D.C. Water Resource Research Center
Annual Technical Report
FY 2003

Introduction

This report summarizes the activities of the District of Columbia Water Resources Research Institute (WRRI) for the period of March 1, 2003 through February 29, 2004. The Institute is in operation with only a Director on full staff and a part-time Masters of Public Administration graduate student as Research Assistant; however, we are progressing toward strengthening a credible program. The Institute is presently working with UDC Cooperative extension Service to hire a Water Quality Extension Agent. The job description has been approved and we anticipate hiring the agent by October, 2004. We are also studying the possibility of expanding and certifying the Environmental Science Water Quality Laboratory which is neither EPA certified nor capable of handling high volume samples for monitoring our stakeholders water quality.

The Seven research proposals submitted to USGS for the 2003 fiscal year were approved and funding provided. Our matching requirements were met with $200,000 worth of non federal in-kind contribution from the Watershed Protection Division of the DC Department of Health/Bureau of Environmental Quality. Five of the seven projects were completed and final reports provided. No cost extensions were approved for the other two projects and one progress report presented. These research projects were related to areas of water chemistry, bio-monitoring of pollutants, vadose zone water quality as related to nutrient management in vegetable production, effects of soil erosion in a DC Park on water quality, and assessing statistical methods for analyzing or evaluating environmental data. These projects provided training for over twenty undergraduate and graduate students as well as DC Public School Teachers. The Institute and researchers continue to accumulate valuable experiences in water resource management as related to water quality and quantity in the District of Columbia.

Water resources information transfer via the Institute website remains a problem and major obstacle to serve our stakeholders. Our expectation is that the new water quality extension agent will significantly impact the Institutes outreach capacity. The effort to enhance the Institutes website for added visibility and continues to be delayed because UDC website, which hosts WRRI webpage, is also being upgraded. We anticipate that UDC new website, with the Institutes upgrade, will be functional soon. The Institutes Directory of Water Resources Experts in the District continues to be updated. This has enabled us to reach out to a greater number of researchers in the consortium of DC Universities. Past publications are being scanned or electronic files converted into PDF files for future availability via our website. This project, though time consuming, is in progress and we anticipate completion by the end of FY 2004. The establishment of an advisory council is still in progress and will be completed by the end of FY 2004.

Collaborations with DC and Federal Agencies, DC Council of Government, and the Chesapeake Watershed Cooperative Ecosystem Studies Unit, of which UDC is a partner, indicate a promising future for additional research and technical funding for capacity building to address DC water resource problems, train students, and better serve the residents of DC through outreach programs.

Research Program

Though the environmental quality of our Anacostia River continues to be the most urgent long term water resources problem in the District, the recent lead contamination of DC drinking water has become the forerunner of immediate and pressing research needs. Published media reports of high lead levels in DC tap water began in late January 2004; however, the Institute became aware of this situation in August of 2003 when we decided to focus research efforts for 2004 on the water treatment and distribution system at DC Water and Sewer Authority (WASA). The 2002 Drinking Water Quality Report of WASA highlights that Your Water is Safe and is also proud to report that Washington DCs drinking water met or surpassed all requirements of the federal safe drinking water act (SDWA) every single day in 2002. However, most DC residents when asked still drink either bottled or filtered water verses tap water. Unfortunately, the perception of DC drinking water quality became real before the Institute had an opportunity to validate WASA report through research.

In an effort to assist in ascertaining and maintaining high drinking water quality in the District, WRRI had a meeting with the Director of Water Services at WASA to determine their research needs and how the Institute could partner or collaborate with WASA to assist in providing solutions to their problems. Critical areas identified for research were:

1. Determining sources of heavy metals, especially lead, in drinking water 2. Evaluating biofilm as a process of mitigating heavy metals 3. Impact of chloramines vs. chlorine as disinfectants on biofilm 4. Determining new mechanisms or indicators for identifying and eliminating dead-ends 5. Determining or evaluating diagnostic methods of leaks leading to water main breaks

Hence, our request for research proposals was focused on solving these problems. A commitment letter for $300,000 non-federal in-kind contributions was also provided by WASA to fulfill the Institutes matching requirements. Unfortunately, only three of the five proposals received were focused on lead contamination. Our 2005 fiscal year research focus will continue in this direction.

The issue of high lead levels in DC drinking water is not new. Past WRRI research publications indicate that two projects related to lead in drinking water, by Dr. Ocran at Howard University, were funded and completed. Lead Profiles in the District of Columbia: A Background Report and Lead in Residential Drinking Water: Risk Assessment were published in May 1993 and March 1996 respectively. Apparently, concerns and recommendations reported were tabled by DC Agencies and the problem reappeared. As a solution, WASA provided filters to affected residents and a proposal is in place to have all lead pipes replaced.

The Anacostia Watershed still suffers from severe problems of non-point source pollution (NPS) associated with urban run-off, combined sewer overflows, and sediments made toxic by past dumping and industrial activities. The destruction of wetlands and marshes has resulted in the loss of the watershed buffering or filtration capacity. This continued degradation of a once beautiful river has incited the involvement of several concerned stakeholders to form clean-up and monitoring groups such as the Anacostia Watershed Toxic Alliance (AWTA), the Anacostia Watershed Society (AWS), and the Anacostia Watershed Restoration Committee (AWRC). These groups continue to pool knowledge, expertise, and resources to make the river swimmable and fishable once more.

The DC Water Resources Research Institute continues to provide the District with inter-disciplinary research support to both identify and contribute to the solution of DC water resources problems. Two proposals for external funding were submitted, but remain to be funded. The proposal Monitoring DC Ground Water for Pesticides, Nutrients, and Heavy Metals was presented to the District of Columbia Department of Health/Division of Toxic and Hazardous Substance. Another proposal entitled Soil Erosion Assessment of District of Columbia Park Facilities: Phase II. Analysis of Soil Properties was also submitted to the DC Natural Resources Conservation Services.

The results of the five completed projects are included in this report while the other two projects had approval for no cost extension. One progress reports was provided while the other will begin and end their field study during the summer of 2004. Dr. Harriette Phelps of UDC continued to bio-monitor the Anacostia Watershed using Corbicula. She and five undergraduate students focused on upstream sites as possible sources of the chlordane and PCBs responsible for the fishing advisory. They identified specific tributaries as contributors of pollutants important for the Anacostia fishing advisory, and also located tributary sources of pollutants associated with toxic river sediment. They also recommend that these findings be used as guidelines for more intensive monitoring leading to remediation action for the watershed sources of Anacostia River contamination.

Dr. Reza Modarres and two graduate students at George Washington University investigated statistical properties of environmental data. They assessed accuracy of some commonly used estimators of upper quantiles of a right skewed distribution of data under both parameter and model uncertainties. They found that the consequences of assuming log-normality when the true distribution is log-logistic or log-double exponential in moderate sample size are not severe and for large sample size, selection estimator performs fairly well. The tail-exponential method is a good alternative for small sample size.

Dr. May of Catholic University and Dr. Eng of the University of the District of Columbia collaborated and researched speciation of triorganotins compounds clays and sand in sediments of the Anacostia River using the Mossbauer Spectrometer. Along with four graduate students, they also determined the effect of bacteria (E. Coli) interaction with the triorganotins species.

The progress report of Dr. Allen indicates that the field design and plots with collard and butterbeans at the UDC Agricultural Experiment farm have been established. He is studying the effect of pelletized poultry manure on vegetable and vadose zone water quality. The lysimeters have been ordered and will be installed during the 2004 summer. Sampling will begin after installation of lysimeters is complete.

The seed grant program allows faculty members access to new technologies and equipment that develop their expertise in water resource management. Specifically, over twenty undergraduate and graduate students as well as DC Public School Teachers benefited from the program. Through these research projects, students interact with employers at federal and local agencies essential for future job opportunities. The Institute and researchers continue to accumulate valuable experiences in water resource management as related to water quality and quantity in the District of Columbia.

Assessment of Soil Erosion at Hillcrest Park Facility and Its Potential Effects on the Quality of DC Water Resources

Basic Information

Title:	Assessment of Soil Erosion at Hillcrest Park Facility and Its Potential Effects on the Quality of DC Water Resources
Project Number:	2003DC32B
Start Date:	3/1/2003
End Date:	2/28/2004
Funding Source:	104B
Congressional District:	District of Columbia
Research Category:	Not Applicable
Focus Category:	Sediments, Solute Transport, Water Quality
Descriptors:	
Principal Investigators:	Inder J. Bhambri, Philip L. Brach, Ahmet Zeytinci

Publication

1. **Project Number:**

2. **Title:** Assessment of Soil Erosion at Hillcrest Park Facility and Its Potential Effect on the Quality of DC Water Resources

3. **Focus Categories:** SED, WQL, REC

4. **Keywords:** Sediments Transport, Water Quality Erosion, Assessment, Suspended Solids

5. **Duration:** Twelve Months

6. **FY 2003 Federal Fund:** $11,136

7. **FY 2003 Non-Federal Fund:** $22,276

8. **Principal Investigators:**
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9. **Congressional District:** District of Columbia

10. **Problem and research objectives:**

Sediments transported from soil erosion contribute significantly to the total suspended solids (TSS) pollution load of DC water resources. According to the Anacostia River Total Maximum Daily Loads (TMDL) for TSS report by DC Department of Health/Bureau of Environmental Quality, there are excessive concentrations of TSS in DC water resources. Potential pollution sources identified are Combined Sewer Overflows, storm sewer flow, and storm water runoff or soil erosion. Recent observations indicate that many of DC Park/Recreation facilities have soil erosion problems, potentially contributing to increase TSS. This is especially so for the Hillcrest Recreation Facility located on 3100 Denver St. Washington DC. It has a stream in close proximity that receives eroded material. In an effort to reduce TSS load to DC water resources, a detailed assessment study of soil erosion at the Hillcrest Recreation Facility will be conducted.

This assessment will include sources and forms of soil erosion, annual soil loss from site, distance to water resources, soil transport mechanisms, and effects of total suspended solids on nearby water resources. A cost analysis with recommendations for corrective actions and site maintenance will be provided. This assessment can be used as a model for future assessments of DC Park facilities and similar recommendations implemented as corrective and/or maintenance actions.

11. Methods, Procedures, and Facilities:

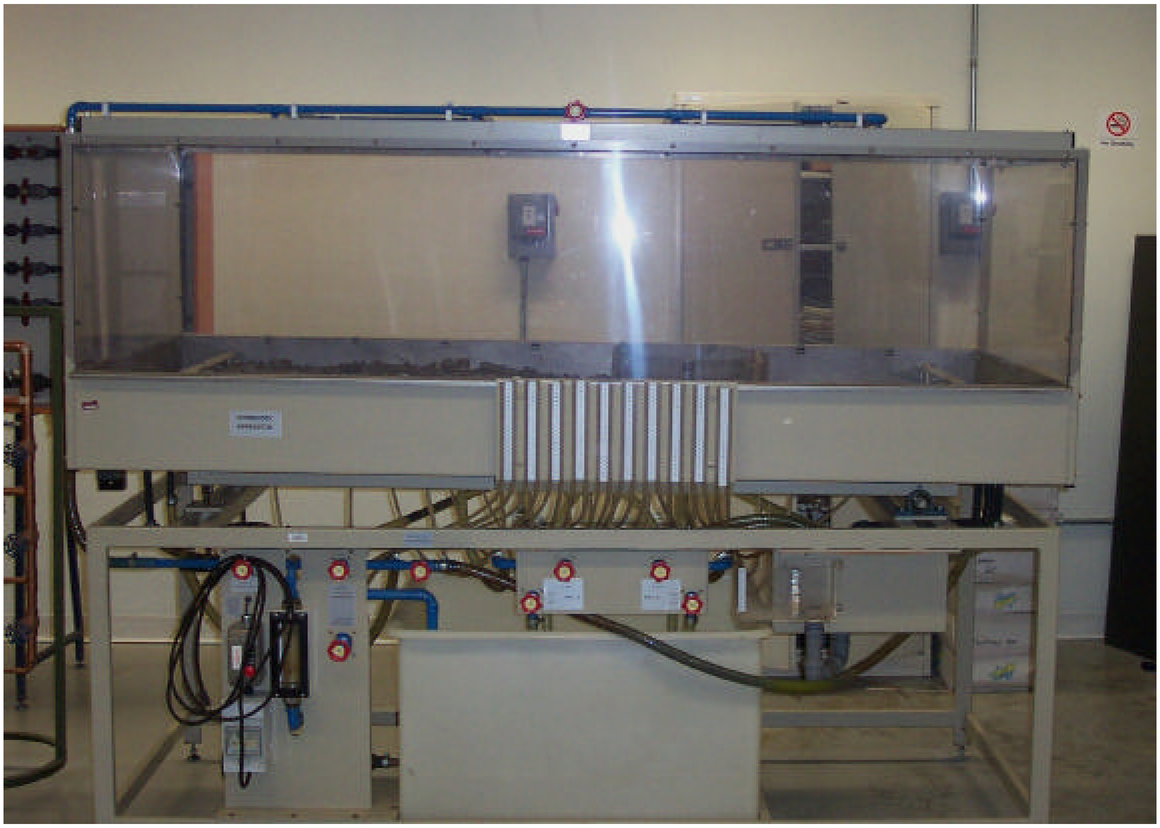
In an initial visit to the park preliminary information regarding the topography, soil erosion problems, soil types and any existing corrective action in place will be documented. Thereafter the facility will be mapped using GPS technology. Sites with conditions that have the potential for soil erosion will be identified and characteristics documented by site inspection. Sod and /or soil samples will be collected from the site for evaluation in the laboratory. Seepage and erosion characteristics will be assessed using hydrology and soils test equipment.

Based on the field and laboratory studies the following outcomes will be reported:

1. Identification of sites with existing soil erosion problems,
2. Identification of sites with significant potential of soil erosion,
3. An estimation of annual soil loss from the park,
4. Preliminary engineering designs and cost estimates of potential corrective measures to minimize soil erosion,
5. Propose design considerations for the prevention of future soil erosion,
6. Preliminary engineering designs and cost analysis of containment measures for sites with existing significant soil erosion.

The University of the District of Columbia maintains an excellent state of the art soils laboratory which is equipped to perform virtually all test needed to evaluate erosion characteristics of soil. Additionally, a hydrological test apparatus [see attached photo] will be used to study soil seepage, effect of rainfall on soil with and without sod, and flow of water through soil samples collected at the site.

It is intended that this study will serve as a model to establish a “study procedure and process” that may be applied to other park facilities with similar problems.



Sources of Bioavailable Toxic Pollutants in the Anacostia Watershed (Part III)

Basic Information

Title:	Sources of Bioavailable Toxic Pollutants in the Anacostia Watershed (Part III)
Project Number:	2003DC34B
Start Date:	3/1/2003
End Date:	2/28/2004
Funding Source:	104B
Congressional District:	District of Columbia
Research Category:	Not Applicable
Focus Category:	Toxic Substances, Water Quality, None
Descriptors:	
Principal Investigators:	Harriette Phelps

Publication

Sources of Bioavailable Toxic Pollutants in the Anacostia Watershed (Part 111)

Final Report to the DC Water Resources Research Center Dr. Harriette L. Phelps June 8, 2004

ABSTRACT

This report summarizes results of the first three phases of this study on finding watershed pollutant sources to DC's Anacostia River freshwater estuary. EPA Priority Pollutants (PAHs, PCBs, Aroclors and Pesticides) and seven metalsCd, Cu, Cr, Fe, Pb, Zn) were biomonitored in the Anacostia River estuary and its five major tributaries using Asiatic clams *(Corbicula fluminea)* translocated from the nearby Potomac River estuary. Biomonitored sites included four Anacostia estuary sites and 16 tributary sites: two in DC and 14 in Maryland. Total metals (As, Cd, Cu, Cr, Fe, Pb, Zn) in clam tissue exceeded reference (Potomac) concentration at one tributary site. Total PAHs (18) in translocated clam tissues significantly exceeded reference Potomac clams at all four Anacostia River sites and 14/18 tributary sites. Total PCBs (26 congenors) and Aroclors (4) in translocated clam tissue significantly exceeded reference at all Anacostia estuary sites, the lower Northeast Branch and two sites in one tributary, Lower Beaverdam Creek. Total pesticides (20) in translocated clam tissue significantly exceeded reference in three tributaries and including over 80% chlordane in Watts Branch and Northeast Branch tributaries. All but one MD tributary site with tPAH, tPCB and tpesticide levels significantly exceeding reference were in the Northeast Branch (Prince George's County) which has a number of industrial parks. Translocated Asiatic clams reached maximum tissue contaminant load in two weeks.

INTRODUCTION

The 10 km freshwater contaminated Anacostia River estuary is one of three Areas of Concern in the Chesapeake Bay and listed among America's 10 worst rivers. In contrast to the confluent healthy Potomac River estuary the Anacostia resident fish (catfish) have a high tumor incidence (Pinkney et al 2000, Washington Post 2004b)) and there are few surviving benthic animals, including *Corbicula* clams (Phelps 1985). In spite of posted fish consumption warnings due to chlordane and PCBs (Velinsky and Cumming 1994) there is fishing in the Anacostia, especially by low-income residents. Planned development of the DC waterfront is increasing interest in the Anacostia (Washington Post 2003). A major suspected source of contaminants has been the contaminated sediments of the Anacostia estuary (Phelps 1983, AWTA 2000). There has been little study of possible tributary sources which may be even more important (Warner et al. 1997, Washington Post 2004a).

Translocation of molluscs for bioaccumulation of water pollutants is considered a significant method for detecting bioavailable low-level variable water contamination (DeKock and Kramer 1994). The *Corbicula* clam is recognized for freshwater biomonitoring because it is nonendangered and can bioconcentrate and store contaminants without chemical alteration or toxic effects (Colombo et al. 1995, Crawford and Luoma 1993, Dougherty and Cherry 1994).

Corbicula clams from the large population in the nearby Potomac river were translocated for biomonitoring to sites in the Anacostia River estuary and watershed. The first research objective of the present study was to identify upstream tributaries with high levels of bioavailable PCBs and chlordane within the Northeast Branch (MD) and Lower Beaverdam Creek (MD) tributaries, based on previous studies (Phelps 2002, Phelps 2003). The second objective was to find minimum translocation time for maximum contaminant bioaccumulation.

METHODOLOGY

For the translocation studies, 20 - 35 mm Asiatic clams (Corbicula *fluminea)* were collected by sieving the near-shore sandy sediment at Fort Foote (MD) which is on the Potomac estuary 5 km below the mouth of the Anacostia River estuary. The Fort Foote site (FF) is the reference site for clam contaminant levels because of the healthy condition of the freshwater estuarine Potomac there now the second ranking large-mouth bass fishing area in the U.S. and considered a Chesapeake Bay restoration success (Phelps 1994; Orth et al. 1996).

Clams were collected at AM low tide and held cool and dry until placed in shellfish bags or boxes at Anacostia locations within 8 hours. TidbiT continuous temperature monitors were attached to bags at two locations. When clams were recovered they were depurated 24 hours with three changes of spring water, then frozen and thawed to remove tissues. All clams at a site (20-40) were combined for a single tissue sample of over the 60 gm needed for complete analysis. Refrozen tissues were hand-carried to Severn-Trent Laboratories (STL) of Sparks, MD, which forwarded them to Severn-Trent Laboratories of Burlington, VT, for analysis. Tissue samples were analyzed for EPA Priority Pollutants: 20 pesticides, 28 PCB congenors, 18 PAHs, and seven metals (As, Cu, Cd, Cr, Fe, Pb and Zn). Electronic results were available within five weeks. The STL analytical variability was SD = 0.175 (mean)- 1.12 (n = 9) (Phelps 2002). Statistical comparison was by t test and the 95% confidence limits of the mean were calculated as 2.05 SD = 0.36 (mean), used for graphical error bars.
Asiatic clams were collected from the Potomac on 5/24/03 for the long-term bioaccumulation study and placed in the upper end of the Anacostia estuary at Bladensburg Marina (BM) with samples taken at 2,4, 8 and 11 weeks.

Anacostia watershed biomonitoring sites were selected in 2003 to find the tributary origins of high levels of pesticides (chlordane) and PCBs based on previous studies (Phelps 2002, Phelps 2003). For the high pesticides in the Northeast Branch (particularly chlordane) clams were placed at the 2001 Northeast Branch site (NEB03) and just upstream of NEB03 at Riverdale Park (RDP) on 5/24/03. On 10/5/03 clams were placed at a third site in the Northeast Branch tributary slightly further upstream at the entrance of the second order stream Brier Ditch Creek (BDT). For PCBs in Lower Beaverdam Creek, clams were placed on 10/5/03 at the biomonitoring site upstream of LBC on Beaver Road (BVR). Since the first translocation (5/24/03) established that two weeks were sufficient for maximum contaminant accumulation, the second translocation set (BDT, BVR, 10/5/03) was for two weeks. The Fort Foote clams collected for translocation on 10/5/03 were brooding.

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RESULTS

Clams were translocated to six Anacostia sites in 2003 for biomonitoring.

Table l. 2003 biomonitoring site locations (GPS) and dates of clam translocation and collection.

Site	Date Transl.	Date Coll.	GPS
Potomac River estuary			
Fort Foote MD (FF03)		5/24/03	N38o46.460',W077o01.770'
Fort Foote MD (FF03b)		10/5/03	« «
Anacostia River estuary			
Bladensburg Marina (BM2)	5/24/03	6/9/03	N38o57.621',W078o55.583'
Bladensburg Marina (BM4)	5/24/03	6/21/03	« «
Bladensburg Marina (BM8)	5/24/03	7/23/03	« «
Bladensburg Marina (BMI 1)	5/24/03	8/13/03	« «
Anacostia Tributaries			
Northeast Branch (NEB03)	5/24/03	7/28/03	N38o57.621',W078o55.583'
Riverdale Park (RDP)	5/24/03	7/28/03	N38o57.621',W078o56.312'
Brier Ditch Creek (BDT)	10/5/03	10/20/03	N38o58.250',W076o54.909'
Beaver Road (BVR)	10/5/03	10/20/03	N38o55.157',W076o54.362

For the long-term bioaccumulation study, clams collected from Fort Foote (Potomac) on 5/24/03 were placed in the upper Anacostia estuary at the Bladensburg Marina dock (MD) and collected at 2, 4, 8 and 11 weeks for analysis (Table 2, Fig. 1).

Table 2. Long-term clam contaminant bioaccumulation study, Bladensburg Marina.

Date collected	Week (sample)	Temp (deg.C)	S/T	Mortality (percent)	tMetal mg/kg	tPCBs ug/kg	tArocl ug/kg	tPAH lmg/kg	tPest. ug/kg	tChlordane ug/kg
5/24/03	0 (FF03)	15.6		0	88.2	97	128	441	90	29
6/9/03	2(BM2)	19.7	3.96		93.9	137	203	478	148	73
6/21/03	4(BM4)	18.8	3.66		85.9	97	180	460	137	65
7/23/03	8(BM8)	25.1	3.38	13%	31.9	158	255	403	107	68
8/13/03	11(BMl1)	25.5	3.31	29%	66	137	251	336	112	90

Key: S/T= total shell weight/total tissue weight

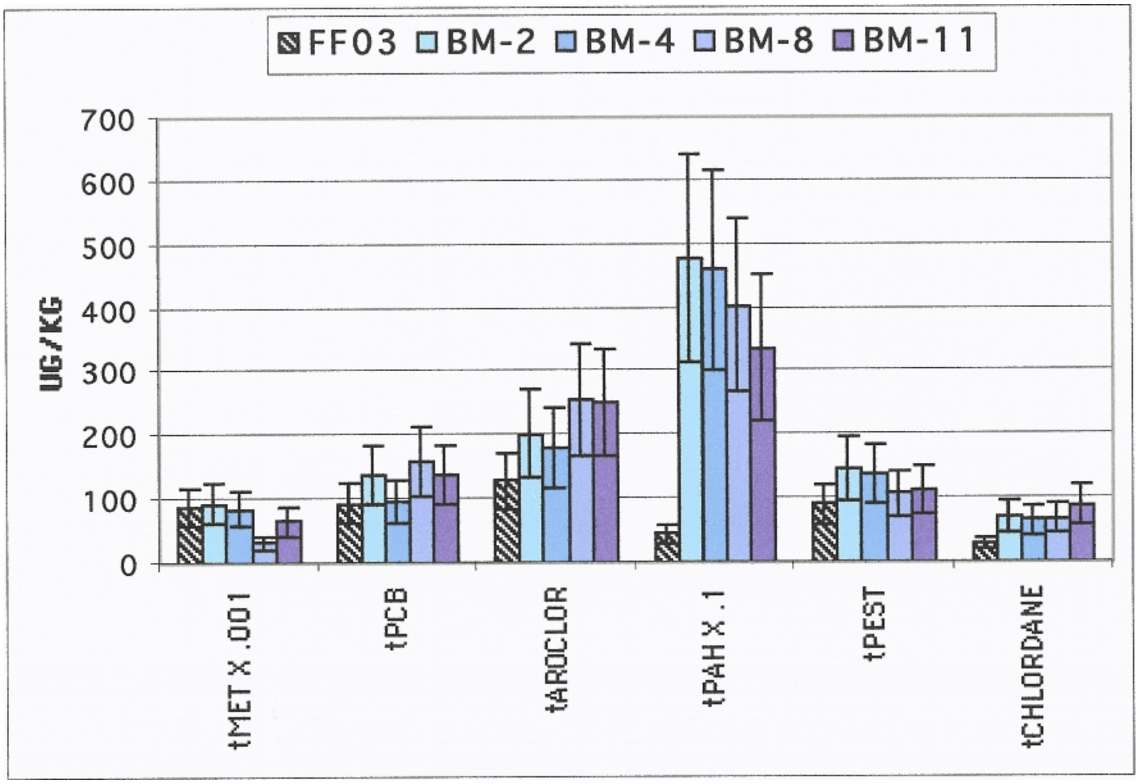


Figure l. Clam tissue EPA Priority Pollutants at Bladensburg Marina +l- 2 SD.

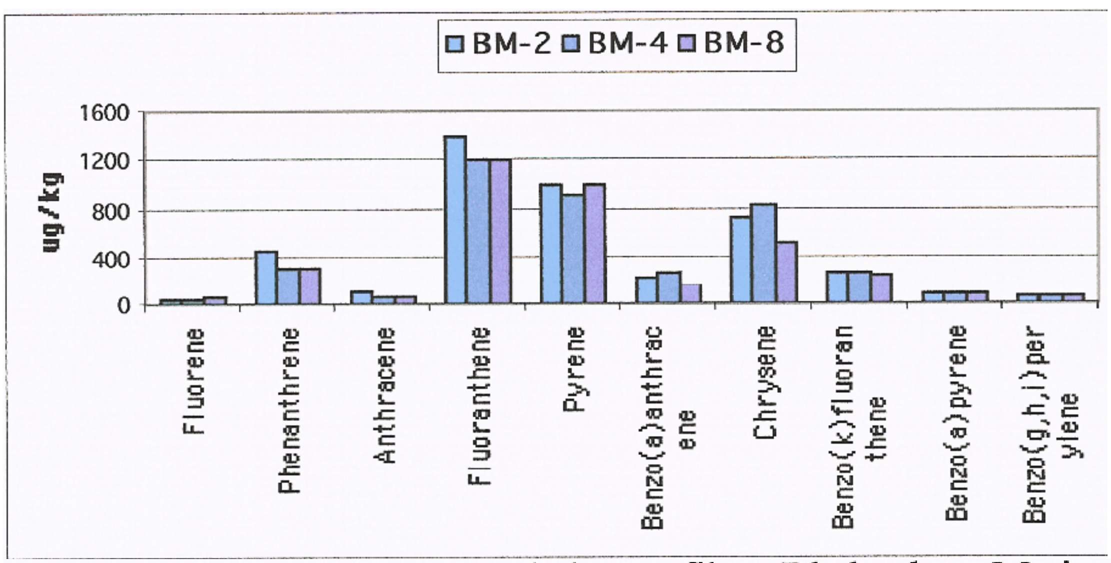


Figure 2. Clam PAH bioaccumulation profile at Bladensburg Marina.

Pesticides in clams translocated to sites in the Northeast Branch tributary (NEB03, RDP and BDT) did not show the high levels of the earlier NEBO l site study (Phelps 2002) (Table 4). However there was a statistically significant increase in chlordane in clams at the Northeast Branch site (NEB03) and just upstream at Riverdale Park (RVP). Chlordane increase was not found in the secondary subtributary of Brier Ditch Creek (BDT) (Table 3, Table 4, Figure 3, Figure 5). Increased total PCBs and pesticides were found in the Lower Beaverdam Creek upstream site of Beaver Road (BVR) where the primary pesticide was DDT (Table 3, Table 4, Figure 3, Figure 6).

Table 3. Clam tissue pollutant totals at Northeast Branch tributary sites (NEB03, RDP, BDT), Lower Beaverdam Creek tributary site (BVR) and the control site at Fort Foote, MD.

Site	tMetal	tPC13	tAroclors	tPAH	tPest	CChoordan
Fort Foote (FF03b)	53	69	256	279	60	23
Northeast Branch (NEB03)	*	118	214	*	72	40
Riverdale Park (RDP)	*	*	203	*	72	39
Brier Ditch Creek (BDT)	49	70	310	419	93	29
Beaver Road (BVR)	61	230	900	601	109	52

Key: * not measured

Figure 4. Anacostia watershed sites where clam tissue total PAH bioaccumulation statistically exceeded reference (Table 4, p<.05).

Anacostia watershed sites with clam tPAHs statistically exceeding the Potomac control value

Table 4 summarizes clam tissue contaminant totals at all Anacostia watershed translocation sites for Phases I, II and III. Reference clam tissue contaminant totals for statistical purpose were taken as the average of all the Fort Foote contaminant totals, except where noted.

Table 4. Anacostia site summary of clam survival and tissue contaminant totals (ug/Kg dry weight)

Site, M/D/Y	Survival	tMetals	tPAHs	tPCBs	tPesticides percent x.001
Potomac River Estuary at Fort Foote MD (Control and Collection Site)					
Fort Foote 5/16/99 (MD) (FF)		49	421	46	25
Fort Foote 4/5/01		94	384	173	100
Fort Foote 7/15/01		74	457	131	70
Fort Foote 9/29/01		71	354	97	53
Fort Foote 5/3/02		77	391	79	48
Fort Foote 7/2/02		73	598	73	30
Fort Foote 5/24/03		88	441	94	90
Fort Foote 10/5/03		53	279	69	60
Average		72	415	102	64
Anacostia Estuary Sites					
Bladensburg Marina (MD) (BM)	98	79	2350*	239*	94
Navy Yard (DC) (NY)	98	75	1366*	186*	102
O Street Outfall (DC) (OS)	51	47	1262*	175*	124
Washington Gas (DC) (WG)	97	90	1502*	212*	128
Anacostia Watershed Tributaries, first order streams					
Hickey Run 0 1 (DC) (HRHO1) 97		50	785*	97	42
Hickey Run 02 (DC) (HRH02) 97		90	1888*	59	63
Lower Beaverdarn Creek 01(MD) (LBCO1) 95		189*	855*	666*	295*
Lower Beaverdam Creek 02 (MD) (LBC02) 95		166*	1345*	326*	68
NorthEast Branch 0 1 (MD) (NEBO1) 100		73	1442*	187*	740*
NorthEast Branch 03 (MD) (NEB03) 42		--	--	118	72
NorthWest Branch 01(MD) (NWBO1) 100		66	637	83	77
NorthWest Branch 02 (MD) (NWBO1) 100		100	933*	64	58
Watts Branch A 02 (DC) (WATA) 66		62	4612*	130	103*
Watts Branch B 02 (DC) (WATB) 100		94	1193*	115	106*
Anacostia Watershed Subtributaries, second order streams					
Beaverdarn Creek (MD) (BDC) 79		90	431	59	42
Beaver Road (MD) (BVR)		61	601	230*	109*
Brier Ditch Creek (Mm) (BDT)		49	419	49	93
Indian Creek High (MD) (ICH) 99		96	2581 *	126	63
Indian Creek Low (MD) (ICL) 100		66	2789*	86	97
Lower Beaverdam Creek High (MD) (LBH) 95		108	2183*	88	72
Lower Paint Branch (MD) (LPB) 95		65	905*	131	76
Paint Branch Longterm 1 (MD) (PBL) 100		73	1804*	128	50
Paint Branch Longterm 2 (MD) 100		73	882*	107	43
Riverdale Park (MD) (RDP)		--	--	72	39
Watts Branch High (MD) (WATH) 97		--	1126*	--	98
Watts Branch Low (MD) (WATL) 34		--	1576*	--	225*

<u>Selected Fort Foote Reference contaminant levels</u>

* >statistically exceeding Reference average ($p < .05$)

Figure 4. Anacostia watershed sites where clam tissue total PAH bioaccumulation statistically exceeded reference (Table 4, p<.05).

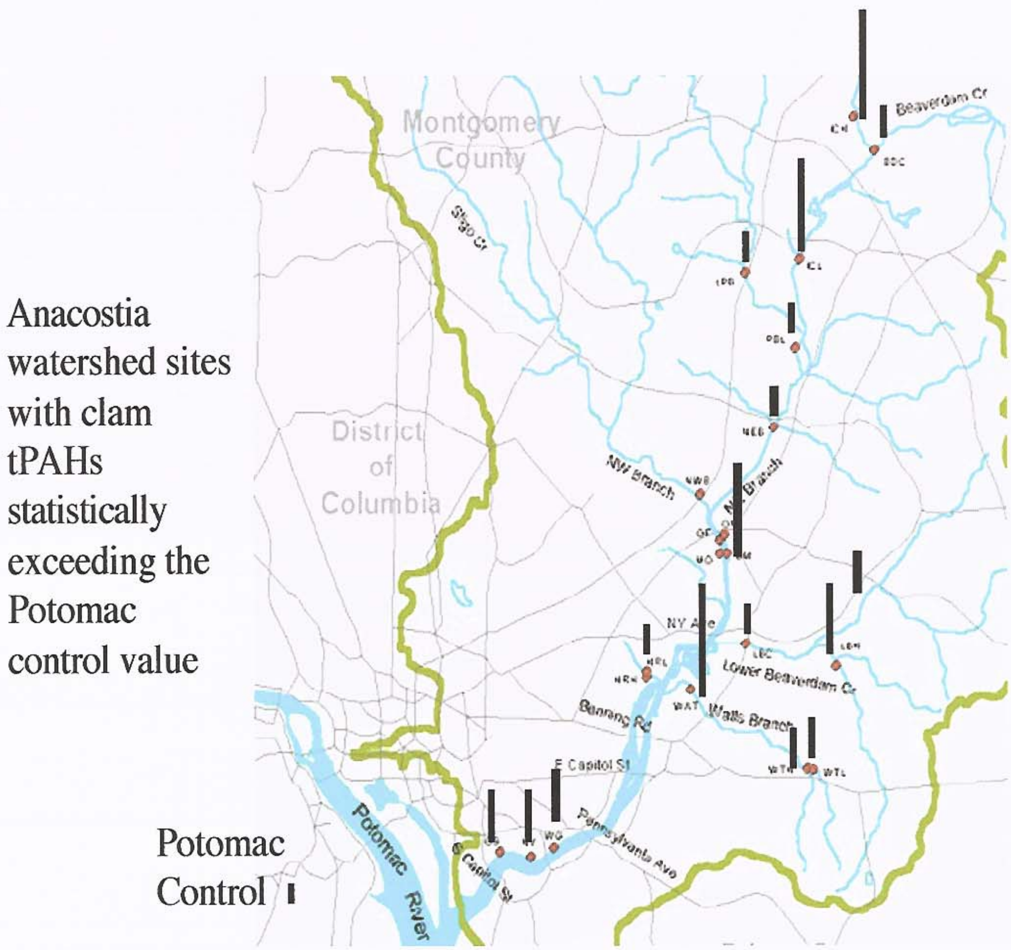


Figure 5. Anacostia watershed sites where clam tissue total pesticide bioaccumulation statistically exceeded reference (Table 4, p<.05).

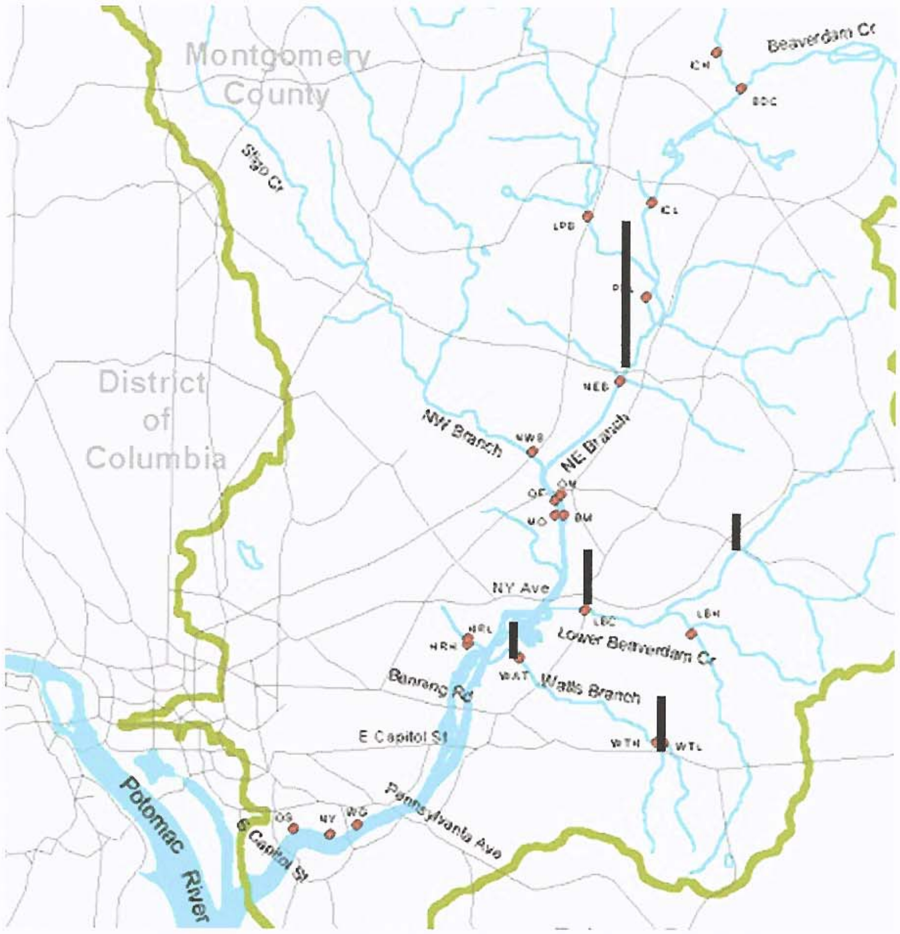
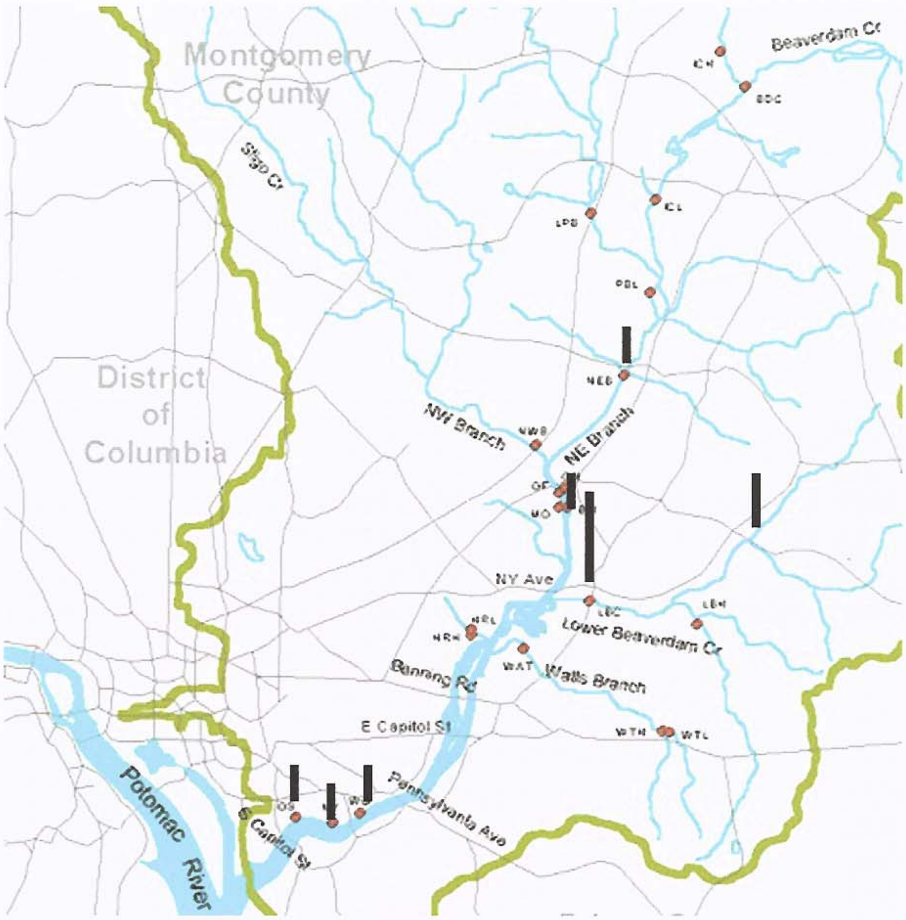


Figure 6. Anacostia watershed sites where clam tissue total PCB bioaccumulation statistically exceeded reference (Table 4, p<.05).



DISCUSSION AND CONCLUSIONS

Asiatic clams placed in the upper Anacostia River estuary at Bladensburg Marina showed no statistical difference in total tissue concentrations of PCBs, Aroclors, PAHs, pesticides and metals from 2 to 11 weeks. Rapid bioaccumulation might be expected from the *Corbicula fluminea* clearance rate which is the highest of any clam (Laritsen 1986), and similar to the oyster which shows a PAH accumulation plateau in 2 to 4 weeks (Huggett e.a. 1985). Both mollusc species produce pseudofeces and can filter continuously. Compared to reference (Potomac) clam contaminants, the Bladensburg Marina clams had no significant increase in total metals and only a slight increase in total PCBs, Aroclors or pesticides over the 11 weeks deployment. The clams did have significant increases in chlordane and total PAHs, which were primarily 4-ring PAH pyrogenic combustion byproducts. Over the 11 weeks deployment the clams had decreasing shell/tissue ratio and increasing mortality which suggested both growth and stress. It was decided to use a two week bioaccumulation time for all future studies.

Total metal levels in translocated clams did not significantly exceed levels in reference Potomac clams at all but one site. At the lowest Lower Beaverdam Creek site (LBC) just downstream from a recycling center on Addison Road iron (Fe) levels exceeded control.
Clams placed at the lowest Northwest Branch site (NWB) just above head of tide in 2001 had no contaminant bioaccumulation totals exceeding Potomac reference values, and in 2002 only had low tPAH concentration exceeding reference. The Northwest Branch is in Montgomery County, contributes about 32% of Anacostia tributary input, and is considered relatively uncontaminated (Warner et al 1997).
The present study focussed on upstream sites as possible sources of the chlordane and PCBs responsible for the fishing advisory. High chlordane levels in clams had been found in earlier studies at the lowest Northeast Branch tributary site (NEB), and at lower (WAT) and upper (WBL) Watts Branch tributary sites (Phelps 2002). Elevated chlordane at the Bladensburg Marina estuary site (BM) downstream from the confluence of the Northeast and Northwest branches is reported in the present study. Upstream Northeast Branch subtributary studies have not found chlordane bioaccumulation in clams placed at Paint Branch (PBL) or Indian Creek (ICL) sites (Phelps 2003), or Riverdale Park (RVP) or Brier Ditch Creek (BDT) sites (present study Table 3). The Northeast Branch in Prince George's County contributes about 45% of Anacostia tributary input (Warner et al 1997). Finding the source of Northeast Branch chlordane should be an objective of more study.

Previous Anacostia watershed translocation studies have found high clam tissue PPCBs exceeding FDA food action levels at the lower end of Lower Beaverdam Creek site (LBC). Significantly increased pesticide (DDT) and metal (Fe) levels in clams were also found at LBC. Lower Beaverdam Creek contributes about 12% of Anacostia tributary flow and has the greatest percent industrial area of the Anacostia tributaries (Warner et al 1997). In the present study, clams placed in Lower Beaverdam Creek at the upstream Beaver Road site (BVR) showed significant accumulation of low-molecular-weight PCBs. BVR is upstream from several industries on Addison Road but downstream from Ardwick Industrial Park. Additional Lower Beaverdam Creek upstream sites should be explored for PCBs.

Bioavailable total PAHs (18) in translocated clams significantly exceeded reference Potomac clam levels at all four Anacostia River estuary sites, high and low, and 14/18 tributary sites. PAHs are known to be carcinogenic, transported by sediments and are probably the major cause of fish tumors and the reduced benthic fauna of the Anacostia River estuary. PAHs have a number of pyrogenic and petrogenic carbon origins. High pyrogenic PAHs in translocated clams were found at sites downstream from some industrial parks of Prince George's County, MD such as the Indian Creek High site (ICH) downstream from Beltsville Industrial Park and the Beaver Road site (BVR) downstream from Ardwick Industrial Park. PAHs were not an object of the present study but should be examined further.

Biomonitoring by translocated Asiatic clams in the Anacostia River watershed has identified specific tributaries as contributors of pollutants important for the Anacostia fishing advisory, and also located tributary sources of pollutants associated with toxic River sediment. These findings could be used as guidelines for more intensive monitoring leading to remediation actions for watershed sources of Anacostia River contamination.

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PRESENTATIONS:

9/15/03 "Finding sources of PAHs, PCBs and pesticides to the Anacostia estuary, DC, using Asiatic Clam (Corbicula *fluminea)* Translocation." Poster Presentation: Estuarine Research Federation meeting, Seattle, WA. Abstract
3/25/04 "Biomonitoring the Anacostia Watershed for Pollutants" Olunbunmi Adekanye, Clemantine Assi, Moina Cook, Nicole McCrea, Danell Sorinmade and Harriette Phelps. Poster Presentation: Atlantic Estuarine Research Society, Norfolk, VA. Abstract

4/22/04 "Biomonitoring the Anacostia Watershed for Pollutants" Olunbunmi Adekanye, Clemantine Assi, Moina Cook, Nicole McCrea, Danell Sorinmade and Harriette Phelps. Poster Presentation: Chesapeake and Potomac Regional Chapter (CPRC) of the Society for Toxicology and Chemistry, Salisbury, MD.

Pesticides in clams translocated to sites in the Northeast Branch tributary (NEB03, RDP and BDT) did not show the high levels of the earlier NEB01 site study (Phelps 2002) (Table 4). However there was a statistically significant increase in chlordane in clams at the Northeast Branch site (NEB03) and just upstream at Riverdale Park (RVP). Chlordane increase was not found in the secondary subtributary of Brier Ditch Creek (BDT) (Table 3, Table 4, Figure 3, Figure 5). Increased total PCBs and pesticides were found in the Lower Beaverdam Creek upstream site of Beaver Road (BVR) where the primary pesticide was DDT (Table 3, Table 4, Figure 3, Figure 6).

Table 3. Clam tissue pollutant totals at Northeast Branch tributary sites (NEB03, RDP, BDT), Lower Beaverdam Creek tributary site (BVR) and the control site at Fort Foote, MD.

Site	tMetal	tPCBs	tAroclors	tPAH	tPest	tChlordane
Fort Foote (FF03b)	53	69	256	279	60	23
Northeast Branch (NEB03)	*	118	214	*	72	40
Riverdale Park (RDP)	*	*	203	*	72	39
Brier Ditch Creek (BDT)	49	70	310	419	93	29
Beaver Road (BVR)	61	230	900	601	109	52

Key: * not measured

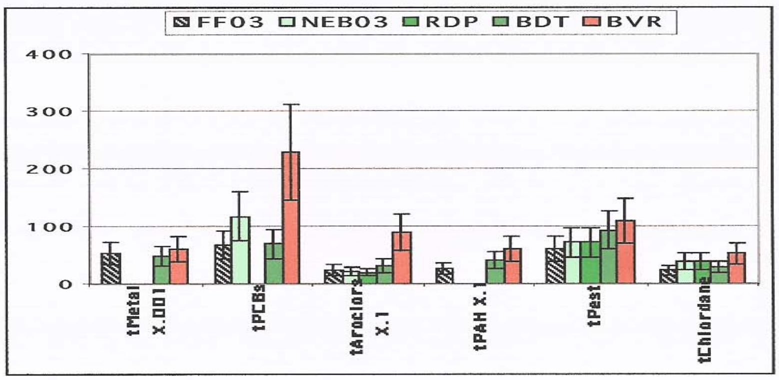

Figure 3. Clam tissue contaminant totals at 2003 Anacostia watershed sites, +/- 2 SD.
Key: FF03b (Fort Foote Reference site), NEB03 (Northeast Branch), RDP (Riverdale Park), BDT (Brier Ditch Creek), BVR (Beaver Road).

Effect of Pelletized Poultry Manure and Vegetable Production on Vadose Zone Water Quality

Basic Information

Title:	Effect of Pelletized Poultry Manure and Vegetable Production on Vadose Zone Water Quality
Project Number:	2003DC35B
Start Date:	3/1/2003
End Date:	2/28/2004
Funding Source:	104B
Congressional District:	District of Columbia
Research Category:	Not Applicable
Focus Category:	Water Quality, Solute Transport, Nutrients
Descriptors:	
Principal Investigators:	James R. Allen, James R. Allen

Publication

Effect of Pelletized Poultry manure on Vegetable and Vadose Zone Water Quality

DC Water Resources Research Institute Progress Report

Principal Investigator: **Dr. James R. Allen**
Agricultural Experiment Station
University of the District of Columbia

Objectives

1. To determine the extent to which pelletized poultry manure affect vadose zone water quality when used as a soil amendment in growing vegetables.

2. To determine the feasibility of using pelletized poultry manure as a substitute for commercial fertilizer in the growing of vegetables in urban areas.

3. To determine the effectiveness of rye in nutrient uptake following vegetable production and preventing leaching.

Progress toward achieving objectives

Implementation of the project is still in the preliminary stages. The experimental site has been prepared and ready for planting. Treatments to be used include for the following:

1. A high fertility rate of 1800 lbs of pelletized chicken manure + 400 lbs of 10-10-10.

2. The same rate of 10-10-10 (400 lbs) but no pelletized chicken manure.

3. Half the rate of pelletized chicken manure used in treatment #1 (900 lbs) + 400 lbs of 10-10-10.

4. The same amount of chicken pelletized manure used in treatment #1 (1800 lbs) but no added fertilizer.

5. Half the rate of pelletized chicken manure used in treatment #1 (900 lbs) but no added fertilizer.

6. Control treatment which will have no added pelletized chicken manure or fertilizer (10-10-10).

The experimental design which is being used is a randomized block with three replications per treatment. Treatments and blocks will be the same. The experimental design has been modified to include three crops. These crops will be collards and butterbeans as summer vegetables and rye as a fall crop. Plot size will be 15 x 10 feet with three rows per plot. Collards will be planted as six weeks old seedlings and butterbeans and rye will be direct seeded. Determination of rye's effectiveness in nutrient uptake to prevent leaching will also be determined.

For measurements of water quality, two lysimeters will be installed in each block, one at 24" and the other at 36". The lysimeters have been ordered and as soon as they arrive treatments will be added and lysimeters installed at the above mentioned depth. Plant, soil, and water samples will be collected and tested for available nitrogen and phosphorus.

Effect of Microorganisms on the Speciation of Tributyltin and Triphenyltin compounds in clays from Sediments Using Mossbauer Spectroscopy

Basic Information

Title:	Effect of Microorganisms on the Speciation of Tributyltin and Triphenyltin compounds in clays from Sediments Using Mossbauer Spectroscopy
Project Number:	2003DC39B
Start Date:	3/1/2003
End Date:	2/28/2004
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Focus Category:	Toxic Substances, Sediments, Water Quality
Descriptors:	
Principal Investigators:	Leopold May, George Eng

Publication

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Speciation of Tributyltin and Triphenyltin Compounds in Clays from Sediments Including the Effect of Microorganisms Using Mõssbauer Spectroscopy

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Introduction

Previously, we had examined the speciation of tributyltin(TBT) and triphenyltin (TPT) compounds directly in sediments from the Chesapeake Bay (1-3) and waterways in the Chesapeake Bay watershed: Anacostia River (4), Baltimore Harbor (5), and Potomac River (4). To determine the nature of the tin compounds directly in the sediments, tin Mössbauer spectroscopy was used. It was found that the speciation of triorganotin compounds varies with the nature of the sediment. It is important to determine which component or components of the sediment are involved in the speciation of the tin compound. The Anacostia and Potomac Rivers are in the Washington Quadrangle of which one-fourth is in the Piedmont Plateau and the remainder in the Coastal plain (6). Clays and sand are important components of these formations. For example, it was reported that kaolin is one of the clays that have been found in the sediment of the Anacostia River (6, p. 27). In 1992, we observed that TPTCl spiked anaerobic and aerobic sediments from the Chesapeake Bay contained microorganisms by streaking agar plates with these sediments. In anaerobic sediments the microorganisms are both facultative and anaerobic, but in aerobic sediments, only facultative microorganisms are found (1). Experiments were performed to determine the speciation of tributyltin and triphenyltin compounds in components of sediments, such as different clays and sand. The effect of microorganisms on the fate of tributyltin and triphenyltin compounds in components of sediments was also examined by including *E. coli* in the mixtures.

X-Ray Diffraction of Sediments

To determine if clays other than kaolin were in the sediments of the Anacostia and Potomac Rivers, the x-ray diffraction patterns of dried sediments from the Anacostia (AR-1) and Potomac Rivers (PR10) were measured using the LabX, XRD-6000 (Shimadzu, Co.). For comparison, the pattern for a sample from Colgate Creek (25 cm below sea level), a tributary of Chesapeake Bay was also measured. The x-ray results are given in Table 1. The samples contained as a major constituent, α-quartz (sand), and clays plus other constituents such as goethite. The clays included chlorite, illite, kaolinite, montmorillonite, and nontronite or smectite (7).

pH of Clay-Water Mixtures

To assist in the interpretation of the speciation experiments with spiked clays, the pH of the various clays in distilled water were measured using a glass pH electrode and the Vernier LabPro. The clay and distilled water were mixed thoroughly and the clay allowed to separate from the solution before the pH was read. The results are given in Table 2. The pH of the water suspensions of clay and sand varies in some cases from the pH of the distilled water alone (pH = 5.7) although with most of the clays, the suspensions have about the same pH as the distilled water. With kaolinite, the pH is much lower at 2.7 and higher in sand at 7.0. The pH also varies with the tin compound added with the highest pH found with TBTO and the lowest with TPTCl. Thus, some component or components of the clay and the tin compound contribute to the acidity of the suspensions.

Spiking of Tin Compounds in Clays and Sand using Mössbauer Spectroscopy

The following procedure was used in all experiments: Mixtures of 5 g of the clay sample and 5 mL or 100 mL of solution containing the organotin compound amounting to 3.3 % of the weight of the clay were shaken mechanically in closed test tubes or Erlenmeyer flasks for two weeks at room temperature. To determine the effect of bacteria on the speciation, E.coli and broth was added. After remaining at room temperature for two additional weeks, the clay was removed by gravity filtration and kept frozen until the Mössbauer spectrum is measured. The Mössbauer spectra were measured at 80K on a Mössbauer spectrometer model MS-900 (Ranger Scientific Co.) in the acceleration mode with moving source geometry. The velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed by a least-square fit to Lorentzian shaped lines.

Mössbauer Spectroscopic Results with Spiked Clays and Sand

The Mõssbauer spectral parameters, quadrupole splitting, Δ, and isomer shift, δ, found with the spiked clays, spiked sand, and spiked sediments from the Anacostia River are given in Tables 3 and 4. In Table 5, the results found with spiked clays mixed in the presence of the microorganism, *E. colil*, are recorded. Duplicate spectra of the clay spiked with a particular TBTCl or TPT compound do not always give reproducible values. The results will be considered based upon those values that are duplicated within experimental error.

The Δs in the spectra of TBTCl in spiked Illite and kaolinite are close to the Δ in the spectrum of the pure compound, but the δ is lower in most spectra. For comparison, the average of the parameters in spiked sediments from the Anacostia River is lower than the parameters of the spectra of the pure TBTCl or in the clays.

The situation is different in the case of the TBTO spiked samples where the Δ in the spectrum of the pure compound is the lower than in any sample. The δs are about the same except for the spectra of the spiked Illite where both parameters are larger than in the other spectra. The TBTO exists as TBT-O-TBT in the solid and dissociates into TBT^+ when dissolved in water. The cation then interacts with the clay and sediments resulting in Mössbauer spectra with parameters different from those in the pure compound. The average Δ in the spectra of the spiked sediments from the Anacostia River is greater than in the pure compound or spiked clay and sand samples. However, the average δ is intermediate between values found in the pure compound, sands and some clays and Illite.

The Δs in the spectra of the kaolinite and sand, spiked with TBTAc are larger than the Δ in the spectrum of the pure TBTAc. The δs for most of the spiked samples and the pure compound are about 1.4 mm/s. The TBTAc in water undergoes the following reactions:

$$TBTAc + H_2O \leftrightarrow TBT(H_2O)^+ + Ac^-$$

$$Ac^- + H_2O \leftrightarrow HAc + OH^-$$

The amount of the TBTAc that will exist as the cation or the molecule will depend upon the pH. As can be seen from Table 2, the pH varies with the clay so the Mössbauer parameters will reflect this.

The Mössbauer parameters are different in the spectra of TPTCl spiked clays and sand. In spiked sand and kaolinite, the Δs are greater than the Δ in the spectrum of the pure compound, but the δs are the same. However, in spiked montmorillonite and nontronite, the parameters are less than the parameters in the pure compound. For illite, the Δs are the same but the δ in spectrum of the spiked sample is less than the pure compound. The average Mössbauer parameters in the spectra of the spiked sediments from the Anacostia River is different from those in the spectra of the spiked clays and sand and the pure compound.

In TPTOH spiked clays and sand, the Δs are lower than in the pure compound whereas the δs are about the same. This is also true for the average of the values in TPTOH spiked sediments from the Anacostia River (5).

With TPTAc spiked clays, the Δs are less than the value in the pure compound. The δs of all spectra were about the same. This suggests that the TPT species are different in the spiked samples from the pure compound. The reactions of the TPTAc are similar to those of the TBTAc so we find differences in the spectra in the different clays and sand.

The variation in the Mössbauer parameters would reflect the variation in the clays and sand whose chemical nature changes differently with the pH. The TBT or TPT structure that interacts with the clay or sand will also vary with the pH. The possible heterogeneity of the clays and sand seems to partly explain the poor reproducibility of some combinations. Additional mixtures are being run to resolve this problem.

Effect of Microorganisms on the Speciation of the Organotin Compounds

The preliminary results of mixing *E. coli* with nontronite and the triorganotin compounds are given in Table 4. There are changes in both Δ and δ which suggests that the microorganism is affecting some change in the structure of the tin compound. These mixtures included the broth used for growing the *E. coli,* and the chemicals included in the broth may have interacted with the tin compound and/or the clay. Additional studies are needed to confirm this.

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Table 1. Prominent Lines in the X-ray Diffraction of Sediments from the Anacostia and Potomac Rivers and Chesapeake Bay, $2\Theta^a$.

Component	Anacostia River	Potomac River	Chesapeake Bay
Quartz	20.9, 26.7, 50.2	20.9, 26.7, 50.2	20.9, 26.7, 50.2
Illite	8.9	61.9	8.9
Kaolinite	45.6		23.1, 45.6
Chlorite	60.0	60.0	60.0
Nontronite		5.8	6.2
Montmorillonite			61.8
Goethite	17.8	17.9	17.8
Calcite	45.5		

[a]Sediment from Chesapeake Bay was sampled 25 cm below sea level at Colgate Creek.

Table 2. pH Measurements of Tributyltin (TBT) and Triphenyltin (TPT) Compounds in Aqueous Suspensions of Clays and Sand.

Compound	pH	Compound	pH
		Illite	
Water	5.7	TBTCl	6.0
TPTCl	6.4	TBTO	7.9
TPTAc	7.3	TBTAc	6.0
		Sand	
Water	7.0	TBTCl	6.0
TPTCl	3.0	TBTO	8.0
TPTOH	.5.8	TBTAc	4.9
TPTAc	4.1		
		Kaolinite	
Water	2.7	TPTCl	2.9
		Nontronite	
Water	5.4	TPTAc	4.8
		Montmorillonite	
Water	5.7		

[a]Water is distilled water.

Table 3. Mössbauer Spectra of Tributyltin (TBT) Compounds in Sediments and Components[a]

Compd	Clay	Δ	δ
TBTCl	Neat	3.43(4)	1.56(1)
	Kaolinite	3.43(3)	1.47(7)
	Kaolinite	2.64(3)	1.29(1)
	Kaolinite	3.45(3)	1.48(1)
	Sand	2.60(3)	1.30(1)
	Sand	3.63(4)	1.43(1)
	Nontronite	4.03(4)	1.58(1)
	Nontronite	3.75(6)	1.48(1)
	Illite	3.19(5)	1.34(1)
	Illite	3.47(1)	1.497(3)
	Illite	3.41(3)	1.48(2)
	Montmorillonite	3.03(7)	1.51(5)
	Montmorillonite	4.12(2)	1.65(1)
	AR- Average	3.22(22)	1.39(11)
TBTO	Neat	1.55(5)	1.11(1)
	Kaolinite	3.84(3)	1.49(1)
	Kaolinite	2.16(3)	1.03(1)
	Kaolinite	2.13(3)	0.98(1)
	Kaolinite	2.61(2)	1.09(1)
	Sand	2.96(5)	1.42(1)
	Sand	2.11(3)	1.05(1)
	Sand	2.06(2)	0.96(1)
	Nontronite	2.16(3)	1.01(1)
	Illite	2.62(5)	1.25(1)
	Illite	3.176(4)	1.482(2)
	Illite	3.354(8)	1.523(5)
	Illite	3.14(7)	1.63(5)
	Sand	2.56(5)	1.34(1)
	Sand	3.92(5)	2.62(1)
	Montmorillonite	2.37(8)	1.49(6)
	Montmorillonite	2.45(4)	1.24(2)
	Montmorillonite	2.86(5)	1.22(1)
		4.12(3)	1.85(1)
	AR-Average	3.25(6)	1.43(5)

Table 3. (Continued). Mössbauer Spectra of Tributyltin (TBT) Compounds in Sediments and Components[a]

Compd	Clay	Δ	δ
TBTAc	Neat	3.52(4)	1.46(1)
	Kaolinite	3.70(2)	1.46(4)
	Kaolinite	3.77(3)	1.47(1)
	Kaolinite	3.85(7)	1.58(4)
	Sand	3.45(6)	1.47(2)
	Sand	2.79(6)	1.40(2)
	Sand	3.729(5)	1.486(3)
	Illite	3.09(5)	1.42(1)
	Illite	3.35(3)	1.51(2)
	Montmorillonite	2.96(6)	1.48(3)
	Montmorillonite	4.03(2)	1.67(1)

[a]Compd = Compound. All values are relative to $BaSnO_3$ at 80K in mm/s.

Table 4. Mössbauer Spectra of Triphenyltin (TPT) Compounds in Sediments and Components

Compd	Clay	□	□
TPTCl	Neat	2.52(7)	1.35(2)
	Kaolinite	2.70(3)	1.34(1)
	Kaolinite	2.61(5)	1.26(1)
	Kaolinite	3.042(4)	1.455(1)
	Sand	2.56(5)	1.34(1)
	Sand	3.92(5)	2.62(1)
	Sand	2.75(1)	1.39(1)
	Montmorillonite	2.45(4)	1.24(2)
	Montmorillonite	2.23(4)	1.15(2)
	Nontronite	2.46(7)	1.27(3)
	Illite	2.58(3)	1.29(1)
	AR- Average	2.74(10)	1.24(6)
TPTOH	Neat	2.95(7)	1.23(7)
	Kaolinite	2.73(2)	1.14(1)
	Kaolinite	2.94(4)	1.26(2)
	Sand	2.78(5)	1.20(1)
	Sand	2.979(3)	1.241(2)
	Sand	2.80(2)	1.27(1)
	Nontronite	1.84(7)	1.10(2)
	Illite	2.76(2)	1.23(1)
	Illite	3.16(4)	1.37(1)
	Montmorillonite	2.65(3)	1.22(2)
	AR-Average	2.79(8)	1.19(2)
TPTAc	Neat	3.31(7)	1.29(2)
	Illite	2.31(4)	1.11(1)
	Illite	4.67(5)	1.95(3)
	Illite	2.37(5)	1.15(3)
	Sand	3.14(1)	1.22(1)
	Sand	3.07(3)	1.27(1)
	Nontronite	2.13(2)	1.10(1)
	Montmorillonite	2.01(6)	1.20(4)
	Montmorillonite	2.16(3)	1.04(1)
	Kaolinite	3.12(4)	1.25(2)

Table 5. Mössbauer Spectra of Tributyl (TBT) and Triphenyltin (TPT) Compounds in Clays in the presence of *E. coli*.

Clay	Compound	No *E. coli*		In presence of *E. coli*	
		Δ	δ	Δ	δ
Nontronite	TBTO	3.50(2)	1.48(12)	2.16(3)	1.01(1)
Nontronite	TBTCl	3.66(1)	1.57(1)	3.75(6)	1.48(1)
Nontronite	TPTAc	2.44(2)	1.19(1)	2.13(2)	1.10(1)

[a]All values are relative to $BaSnO_3$ at 80K in mm/s.

Analysis of Positive, Right Skewed, and Unimodal Observations

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Estimation of Upper Quantiles Under Model and Parameter Uncertainty

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Abstract.

In this paper we assess accuracy of some commonly used estimators of upper quantiles of a right skewed distribution under both parameter and model uncertainty. In particular, for each of log-normal, log-logistic, and log-double exponential distributions, we study the bias and mean squared error of the maximum likelihood estimator (MLE) of the upper quantiles under both the correct and incorrect model specifications. We also consider two data dependent or adaptive estimators. The first (tail–exponential) is based on fitting an exponential distribution to the highest ten to twenty percent of the data. The second selects the best fitting likelihood-based model and uses the MLE obtained from that model. The simulation results provide some practical guidance concerning the estimation of the upper quantiles when one is uncertain about the underlying model. We found that the consequences of assuming log-normality when the true distribution is log-logistic or log-double exponential are not severe in moderate sample sizes. For extreme quantiles, no estimator was reliable in small samples. For large sample sizes the selection estimator performs fairly well. For small sample sizes the tail-exponential method is a good alternative. Presenting it and the MLE for the log-normal enables one to assess the potential effects of model uncertainty.

Keywords: Quantile Estimation; Model Uncertainty; Parameter Uncertainty; Model Selection; Likelihood; Tail-exponential; Log-symmetric; Monte Carlo Simulation.

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1. Introduction

Estimation of upper quantiles of distributions is important in many applications. Estimates of the upper quantiles of the distribution of a risk factor or an exposure index are commonly used to assess the risk to human health as a result of exposure to chemicals and microbes in the environment, or to determine if concentration levels of contaminants exceed specified limits. Quantitative risk assessment using Monte Carlo methods requires selection of appropriate probability distributions for the risk factors. When the distribution of an important factor is modeled by an incorrect distribution, inaccurate risk estimates may result. Haas (1997) discussed the importance of the distributional form when specifying inputs to Monte Carlo risk assessment. In particular, he showed that the tail behavior of distributions from different families with the same mean and same variance may differ substantially when the variance is large. He also demonstrated that correctly identifying the true model with high probability requires large sample sizes. These considerations indicate that quantile estimates may also be sensitive to the assumed distributional form. Thus, it is important to examine the effects of model selection, and mis-specification on risk estimates. In this paper we investigate the accuracy and robustness of certain quantile estimators under both correct and incorrect model specifications.

The Safe Drinking Water Act requires the United State Environmental Protection Agency (USEPA) to set drinking water standards to control the level of contaminants in drinking water. The National Primary Drinking Water Regulations codify these enforceable standards. Such standards protect the public from the effects of contaminants by limiting their levels in drinking water. Maximum Contaminant Level is the highest level of a contaminant that USEPA allows in drinking water. The maximum contaminant levels for a host of microorganisms, disinfectants and disinfection by-products, inorganic and organic chemicals, and radio nuclides have been established (USEPA, 2001).

The size of the environmental samples are usually small. Sampling for compliance purposes, for example, may be required to be performed monthly or annually since the sampling process may cause disruption in the plant operation. In some instances measuring procedures and laboratory determinations for such substances in water, air, or soil samples are expensive, leading to small sized samples. For example, Frey and Burmaster (1999) study estimates of the $95th$ percentile based on datasets of sizes 19, 9 and 5. Estimating upper quantiles based on small to moderate sample sizes cannot be avoided as it may be mandated by regulation. For example, USEPA (1985) provides guidance for setting and monitoring aquatic standards on toxic chemicals based on the estimates of the *95th* percentile. The upper quantiles are often used in regulatory settings to reflect a degree of prudence in the decision-making process. This is especially true when the issues involved concern human health or the protection of natural resources.

In this paper, we focus on continuous distributions. Let the probability and cumulative distribution functions of Y be denoted by f and F, respectively. Then, the *pth* quantile of Y is defined as $Q_Y(p) = F^{-1}(p)$, which is the smallest y such that $F(y) = p$. Since regulatory decisions rely on the upper tail of a distribution, we are concerned with estimating the upper quantiles and extreme upper quantiles of Y based on a random sample $y_1 \ldots, y_n$ of observations from the distribution of Y. We define upper quantiles to refer to quantiles that correspond to $0.90 \leq p < 0.99$ and extreme upper quantiles will refer to quantiles that are at or above the *99th* percentile.

In a parametric approach, one assumes that the true distribution of Y belongs to a family of distributions $\mathcal{F} = \{f_\theta(y), \theta \in \Theta\}$ indexed by a parameter θ, which may be vector valued. Under such a model, the quantiles are functions of the parameters of the model, and hence estimation of quantiles amounts to estimation of certain parametric functions, namely, estimation of $Q_Y(p) = F_\theta^{-1}(p)$, where $F_\theta(p)$ is the cumulative distribution function (CDF) of Y and θ is the true value of the parameter. These quantities can be estimated using the maximum likelihood method according to which the estimate of $Q_Y(p)$ is $\hat{Q}(p) = F_{\hat{\theta}}^{-1}(p)$, where $\hat{\theta}$ is the MLE of θ under the specified model $\mathcal{F}$. It may be noted that estimation of upper and extreme quantiles is a difficult task. Letting $p = F(y) = \int_{-\infty}^{y} f(t)dt$, and $y = F^{-1}(p) = Q_Y(p)$, it is seen that $dy/dp = dQ_Y(p)/dp = 1/f(y)$. Therefore, the quantile values, $Q_Y(p)$, change very rapidly with p when $f(y)$ is small, i.e., in the upper and extreme upper tails of the underlying distribution. Thus, for accurate estimation of upper and extreme quantiles one needs very accurate estimate of the upper tail of the distribution. This is difficult as very few observations from the upper and extreme upper tails occur in modest sized samples.

Usually, a parametric distributional model is chosen based on physical or biological grounds (Kapteyn, 1903). For example, Ott (1990, chapter 8) discusses the dilution of pollutants in the environment and argues that repeated dilution of a contaminant with water results in a gamma distribution. The log-normal distribution arises as the product of many independent random factors (Aitchison and Brown, 1973). In such cases, there is little uncertainty about the underlying distribution, and a suitable model can be identified apriori.

In many environmental applications, however, we do not have adequate physical, biological, or empirical knowledge to suggest the functional form of the underlying distribution, i.e., to suggest one distributional model. But, we may have enough knowledge to suggest that the true distribution belongs to one of certain specific families. In such cases, one may assume that F is a member of a set of parametric families $\mathcal{F}_i,\ i = 1, \ldots, k$ as in robustness studies (Gastwirth, 1966; Andrews et al. 1977). For example, for unimodal and right skewed variables with unbounded support, one may assume that the true distribution is either log-normal, or log-logistic, or log-double exponential. Then, one may investigate the data by various exploratory techniques (Hoaglin et. al., 1983) and confirmatory tests of hypotheses (D'Agostino and Stephens, 1986) in order to identify a single model that best describes the observations. That is, the information provided by the sample may be used to identify a single best model (Draper, 1995) as measured by some criteria. The investigation can be exploratory or confirmatory in nature. There are several techniques of model selection, including optimal and sub-optimal invariant rules (Quesenberry and Kent, 1982), maximum likelihood rules (Dumonceaux and Antle, 1973; Kappenman, 1982), and rules based on goodness-of-fit statistics (Dyer, 1973). Clearly, the choice of the methods and criteria for data based model selection involves some judgment.

Alternatively, in the presence of model uncertainty one may use non-parametric estimators, which are based on minimal and mild assumptions regarding F, such as continuity or existence of moments (Lehman, 1983). This avoids parametric model selection which requires additional assumptions about the functional form of F. In non-parametric approaches, the empirical distribution function, in various interpolated forms, or a quasi-empirical distribution are used to estimate F. The estimated distribution function is then inverted to obtain quantile estimates. Specifically, we shall consider quantile estimates that are based on the empirical quantile function, or the tail-exponential method described in Section 3.

Generally, non-parametric estimators are less efficient than parametric estimators when the assumed parametric model is correct. Parametric estimators are more attractive when there is not much uncertainty about the model. They run the risk of being inaccurate as the assumed model may not be the true model. However, the choice of the model may or may not have crucial effects on the final inferences. For example, in the context of general linear models, McCullagh and Nelder (1989) and Atkinson (1982) have suggested that assuming a log-normal distribution will in many cases produce the same conclusions as assuming a gamma distribution. On the other hand, Wiens (1999) showed that the two competing models, log-normal and gamma, yielded different conclusions in the analysis of the effects of an investigational vaccine. For estimation in regression models with multiplicative errors, Firth (1988) showed that maximum likelihood estimates based on gamma errors are more efficient than those based on a log-normal distribution under reciprocal misspecification.

To examine the effects of model uncertainty, in this paper, we consider the log-normal, log-logistic, and log-double exponential families, and investigate the properties of the maximum likelihood estimators (MLE) of certain quantiles under both correct and incorrect model specifications. For example, when the true distribution is log-normal, we investigate the bias and mean squared error (MSE) of the maximum likelihood estimators of quantiles derived under the assumption that the true distribution is log-normal (i.e., under correct model specification), as well as under the assumptions that the true distribution is log-logistic, and log-double exponential, respectively (i.e., under incorrect model specifications). We focus on maximum likelihood estimators because they are used frequently in practice. While some asymptotic properties of maximum likelihood estimators of quantiles under a mis-specified general linear model have been discussed by Séménou (1996), we investigate small sample properties by simulation. We also compare the MLEs with non-parametric estimators, and a natural estimator. For the last estimator we first select a model, among log-normal, log-logistic, and log-double exponential, and then calculate the MLE based on the selected model. In this context, we select the model for which the maximized likelihood is the largest. Thus, our selection estimator is also the MLE under the union of the three models. As the selection estimator deals with both model and parameter uncertainty, it is expected to have larger sampling variation than the MLE based on the correct model. Note that if the correct model is identified apriori, only uncertainty about the parameters leads to error in estimation of $Q_Y(p)$. Effects of model mis-specification on the width and coverage probability of confidence intervals is also an important issue, but we do not investigate it in this paper.

In the next section, we review some basic properties of the log-normal, log-logistic, and log-double exponential families of distributions. These three families are log-symmetric, and have been found useful for modeling environmental data. Also, they are location-scale families on the log scale. To compare the three families we study their quantile plots simultaneously. Section 3 considers the empirical distribution function and discusses the tail-exponential method for estimating the upper values of the quantile function. Section 4 describes a simulation study and compares the performance of the quantile estimators. An example is discussed in section 5. The final section is devoted to summary and recommendations.

2. Distributions

In this section, we discuss three symmetric location-scale distribution families on the log scale. A location-scale family is obtained by considering location and scale transformations of a random variable with a specified distribution. Let Z be a random variable with density f_Z, distribution function F_Z, and quantile function $Q_Z(p)$. Consider the transformation $X = a + bZ$, $a \in R$, $b > 0$. Then, it can be seen that X has density $f_X(x) = \frac{1}{b} f_Z(\frac{x-a}{b})$, distribution function $F_X(x) = F_Z(\frac{x-a}{b})$, and quantile function $Q_X(p) = a + bQ_Z(p)$. Further if the distribution of Z is symmetric about zero, i.e. $f_Z(-z) = f_Z(z)$ for all z, then the distribution of X is symmetric about a, i.e., $f_X(a-t) = f_X(a+t)$ for all t. If Z is symmetric about 0, it also follows that $F_Z(z) = 1 - F_Z(-z)$ for all z, and $Q_Z(p) = -Q_Z(1-p)$ for all p. The parameters a and b of a location-scale family determine the center, and the dispersion of the distribution, respectively. The Normal, logistic, and double exponential are three well known symmetric location-scale families of distribution.

We shall however, assume that the risk factor Y is such that the distribution of its logarithm belongs to a symmetric location-scale family. Thus, $Y = \exp(X) = \exp(a + bZ)$ for some $a \in R$ and $b > 0$, where Z has a known distribution which is symmetric around 0. Being a continuous and increasing function, the exponentiation leads to distributions that are unimodal and right skewed. This transformation alters the spacing while preserving the order of the observations. It can be seen that Y has density $f_Y(y) = \frac{1}{y} f_X(\ln y) = \frac{1}{by} f_Z(\frac{\ln(y)-a}{b})$, and quantile function $Q_Y(p) = \exp(Q_X(p)) = \exp(a + bQ_Z(p))$. Thus, the distribution, the quantile function and other properties of the distribution of Y can be obtained readily from the distribution of Z. We next review some specific properties of three distribution families. As the interpretations of the parameters a and b are different for the three families, we express them in terms of the mean μ_y and coefficient of variation, $\nu_y = \sqrt{Var(Y)}/E(Y)$ of Y. It may be noted that under the assumption that log Y has a symmetric location-scale distribution, the CV of Y depends only on the scale parameter b and not on the location parameter a.

Log-normal distribution

The Log-normal distribution is basic in the modeling of environmental, economic, and industrial observations. It has been used to fit air quality data (Mage, 1981), water consumption rates (Rosebury and Burmaster, 1998), and trace elements in human tissue (Rustagi, 1964). Many exposure factors such as body weight as a function of age (Burmaster and Crouch, 1997), total skin area as a function of body weight (Burmaster, 1998), and fish consumption rates (Murray and Burmaster, 1994) have also been modeled by log-normal distributions.

A random variable Y has a log-normal distribution if $Y = \exp(X)$, and X has a normal distribution. Here the parameters a and b are the mean μ and standard deviation σ of X. Standard calculations show that $\mu_y = \exp(\mu + \sigma^2/2)$, and $\nu_y = \sqrt{\exp(\sigma^2) - 1}$ (see Table 1). So, for given ν_y and μ_y, the corresponding values of μ and σ^2 are $\mu = \ln(\mu_y) - \frac{1}{2}\ln(\nu_y^2 + 1)$, and $\sigma^2 = \ln(\nu_y^2 + 1)$. The quantiles of log-normal distributions are obtained from the quantiles of the standard normal distribution by noting that $Q_Y(p) = \exp(\mu + \sigma Q_z(p))$, where $Q_z(p) = \Phi^{-1}(p)$, and $\Phi^{-1}(p)$ is the quantile function of the standard normal distribution. This indicates that the upper quantiles of the log-normal distribution are affected by the scale (σ) of the underlying normal distribution. For further reviews of this distribution we refer to Aitchison and Brown (1973), and Johnson et. al. (1995).

Log-logistic distribution

The logistic distribution with location parameter a and scale parameter b has the density function

$$f(x) = \frac{\exp[-(x-a)/b]}{b[1+\exp(-(x-a)/b)]^2}, \quad -\infty < x < \infty, \quad b > 0, \quad -\infty < a < \infty.$$

One can show $E(X) = a$ and $Var(X) = b^2\pi^2/3$ (see Table 2). The distribution of $Y = \exp(X)$ is given by

$$g(y) = \frac{\exp(a/b)y^{-(1/b)-1}}{b[1+\exp(a/b)y^{-1/b}]^2}, \qquad y > 0.$$

It can be shown that $E(Y^r) = (\pi r b)\exp(ra)csc(\pi r b)$, and $\nu_y = \sqrt{\frac{1}{\pi b}\tan(\pi b) - 1}$. Using these relationships we can find the values of a and b corresponding to given values of μ_y and ν_y. For that we need to solve $\nu_y^2 + 1 = \frac{1}{\pi b}\tan(\pi b)$ for b and calculate $a = \ln([\mu_y/\pi b]sin(\pi b))$. For further discussion of the log-logistic distribution we refer to Johnson et. al. (1995).

The log-logistic distribution has been used to model survival data (Bennett, 1983) and business failure data (Dubey, 1966). The shape of the log-logistic distribution is similar to a log-normal distribution as the normal and logistic distributions are very similar in shape. Johnson et. al. (1995) show that $|[1+\exp(-\pi x/\sqrt{3})]^{-1} - \Phi(\frac{16x}{15})| < 0.01$, where $[1+\exp(-\pi x/\sqrt{3})]^{-1}$, and $\Phi(x)$ are the distribution functions of standard logistic and standard normal distributions, respectively. They also suggest that, on suitable occasions, the normal can replace the logistic to simplify the analysis. Due to their similarity, statisticians often do not concern themselves with whether the normal or logistic distributions underlie the data. It is also very difficult to distinguish between these two distributions at small sample sizes. Even though logistic provides a good approximation in the central part of the normal distribution, there can be substantial differences in the upper and extreme upper quantiles. With a kurtosis of 4.2, the standard logistic distribution has a longer tail than the normal, which has kurtosis 3.0. In fact the logistic distribution has been shown to be better approximated by a t distribution with nine degrees of freedom (Mudholkar and George, 1978). Differences in the upper quantiles of normal and logistic are further magnified when they are exponentiated to get log-normal and log-logistic distributions.

Log-double exponential distribution

The log-double exponential distribution is briefly discussed in Johnson et. al. (1995). Let X have a double exponential distribution with location parameter a and scale parameter b. That is,

$$f(x) = \frac{1}{2b}\exp(-|x-a|/b), \quad -\infty < x < \infty, \quad b > 0, \quad -\infty < a < \infty.$$

The density function of $Y = \exp(X)$ can be expressed as

$$g(y) = \begin{cases} \frac{1}{2b}\exp(-a/b)\ y^{1/b-1}, & \text{if } \ 0 \le y \le \exp(a) \\ \frac{1}{2b}\exp(a/b)\ y^{-1/b-1}, & \text{if } \ y \ge \exp(a). \end{cases}$$

It is straight forward to verify that $E(y^r) = [1-(rb)^2]^{-1}\exp(ra)$ for $r < 1/b$, and $1+\nu_y^2 = (\alpha^2-2\alpha+1)/(\alpha^2-4\alpha)$, where $\alpha = 1/b^2$. Then, letting $k = 1+\nu_y^2$ we see that

$$(1-k)\alpha^2 + (4k-2)\alpha + 1 = 0$$

and the values of a, and b corresponding to given values of μ_y and ν_y are

$$b = [\frac{2-4k-\sqrt{(4k-2)^2-4(1-k)}}{2(1-k)}]^{-1/2}$$

and $a = \ln(\mu_y(1-b^2))$ (see Table 3).

Johnson (1949) discussed a system of three transformations, including a log transformation, of normal and double exponential distributions. Takikamalla and Johnson (1982) discussed the same system of transformations applied to the logistic distribution. Log-double exponential distribution, also called log-Laplace distribution, has been used to model dose-response data (Uppuluri, 1980).

To compare the three families of distributions Figures 1–4 simultaneously plot their quantile functions in the upper region ($0.90 < p < 0.999$) for several identical values of the mean and CV. A change in the mean results in a shift in the plot but a change in the CV changes the shapes of the graphs and the ordering of the extreme quantiles. Examination of the three quantile functions $Q(p)$ over the entire region of p indicate that they are very close to each other over an interval $(0, p_1)$ of values of p. The value of p_1 depends on the CV and increases with the CV. For example, investigating the entire range of p and several values of CV indicate that, the value of p_1 is around .50 for CV = 0.1, and around .93 for CV = 10. As the value of p exceeds this value p_1, the quantile functions separate from each other. For small to moderate values of the CV, the quantile functions cross each other again at a value p_2, which is between p_1 and 1. The value of p_2 also increases with the CV. For example, p_2 is around .955 when the CV = 0.1, and around .998 for CV = 1. For much larger CV values this crossing does not occur.

Figures 1–4 shows the differences among the upper and extreme quantiles (i.e., for p between .90 and .999) of the log-normal, log-logistic, and log-double exponential distributions for $\mu_y = 1$, and CV = 0.1, 1. For the values of p that are between p_1 and p_2, the quantiles for the log-normal are larger than the corresponding quantiles under log-logistic, which in turn are larger than those for the log-double exponential. This ordering is reversed for values of p that are larger than p_2 when the crossing takes place, i.e., for small values of the CV. Thus, for the same mean and CV, the ordering of the quantiles $Q(p)$ under the three models depends on p as well as the CV. It is interesting to note that for small and moderate CV the log-double exponential has the longest tail, and log-normal has the shortest tail but, this ordering is reversed for large CV.

3. Empirical Distribution Function

Not knowing the general form of F, we would ideally like to find accurate estimates of $Q_Y(p) = F^{-1}(y)$ for $0 < p < 1$ under mild assumptions, such as existence of moments, or continuity of F. In such settings, $F_n(y) = \frac{1}{n}\#\{y_i \leq y\}$, the empirical distribution function, is a natural estimator of $F(y)$. This estimator places equal probability mass $1/n$ at each sample point y_i and is the non-parametric maximum likelihood estimate of $F(y)$ (Efron and Tibshirani, 1993, P. 310).

Being more revealing for our purposes, the empirical distribution function (EDF) can also be defined in terms of the ordered sample values $y_{(1)} < y_{(2)} \ldots < y_{(n)}$ as

$$F_n(y) = \begin{cases} 0, & \text{if } \ y < y_{(1)}; \\ \frac{i}{n} & \text{if } \ y_{(i)} \leq y < y_{(i+1)}; \\ 1 & \text{if } \ y \geq y_{(n)}. \end{cases} .$$

Direct inversion of the CDF is not very helpful for estimating the quantile function. As $F_{(n)}(y)$ is a step function, its inverse $F_n^{-1}(p)$ exists only for a finite number of values, $p = i/n, \quad i = 1, \ldots, n$. Inversion of the EDF does not produce any estimate of $F^{-1}(p)$ if p is not in the set $1/n, 2/n, \ldots, 1$. It is necessary to use interpolation to get estimates of $F(p)$ for all values of p. For example, a linearly interpolated empirical quantile function has the form,

$$Q_n(p) = y_{(i)} + n(p - i/n)(y_{(i+1)} - y_{(i)})$$

where $Q_n(0) = 0$, $Q_n(1) = y_{(n)}$, and i is such that $\frac{i}{n} \leq p < \frac{i+1}{n}$.

According to the EDF all the probability is concentrated between the minimum and maximum of the sample observations. Thus, when estimating a true distribution by an EDF we truncate the tails of the distribution, which alters the resulting estimates of upper and extreme quantiles. In many cases the distribution of the observations in the upper tail is well approximated by a two parameter exponential distribution. Motivated by this fact Breiman et. al. (1979) proposed the tail exponential method for estimating the upper quantiles. As discussed in Ott (1995), this method seeks to fit an exponential distribution to the upper r percent of the observations. Let $y_c = Q_n(1-r)$, where r is a specified tail proportion, usually 10 to 20 percent. Assume that the conditional distribution of Y given $Y > y_c$ is two parameter exponential with parameters y_c and η. Then, for $y > y_c$, the unconditional distribution function of Y is $F(y) = 1 - r\exp[-(x-x_c)/\eta]$, and hence for $p > 1-r$ the tail exponential quantile function is $Q_n(p) = y_c - \eta\ln(\frac{1-p}{r})$. The parameter η of the tail exponential model is estimated as $\hat{\eta} = \bar{y}_c - y_c$ where $\bar{y}_c$ is the mean of the observations above y_c.

4. Simulation Study

We performed a simulation study to assess the accuracy of upper and extreme upper quantile estimates for log-normal, log-logistic and log-double exponential distributions. For each model we considered the combinations of $\mu_y = 1$, CV= $[0.1, 1.0]$, $n = [10, 30, 100, 1000]$, and $p = [0.95, 0.99, 0.999]$. In each case we generated 2000 samples of size n and estimated the pth percentile. Three of the estimates are the maximum likelihood estimates under the assumptions that the population distribution is (i) log-normal, (ii) log-logistic, and (iii) log-double exponential, respectively. For the log-normal distribution the log of the likelihood function is $-n(\ln b\sqrt{2\pi}) - \sum_{i=1}^{n}\ln y_i - \frac{1}{2b^2}\sum_{i=1}^{n}(\ln y_i - a)^2$. The log of the likelihood function for the log-logistic distribution is $n(\ln(1/b) + a/b) - (1/b+1)\sum_{i=1}^{n}\ln y_i$ and for the log-double exponential distribution is $-\ln b - a/b + (1/b-1)\ln y_i - \ln 2$ if $0 \leq y \leq \exp(a)$ and $-\ln b + a/b - (1/b+1)\ln y_i - \ln 2$ if $y \geq \exp(a)$.

The maximum likelihood estimators of the parameters exist in closed form under a log-normal distribution with $\hat{a} = \frac{1}{n}\ln y_i$ and $\hat{b}^2 = \frac{1}{n}(\sum_{i=1}^{n}\ln^2 y_i - \hat{a}^2)$ and under a log-double exponential distribution with $\hat{b} = \frac{1}{n}\sum_{i=0}^{n}|y_i - \hat{a}|$ and $\hat{a} = median(y_i)$. Clearly, in one of these three cases, the model is correctly specified, and in the other two cases the model is mis-specified. We consider the three cases to assess parameter uncertainty as well as effects of incorrect model specification. The fourth estimator is a nonparametric estimator. Table 4 specifies the method of estimation as a function of n and p, i.e., it specifies when we use the empirical distribution function and when we use the tail-exponential method. The fifth estimator is the MLE based on a selected model. In this approach, the selected model is the family, out of log-normal, log-logistic, and log-double exponential, which has the largest maximized likelihood. This fifth estimator is also the MLE under the assumption that the true distribution is either log-normal or log-logistic or log-double exponential.

The simulations were performed using SAS/IML. The inverse transformation method was used to generate variates from the logistic and double exponential distributions. Uniform and normal variates were generated using Rannor and Ranuni functions of SAS. The variates were exponentiated to generate values from LL, LN, and LDE distributions. The MLEs of the parameters for log-logistic distribution are obtained by applying the Newton–Raphson root finding procedure to the likelihood equations. We use the criterion of bias and root mean squared error (RMSE) in order to assess the accuracy of the estimates. The simulation results are presented in Tables 5–10. The values of bias that are less than 5% , greater than 25% and 50% of the true parameter values at $P = 0.95, 0.99$ and 0.999 are marked with $*$, $+$, and $>$, respectively.

The first blocks of numbers in Tables 5–10 correspond to the cases where the true model is specified correctly. As expected, the accuracy of the estimators generally increase as the sample size (n) increases and/or the CV decreases. Note that as p increases, i.e., the quantiles become more extreme, the accuracy decreases. The MLEs are not unbiased although the bias decreases to 0 as the sample size increases. The direction and magnitude of bias depends on the specific combination. For small CV (CV $= 0.1$) the biases are negative but quite small, and the RMSEs are also fairly small. Also, for CV $= .1$, the MLE is most reliable, judged by both bias and RMSE, for the log-normal model, and least reliable for log-double exponential model. For larger CV, however, the biases are generally positive, and they increase in magnitude as n decreases or the CV increases or p increases. Simulation experiments with larger values of CV (CV=10) indicate that the biases (and the RMSEs) are severe for log-normal model unless n is large. Thus, when the CV is large and the sample size is small or moderate, the MLE should not be used for estimating the upper and extreme quantiles. One should use other estimators with no or smaller bias.

We next consider the second and third blocks in Tables 5–10 to discuss the effect of model mis-specification. The results for $n = 1000$ exhibit the systematic effect of mis-specification as the sampling variability in this case is rather small. When the true distribution is log-normal, from Tables 5–6 we see that modeling the data using a log-logistic or log-double exponential distribution usually results in a positive bias. Interestingly, for $p = .95$ and $n \leq 100$, the bias and RMSE values under the log-logistic assumption are similar to the corresponding values under the correct assumption of log-normality. Thus, mis-specification of a log-normal model by a log-logistic does not seem to have serious consequences for estimating the 95th percentile, unless the sample size is very large. For larger values of p, this mis-specification substantially reduces the accuracy of the estimates. Further, the bias and RMSE increase as p and/or the CV increase. When the data follow a log-normal model, the effects of wrongly using log-double exponential distribution are generally much more serious than using the log-logistic to fit the data.

The bias due to mis-specification of a log-logistic distribution by log-normal, reported in Tables 7–8, depends on the values of p and CV. When the CV = .1, they are generally negative, but when the CV = 1.0, they are negative for $p = .99$, .999 and positive for $p = .95$. For $n = 1000$ these biases are generally quite large, and the RMSEs are much larger than the RMSEs of the MLE under the correct assumption of log-logistic distribution. However, for smaller sample sizes the RMSE values are fairly comparable. Interestingly, the RMSEs under the log-normal assumption are smaller than the RMSEs under log-logistic assumption for $n = 10, 30$, $p = .99, .999$, and CV = 1.0. Thus, assuming log-normality when the true distribution is log-logistic does not appear to have a major impact on the estimates of the upper and extreme quantiles in samples of size $n \leq 30$. In contrast, the assumption of log-double exponential generally induces positive biases, whose magnitude tend to increase with CV and p. Their overall properties are markedly inferior except possibly for CV = .1 and $p = .95$.

Tables 9–10 report the effects of mis-specification of a true log-double exponential distribution. The MLEs under log-logistic assumption are negatively biased, but their RMSEs are close to the RMSEs under log-double exponential for small to moderate sample sizes. Actually, for $n \leq 30$, the RMSEs under mis-specification by log-logistic are mostly smaller than the RMSEs under the correct assumption of log-double exponential distribution. Mis-specification by the log-normal leads to negative biases for $p = .99$ and .999; for $p = .95$, they are positive for CV=1. The RMSEs are close (and even smaller in several cases) to those under the correct assumption for smaller ($n \leq 30$) sample sizes and $p \leq 0.99$. When $p = 0.999$, however, the negative bias remained and the RMSE's were high regardless of which model was fit. The log-normal mis-specification is slightly worse than the log-logistic mis-specification. Overall, mis-specification of log-double exponential by log-normal or log-logistic is fairly innocuous for estimating upper percentiles from small or moderate sized data sets.

Considering effects of all incorrect specifications of the model, we conclude that when the sample size is not very large, the assumption of log-normality is fairly harmless for estimating upper percentiles. Extreme upper percentiles are difficult to estimate accurately even when one knows the correct underlying model. When the sample size is large, significant biases result from assuming an incorrect model. In such cases, however, it is much easier to identify the correct model using goodness of fit tests or the selected estimator can be used.

Now we discuss the behavior of the EDF estimator. Expectedly, the RMSE values are fairly large in the cases where the fully nonparametric method has been used (see Table 4). They are mostly larger than the RMSE values under the log-normal assumption, even when that assumption is not correct. However, the tail exponential approach performs fairly well for log-normal and log-logistic distributions, especially for large CV. But, it does not work well for log-double exponential distribution. In that case, even the MLE under the incorrect assumption of log-normality performs better.

Finally, we discuss performance of the selection estimator, which is the MLE under the selected model. The selection probabilities of different families, for different true distributions with CV = 1, are presented in Table 11. We report them only for CV = 1 as they changed very little with the CV. For $n = 1000$, the true model is selected with probability at least 0.98, and hence the resulting estimator generally performs almost as well as the MLE under the correct distribution. Only for log-normal data with CV = 1.0, the estimators of $99th$, and $99.9th$ percentiles have noticeably larger RMSE than the MLE for the log-normal. For $n \leq 100$, its performance is roughly comparable to the MLE under the log-normal assumption; neither one is uniformly better than the other.

Based on the simulation results we come to the following conclusions. For large n, we suggest using the data to select a model, and then estimate the quantiles based on the selected model. For smaller sample sizes it is difficult to identify the correct model, (see Table 11, and Haas, 1997), and hence one cannot rely on the estimates derived under the selected model. In such cases, one should try to choose a model by examining the subject matter and related studies. If one has considerable uncertainty about the correct model, we believe one should obtain multiple estimates using different methods. For moderate sample sizes, the MLE under the log-normal assumption, and the selection estimates appear to be two reasonable alternatives. For small sample sizes, selection estimates are unreliable, especially for large p. For estimating upper and extreme quantiles based on a small sample ($n \leq 30$), we suggest reporting the tail exponential estimates, and the MLE under the log-normal assumption. The inherent model uncertainty should be reflected in the differences between them.

5. An Example

Nickel is a metal found only in combined form in nature. Used in electronics industry, coal gasification, petroleum refining, and hydrogenation of fats and oils, nickel is a potential ground and surface water pollutant. There is currently no legal limit on the amount of nickel in drinking water. Nickel has not been found to potentially cause health effects from acute exposures at levels below 0.1 mg/L. USEPA (2001) contains various fact sheets about this and other contaminants. We will investigate estimation of the upper quantiles of a data set of nickel concentrations from four monitoring wells. The data set appears in a guidance document on analysis of ground-water monitoring data (USEPA, 1992) and is discussed by Millard (1998).

The data set consists of $n = 20$ nickel concentrations in parts per billion. We use these data, which appear in Table 12 along with some summary measures, for illustrative purposes. Millard (1998) considered $\mathcal{F}$ to only contain the log-normal distribution. We will enlarge $\mathcal{F}$ to include log-logistic and log-double exponential families. Table 13 displays the values of the MLE, log-likelihood, and three estimated quantiles for all three distributions. The model with the largest likelihood is Log-normal. Note that none of the listed distributions are rejected at a 05% confidence level. The log of the likelihoods are very close. Anderson-Darling test for normality of ln(nickel) produces a P-value in excess of 0.25. The same test for a logistic and double exponential distributions produce p-values larger than 0.15. There seems to be some uncertainty about the underlying model.

Estimated quantiles based on the tail-exponential method corresponding to a 10, and a 20 percent tail proportion also appear in Table 13. The estimates vary substantially for each value of p. The exponential method leads to estimated quantiles that are smaller than the ones obtained under parametric models. As there is considerable uncertainty about an effective model, we believe one should utilize the estimates under different models to draw conclusions. Estimates under the Log Double Exponential model are substantially larger than all other estimates. The estimates under the log-normal and log-logistic distributions are comparable for $p = 0.95$, but differ substantially for $p = 0.999$. In this example, one might consider an interval at the *95th*(*99th*) percentile ranging from the Log-normal estimates (903.7)(2990.2) to (1032.2)(5527.1) from the log-logistic model. A formal confidence interval would be much larger.

6. Summary and recommendations

In this paper, we considered the accuracy of upper and extreme tail estimates of three right skewed distributions under model and parameter uncertainty. We used the criteria of bias and root mean squared error in order to assess the accuracy of the estimates. The distributions considered are log-transformation of three well-known and symmetric distributions, the log-normal, log-logistic and log-double exponential distributions. We examined and compared performances of the MLE and non-parametric estimators based on the empirical or a quasi-empirical quantile function (tail-exponential method). We considered four cases that are encountered in practice. In particular, we considered the cases where *i)* the model is correctly specified, *ii)* the model is mis-specified, *iii)* the best model is selected using the data, and *iv)* no form is assumed for the model.

In practice it is important to report standard errors or confidence intervals along with the point estimates to provide information about the reliability of the point estimates. Thus, the effects of model mis-specification on the width and coverage probability of confidence intervals deserve further investigation. For a given dataset, the true (correct) model is unknown and its analysis should be guided by *(i)* identification of a reasonable model and *(ii)* the robustness of the proposed methodology. We should know how an analysis based on an assumed model perform when it differs from the true model. Identification of a useful and effective model is easier for large datasets. For smaller datasets, one needs to rely on more robust methods. Fully nonparametric methods are robust, but may not be very efficient for some models. It is useful, therefore, to use a method that works well for a class of sufficiently realistic models. In this paper we have studied the robustness of estimates of upper and extreme percentiles when the true model is either log-normal, log-logistic or log double exponential, all of which are symmetric location-scale families on the log-scale.

Generally speaking, when the model is specified correctly, the accuracy of the estimators increase as the sample size increases and/or the CV decreases and/or p decreases. Under model mis-specification, we observed the following. The assumption of log-normality when the true distribution is log-logistic does not appear to have a major effect on the estimates of upper and extreme quantiles. The mis-specification of a log-double exponential by a log-normal or log-logistic is fairly innocuous for estimating upper percentiles from small or moderate sized data sets but become quite noticeable for larger samples. Considering effects of all the incorrect specifications of a model, we conclude that when the sample size is not very large, the assumption of log-normality is relatively harmless for estimating the upper percentiles. The extreme percentiles were difficult to reliably estimate in modest sized samples for all three distributions. When the sample size is large, significant biases result from assuming an incorrect model. In such cases, however, it is much easier to identify the correct model using goodness of fit tests.

When the size of the sample is large we should use the data to select a model, and then estimate the quantiles based on the selected model. For smaller sample sizes it is difficult to identify the correct model and hence one cannot rely on the estimates derived under the selected model. In such cases, one should try to choose a model by examining the subject matter and related studies. But, if one has considerable uncertainty about the correct model, we believe it is helpful to obtain multiple estimates using different methods. For moderate sample sizes, the MLE under log-normal assumption, and the selection estimates appear to be two reasonable alternatives. Considering the non-parametric estimators, the tail exponential approach works fairly well for log-normal and log-logistic distributions, especially when the CV is large. Unfortunately, it does not work well for log-double exponential distribution. For small sample sizes, selection estimates are unreliable, especially for large p. For estimating upper and extreme quantiles based on a small sample ($n \leq 30$), we suggest reporting the tail exponential estimates, and the MLE under log-normal assumption.

The coefficient of variation has a great impact on the results in all four situations. Even when the parent distribution is identified apriori, the extreme upper tail estimates are not accurate at small sample sizes and large values of CV. Caution must be exercised when identifying a distribution apriori as model mis-specification can result in high bias and mean squared error at large values of CV. Large values of CV also impact the identification of the correct model. Estimates based on the selection method may be suspect for small sample sizes and high values of CV. Large sample sizes are necessary to reduce the mis-classification rates.

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$Distribution$	$Log - Normal$
PDF, $f(y)$	$y = \exp(x), \quad x \sim N(a, b^2)$ $\frac{1}{b\sqrt{2\pi}y} \exp(\frac{-(\ln y - a)^2}{2b^2}), \quad y > 0, \quad b > 0$
CDF, $F(y)$	$\Phi(\frac{\ln(y)-a}{b})$, Φ is the standard Normal CDF
Quantile Function, $Q_Y(p)$	$\exp(a + b\Phi^{-1}(p))$
Mean, μ_y	$\exp(a + b^2/2)$
Variance, σ_y^2	$\exp(2a + b^2)(\exp(b^2) - 1)$
Skewness, $\eta_3 = \mu_3/b^3$	$(\exp(b^2) + 2)\sqrt{\exp(b^2) - 1}$
Coefficient of Variation, ν	$\sqrt{\exp(b^2) - 1}$
log(Likelihood)	$-n(\ln b\sqrt{2\pi}) - \sum_{i=1}^{n} \ln y_i - \frac{1}{2b^2} \sum_{i=1}^{n} (\ln y_i - a)^2$
Parameter MLE	$\hat{a} = \frac{1}{n} \ln y_i$ and $\hat{b}^2 = \frac{1}{n}(\sum_{i=1}^{n} \ln^2 y_i - \hat{a}^2)$

Table 1. Log-Normal Properties.

$Distribution$	$Log - Logistic$
PDF, $f(y)$	$y = \exp(x), \quad x \sim L(a, b), \quad b > 0$ $(1/b)\exp(a/b)y^{-1/b-1}(1 + \exp(a/b)y^{-1/b})^{-2}, \quad y > 0$
CDF, $F(y)$	$(1 + \exp(a/b)y^{1/b})^{-1}$
Quantile Function, $Q_y(p)$	$\exp(a)(\frac{p}{1-p})^b$
Mean, μ_y	$b\pi \exp(a) \csc(b\pi)$
Variance, σ_y^2	$b\pi \exp(2a)(\tan(b\pi) - b\pi)\csc^2(b\pi)$
Skewness, $\eta_3 = \mu_3/\sigma_y^3$	Note: $E(y^r) = (b\pi r)\ \exp(ar)\csc(b\pi r), \quad r < 1/b$
Coefficient of Variation, ν	$\sqrt{1/(b\pi)\ \tan b\pi - 1}$
log(Likelihood)	$n(\ln(1/b) + a/b) - (1/b + 1)\sum_{i=1}^{n} \ln y_i$ $-2\sum_{i=1}^{n} \ln(1 + \exp(a/b){y_i}^{-1/b})$
Parameter MLE	No closed form expression

Table 2. Log-Logistic Properties.

Distribution	Log-Double Exponential
PDF, $f(y)$	y=exp(x), $x \sim DE(a,b)$ $\frac{1}{2b}\exp(-a/b)x^{1/b-1}$ $0 \le x \le \exp(a)$ $\frac{1}{2b}\exp(a/b)x^{-1/b-1}$ $x \ge \exp(a)$
CDF, $F(y)$	$\frac{1}{2}\exp(-a/b)x^{1/b}$ $x \ge \exp(a)$ $1-\frac{1}{2}\exp(a/b)x^{-1/b}$ $x \ge \exp(a)$
Quantile Function, $Q_Y(p)$	$(2\ p\ \ \exp(a/b))^b$ $0 \le p \le 1/2$ $(2(1-p)\exp(-a/b))^{-b}$ $1/2 \le p \le 1$
Mean, μ_y	$(1-b^2)^{-1}\exp(a), \quad b<1$
Variance, σ_y^2	$\exp(2a)((1-4b^2)^{-1}-(1-b^2)^{-2}), \qquad b<2$
Skewness, $\eta_3 = \mu_3/\sigma_y^3$	Note: $E(y^r) = [(1-(rb)^2]^{-1}\exp(ra), \qquad b<1/r$
Coefficient of Variation, ν	$\sqrt{\frac{(1-b^2)^2}{1-4b^2}-1}, \qquad b<2$
log(Likelihood)	$-\ln b - a/b + (1/b-1)\ln y_i - \ln 2$ $0 \le y \le \exp(a)$ $-\ln b + a/b - (1/b+1)\ln y_i - \ln 2$ $y \ge \exp(a)$
Parameter MLE	$\hat{b} = \frac{1}{n}\sum_{i=0}^{n}\lvert x_i - \hat{a}\rvert$ $\hat{a} = median(x_i)$

Table 3. Log-Double Exponential Properties.

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Speciation of Triorganotins in Sediments of the Anacostia and Potomac River Sediments as the Result of their Interaction with Bacteria

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Speciation of Triorganotins in Sediments of the Anacostia and Potomac River As the Result of Their Interactions with Bacteria

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Speciation of Triorganotins in Sediments of the Anacostia and Potomac River as the Result of Their Interactions with Bacteria

Introduction

The Anacostia and Potomac rivers are two major waterways located in the District of Columbia. Each year these rivers play host to extensive recreational activities for the residents of the metropolitan area. The majority of these activities involve boating and fishing. Optimally, these rivers should be free of hazardous chemicals and/or agents that can be detrimental to the aquatic biota. If this is not possible, then it is imperative to know what hazardous species are present and their interactions and/or relationships with the aquatic biota. Armed with this type of knowledge beforehand, potential problems such as the recent *Pfiesteria piscicida* outbreak can be avoided. Two classes of pollutants that find their way into the Anacostia and Potomac rivers, as well as other waterways that have high boat traffic, are tributyltins (TBTs) and triphenyltins (TPTs) since they are the toxic additives added to antifoulant marine paints. Marine paints are used to inhibit the attachment of barnacles, sea grass, hydroids and other marine organisms to the bottom of ships and other submerged marine structures. Organotin marine paints contain as much as 20% by weight of the antifoulant (1). One mode of entry of these triorganotins into the various waterways is through their release from vessels and underwater structures, such as piers and docks that have been treated with antifoulant paints. The leaching of these compounds from marine paints results in higher concentrations of these chemicals in static environments, such as harbors, estuaries, marinas and bays, than in open waters. Studies have shown that the level of TBT observed is directly related to the amount of boating activity (2). For example, Seligman *et al.* (2) observed that the level of TBT was highest in the vicinity of a commercial shipyard along the Elizabeth River with the concentrations decreasing as the distance from the shipyard increased. Similar findings were reported by Matthias *et al.*(3,4) who found low levels of TBT compounds in the open waters of the Chesapeake Bay, while elevated levels were detected in the Annapolis marina areas. The use of triorganotin compounds in the United States has been restricted by the Organotin Act (5), which prohibits the use of organotin-based paints on vessels smaller than 25 meters. However, vessels larger than 25 meters may still use marine paints containing organotins and a number of these larger vessels still travel these rivers, particularly the Anacostia river, where a naval shipyard is located. Even with the restricted use of these antifouling marine paints, these compounds have already entered various water systems during their previously unrestricted use. In the aquatic environment, triorganotin compounds are known to have low aqueous solubility and mobility, and exhibit strong binding to sediments (6). Therefore, particulate matter in the water, which upon settling to the bottom, can be incorporated into the sediment, easily absorbs these compounds. Any disturbance of the sediment will permit the direct and continuous re-introduction of the triorganotins back into the water column, where they can have adverse effects on non-targeted species such as crustaceans and fish (7). Furthermore, these compounds still possess a major threat to the aquatic environment even after government regulations have restricted their use. For example, a recent study of Canadian water and sediment samples (8) done after the banning of TBTs indicated that while there has been a reduction of TBT concentrations in fresh waters, such a reduction was not evident in sea water. The study also revealed that at many sites, the TBT concentrations were still high enough to cause acute and chronic toxicity to aquatic and benthic organisms. Another recent study from Canada (9) indicated that since 1989, when the use of TBTs was banned, there was an actual increase in the TBTs contained in sediments from large vessel harbor sites.

Several countries (8) have made attempts to assess the effectiveness of their TBT regulations. In general, it was found that with restricted usage, there was a reduction of the TBT contamination of water and some organisms. Some recovery of the populations of some organisms has been observed, particularly those close to marinas (8). However, this reduction was not observed in areas where the boat traffic involved vessels larger than 25 meters since the ban of TBT does not apply to them. Reductions of TBT concentrations in water systems have been observed in France (10), the United Kingdom (11 - 14), Ireland (15, 16) and Switzerland (17, 18). However, the concentrations of TBT in water still exceeded the guidelines for a particular jurisdiction in some of these countries (12). Furthermore, in some sampling sites in the United Kingdom (19) and the Netherlands (20), there was little or no decrease in TBT concentrations in the water at the time of sampling. In addition, many workers have reported that little or no reduction in

TBT concentrations was observed in sediments several years after the enactment of the TBT regulations (13, 14,17, 18, 21 - 23). This non-reduction was attributed to the appreciable persistence of TBT in sediments, most probably due the their strong binding to the sediments. Thus, TBT contaminated sediments may continue to pose a hazard to benthic organisms and other organisms in the water column, either through sediment re-suspension directly or indirectly through benthic eating organisms.

While there have been numerous speciation studies of organotin compounds in various bodies of water around the world, there have been no similar extensive studies in DC waterways. While most investigators have focused on the determination of organotin species and their concentrations in the environment, only a few studies have been initiated to study triorganotins in sediments as a result of their interactions with bacteria. Thus, a study of the speciation of triorganotins in sediments of the Anacostia and Potomac rivers, as a result of their interaction with bacteria, would be essential for a more complete understanding of the effects of triorganotins on the aquatic environment. The results from this study will alert those responsible for water quality to the long term impact of these hazardous chemicals and, therefore, allow them to plan accordingly.

Experimental

Chemicals.

Tributyltin chloride (TBTCl) was obtained from Gelest, Inc., Tullytown, PA, USA. Triphenyltin chloride (TPTCl) was obtained from Aldrich Chemical Co., Inc., Milwaukee, WI, USA. The compounds contained the normal abundance of ^{119}Sn and were used as received without further purification to spike the sediment samples.

Sediment Samples.

Sediment samples were obtained as grab samples from the Potomac River in the DC metropolitan area. The samples were kept frozen until they were ready to be spiked. The locations of the various sites are given in Table 1.

Bacterium

The *E. coli* was obtained from the Biology Department at the University of the District of Columbia, Washington, DC, 20008. The concentration of the *E. coli* was determined by measuring its absorbance at 540 nm.

Preparation of Sediment Samples.

Five grams of sediment, 0.1 grams of the triorganotin, 10^6 cells of *E. coli* were added to 100 mL of nutrient agar broth since the *E. coli* did not survive in deionized water alone. The mixture containing the sediment, triorganotin, *E. coli*, and nutrient agar broth was then mechanically shaken in the dark for a period of two weeks at ambient temperature. The samples were kept in the dark for an additional week. Samples were shaken in the dark to simulate the natural environment of the sediment Also some triorganotins are known to degrade to other species when exposed to sunlight or UV light in a laboratory photo reactor (24). After three weeks, the sediment samples were filtered and frozen until the Mössbauer spectra were recorded. To identify the organotin species present, the experimental spectra were compared to spectra of known triorganotin compounds. Controls consisting of sediment, triorganotin and nutrient agar broth were also prepared and their Mössbauer were also used for comparison.

Mössbauer Spectral Studies.

The Mössbauer spectra were recorded using a Model MS-900 (Ranger Scientific Co., Burleson, TX) spectrometer in the acceleration mode with a moving source geometry. A 5 mCi $Ca^{119m}SnO_3$ source was used, and counts of 30,000 or more were accumulated for each spectrum. The spectra were measured at 80K using a liquid-nitrogen cryostat (CRYO Industries of America, Inc., Salem, NH). The velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed by a least-square fit to Lorenzian shaped lines.

Results and Discussion

Determination of structures of triorganotin compounds using various spectroscopic techniques is well documented in the literature. Mössbauer spectroscopy has proven very useful for determining the coordination and bonding in organotin compounds (1). Mössbauer spectroscopy yields two parameters, the isomer shift (IS) and quadrupole splitting (QS) values. The former is primarily sensitive to changes in *s*-electron density at the tin nucleus and the latter to the stereochemistry about the tin atom. The ratio of the quadrupole splitting to isomer shift values (ρ = QS/IS) has been used to determine the coordination number of the central tin atom. Tin compounds which are four coordinated have ρ values smaller than 1.8 while ρ values larger than 2.1 are indicative of compounds with greater than four coordination.[21]

A comparison of the QS and IS values of the pure compounds and the spiked compounds (control and bacterial) at the various sites indicate that the sediments affect the speciation of the compounds. This conclusion is based on the observation of the differences in the QS and IS Mössbauer parameters.

While the sediments affect the speciation of the compounds, the characteristics of the sediments at the different sites do not appear to affect the speciation. For example, the QS values in Table 2 for the TBTCl control samples (3.14 – 3.34 mm s^{-1}) in sites I, II, IV and V are within experimental error of each other. This is also true for the TBTCl samples containing bacteria whose QS values ranged from 3.14 to 3.41 mm s^{-1}. These findings, with the exception of site III, would suggest that, in general, the speciation of the TBTCl is independent of the characteristics of the sediments at these sites.

Similarly, the speciation of the TPTCl was independent of the sediment characteristics in sites I, II and IV. The QS values for the controls ranged from 2.77 to 2.86 mm s^{-1} while the bacterial samples ranged from 2.77 to 2.96 mm s^{-1}.

The stereochemistry of the tin atom can be deduced from the ρ values. As can be seen in Table 2, all the TBTCl spiked anaerobic samples have ρ values in the range 2.08 to 2.46, indicative of triorganotin compounds that are five coordinated. This is also true for the TPTCl spiked anaerobic samples (Table 3) with the exception of samples from sites III and V. The tin atoms in these samples are four coordinated.

In is also observed that the QS values for TPTCl spiked samples are lower than for the TBTCl spiked samples, which indicate that the geometry of the tin atoms in these samples are more symmetrical. This is not surprising since the phenyl groups are more symmetrical as compared to the butyl groups and thus, expected to lead to a more symmetrical species.

The higher observed IS values for the TBTCl can be rationalized by its electron donating abilities. It has been reported that an increase in electron density at the tin atom will increase the IS value (1). The data in tables 2 and 3 support this conclusion. In addition, the lower observed IS values for the TPTCl spiked samples indicate that there is less *s*-character in the tin atoms for these species.

The average QS and IS values for both TBTCl and TPTCl in the control and bacterial samples (Tables 2 and 3) are within experimental error, suggesting that the bacteria had no effect on the speciation of either compound. However, on closer examination, the data in Tables 2 and 3 indicate that there is a difference, beyond experimental error, in the QS values of the sediments with and without the bacteria, *E. coli,* for several sites. This would suggest that the *E. coli* is affecting the speciation of the triorganotins, however, the mechanism is not clear at present.

This study clearly indicates that the speciation of the triorganotins as well as the bacterial effects on the speciation is a function of several factors. These factors would include variation in the components of the sediments and the heterogeneous nature of the sediments. A fuller understanding of these variations awaits analyses of the structure of the sediments.

Table 1. Location of Potomac River Sediment Samples.

Site	Latitude	Longitude
1	38.89997 N	77.07510 W
2	38.89464 N	77.06253 W
3	38.88553 N	77.05939 W
4	38.85290 N	77.03464 W
5	38.82120 N	77.03790 W

Table 2. Mössbauer spectral parameters (mm s^{-1}) of anaerobic Potomac River Sediments spiked with tributyltin chlorides in the presence and absence of *E. coli*.

	TBTCl					
Site	**Control**			**Bacteria**		
	QS	IS	ρ	QS	IS	ρ
I	3.20	1.36	2.35	3.22	1.33	2.42
II	3.14	1.44	2.18	3.41	1.45	2.35
III	3.09	1.41	2.19	2.87	1.38	2.08
IV	3.34	1.34	2.54	3.14	1.43	2.20
V	3.27	1.42	2.37	3.34	1.36	2.46
Average	3.21	1.39	2.33	3.20	1.39	2.30
Pure Compound	3.38	1.54	2.19	---	---	---

Table 3. Mössbauer spectral parameters (mm s^{-1}) of anaerobic Potomac River Sediments spiked with triphenyltin chlorides in the presence and absence of *E. coli.*

	TPTCl					
Site	**Control**			**Bacteria**		
	QS	IS	ρ	QS	IS	ρ
I	2.86	1.21	2.36	2.77	1.16	2.39
II	2.85	1.19	2.39	2.96	1.18	2.51
III	2.38	1.12	1.92	2.08	1.17	1.78
IV	2.77	1.21	2.30	2.91	1.20	2.42
V	2.13	1.05	2.03	2.40	1.12	1.97
Average	2.60	1.16	2.20	2.62	1.17	2.21
Pure Compound	2.53	1.31	1.93	---	---	---

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Information Transfer Program

Water resources information transfer via the Institute website remains a problem and major obstacle to serve our stakeholders. Our expectation is that the new water quality extension agent will significantly impact the Institutes outreach capacity. The effort to enhance the Institutes website for added visibility and continues to be delayed because UDC website, which hosts WRRI webpage, is also being upgraded. We anticipate that UDC new website, with the Institutes upgrade, will be functional soon. The Institutes Directory of Water Resources Experts in the District continues to be updated. This has enabled us to reach out to a greater number of researchers in the consortium of DC Universities. Past publications are being scanned or electronic files converted into PDF files for future availability via our website. This project, though time consuming, is in progress and we anticipate completion by the end of FY 2004.

Dr. Jo Anne Favors at UDC trained 9 DC Public School Teachers through the Water Environment Studies in Schools Teacher Training Institute of the Agricultural Experiment Station. This report evaluates the effectiveness of the training program and its effect on some of DC Public Schools science programs ans students.

Water Environment Studies in Schools Training Program

Basic Information

Title:	Water Environment Studies in Schools Training Program
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Publication

WATER ENVIRONMENT STUDIES IN SCHOOLS
TEACHER TRAINING INSTITUTE

WATER ENVIRONMENT STUDIES IN SCHOOLS PROGRAM EFFECTIVENESS EVALUATION

Year - Three

Dr. Jo Anne Favors
UDC AGRICULTURAL EXPERIMENT STATION

WATER ENVIRONMENT STUDIES IN SCHOOLS PROGRAM EFFECTIVENESS EVALUATION

WATER ENVIRONMENT STUDIES IN SCHOOLS
TEACHER TRAINING INSTITUTE

CONTENTS

PROGRAM SUMMARY

INTRODUCTION

The University of the District of Columbia ("UDC") Agricultural Experimental Station ("AES") and Water Resource Research Center (WRRC), in collaboration with Kramer Middle, Browne Junior High, Terrell Jr High and Backus Jr. High Schools is proposing **Water Environment Studies In Schools ("WESS")** to engage students in the exploration, analysis and restoration of selected areas of the Anacostia River Watershed. This **WESS Teacher Training Institute** is designed as a pilot project to 32 Junior High and Middle High School teachers in two Institutes - 16 teachers in each Institute - during the summer. These Institutes will engage teachers in ten-days of extensive training in water quality assessment and conservation, with a follow-up ten-day summer program practicum with students. Teachers will implement the program in school during the academic year.

Program Overview

The **WESS** program is designed to respond to the need for: 1. environmental education in the schools, 2. teachers proficient in the writing of curriculum around the newly designed performance standards, and, 3. innovative practices to improve math and science teaching and learning of teachers and students as expressed by DCPS administrators and teachers. The **WESS** program's focus is the Anacostia River Watershed in which the students and teachers are residents. The goals of **WESS** provide for: 1. training for the schools' teachers in math, science, technology, art and humanities within water environmental studies; 2. involvement of students in the same discipline areas as required for the restoration and conservation of the Anacostia River and its flora and fauna; and 3. the development of a plan that engages the total community in the conservation of the Anacostia Watershed.

Program Goals

1. To establish a core group of teachers trained in the knowledge and technology to integrate environmental education into the total junior high school and middle school curriculum.

2. To provide teachers with the expertise to write curriculum that integrates the current performance standards and allows for their application and reinforcement in mathematics, science, arts and humanities through environmental education.

3. To provide teachers with the skills to help students to achieve and maintain the

academic standards necessary to bridge the transition from high school to college in science, mathematics and technology.

4. To increase the participation of minority youth in environmental issues and enhance their perspective of the effect they have on the environment through project focus on the Anacostia River.

5. To create a community movement to benefit the local environment issue which, in this case, is the Anacostia River.

Program Objectives

1. To engage teachers in the **WESS** Teacher Training Institute for a ten-day training session on the information and technology for implementing water environment studies programs with students.

2. To engage students in environmental studies that can reinforce skills and performance standards in math, science and computer technology, primarily; and arts and humanities in the process of learning the tasks necessary for the restoration and preservation of the Anacostia River Watershed.

3. To design a plan to improve the ecological integrity and aquatic diversity of the Anacostia River Watershed that includes strategies for reducing pollutant loads to improve water quality.

4. To establish collaborative and working partnerships with community residents and watershed restoration groups that can increase public awareness and participation in the clean up and restoration of the Anacostia River Watershed.

5. To familiarize youth and teachers with the unique careers in environmental and water quality management.

WESS Teacher Training Institute

The **WESS** Teacher Training Institute is designed to equip teachers with:

1. Knowledge and skills in the scientific testing, measurement and assessment and remote sensing of rivers, particularly the Anacostia River.

2. Curriculum development skills that integrate the Anacostia River scientific, social/political, and cultural aspects with the school’s performance standards, career development and college preparation.

3. A critical overview of the need for a citizenry knowledgeable of their environment and the causes and effects of their own actions. Specifically using the Anacostia River as the model in this case.

4. Planning Methods and Strategies for implementing Water Studies program that:

   -Utilize the research of AES and WRRC, provides experiences in data gathering and increases academic achievement for students;
   -Provide resources and skills for independent searching for appropriate materials and equipment;
   -Use the metropolitan area as a bank of people, places and things that serve as viable elements of a hands-on curriculum.

5. The ability to lead students to design and implement a plan and process for restoring the River.

**WATER ENVIRONMENT STUDIES IN SCHOOLS PROGRAM
EFFECTIVENESS EVALUATION
Year – Three**

Introduction

This report reflects highlights and summarizations of the major findings of the Water Environment Studies in Schools (WESS) Program, Teacher Training Institute (TTI), for Year Three. These highlights and summarizations are based upon evaluation measures that document the effectiveness of the goals and objectives of the program. This report also addresses the program's strengths as well as areas for improvement.

Methodology

Pre-post program surveys and daily testimonial (evaluation/comment) forms for each workshop session during the institute were completed by the participants, and workshop observations and monitoring critiques were conducted by the evaluator. The process for collecting the data follows:

- Pre Program Surveys were conducted at the beginning of each (TTI).
- Program Testimonial Forms were completed by the participants on a daily basis and collected at the end of each session.
- Post Program Surveys were conducted at the end of the TTI.
- Evaluator's Observation and Monitoring Critiques were conducted during intermittent workshops for each TTI session.

Overview

The Anacostia Watershed is the focus of the **Water Environment Studies in Schools (WESS)** Program of the Agricultural Experiment Station ((AES) and Water Resources Research Center (WRRC) of the University of the District of Columbia (UDC). This project is designed to respond to the school's needs for: 1) environmental education, 2) curriculum developed around the performance standards, and 3) innovative practices to improve math and science teaching and learning of teacher and students as expressed by DCPS administrators and teachers.

The targeted area and participants for this project are schools and residents (including teachers and students) of the Anacostia River Watershed. This WESS TTI was designed as a pilot project to engage 32 Junior High and Middle School teachers in two Institutes – 16 teachers in each Institute during the summer. Kramer Middle, Backus Middle, Browne Junior High, and Terrell Junior High Schools were identified as the pilot schools. However, due to constraints within DCPS during the first year of the project, the pilot schools were altered and a mixed cadre of schools and teachers participated in the WESS Program. Each year, since the pilot program, a variety of schools within the targeted area have participated in the project with emphasis being placed upon the participation of middle and junior high schools.

WESS Teacher Participants

This year, the project continued its expansion with a diverse population of teachers participating in the TTI. The thirty-two participants included teachers from elementary schools, education centers, middle, junior, and senior high schools as well as one college student. Some teachers were from schools of former participants and other teachers were from schools new to the program. The schools of former participants are: Backus MS, Kramer MS, Browne JHS, and P.R. Harris Education Center. The schools new to the program are: Birney ES, Wheatley ES, Garnet- Patterson MS, MacFarland MS, Jefferson JHS, Dunbar SHS, Mamie D. Lee School, and Clara Muhammad Charter School, as well as, Flowers SHS (PG County, Maryland) and UDC. The teacher from Flowers SHS (PG County, Maryland) and the student from UDC participated on a trial/pilot basis.

The pool of teachers consisted of two senior high, five junior high, eighteen middle level, five elementary, one special education, and one environmental education college student. This cadre included science, mathematics and technology teachers; reading, language arts, English, foreign language and social studies teachers; as well as a variety of specialists – media and special education.

The diverse composition of this group of teachers supported the purpose of this progam by helping to ensure that the message of the project was carried to many venues through a variety of disciplines. Further the diversity of the group provided for reinforcement throughout the various disciplines, and carried a linked and unified message from level to level (elementary to middle to junior to secondary to college level).

WESS TTI Workshops

The WESS TTI provided teachers with an overview of the Anacostia River Watershed, focusing on the environmental impact of the community's actions and the need for citizenry knowledge of their environment. This focus was addressed through a series of workshops that not only provided a pathway to water environmental studies, but also provided a model to introduce and/or enhance environmental education in the schools. The model also provided strategies and tools for teachers to use as a support in the design of their school's standards-based (national and local, performance and content standards) water environmental studies curriculum.

Through the multifaceted workshops that included cross-curricular components, teachers were able to observe, demonstrate and apply innovative practices and skills that are designed to improve mathematics and science teaching and learning of teachers and students. Through the use of technology and interpersonal connections, the teachers were able to form allies in soliciting and obtaining community support for the implementation of their school's environmental project.

A summary of each workshop follows:

Project WET – This workshop promoted awareness, appreciation, knowledge, and stewardship of water resources through the development and dissemination of classroom-ready teaching aids and through the establishment of state and internationally sponsored Project WET programs. Teachers received the Project WET Curriculum Guide and Rain Stick Book as well as learned modeling techniques to promote the enhancement of critical thinking skills in learners.

The Anacostia Watershed Society – Participants engaged in a discussion on the history and culture of the Anacostia River and experienced a canoe trip on the river. They also engaged in hands-on activities that can be used in the classroom.

USA TODAY Education – *Bringing Life into the Classroom with Real World Activities* is a workshop that demonstrated how cross-curricular topics can be taught utilizing relevant and timely articles found in the newspaper. Teachers engaged in hands-on exercises utilizing today's USA TODAY, examined environmental snapshops, explored *Before, During and After* learning strategies and surfed the net for additional online resources.

Wetland Nursery Pond – Participants worked with the staff from the National Aquarium of Baltimore to gain experience in constructing a Wetland Nursery Pond. The actual experience included preparing the area to hold water, separating and setting out plants, filling the pond with water and engaging in activities to support an understanding of the importance wetland areas.

Water Quality and Analysis – This workshop focused on the importance of water; properties of water; assessment, calculations and projections of water quality. Basic instruction was provided through lecture, discussion and hands on investigations; and then followed with internet explorations to acquire information for interpretation and application. As the study continued, teachers conducted water quality tests and analyzed the results of actual water samples from various points around the metro area including selected points along the Anacostia River.

Satellite Remote Sensing – The presenter of this workshop employed the use of U.S. Geological Maps and cartography to explain the science of remote sensing. Teachers explored "on-line" visuals and photographs of remote sensing graphics. Through the use of Excel software demonstrations and analyses were used to provide a more in depth understanding of this technology and it's application to the Anacostia Watershed.

The Value of Environmental Education – This workshop addressed local, national and international levels of environmental education. The teachers were able to make connections as to how local issues can impact national and international issues.

They explored the environmental monitoring activities of Green Peace, an international organization and engaged in activities relative to The Healthy and Safe Communities Campaign: "*Working to Protect Our Children, Families and Communities From Enviromental Threats and Hazards!!!*" and related those activities to the Anacostia River Watershed.

<u>The Value of Student Research on the Anacostia River</u> –This workshop provided teachers with data from student research projects. The data was presented for observation, analysis, and interpretation. Teachers were provided instruction on the use of Excel and other software to construct charts and graphs that revealed the impact and value of environmental monitoring.

<u>Art: The Design of Environmental Models and Variety of Materials Available</u> – This workshop demonstrated how art could be used as an intricate part of environmental education studies. The workshop focused on "recycling" and "reusing" materials in order to "reduce" trash. Sample activities included making use of such materials in the construction of costumes, jewelry, and models. In addition, teachers wrote poetry and short stories about the environment and conservation.

<u>Language Arts: The Inclusion of Literature, Writing and History into Environmental Studies</u> – During this workshop, a variety of venues, such as music, art, poetry and literature were used to address the topic, *Water Matters*. Overall, the workshop provided a link to connect environmental studies with other disciplines. Effective communication skills (reading, writing, speaking and listening) were emphasized and numerous opportunities were provided for the participants to demonstrate the use of these skills. Activities such as writing poetry, short stories and letters, or conducting a mock forum to express views and concerns about water issues, the Anacostia River in particular, were examples that demonstrated a means for curriculum integration.

<u>Applied Learning:</u> <u>Standards and Other Support</u> - The teaching and learning standards were a key component of the WESS TTI. The national and local, performance and content standards for mathematics, science, art, and language arts/humanities were addressed throughout each workshop. Teachers were provided opportunities to review standards documents and to align appropriate standards in preparation for the development of their lesson plan. Throughout the course of the TTI, teachers were provided with model lesson and unit plans, and a template to use in the development of their own lesson plan. They were provided with instructional expertise via the master teacher and technology-based information via the internet. They were provided with classroom instructional materials (kits, books, videos, measurement apparatus, etc.) and hands-on/guided instructions to support the development of their lesson and ultimately support their classroom instruction. Additionally, teachers were able to collaborate with their colleagues and share information and ideas on an informal professional level, which in turn supported their growth in knowledge and their understanding of standards, water studies and instructional techniques and strategies.

SUMMARY OF EFFECTIVENESS EVALUATION

Pre-Program Survey Responses

The responses from the Pre-Program Survey represent the prior experiences of the teachers and their initial attitude regarding formal environmental education before their experience and participation in the Institute. Twenty-nine (29) participants responded to the survey. Each provided a response to all of the questions.

1. Do you have a formal environmental education program at your school?

   Responses: Yes - 0% Maybe - 14% No – 86%

2. Have you led your students or co-workers in any environmental workshops or classes?

   Responses: Yes – 14% Maybe – 0% No – 86%

3. Do you believe you have the expertise to conduct classes of youth in water environmental studies?

   Responses: Yes – 28% Maybe – 14% No – 58%

4. Do you believe you have the competency to write a lesson plan on water environmental studies?

   Responses: Yes – 52% Maybe – 17% No – 31%

5. Do you feel competent to match lesson activity to the school's performance standards?

   Responses: Yes – 69% Maybe – 7% No – 24%

6. How do you expect to benefit from this Institute?

   Written responses (all) were among or similar to the following comments :

   - will gain information to improve writing skills and constructing lesson plans;
   - will be able to integrate water studies and environmental activities into the curriculum;
   - will use the information to make the students, teachers and staff aware of water pollution and conservation;
   - will gain knowledge to engage students in hands-on water environmental studies;
   - will grow professionally in the field of environmental studies.

7. How will your school benefit from this Institute?

   Written responses (all) were among or similar to the following comments:

   - will use ideas and strategies gained from TTI to form a school-wide interdisciplinary water environmental group to coordinate activities for our students;
   - will share with students, teachers and staff the importance of having an environmental studies program and knowing about water pollution;
   - will sensitize students to become wards of their environment;
   - will be able to test water quality in streams near the local school; and
   - will network and open avenues for our teachers to benefit through my professional development.

Summation of Pre-Program Survey Responses

The response data for question no. 1 indicates that the majority of the schools (86%) do not have a formal environmental education program, while a very low percentage of the schools (14%) may have a program.

The response data for question no. 2 indicates that the majority of the teachers (86%) have not led students or co-workers in environmental workshops or classes. Again, a very low percentage (14%) of the teachers have led either a workshop or a class for students and teachers.

The response data for question no. 3 indicates that a little more than half (58%) of the teachers do not believe they have the expertise to conduct classes of youth in water environmental studies, however they indicated they are willing to learn. 3% of the teachers believe they may be able to conduct classes of youth in water environmental studies with additional training and 37% believe they can conduct classes of youth in water environmental studies.

The response data for question no. 4 indicates that approximately two-thirds (73%) of the teachers believe that they have the competency to write a lesson plan on water environmental studies for youth. A few teachers (6%) indicate that they might be able to write the lesson plan with the support of the training staff. 31% of the teachers indicate that adequate training is needed in order to write the lesson plan.

The response data for question no. 5 indicates that the majority (75%) of the teachers feel competent to match lesson activity to school's performance standards. 6% indicate that they might be able to match the activity with the standards and the remaining 19% indicate that they are not ready.

The response data for question no. 6 indicates that the teachers in this Institute expect to gain knowledge about water pollution and conservation as well as strategies and activities that can be used to integrate the curriculum; and will gain information to increase environmental awareness for teachers, students and staff.

The response data for question no. 7 indicates that the schools will benefit from the teachers' experiences in the TTI in terms of their sharing their professional development; knowledge and understanding of water environmental studies; and through the formation of school-wide interdisciplinary water environmental groups to promote awareness, stewardship and hands-on learning.

There was no response data for the additional comments section.

Post-Program Survey Responses

The responses from the Post-program Survey represent the experiences of the teachers and their attitude regarding formal environmental education after their participation and closing experience in the Institute. Thirty (30) of the participants responded to the survey. Each provided a response to all of the questions.

Part I. Attitude Survey

1. Would you like to establish a formal environmental education program at your school?

   Responses:

Definitely not	0%
Probably not	0%
Don't know	3%
Probably yes	40%
Definitely yes	57%

2. Has the Teacher Training Institute provided you with the tools to lead your students or co-workers in any environmental workshops or classes in the coming academic year?

   Responses:

Definitely not	0%
Probably not	0%
Don't know	0%
Probably yes	30%
Definitely yes	70%

3. Do you believe you now have the expertise to conduct classes for youth in water environmental studies?

   Responses:

Definitely not	0%
Probably not	7%
Don't know	3%
Probably yes	40%
Definitely yes	50%

4. Do you believe you have the competency to write a lesson plan on water environmental studies for youth?

Responses:

Definitely not	0%
Probably not	0%
Don't know	0%
Probably yes	33%
Definitely yes	67%

5. Do you feel competent to match lesson activity to your school's performance standards?

Responses:

Definitely not	0%
Probably not	0%
Don't know	0%
Probably yes	40%
Definitely yes	60%

Part II: Best Experiences and Challenges - Responses

The following questions invite you to discuss further your reactions to the Teacher Training Workshop. Please help AES by highlighting both the successes and areas where you would recommend change.

6. Please explain the following:

Responses:

A. What has been the best experience for you in this training workshop?

- all aspects of the program;
- varied exercises and experiences;
- the canoe trip and Anacostia Watershed Society;
- learning about Project WET;
- using hands-on activities;
- interacting with others in class;
- learning about wetland ponds;
- discussions on water environment.

B. What has been the greatest success for you personally?

- sharing in thought provoking experiences and discussions;
- gaining information about the impact of racism and government policies in regards to environmental factors;
- gaining hands-on experiences with developing a wetlands pond;
- receiving and using excellent materials;
- gaining information on how to integrate subject areas through water studies;
- learning about the Anacostia River and experiencing the canoe trip;
- gaining information that will be used to educate students on how to help clean up the environment.

C. Has the workshop met your expectations?

- 20% - yes, the workshop has met my expectations;

D. Exceeded you expectations?

- 80% - yes, the Institute far exceeded my expectations;

E. Fallen short of your expectations?

- 0% - The workshops did not meet my expectations. One participant stated "some days seemed too long for a presenter."

F. How will your school benefit from the experience that you have had?

- information will be used to help educate the students on how to help clean up our environment;
- workshops on environmental water studies will be conducted for teachers at school.

7. Please explain the following:

Responses:

A. What unmet needs remain for you?

- more information on subject areas;
- more trips to water sites;
- more support with incorporating knowledge gained into lesson plans;
- testing products and materials (system and/or standardized) in order to conduct classes with students.

B. *What else needs to happen if you are to be able to offer water environmental studies for students in your school – as a lesson, a class or workshop, or a formal program?*

- access to more materials and supplies such as water testing products;
- support of administration and teachers participating in the program;
- to have environmental science put back into the curriculum;
- to have city officials be concerned enough to provide financial resources to further support the project.

C. *What challenges remain?*

- determining how to help others understand the need to save our water;
- securing funds to support hands on activities and field lab experiences for students;
- organizing my thoughts, resources and materials in order to construct a meaningful curriculum.

D. *What further help would you like from Agriculture Experiment Station?*

- follow-up service to this institute by providing a one-day or half-day meeting, later in the year to discuss up-dates and classroom/student experiences;
- the provision of speakers for school programs;
- assist with a series of water studies workshops conducted at the school level.

E. *What help would you like from school administrators?*

- support from the administrators;
- assistance with funding materials and resources for the program.

F. *From other teachers at your school?*

- encourage fellow teachers in the local school's science department to use the resources of the program.
- encourage fellow teachers in the local schools to participate in the TTI.

G. *From others in the workshop?*

- teachers should work cooperatively to develop a more clear understanding of what to do back at school by producing a plan of action.

8. Please explain the following:
   Responses:

   A. What would you like to recommend to UDC Agricultural Experiment Station for future Teacher Training Workshops?

   - the TTI workshops are excellent as presented;
   - that every presenter use hands-on activities;
   - train special group of students along with teachers to form an outreach group and promote stewardship;
   - a follow-up component to see the progression of the wetlands pond;
   - additional workshops during the school year;
   - provide handouts on CD/disk to save paper;
   - more trips to different waterways, Rock Creek;
   - more outdoor activities;
   - shorten the canoe trip, 5 miles is too long for new canoers;
   - provide parking.

   B. For other activities that could help launch formal environmental education programs in elementary, middle and secondary schools?

   - continue this environmental program as a means to benefit our schools in their awareness of water studies;
   - encourage the science department (DCPS) to include these tours and speakers as a support to the on-going curriculum;
   - provide information regarding the TTI earlier in the spring to allow more teachers to participate;
   - present the Institute more than once per year.

Part III. Plans for the coming year

9. Over the next academic year, are you now planning to do any of the following:

   Responses:

   • Use the Internet to collect further information on the environment

   Yes – 97%   Maybe - 3%   No - 0%

   • Acquire print resources from EPA, NASA or other sources on the environment

   Yes – 77%   Maybe - 23%   No - 0%

- Take further classes on environmental studies

  Yes – 50%   Maybe - 50%   No - 0%

- Offer a lesson or lessons in water environmental studies to students

  Yes – 90%   Maybe - 10%   No - 0%

- Involve students in environmental research projects

  Yes – 80%   Maybe - 20%   No - 0%

- Offer an environmental workshop to co-workers

  Yes – 44%   Maybe - 43%   No - 13%

- Take students on field trips to study the environment

  Yes – 84%   Maybe - 13%   No - 3%

- Launch an environmental research program in your school

  Yes – 47%   Maybe - 50%   No - 3%

Summation of Post-Program Survey Responses

Part I: Attitude Survey

The response data for question no. 1 indicates that more than half of the participants (57%) would like to establish a formal environmental education program at their school. Slightly less than half of the responses indicate that 40% probably would establish a program.   Only one person (5%) indicated that they are not sure whether or not they would establish a formal environmental education program.

The response data for question no. 2 indicates that the majority of the participants (70% definitely yes and 30% probably yes) consider that they have been provided with tools to lead students or co-workers in any environmental workshops or classes during the coming year.

The response data for question no. 3 indicates that the majority of participants (50% yes and 40% probably yes) believe that they have the expertise to conduct classes for youth in water environmental studies. One participant (3%) is not sure of their expertise and two participants (7%) believe that they probably lack the expertise to conduct the class.

The response data for question no.4 indicates that the majority (67% yes and 33% probably yes) believes that they have the competency to write a lesson plan on water environmental studies for youth.

The response data for question no. 5 indicates that the majority (60% yes and 40% probably yes) feels competent to match lesson activity to the school's performance standards.

Part II: Best Experiences and Challenges

These questions invited the participants to discuss their reactions to the Teacher Training Workshop. They included both successes and areas of recommendation for change.

The response data to question no. 6 resulted in a variety of answers in terms of the best experiences, greatest personal successes, workshop expectations and benefits to schools.

> Many participants indicated all aspects of the program were the best, while others sited specific components of the program such as, but not limited to Project WET, the canoe trip, hands-on experiences, and sharing interactive information with and among classmates. Though this compilation of responses each segment was sited as a best experience.
>
> Responses to the greatest personal success focused on three categories: interacting through thought provoking discussions and gaining new ideas; coming to the realization of the impact of racism and government policies on environmental issues; and hands-on experiences (involving the Anacostia River and AWS as a whole) that will be incorporated into instructional practices to educate the students.
>
> The responses to workshop expectations indicated that the workshops either met expectations (20%) or exceeded expectations (80%). There were no responses indicating that the workshop did not meet their expectations, however, one participant stated "some days seemed too long for a presenter."
>
> Responses defining school benefits from teacher experiences indicate that information on environmental studies and the Anacostia River Watershed will be shared through classes for students and teacher workshops.

The response data to question no. 7 represents needs and recommendations for the program.

> The majority of the responses indicated that there were no unmet needs. However the remaining responses indicated the following recommendations: 1) a need for prepared testing products and materials to use with students in order to support further alignment of this program with school standards and curriculum;

2) a need for additional support with developing lesson plans; and 3) a need for environmental science to be put back into the schools' curriculum.

Responses to challenges indicated a personal need for time to conduct research work in order to collect data on resources and work on plans to support the implementation of the program; and a need for promotional strategies to support the development of the program in the community with students and citizens.

Responses to further the assistance from AES indicate a need for follow-up service to the workshop by promoting a one-day or half day meeting later during the school year to provide updates and classroom/student experiences.

Responses regarding the help participants would like from school administrators indicate a need for administrative and financial support to ensure the implementation of the program.

The responses regarding help the participant would like from other teachers indicate that fellow teachers within the school should be encouraged to use the resources of the program and should be encouraged to participate in the training.

The response regarding help the participant would like from others in the workshop indicate that all teachers should work cooperatively to develop a clear, detailed school action plan for implementing and sharing the program.

The response data to question no. 8 represents recommendations to AES for the future Teacher Training Workshops.

Responses indicate that UDC AES consider the following recommendations for future Teacher Training Workshops: ensure that every instructor present hands-on activities; include a special group of students in the summer training component; provide handouts on CDs to conserve paper; provide a follow-up component including revisiting field trips (i.e., wetlands pond) and up dating experiences with fellow Summer Institute classmates.

Responses regarding activities that could be used to launch formal environmental education programs in other schools indicate that the WESS program should visit schools to help tie program into the existing curriculum and present the TTI more than once per year.

Responses to no. 9 indicate that the participants are considering the following plans for the coming year. The majority (97% yes and 3% maybe) will further their use of the Internet to collect information on the environment. The majority (90% yes and 10% maybe) will teach water environmental studies lessons to students. The majority of participants (84% yes and 13% maybe) will take field trips and involve their students in environmental research projects, while one participant (college student) responded no. The majority (77% yes and 23% maybe) will acquire print resources from environmental organizations. 50% yes and 50% maybe indicate they will take further environmental education classes. Less than one-half (44%) will offer workshops to their co-workers, 43% indicated maybe and 13% indicated no. Slightly less than one-half (47%) responded yes to - launch an environmental research program in your school, while 50% responded maybe and one participant (college student) responded no.

WESS TTI Monitor's Critique for Sessions I and II - Sampling

During each of the sessions various workshops were monitored and critiqued. The observations assessed the presenter's strategies, the engagement and participation of the teachers, and the relevancy of the activities as they pertain to the WESS program. The following review will provide an overview of the session and will include the strengths, areas of improvement needed, and recommendations as they apply to the session.

- Project WET: The presenter engaged teachers in numerous hands-on experiences and modeled for them a variety of ways to teach water studies through an integrated curriculum. The strategies included such examples as conducting investigations to determine water quality; solving number-based problems; reading for understanding and interpretation; and identifying water-forms and habitats. This workshop also modeled the use of making various cultural connections in an effort to personalize the activities as well as bring in historical facts for students. This workshop was rated highly among the participants and often listed as a favorite in their daily testimonials.

- Wetlands Pond: This workshop was facilitated by a team of instructors who helped the participants form cooperative learning groups in an effort to prepare for the setting up process of the pond. An overview along with modeling instructions for each activity associated with the set up process for the pond was provided for the class. Each team was given an opportunity to engage in the various segments of the pond set up process which included: preparing the area and constructing the pond; identifying, sorting and separating the grasses; planting the grasses; and filling the pond with water. Following these activities the participants then proceeded to engage in activities that would simulate a study of the wetlands. All participants were given materials to design a model of a wetland area and resource materials to help support their understanding of the concept. It was further noted that these materials could serve as a tool for the participants to use with their students in teaching "the need to care for the survival of wetlands." The presentation and the involvement of participants with the activities were in direct alignment with the goals of the WESS Program. There was high enthusiasm for this workshop and it was also reflected in the participants' daily testimonials.

To support the effectiveness of this workshop the recommendation would be to plan a follow-up visit for the teachers and more importantly to provide an opportunity for the students from the schools to visit the site and conduct investigations.

WESS TTI Testimonial Responses for Sessions I and II - Sampling

The following data represents a sampling of the participants' responses to the testimonials that were collected each day. The sampling shows the correlation of the workshops presented throughout the Institute and represents on-site instructional lab activities and off-site first hand field lab experiences. This sampling includes responses from both TTI sessions for the Water Quality and Analysis workshop and the Anacostia Watershed workshop. The testimonials are in response to the following statement:

> The overall objectives of the Water Environment Studies In Schools program is to empower teachers to engage their students in: water quality assessment, wetlands studies, environmental monitoring, the application of computer technology in program development and problem solving activity, and the formation of community support for environmental conservation.

<u>Workshop: Water Quality and Analysis</u>

What do you believe you learned today?

- *Water Quality Assessment, Wetlands*
  - how important water and the quality of water is to the environment;
  - basic facts about water (physical and chemical qualities of water);
  - how to test water with chemicals and various instruments;
  - how pollution affects the Anacostia River; and
  - how DC water compares to bottled water.

- *Technology Application*
  - how to conduct a computer search, analysis, charting and graphing;
  - learned good websites; and
  - how to prepare a presentation on water using power point.

- *Environmental Monitoring Plan*
  - learned planning methods and strategies for implementing a water studies program;
  - learned history of the Anacostia River; and
  - learned to organize information to support the design of the curriculum.

- *Community Support*

  - how to apply the WESS program to a school/community project through classroom instruction, technology and field trips; and
  - think clearly about activities and resources for the enhancement of community support.

2. What helped you reach your goal?

   - using the computer to compute, analyze and chart graphics;
   - using the computer to problem solve and to access information;
   - environmental conservation and environmental monitoring; and
   - collaboration among team colleagues.

3. Favorite part of the program so far?

   - testing water for impurities;
   - hands-on activities;
   - discussions - environmental factors that are affected by water;
   - using computers to make charts; and
   - discovering new experiences.

<u>Workshop: Anacostia Watershed Society</u>

1. What do you believe you learned today?

- *Water Quality Assessment, Wetlands*
  - how pollutants affect the Anacostia River;
  - how the pollution in the Anacostia River and other water forms affects all living creatures; and
  - observed and learned basic facts about wetland revitalization of marshland.

- *Technology Application*

  - how to use various instruments to conduct water quality test.

- *Environmental Monitoring Plan*

  - learned more about the history of the Anacostia River; and
  - learned to canoe a boat along the river in order to collect samples to make first hand observations.

- *Community Support*

  - how to apply the WESS program to a school/community project through classroom instruction, technology and field trips; and
  - think clearly about activities and resources for the enhancement of community support; and
  - the importance of sharing the message to keep the rivers clean.

What helped you reach your goal?

- canoeing along the river;
- using instruments to collect actual data along the river;
- environmental conservation and environmental monitoring; and
- collaboration among team colleagues.

Favorite part of the program so far?

- the canoe trip;
- hands-on experiences;
- real-life learning, learning by doing;
- exploring materials shared by the instructors and interacting with colleagues.

Summation of Testimonials

Each day, participants completed a form, addressing the above questions. The responses for question no. 1 indicate what the participants have learned for the day in regards to water quality assessment, wetlands studies, environmental monitoring, the application of computer technology in program development and problem solving activity, and the formation of community support for environmental conservation. These items address the goals and objectives of the program. Favorable responses to these questions indicates that the participant is on target and is meeting the goals and objectives for the program.

Questions no. 2 and no. 3 serve as reinforcement to question no. 1. These testimonials indicate that the participants are learning how to operate and/or become more proficient with the use of a computer, as well as use other technical support to study the overall facts about water and how pollution affects the river. The complete set of testimonials may be found in the appendix.

The two sets of data show the correlation between the sessions and how the participants are able to build upon the acquired knowledge in each of the workshops.

Summary Of Survey Results

This information documents the analysis of the results of participant responses to Pre-Program and Post-Program Surveys. This information is reflective of 29 pre-program responses and 30 post-program responses of the 32 participants who represent 14 schools.

The Pre-Program Survey responses indicated that of the 14 schools participating, four may have formal environmental programs. The responses indicated that 4 of the 29 teachers have previously led student or coworker environmental workshops. The responses indicated 8 of the 29 participants believe they have the expertise to conduct classes in environmental studies for youth. Fifteen of the 29 teachers believe they have competency to write a plan on water environmental studies and 20 of 29 feel competent to match lesson activity to performance standards.

The Testimonial responses provided indications of self-growth, confidence, and personal accomplishments as a result of their participation in the WESS Teacher Training Institute.

Post-Program Survey responses indicated that all schools to a degree (yes/probably yes) with the exception one would like to establish a formal environmental program. The one exception being the college student, with a response of "don't know."

All participants, to a degree (yes/probably yes), indicated that the TTI provided them with tools to lead students or co-workers in any environmental workshop course.

The majority of the participants, to a degree (yes/probably yes), indicated that they have the expertise to conduct classes for youth on water studies. One response indicated "don't know" and two responses indicated "probably not."

All participants, to a degree (yes/probably yes), indicated that they have competency to write a lesson plan on water environmental studies.

All participants, to a degree (yes/probably yes), indicated that they feel competent to match lesson activity to their school's performance standards.

Indication of Goals and Objectives Met:

In general, the responses indicate that the WESS Teacher Training Institute participants have gained an awareness of water environmental education, in particular, the Anacostia Watershed. The responses indicate that the workshops were facilitated and guided by knowledgeable, expert presenters, whose instructional skills enhanced the participants' use of technology and their use of the Internet to access information and apply it to the development of personalized standards-based curricular for their schools. This curricular includes a match of national and district, content and performance standards.

Further, the responses indicate that during the workshop sessions, participants have engaged in activities that provided knowledge and skills to support student improvement in mathematics, science and technology. They also gained instructional strategies that support the integration of scientific, social and cultural aspects of teaching and learning. They have designed a plan that engages the community in the conservation of the Anacostia Watershed. The responses also indicate that the participants will promote citizenry knowledge of the Anacostia River Watershed through classroom instruction, workshops and community forums with the support of environmental speakers and environmental projects.

Additionally, the daily testimonials and the monitors critique support the responses to the post survey summary.

Strengths of the WESS TTI

Based upon the evaluation of the program the following strengths are documented:

- Range of Schools: The broad range of schools from elementary to middle level to junior high to senior high provides a continuum of the program and prepares building blocks for each level of awareness of environmental studies. The inclusion of the college student and teacher from Prince George County Public Schools, Maryland furthered the broadening concept of the program.

- Diversity of Subject Area Teachers: The inclusion of teachers in all subject areas helps to strengthen the program by broadening the instructional base for broadcasting the importance of water studies and water conservation.

- Use of Standards: The inclusion of standards (national and local, performance and content) makes for a complete curriculum for lessons and units in relation to the school's required standards.

- Integration of Discipline: The integration of the disciplines (science, mathematics, art, language arts/literature) again helps to ensure that the environmental message is being delivered to the students as well as the community through a variety of venues.

- Variety of Environmental Workshop Sessions: The variety of environmental education sessions associated with the importance of water and water quality helps enlighten the participants as far as their responsibility in communicating the message "to help conserve the environment and keep water safe." The variety of sessions also models different means for broadcasting the message and levels of involvement.

- Field Trips: The inclusion of the field trips provides a concrete hands-on experience that vividly identifies for the participants the need to help protect "our" water sources.

- Use of Resources in the Program: The use of the computer and Internet accessibility, the newspaper connection and supplemental resources, and integrated water programs (Project Wet) enhance the participants ability to gather information and supports the structural development and design of lesson plans.

- Expertise of Instructors: The knowledgeable and expert instructors provide a wealth of information in terms of content, instructional skills, innovative practices, and resources.

Need for Improvement:

Based upon the evaluation of the program the following areas of improvement are needed:

- Providing a variety of teaching/learning strategies to ensure that each participant is understanding (connecting) with the material being presented.

- Explaining how the goals of the project relate to each workshop in an effort to ensure each participants understanding and connection.

Recommendations for WESS TTI:

Based upon the evaluation of the program the following recommendations are made:

- Establish a forum whereby participants can meet to collaborate, reflect and share ideas and strategies to support the program.

- Plan a follow-up for teachers to visit the Wetlands Nursery Pond and (if possible, avail this opportunity for the students from the participating schools so that they can conduct on-site investigations).

- Re-institute student involvement through the summer program.

- Continue to share environmental education grant opportunities with participants in an effort to support their acquisition of additional funding sometimes needed to assist the development environmental programs.

- Invite school administrators to participate in the program on a part-time or full time basis to help ensure their support of the program.

The overall study of the WESS Program indicates that there is continued growth among the participating teachers and that they have gained an awareness of the importance of water environmental studies. Further, they recognize the importance of continuing this program.

Student Support

None

Notable Awards and Achievements

Publications from Prior Projects