike recoveries for large volumes (6-10 L) and small volumes (1-4 L). Abbreviations are as follows: ALD=aldrin; OXY=oxychlordane; GCH=gamma-chlordane; ACH=alpha-chlordane; DLD=dieldrin; DDT=4,4'-DDT; PCB=total PCBs; PAH=total PAH; PR=Potomac River; DW=distilled water.

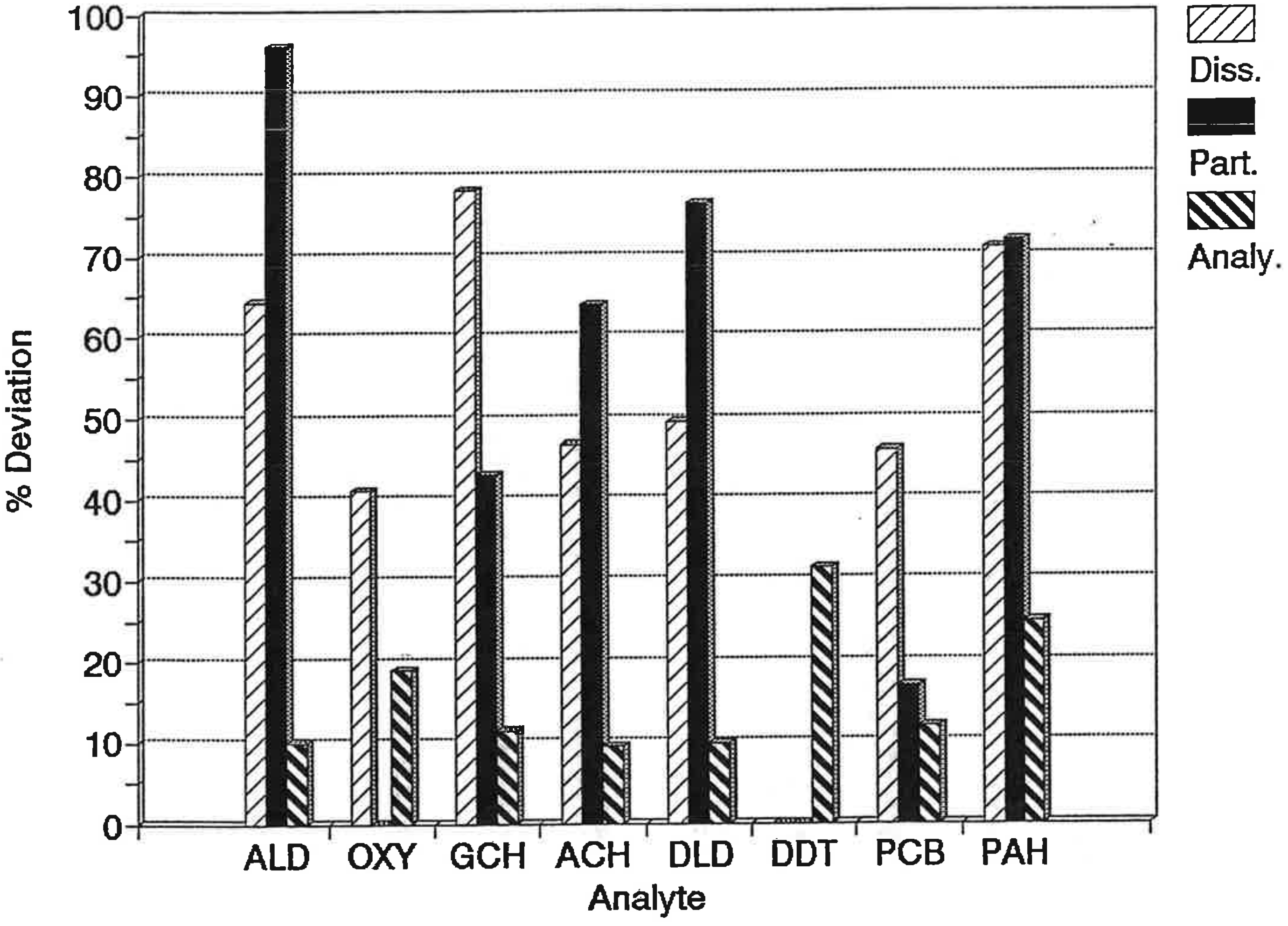

Figure 3. Average duplicate sample uncertainties and analytical relative uncertainties (% relative standard deviations) expressed as percent deviations (% Deviation). Analyte abbreviations conform to those provided in Figure 2; Diss.=dissolved phase; Part.=particulate phase; and Analy.=%RSDs for sample analysis.

Sediment Concentration Results

In Tables 3 - 5 are the polycyclic aromatic hydrocarbon (PAH), pesticides, and polychlorinated biphenyls (PCB) bed sediment data for the marina study. Methods used are similar to those described in the text.

Table 3. Organic contaminants in Anacostia River bed sediment.

ANALYTE	ANA #3 Rep 1	ANA #3 Rep 2	ANA #4 Rep 1	ANA #4 Rep 2	ANA #5 Rep 1	ANA #5 Rep 2
Aldrin	0.00	n/a	0.33	n/a	0.53	0.67
trans-Chlordane	0.52	n/a	3.8	2.8	6.8	5.9
cis-Chlordane	0.40	n/a	2.7	2.6	5.7	5.3
Dieldrin	0.00	n/a	0.59	0.20	1.3	0.09
4,4'-DDT	0.24	n/a	1.5	3.4	0.0	1.5
total-PCB	3.8	2.5	28.2	n/a	13.4	9.3
total-PAH	640	1100	6300	9100	14000	14000
% Silt+Clay	76	n/a	11	n/a	56	n/a
% Organic Matter	5.0	n/a	1.4	n/a	7.6	n/a

Concentrations are reported in ng/g of bed sediment dry weight except grain size and organic matter which are in percent. n/a - not analyzed.

% Organic Matter determined after combustion at 450oC for 2 hours.

Table 4. Polynuclear Aromatic Hydrocarbon concentrations in bed sediments.

Analyte	ANA #3 Rep 1	ANA #3 Rep 2	ANA #4 Rep 1	ANA #4 Rep 2	ANA #5 Rep 1	ANA #5 Rep 2
Naphthalene	0.0	0.0	0.0	0.0	0.0	0.0
Acenapthylene	1.2	2.6	14.8	26.4	32.0	52.7
Acenaphthene	2.9	4.3	19.0	32.2	109.2	112.7
Flourene	4.7	6.6	33.1	50.5	180.0	208.7
Phenanthrene	70.4	130.2	679.0	1034.5	2075.3	2039.7
Anthracene	8.7	7.2	61.0	71.0	170.6	1807.1
Flouranthene	229.3	377.8	1835.9	2115.5	2558.7	2172.8
Pyrene	216.5	333.3	1721.4	1835.2	2068.8	1813.7
Benz(a)anthracene	35.4	67.0	428.4	595.3	1064.5	985.5
Chyrsene	32.4	86.2	541.6	860.2	1342.4	1231.6
Benzo(b)flouranthene	n/a	n/a	n/a	n/a	n/a	n/a
Benzo(k)flouranthene	21.4	55.5	477.5	1088.0	2070.6	2063.0
Benzo(a)pyrene	9.3	29.6	221.0	556.0	1057.2	1071.4
Indeno(123-cd)pyren	4.1	16.8	159.6	428.9	703.2	0.0
Dibenz(ah)anthracen	0.0	0.0	35.9	95.3	173.6	54.6
Benzo(ghi)perylene	3.0	11.9	119.0	317.3	502.1	0.0
TOTAL PAHs	639.2	1129.0	6346.9	9106.5	14108.2	13613.4

Concentrations are reported in ng/g dry weight.
n/a - Not analyzed

Table 5. PCB Congeners in Anacostia River sediments.

Congener #	ANA #3 Rep 1	ANA #3 Rep 2	ANA #4 Rep 1	ANA #4 Rep 2	ANA #5 Rep 1	ANA #5 Rep 2
4/10	0.00	0.00	0.00	n/a	0.00	0.00
7/9	0.00	0.00	0.00	n/a	0.00	0.00
6	0.00	0.00	0.00	n/a	0.00	0.00
5/8	0.00	0.00	0.00	n/a	0.00	0.00
19	0.00	0.00	0.02	n/a	0.00	0.04
18	0.00	0.04	0.29	n/a	0.51	0.46
15/17	0.00	0.05	0.00	n/a	0.46	0.42
24/27	0.00	0.00	0.14	n/a	0.00	0.00
16/32	0.03	0.02	0.14	n/a	0.00	0.25
26	0.00	0.00	0.00	n/a	0.00	0.00
25	0.00	0.00	0.00	n/a	0.00	0.00
28/31	0.00	0.00	0.75	n/a	1.73	0.00
20/33/53	0.00	0.00	0.00	n/a	0.00	0.00
22/51	0.00	0.00	0.00	n/a	0.00	0.00
45	0.00	0.00	0.00	n/a	0.00	0.00
46	0.00	0.00	0.00	n/a	0.00	0.00
52	0.16	0.09	1.18	n/a	0.00	3.03
49	0.00	0.00	0.00	n/a	0.00	0.00
47/48/75	0.00	0.00	0.00	n/a	0.00	0.00
44	0.12	0.00	0.00	n/a	0.00	1.62
37/42/59	0.04	0.00	0.19	n/a	0.28	0.00
41/64	0.00	0.00	0.00	n/a	0.00	0.00
40	0.00	0.00	0.00	n/a	0.00	0.00
67/100	0.00	0.00	0.00	n/a	0.00	0.00
63	0.00	0.06	0.16	n/a	0.00	0.00
74	0.08	0.00	0.00	n/a	0.00	0.00
70	0.16	0.00	0.00	n/a	0.00	0.00
66/95	0.31	0.00	0.00	n/a	0.00	0.00
91	0.00	0.00	0.00	n/a	0.00	0.00
56/60	0.00	0.00	0.00	n/a	0.71	0.00
84	0.00	0.00	0.48	n/a	0.00	0.00
90	0.00	0.00	0.00	n/a	0.00	0.95
101	0.33	0.00	2.22	n/a	0.00	0.00
99	0.00	0.00	0.00	n/a	0.00	0.00
119	0.00	0.00	0.00	n/a	0.00	0.00
83	0.02	0.00	0.00	n/a	0.00	0.00
97	0.00	0.00	0.00	n/a	0.00	0.00
87/115	0.00	0.00	0.00	n/a	0.00	0.00
85/p,p'-ddt	0.00	0.00	0.00	n/a	0.00	0.00
136	0.00	0.00	0.00	n/a	0.00	0.00
77/110	0.27	0.00	1.98	n/a	0.00	0.00
82/151	0.11	0.10	0.00	n/a	0.00	0.00
135	0.08	0.07	0.00	n/a	0.00	0.00
107	0.00	0.00	0.00	n/a	0.00	0.00
123/149	0.19	0.18	0.00	n/a	0.00	0.00
118	0.12	0.10	0.00	n/a	0.00	0.00
134	0.00	0.00	0.00	n/a	0.00	0.00
114/122/131	0.00	0.00	0.00	n/a	0.00	0.00
146	0.05	0.04	0.48	n/a	1.45	0.00
153/132	0.35	0.36	6.45	n/a	0.00	0.00
105	0.08	0.10	0.00	n/a	0.00	0.00
141/179	0.09	0.08	1.14	n/a	1.85	0.00
176	0.02	0.02	0.27	n/a	0.00	0.00
137	0.00	0.00	0.00	n/a	0.00	0.11
138	0.17	0.17	2.25	n/a	3.66	0.00
158	0.04	0.03	0.35	n/a	0.00	0.00
129/178	0.07	0.07	0.86	n/a	1.62	0.00
175	0.00	0.00	0.13	n/a	0.00	0.00
187	0.08	0.07	0.93	n/a	0.00	0.00
183	0.03	0.03	0.45	n/a	0.00	0.72
128	0.05	0.06	0.00	n/a	0.00	0.00
185	0.02	0.03	0.31	n/a	0.63	0.63
174	0.08	0.08	0.00	n/a	0.00	0.00
177	0.05	0.06	0.57	n/a	0.00	0.00
156/171/202	0.19	0.21	1.40	n/a	0.00	0.00
172	0.01	0.01	0.22	n/a	0.00	0.40
180	0.15	0.14	2.20	n/a	0.00	0.00
193	0.00	0.00	0.00	n/a	0.00	0.00
191	0.00	0.00	0.05	n/a	0.00	0.00
199	0.02	0.01	0.11	n/a	0.00	0.00
170/190	0.10	0.08	1.37	n/a	0.00	0.00
198	0.00	0.00	0.00	n/a	0.00	0.00
201	0.03	0.02	0.32	n/a	0.00	0.00
196/203	0.05	0.03	0.43	n/a	0.00	0.00
189	0.01	0.00	0.00	n/a	0.00	0.00
195/208	0.02	0.02	0.21	n/a	0.31	0.34
207	0.00	0.00	0.03	n/a	0.04	0.07
194	0.03	0.02	0.00	n/a	0.00	0.00
205	0.00	0.00	0.00	n/a	0.00	0.00
206	0.01	0.02	0.14	n/a	0.18	0.23
Total PCB	3.84	2.50	28.19		13.45	9.27

Concentrations in ng/g dry weight.
n/a - Not analyzed

Appendix 1. Summary of matrix spike distribution for organochlorines in large volume (6-10 L) Potomac River and distilled water samples.

		Aldrin	Oxychlordane	gamma-Chlordane	alpha-Chlordane	Dieldrin	4,4'-DDT	Total-PCBs
Potomac River Matrix								
Replicate 1:								
Front trap	nanograms	924.1	776.2	822.2	676.3	1239.5	1088.6	724.0
Can Rinse	nanograms	0.0	7.3	8.5	20.2	4.0	8.1	12.5
TOTAL ng REC	percent	924.1	783.5	830.7	696.5	1243.5	1096.7	736.5
TOTAL % REC	percent	87.5%	63.6%	69.8%	75.7%	112.0%	97.9%	62.9%
Replicate 2:								
Front trap	nanograms	349.3	784.0	898.4	739.9	1065.6	791.4	na
Can Rinse	nanograms	1.5	9.5	7.7	19.0	7.7	4.4	na
TOTAL ng REC	percent	350.8	793.5	906.2	758.9	1073.3	795.8	na
TOTAL % REC	percent	33.2%	64.4%	76.2%	82.5%	96.7%	71.1%	na
Replicate 3:								
Front trap	nanograms	495.7	845.1	932.3	797.2	1212.9	1244.0	611.7
Can Rinse	nanograms	0.0	6.7	9.1	21.3	2.5	11.6	6.2
TOTAL ng REC	percent	495.7	851.8	941.5	818.6	1215.4	1255.7	617.9
TOTAL % REC	percent	46.9%	69.1%	79.1%	89.0%	109.5%	112.1%	52.8%
AVG. Rec. %	percent	55.9	65.7	75.0	82.4	106.1	93.7	57.9
Distilled water matrix								
Replicate 1:								
Front trap	nanograms	501.2	684.8	828.7	691.1	1016.4	1020.7	710.8
Back trap	nanograms	6.1	7.1	5.8	12.3	3.6	10.9	11.8
Front MeOH	nanograms	1.2	4.0	0.0	3.9	6.6	0.0	12.7
Can Rinse	nanograms	1.4	21.3	32.1	29.6	10.3	53.9	12.2
TOTAL ng REC	nanograms	508.5	695.9	834.5	707.4	1026.6	1031.6	735.3
TOTAL % REC	percent	48.2%	56.5%	70.1%	76.9%	92.5%	92.1%	62.8%
Replicate 2:								
Front trap	nanograms	408.7	613.9	696.2	585.0	791.6	833.0	697.8
Back trap	nanograms	9.9	9.9	8.7	13.9	5.4	16.6	14.7
Front MeOH	nanograms	2.2	2.7	0.0	2.7	3.7	0.0	35.7
Can Rinse	nanograms	0.7	10.1	20.0	16.3	6.4	36.0	11.3
TOTAL ng REC	nanograms	421.5	636.7	724.8	618.0	807.1	885.6	759.5
TOTAL % REC	percent	39.9%	51.7%	60.9%	67.2%	72.7%	79.1%	64.9%
TOTAL AVG. %	percent	44.0	54.1	65.5	72.0	82.6	85.6	63.9