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**D.C. DEPARTMENT OF HEALTH**

*Environmental Health Administration*

*Bureau of Environmental Quality*

*Water Quality Division*

**TAM/WASP TOXICS SCREENING LEVEL MODEL  
FOR THE TIDAL PORTION OF THE ANACOSTIA RIVER  
Final Report**

**April 2003**



Government of the  
District of Columbia  
Anthony A. Williams, Mayor

D.C. DEPARTMENT OF HEALTH  
ENVIRONMENTAL HEALTH ADMINISTRATION  
BUREAU OF ENVIRONMENTAL QUALITY  
WATER QUALITY DIVISION

TAM/WASP TOXICS SCREENING LEVEL MODEL  
FOR THE TIDAL PORTION OF THE ANACOSTIA RIVER  
Final Report

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## TABLE OF CONTENTS

LIST OF TABLES .....	<a href="#">vi</a>
LIST OF FIGURES .....	<a href="#">viii</a>
ACKNOWLEDGMENTS .....	<a href="#">xii</a>
EXECUTIVE SUMMARY .....	<a href="#">xiii</a>
CHAPTER 1: INTRODUCTION .....	<a href="#">1</a>
1.1. Background .....	<a href="#">1</a>
1.2. TAM/WASP Modeling Framework .....	<a href="#">2</a>
1.3. Sediment Transport Model Component .....	<a href="#">4</a>
1.4. Data Support .....	<a href="#">5</a>
1.4.1. Storm and Non-Storm Monitoring Data .....	<a href="#">5</a>
1.4.2. Main Channel Water Column Data .....	<a href="#">6</a>
1.4.3. Bed Sediment Chemical Concentration Data .....	<a href="#">7</a>
1.5. Model Constituents .....	<a href="#">9</a>
1.5.1. Inorganic Chemicals Sub-Models .....	<a href="#">9</a>
1.5.2. PCB Sub-Model .....	<a href="#">9</a>
1.5.3. PAH Sub-Model .....	<a href="#">11</a>
1.5.4. Chlordane/Heptachlor Epoxide Sub-Model (PEST1) .....	<a href="#">12</a>
1.5.5. Dieldrin Sub-Model (PEST2) .....	<a href="#">12</a>
1.5.6. DDT Sub-Model .....	<a href="#">13</a>
CHAPTER 2: MODEL INPUTS .....	<a href="#">21</a>
2.1. Hydrodynamic Model Inputs .....	<a href="#">21</a>
2.2. Sediment Transport Model Inputs .....	<a href="#">23</a>
2.3. Partition Coefficients .....	<a href="#">25</a>
2.4. Chemical Load Inputs .....	<a href="#">31</a>
2.4.1. Upstream Loads .....	<a href="#">32</a>
2.4.2. CSO Loads .....	<a href="#">32</a>
2.4.3. Lower Beaverdam Creek Loads .....	<a href="#">33</a>
2.4.4. Other Tributaries and Separate Storm Sewer Loads .....	<a href="#">33</a>
2.5. Confidence Intervals for Upstream Storm Concentration Estimates .....	<a href="#">38</a>
CHAPTER 3: MODEL CALIBRATION/VERIFICATION .....	<a href="#">41</a>
3.1. General Calibration Strategy .....	<a href="#">41</a>
3.2. Discussion of Calibration Data .....	<a href="#">43</a>
3.2.1. Estimation of Bed Sediment Segment Concentration Averages .....	<a href="#">43</a>
3.2.2. Estimates of Ambient Water Column Concentrations From Fish Tissue Data .....	<a href="#">47</a>

3.3. Calibration Results .....	<a href="#">62</a>
3.3.1. Metals (Metals1) Sub-Model .....	<a href="#">62</a>
3.3.2. Arsenic (Metals2) Sub-Model .....	<a href="#">95</a>
3.3.3. PCB Sub-Model .....	<a href="#">101</a>
3.3.4. PAH Sub-Model .....	<a href="#">125</a>
3.3.5. Chlordane and Heptachlor Epoxide (PEST1) Sub-Model .....	<a href="#">143</a>
3.3.6. Dieldrin (PEST2) Sub-Model .....	<a href="#">155</a>
3.3.7. DDT Sub-Model .....	<a href="#">163</a>
 CHAPTER 4: CONCLUSION .....	 <a href="#">174</a>
 LIST OF ACRONYMS AND ABBREVIATIONS .....	 <a href="#">177</a>
 REFERENCES .....	 <a href="#">178</a>

**LIST OF TABLES**

Table 1-1. Number of Surficial Sediment Sampling Stations per Chemical from AWTA/NOAA Database ..... [8](#)

Table 1-2. Constituents Represented ..... [14](#)

Table 1-3. Rational for PCB Groupings ..... [15](#)

Table 1-4. Rational for PAH Groupings ..... [16](#)

Table 2-1. Model Flow Input Summary ..... [23](#)

Table 2-2. TAM/WASP Annual Sediment Load Estimates ..... [25](#)

Table 2-3. Summary of Anacostia River (AR), Northeast/Northwest Branches (NE/NW) and Literature  $K_d$  Values (L/kg/1000) ..... [28](#)

Table 2-4. Summary of Storm flow (SF) and Base flow (BF) Concentration Estimates Based on Available Monitoring Data ..... [35](#)

Table 2-5. Sampling Methods and Detection Limits for Water Column Data Sets ..... [36](#)

Table 2-6. Statistical Uncertainty in Northeast/Northwest (NE/NW) Branches Storm flow Concentration Means ..... [39](#)

Table 3-1. Average Segment Sediment Concentrations (ng/g dry weight) ..... [45](#)

Table 3-2. Estimated Water Column Concentration for Selected Chemicals Based on Fish Tissue Concentrations ..... [47](#)

Table 3-3. Sensitivity Test Results: Predicted Total Mass in Bed Sediment ..... [66](#)

Table 3-4. WASP Input Parameters for Metals1 Sub-Model ..... [67](#)

Table 3-5. Concentrations Used to Compute Metals1 Sub-Model Calibration Run Input Loads ..... [68](#)

Table 3-6. Average Annual Load Contributions and Losses by Source for Calibrated Metals1 Sub-Model ..... [70](#)

Table 3-7. WASP Input Parameters for Metals2 Sub-Model ..... [96](#)

Table 3-8. Concentrations Used to Compute Metals2 Sub-Model Calibration Run Input Loads ..... [97](#)

Table 3-9. Average Annual Load Contributions and Losses by Source for Calibrated Metals2 Sub-Model ..... [100](#)

Table 3-10. Estimated Annual Atmospheric Deposition of Total PCBs to the Anacostia River ..... [105](#)

Table 3-11. Concentrations Used to Compute PCB Sub-Model Calibration Run Input Loads (ug/L) ..... [106](#)

Table 3-12. WASP Input Parameters for PCB Sub-Model ..... [107](#)

Table 3-13. Measured Atmospheric Concentrations of PCB Homologs ..... [108](#)

Table 3-14. Average Annual Load Contributions and Losses by Source for Calibrated PCB Sub-Model ..... [109](#)

Table 3-15. Concentrations Used to Compute PAH Sub-Model Calibration Run Input Loads (ug/L) ..... [130](#)

Table 3-16. WASP Input Parameters for PAH Sub-Model ..... [131](#)

Table 3-17. Comparison of Washington Gas Annual PAH Load (kg/year) Estimates Based on Average PAH Concentrations in Groundwater and Sediment ..... [132](#)

Table 3-18. Measured Atmospheric Concentrations of PAHs ..... [133](#)

Table 3-19. Estimated Annual Atmospheric Deposition of Total PAHs to the Anacostia River ..... [133](#)

Table 3-20. Average Annual Load Contributions and Losses by Source for Calibrated PAH Sub-Model ..... [134](#)

Table 3-21. Comparison of Average Annual PAH Kinetic Losses ..... [134](#)

Table 3-22. Concentrations Used to Compute PEST1 Sub-Model Calibration Run Input Loads (ug/L) ..... [146](#)

Table 3-23. WASP Input Parameters for PEST1 Sub-Model ..... [147](#)

Table 3-24. Average Annual Load Contributions and Losses by Source for Calibrated PEST1 Sub-Model ..... [148](#)

Table 3-25. Concentrations Used to Compute PEST2 Sub-Model Calibration Run Input Loads (ug/L) ..... [157](#)

Table 3-26. WASP Input Parameters for PEST2 Sub-Model ..... [158](#)

Table 3-27. Average Annual Load Contributions and Losses by Source for Calibrated PEST2 Sub-Model ..... [159](#)

Table 3-28. Concentrations Used to Compute DDT Sub-Model Calibration Run Input Loads (ug/L) ..... [166](#)

Table 3-29. WASP Input Parameters for DDT Sub-Model ..... [167](#)

Table 3-30. Average Annual Load Contributions and Losses by Source for Calibrated DDT Sub-Model ..... [167](#)

Table 4-1. Model Predictions of Total Accumulated Mass in Bed Sediment ..... [176](#)



**LIST OF FIGURES**

Figure 1-1. Anacostia Watershed ..... [17](#)

Figure 1-2. TAM/WASP Version 2 Model Water Column Segmentation ..... [18](#)

Figure 1-3. Schematic Representation of Model Bed Sediment Segmentation ..... [19](#)

Figure 1-4. Bed Sediment Chemical Concentration Sampling Locations ..... [20](#)

Figure 2-1. TAM/WASP Model Sub-sheds and Sub-shed Types ..... [40](#)

Figure 3-1. Estimated zinc concentrations (ppm) in Anacostia River surficial bed sediments . [48](#)

Figure 3-2. Estimated lead concentrations (ppm) in Anacostia River surficial bed sediments . [49](#)

Figure 3-3. Estimated copper concentrations (ppm) in Anacostia River surficial bed sediments  
..... [50](#)

Figure 3-4. Estimated arsenic concentrations (ppm) in Anacostia River surficial bed sediments  
..... [51](#)

Figure 3-5. Estimated total PCBs concentrations (ppb) in Anacostia River surficial bed  
sediments ..... [52](#)

Figure 3-6. Estimated phenanthrene (representative of PAH Group 1) concentrations (ppb) in  
Anacostia River surficial bed sediments ..... [53](#)

Figure 3-7. Estimated benz[a]anthracene (representative of PAH Group 2) concentrations (ppb)  
in Anacostia River surficial bed sediments ..... [54](#)

Figure 3-8. Estimated benzo[a]pyrene (representative of PAH Group 3) concentrations (ppb) in  
Anacostia River surficial bed sediments ..... [55](#)

Figure 3-9. Estimated total chlordane concentrations (ppb) in Anacostia River surficial bed  
sediments ..... [56](#)

Figure 3-10. Estimated heptachlor epoxide concentrations (ppb) in Anacostia River surficial bed  
sediments ..... [57](#)

Figure 3-11. Estimated dieldrin concentrations (ppb) in Anacostia River surficial bed sediments  
..... [58](#)

Figure 3-12. Estimated p,p' DDD concentrations (ppb) in Anacostia River surficial bed  
sediments ..... [59](#)

Figure 3-13. Estimated p,p' DDE concentrations (ppb) in Anacostia River surficial bed  
sediments ..... [60](#)

Figure 3-14. Estimated p,p' DDT concentrations (ppb) in Anacostia River surficial bed  
sediments ..... [61](#)

Figure 3-15. Metals Bed Sediment Results: Base Model and Calibrated Model (Upstr Lead  
Loads x 0.5) ..... [71](#)

Figure 3-16. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: Calibrated  
Model;  $K_d$ 's x 4;  $K_d$ 's/4 ..... [72](#)

Figure 3-17. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: Calibrated  
Model;  $K_d$ 's x 4;  $K_d$ 's/4 ..... [73](#)

Figure 3-18. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results:  
Calibrated Model;  $K_d$ 's x 4;  $K_d$ 's/4 ..... [74](#)

Figure 3-19. Dissolved Zinc Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x 4;  
 $K_d$ 's/4 ..... [75](#)

Figure 3-20. Dissolved Lead Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x

4; $K_d$ 's/4	<u>76</u>
Figure 3-21. Dissolved Copper Water Column Sensitivity Test Results: Calibrated Model; $K_d$ 's x 4; $K_d$ 's/4	<u>77</u>
Figure 3-22. Summary of Average Annual Loads and Losses for the Calibrated Metals1 Sub-Model	<u>78</u>
Figure 3-23. Metals Bed Sediment Sensitivity Test Results: $K_d$ 's x 4; $K_d$ 's/4	<u>79</u>
Figure 3-24. Metals Bed Sediment Sensitivity Test Results: Med $K_d$ /Fine $K_d$ Changed to 1; to 1/10	<u>80</u>
Figure 3-25. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: Med $K_d$ /Fine $K_d$ Changed 1; to 1/10	<u>81</u>
Figure 3-26. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: Med $K_d$ /Fine $K_d$ Changed 1; to 1/10	<u>82</u>
Figure 3-27. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results: Med $K_d$ /Fine $K_d$ Changed 1; to 1/10	<u>83</u>
Figure 3-28. Dissolved Zinc Water Column Sensitivity Test Results: Med $K_d$ /Fine $K_d$ Changed 1; to 1/10	<u>84</u>
Figure 3-29. Dissolved Lead Water Column Sensitivity Test Results: Med $K_d$ /Fine $K_d$ Changed 1; to 1/10	<u>85</u>
Figure 3-30. Dissolved Copper Water Column Sensitivity Test Results: Med $K_d$ /Fine $K_d$ Changed 1; to 1/10	<u>86</u>
Figure 3-31. Metals Bed Sediment Results - Calibrated Model (Version 2.3) vs. Sediment Model (Version 2.1)	<u>87</u>
Figure 3-32. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: TAM/WASP V2.3 (Calibrated Model) vs. V2.1	<u>88</u>
Figure 3-33. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: TAM/WASP V2.3 (Calibrated Model) vs. V2.1	<u>89</u>
Figure 3-34. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results: TAM/WASP V2.3 (Calibrated Model) vs. V2.1	<u>90</u>
Figure 3-35. Metals Bed Sediment Results: Potomac Boundary Conditions x 2; x 1/2	<u>91</u>
Figure 3-36. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: Potomac Boundary Conditions x 2; x 1/2	<u>92</u>
Figure 3-37. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: Potomac Boundary Conditions x 2; x 1/2	<u>93</u>
Figure 3-38. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results: Potomac Boundary Condition x 2; x 1/2	<u>94</u>
Figure 3-39. Arsenic Bed Sediment Results	<u>98</u>
Figure 3-40. Predicted vs. Measured Water Column Concentrations for Total Arsenic	<u>99</u>
Figure 3-41. Summary of Average Annual Loads and Losses for Arsenic (Metals2) Sub-Model	<u>100</u>
Figure 3-42. PCB Bed Sediment Results: Base Scenario and Calibrated Model (Loads x 3)	<u>110</u>
Figure 3-43. Summary of Average Annual Loads and Losses for the Calibrated PCB Sub-Model	<u>111</u>
Figure 3-44. PCB1 Water Column Results for the Base Scenario	<u>112</u>

Figure 3-45. PCB2 Water Column Results for the Base Scenario ..... [113](#)

Figure 3-46. PCB3 Water Column Results for the Base Scenario ..... [114](#)

Figure 3-47. PCB1 Water Column Results for the Calibrated (3 x Loads) Scenario ..... [115](#)

Figure 3-48. PCB2 Water Column Results for the Calibrated (3 x Loads) Scenario ..... [116](#)

Figure 3-49. PCB3 Water Column Results for the Calibrated (3 x Loads) Scenario ..... [117](#)

Figure 3-50. PCB Bed Sediment Sensitivity Test Results: All  $K_d$ 's x 10; All  $K_d$ 's x 1/4 .... [118](#)

Figure 3-51. PCB1 Water Column Sensitivity Test Results: Both  $K_d$ 's x 1/4 ..... [119](#)

Figure 3-52. PCB2 Water Column Sensitivity Test Results: Both  $K_d$ 's x 1/4 ..... [120](#)

Figure 3-53. PCB3 Water Column Sensitivity Test Results: Both  $K_d$ 's x 1/4 ..... [121](#)

Figure 3-54. PCB1 Water Column Sensitivity Test Results: Both  $K_d$ 's x 10 ..... [122](#)

Figure 3-55. PCB2 Water Column Sensitivity Test Results: Both  $K_d$ 's x 10 ..... [123](#)

Figure 3-56. PCB3 Water Column Sensitivity Test Results: Both  $K_d$ 's x 10 ..... [124](#)

Figure 3-57. PAH Bed Sediment Results: Base Model and Calibrated model (Loads x 1.5) . [135](#)

Figure 3-58. Total (Dissolv. + Partic.) PAH Water Column Results, Calibrated Model Versus Katz et al. (2000) Single Event Data ..... [136](#)

Figure 3-59. Particulate PAH1 Water Column Results, Calibrated Model Versus Coffin et al. (1998) Data ..... [137](#)

Figure 3-60. Particulate PAH2 Water Column Results, Calibrated Model Versus Coffin et al. (1998) Data ..... [138](#)

Figure 3-61. Particulate PAH3 Water Column Results, Calibrated Model Versus Coffin et al. (1998) Data ..... [139](#)

Figure 3-62. Summary of Average Annual Loads and Losses for the Calibrated PAH Sub-Model ..... [140](#)

Figure 3-63. PAH Bed Sediment Sensitivity Test Results: Addition of Decay Interactions .. [141](#)

Figure 3-64. PAH Bed Sediment Sensitivity Test Results: Changes in Decay Constants .... [142](#)

Figure 3-65. Chlordane/Heptachlor Epoxide Bed Sediment Results: Base Model and Calibrated Model (Loads x 0.7) Predictions ..... [149](#)

Figure 3-66. Summary of Average Annual Loads and Losses for the Calibrated PEST1 Sub-Model ..... [150](#)

Figure 3-67. Chlordane Water Column Results for Base/Calibrated Model ..... [151](#)

Figure 3-68. Chlordane/Heptachlor Epoxide Bed Sediment Sensitivity Test Results: Calibrated Model Predictions with Air Concentrations Reduced to 0. .... [152](#)

Figure 3-69. Chlordane/Heptachlor Epoxide Bed Sediment Sensitivity Test Results: Potomac Boundary Concentrations x 10, x 100. .... [153](#)

Figure 3-70. Heptachlor Epoxide Bed Sediment Sensitivity Test Results:  $K_d \rightarrow K_d/2$  ..... [154](#)

Figure 3-71. Dieldrin Bed Sediment Results for Base/Calibrated Model ..... [160](#)

Figure 3-72. Summary of Average Annual Loads and Losses for the Calibrated Dieldrin (PEST2) Sub-Model ..... [161](#)

Figure 3-73. Dieldrin Bed Sediment Sensitivity Test Results - Potomac Boundary Concentration x 10 ..... [162](#)

Figure 3-74. DDT Bed Sediment Results: Base and Calibrated (with Load Adjustments) Models ..... [168](#)

Figure 3-75. DDE Base Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data ..... [169](#)

Figure 3-76. DDT Base Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data ..... [170](#)

Figure 3-77. DDE Calibrated Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data ..... [171](#)

Figure 3-78. DDT Calibrated Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data ..... [172](#)

Figure 3-79. Summary of Average Annual Loads and Losses for the Calibrated DDT Sub-Model ..... [173](#)

Figure 4-1. TAM/WASP Toxic Screening Level Model Predictions of Total Accumulated Mass in Bed Sediment (upper 1 cm; before load adjustments) ..... [176](#)

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## EXECUTIVE SUMMARY

The Anacostia River runs through the heart of our nation's capital and drains an urban/suburban watershed that covers a portion of the District of Columbia and its Maryland suburbs. The Anacostia has long suffered from ills common to urban rivers, including low levels of dissolved oxygen, high sedimentation rates, high bacteria counts, and problems arising from the presence of toxic chemicals. Toxic chemicals including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), metals, and pesticides such as chlordane and dichloro-diphenyl-trichloroethane (DDT) have been detected in the river's bed sediments. Fish consumption advisories have been in place since 1987 due to unacceptable levels of PCBs and chlordane in certain Anacostia fish. PAHs are suspected to be the cause of the high rate of tumors in brown bullheads in the Anacostia reported by the U.S. Fish and Wildlife Service. A preliminary risk assessment for the Anacostia Watershed Toxics Alliance (AWTA) found that a variety of species of aquatic life, birds, and mammals were potentially at risk due to the presence of toxic chemicals in the river. Because of problems related to toxic chemicals, the Anacostia was designated a "Region of Concern" by the Chesapeake Bay Program in 1993.

The District of Columbia Department of Health (DC DOH) has developed the *Anacostia River Toxics Management Action Plan* to serve as a guide for addressing the problem of toxic chemicals in the river. The Anacostia has been placed on the District's 303(d) list of impaired waterbodies, and the District has in place a program to determine Total Maximum Daily Load (TMDL) allocations for toxic chemicals that will allow the Anacostia to meet water quality standards.

To assist in the TMDL allocation process, DC DOH has asked the Interstate Commission on the Potomac River Basin (ICPRB) to construct a computer model capable of simulating the daily concentrations of toxic chemicals in the District's portion of the Anacostia River, and of predicting the changes in these concentrations under potential load reduction scenarios. This model, the TAM/WASP Toxics Screening Level Model, simulates the loading, fate, and transport of toxic chemical contaminants in the tidal portion of the Anacostia River, and can predict the changes over time of concentrations of these contaminants in both the river's water and in the surficial bed sediment. The model includes three primary components:

1. A hydrodynamic component, based on the Tidal Anacostia Model (TAM), originally developed at MWCOG in the 1980's. This component simulates the changes in water level and water flow velocities throughout the river due to the influence of tides and due to the various flow inputs entering the river.
2. A load estimation component Water containing sediment and chemicals flows into the river every day from a variety of sources, including the upstream tributaries (the Northeast and Northwest Branches), the tidal basin tributaries (Lower Beaverdam Creek, Watts Branch and others), the combined sewer system overflows, the DC separate storm sewer system, and ground water. The ICPRB load estimation component estimates daily water flows into the river based on local stream flow and precipitation data, and estimates daily sediment and chemical loads into the river, based on available monitoring data.

3. A water quality component, based on the EPA's Water Quality Analysis Simulation Program, Version 5 (WASP-TOXI5) for sediments and toxic contaminants. This component simulates the physical and chemical processes that transport and transform chemical contaminants that have entered the river. The WASP sediment/toxics transport module has been enhanced by ICPRB to more realistically simulate sediment erosion and deposition processes based on hydrodynamic conditions.

The TAM/WASP Toxics Screening Level Model consists of seven sub-models which simulate the loading, fate, and transport of zinc, lead, copper, arsenic, PCBs, PAHs, chlordane, heptachlor epoxide, dieldrin, and DDTs in the tidal portion of the Anacostia River. The underlying sediment transport model is the same as that which was used, with only very minor changes, for development of the District's sediment TMDL for the Anacostia. It simulates the loading and transport of three classes of sediment grain sizes ( $< 30 \mu\text{m}$ ,  $> 30 \mu\text{m}$  and  $< 120 \mu\text{m}$ ,  $> 120 \mu\text{m}$ ), and quite successfully predicts the observed spatial pattern of grain-size distribution in the river bed sediment.

The seven sub-models were calibrated individually with varying amounts of data support, and only a few changes were made to model input parameters during the calibration process. For all constituents but arsenic, site-specific data was available to estimate values for  $K_d$ 's, the parameters which govern partitioning between the dissolved and solid phases. During the calibration process,  $K_d$ 's for some constituents were adjusted in order to improve model predictions of water column dissolved concentrations. Also, for constituents for which there was no data on Potomac River concentrations, downstream boundary condition concentrations were estimated via calibration to bed sediment data. Finally, when long-term predictions of model segment bed sediment concentrations (last day of six-year run) were very different from segment averages computed from available data, calibration adjustments were made to initial constituent load estimates. Calibration load adjustments were made for lead, heptachlor epoxide, PCBs, PAHs, and DDTs.

Overall, the TAM/WASP Screening Level Toxics Model does a good job in accounting for load inputs of toxic chemicals to the tidal Anacostia. Though the total mass of various contaminants residing in the surficial bed sediment (upper 1 centimeter) varies over five orders of magnitude, from about 0.02 kg for heptachlor epoxide to almost 8,000 kg for zinc, model predictions of total mass vary from 13% to 252% of observed mass, before calibration load adjustments are made. After calibration load adjustments, model predictions of sediment mass range from 49% to 182% of observed mass. In cases in which data is available, predictions of the calibrated model match observed water column concentrations reasonably well. Also, the model is able to reproduce to some extent the spatial pattern of contaminant concentrations observed in the bed sediment, with concentrations generally highest in the wider, slower moving downstream portion of the river.

From the error analysis of upstream storm concentration estimates and the various sensitivity test runs, it appears that model errors are dominated by uncertainties in the load estimates, with load confidence intervals likely in the range of -50% to +300%. The use of the calibration load adjustment factors was an effort to use information from contaminant bed sediment data to

reduce this error. There is also a great deal of uncertainty in the  $K_d$  values used as model inputs because of the high variability of  $K_d$ 's computed from site-specific data. However, sensitivity test runs for metals and PCBs indicate that changes in  $K_d$ 's have little effect on bed sediment concentration predictions for many of the contaminants modeled, though they do have a significant effect on dissolved water column concentration predictions. An analysis supports this finding by showing that, for constituents with relatively large  $K_d$ 's (say  $> 200$  L/g), particulate concentrations are relatively insensitive to changes in  $K_d$ 's, while dissolved concentrations are approximately proportional to  $1/K_d$ .

Additional data support is necessary to address the current limitations of the TAM/WASP Screening Level Model. Key data gaps and corresponding model uncertainties include:

- Uncertainties in chemical load estimates, currently probably in the range of about -50% to +300%, could be reduced by additional storm water monitoring data for the upstream tributaries, Lower Beaverdam Creek, and the separate sewer and combined sewer systems, especially from outfalls in the vicinity of apparent sediment “contaminant hot spots”. In order to support quantification of toxic chemical loads, it is necessary to use analytical techniques with sufficiently low detection limits.
- Uncertainty concerning the importance of ground water load inputs could be improved by the collection of ground water monitoring data at several locations adjacent to the river, again, using sufficiently low analytical detection limits. Currently, the model uses upstream base flow monitoring results to estimate chemical concentrations in ground water inputs.
- Lack of information concerning decay processes, such as biodegradation and photolysis, for chemicals such as PAHs, could be addressed by collection of a comprehensive water column calibration data set, including data to assess seasonal variations in concentrations. Decay rate coefficients are currently estimated by using values found in the published literature, which often vary by several orders of magnitude.
- Lack of understanding of the importance of potential mixing processes, such as bioturbation, methane gas bubble generation, and tidal pumping effects, could be addressed by the collection of radioisotope and other types of data to characterize vertical mixing in the sediment bed. At this time it is not possible to assess the potential for recontamination of recently deposited sediments by underlying sediments due to these processes, and sediment bed mixing processes are not currently simulated by the model.

At the time of preparation of this report, a number of studies, funded by the DC DOH, AWTA, and other groups, are being conducted to begin filling in some of these data gaps. A better understanding of some of the issues listed above will lead to improvements in the predictive capabilities of the TAM/WASP Screening Level Toxics Model.



## CHAPTER 1: INTRODUCTION

The Anacostia River runs through the heart of our nation's capital and drains an urban/suburban watershed that covers a portion of the District of Columbia and its Maryland suburbs. The Anacostia has long suffered from ills common to urban rivers, including low levels of dissolved oxygen, high sedimentation rates, high bacteria counts, and problems arising from the presence of toxic chemicals. Toxic chemicals including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), metals, and pesticides such as chlordane and dichloro-diphenyl-trichloroethane (DDT) have been detected in the river's bed sediments (Velinsky et al., 1992; Velinsky et al., 1994; Wade et al., 1994; Velinsky et al., 1997; Velinsky and Ashley, 2001). Fish consumption advisories have been in place since 1987 due to unacceptable levels of PCBs and chlordane in certain Anacostia fish. PAHs are suspected to be the cause of the high rate of tumors in brown bullheads in the Anacostia reported by the U.S. Fish and Wildlife Service (Pinkney et al., 2000; 2002). A preliminary risk assessment for the Anacostia Watershed Toxics Alliance (AWTA) found that a variety of species of aquatic life, birds, and mammals were potentially at risk due to the presence of toxic chemicals in the river (Syracuse Research Corporation, 2000). Because of problems related to toxic chemicals, the Anacostia was designated a "Region of Concern" by the Chesapeake Bay Program in 1993.

The District of Columbia Department of Health (DC DOH) has developed the *Anacostia River Toxics Management Action Plan* (DC Environmental Regulation Administration, 1996) to serve as a guide for addressing the problem of toxic chemicals in the river. The Anacostia has been placed on the District's 303(d) list of impaired waterbodies, and the District has in place a program to determine Total Maximum Daily Load (TMDL) allocations for toxic chemicals that will allow the Anacostia to meet water quality standards. To assist in the TMDL allocation process, DC DOH has asked the Interstate Commission on the Potomac River Basin (ICPRB) to construct a computer model capable of simulating the daily concentrations of toxic chemicals in the District's portion of the Anacostia River, and of predicting the changes in these concentrations under potential load reduction scenarios.

### 1.1. Background

The Anacostia River begins in Bladensburg, Maryland, at the confluence of its two major tributaries, the Northeast Branch and the Northwest Branch, and flows a distance of approximately 8.4 miles before it discharges into the Potomac River in Washington, DC. Its watershed encompasses an area of approximately 176 square miles in the District of Columbia and Maryland. The watershed lies within two physiographic provinces, the Piedmont Plateau and the Coastal Plain, whose division runs approximately along the Montgomery/Prince Georges County line. The upper northwestern portion of the watershed lies within the Piedmont Plateau province, characterized by steep stream valleys and well-drained loamy soils underlain by metamorphic rock. The remainder of the basin lies within the Coastal Plain province, a wedge-shaped mass of primarily unconsolidated sediments drained by slowly meandering streams. The location of the watershed and its three major drainage areas, the Northeast Branch, the Northwest

Branch and the tidal drainage areas, are depicted in Figure 1-1. The drainage areas of the Northeast and Northwest Branches, 53 mi<sup>2</sup> and 76 mi<sup>2</sup>, respectively, comprise approximately 73% of the total area of the watershed. Because of its location in the Washington metropolitan area, the majority of the watershed is highly urbanized, with a population of 804,500 in 1990 and a projected population of 838,100 by the year 2010 (Warner et al., 1997). An analysis of GIS layers prepared by the Metropolitan Washington Council of Governments (MWCOG), indicates that land use in the watershed is approximately 43% residential, 11% industrial/commercial, and 27% forest or wetlands, with 22.5% of the area of the watershed covered by impervious surfaces (see Shepp et al., 2000).

The Anacostia River is actually an estuary, with tidal influence extending some distance into the Northeast and the Northwest Branches, approximately to the United States Geological Survey (USGS) gage stations 01649500 at Riverdale Road, and 01651000 at Queens Chapel Road (see Figure 1-1). However, water in the tidal portion of the river is fresh water, with negligible values of salinity. The variation in the river's water surface elevation over a tidal cycle is approximately 3 feet. From an analysis by the National Oceanographic and Atmospheric Administration (NOAA) of sounding data taken by the US Army Corps of Engineers prior to a 1999 dredging project combined with additional bathymetry data taken by the Navy in the summer of 2000, the volume of the tidal portion of the river at mean tide is approximately 10,000,000 cubic meters (m<sup>3</sup>), with a surface area of approximately 3,300,000 square meters (m<sup>2</sup>). The width of the river varies from approximately 60 meters (m) in some upstream reaches to approximately 500 m near the confluence with the Potomac, and average depths across channel transects vary from approximately 1.2 m upstream of Bladensburg to about 5.6 m just downstream of the South Capital Street Bridge. The average daily combined discharge of the Northeast and Northwest Branches into the tidal river is approximately 370,000 m<sup>3</sup>. During non-storm conditions, measured flow velocities during the tidal cycle have been in the range of 0 to 0.3 m/sec (Katz et al., 2000; Schultz and Velinsky, 2001).

## **1.2. TAM/WASP Modeling Framework**

The TAM/WASP Toxics Screening Level Model simulates the loading, fate, and transport of toxic chemical contaminants in the tidal portion of the Anacostia River, and can predict the changes over time of concentrations of these contaminants in both the river's water and in the surficial bed sediment. The toxics model is based on ICPRB's TAM/WASP modeling framework, which was first used to construct a eutrophication/sediment oxygen demand model for the District's dissolved oxygen TMDL (Mandel and Schultz, 2000). The sediment transport capabilities of the model were then further developed, resulting in TAM/WASP Version 2.1 (Schultz, 2003), which was used by the District to develop its suspended solids TMDL. The TAM/WASP Toxics Screening Level Model, TAM/WASP Version 2.3, uses, with only minor changes, the hydrodynamic model and the sediment transport model components of Version 2.1.

The TAM/WASP Toxics Screening Level Model includes three primary components:

1. A hydrodynamic component, based on the Tidal Anacostia Model (TAM), originally

- developed at MWCOG in the 1980's (Sullivan and Brown, 1988). This component simulates the changes in water level and water flow velocities throughout the river due to the influence of tides and due to the various flow inputs entering the river. The original 15 segment hydrodynamic model has been upgraded by ICPRB to a 36 segment model with side embayments (Schultz, 2003).
2. A load estimation component, constructed by ICPRB using Microsoft ACCESS. Water containing sediment and chemicals flows into the river every day from a variety of sources, including the upstream tributaries (the Northeast and Northwest Branches), the tidal basin tributaries (Lower Beaverdam Creek, Watts Branch and others), the combined sewer system overflows (CSOs), the DC separate storm (SS) sewer system, and ground water. The ICPRB load estimation component estimates daily water flows into the river based on USGS gage data for the Northwest and Northeast Branches and National Airport daily precipitation data for flows from other sources. It also estimates daily sediment and chemical loads into the river, based on available monitoring data.
  3. A water quality component, based on the EPA's Water Quality Analysis Simulation Program, Version 5 (WASP-TOX15) for sediments and toxic contaminants (Ambrose et al., 1993). This component simulates the physical and chemical processes that transport and transform chemical contaminants that have entered the river. The WASP sediment/toxics transport module has been enhanced by ICPRB to more realistically simulate sediment erosion and deposition processes based on hydrodynamic conditions (see Schultz, 2003).

TAM/WASP is a one-dimensional (1-D) model, that is, it simulates processes in the river by idealizing the river as a long channel where conditions may vary along the length of the channel but are assumed to be uniform throughout any channel transect (i.e. from left bank to right bank). Approximating the river as a one-dimensional system is reasonable given the results of the summer 2000 SPAWAR study (Katz et al., 2001), which concluded that throughout a channel transect, the water in the river was generally well-mixed, and current velocities were relatively homogenous and primarily directed along the axis of the channel. It is also supported by model simulations carried out subsequent to a dye study conducted in 2000 by LimnoTech, Inc. (LTI) (LTI, 2000). These results showed that a 35 segment 1-D model was capable of simulating fairly well the time evolution of dye concentrations in the tidal river (DC WASA, 2001; Schultz, 2003)

In ICPRB's TAM/WASP Version 2, the main channel is divided along its length into 35 model water column segments, extending from the Bladensburg Road bridge in Prince Georges County, MD, to the Anacostia's confluence with the Potomac in Washington, DC (see Figure 1-2). Additionally, WASP model segment 36, representing Kingman Lake, adjoins segment 19. (Kingman Lake is represented as a tidal embayment to segment 19 in ICPRB's upgraded version of the TAM hydrodynamic model.) Each of these 36 water column segments is underlain by a surficial sediment segment (segments 37 to 72), and each surficial sediment segment is underlain by a segment of the lower sediment layer (segments 73 to 108), as shown schematically in Figure 1-3. Surficial sediment segment 72 and lower sediment segment 108 underlie water column segment 36, representing Kingman Lake, and are not represented in Figure 1-3. In all but the PCB sub-model, the surficial bed sediment layer is 1 centimeter (cm) in thickness and the lower

bed sediment layer is 5 cm in thickness. Unlike the other TAM/WASP sub-models, the PCB sub-model has four bed sediment layers instead of two (see Chapter 3).

### 1.3. Sediment Transport Model Component

A complete description of the TAM/WASP Version 2 sediment transport model is available in ICPRB's report on the model calibration (Schultz, 2003). A brief summary of the model is given below.

It is known that the transport properties of sediments depend on sediment grain size. The WASP model allows the simulation of the fate and transport of up to three sediment grain size fractions. In TAM/WASP Version 2, the three sediment size fractions modeled are:

<u>Frac1</u> : coarse-grained sediments:	> 120 $\mu\text{m}$	(fine sands to gravel)
<u>Frac2</u> : medium-grained sediments:	> 30 $\mu\text{m}$ and < 120 $\mu\text{m}$	(fine silts to very fine sands)
<u>Frac3</u> : fine-grained sediments	< 30 $\mu\text{m}$	(clays and very fine silts)

In TAM/WASP Version 1, a new capability was added to WASP-TOXI5 by ICPRB to allow simulation of sediment transport based on model hydrodynamics (Mandel and Schultz, 2000). This capability has undergone further development in TAM/WASP Version 2, to support the use of the model for the prediction of fate and transport of toxic chemicals (Schultz, 2003). The fine-grained and medium-grained sediment fractions are treated in TAM/WASP as cohesive sediments, and the algorithms governing their transport follow the approach developed by Partheniades (1962) and Krone (1962), which has frequently been employed in other models, such as the Hydrologic Simulation Program FORTRAN, (HSPF) model (Bicknell et al. 1993) and the Army Corps of Engineer's HEC-6.

For the two cohesive sediment fractions, erosion and deposition are a function of bed shear stress. Erosion occurs when shear stress exceeds a critical shear stress and is proportional to the extent it exceeds the critical shear stress. Similarly, the deposition of cohesive sediment occurs when shear stress is less than a critical threshold--distinct from the critical shear stress for erosion--and occurs in proportion to the drop in shear stress below the threshold. Bed shear stress is calculated from the slope of the energy grade line, which is determined by solving Manning's equation, resulting in a relationship between bed shear stress and flow velocity. Distinct values of the zero-flow settling velocity, the erosion velocity multiplier, critical shear stress, and the critical deposition threshold are entered by the user for fine-grained and medium-grained sediment fractions.

To model the transport of the coarse-grained sediment fraction, a simple power law method is used. The transport of the coarse-grained sediment fraction (i.e. sand and gravel) is modeled by

determining the carrying capacity of the flow, which in turn is dependent on the flow's hydrodynamic properties. If flow conditions change so that the carrying capacity exceeds the concentration of sand currently being transported, additional sand will be eroded from the bed. If the concentration of sand exceeds its carrying capacity, sand will be deposited.

The TAM/WASP sediment transport model, in addition to predicting water column concentrations of total suspended solids (TSS) that are in reasonably good agreement with available data, does a good job of predicting the spatial pattern of bed sediment grain size distribution, including the high proportion of coarse-grained sediment found near the mouths of the upstream tributaries and Watts Branch and the high proportion of fine-grained sediment found in the downstream portion of the tidal river.

#### **1.4. Data Support**

This modeling effort relies upon a number of data sets to compute model inputs and to provide data for model calibration and verification. The data sets used to support the hydrodynamic and sediment transport components of the model were discussed in the report on the sediment transport model calibration (Schultz, 2003). The primary data sets used to support the toxic chemical fate and transport component of the model are described in the sections below.

##### **1.4.1. Storm and Non-Storm Monitoring Data**

Storm and non-storm monitoring data are used to compute daily storm flow and base flow load inputs for the model. The following three data sets were those primarily used for load calculations:

Upstream tributary study by Gruessner et al. (1998) ICPRB conducted a study for DC DOH on toxic chemical concentrations in the upstream tributaries to the Anacostia, the Northeast and Northwest Branches. For this study, water samples were collected from both tributaries in 1995-96 during four storm events and six non-storm events and concentration values were reported for all chemicals modeled except arsenic. Chemical analyses were performed at detection limits low enough to quantify loads. Sample collection locations were at the US Geological Survey's Northeast Branch and Northwest Branch gage stations, Stations 01649500 and 01651000, shown in Figure 1-1.

District of Columbia MS4 monitoring data (Nicoline Shelterbrandt, private communication, 2002) The Water Quality Division of the DC DOH is conducting Municipal Separate Storm Sewer System (MS4) monitoring at a number of locations as part of the requirements for the District's National Pollutant Discharge Elimination System (NPDES) permit (MS4 NPDES Permit No.DC0000221, First Annual Review, Volume III). For this modeling effort, ICPRB had available MS4 monitoring data collected from June 1, 2001 through June 13, 2002 at the following locations in the Anacostia tidal basin: Stickfoot sewer, O St. pumping station (separate

sewer line), Gallatin at 14 St., Varnum and 19th Place (later Varnum and 22<sup>nd</sup> Place), Nash Run, Hickey Run at V St. and 33<sup>rd</sup> St., Oklahoma and D St., and East Capitol Street (west). In this dataset, for some of the chemicals modeled, results have been reported at detection limits low enough to quantify loads.

Prince Georges County Monitoring Data (Dr. Mou Soung Cheng, private communication, 2001) Prince Georges (PG) County collects samples from Lower Beaverdam Creek and Watts Branch at locations in PG County as part of its storm water monitoring program, and these samples are analyzed for a variety of chemicals including zinc, lead, and copper and other metals. For this modeling effort, ICPRB had available data from the years 1994-99.

DC Water and Sewer Authority Long Term Control Plan Monitoring In 1999 and 2000 the District of Columbia Water and Sewer Authority (DC WASA) conducted monitoring of storm water discharges from CSOs as well as some tributaries and SS locations, in support of its development of its Long Term Control Plan (LTCP) to address the CSO problem (DC WASA, 2000a; 2000b; 2000c). Though the primary aim of the monitoring study was to better understand loads of constituents contributing to the dissolved oxygen problem in the river, some analyses were also done for toxic contaminants. Though detection limits used for analyses for organic chemicals were not low enough to provide data to quantify loads, useful data was obtained for metals.

#### **1.4.2. Main Channel Water Column Data**

Data on water column concentrations of chemicals in the main channel of the Anacostia make possible a comparison of model predictions with empirical observations, and are used in the model calibration and verification process. Data from the following studies was used in the calibration/verification of the TAM/WASP Toxics Screening Level Model:

Study on the effects of stormwater runoff (Velinsky et al., 1999) In this study, water samples were collected in 1998 at seven stations in the main channel of the Anacostia, as well as at three additional locations: in the Potomac River near the confluence with the Anacostia, and at the Northeast and Northwest Branches. Samples were collected on four days prior to storm events, and on five days subsequent to storm events. Data is available for some of the chemicals included in the model, with detection limits low enough to be suitable for comparison with model predictions.

Study on the fate and transport of sorbed PAHs (Coffin et al., 1998) In this study, water samples were collected at four stations in the main channel of the Anacostia during 3 sampling events (November 1997, February 1998, and May 1998). Water samples were analyzed for concentrations of sorbed PAHs only (i.e. total and dissolved constituents not reported).

Study on the distribution of PAHs along the tidal Anacostia (Katz et al., 2000) In this study, water samples were collected at 14 stations in the main channel of the Anacostia during a 1-day

sampling period, on July 12, 2000. Water samples were analyzed for concentrations of total PAHs, as well as other constituents.

### **1.4.3. Bed Sediment Chemical Concentration Data**

Data on toxic chemical concentrations in the river's bed sediment is used, with the help of Geographic Information System (GIS) software, to characterize the spatial pattern of chemical contaminants in the river bed (see Section 3.2.1). These empirical results are then compared with model predictions of bed sediment contaminant concentrations as part of the model calibration and verification process. The most comprehensive bed sediment concentration data set was collected by Velinsky and Ashley in 2000. In addition, several smaller historical (post-1994) data sets were used to provide information on contaminant concentrations in areas immediately adjacent to facilities that are thought to be potential sources of certain contaminants. Figure 1-4 shows the sediment sampling locations for the studies listed below:

#### Study of chemical contaminants in Anacostia River bed sediments (Velinsky and Ashley, 2001)

In September of 2000, in a study sponsored by the DC DOH and the AWTA, bed sediment samples were collected from 128 locations within the main channel of the Anacostia or nearby areas in the Potomac. Samples were analyzed for a wide variety of chemical contaminants, including all of the constituents considered in this modeling effort.

AWTA/NOAA Database NOAA has constructed a database for the Anacostia Watershed Toxics Alliance containing a number of historical data sets with bed sediment contamination data (NOAA, 2001). Many of these data sets are a result of site investigations conducted by individual facilities located adjacent to the river. For the calibration of the TAM/WASP Toxics Screening Level Model, the post-1994 data sets from this database were combined with the data collected by Velinsky and Ashley to provide a picture of sediment contamination in the Anacostia. Table 1-1, below, contains a summary of the relevant studies extracted from this database as well as the number of stations for each chemical.

**Table 1-1. Number of Surficial Sediment Sampling Stations per Chemical from AWTA/NOAA Database**

Study <sup>1</sup>	Zinc	Lead	Copper	Arsenic	PCB	PAH	Chlordane	Hepta Epox	Dieldrin	DDT
1995 PEPCO	5	5	x	x	5	x	6	4	5	5
1995 Washington Navy Yard	7	7	7	7	1	40	x	x	x	7
1996 FWS PAH/PCB - Mason Neck	x	x	x	x	x	x	x	x	x	2
1996 WA Gas - East Station Project	8	8	8	7	x	7	x	x	x	x
1996 Wetland Restoration - Kenilworth	2	2	2	2	x	x	2	2	x	x
1997 DC Sed Core Analysis	6	6	6		6	x	6	1	6	6
1998 USACE Federal Navy Channel	4	4	4	4	x	x	x	x	x	4
1999 WA Navy Yard RI	32	32	32	30	x	x	x	x	x	x
2000 Velinsky AR Sed <sup>2</sup>	128	128	128	x	126	125	122	122	119	120
Total # of Stations	192	192	187	50	138	172	136	129	130	144

<sup>1</sup> All data from studies extracted from AWTA/NOAA database (NOAA, 2001) with the exception of 2000 Velinsky AR Sed.

<sup>2</sup> source: Velinsky and Ashley (2001).



## 1.5. Model Constituents

The TAM/WASP Toxics Screening Level Model uses WASP-TOXI5 to simulate many of the chemical and physical transformation processes that affect the fate of toxic chemicals in the river. Because WASP-TOXI5 can only simulate three chemicals at a time, a total of seven sub-models have been constructed. Most of the organic chemicals considered are actually classes of related constituents, including isomers and breakdown products. For a given class of chemicals, for example, DDTs, data was not available for all of constituents in the class, and therefore the sub-model only includes those constituents for which there is adequate data support. Also, for some sub-models, constituents are grouped together for convenience because of WASP's limitation of three chemicals. In these cases an effort is made to group together constituents with similar physical and chemical properties. The sub-models and the constituents represented in each of them are given in Table 1-2. Tables 1-3 and 1-4 list some of the physical and chemical properties by sub-model grouping of PCB homologs and of individual PAHs, and are meant to provide a rationale for the choice of groupings.

### 1.5.1. Inorganic Chemicals Sub-Models

Two sub-models have been constructed to simulate the fate and transport of inorganic chemicals in the tidal Anacostia. The METALS1 sub-model simulates the fate and transport of zinc, lead, and copper, and the METALS2 sub-model simulates the fate and transport of arsenic. These substances are widely used and ubiquitous in our environment. Zinc is commonly used as a protective coating for other metals, a component of many common metal alloys, and in many manufacturing processes and household goods, including batteries, pigments, and pharmaceuticals. Though environmental concerns have significantly decreased the use of lead in our society, it was formerly used widely as a gasoline additive, a paint additive, and in solder for drinking water pipes. Lead is still used in automotive and other types of batteries. Copper is widely used in metal alloys, and it is also used in fungicides and insecticides, and as a nutrient in fertilizers and animal feeds. Arsenic is used in wood preservatives, as a additive of metal alloys, in the manufacture of materials used in semiconductors, as a livestock feed additive, and in herbicides and pesticides. (From ATSDR, 1994a; 1999; 2002a; 2000a.)

### 1.5.2. PCB Sub-Model

Polychlorinated biphenyls (PCBs) are a group of 209 related compounds (congeners) that are formed by the addition of one or more chlorine atoms to a biphenyl molecule. The biphenyl structure consists of two 6-carbon rings linked by a single carbon-carbon bond and has ten binding sites that can be occupied by either chlorine or hydrogen atoms. Individual congeners differ in the number and position of the chlorine atoms on the biphenyl, and congeners with the same number of chlorines are chemical homologs. For example, PCBs containing two chlorines are called dichlorobiphenyls, and the congeners 2,2' dichlorobiphenyl and 2,4 dichlorobiphenyl belong to the same homolog group, dichlorobiphenyl. Depending on the

number of chlorine atoms (1 to 10) , homologs are called mono, di, tri, tetra, penta, hexa, hepta, octa, nona, or deca chlorobiphenyl.

PCBs were commercially produced in the United States from 1929 until 1977 when their production was banned and were sold as complex mixtures mostly under the Aroclor trade name. Most PCBs are light colored oily liquids, but some are also waxy solids. Because PCBs are chemically and thermally inert and have a high dielectric constant, they were widely used as heat transfer, hydraulic, and dielectric fluids, but were also used in variety of industrial applications including the production of inks, carbonless copy paper, paints, pesticides, adhesives, and plasticizers in rubber and plastic products (ATSDR 2000b).

Accidental releases and inappropriate disposal techniques coupled with the general inertness of PCBs has led to extensive environmental contamination. Once released into the environment, PCBs are taken up by biota. Due to their lipophilicity, they are stored in the fatty tissues of animals and bioaccumulate up the food chain. Concern over the environmental persistence and toxicity of PCBs led Congress to enacted Section 6 of the Toxic Substances Control Act in 1976, which, among other items, provides EPA with the authority to regulate the manufacture, processing, distribution in commerce, use and disposal of PCBs. These regulations have been amended several times, but currently ban the production of PCBs in the United States, restrict the use of PCB-containing materials still in service, prohibit the discharge of PCB-containing material, regulate the disposal of materials contaminated by PCBs, and allow the import or export of PCBs only through exemptions granted by EPA (EPA 1977b, 1979a, 1979f, 1979g, 1988c, 1988e).

In the TAM/WASP PCB sub-model, PCB congeners are grouped into three classes by PCB homolog, as given in Table 1-2. The first group, PCB1, consists of di- and tri-chlorobiphenyls (homologs 2 and 3), the second group, PCB2, consists of tetra-, penta-, and hexa-chlorobiphenyls (homologs 4, 5, and 6), and the third group, PCB3, consists of hepta-, octa-, and nona-chlorobiphenyls (homologs 7, 8, and 9). It should be noted that in the data sets used in this project, concentrations for typically only roughly one half of the possible 209 PCB congeners were reported. Furthermore, the particular congeners with reported values differed somewhat from data set to data set, leading to some degree of inconsistency for different model components in the computed sums of congeners concentrations for the three PCB groupings.

Monochlorobiphenyls, which include congeners #1, #2, and #3, are currently not included in the model due to limited data support. Congener #1 has been found in significant quantities in the sediment (Velinsky and Ashley, 2001) but has not been reported in either the Anacostia River (Velinsky et al., 1999) or in the Northeast and Northwest Branches (Gruessner et al., 1998) water columns. Congener #2 has not been reported in any of the three studies. Congener #3 was detected by Velinsky and Ashley (2001) in the Anacostia River sediment, was reported as below the detection limit in the Gruessner et al. (1998) Northeast and Northwest Branches water column data set, and was not reported in the Anacostia River by Velinsky et al. (1999).

The decachlorobiphenyl (congener #209) is not included because it has neither been reported in

the Gruessner et al. (1998) nor the Velinsky et al. (1999) water column data sets, and most of the decachlorobiphenyl sediment data as reported by Velinsky and Ashley (2001) is below the detection limit. The limited amount of sediment data that does exist could be incorporated into the model; however, ICPRB found that it has little effect on model predictions.

In support of the groupings used in the PCB sub-model, Table 1-3 gives values for the molecular weights (MW), partition coefficients ( $K_d$ 's), Henry's Law coefficients (HLCs), and reported aerobic biodegradation potential for homologs 2 to 9. The average partition coefficients listed were computed from 1998 Anacostia River water column data (Velinsky et al., 1999).

### **1.5.3. PAH Sub-Model**

Polycyclic aromatic hydrocarbons (PAHs) are a large class of compounds some of which are acutely toxic, carcinogenic, mutagenic, or teratogenic to aquatic organisms, and some of which are thought to be human carcinogens. They are formed during the incomplete combustion of organic substances such as wood, gasoline and other fossil fuels, garbage, and even grilled foods. Other sources of these pollutants include crude oil spills, oil refinery wastes, and petrogenic industrial effluents. PAHs are ubiquitous pollutants in the environment, and occur only as complex mixtures when formed naturally. PAHs can also be manufactured individually, and some are used in dyes, plastics, pesticides, and medicines. The commercial production of PAHs, however, does not create a significant environmental burden (ATSDR 1995). In the pure state, PAHs are colorless, yellow, or pale-green solids and are made up entirely of carbon and hydrogen. Their basic structure is based on fused benzene rings. For example, naphthalene, the simplest PAH, consists of two joined benzene rings.

The TAM/WASP PAH sub-model includes the 16 individual PAHs that had reported values in both the 1995-96 study on upstream loads (Gruessner et al., 1998) and the 2000 study of bed sediment concentrations by Velinsky and Ashley. The PAH sub-model simulates the fate and transport of three groups of the individual PAHs, as listed in Table 1-4 (also see Table 1-2). The first group, PAH1, is the sum of six 2- and 3-ring PAHs: naphthalene, 2-methyl naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene. The second group, PAH2, consists of four 4-ring PAHs: fluoranthene, pyrene, benz[a]anthracene, and chrysene. The third group, PAH3, consists of six 5 and 6-ring PAHs: benzo[k]fluoranthene, benzo[a]pyrene, perylene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene, and dibenz[a,h+ac]anthracene.

In support of the groupings used in the PAH sub-model, Table 1-4 gives values for the molecular weights (MW), partition coefficients ( $K_d$ 's), and Henry's Law coefficients (HLCs) for the 16 PAHs included in the model. The average partition coefficients listed were computed from 1995-96 Northeast and Northwest Branch water column data (Gruessner et al., 1998).

#### **1.5.4. Chlordane/Heptachlor Epoxide Sub-Model (PEST1)**

The TAM/WASP PEST1 sub-model simulates the fate and transport of total chlordane and heptachlor epoxide. In this modeling study, the definition of total chlordane, determined by data availability, is the sum of three chlordane isomers/metabolites: cis-chlordane, trans-nonachlor, and oxychlordane.

Chlordane was used as a pesticide in the United States from 1948 to 1988. It was initially used as a general pesticide for agricultural crops, lawns, and gardens. In 1978, the EPA began restricting the use of chlordane because of growing environmental and human health concerns, and from 1983 until 1988, it's only approved usage was for termite control. It was sold under the trade names of Chlordan, Velsicol1068, Octachlor, and others. Technical chlordane is a viscous, relatively insoluble liquid, ranging in color from clear to amber. Though technical chlordane is a mixture of more than 140 related compounds, it primarily consists of the two isomers, cis-chlordane and transchlordane (60-85%). Other components include cis- and trans-nonachlor (~7%) and heptachlor (~10%). Chlordane appears to be resistant to breakdown in the natural environment, and is a bioaccumulative substance that is commonly detected in the fatty tissues of fish, birds, and mammals, including humans.

Heptachlor epoxide is a breakdown product of heptachlor, which was used in the United States beginning in 1953 as both an agricultural and household pesticide. The use of heptachlor became more restricted in 1974 and was banned in 1988 (ATSDR, 1993). Technical grade heptachlor, which is a white powder, is actually a mixture of compounds consisting of approximately 72% heptachlor and 28% other compounds including trans-chlordane, cis-chlordane and nonachlor. Also, technical grade chlordane contains about 10% heptachlor (see above). It was sold commercially under the trade names, Heptagran, Heptamul, Heptagranox, Heptamak, Basaklor, Drinox, Soleptax, Gold Crest H-60, Termide, and Velsicol 104. In the natural environment, heptachlor is believed to be rapidly converted to heptachlor epoxide. No significant concentrations of heptachlor were found in the Northeast/Northwest Branches water monitoring samples (Gruessner et al., 1998), but heptachlor was found to be present in Anacostia River bed sediment samples (Velinsky and Ashley, 2001).

#### **1.5.5. Dieldrin Sub-Model (PEST2)**

Dieldrin is modeled individually in the TAM/WASP PEST2 sub-model. Dieldrin was used as popular broad spectrum insecticide from 1950 to the early 1970s when EPA restricted its use to termite control and non-food seed and plant treatment. Its use was completely banned in 1987. Dieldrin was manufactured by the epoxidation of another banned pesticide, aldrin, and is also a degradation product of aldrin. Dieldrin is a white powder when pure and tan as technical-grade and was sold under the trade names Alvit, Dieldrix, Red Shield, and others. Dieldrin is very persistent in the environment and can still be detected in soil, sediment, foods, aquatic organisms, wildlife, and humans. (From ATSDR 2000c.)

### 1.5.6. DDT Sub-Model

The DDT sub-model simulates the fate and transport of p,p' DDT (the p,p' isomer of dichloro-diphenyl-trichloroethane), as well as the p,p' isomer of DDE (dichloro-diphenyl-ethane), and DDD (dichloro-diphenyl-dichloroethane). As a group, DDT and its metabolites are sometimes referred to as DDX's. From 1939 until 1970, DDT was used extensively in the United States to control crop and forest pests as well as insect vectors that spread malaria, typhus and other diseases. It was sold under the following names: Dinocide, Digmar, ENT 1506, Genitox, Ixodex, Micro DDT 75, Pentachlorin, and others. In 1969, the US Department of Agriculture canceled the registration of DDT for application on tobacco and shade trees, in the home, and in aquatic environments. In 1970, its use for crops, commercial plants, wood products, and building purposes was banned by the EPA. In 1973, all use of DDT and DDT metabolites were canceled, except for public health emergencies and some other applications permitted on a case-by-case basis (ATSDR 2002b). These remaining uses were voluntarily canceled in 1989. DDD was also occasionally used as a pesticide.

DDT is a white crystalline powder, and the technical grade is comprised of up to 14 chemical compounds, including 65-80% of the active ingredient p,p'- DDT, 15-21 % of the nearly inactive 2,4'- DDT, up to 4% of p,p'- DDD, and up to 1.5% of 1-(p-chlorophenyl)-2,2,2-trichloroethanol (ATSDR 2002b). DDT and its degradation products, DDE and DDD are very persistent in the environment, tend to accumulate in the fatty tissue of organisms, and biomagnify up the food chain.

**Table 1-2. Constituents Represented**

Constituent	WASP Variable
<b>Metals 1 Model</b>	
zinc	CHEM1
lead	CHEM2
copper	CHEM3
<b>Metals 2 Model</b>	
arsenic	CHEM1
<b>PCB Model</b>	
homolog 2 (dichlorobiphenyls)	CHEM1 (PCB1)
homolog 3 (trichlorobiphenyls)	
homolog 4 (tetrachlorobiphenyls)	CHEM2 (PCB2)
homolog 5 (pentachlorobiphenyls)	
homolog 6 (hexachlorobiphenyls)	
homolog 7 (heptachlorobiphenyls)	CHEM3 (PCB3)
homolog 8 (octachlorobiphenyls)	
homolog 9 (nonachlorobiphenyls)	
<b>PAH Model</b>	
napthalene	CHEM1 (PAH1) (2 and 3 ring PAHs)
2-methyl napthalene	
acenaphthylene	
acenaphthene	
fluorene	
phenanthrene	
fluoranthene	CHEM2 (PAH2) (4 ring PAHs)
pyrene	
benz[a]anthracene	
chrysene	
benzo[k]fluoranthene	CHEM3 (PAH3) (5 and 6 ring PAHs)
benzo[a]pyrene	

**TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report**

Constituent	WASP Variable
perylene	
indeno[1,2,3-c,d]pyrene	
benzo[g,h,i]perylene	
dibenz[a,h+ac]anthracene	
<b>PEST1 Model</b>	
chlordanes (cis-chlordane + trans-nonachlor + oxychlordane)	CHEM1
heptachlor epoxide	CHEM2
<b>PEST2 Model</b>	
dieldrin	CHEM1
<b>DDT Model</b>	
p,p'-DDD	CHEM1
p,p'-DDE	CHEM2
p,p'-DDT	CHEM3

**Table 1-3. Rational for PCB Groupings**

Grouping for WASP	PCB Homolog	MW (g/mole)	Mean Base flow $K_d^1$ ( $L_w/kg_s$ )	Average HLC <sup>2</sup> ( $atm - m^3/mole$ )	Aerobic Biodegradation Potential
PCB1	dichlorobiphenyl	223.1	19,988	2.34E-04	rapid
	trichlorobiphenyl	257.5	52,291	1.88E-04	rapid
PCB2	tetrachlorobiphenyl	292.0	136,823	1.49E-04	slow
	pentachlorobiphenyl	326.4	181,487	0.84E-04	resistant
	hexachlorobiphenyl	360.9	259,465	0.36E-04	resistant
PCB3	heptachlorobiphenyl	396.3	765,233	0.15E-04	resistant
	octachlorobiphenyl	429.8	558,671	0.13E-04	resistant
	nonachlorobiphenyl	464.2	insufficient data	not reported	resistant

<sup>1</sup> Mean  $K_d$  based on tidal Anacostia base flow water column data (Velinsky et al., 1999)

<sup>2</sup> Adapted from Brunner et al., 1990

**Table 1-4. Rational for PAH Groupings**

<b>Grouping for WASP</b>	<b>PAH Analyte</b>	<b>MW (g/mole)</b>	<b>Mean Base flow <math>K_d^1</math> (L<sub>w</sub>/kg<sub>s</sub>)</b>	<b>HLC<sup>2</sup> (atm – m<sup>3</sup>/mole)</b>
CHEM1 (2- and 3- ring PAHs)	naphthalene	128.2	10775	4.40E-04
	2-methyl naphthalene	142.2	35,470	5.18E-04
	acenaphthylene	152.2	66,426	1.14E-04
	acenaphthene	154.2	17320	1.84E-04
	fluorene	166.2	9,584	9.62E-05
	phenanthrene	178.2	65,194	4.23E-05
CHEM2 (4-ring PAHs)	fluoranthene	202.2	268,884	8.86E-06
	pyrene	202.3	491,870	1.19E-05
	benz[a]anthracene	228.3	678,999	1.20E-05
	chrysene	228.3	695,794	5.23E-06
CHEM3 (5- and 6- ring PAHs)	benzo[k]fluoranthene	252.3	1,517,320	5.84E-07
	benzo[a]pyrene	252.3	2,276,973	4.57E-07
	perylene	252.3	513,160	3.65E-06
	indeno[1,2,3-c,d]pyrene	276.3	1,769,475	3.48E-07
	benzo[g,h,i]perylene	276.3	5,832,155	3.31E-07
	dibenz[a,h+ac]anthracene	278.4	901,534	1.23E-07

<sup>1</sup> Computed from Northeast/Northwest Branches base flow data; see Section 2-3.

<sup>2</sup> From SRC Physical Properties Database: <http://esc.syrres.com/interkow/physdemo.htm>.



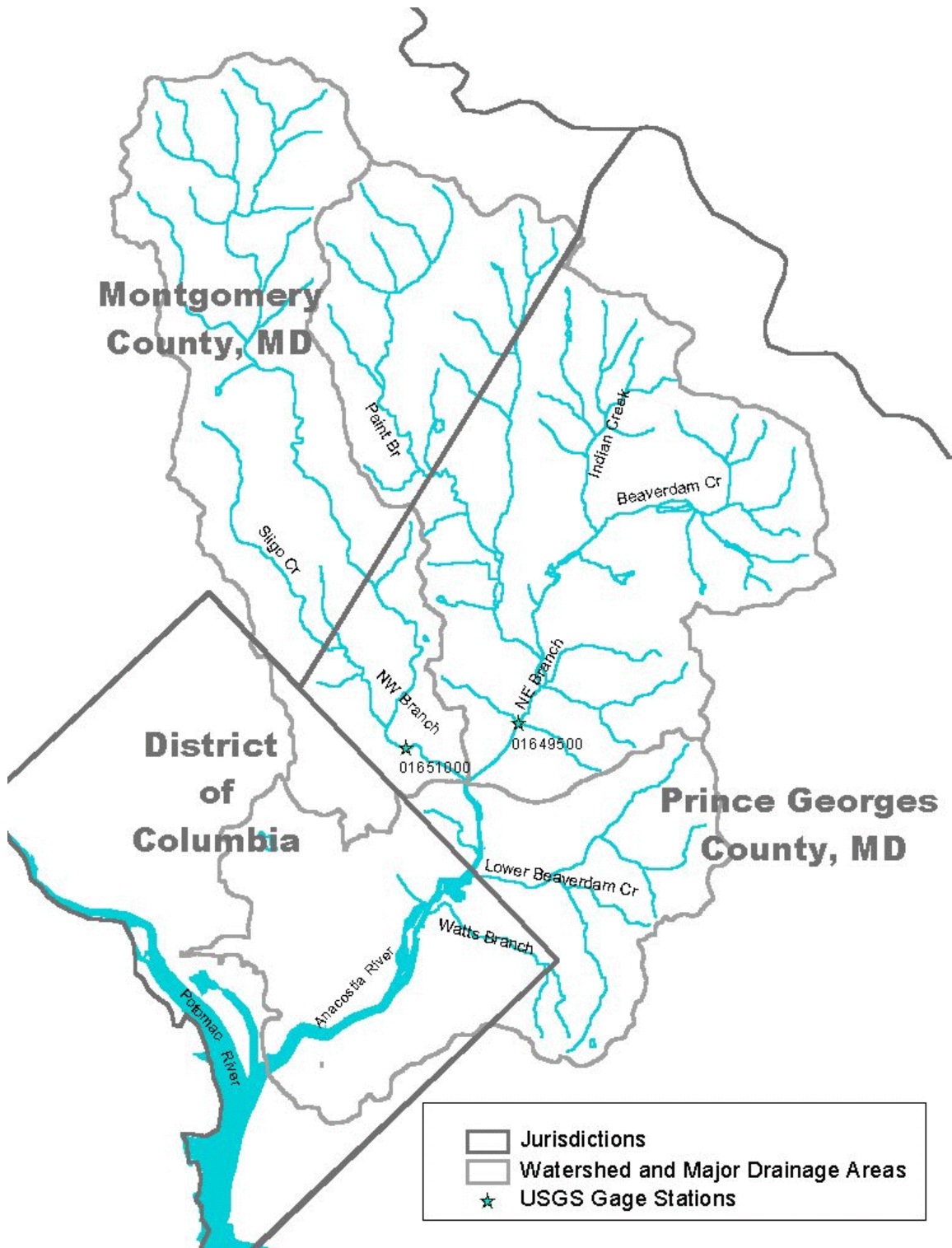


Figure 1-1. Anacostia Watershed

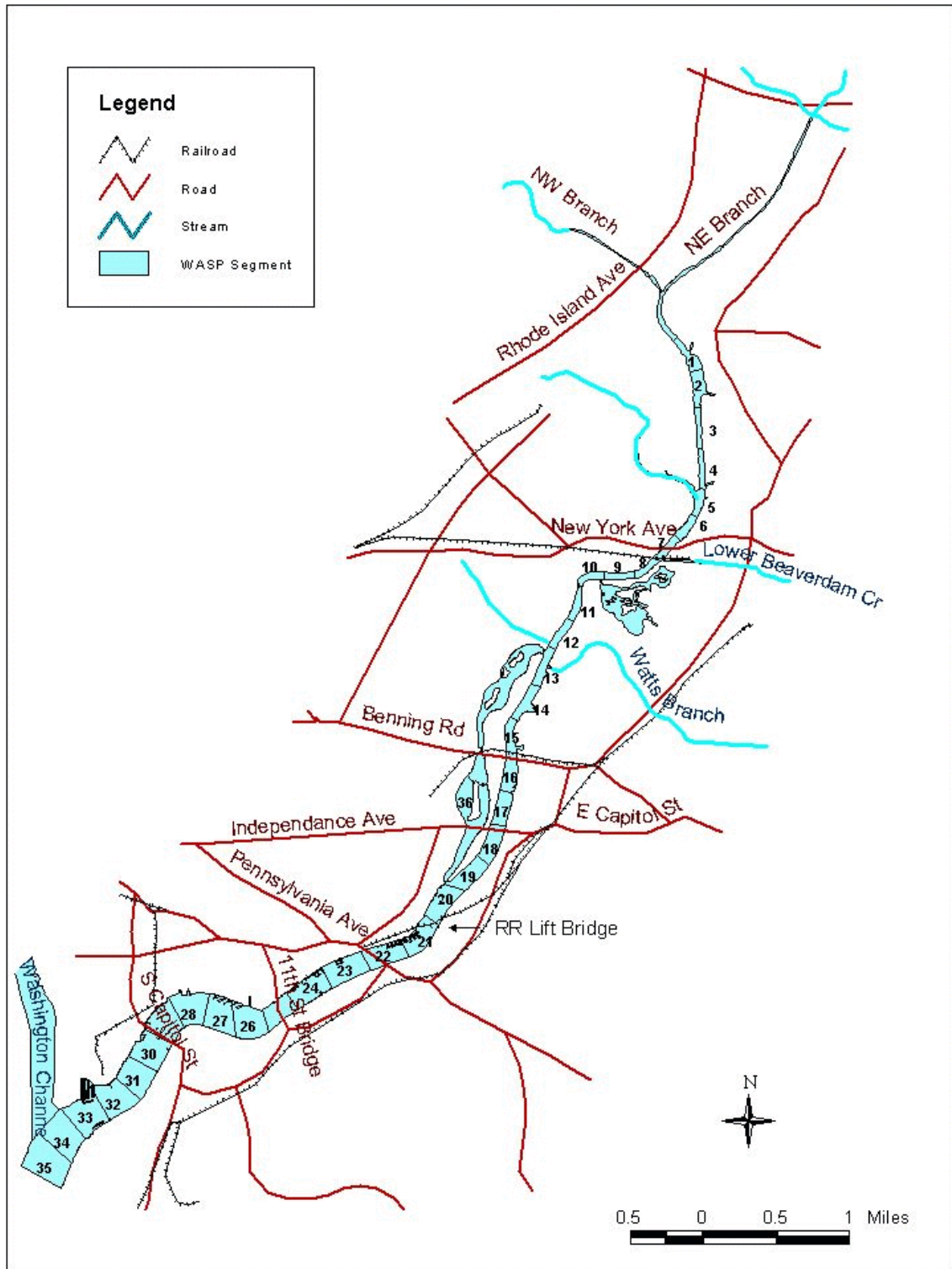
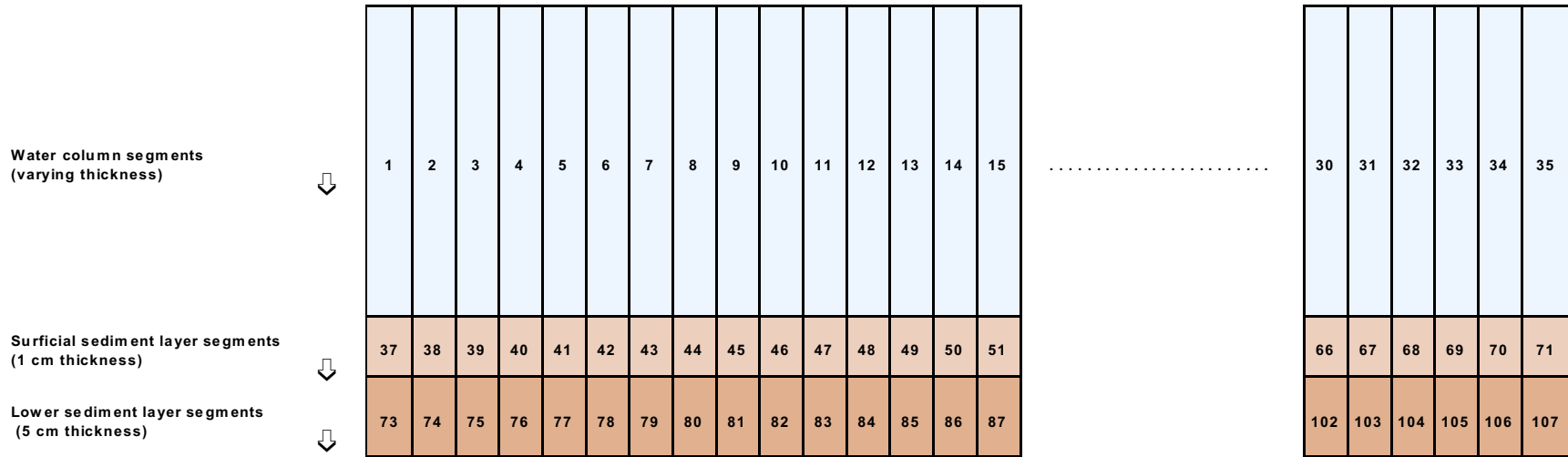


Figure 1-2. TAM/WASP Version 2 Model Water Column Segmentation



**Figure 1-3. Schematic Representation of Model Bed Sediment Segmentation (not showing water column segment 36, representing Kingman Lake, adjoining segment 19, and underlying sediment segments 72 and 108 underlying segment 36)**

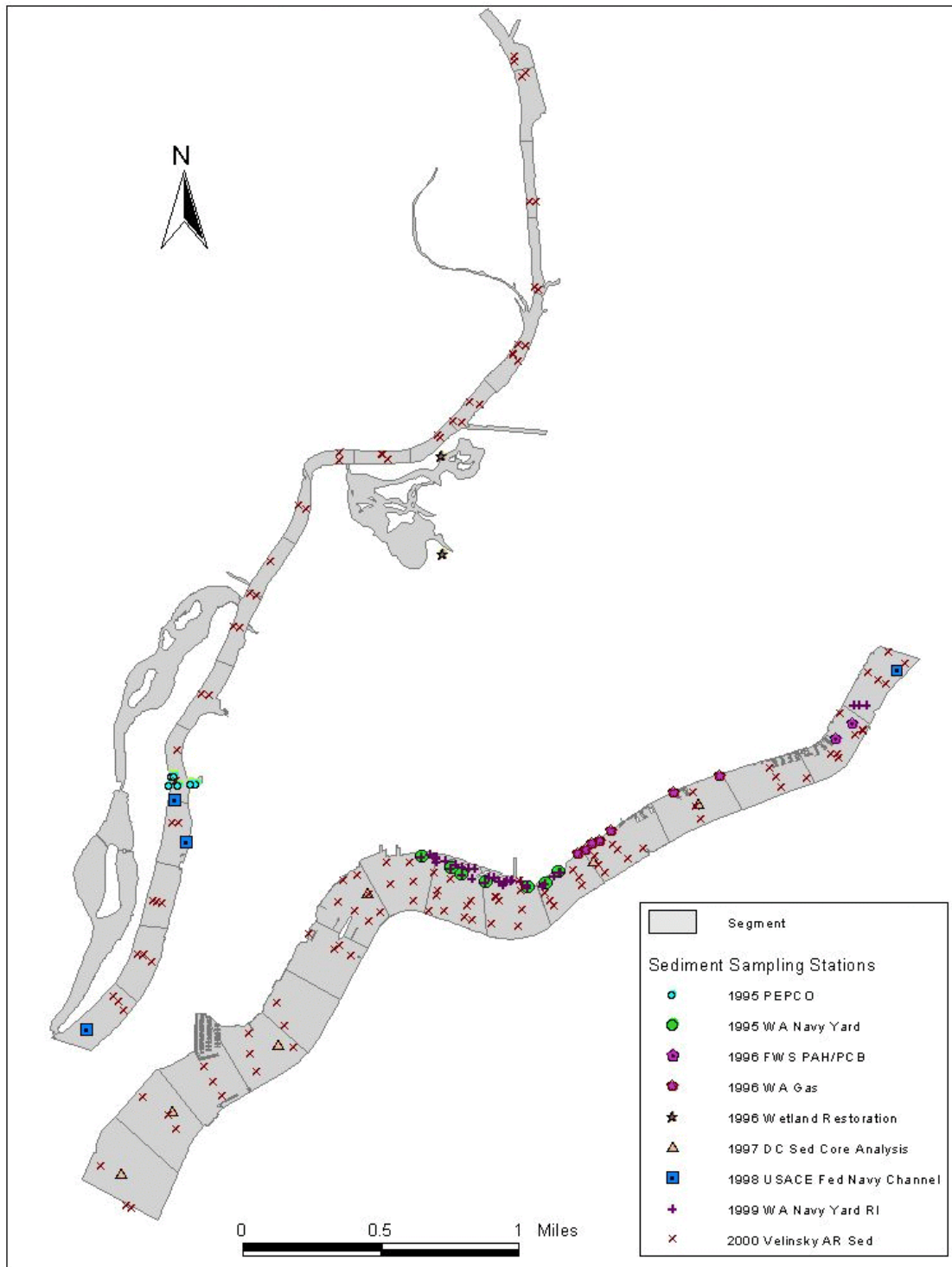


Figure 1-4. Bed Sediment Chemical Concentration Sampling Locations

## CHAPTER 2: MODEL INPUTS

A variety of information must be provided to the TAM/WASP model in order to simulate the processes that determine toxic chemical concentrations in the tidal portion of the Anacostia River. Required model inputs include hourly tidal elevations at the Anacostia-Potomac confluence, daily flows discharging into the river, daily sediment and chemical loads entering the river, the dissolved phase/solid phase partition coefficients, average chemical concentrations at the Potomac boundary, and information on water and air temperature. Methods used to estimate these quantities are discussed in the sections below. The WASP water quality component of the model also requires the specification of certain additional parameters that govern simulated physical/chemical transformation processes, and determination of these additional parameters is discussed in Chapter 3: Model Calibration. Many of the required inputs are identical to those used in the TAM/WASP sediment transport model, Version 2.1, and are discussed in more detail in the report by Schultz (2003).

### 2.1. Hydrodynamic Model Inputs

The TAM hydrodynamic component of the TAM/WASP sediment transport model simulates water depths and flow velocities based on equations for continuity and momentum conservation (Sullivan and Brown, 1988). The hydrodynamic inputs to TAM/WASP Version 2.3 are identical to those of Version 2.1, with the exception of the inclusion of flows representing ground water inputs from the CSO sub-sheds, described at the end of this section. The primary hydrodynamic inputs are the model segment geometry, daily tidal gage heights near the downstream boundary of the model, daily flow discharges from the two upstream tributaries, the Northeast and Northwest Branches, and daily flow discharges into each model segment from the tidal drainage area. Each of these inputs is described below and described in greater detail in the report on TAM/WASP Version 2.1 (Schultz, 2003).

The model segment geometry used in TAM/WASP Version 2.3 is identical to that used in Version 2.1. Segment widths were obtained using the GIS representation of the tidal river prepared by NOAA for the AWTA, based primarily on the National Capitol Parks - East GIS layer of the Anacostia River, and are consistent with available aerial photos of the river. Average mean-tide segment depth estimates were based on 1999 depth sounding data provided by the U.S. Army Corps of Engineers (U.S. ACE, 1999) and an additional data set collected in the summer of 2000 for AWTA by the SPAWAR's data collection team (see Katz et al., 2000). NOAA used ESRI's Arcview Spatial Analyst software interpolation capabilities to estimate river depths at each point on a 10 ft by 10 ft grid. Average segment depths were then computed by averaging depths at all grid points within the segment.

Hourly tidal heights were obtained from NOAA for Station 8594900, "Washington, Potomac River, DC", which is located in the Washington Ship Channel. Tidal heights were downloaded from the NOAA website, in units of meters, from the vertical datum, MLLW (mean lower low water) for the tidal epoch, 1960 to 1978. Adjustments were made to this data set to account for

several periods of time for which no data were available and several days when extremely low tides caused de-watering of some model segments, a condition that cannot be handled in the current TAM/WASP framework.

Water flows into the tidal portion of Anacostia from the Northeast Branch and Northwest Branch upstream tributaries, from CSO and SS outfalls, from the Watts Branch, Lower Beaverdam Creek and other tidal tributaries, from direct drainage (i.e. overland flow from areas adjacent to the river banks) and from ground water discharges. TAM/WASP model sub-sheds and sub-shed types are shown in Figure 2-1 and described in detail in the report on the TAM/WASP sediment transport model (Schultz, 2003). Flows from each of these sub-sheds are represented in TAM/WASP as daily flow volume inputs into appropriate model segments. Daily flows from each sub-shed are conceptually divided into two components: 1) a storm flow volume, and 2) a non-storm flow volume. The non-storm flow represents tributary base flow and/or ground water flow from the sub-shed.

Flow estimates for the Northeast Branch and Northwest Branch drainage areas are obtained directly from USGS gage station data from Station 01649500 on the Northeast Branch at Riverdale Road and Station 01651000 on the Northwest Branch at Queens Chapel Road. Northeast Branch and Northwest Branch daily flow values were separated into base flow and storm flow components using the USGS hydrograph separation program, HYSEP, using the local minimum method. Flow estimates for CSOs for the three-year model calibration time period (using 1988-90 hydrology to represent “typical” hydrology) were obtained from DC WASA from their model developed for the Long Term Control Plan (Andrea Ryon, MWCOG, private communication). These CSO flow estimates were computed assuming “current conditions” of the CSO system. CSO flow estimates for other time periods were estimated by ICPRB (see Mandel and Schultz, 2000). Flow estimates for Lower Beaverdam Creek were obtained using the HSPF model developed by Tetra Tech, Inc. for Prince Georges County (Tetra Tech, 2000).

Flow estimates for the Watts Branch sub-shed and for sub-sheds drained by other minor tributaries and by the District SS system were computed using ICPRB’s Watts Branch HSPF model, based on the delineation of sub-sheds as depicted in Figure 2-1, land use analysis, and precipitation data from Reagan National Airport. The land use types considered in the Watts Branch HSPF model are: i) impervious surfaces, ii) urban pervious surfaces, and iii) forested pervious surfaces. Daily storm flows for these sub-sheds were calculated as the product of the storm flow per unit area from each land use type, as determined from the Watts Branch HSPF model, and the area of that type within the sub-shed. Daily non-storm flows were calculated as the product of the base flow per unit area from each land use type, as determined from the Watts Branch HSPF model, and the area of that type within the sub-shed.

As mentioned at the beginning of this section, the TAM/WASP Toxics Screening Level Model, TAM/WASP Version 2.3, uses a hydrodynamic model identical to that used in TAM/WASP Version 2.1 with one minor change. Version 2.3 includes additional flows representing the volume of ground water from surface recharge from the CSO sub-sheds, based on predictions of base flow per unit area of land use type from the Watts Branch HSPF model. This change has

only a minor impact on model results because the added flow volume is only approximately 2% of the total. A breakdown of average annual flow contributions according to sub-shed type is given in Table 2-1, where CSO flows are WASA estimates assuming “current” system conditions. The average annual flow input percentages are quite close to the corresponding drainage area percentages, as would be expected. Note that the CSO sub-sheds are expected to contribute less flow than would be estimated from their relative areas, because a portion of the runoff from the CSO sub-sheds is carried to the Blue Plains sewage treatment plant.

**Table 2-1. Model Flow Input Summary**

Source	Area (acres)	Area (%)	Average Annual Flow (1000 m <sup>3</sup> )	Average Annual Flow (%)
Upstream Drainage Areas	77,800	72.0%	136,183	69.6%
Tidal Drainage Area: Watts Branch	2,470	2.2%	4,987	2.5%
Tidal Drainage Area: Lower Beaverdam	10,466	9.3%	23,390	12.0%
Tidal Drainage Area: Separate Sewers and Minor Tributaries	10,501	10.0%	20,952	10.7%
Tidal Drainage Area CSO sub-sheds	6,946	6.4%	5,637	2.9%
Storm Overflows: Ground Water Recharge:			4,468	2.3%
Total Watershed	108,183	100.0%	195,617	100.0%

## 2.2. Sediment Transport Model Inputs

The TAM/WASP Toxics Screening Level Model sediment transport component simulates daily changes in sediment concentrations in both the water column and the bed sediment by simulating the processes of advective transport, dispersive transport, deposition, and erosion. In this report the term “sediment” is used to refer to all solid material entering the system, including the inorganic and organic solids fractions. The inputs to the Toxics Screening Level Model, TAM/WASP Version 2.3, are identical to those in TAM/WASP Version 2.1, with two minor exceptions. The value specified for the advection factor in Version 2.3 is 0.25 rather than 0.0, based on examination of dye study simulation results (Schultz, 2003). Also, the sediment concentration values specified for the Potomac boundary condition have been changed, as described in detail at the end of this section. Results of a sensitivity run investigating the differences between Versions 2.1 and 2.3 are given in Section 3.3.1 and are shown to be minor. Each of the inputs to the sediment transport component of the model is described below and described in greater detail in the report on TAM/WASP Version 2.1 (Schultz, 2003).

Daily sediment load inputs to the model are based on estimates of daily flows discharging into

the tidal river, discussed above, and on estimates of sediment concentrations in these flow volumes. Daily sediment loads are calculated by multiplying daily storm flow and base flow volumes by daily storm flow and base flow TSS concentration estimates. Estimates for average base flow and storm flow TSS concentrations are based on tributary, separate storm sewer, and CSO monitoring data, and the values used in TAM/WASP version 2.3 are identical to those used in Version 2.1, discussed in more detail in the report by Schultz (2003). Daily sediment loads for the Northeast and Northwest Branches were estimated based on monitoring data collected in 1999 and 2000 as part of the WASA Long Term Control Plan program for combined sewer system overflows and on calibration results. Daily TSS loads from the Watts Branch tributary were estimated by based on the MWCOG Pope Branch open channel result (Shepp et al., 2000). A non-storm TSS concentration for the Watts Branch was estimated from available DC DOH routine monitoring data for station TWB01 (time period 4/20/82 to 12/9/97). Output from the Prince Georges County/TETRA TECH HSPF model of Lower Beaverdam Creek was used to generate daily TSS loads from Lower Beaverdam Creek. TSS daily load estimates for CSOs are from WASA's model developed for the LTCP, contained in a file named "cso\_c2.ana", (Andrea Ryan, MWCOG, private communication). These daily load estimates are based on 1988-1990 hydrology and a CSO system "with current conditions". Storm concentrations for the three minor tributaries, Nash Run, Fort Dupont, and Pope Branch, use MWCOG-estimated storm concentrations based on Pope Branch monitoring data (Shepp et al., 2000), following the MWCOG designation of these sub-sheds as primarily open channel systems. TSS storm concentrations for the remaining SS and minor tributary sub-sheds, including direct drainage areas, were based on WASA LTCP provisional results (T.J. Murphy, MWCOG, private communication). A summary of the model's annual sediment load estimates is given in Table 2-2.

The model classifies sediments into three grain sizes: coarse-grained, medium-grained, and fine-grained particle size fractions. Because no monitoring data is available to determine the relative proportions of the individual grain size fractions in sediment loads entering the river, the percentage of each size fraction in daily input loads was estimated from the bed sediment grain size data collected by GeoSea for the AWTa (Hill and McLaren, 2000) and combined with sediment transport model calibration results. The percentages used in the model to estimate loads for each size fraction are:

Frac1 (grain sizes > 120 $\mu\text{m}$ ):	17%
Frac2 (grain sizes > 30 and < 120 $\mu\text{m}$ ):	15%
Frac3 (grain sizes < 30 $\mu\text{m}$ ):	68%

The TAM/WASP sediment transport model requires that the user input a time series of downstream boundary conditions for each of the three sediment size fractions, representing daily average water column concentrations of each of the suspended sediment size fractions in the Potomac River. Constant boundary condition values of 0 mg/L for coarse-grained sediment, 2 mg/L for medium-grained sediment, and 12 mg/L for fine-grained sediment were used for initial calibration runs of TAM/WASP Version 2.1. These values were based on an average TSS



concentration of 14 mg/L from available DC DOH routine monitoring data at Station ANA29, near the confluence of the Anacostia and the Potomac River, and an average relative suspended sediment size fraction composition of 0% coarse-grained / 14% medium-grained / 86% fine-grained found in samples taken at Station ANA29 by the Academy of Natural Sciences (Schultz and Velinsky, 2001). Based on final calibration results, in Version 2.1 these were changed to 0 mg/L for coarse-grained sediment, 2 mg/L of medium-grained sediment, and 20 mg/L of fine-grained sediment. In TAM/WASP Version 2.3, based on a further review of calibration results, the boundary conditions were changed back to values close to those originally used: 0.04 mg/L for coarse-grained sediment, 1.5 mg/L for medium-grained sediment, and 12 mg/L for fine-grained sediment.

**Table 2-2. TAM/WASP Annual Sediment Load Estimates**

Source	Average Annual Sediment Load (1000 kg)	Average Annual Sediment Load (%)
Upstream	27,642	89.2%
Watts Branch	655	2.1%
Lower Beaverdam	682	2.2%
Separate Sewers and Minor Tributaries	1,223	3.9%
CSOs	788	2.5%
Total Annual Load	30,990	100.0%

### 2.3. Partition Coefficients

Adsorption onto solid material is an important process affecting the fate and transport of contaminants in the river. Contaminants in the water column that are sorbed onto sediment particles may settle to the river bottom and be buried, and contaminants in the bed sediment that are sorbed onto sediment particles may re-enter the water column if erosion occurs and sediments are re-suspended. In WASP-TOXI5, the process of adsorption is modeled using the assumption of instantaneous equilibrium partitioning, where the partitioning between the solid phase and the dissolved phase is assumed to be linear (Karickhoff, 1984), that is,

$$C_s = K_d C_w \quad (2-1)$$

where:

- $C_s$  = concentration of contaminant on solid phase (mg/kg)
- $C_w$  = concentration of contaminant in dissolved phase (mg/L)
- $K_d$  = partition coefficient (L/kg)

The assumption of instantaneous partitioning is only an approximation, because it is believed that for many hydrophobic organic chemicals introduced into an aquatic environment, it may take several days to reach a solid-phase/dissolved phase equilibrium state. However, as discussed below, this assumption should be adequate given the current model data support because in most cases discussed below, the mean  $K_d$ 's computed from base flow data did not differ statistically from the mean  $K_d$ 's computed from storm flow data (at the 5% significance level, under the assumption that values are normally distributed). The TAM/WASP Toxics Screening Level Model uses a two-phase partitioning model, completely described by Equation 2-1.  $K_d$ 's for each constituent modeled were computed from site-specific water column data, using data, if available, from two studies, the upstream monitoring study by Gruessner et al. (1998) and the storm water runoff study by Velinsky et al. (1999). Separate base flow and storm flow  $K_d$ 's were computed from pooled Northeast Branch and Northwest Branch monitoring data from both studies. Also, separate base flow and storm flow  $K_d$ 's were computed from the Anacostia River data (excluding the Northeast and Northwest Branches samples and the Potomac River samples) from the Velinsky study for the chemicals for which data was available. Sample points with non-detect or below-quantitation-limit concentrations for either the solid phase or dissolved phase were not used in the computations. Mean base flow and storm flow  $K_d$ 's appear in Table 2-3, along with ranges, standard deviations and sample sizes. A corresponding range of values for  $K_d$ 's found in the water quality literature is given in the last column of the table.

For metals, most mean  $K_d$  values fell within the range of reported literature values. For the Anacostia River zinc, lead and copper data, none of the base flow mean  $K_d$ 's differed significantly, at the 5% confidence level, from the corresponding storm flow means, though it should be noted that in the Velinsky 1998 data set, no samples were actually taken during storm events, but rather on the 1<sup>st</sup> or 2<sup>nd</sup> day following a storm event. For the Northeast/Northwest Branches data, mean lead base flow and storm flow  $K_d$ 's did not differ significantly, but the mean storm flow zinc  $K_d$  is significantly smaller than the mean base flow  $K_d$ , and the mean storm flow copper  $K_d$  is significantly greater than the mean base flow value. Finally, when mean base flow metal  $K_d$ 's computed from the Anacostia River data were compared with those computed from the Northeast/Northwest Branches data, no statistically significant difference was found.

For the organic chemicals modeled, it was also found that there was little statistically significant difference between mean  $K_d$  values computed from storm flow and from base flow data. PCB mean  $K_d$  values were computed for each homolog, and some means fell outside the range of reported literature values. For the Anacostia River data set, base flow means did not differ significantly, at the 5% confidence level, from the corresponding storm flow means except in the case of homolog 6. For PAHs, the only data currently available for computing  $K_d$  values is the Northeast/Northwest Branches data set of Gruessner et al. (1998). Site-specific  $K_d$ 's computed for PAHs were generally quite a bit higher than values found in the literature. For the 16 PAHs included in the PAH sub-model, none of the base flow mean  $K_d$ 's differed significantly, at the 5% confidence level, from the corresponding storm flow mean  $K_d$ 's. For the pesticides modeled, there was no significant difference between the mean base flow  $K_d$ 's and the mean storm flow  $K_d$ 's for cases where there were a sufficient number of sample points to carry out the statistical tests.

The summary of site-specific and literature values for  $K_d$  in Table 2-3 was used as a starting point in the calibration of the TAM/WASP Toxics Screening Level Model. When available, site-specific mean  $K_d$ 's from the Anacostia River sample set were used in initial calibration runs; otherwise, mean  $K_d$ 's from Northeast/Northwest Branches data were used. Contaminants were assumed to sorb to fine-grained and medium-grained particles only, with the amount of contaminants sorbed to coarse-grained material assumed to be negligible. Because contaminants are thought to sorb more strongly to fine-grained material, separate  $K_d$  values were used for the fine-grained and medium-grained sediment fractions, and adjustments were made to these values during model calibration (see Chapter 3). When reported literature values were given in terms of adsorption to the organic fraction of solids, i.e. as  $K_{oc}$ 's, corresponding  $K_d$ 's were estimated from the relationship,  $K_d = f_{oc} * K_{oc}$ , where  $f_{oc}$ , the fraction of organic carbon in the solid material, was assumed to be 0.09, the mean fraction of organic carbon in Anacostia River from the Velinsky 1998 data.

**Table 2-3. Summary of Anacostia River (AR), Northeast/Northwest Branches (NE/NW) and Literature  $K_d$  Values (L/kg/1000)**

Constituent	Baseflow Data $K_d$ Range	Baseflow Data $K_d$ Mean	Baseflow Data $K_d$ Stdev	Baseflow Data $K_d$ Sample Size	Stormflow Data $K_d$ Range	Stormflow Data $K_d$ Mean	Stormflow Data $K_d$ Stdev	Stormflow Data $K_d$ Sample Size	Literature $K_d$ Values
Zinc - AR <sup>a</sup>	101 - 3217	798	1035	14	10 - 1646	273	340	31	10 - 631 <sup>c</sup>
Zinc - NE/NW <sup>b</sup>	2 - 1627	379	460	20	4 - 427	84	95	32	
Lead - AR	146 - 4370	663	1106	13	42 - 3649	434	637	30	63 - 10,000 <sup>c</sup>
Lead - NE/NW	3 - 7497	1342	2741	7	1 - 24,570	1813	4891	26	
Copper - AR	30 - 183	94	50	12	25 - 108	66	23	31	3 - 316 <sup>c</sup>
Copper - NE/NW	1 - 6152	884	1892	15	9 - 229	66	62	31	
Arsenic	NA	NA	NA	NA	NA	NA	NA	NA	30 - 150 <sup>d</sup>
PCB Homolog 2 - AR	2 - 53	20	22	5	2 - 107	32	36	11	6 <sup>f</sup>
PCB Homolog 3 - AR	2 - 339	52	60	51	1 - 239	43	50	68	19 <sup>f</sup> , 29
PCB Homolog 4 - AR	9 - 2865	137	351	69	8 - 17,054	316	1773	92	54 <sup>f</sup>
PCB Homolog 5 - AR	20 - 870	181	150	77	6 - 780	213	169	111	164 <sup>f</sup> , 29 - 483
PCB Homolog 6 - AR	56 - 714	259	128	35	42 - 1667	404	360	52	375 <sup>f</sup> , 350 - 1362
PCB Homolog 7 - AR	88 - 16,716	765	2045	64	48 - 107	1655	10,619	100	964 <sup>f</sup> , 1676
PCB Homolog 8 - AR	1 - 3636	559	770	23	29 - 1602	239	319	31	2537 <sup>f</sup>
PCB Homolog 9 - AR	NA	NA	NA	0	NA	146	NA	1	5811 <sup>f</sup>

**TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report**

Constituent	Baseflow Data K <sub>d</sub> Range	Baseflow Data K <sub>d</sub> Mean	Baseflow Data K <sub>d</sub> Stdev	Baseflow Data K <sub>d</sub> Sample Size	Stormflow Data K <sub>d</sub> Range	Stormflow Data K <sub>d</sub> Mean	Stormflow Data K <sub>d</sub> Stdev	Stormflow Data K <sub>d</sub> Sample Size	Literature K <sub>d</sub> Values
naphthalene - NE/NW	6 - 16	11	7	2	1 - 11	4	4	5	
2-methyl naphthalene - NE/NW	1 - 155	35	48	9	1 - 228	39	77	8	
acenaphthylene - NE/NW	17 - 176	66	50	9	8 - 140	40	47	7	0.002 <sup>e</sup>
acenaphthene - NE/NW	6 - 43	17	17	4	2 - 42	20	14	7	0.4 <sup>e</sup>
fluorene - NE/NW	2 - 18	10	6	6	2 - 51	20	16	8	0.7 <sup>e</sup>
phenanthrene - NE/NW	11 - 180	65	70	8	14 - 648	210	217	7	1 <sup>e</sup>
fluoranthene - NE/NW	23 - 1598	269	447	12	37 - 405	172	136	8	3 <sup>e</sup>
pyrene - NE/NW	11 - 3754	492	1113	11	29 - 778	309	249	8	3 <sup>e</sup>
benz[a]anthracene - NE/NW	12 - 4150	679	1236	11	122 - 1713	686	562	7	18 <sup>e</sup>
chrysene - NE/NW	89 - 4141	696	1101	12	217 - 1997	897	658	8	18 <sup>e</sup>
benzo[k]fluoranthene - NE/NW	113 - 10,133	1517	2793	12	31 - 1539	785	558	5	49 <sup>e</sup>
benzo[a]pyrene - NE/NW	41 - 12,640	2277	4392	9	250 - 1273	850	403	6	495 <sup>e</sup>
perylene - NE/NW	35 - 1770	513	509	11	56 - 2818	699	1202	5	
indeno[1,2,3-c,d]pyrene - NE/NW	103 - 11,614	1769	3719	9	7 - 599	237	190	8	143 <sup>e</sup>
benzo[g,h,i]perylene - NE/NW	296 - 30,669	5832	8814	12	310 - 2574	1187	955	8	143 <sup>e</sup>

**TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report**

Constituent	Baseflow Data K <sub>d</sub> Range	Baseflow Data K <sub>d</sub> Mean	Baseflow Data K <sub>d</sub> Stdev	Baseflow Data K <sub>d</sub> Sample Size	Stormflow Data K <sub>d</sub> Range	Stormflow Data K <sub>d</sub> Mean	Stormflow Data K <sub>d</sub> Stdev	Stormflow Data K <sub>d</sub> Sample Size	Literature K <sub>d</sub> Values
dibenz[a,h+ac]anthracene - NE/NW	48 - 3563	902	1332	6	87 - 2498	605	963	6	298 <sup>e</sup>
cis-chlordane - NE/NW	28 - 161	62	52	6	25 - 795	186	301	6	
nonachlor - NE/NW	31 - 332	102	100	8	42 - 1589	336	560	7	
oxychlordane - NE/NW	10 - 35	20	11	4	10 - 31	16	10	4	0.73 <sup>g</sup>
heptachlor epoxide - NE/NW	5 - 190	28	61	9	2 - 98	18	35	7	0.2 - 2.1 <sup>e</sup>
dieldrin - NE/NW	9 - 98	51	29	6	13 - 818	287	460	3	421 <sup>e</sup>
p,p'-DDD - AR	NA	NA	NA	NA	NA	NA	NA	NA	14 <sup>e</sup>
p,p'-DDD - NE/NW	NA	77	NA	1	24 - 48	36	17	2	
p,p'-DDE - AR	3 - 326	100	100	12	1 - 283	90	76	18	5 <sup>e</sup>
p,p'-DDE - NE/NW	7 - 15	10	4	3	NA	NA	NA	NA	
p,p'-DDT - AR	243 - 326	285	59	2	41 - 347	156	136	4	14 <sup>e</sup>
p,p'-DDT - NE/NW	NA	190	NA	1	1 - 24	10	13	3	

<sup>a</sup> All AR statistics computed from data in Velinsky et al., 1999.

<sup>b</sup> All NE/NW Branches statistics computed from data in Gruessner et al., 1998.

<sup>c</sup> As compiled by Sigg, 1998.

<sup>d</sup> From Diamond et al., 1990; Diamond, 1995.

<sup>e</sup> ATSDR - K<sub>d</sub> values were derived from median K<sub>oc</sub> values, where K<sub>d</sub> = K<sub>oc</sub>\*f<sub>oc</sub> and using f<sub>oc</sub> = 0.09.

<sup>f</sup> Delaware River Basin Commission.

<sup>g</sup> TOXNET.

## 2.4. Chemical Load Inputs

Water discharging into the tidal portion of the river from tributaries, sewer outfalls, and groundwater may carry with it measurable quantities of chemical contaminants. The daily quantities of these constituents entering the river, referred to as daily loads, have been estimated by ICPRB based on available toxic chemical monitoring data. Though it is possible in the model to specify distinct non-storm flow and storm flow chemical concentrations from each of the 34 individual tributary or outfall sub-sheds depicted in Figure 2-1, available monitoring data are limited. For this reason the model currently represents the entire Anacostia watershed as relatively homogenous in terms of storm water quality (and base flow/groundwater quality). For example, because the only available monitoring data for PAHs, chlordane, heptachlor epoxide, and dieldrin are from samples taken from the upstream tributaries, the Northeast and Northwest Branches (Gruessner et al, 1998), the average concentrations computed from this data are used to estimate PAH, chlordane, heptachlor epoxide, and dieldrin loads for all Anacostia basin sub-sheds. The situation is somewhat better for the metals included in the model, namely zinc, lead, and copper, where monitoring data is available from several sources, including the Northeast/Northwest Branch study, the recent CSO Long Term Control Plan study, recent MS4 program monitoring data, and several historical studies.

For all of the sources considered, chemical loads are estimated by using estimated average non-storm flow and storm flow concentrations that are assumed to not vary with respect to time. For each constituent considered in the model, ICPRB's Microsoft ACCESS input routine estimates a daily load from each of the sub-sheds depicted in Figure 2-1. For each constituent, for each sub-shed, the daily load, in units of kilograms, is estimated to be

$$\begin{aligned} \text{Daily Load} &= (\text{daily sub-shed non-storm flow volume}) * (\text{sub-shed non-storm flow} \\ &\quad \text{concentration}) \\ &+ (\text{daily sub-shed storm flow volume}) * (\text{sub-shed storm flow} \\ &\quad \text{concentration}) \end{aligned}$$

A summary of estimated average storm flow and base flow chemical concentrations from available monitoring data is given in Table 2-4. Because it appears that little useful data is currently available on ground water concentrations in the basin, ground water data was not compiled. Information on detection limits for the primary water column data sets used in this study appears in Table 2-5. Though monitoring data for toxic contaminants are limited, loads from the upstream portion of the watershed, which accounts for approximately 70% of the water discharging into the tidal river, can be estimated from data in the Northeast/Northwest Branch study for all chemicals except arsenic. Also, as discussed above, when no other data are available, results for the upstream tributaries are extrapolated throughout the watershed. Because data from the Northeast/Northwest Branch study is heavily relied upon in the current TAM/WASP toxics chemical model simulations, a discussion of the uncertainty associated with estimates made using this data set is given at the end of this section.

### 2.4.1. Upstream Loads

Because the two upstream tributaries, the Northeast Branch and the Northwest Branch, drain over 70% of the Anacostia watershed, upstream loads have the potential to be a highly significant source of contamination for the tidal portion of the river. Currently, two studies contain data that can be used to help estimate upstream loads. The study by Gruessner et al. (1998) contains concentration data for metals and a variety of organic contaminants from samples collected during six base flow and four storm flow sampling events, for both the Northeast Branch and the Northwest Branch. During each storm event, grab samples were collected during the rising limb, the approximate peak, and the falling limb of the storm's hydrograph. For each storm, the rising limb, peak, and falling limb samples for metals were analyzed individually, but the three samples were composited before being analyzed for organics. A limited amount of Northeast and Northwest Branch data is also available from a second study (Velinsky et al., 1999).

The first two columns of Table 2-4 contain estimates of Northeast and Northwest Branch base flow and storm flow concentrations for each of the toxic constituents, or constituent groups, modeled. For each constituent or group of constituents, separate base flow and storm flow mean concentrations were computed by assuming that the concentration values have a log normal distribution (Gilbert, 1987), as discussed in more detail in the last section of this chapter. Base flow metals concentrations were computed by combining base flow data from the Gruessner et al. (1998) and the Velinsky (1999) monitoring studies. Storm flow metals concentrations were computed from event mean concentrations (EMCs) for the four storm events in the Gruessner et al. (1998) data set. The metals post-storm data from the Velinsky study was not used because it was not deemed to be comparable to the storm data in the Gruessner study. Mean base flow concentrations for organics were computed from the six base flow concentrations reported in the Gruessner study, and mean storm flow organics concentrations were computed from the four storm composite concentrations from the Gruessner study. To construct the time series of daily loads for input into WASP, Northeast Branch and Northwest Branch daily flow values were separated into base flow and storm flow components using the USGS hydrograph separation program, HYSEP, using the local minimum method.

### 2.4.2. CSO Loads

Estimates for metals concentrations in CSO discharges are available from WASA (DC WASA, 2000a; 2000b; 2000c). Based on data collected in 1999 - 2000 for the LTCP, EMCs were computed for zinc, lead, and copper for several CSO sub-drainage areas. Data was included from the Northeast Boundary (NEB) Sewer, both from discharge treated by the swirl concentrator facility and discharge that bypassed the swirl facility. The WASA CSO EMCs are included in Table 2-4, below.

Because no CSO data exists for organic chemicals at detection limits low enough to quantify loads, concentrations of organic chemicals in CSO discharges were assumed to be the same as concentrations in the District's SS system. Therefore, for organic chemical concentrations in



CSOs, mean concentrations from the District's MS4 monitoring data were used when available. Otherwise, mean values from the Northeast and Northwest Branches data set were used. Arsenic was treated similarly.

A non-storm load from CSO sub-sheds was also included in the model, representing a load from ground water attributable to surface recharge from the CSO sub-sheds. As discussed in Section 2.1, the ground water flow volumes were computed based on predictions of base flow per unit area of land use type from the Watts Branch HSPF model. The ground water contaminant concentrations are based on Northeast/Northwest Branches base flow data, due to lack of ground water data at sufficiently low detection limits to compute load estimates.

#### **2.4.3. Lower Beaverdam Creek Loads**

Storm flow and base flow data for metals are available for Lower Beaverdam Creek from the Prince Georges County storm water monitoring program (M. Cheng, private communication). Average storm flow and base flow concentrations values for computing zinc, lead, and copper loads for Lower Beaverdam were obtained using 1998-99 data for Station 006, located in Prince Georges County upstream of the confluence with the Anacostia. Mean storm flow concentrations for zinc, lead, and copper were computed from 22 storm EMCs, and mean base flow concentrations were computed from 3 dry weather samples.

Because no Lower Beaverdam Creek data exists for organic chemicals at detection limits low enough to quantify loads, concentrations of organic chemicals in this tributary were assumed to be the same as concentrations in the District's SS system. Therefore, for organic chemical concentrations in Lower Beaverdam, mean concentrations from the District's MS4 monitoring data were used when available. Otherwise, mean values from the Northeast and Northwest Branches data set were used. Arsenic was treated similarly.

#### **2.4.4. Other Tributaries and Separate Storm Sewer Loads**

All tidal sub-basin tributary sheds and separate sewer system sheds, including the Watts Branch tributary, were assumed to have identical storm flow and non-storm flow concentrations for all chemicals modeled. Non-storm concentrations were assumed to represent base flow and/or ground water concentrations in non-storm flow volumes entering the tidal Anacostia from each sub-shed. For the metals, storm flow concentrations were obtained by averaging the WASA LTCP EMCs separate sewer system results (DC WASA, 2000c) with means of the recent DC MS4 monitoring results (see Table 2-5). For arsenic, the DC MS4 monitoring results were used because the WASA EPMC-III results were all below the detection limit. For all four inorganic chemicals modeled, base flow mean values from the Northeast/Northwest Branches data were used for base flow concentrations.

For organic chemicals, means of recent DC MS4 monitoring data were used for storm flow

concentrations when detection limits were adequate (see Table 2-5); otherwise, Northeast/Northwest Branches storm flow averages were used. Base flow mean values from the Northeast/Northwest Branches data were used for base flow concentrations.

**TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report**

**Table 2-4. Summary of Storm flow (SF) and Base flow (BF) Concentration Estimates Based on Available Monitoring Data**

	Upstream BF/SF		WASA LTCP CSO sub-sheds SF				SS and Tribs SF		
	Northeast Br EMC	NW Br EMC	B St /NJ Ave EMC	Tiber Cr EMC	NEB Swirl EMC	NEB Bypass EMC	WASA LTCP EMC	DC MS4 Composite Means	LBD Cr BF/SF EMCs
Zinc (ug/l)	8/77	7/91	194	188	181	256	202	144	22/172
Lead (ug/l)	0.5/49	0.6/103	71	73	64	96	35	20	0.25/35
Copper (ug/l)	3/25	4/43	103	64	40	63	61	52	0.25/24
Arsenic (ug/l)	0.2/NA	0.2/NA	<5	<5	<5	<5	<5	1.4	
PCB1 (ng/l)	0.58/0.66	0.60/0.41						7.80	
PCB2 (ng/l)	2.63/8.81	1.90/6.13						14.97	
PCB3 (ng/l)	0.82/7.31	1.06/4.58						4.08	
PAH1 (ug/l)	0.054/0.271	0.056/0.607							
PAH2 (ug/l)	0.099/1.634	0.193/3.911							
PAH3 (ug/l)	0.044/0.945	0.097/2.631							
chlordane (ng/l)	0.81/4.49	1.19/18.93							
heptachlor epoxide (ng/l)	0.72/1.31	1.21/1.46							
dieldrin (ng/l)	0.55/0.65	0.78/1.70						0.29	
DDD (ng/l)	0.23/1.04	0.23/1.24						0.15	
DDE (ng/l)	0.52/0.07	ND/ND						0.89	
DDT (ng/l)	0.63/0.25	0.60/0.15						1.71	

**Table 2-5. Sampling Methods and Detection Limits for Water Column Data Sets**

Parameter	DC SS outfalls and minor tributaries <sup>1</sup>						NE/NW Branches <sup>2</sup>	Anacostia River <sup>3</sup>
	Sample Type	Bottle Type	Method	MDL for Method (ug/L)	MDL as Reported (ug/L)	Value Used for NDs (ug/L)	Quantitation Limit	Detection Limit
Metals	Composite	(1) 1000 ml Plastic HN03	U.S. EPA 200.8				Grab	Grab
Arsenic, Total				0.25	2.0	1.0		0.005
Copper, Total				1.52	2.0	N/A		0.02 ug/L (D), 0.11 ug/L (TR)
Lead, Total				0.23	2.0	N/A		0.02 ug/L (D), 0.71 ug/L (TR)
Zinc, Total				1.52	2.0	N/A		0.4 ug/L (D), 0.12 ug/L (TR)
Volatile Organic Compounds	Grab	(2) 40 ml Glass Vials; Teflon Lids	U.S. EPA 624	0.5			Composite	Composite
naphthalene					1.4	Only 1 detect	NA; used group average	
acenaphthylene					0.8	N/A	0.010 ng/L (D), 0.500 ng/g (P)	
acenaphthene					0.8	N/A	0.020 ng/L (D), 1.000 ng/g (P)	
fluorene					0.8	N/A	0.010 ng/L (D), 0.100 ng/g (P)	
phenanthrene					0.7	N/A	0.010 ng/L (D), 0.100 ng/g (P)	
fluoranthene					0.6	Only 2 detect	0.010 ng/L (D), 0.200 ng/g (P)	
pyrene					0.8	Only 1 detect	NA; used group average	
benz[a]anthracene					0.7	N/A	0.010 ng/L (D), 0.400 ng/g (P)	
chrysene					0.6	Only 1 detect	0.060 ng/L (D), 0.600 ng/g (P)	
benzo[k]fluoranthene					1.3	N/A	used group average	

**TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report**

Parameter	DC SS outfalls and minor tributaries <sup>1</sup>						NE/NW Branches <sup>2</sup>	Anacostia River <sup>3</sup>
	Sample Type	Bottle Type	Method	MDL for Method (ug/L)	MDL as Reported (ug/L)	Value Used for NDs (ug/L)	Quantitation Limit	Detection Limit
benzo[a]pyrene					0.6	N/A	0.010 ng/L (D), 0.700 ng/g (P)	
indeno[1,2,3-c,d]pyrene					0.6	N/A	used group average	
benzo[g,h,i]perylene					0.7	N/A	used group average	
dibenz[a,h]anthracene					0.6	N/A	used group average	
Pesticides	Composite	(1) 1 Liter Glass Amber Teflon Lids	EPA608	0.01 to 1.7				
cis-chlordane			Values for Total Chlordane		0.34	N/A	0.009 ng/L (D), 0.080 ng/g (P)	5.2 pg/L (D), 0.1 pg/L (P)
trans-nonachlor							0.010 ng/L (D), 0.100 ng/g (P)	
oxychlordane							0.009 ng/L (D), 0.100 ng/g (P)	
Heptachlor Epoxide					0.0002	N/A	0.020 ng/L (D), 0.200 ng/g (P)	
Dieldrin					0.0002	0.001	0.020 ng/L (D), 0.200 ng/g (P)	
p,p' DDD					0.0003	N/A	0.010 ng/L (D), 0.100 ng/g (P)	
p,p' DDE					0.0002	0.0001	0.010 ng/L (D), 0.100 ng/g (P)	
p,p' DDT					0.0004	0.0002	0.020 ng/L (D), 1.700 ng/g (P)	
PCB Congeners	Composite	(2) 1 Liter Glass Amber Teflon Lids	U.S. EPA 8082 modified	0.00025 to 0.005	0.00048 to 0.0005	0.00025	0.130 ng/L (D), 0.100 ng/g (P)	No MDL reported for congeners

<sup>1</sup> Source: DC MS4 Program, Nicoline Shelterbrandt, DC DOH; N/A = not applicable because all non-detects; MDL = Minimum detection limit; ND = non-detect.

<sup>2</sup> Source: Gruessner et al., 1998; D = Dissolved; P = Particulate.

<sup>3</sup> Source: Velinsky et al., 1999; D = Dissolved; P = Particulate; TR = Total Recoverable.

## 2.5. Confidence Intervals for Upstream Storm Concentration Estimates

There are relatively few storm water monitoring studies that have measured concentrations of toxic contaminants at detection limits useful for quantifying loads, especially in the case of hydrophobic organic chemicals. The studies that do exist typically collect samples for only a handful of storm events and a handful of base flow events. This lack of data is primarily due to the high cost of analyzing water samples for toxic chemicals using the very sensitive methods required to attain the accuracy necessary for load estimates. The sample sizes and the high variability of chemical concentrations in storm water result in large uncertainties in the concentration estimates that are used to compute loads. In this section, an effort is made to better understand the uncertainties associated with storm water concentrations estimates from the Northeast and Northwest Branches data.

Table 2-6 shows the results of a statistical analysis of data collected for the ICPRB Northwest/Northeast Branches study (Gruessner et al., 1998), in which four storm samples and six non-storm samples were analyzed for metals and organic contaminants using very low detection limits. This table shows the estimated mean storm flow concentrations of total PCBs, total PAHs, zinc, lead, and copper, which are used in the TAM/WASP model to compute corresponding loads to the river from the Northeast and Northwest Branches sub-sheds. The table also shows estimates of an 80% two-tailed confidence interval around each of the estimated means. Computations of means and confidence intervals were done using the assumption that concentrations have a lognormal distribution, using the methods given in Gilbert (1987). This assumption cannot be tested because of the small number of sample points, but it is generally considered to be a reasonable choice for storm water concentrations.

Though the individual uncertainty estimates themselves are highly unreliable due to the small number of sample points available, results appearing in Table 2.6 imply that estimates of concentration means based on the four sample points may be a factor of two or three or even a hundred times smaller than actual means. Alternatively, estimated concentration means may be 30% to 50% greater than actual means. Thus, the Northeast and Northwest Branches load estimates typically have a confidence interval of roughly (mean - (30% to 50%), mean + (200% to 1000%)). These results emphasize the need in the Anacostia for storm water monitoring studies with larger numbers of sample points per sampling location. Without a substantial amount of additional data, our understanding of where and in what quantities toxic chemicals are entering the Anacostia will be limited.

**Table 2-6. Statistical Uncertainty in Northeast/Northwest (NE/NW) Branches Storm flow Concentration Means**

<b>Data</b> (TPAH - Total PAHs TPCBs - Total PCBs BF - Base flow samples SF - Storm flow samples)	<b>Number of Samples</b>	<b>Range</b>	<b>Estimated Mean - (Lognormal)</b>	<b>Estimated Lower Limit for 80% Confidence Interval - (Lognormal)</b>	<b>Estimated Upper Limit for 80% Confidence Interval - (Lognormal)</b>
<b>TPAHs (ng/L) - NE</b>	4	960 - 4722	2900	1900	8900
<b>TPAHs (ng/L) - NW</b>	4	1268 - 9113	7100	4200	65,000
<b>TPCBs (ng/L) - NE</b>	4	12.8 - 20.9	16.8	14.5	20.4
<b>TPCBs (ng/L) - NW</b>	4	2.1 - 30.7	11.0	6.1	187.2
<b>Total Zn (µg/L) - NE</b>	4	31 - 125	77	53	169
<b>Total Zn (µg/L) - NW</b>	4	37 - 210	91	59	286
<b>Total Pb (µg/L) - NE</b>	4	3 - 76	49	24	1392
<b>Total Pb (µg/L) - NW</b>	4	4 - 282	103	45	44,000
<b>Total Cu (µg/L) - NE</b>	4	11 - 48	25	17	55
<b>Total Cu (µg/L) - NW</b>	4	4 - 80	43	21	481

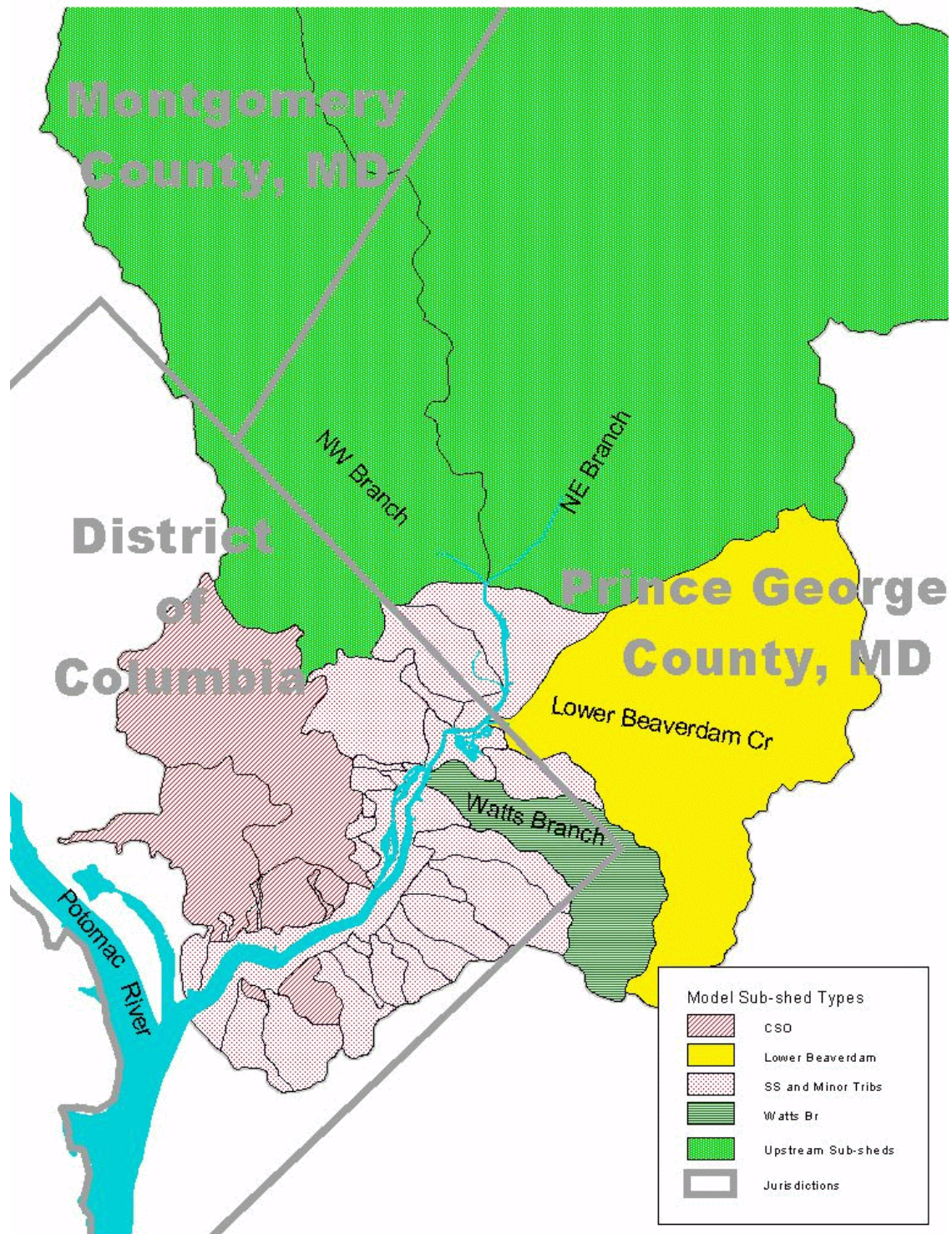


Figure 2-1. TAM/WASP Model Sub-sheds and Sub-shed Types



## CHAPTER 3: MODEL CALIBRATION/VERIFICATION

In the calibration/verification process, predictions of the TAM/WASP Toxics Screening Level Model were compared with available Anacostia River data, and, if necessary, adjustments were made to a limited number of model input parameters to improve model performance. A description of the general strategy used to calibrate and verify the model is given in the first section of this chapter. A discussion of how data was processed for model calibration and verification purposes, including water column concentration data, surficial bed sediment concentration data, and fish tissue data, is given in Section 3.2. Calibration/verification results for the six sub-models are given in Section 3.3.

### 3.1. General Calibration Strategy

The TAM/WASP Toxics Screening Level Model is based on the TAM/WASP sediment transport model, Version 2.3. The primary inputs new to the toxic chemicals component of the model are the chemical load inputs, the solid phase/dissolved phase partition coefficients ( $K_d$ 's), and chemical concentrations at the Potomac River boundary. Additional inputs that have an effect on model predictions are parameters governing air/water exchange and degradation of chemicals. As discussed below, site-specific data was used to estimate chemical load inputs and  $K_d$ 's for initial model runs and, in some cases,  $K_d$ 's and/or loads were adjusted during the calibration process to produce a better match between model predictions and observed concentrations. Potomac River boundary conditions were based on data when available, or otherwise, were estimated based on calibration run results. Inputs governing air/water exchange were based on values found in the literature, and were not adjusted in the calibration process.

Initial model runs were done using load estimates computed from mean storm flow and mean base flow chemical concentrations computed from monitoring data, summarized in Table 2-4, and mean  $K_d$ 's computed from Anacostia River base flow water column data, given in Table 2-3. For chemicals where no Anacostia River  $K_d$ 's were available, Northeast/Northwest Branches mean base flow  $K_d$ 's were used. These initial model runs simulated the deposition of contaminated sediment to the river bottom over a six-year time period, in order to determine whether the model could simulate observed bed sediment contamination patterns. A three-year time period representing 1988 through 1990 hydrology, considered to represent a typical "wet" year, "dry" year, and "average" year in terms of precipitation (Mandel and Schultz, 2000), was used to generate model flows, and this three-year simulation was run twice, using the WASP model's "RESTART" option, to simulate processes over a six-year time period. These model runs began with initial conditions that simulated a "clean" sediment bed, i.e. with chemical concentrations initially set equal to zero in all bed sediment segments. The model uses WASP's variable bed volume option (IBEDV = 1). Most sub-models were configured with a surficial sediment layer 1 cm in depth and a lower sediment layer 5 cm in depth. However, the PCB sub-model was configured with four sediment layers with thicknesses, from top layer to bottom layer, of ¼ cm, ¼ cm, ½ cm, and 5 cm, in order to allow more accurately simulation of burial processes. It was determined that after a six-year simulation, segment contaminant

concentrations in the upper 1 cm of the sediment bed approached a relatively constant, “steady state”, condition, that is, they ceased changing significantly over time. Model predictions for last day of the six-year run for the 35 main channel sediment segments for the upper 1 cm of the bed sediment were compared to averaged bed sediment data for these segments (see Section 3.2.1 below) to determine whether or not the initial load estimates were producing the observed magnitude of contamination in the river’s sediment bed. In a number of cases, namely, for zinc, copper, chlordane, and dieldrin, predicted contaminant concentrations matched observed concentrations fairly well, and it was decided that loads estimated from the available monitoring data were reasonable. For PAHs, PCBs, and DDX’s, the model predictions produced significantly lower concentrations in the sediment bed than is observed, and for lead and heptachlor epoxide, the model predicted significantly higher concentrations than are observed. Given the uncertainty in storm and base flow concentration estimates (see Section 2.5), it is not unexpected that load estimates may be 50% too high, or may be a factor of 2 or 3 or more too low. Therefore, in cases where it appeared to be necessary, the model storm flow and base flow chemical concentrations were increased or decreased to obtain a more reasonable match of model predictions to bed sediment contamination data.

In the second phase of the calibration process, the model was run to simulate daily water column concentrations for time periods in which data was available. Water column data is available for 1998 for zinc, lead, copper, PCBs, p,p' DDE and p,p' DDT. For these chemicals, model predictions for the dissolved phase and for the total (dissolved + particulate) phase concentrations were compared with available data. In some cases, model  $K_d$  values were adjusted to produce a better fit to the dissolved concentration data. For chemicals for which no water column calibration data was available, model predictions were compared to predictions of ambient concentrations based on fish tissue data and bioaccumulation factors (see Section 3.2.2).

As mentioned above, partition coefficients used in the model were based on site-specific data, and in some cases were adjusted in the calibration process. TAM/WASP Version 2.3 can simulate the adsorption of chemical contaminants onto the fine-grained and medium-grained sediment fractions but not onto the coarse-grained fraction. This seems reasonable because it is known that contaminant concentrations are generally higher in finer-grained sediments.  $K_d$ ’s for organic contaminants are proportional to the sediment’s fraction of organic carbon (foc), and higher foc values in the Anacostia have been found to be correlated with smaller average sediment grain sizes (Velinsky and Ashley, 2001). Also, because of their higher mass to surface area ratio, coarse-grained sediments should contain lesser quantities of contaminants on a mass chemical per mass sediment basis. For this reason,  $K_d$ ’s for the fine-grained sediment fraction were initially set equal to mean  $K_d$ ’s computed from base flow data.  $K_d$ ’s for the medium-grained fraction were set, somewhat arbitrarily, to be a factor of 1/4 of the fine-grained  $K_d$ ’s. If adjustments were made to  $K_d$ ’s during the calibration process, the same adjustment factor was applied to both the fine-grained and the medium-grained  $K_d$ ’s. Results of runs to investigate the sensitivity of model predictions to changes in  $K_d$ ’s are presented below in the sections on the metals model calibration and the PCB model calibration.

### **3.2. Discussion of Calibration Data**

Three types of data are used in the model calibration/verification process: water column chemical concentration data, bed sediment chemical concentration data, and fish tissue chemical concentration data. The use of the water column concentration data is relatively straightforward. Model predictions of daily water column concentrations (both total and dissolved) are compared with concentrations measured in water samples collected from the river. However, in the case of the bed sediment concentration data and the fish tissue data, a certain amount of analysis must be done before values can be obtained that are useful for comparison with model results. These analyses are described in Sections 3.2.1 and 3.2.2, below.

#### **3.2.1. Estimation of Bed Sediment Segment Concentration Averages**

Bed sediment concentrations in the tidal sub-basin are based on the Velinsky and Ashley (2001) data set and several historical data sets available in the AWT/NOAA database (NOAA, 2001), as described in Section 1.4.3 of this report. The average sediment concentration in each WASP segment (Table 3-1) were estimated from the data points by Inverse Distance Weighted (IDW) spatial interpolation and zonal statistics using Environmental Systems Research Institute (ESRI) software products, including ArcMap and Spatial Analyst.

Spatial interpolation is a method that allows estimating values for locations where no measured values are available and can be used to create a continuous value surface from data collected at discrete locations (i.e. points) or to explore spatial patterns in point-sampled data. IDW interpolation is a spatial interpolation method that uses weighted moving averages within an area of influence to predict values of grid cells. IDW assumes that each data point has a local influence that diminishes with distance. To predict a value at an unknown location, IDW looks at the measured values surrounding the prediction location and assigns weights that are inversely proportional to the distance to the prediction location, raised to a user-specified power. At a higher power, the nearest data points exert the most influence on the prediction location, creating an interpolated surface that is more detailed but less smooth; whereas at a lower power, the influence of more distant points is increased, creating a surface that is smoother but less detailed. A power of two is commonly used. Because the interpolated surface is a weighted average of data points, the predicted grid cell values cannot be greater than the highest or less than the lowest input value.

There are two common approaches for defining the neighborhood search area: a) fixing the search radius and allowing interpolation between a variable number of data points or b) specifying the number of data points (i.e. nearest neighbors) within a variable search radius to be used for the interpolation. The choice of method depends on the spatial distribution of the data points and the presence of outliers. The fixed radius approach may fail to find neighbors when the data points are spaced too far apart, and as a result the interpolated surface may be discontinuous. The nearest neighbor method, on the other hand, yields a continuous output surface, but the points may be so far apart that the results may be misleading.

Based on sensitivity analyses, ICPRB determined that by using a grid cell size of three meters, a power of two, and six nearest neighbors, IDW predicted the interpolated surface fairly accurately for most of the chemicals. Zonal statistics was then used to estimate the average chemical concentrations in each WASP segment from the grid values. With ArcMap's zonal statistics function, a statistics (e.g., mean sediment concentration) can be calculated for each zone (e.g., WASP segment) in a zone data set based on the values of a value grid (e.g., IDW interpolated sediment concentration grid).

Estimated sediment concentrations of the modeled constituents for the tidal portion of the Anacostia River are shown in comparison to the Thresholds Effects Limit (TEL) and Probable Effects Limit (PEL) (source: Buchman, 1999) or as standard deviations when TEL and PEL were not available in Figures 3-1 to 3-14.

Table 3-1. Average Segment Sediment Concentrations (ng/g dry weight)

Segment	Zinc	Lead	Copper	Arsenic	PCB1	PCB2	PCB3	PAH1	PAH2	PAH3	Total Chlordane	Heptachlor Epoxide	Dieldrin	p,p'-DDD	p,p'-DDE	p,p'-DDT
1	104679	27632	18949	3.3	10.6	19.9	6.2	603	2203	2214	5.4	0.55	0.42	1.5	1.1	0.9
2	124477	28217	42377	3.3	30.1	50.6	16.0	1361	4990	5020	11.9	1.05	1.00	2.9	2.3	1.5
3	263314	57277	46411	3.3	11.4	57.3	33.7	1835	9191	8398	17.9	1.71	1.71	6.5	4.5	3.7
4	252762	57894	49262	3.3	7.5	58.2	31.2	1862	9531	8517	22.8	1.56	1.80	7.5	5.0	3.3
5	220396	51242	48727	3.3	9.9	58.5	28.6	1429	7450	7700	27.6	1.48	3.19	9.2	6.8	2.8
6	251804	58821	60110	3.4	16.7	73.5	34.8	1840	9509	10137	33.8	1.85	5.57	11.1	8.4	3.8
7	199068	49074	38050	3.6	23.7	70.3	23.6	1403	6468	6577	20.2	1.19	3.68	7.6	4.7	2.8
8	172548	37771	33165	3.7	38.5	73.8	18.8	941	4201	4029	13.5	1.18	2.74	11.6	3.7	7.2
9	143411	31352	45854	3.4	22.1	47.5	16.0	689	3547	3114	11.8	0.90	1.36	5.2	3.0	2.5
10	182699	49629	40791	3.2	15.0	56.5	22.0	853	5036	4313	16.4	0.07	1.51	6.5	5.2	2.3
11	189770	43959	51912	3.1	16.5	61.4	25.7	856	4843	4885	18.3	0.01	1.81	7.3	6.3	2.3
12	276725	74125	61978	3.2	21.2	83.9	31.8	1648	7752	9321	24.7	0.01	3.12	11.5	8.9	5.9
13	152750	70512	44137	3.4	10.2	54.8	22.8	1363	4308	4481	9.4	0.28	1.73	6.5	4.0	3.6
14	209450	69465	153845	3.5	33.6	193.5	86.2	667	2299	2376	14.8	0.13	1.42	16.3	12.8	2.3
15	228644	64500	50833	3.2	55.7	326.3	56.7	754	3874	3771	31.9	0.88	1.69	24.1	18.5	4.5
16	270671	74100	62671	4.3	37.6	233.6	51.2	1494	7868	7615	28.8	1.35	1.89	13.4	10.9	4.1
17	234474	73119	51049	4.2	23.8	103.8	31.3	1498	6739	6075	20.3	1.12	1.49	11.6	12.8	7.0
18	230543	63765	48914	3.7	19.0	83.3	28.4	1311	6837	6564	25.5	1.12	2.07	15.9	14.6	4.4
19	276549	88963	67469	3.4	25.4	109.2	42.1	1801	7898	8406	22.4	0.92	3.39	15.2	12.3	3.9
20	270636	92822	65887	4.2	24.8	100.4	34.0	8780	12006	8134	22.8	0.36	3.39	19.1	21.3	4.0
21	232664	96506	51703	4.3	25.9	113.2	32.8	2668	8204	6805	30.5	1.06	3.62	31.0	33.2	10.0
22	213175	114978	52246	5.6	21.4	117.1	33.7	2221	7989	7181	29.6	1.19	2.50	16.9	5.5	15.5
23	210906	122075	53822	6.1	23.7	149.0	51.5	5607	15325	10981	35.1	1.03	2.66	14.7	9.7	6.0
24	254232	69501	70521	8.7	17.2	119.1	40.6	16224	27260	16423	24.6	0.90	2.29	11.9	4.2	17.9
25	327815	93010	90149	5.4	20.9	114.9	54.5	4944	9232	7914	25.5	0.89	3.08	11.0	8.8	4.7
26	328992	98175	92868	6.9	20.1	124.6	59.9	2210	7793	7399	30.5	0.92	3.16	13.2	8.7	12.1
27	329065	100405	97437	6.7	17.3	209.1	139.2	4932	9902	8398	29.0	1.35	2.66	11.7	7.6	17.2
28	495290	202866	145160	7.5	39.1	732.6	567.9	4007	11164	11110	34.3	0.66	2.72	23.5	27.7	32.7

**TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report**

Segment	Zinc	Lead	Copper	Arsenic	PCB1	PCB2	PCB3	PAH1	PAH2	PAH3	Total Chlordane	Heptachlor Epoxide	Dieldrin	p,p'-DDD	p,p'-DDE	p,p'-DDT
29	555629	220679	142153	7.5	57.6	380.0	175.0	1911	7774	8981	38.9	0.28	3.04	22.9	30.1	40.3
30	306851	101132	93611	7.5	14.0	108.3	44.1	1323	4689	5333	18.2	0.21	0.99	8.0	13.5	34.7
31	338812	97763	100016	7.5	12.7	83.1	42.3	930	4210	5063	18.7	0.22	1.29	6.2	10.7	50.3
32	314355	80083	88489	7.5	13.4	82.9	52.3	795	3668	4507	16.1	0.31	1.80	10.1	12.3	27.2
33	276090	63430	79101	7.5	8.6	50.3	28.4	547	2369	3023	11.6	0.28	1.18	21.8	9.1	13.7
34	240419	49007	72135	7.5	6.6	42.6	27.0	447	1831	2442	7.8	0.28	0.81	5.6	7.6	11.9
35	213742	41502	62960	7.5	7.1	47.9	24.7	424	1635	2074	6.7	0.28	0.79	3.3	7.6	9.9

### 3.2.2. Estimates of Ambient Water Column Concentrations From Fish Tissue Data

For some of the chemicals modeled in this study, no water column data is currently available for comparison with model predictions. As a rough means of model verification, data on contaminant concentrations in fish tissue can be used along with published values for bioconcentration factors to estimate ambient water column concentrations. The bioconcentration factor for a given contaminant is defined as the ratio of the fish tissue concentration over the water column concentration (see, e.g., US EPA, 1998). Given a site-specific fish tissue concentration average, an estimate for the ambient water column concentration is then:

$$WC = \frac{TC}{1000 BCF} \quad (3-1)$$

where

TC = tissue concentration in mg/kg (equivalent to mg/L)

BCF = EPA bioconcentration factor in L/kg

WC = water column concentration (estimated) in mg/L

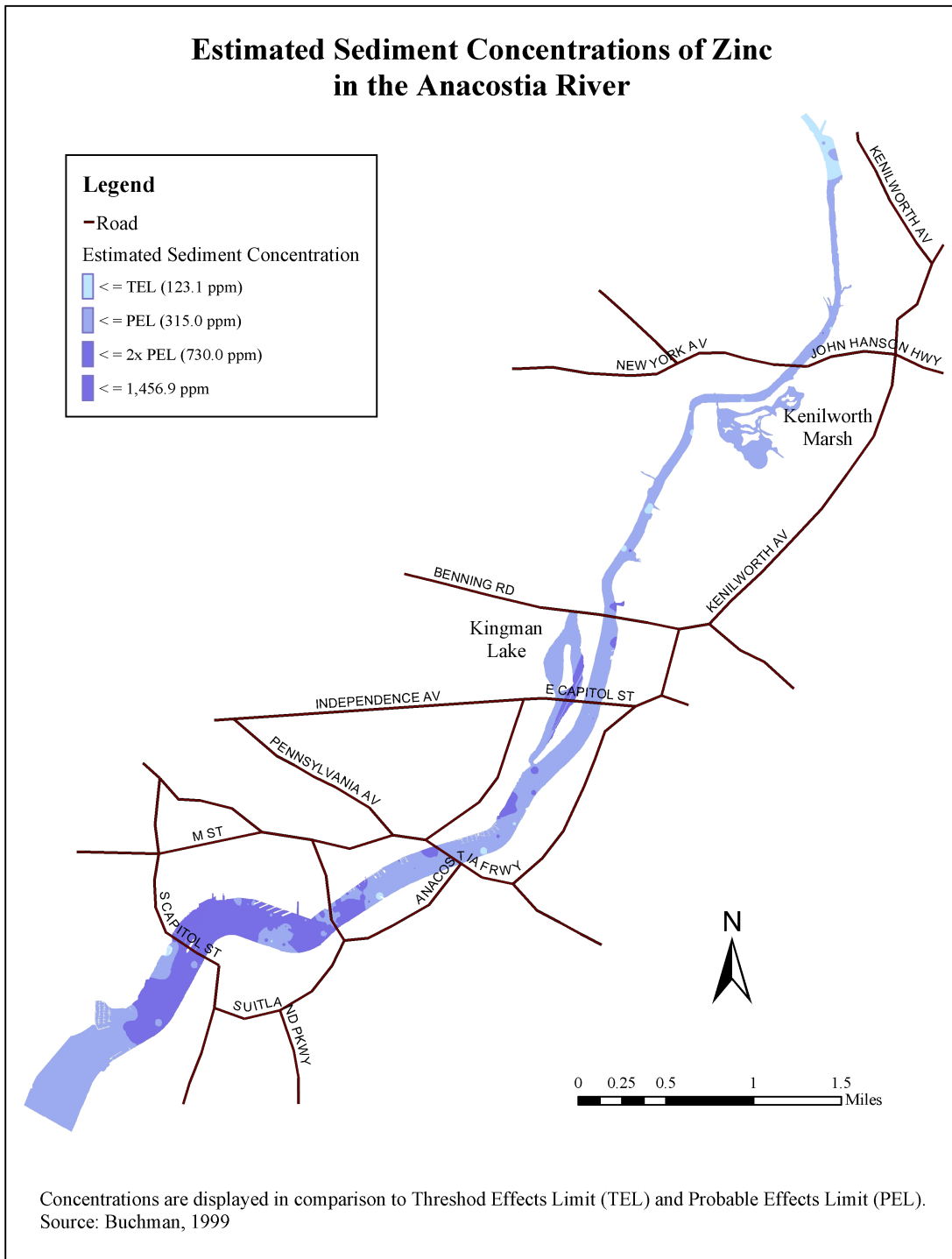
Multiply by 1000 to obtain ug/L

Anacostia River fish tissue concentrations are available (USGS Fred Pinkney, private communication) for several of the modeled chemicals. The data set consists of four fish species (bluegill, carp, channel catfish, and largemouth bass) for a total sample size of 25.

Bioconcentration factors (BCF) were obtained for all modeled chemicals except PAHs, heptachlor epoxide, and zinc. Estimated water column concentrations are provided in Table 3-2.

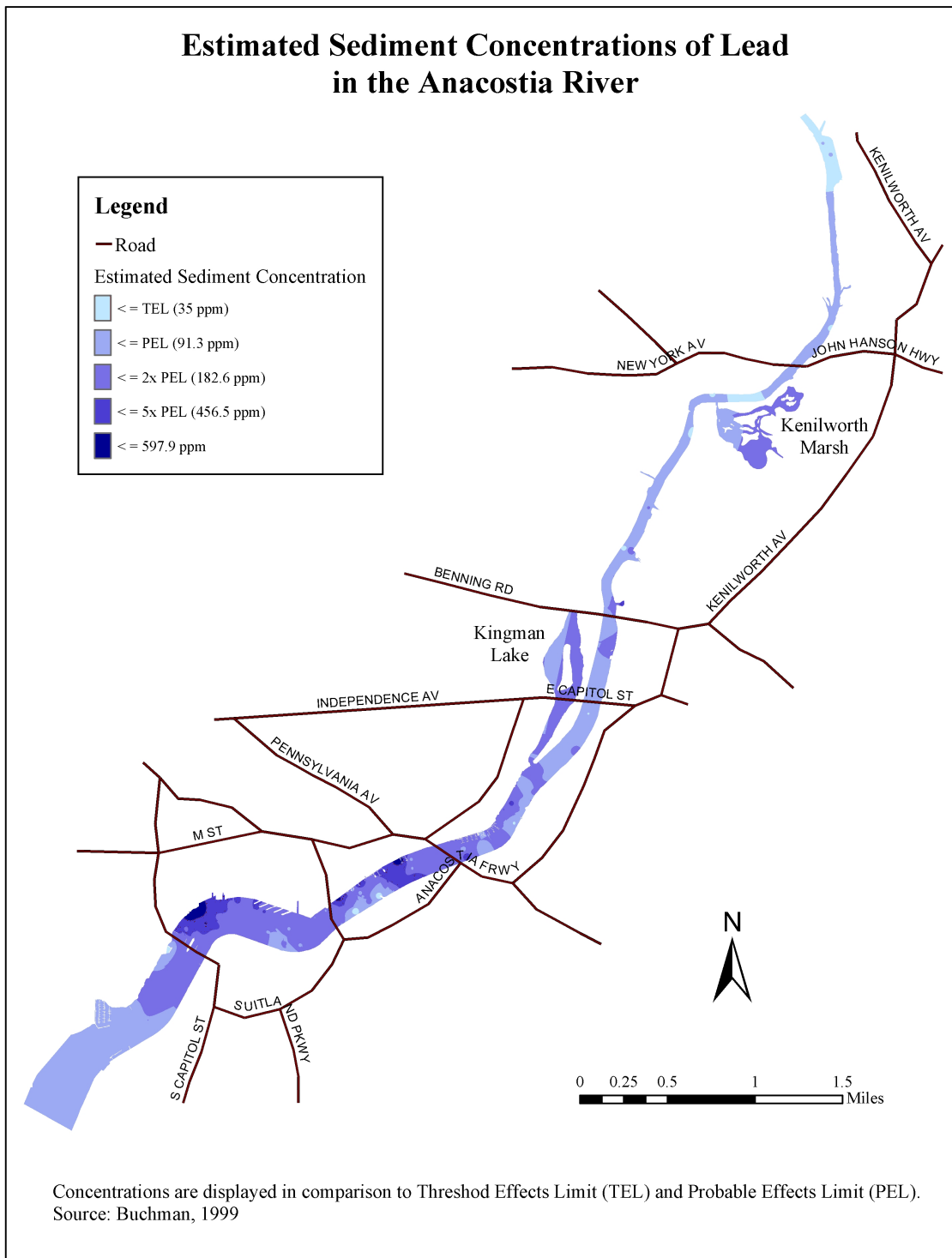
**Table 3-2. Estimated Water Column Concentration for Selected Chemicals Based on Fish Tissue Concentrations**

Chemical	BCF	Est. Water Column Conc (ug/L)
Zn	na	x
Pb	49 (U.S. EPA, 1980f)	1.44
Cu	36 (U.S. EPA, 1980d)	16.93
As	44 (U.S. EPA, 1980b)	1.99
PCB	31,200 (U.S. EPA, 1980g)	2.89E-02
PAH	na	x
Chlordane	14,100 (U.S. EPA, 1980c)	6.62E-03
Heptachlor epoxide	na	x
Dieldrin	4,670 (U.S. EPA, 1980a)	2.34E-03
p,p' DDD	53,600 (U.S. EPA, 1980e)	6.20E-04
p,p' DDE	53,600 (U.S. EPA, 1980e)	1.72E-03
p,p' DDT	53,600 (U.S. EPA, 1980e)	5.19E-05

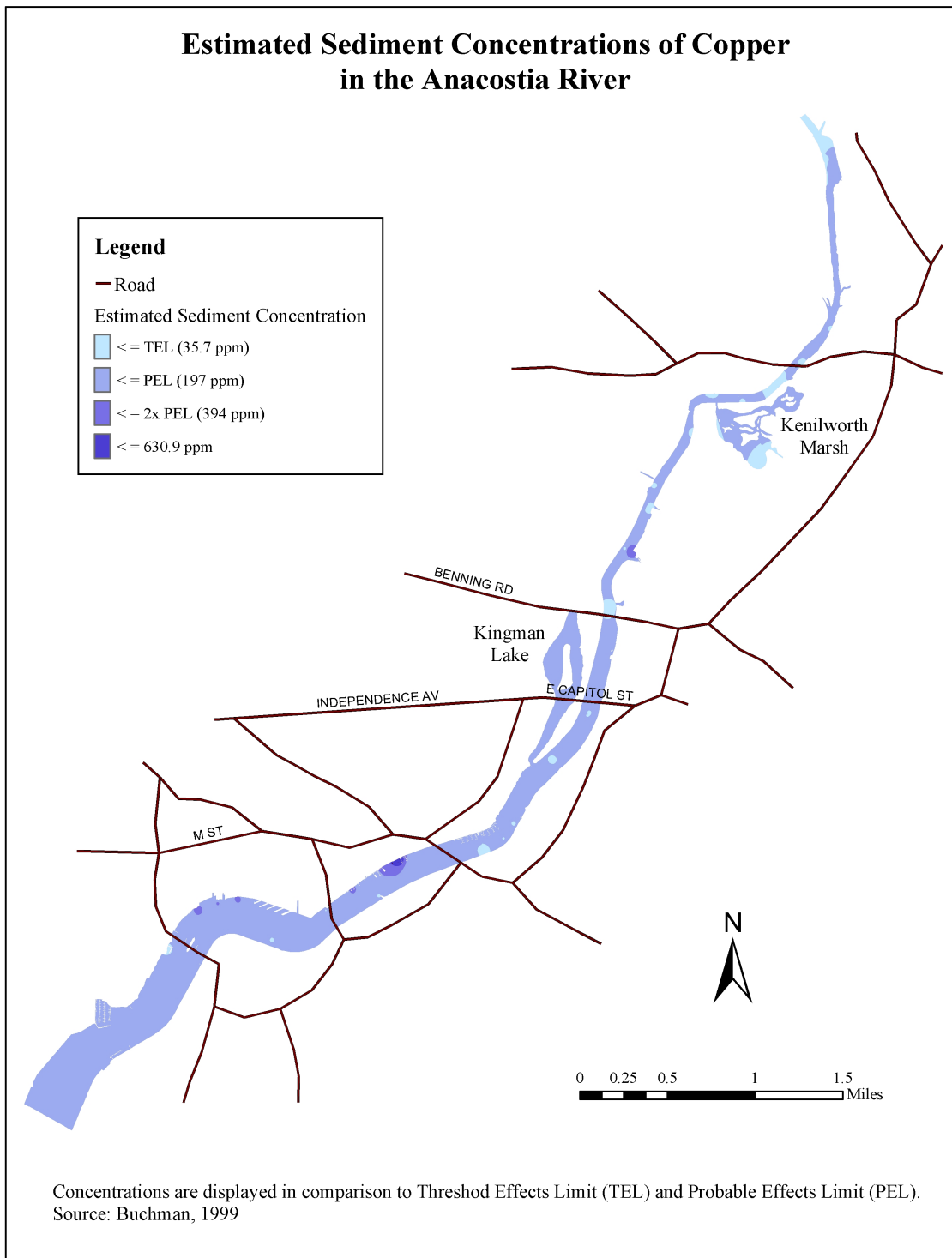


**Figure 3-1. Estimated zinc concentrations (ppm) in Anacostia River surficial bed sediments**

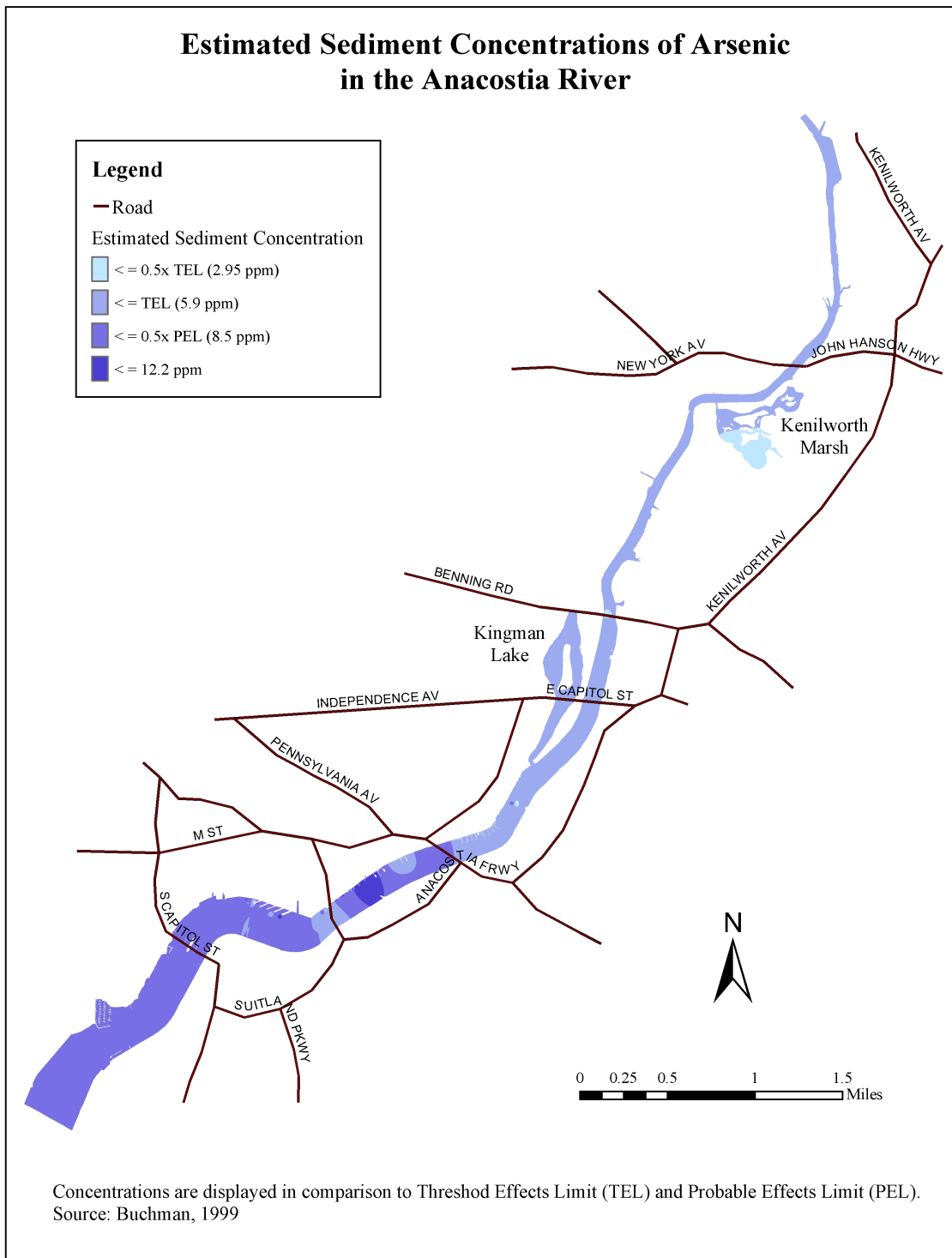




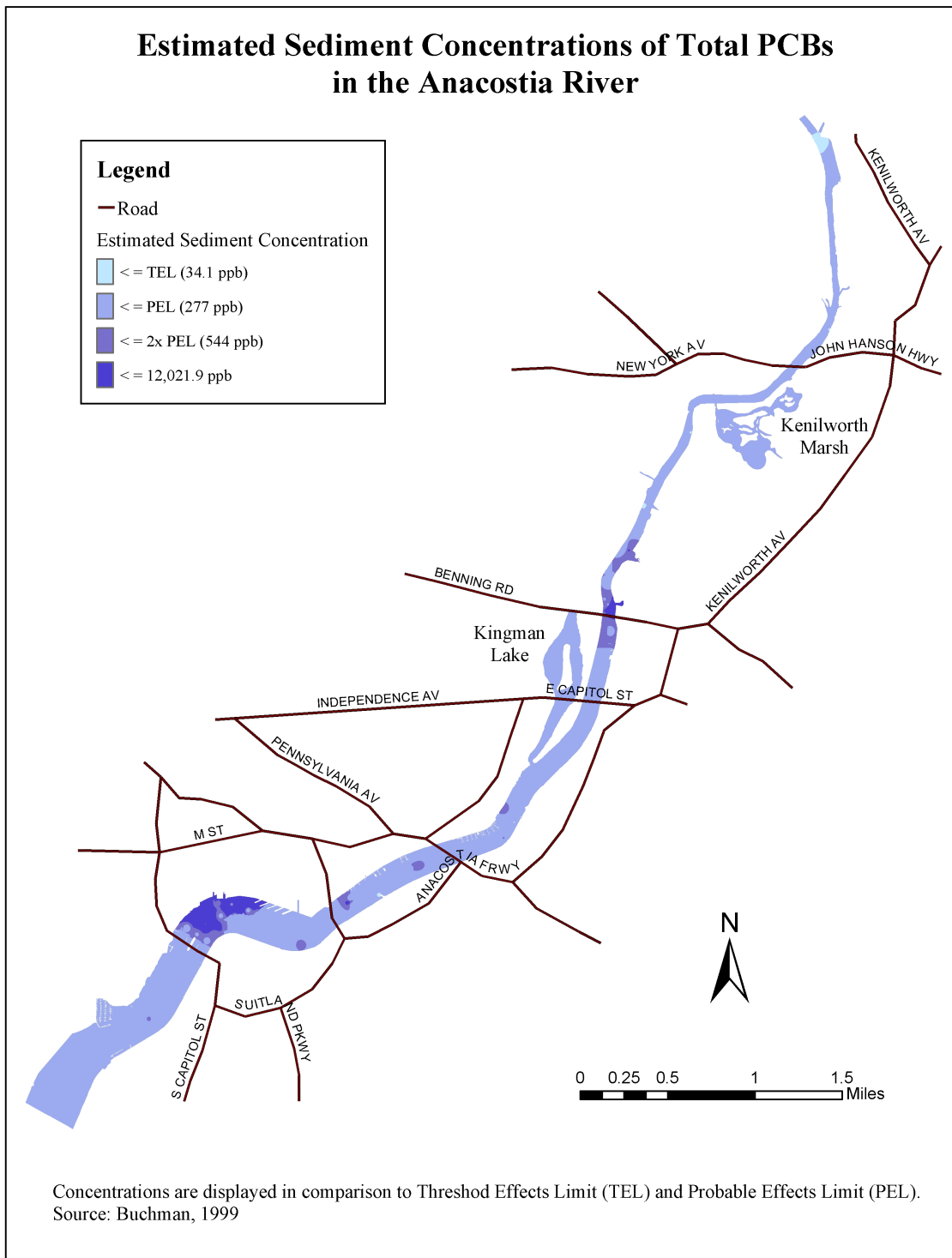
**Figure 3-2. Estimated lead concentrations (ppm) in Anacostia River surficial bed sediments**



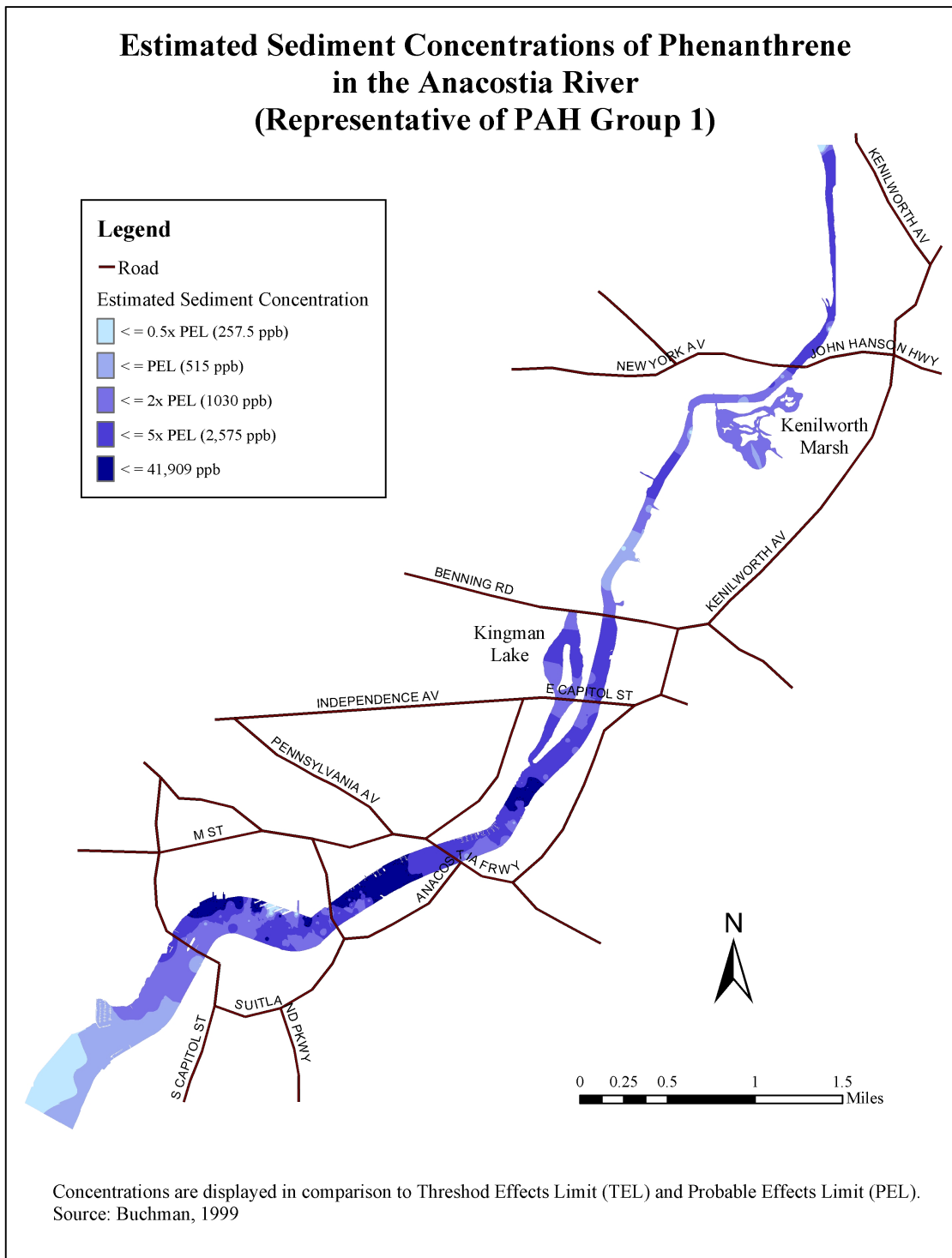
**Figure 3-3. Estimated copper concentrations (ppm) in Anacostia River surficial bed sediments**



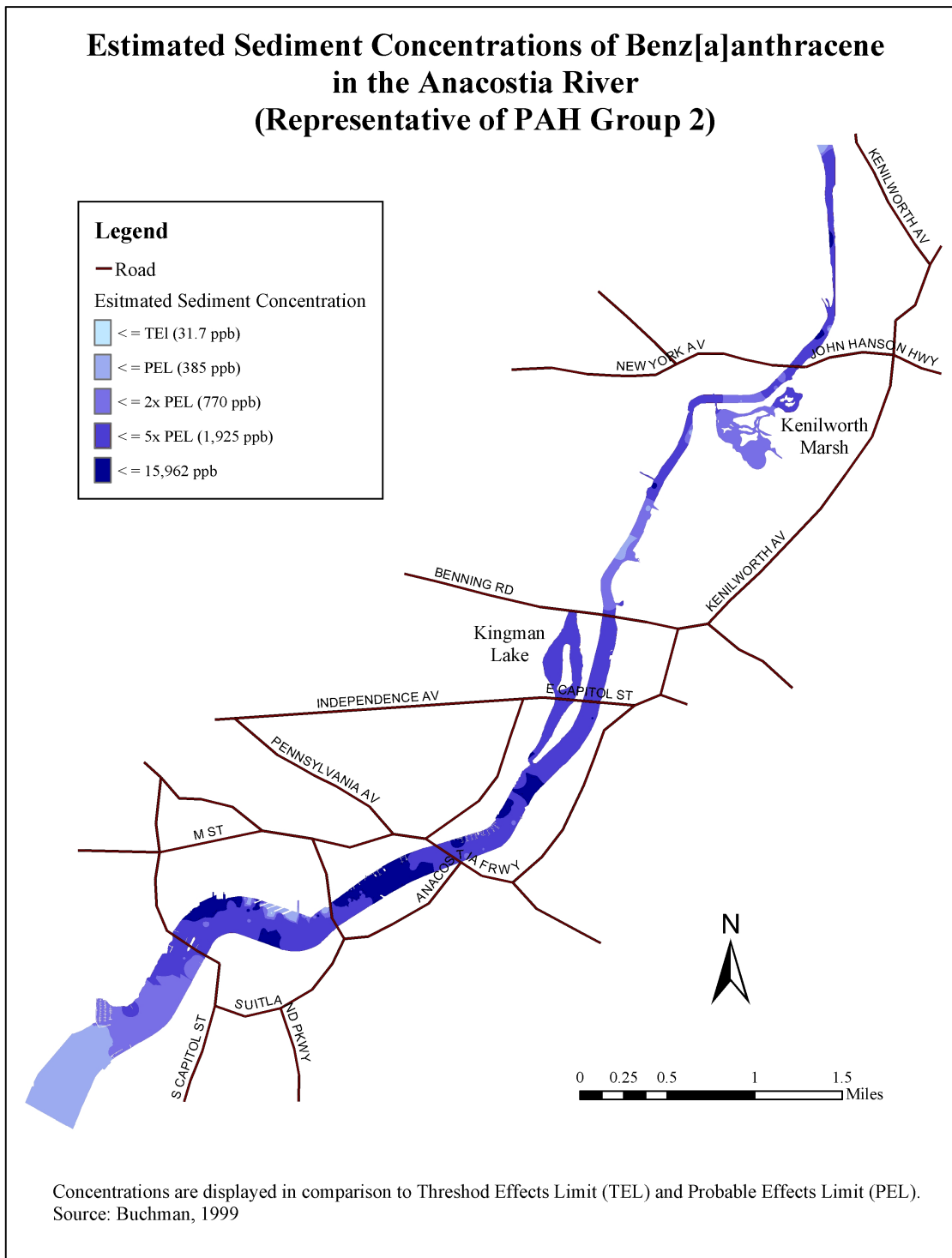
**Figure 3-4. Estimated arsenic concentrations (ppm) in Anacostia River surficial bed sediments**



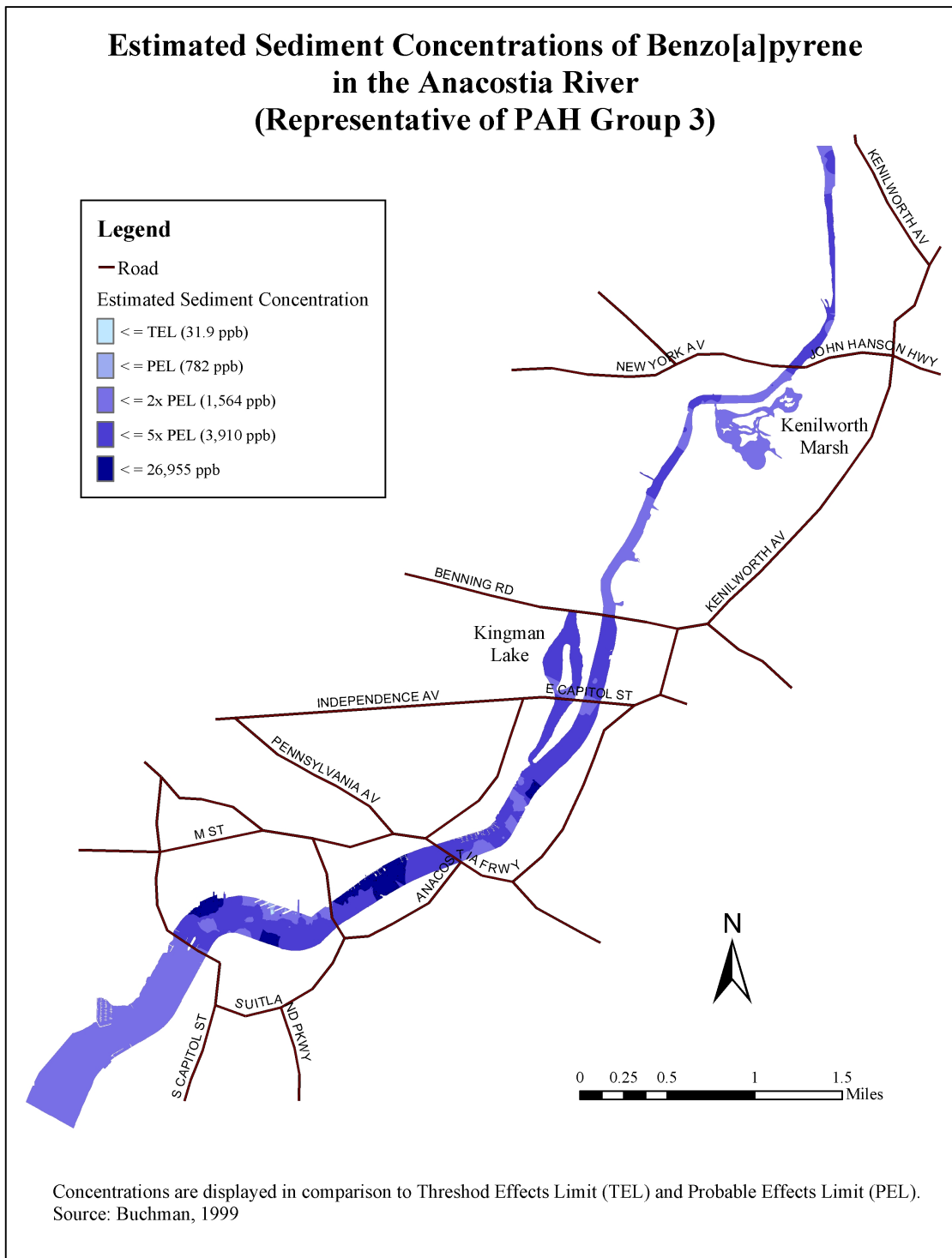
**Figure 3-5. Estimated total PCBs concentrations (ppb) in Anacostia River surficial bed sediments**



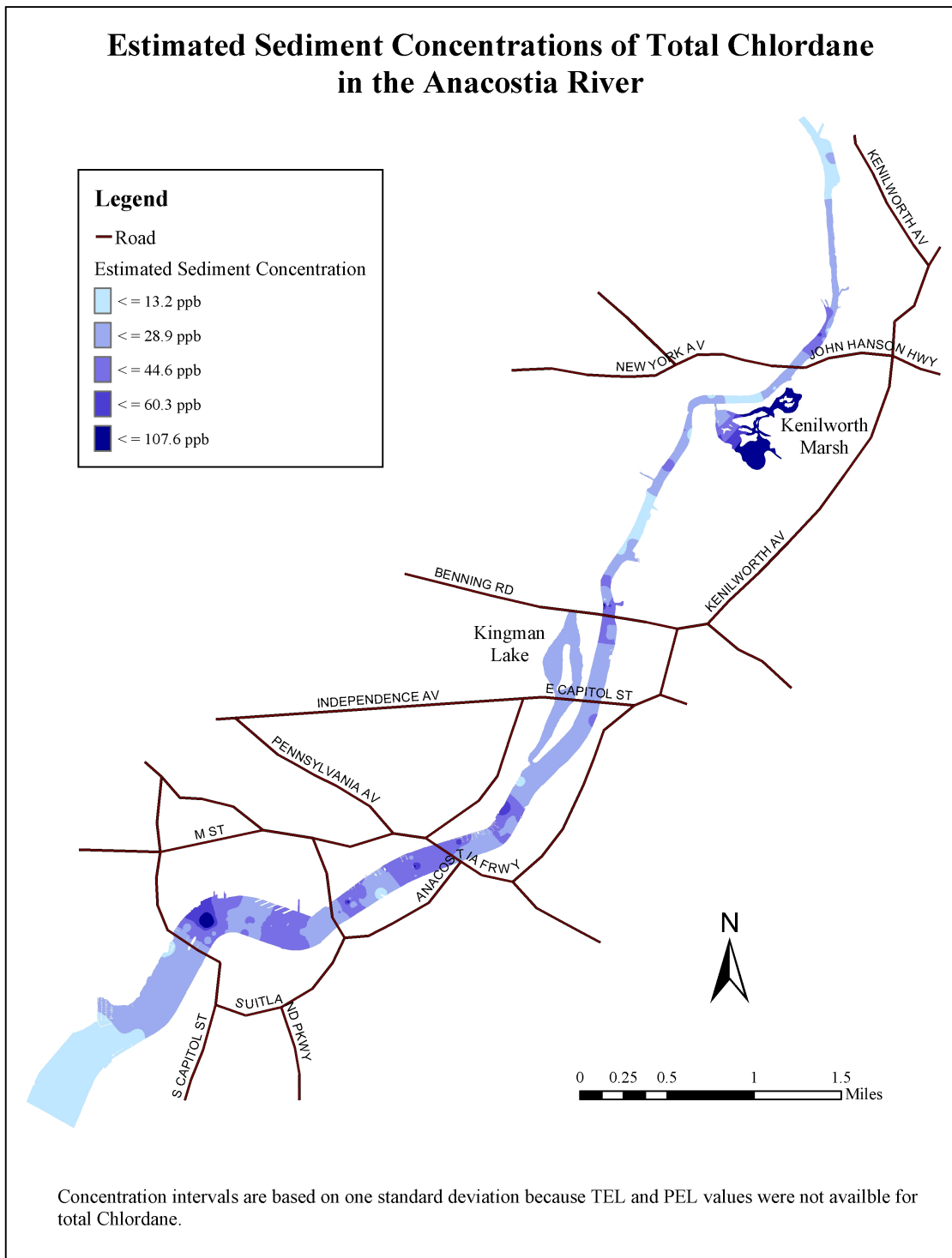
**Figure 3-6. Estimated phenanthrene (representative of PAH Group 1) concentrations (ppb) in Anacostia River surficial bed sediments**



**Figure 3-7. Estimated benz[a]anthracene (representative of PAH Group 2) concentrations (ppb) in Anacostia River surficial bed sediments**

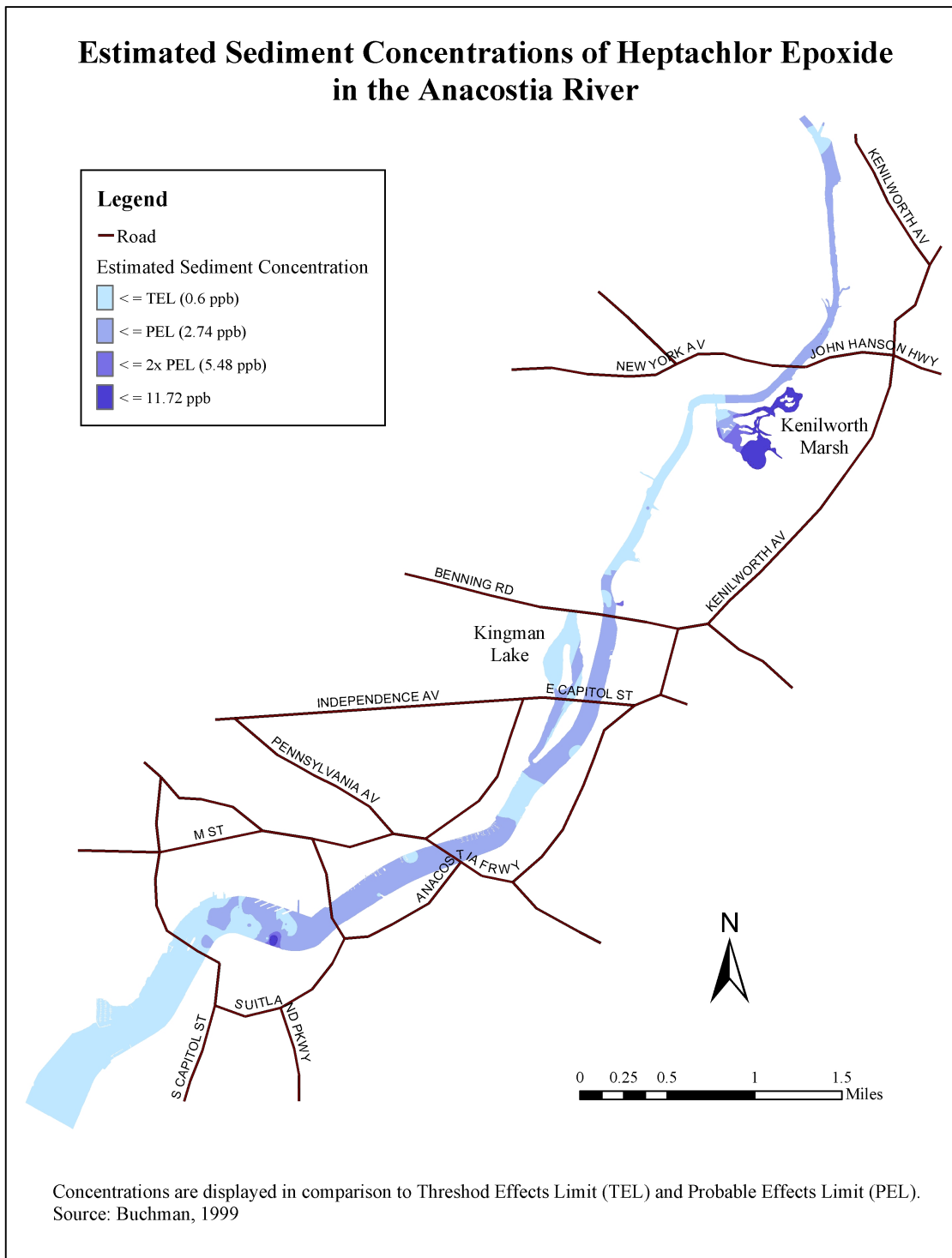


**Figure 3-8. Estimated benzo[a]pyrene (representative of PAH Group 3) concentrations (ppb) in Anacostia River surficial bed sediments**

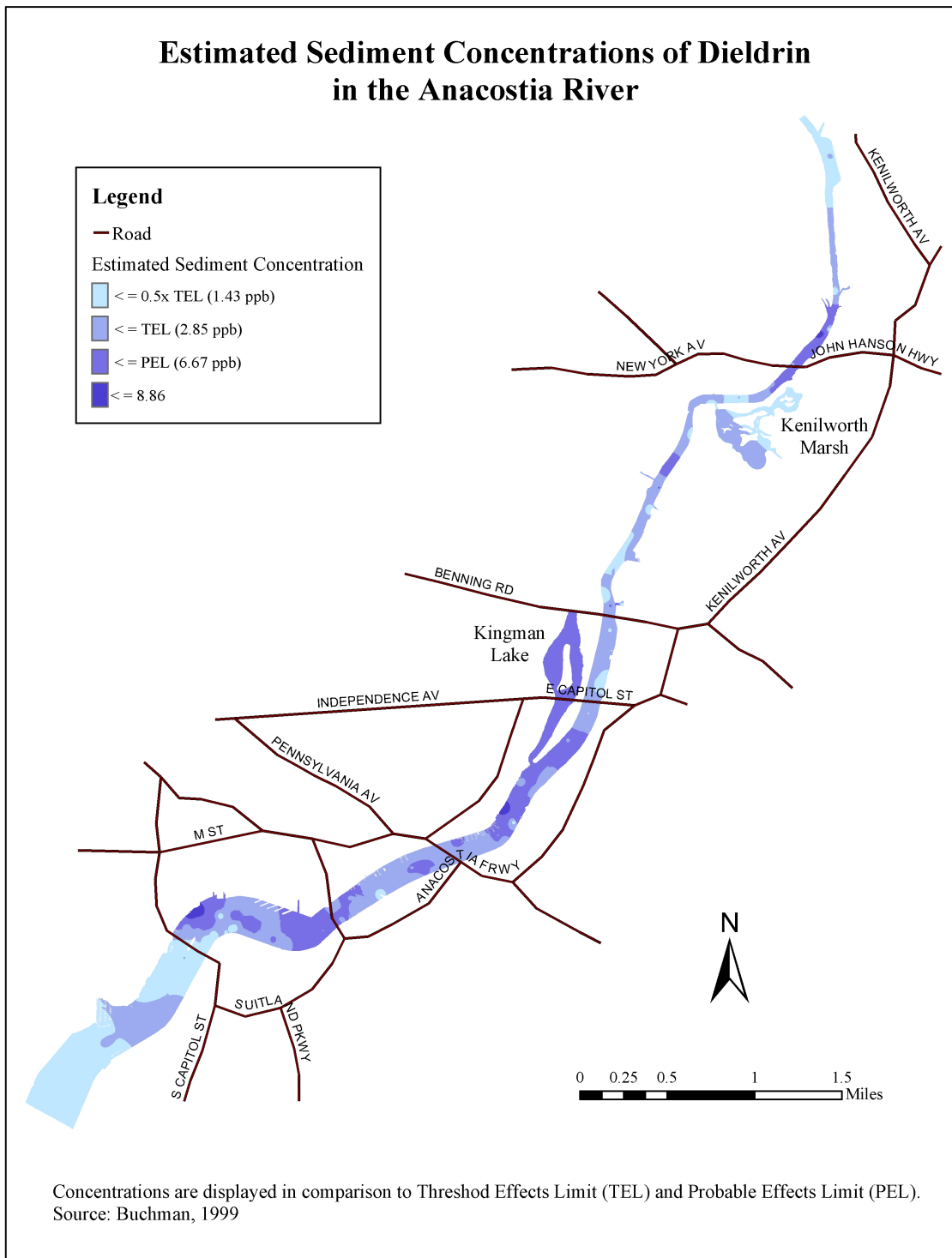


**Figure 3-9. Estimated total chlordane concentrations (ppb) in Anacostia River surficial bed sediments**

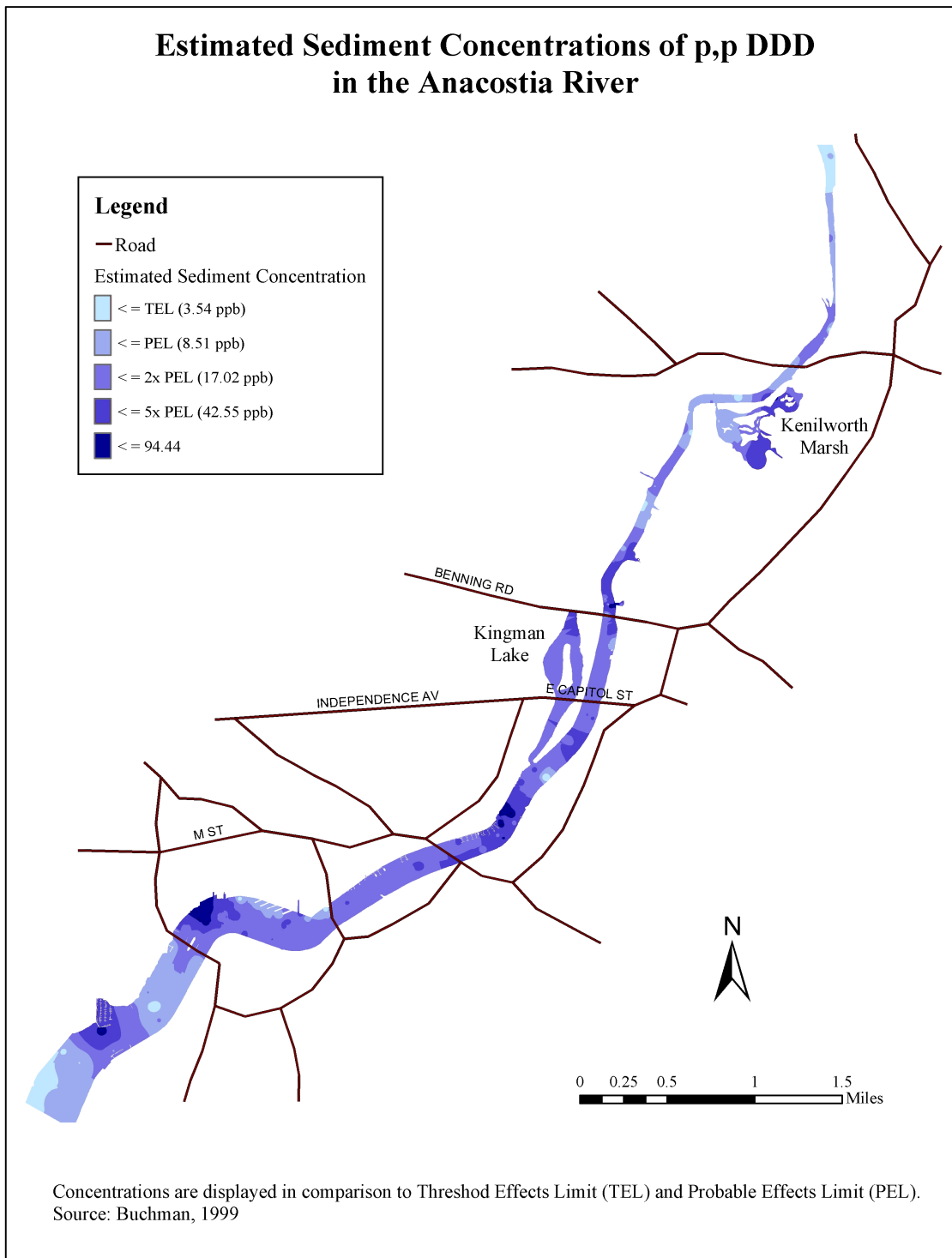




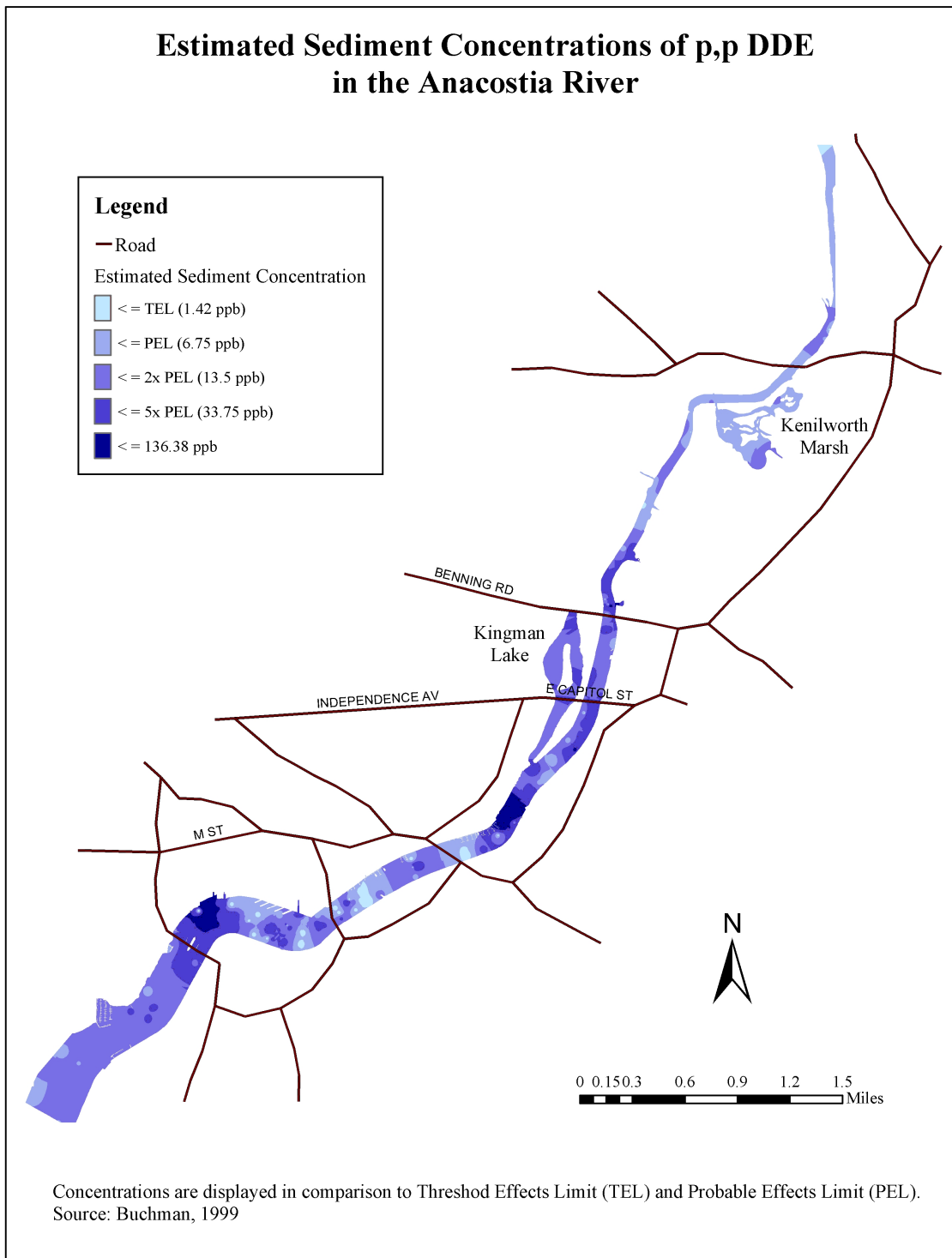
**Figure 3-10. Estimated heptachlor epoxide concentrations (ppb) in Anacostia River surficial bed sediments**



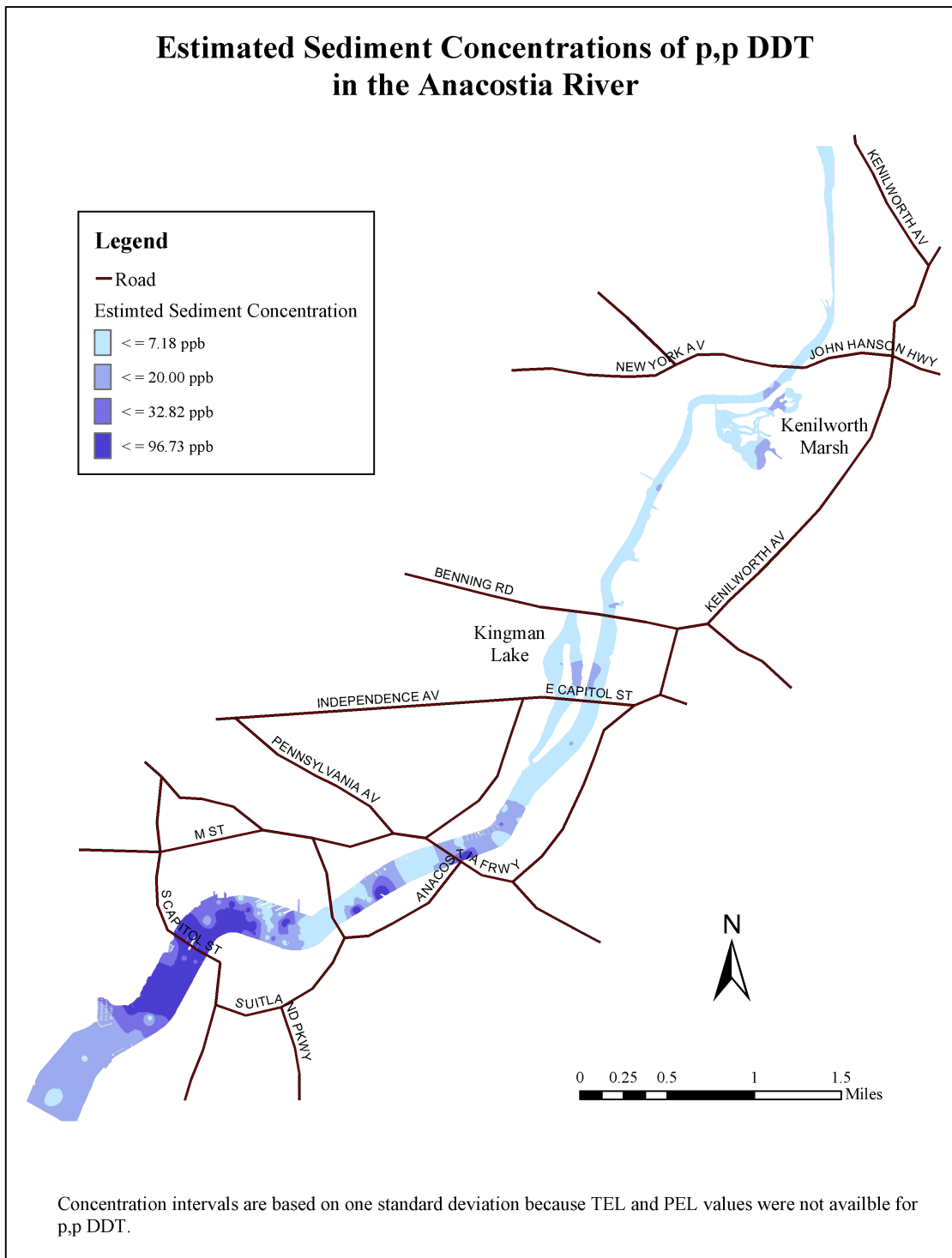
**Figure 3-11. Estimated dieldrin concentrations (ppb) in Anacostia River surficial bed sediments**



**Figure 3-12. Estimated p,p' DDD concentrations (ppb) in Anacostia River surficial bed sediments**



**Figure 3-13. Estimated p,p' DDE concentrations (ppb) in Anacostia River surficial bed sediments**



**Figure 3-14. Estimated p,p' DDT concentrations (ppb) in Anacostia River surficial bed sediments**

### 3.3. Calibration Results

Discussions of the calibration/verification of the six TAM/WASP Toxics Screening Level Model sub-models appear below.

#### 3.3.1. Metals (Metals1) Sub-Model

##### Model Description

The TAM/WASP sub-model for metals (Metals1), has been configured to simulate the loading, fate and transport of total zinc, total lead, and total copper. The only fate and transport process simulated, in addition to advection and dispersion, is adsorption to the medium and fine-grained sediment fractions. Chemical speciation of these three metals is not simulated due to lack of data support.

##### Input Parameters

Proposed partition coefficients for zinc, lead, and copper are given in Table 3-4. These values are based on an analysis of 1998 water column data available in Velinsky et al. (1999), and on water column calibration results. Initial model calibration runs were made using the mean  $K_d$  values computed from base flow Anacostia River data (Table 2-3).  $K_d$  values for zinc and lead were adjusted downward in order to better match observed dissolved water column concentrations. Model boundary conditions at the Potomac confluence, also given in Table 3-4, were set using the mean of four pre-storm Potomac River concentrations reported in the Velinsky 1998 water column data set.

Data to estimate load inputs of zinc, lead and copper to the tidal Anacostia is available from the Gruessner study of upstream loads (Gruessner et al., 1998), the WASA LTCP study of District CSO and separate sewer system pollutant concentrations (DCWASA, 2000a; 2000b; 2000c), the District's MS4 program storm water monitoring data (Nicoline Shelterbrandt, private communication), and the Prince Georges county monitoring program (Dr. Mow Soung Cheng, private communication). Values used in the calibration are given in Table 3-5. As discussed below, upstream lead concentrations used in load computations were reduced by 50% based on calibration results.

##### Model Results

Calibration/verification runs were made to compare model predictions with the bed sediment data and with the water column data collected in 1998 in study by Velinsky et al. (1999). Model predictions of bed sediment concentrations (last day of 6-year run) were compared with estimated bed sediment segment concentration averages (Table 3-1). In early model runs, zinc and lead fine-grained  $K_d$  values were set at 798,000 and 663,000 L/kg, respectively, based on Anacostia River base flow mean values (Table 2-3). These values were reduced to 420,000 and 400,000 L/kg, respectively (Table 3-4), to improve model water column predictions of the dissolved fractions of these constituents. Also, because in initial model runs, made with load estimates based on mean concentrations from monitoring data (base model), predicted lead bed sediment

concentrations for many segments were more than double the observed values, upstream lead load estimates were reduced by a factor of  $\frac{1}{2}$  for the calibrated model (see Table 3-5). Figure 3-15 shows predicted bed sediment concentrations (last day of 6-year run) for both the calibrated model (with upstream lead loads reduced to  $\frac{1}{2}$  of their original value) and the base model (no load adjustment). Water column results for total (= dissolved + particulate) and dissolved concentrations are shown in Figures 3-16 to 3-21. It can be seen in these figures that though the calibrated model has some tendency to over-predict both bed sediment and water column concentrations of these three metals, the general characteristics of the spatial pattern of bed sediment metals contamination are reproduced, and water column predictions match available data reasonably well. The fairly close match between predicted and measured total lead concentrations in the water column lends support to the appropriateness of the factor of  $\frac{1}{2}$  load reduction for upstream lead.

Results of a mass balance analysis for metals appear in Table 3-6 and Figure 3-22. According to model load estimates, the upstream tributaries account for the majority of the metals found in the sediment bed of the tidal river. Lower Beaverdam Creek contributes a higher proportion of the metals load than would be expected from its relative land area. Approximately  $\frac{1}{3}$  of the metals discharged into the tidal portion of the Anacostia are eventually exported to the Potomac River.

### **Model Sensitivity Analysis**

Because the value of model input parameters are only estimates and are subject to some degree of uncertainty, a number of “sensitivity runs” were made to investigate how the metals sub-model predictions change due to changes in input parameters. Because all of the TAM/WASP Toxic Screening Level sub-models have been constructed using a similar framework, many of the results of the metals sensitivity runs are also applicable to other sub-models. Results of metals sub-model sensitivity runs appear in Figures 3-23 through 3-38. Also, at the end of this section a summary is given of changes in predicted (last day of six-year run) total mass contained in the surficial (1 cm thickness) bed sediment layer produced by the various sensitivity scenarios (Table 3-3). All sensitivity runs were done using calibrated loads (i.e., with factor of  $\frac{1}{2}$  adjustment to leads loads).

Initial values for the partition coefficients for the fine-grained sediment fraction were based on mean values computed from site-specific base flow water column data (Table 2-3). For some sub-models, including the Metals1 sub-model, these values were then adjusted during the calibration process based on model predictions of dissolved phase concentrations. Because the computed  $K_d$ 's were highly variable, sensitivity runs were done to investigate changes in model predictions when all metals  $K_d$ 's were multiplied by 4, or all metals  $K_d$ 's were multiplied by  $\frac{1}{4}$ . Bed sediment results are shown in Figure 3-23 and water column results appear in Figures 3-16 to 3-21. It is evident that neither the bed sediment nor the total water column predicted concentrations of zinc or lead are very sensitive to these changes in  $K_d$ 's, though the dissolved lead and zinc concentrations are sensitive. Because copper has a considerably lower  $K_d$  value than lead or zinc, copper concentration predictions are much more sensitive to changes in  $K_d$ 's. However, from Figures 3-18, 3-21, and 3-23, it appears that the calibrated model's copper

predictions are quite good and that model performance for copper is clearly degraded in these sensitivity runs.

The fact that for constituents with large  $K_d$  values, such as zinc and lead, changes in  $K_d$ 's have a significant effect on dissolved water column concentration predictions but little effect on bed sediment concentration predictions can be explained by examining the relationship between dissolved, particulate, and total concentrations in the water column. By combining Equation (2-1), the equation that defines  $K_d$ , with two other simple relationships involving the particulate fraction,  $C_s$ ,

$$C_T = C_w + C_s' \quad (3-2)$$

and

$$C_s' = TSS C_s \quad (3-3)$$

where

$C_T$	=	total concentration ( $\mu\text{g/L}$ )
$C_w$	=	dissolved fraction ( $\mu\text{g/L}$ )
$C_s$	=	particulate fraction ( $\mu\text{g/g}$ )
$C_s'$	=	particulate fraction ( $\text{ug/L}$ )
TSS	=	total suspended solids ( $\text{g/L}$ )

it is possible to write the dissolved fraction,  $C_w$ , and the particulate fraction,  $C_s$ , as functions of the total concentration,  $C_T$ , that is,

$$C_w = \frac{1}{(1 + TSS K_d)} C_T \quad (3-4)$$

and

$$C_s = \frac{K_d}{(1 + TSS K_d)} C_T \quad (3-5)$$

From these relationships, it is clear that for very large  $K_d$ 's,  $C_w \sim C_T / (TSS K_d)$  is proportional to  $1/K_d$  but  $C_s \sim C_T / TSS$  is relatively insensitive to changes in  $K_d$ . Because much of the particulate fraction in the water column eventually settles to the bed sediment,  $C_s$  in the water column determines to a large degree the bed sediment concentration of the constituent.

A second sensitivity test was done to investigate changes in model predictions due to changes in the assumption concerning the ratio of  $K_d$ 's for the medium-grained sediment fraction and the



fine-grained sediment fraction. Though it is known that fine-grained sediments typically have higher fractions of organic carbon and larger partition coefficients than coarser-grained sediments, in the TAM/WASP Toxics Screening Level Model, the ratio of the  $K_d$ 's for the medium-grained sediment fraction to the  $K_d$ 's for the fine-grained sediment fraction was rather arbitrarily set equal to 1/4. Runs to investigate the sensitivity of model results to this choice were done. Figures 3-24 to 3-30 show results of model runs using a ratio of medium-grained to fine-grained sediment  $K_d$ 's of 1 and of 1/10. It is clear from these results that changes in the medium to fine-grained  $K_d$  ratio would not qualitatively change model calibration results for metals, though increasing the ratio to 1 noticeably increases predicted bed sediment concentrations. This increase is most pronounced for copper, the metal with the lowest  $K_d$  values. The primary reason for the model's insensitivity to these changes is probably due to the fact that there are considerably less medium-grained than small-grained sediments in the tidal river, and medium-grained sediments are less likely to undergo resuspension.

The underlying hydrodynamic and sediment transport components of TAM/WASP Version 2.3, used for the Toxics Screening Level Model, are identical to those of Version 2.1, with three exceptions, discussed in Sections 2.1 and 2.2 of this report. The most significant difference is a change in the down stream boundary conditions for the three sediment grain size fractions. Figures 3-31 through 3-33 show the results of a sensitivity test done to compare metals predictions of the two sediment transport model versions. For all three metals, the model's predictions of accumulated mass in the upper 1 cm of the bed sediment drops by roughly 15% when Version 2.1 is used (Table 3-3). These results provide some indication of the uncertainty introduced to the toxic models due to uncertainties in parameters governing the underlying sediment transport model.

Because water from the Potomac enters the Anacostia every day during the rising tide, chemical concentrations in the Potomac River have an effect on concentrations in the Anacostia. Though chemical concentrations in the Potomac are expected to vary daily, in the TAM/WASP Toxics Screening Level Model, these downstream boundary condition (BC) concentrations are set at constant values based on, at best, a handful of measured values. In the case of some chemicals, no Potomac River data was available and Potomac River boundary conditions are based on calibration results. Figures 3-35 to 3-38 show the results of two sensitivity runs done to investigate changes in the metals sub-model predictions if estimated Potomac boundary conditions were halved or doubled. Both the bed sediment and the water column results indicate, as expected, that the Potomac River concentrations have no noticeable effect on concentration predictions for the middle and upper stream segments. However, there is a noticeable difference in predicted concentrations in downstream segments, particularly in segments 29 and below.

Table 3-3 contains a summary of the sensitivity test results in terms of the predicted total mass of zinc, lead, and copper contained in the upper 1 centimeter layer of the bed sediment (as predicted by last day of 6-year run). It can be seen from this table that changes in input parameters made for the sensitivity tests changed predictions of total bed sediment mass by 27% at most, and usually by 15% or less, when compared to the calibrated model. These results lend some confidence to the calibration strategy of applying multiplicative adjustment factors to some of the

initial load estimates, based on bed sediment concentration predictions.

**Summary**

The metals sub-model (Metals1) has better data support than any other of the TAM/WASP Toxic Screening Level sub-models, and therefore provides an important test of the general framework used to construct of this series of models. Two changes were made to the initial input parameters during the calibration process:  $K_d$  values for both zinc and lead were reduced based on predictions of dissolved water column concentrations, and initial upstream load estimates for lead were reduced by a factor of ½. The calibrated metals sub-model performed fairly well in predicting the magnitude and general spatial pattern of contaminant bed sediment concentrations, and also did a reasonable job in matching available water column data for total and dissolved concentrations of these constituents.

**Table 3-3. Sensitivity Test Results: Predicted Total Mass in Bed Sediment (Upper 1 cm)**

	<b>Zn (kg)</b>	<b>Zn (%)<sup>1</sup></b>	<b>Pb (kg)</b>	<b>Pb (%)</b>	<b>Cu (kg)</b>	<b>Cu (%)</b>
<b>Data:</b>	7970	79%	2490	86%	2160	74%
<b>Base model:</b>	10120	100%	4770	164%	2900	100%
<b>Calibrated model:</b>	10120	100%	2900	100%	2900	100%
<b>Kds x 4:</b>	10460	103%	2970	102%	3270	113%
<b>Kds/4:</b>	9150	90%	2660	92%	2130	73%
<b>med-Kd = fine-Kd:</b>	11600	115%	3280	113%	3360	116%
<b>med-Kd = fine-Kd/10:</b>	9810	97%	2810	97%	2800	97%
<b>Sediment transport V 2.1:</b>	8850	87%	2510	87%	2580	89%
<b>BCs x 2</b>	10960	108%	2960	102%	3190	110%
<b>BCs/2</b>	9700	96%	2860	99%	2760	95%

<sup>1</sup> Percentage of mass predicted by calibrated model.

**Table 3-4. WASP Input Parameters for Metals1 Sub-Model**

Process	Parameter	Units	Zinc	Lead	Copper	Source
<i>Adsorption:</i>						
	K <sub>d</sub> for fine-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	420,000	400,000	94,000	Based on 1998 water column data <sup>a</sup>
	K <sub>d</sub> for medium-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	100,000	100,000	23,000	Taken to be 1/4 times K <sub>d</sub> for fine-grained sediment, based on best professional judgement.
<i>Downstream boundary condition:</i>						
	Typical Potomac concentration	ug/L	4.0	0.3	2.0	Mean of non-storm concentrations at Potomac confluence, 1998 water column data <sup>a</sup>

<sup>a</sup> Computed from data in Velinsky et al. (1999)

**Table 3-5. Concentrations Used to Compute Metals1 Sub-Model Calibration Run Input Loads (ug/L)**

Source	Zinc Orig	Suggested Zinc Multiplier	Zinc Draft Final	Lead Orig	Suggested Lead Multiplier	Lead Draft Final	Copper Orig	Suggested Copper Multiplier	Copper Draft Final	Data Source/ Comment
NW Br Base	7	x 1	7	0.6	x 0.5	0.3	4	x 1	4	Gruessner et al. (1998) 1995-96 data and Velinsky et al. 1998 data - mean of 10 values.
NW Br Storm	91	x 1	91	103	x 0.5	51.5	43	x 1	43	Gruessner et al. (1998) 1995-96 data - mean of 4 EMC's.
NE Br Base	8	x 1	8	0.5	x 0.5	0.25	3	x 1	3	Gruessner et al. (1998) 1995-96 data and Velinsky et al. 1998 data - mean of 10 values.
NE Br Storm	77	x 1	77	49	x 0.5	24.5	25	x 1	25	Gruessner et al. (1998) 1995-96 data - mean of 4 EMC's.
LBD Creek Base	22	x 1	22	0.25	x 1	0.25	0.25	x 1	0.25	PG Co. 1998-99 monitoring data at site 006; mean of 3 values.
LBD Creek Storm	172	x 1	172	35	x 1	35	24	x 1	24	PG Co. 1998-99 monitoring data at site 006. Mean of 24 EMCs.
SSTrib Base/GW	7.5	x 1	7.5	0.6	x 1	0.6	3.5	x 1	3.5	Using mean of NE and NW Branches base flow values.

**TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report**

Source	Zinc Orig	Suggested Zinc Multiplier	Zinc Draft Final	Lead Orig	Suggested Lead Multiplier	Lead Draft Final	Copper Orig	Suggested Copper Multiplier	Copper Draft Final	Data Source/ Comment
SSTrib Storm	173	x 1	173	28	x 1	28	57	x 1	57	Average of WASA EPMC-III value and recent 2002 DC MS4 monitoring mean.
B St. NJ Ave/ Tiber Cr CSO	191	x 1	191	72	x 1	72	83	x 1	83	WASA LTCP monitoring: average of B St. NJ Ave. and Tiber Creek results.
NE Swirl and Bypass	256	x 1	256	96	x 1	96	63	x 1	63	WASA LTCP monitoring program result.
All other CSOs	213	x 1	213	80	x 1	80	76	x 1	76	WASA LTCP monitoring program estimate.

**Table 3-6. Average Annual Load Contributions and Losses by Source for Calibrated Metals1 Sub-Model**

Loads/Losses	Zinc		Lead		Copper	
	kg	% <sup>2</sup>	kg	%	kg	%
Upstream	6,927	49	2,744	64	2,698	61
SS Tribs	2,071	15	341	8	692	16
LBD	3,591	25	719	17	493	11
Watts	505	4	83	2	169	4
CSOs	1,061	7	389	9	340	8
Total Input <sup>1</sup>	14,155	100	4,276	100	4,392	100
Export to Potomac	-4,673	-33	-1,506	-35	-1,666	-38

<sup>1</sup> Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.  
<sup>2</sup> % represents the percentage of total input (sum of all loads).

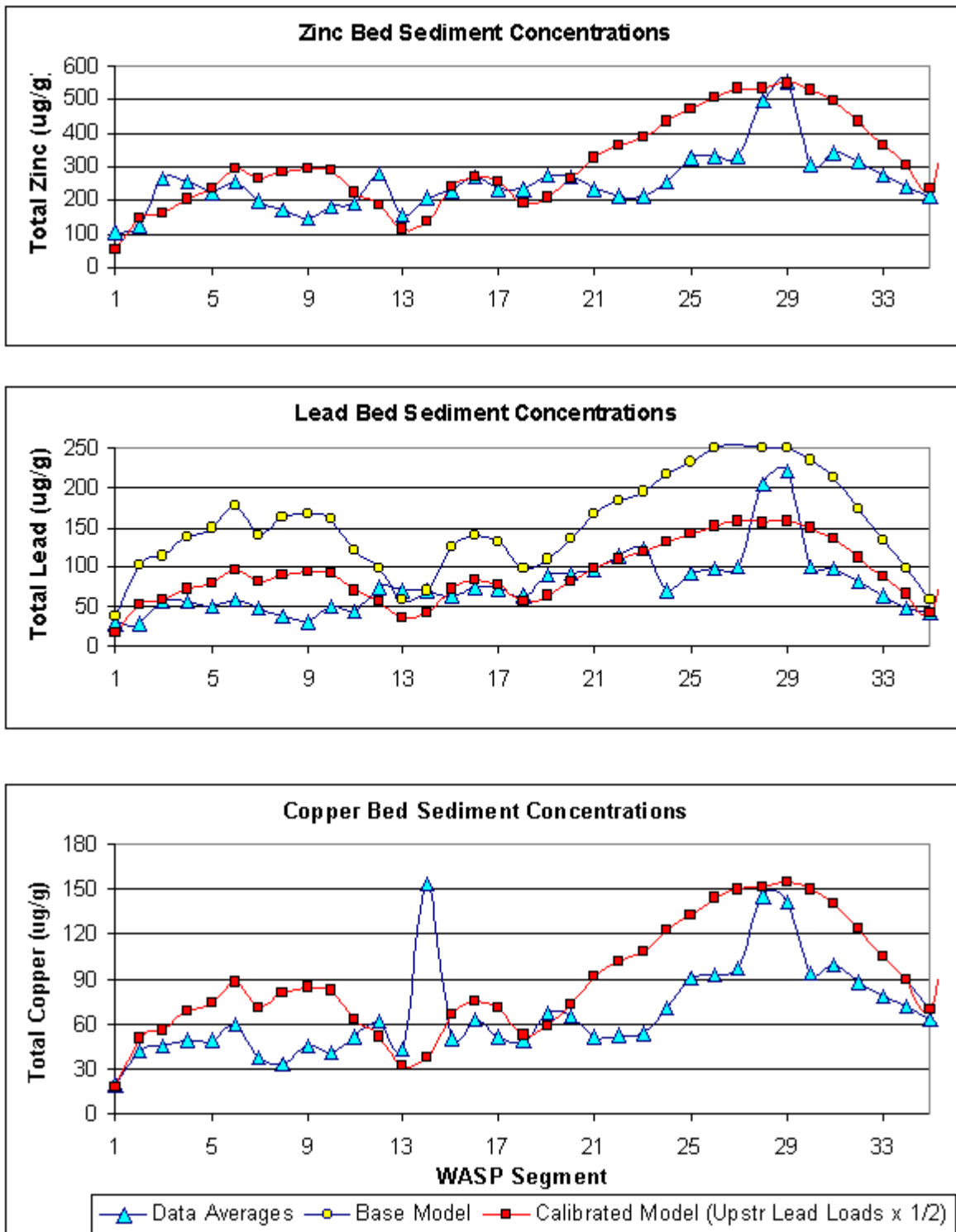


Figure 3-15. Metals Bed Sediment Results: Base Model and Calibrated Model (Upstr Lead Loads x 0.5)

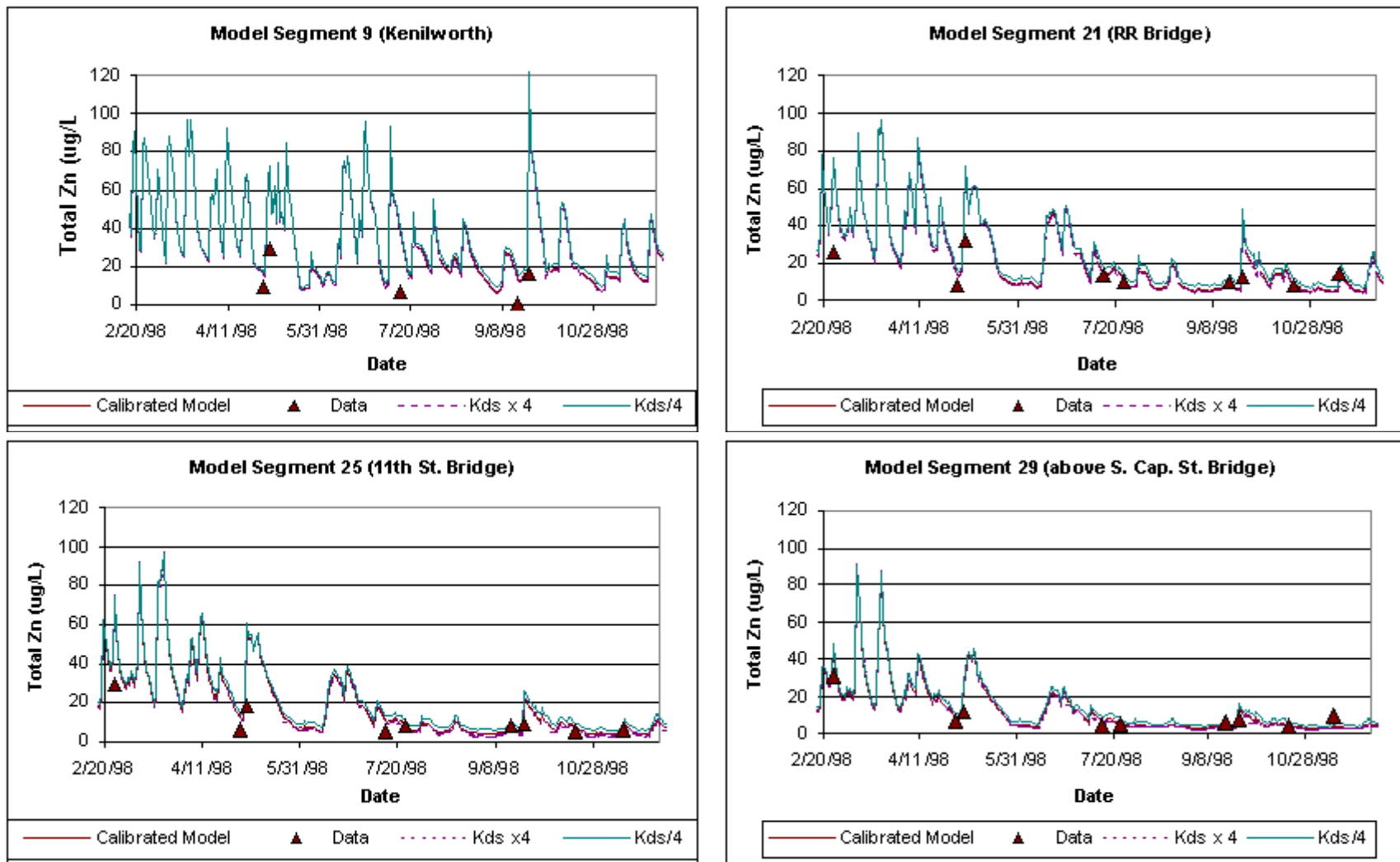


Figure 3-16. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x 4;  $K_d$ 's/4



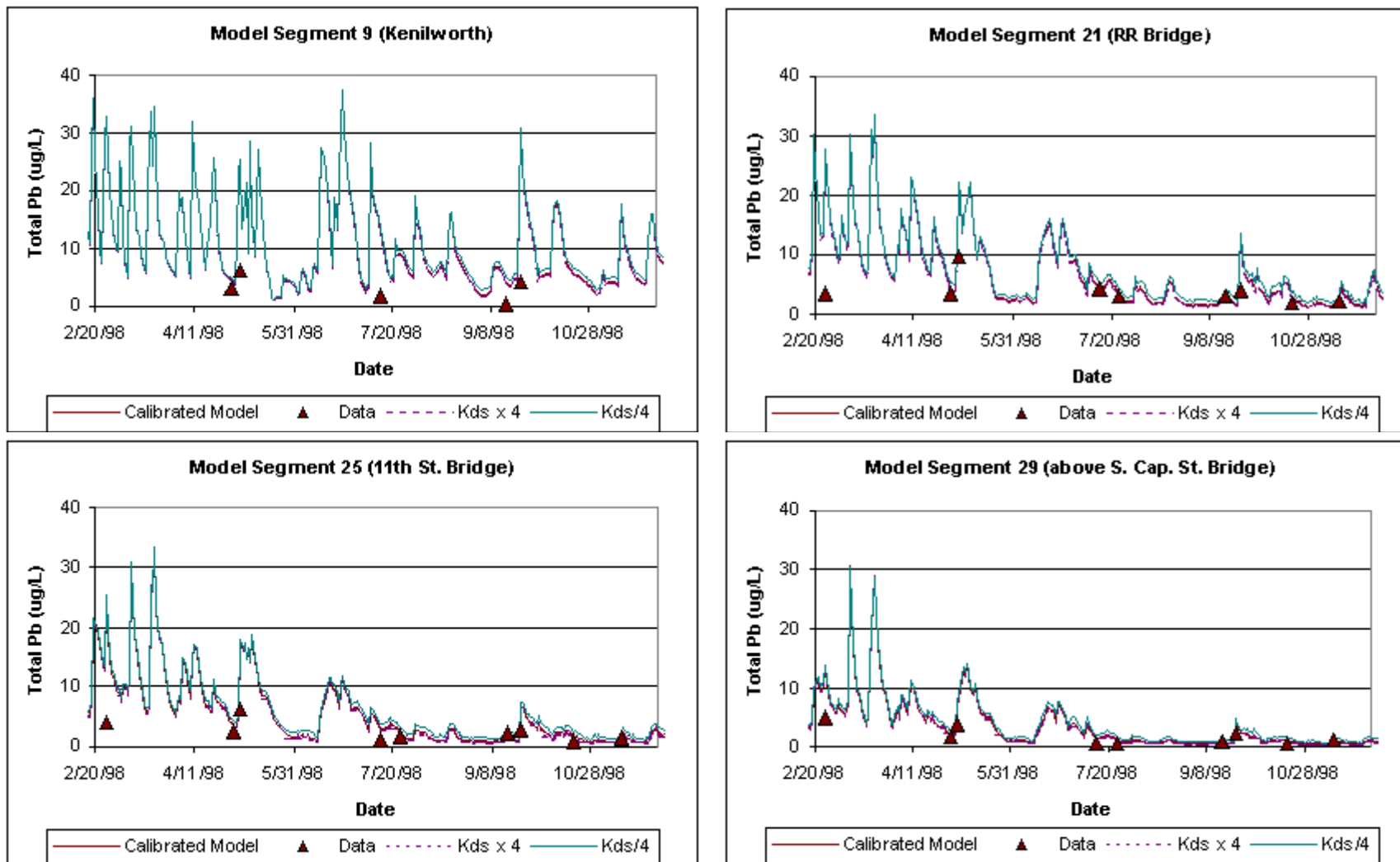


Figure 3-17. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x 4;  $K_d$ 's/4

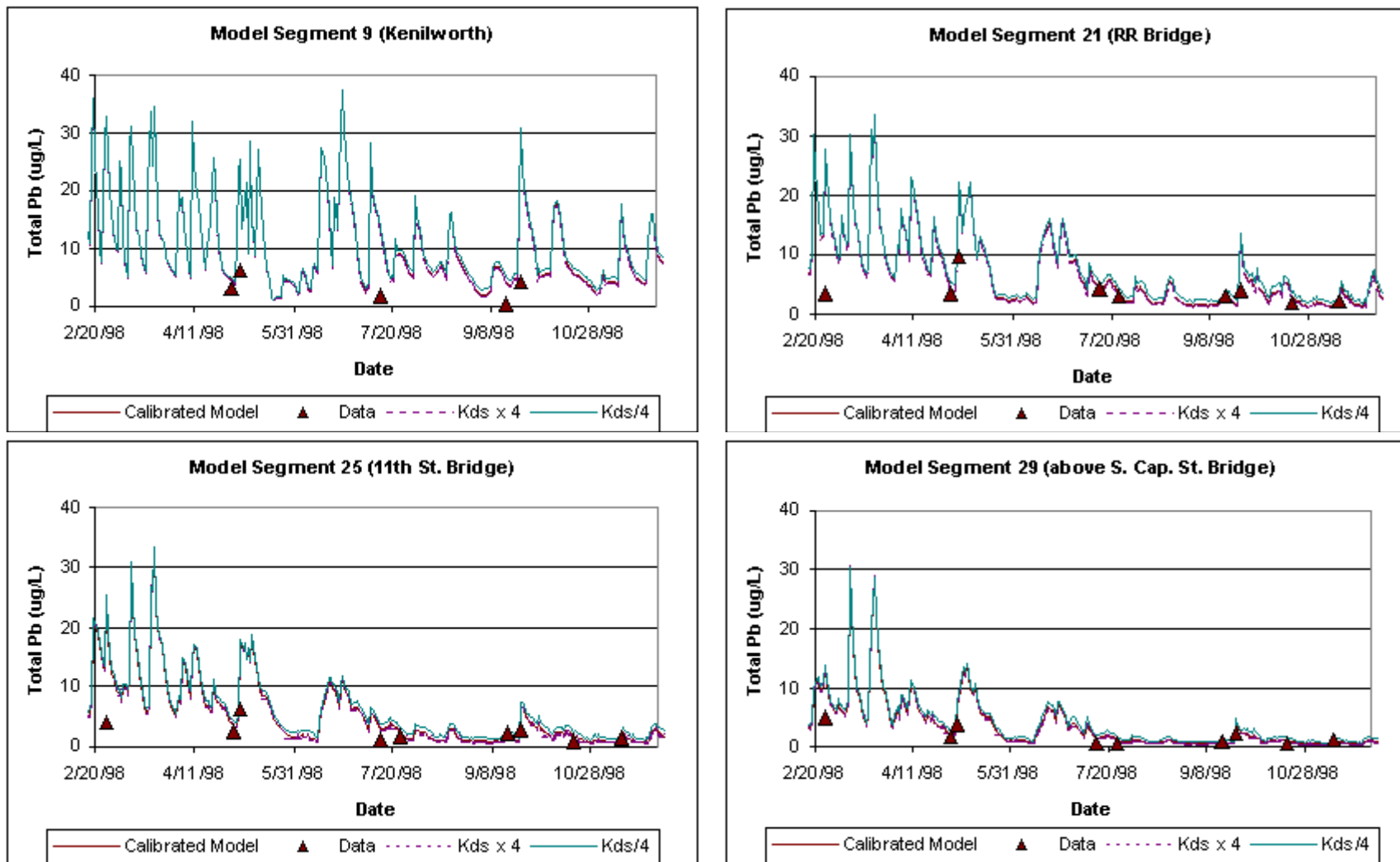


Figure 3-18. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x 4;  $K_d$ 's/4

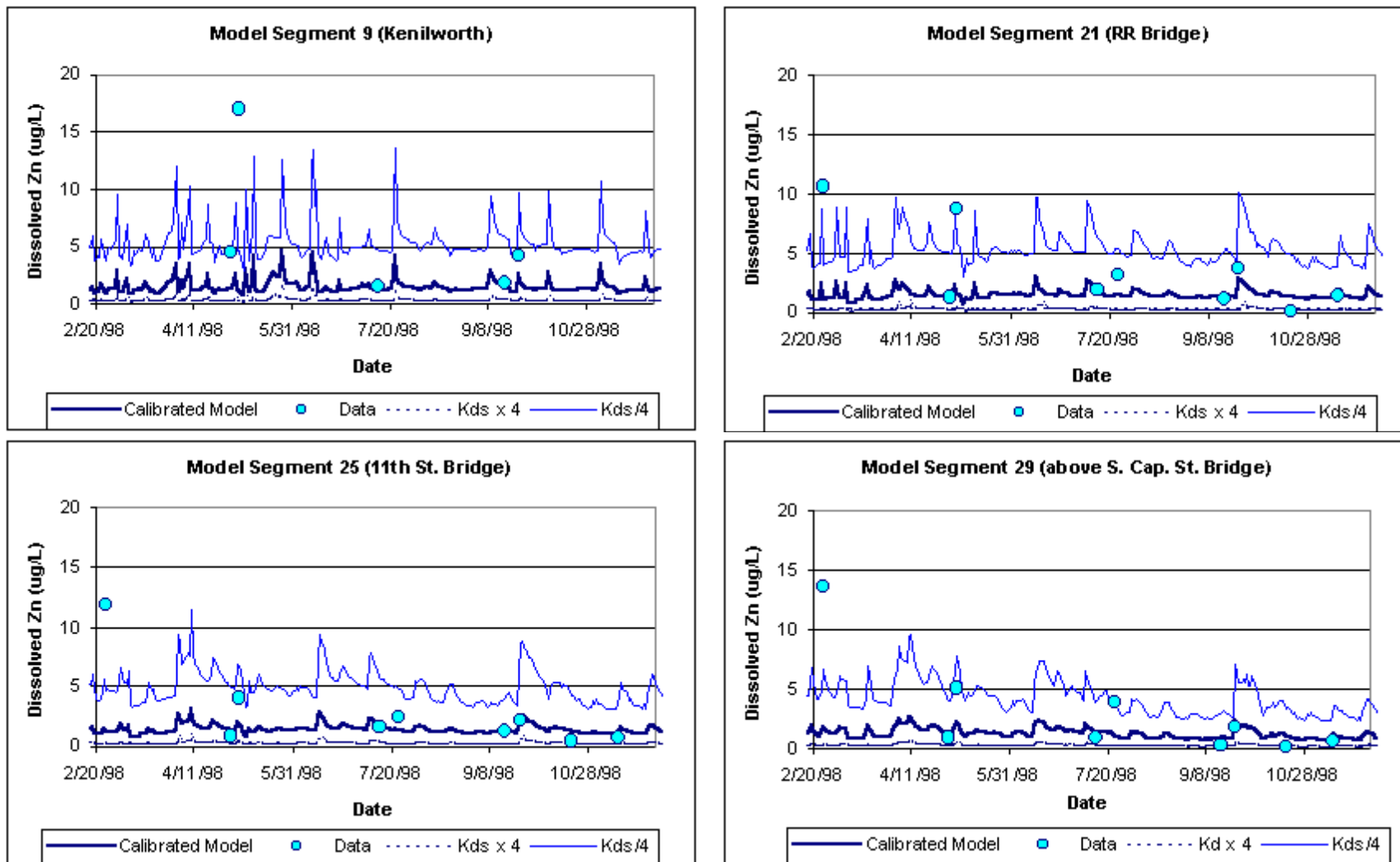


Figure 3-19. Dissolved Zinc Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x 4;  $K_d$ 's/4

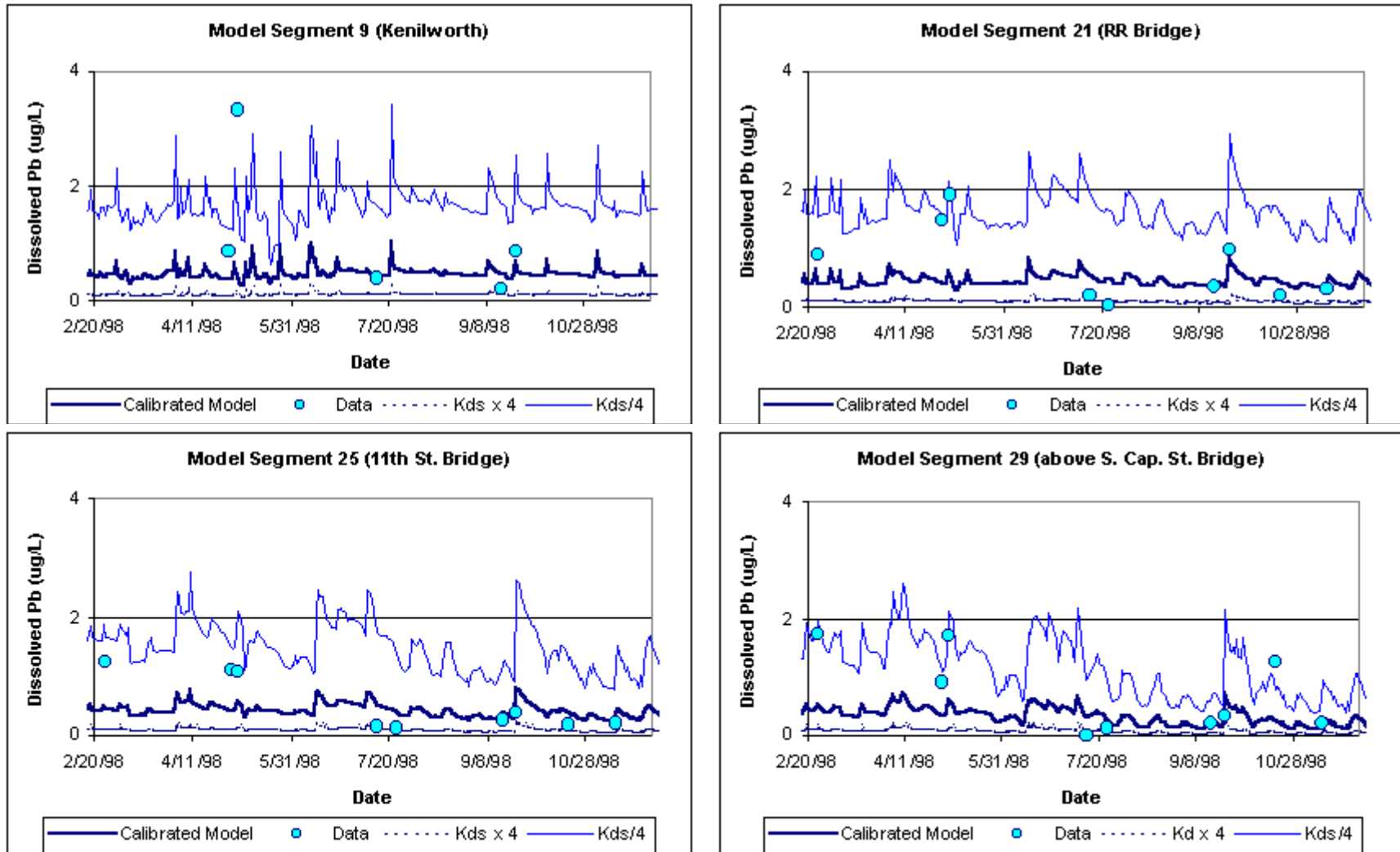


Figure 3-20. Dissolved Lead Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x 4;  $K_d$ 's/4

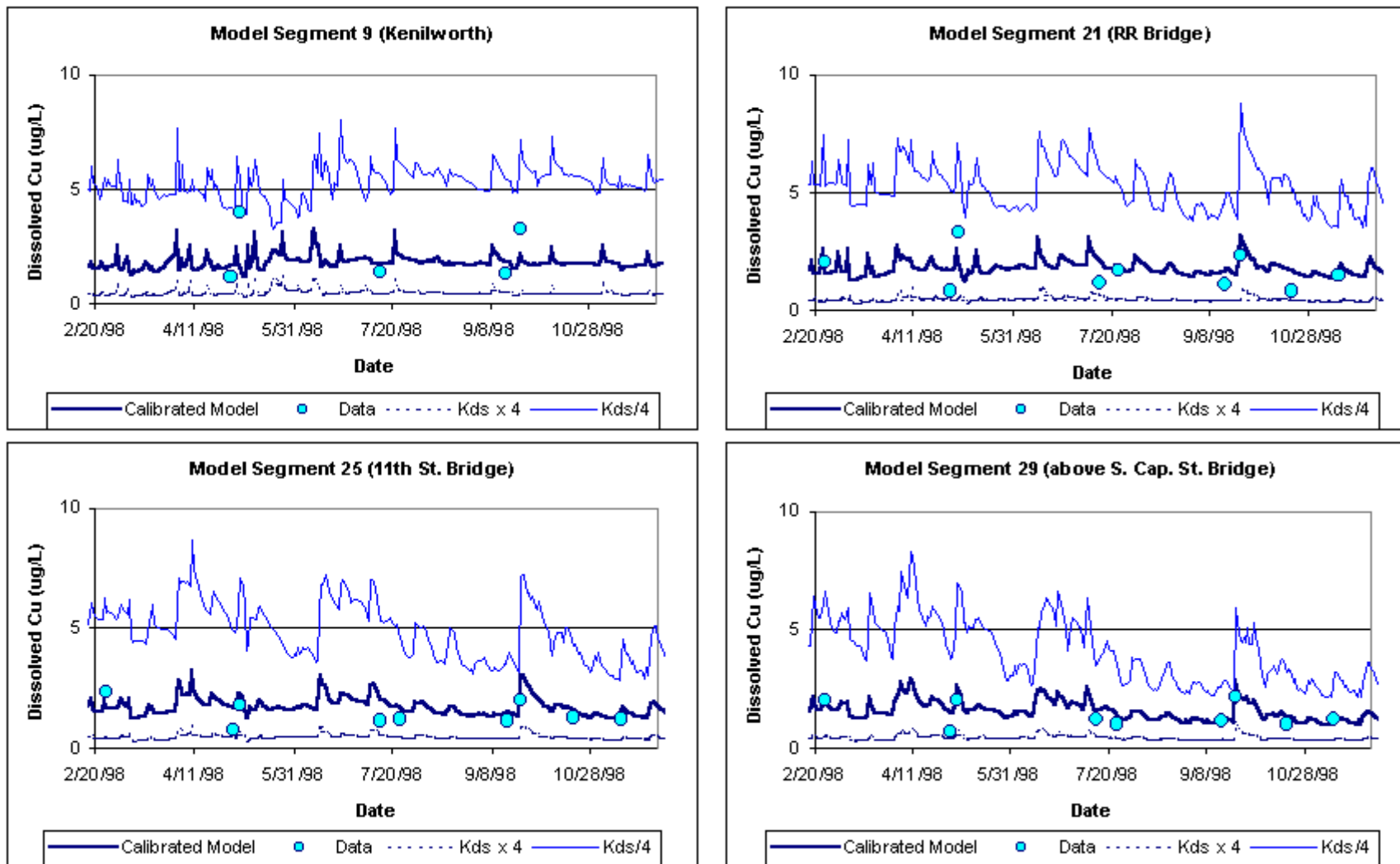


Figure 3-21. Dissolved Copper Water Column Sensitivity Test Results: Calibrated Model;  $K_d$ 's x 4;  $K_d$ 's/4

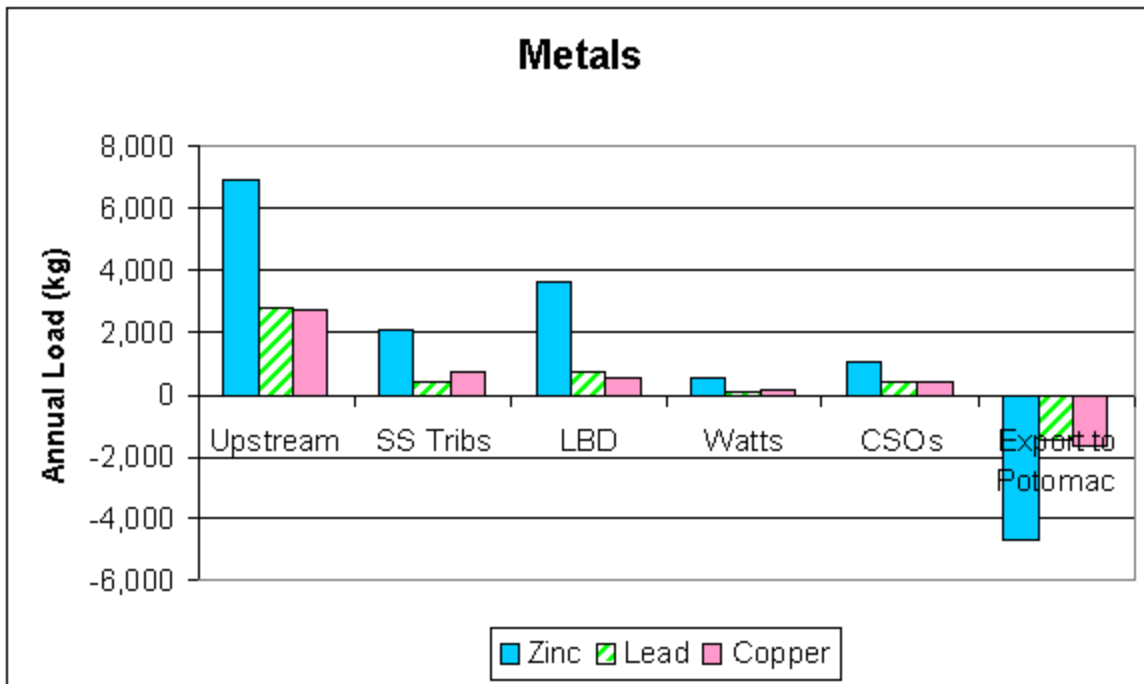


Figure 3-22. Summary of Average Annual Loads and Losses for the Calibrated Metals1 Sub-Model

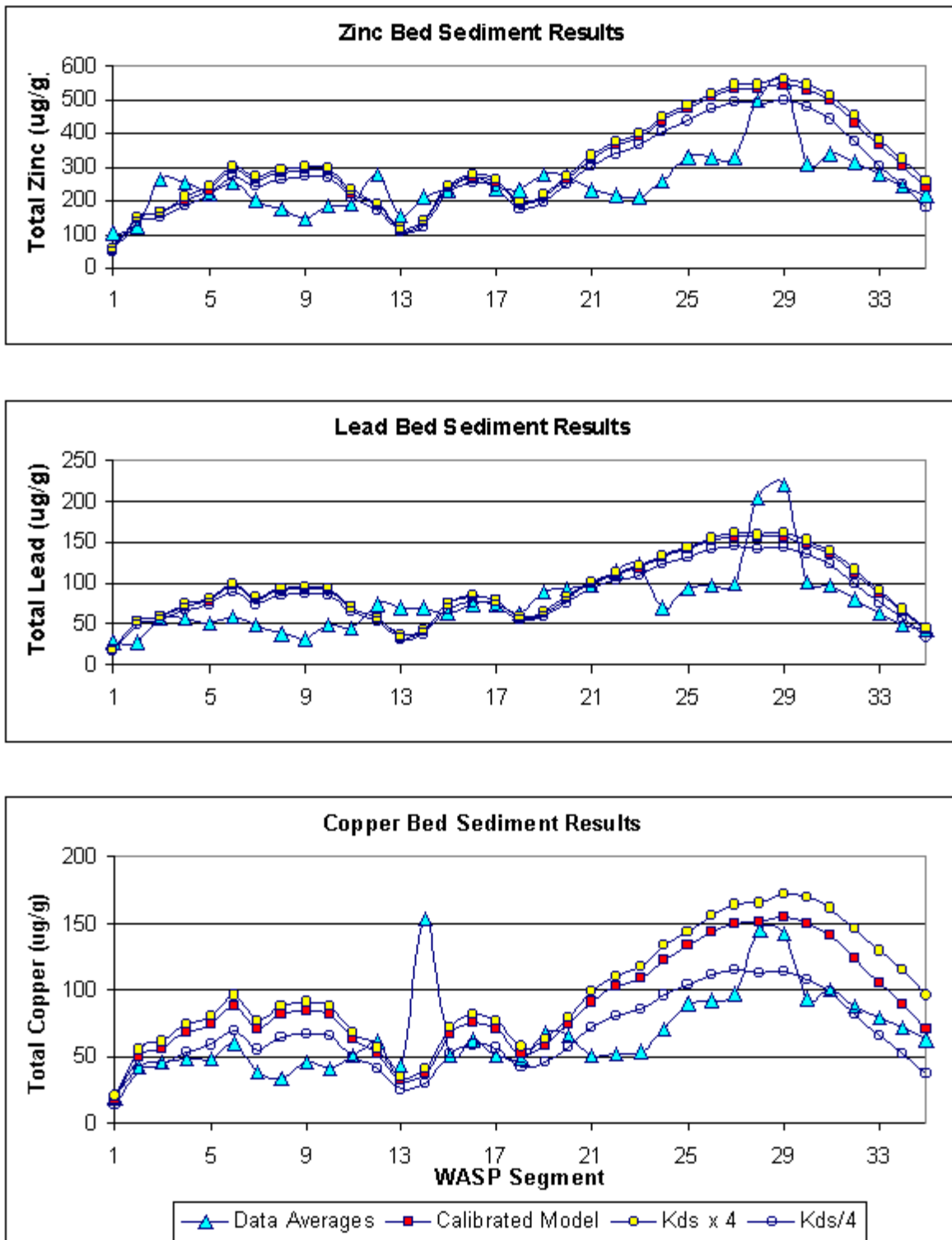


Figure 3-23. Metals Bed Sediment Sensitivity Test Results:  $K_d$ 's x 4;  $K_d$ 's/4

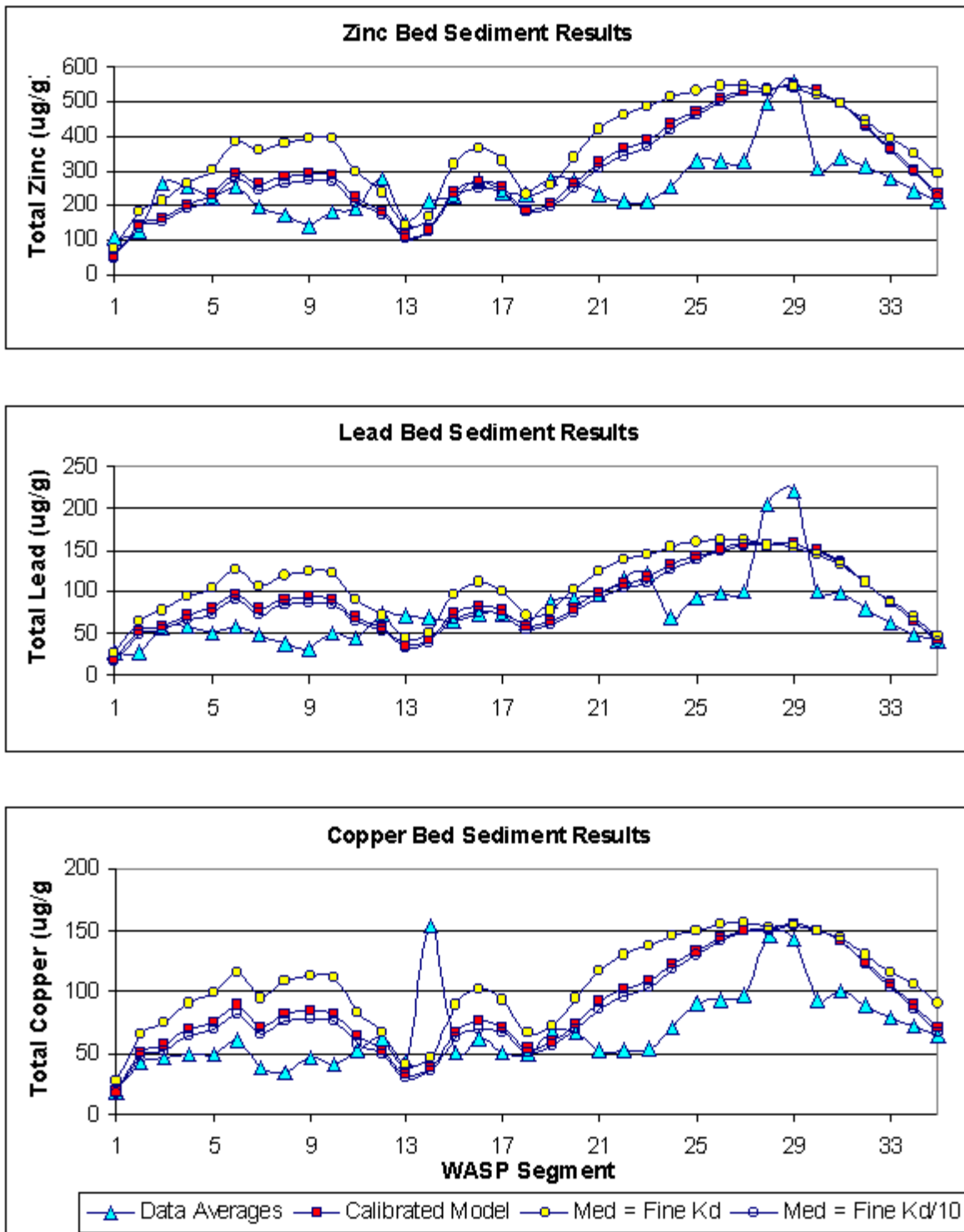


Figure 3-24. Metals Bed Sediment Sensitivity Test Results: Med  $K_d$ /Fine  $K_d$  Changed to 1; to 1/10



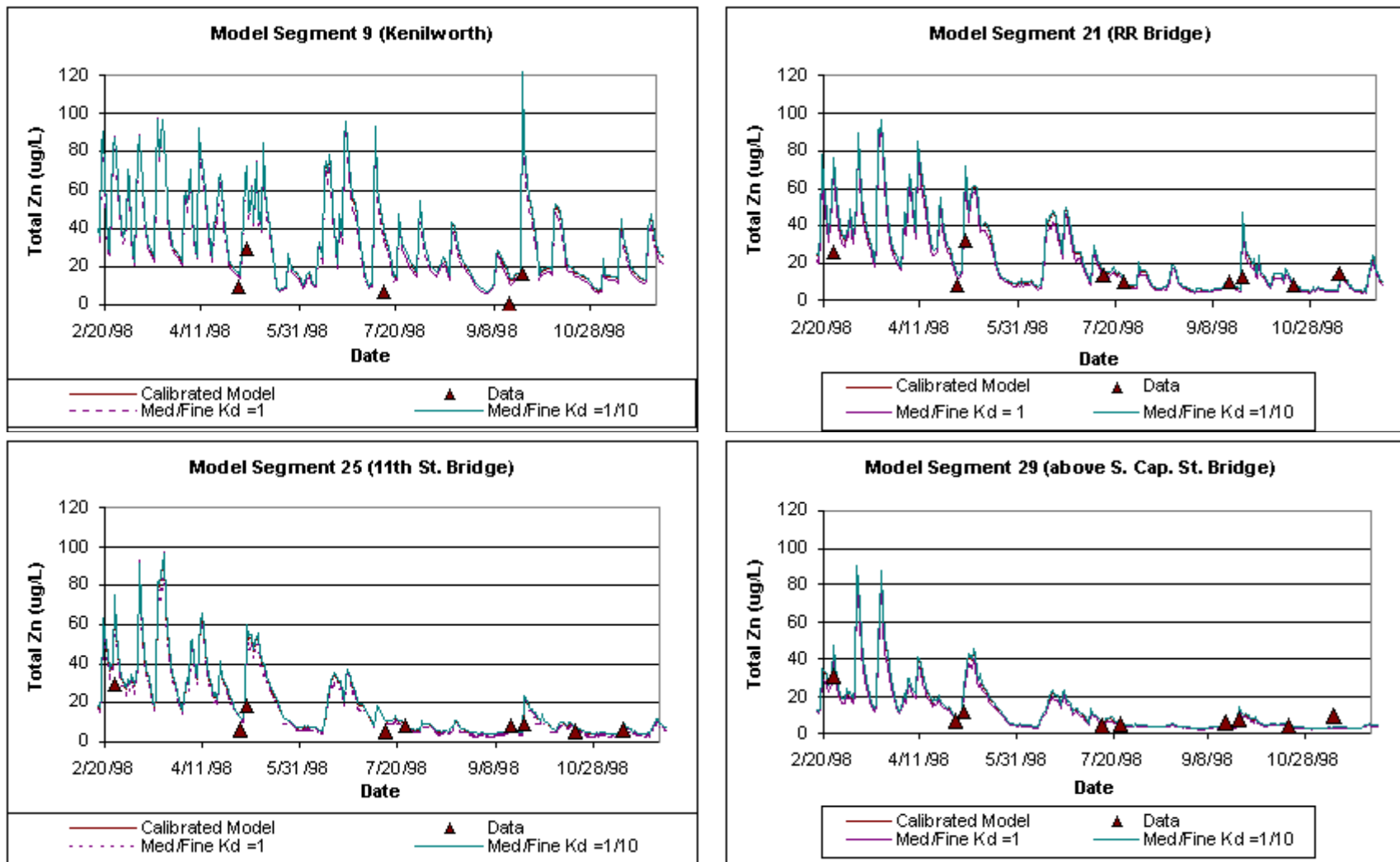


Figure 3-25. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: Med  $K_d$ /Fine  $K_d$  Changed 1; to 1/10

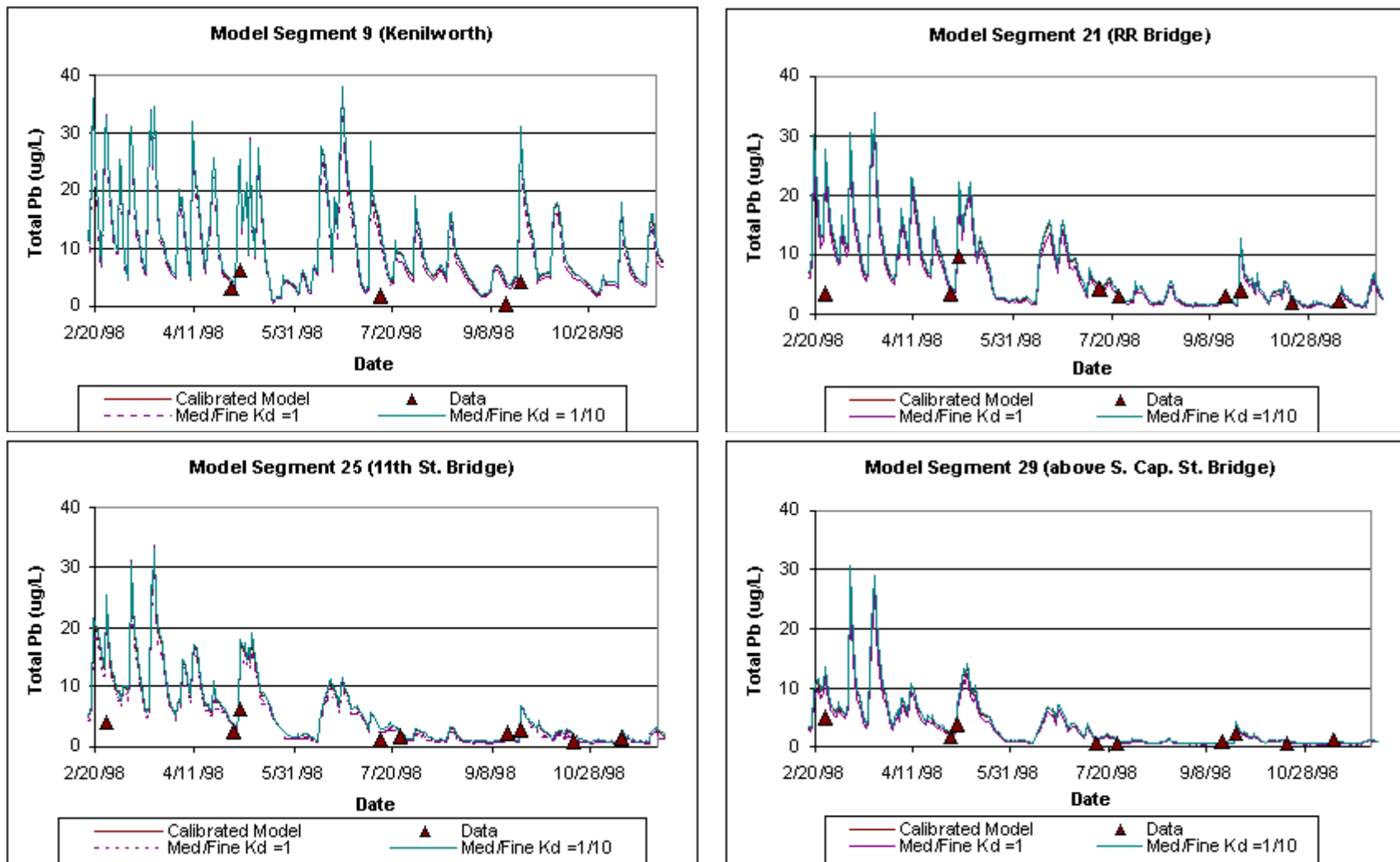


Figure 3-26. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: Med  $K_d$ /Fine  $K_d$  Changed 1; to 1/10

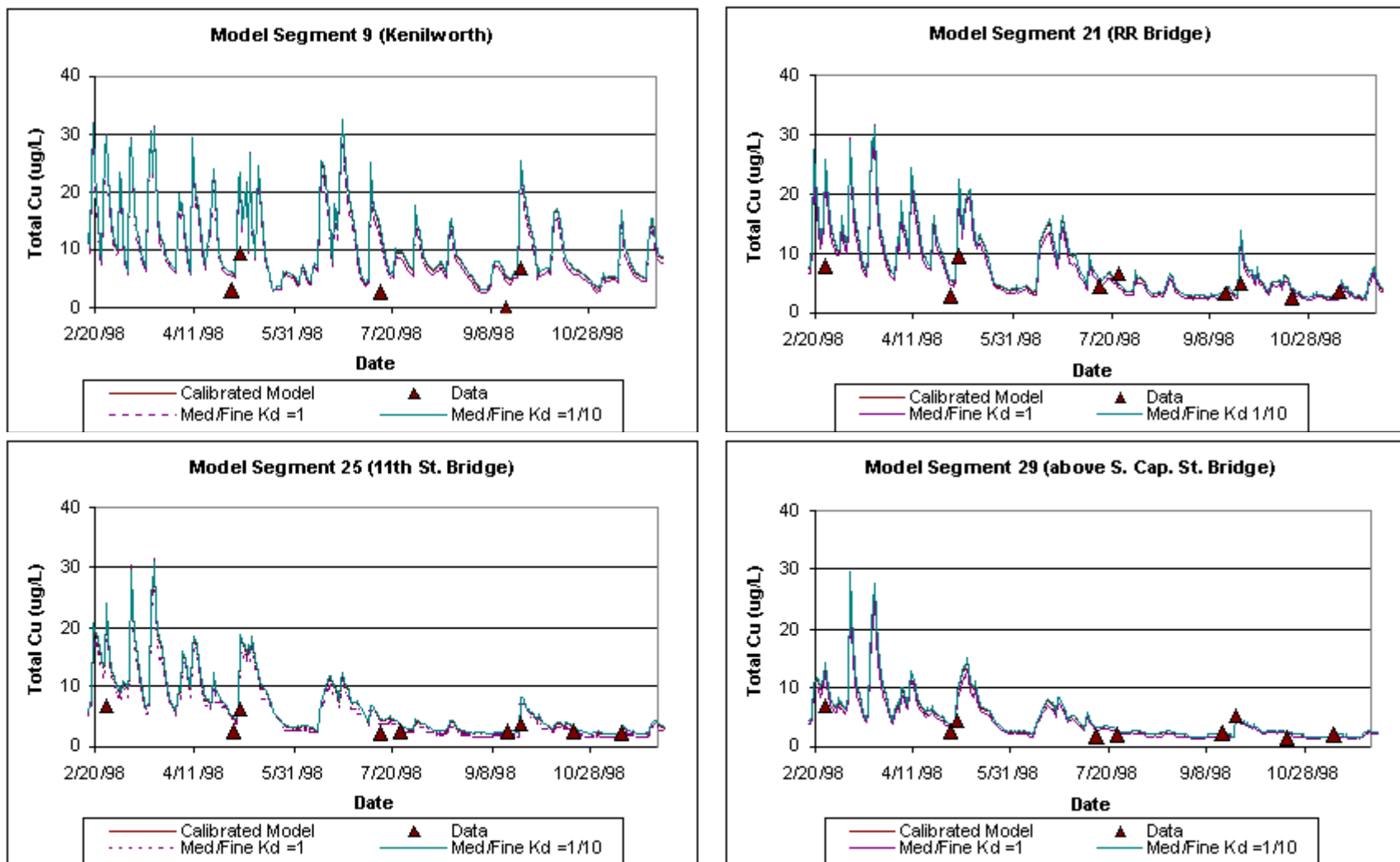


Figure 3-27. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results: Med  $K_d$ /Fine  $K_d$  Changed 1; to 1/10

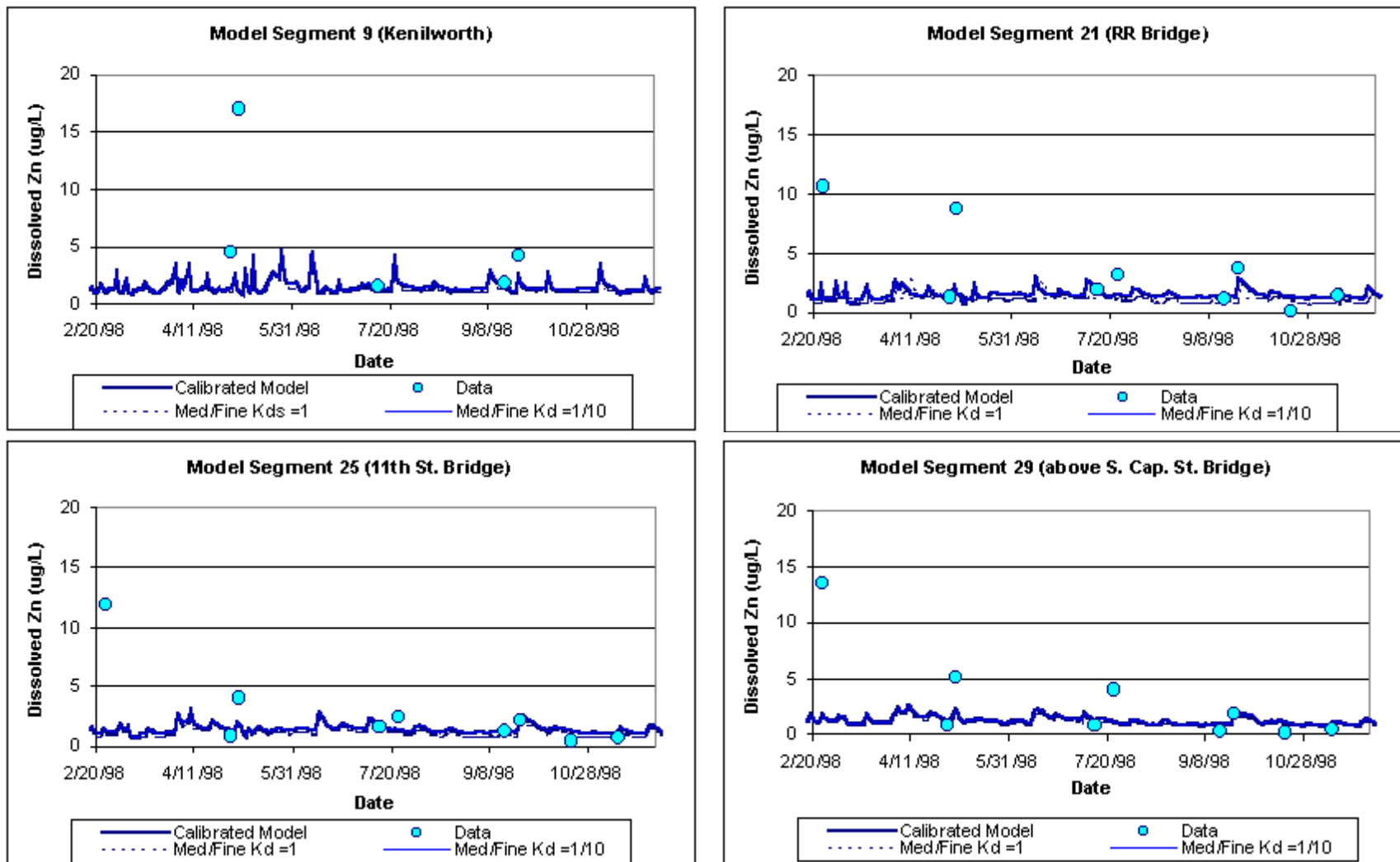


Figure 3-28. Dissolved Zinc Water Column Sensitivity Test Results: Med  $K_d$ /Fine  $K_d$  Changed 1; to 1/10

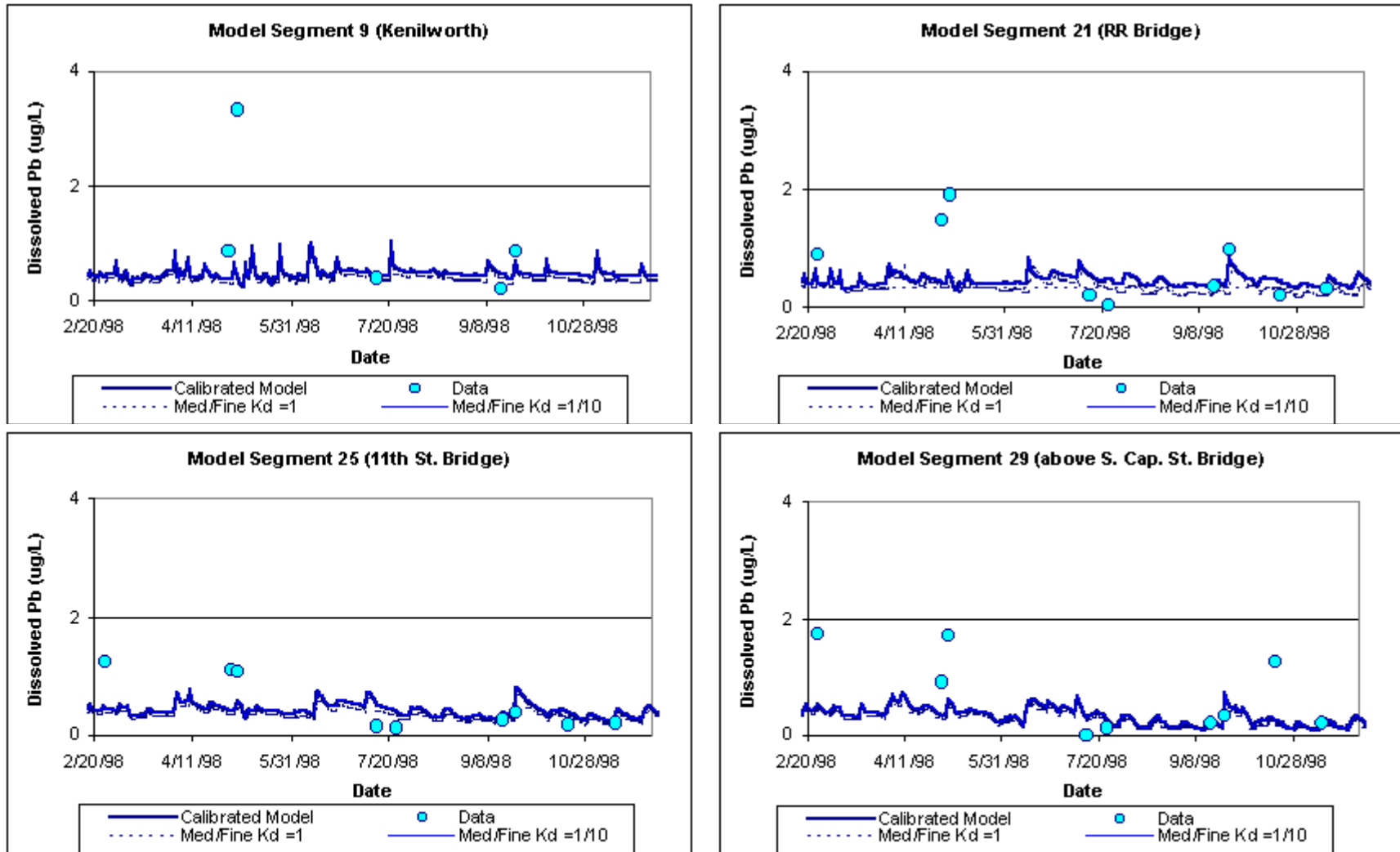


Figure 3-29. Dissolved Lead Water Column Sensitivity Test Results: Med  $K_d$ /Fine  $K_d$  Changed 1; to 1/10

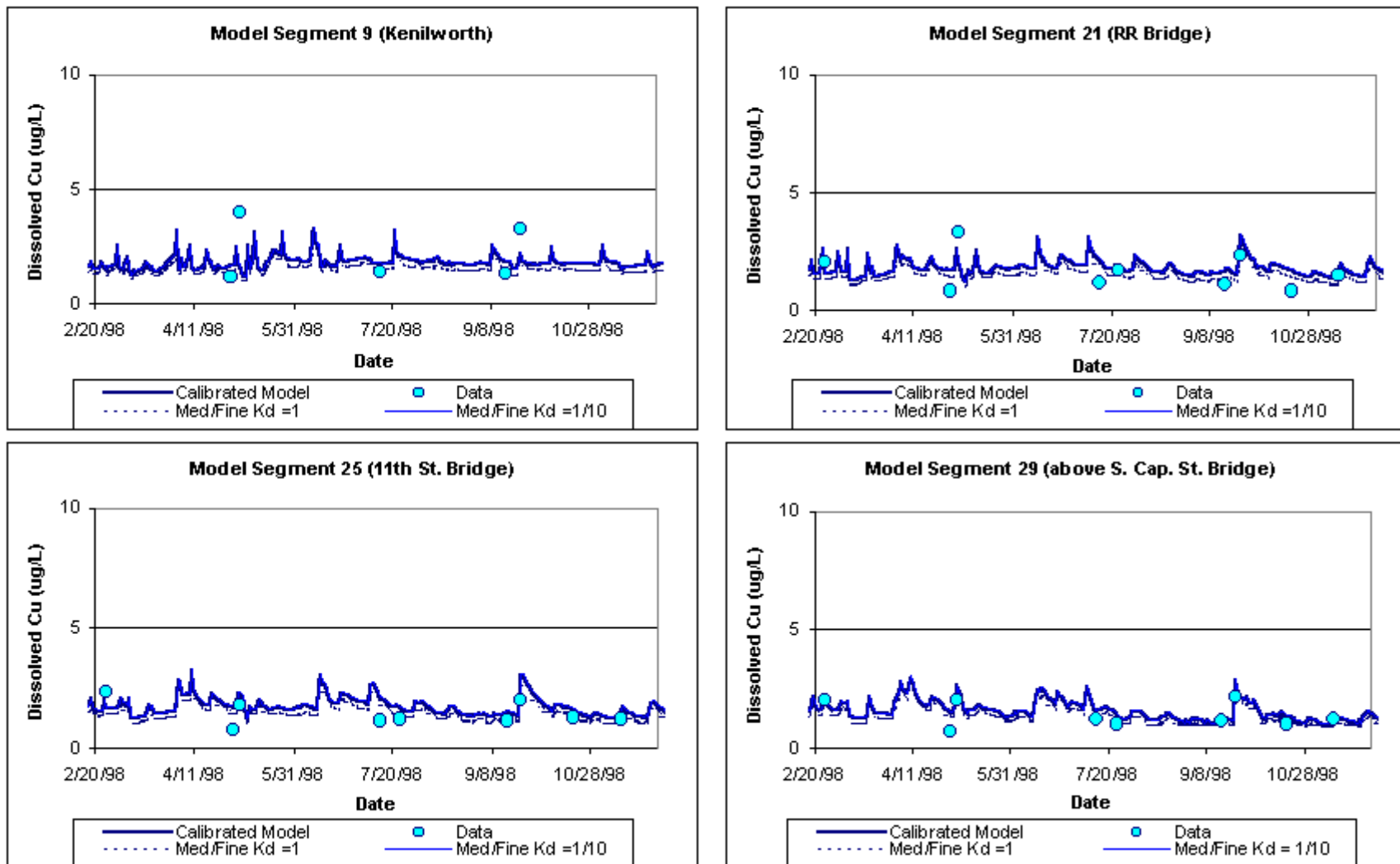


Figure 3-30. Dissolved Copper Water Column Sensitivity Test Results: Med  $K_d$ /Fine  $K_d$  Changed 1; to 1/10

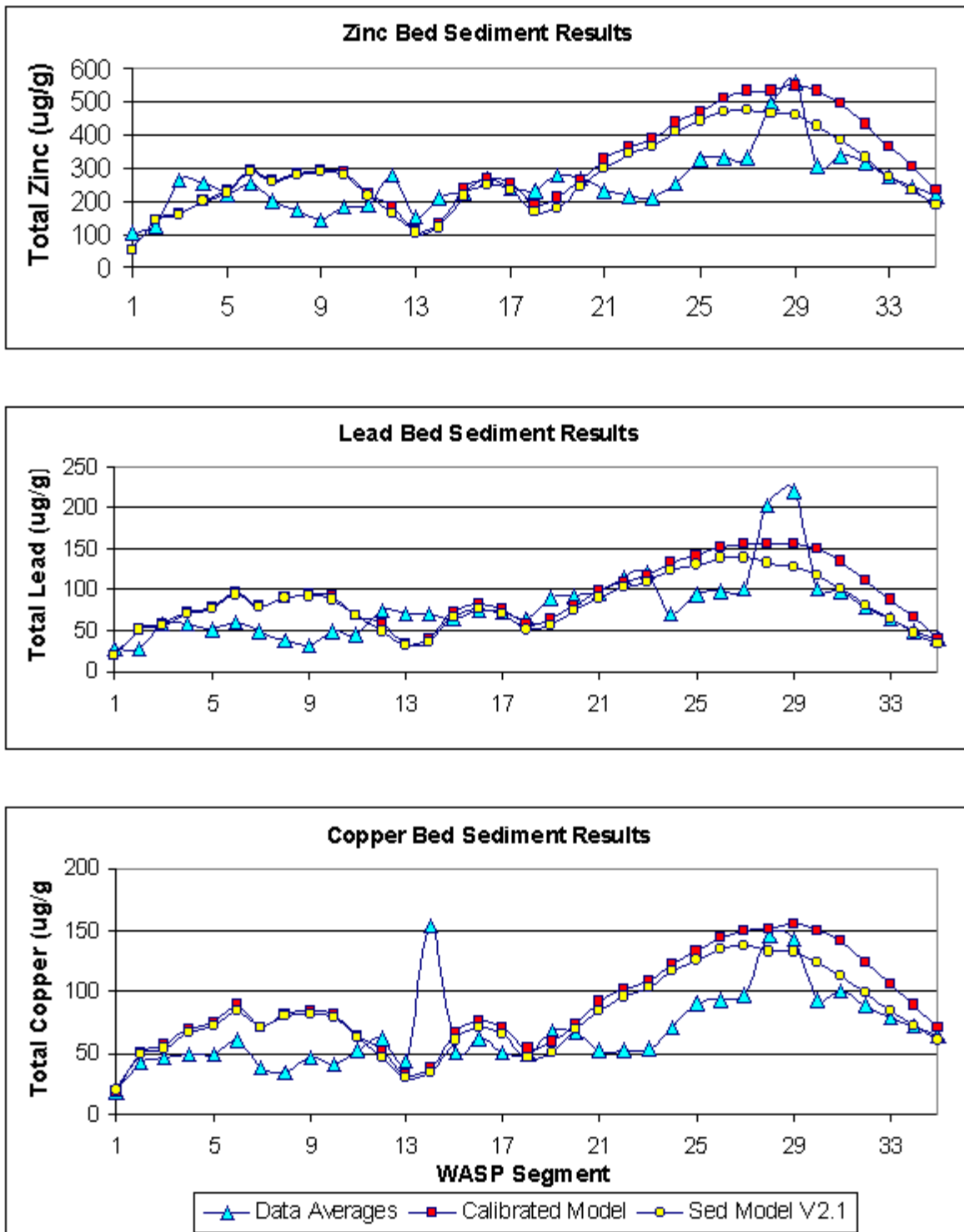


Figure 3-31. Metals Bed Sediment Results - Calibrated Model (Version 2.3) vs. Sediment Model (Version 2.1)

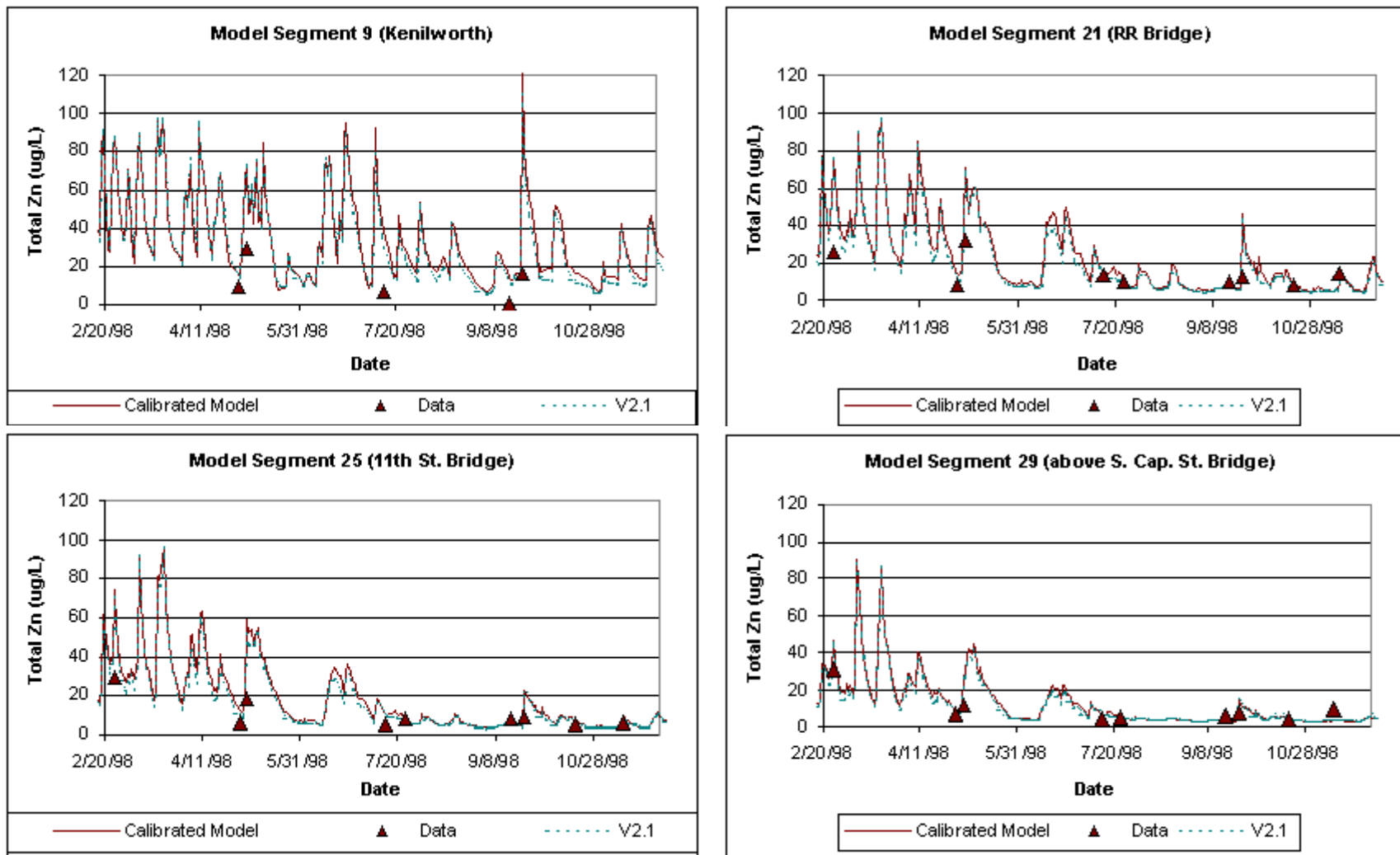


Figure 3-32. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: TAM/WASP V2.3 (Calibrated Model) vs. V2.1



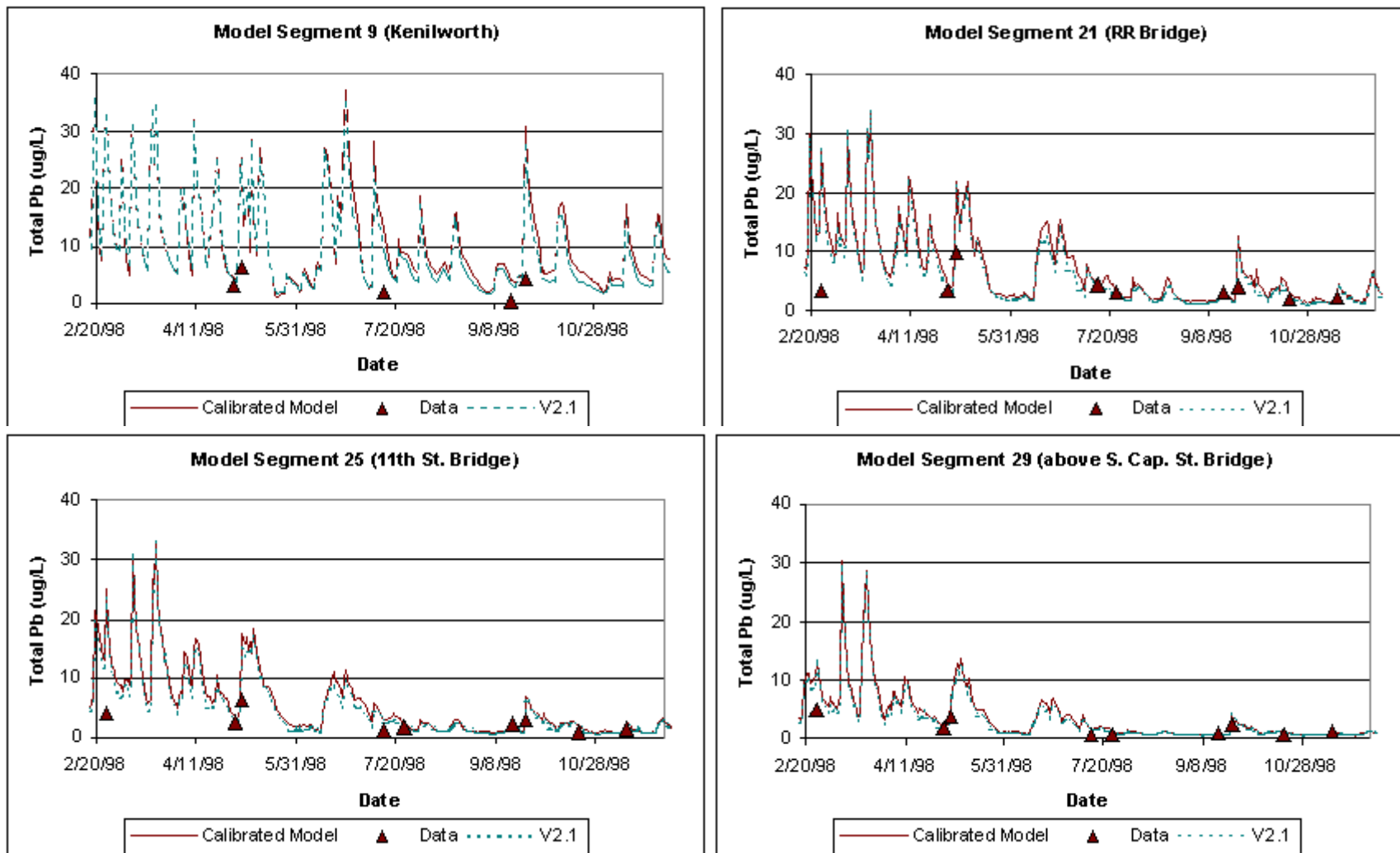


Figure 3-33. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: TAM/WASP V2.3 (Calibrated Model) vs. V2.1

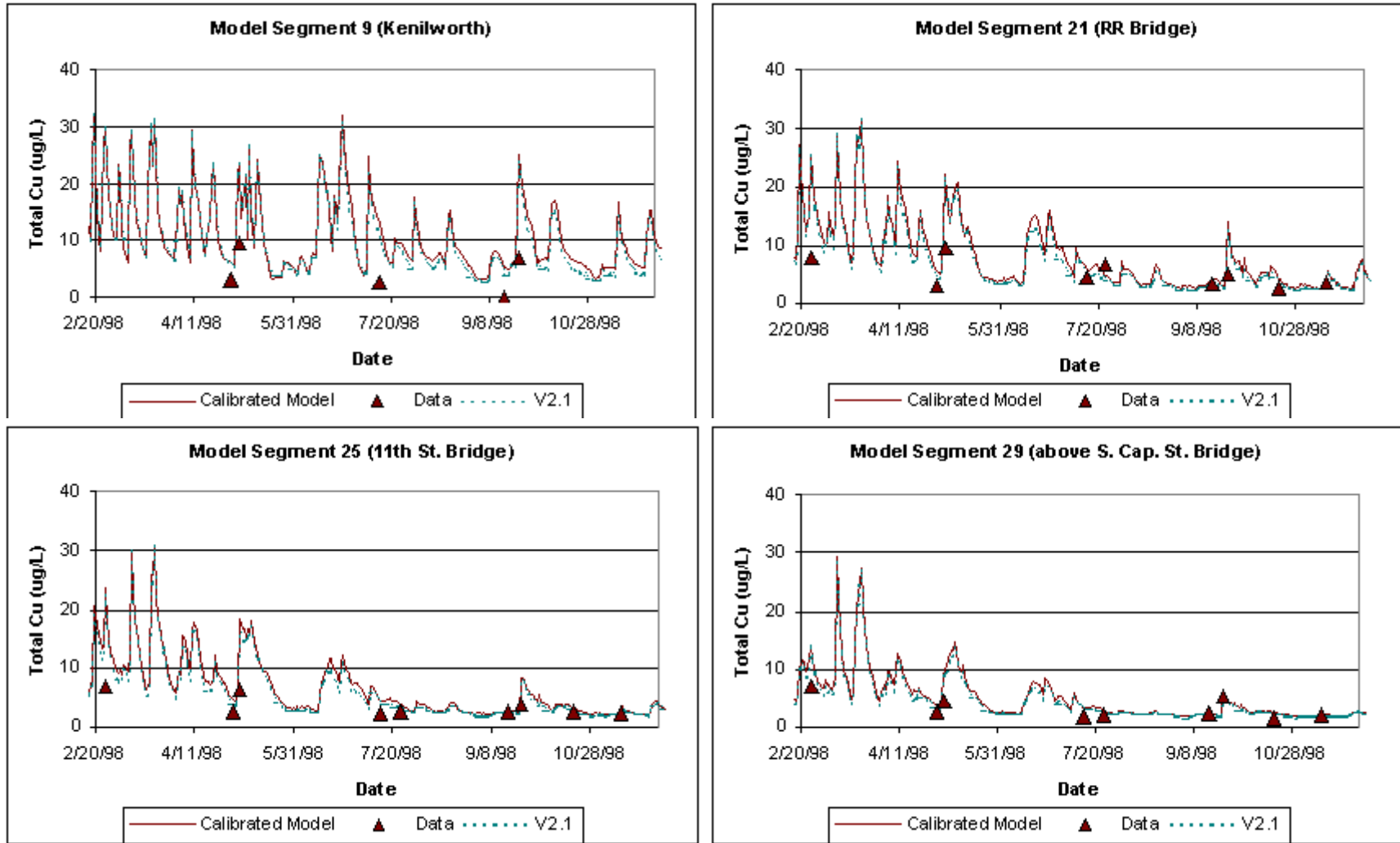


Figure 3-34. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results: TAM/WASP V2.3 (Calibrated Model) vs. V2.1

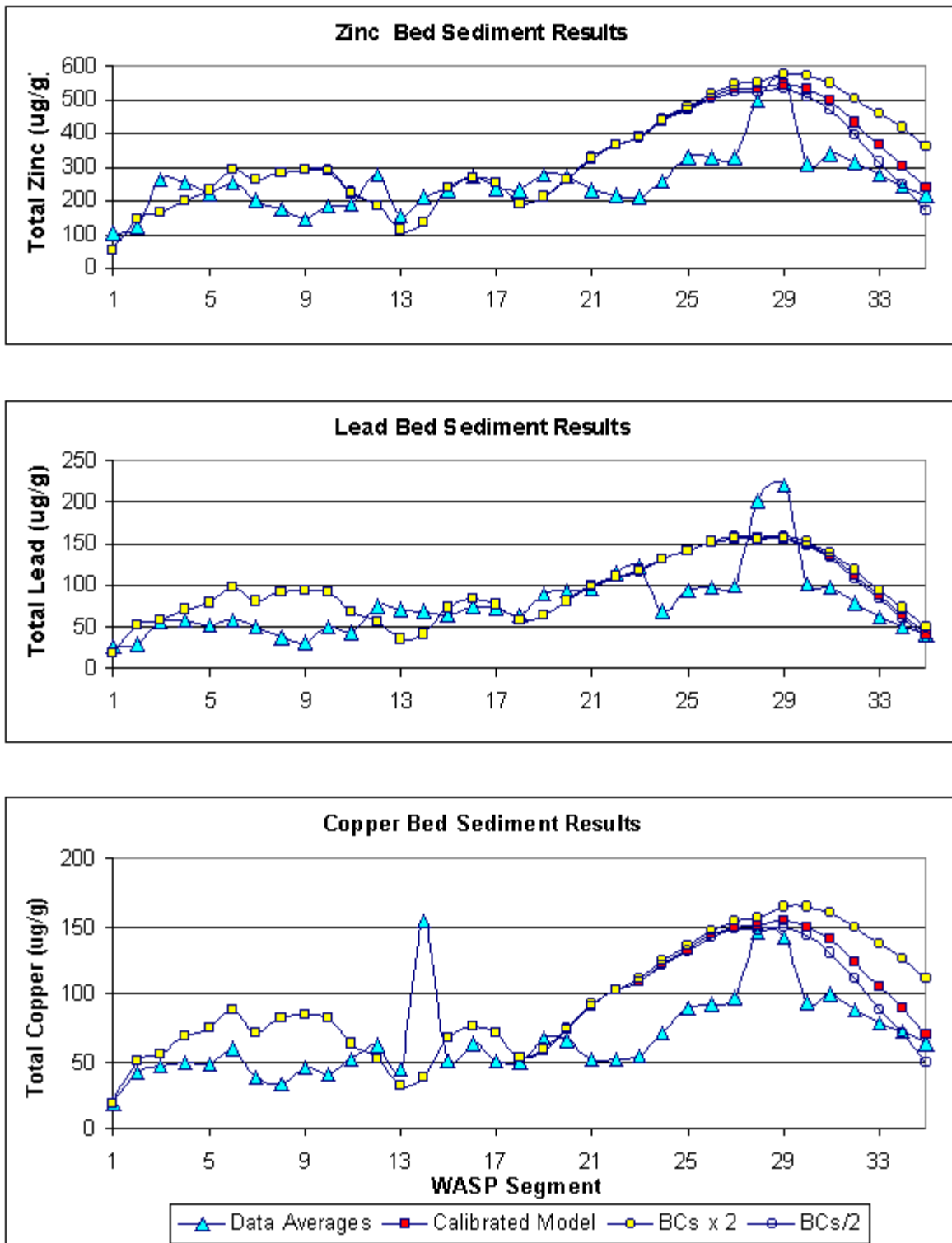


Figure 3-35. Metals Bed Sediment Results: Potomac Boundary Conditions x 2; x 1/2

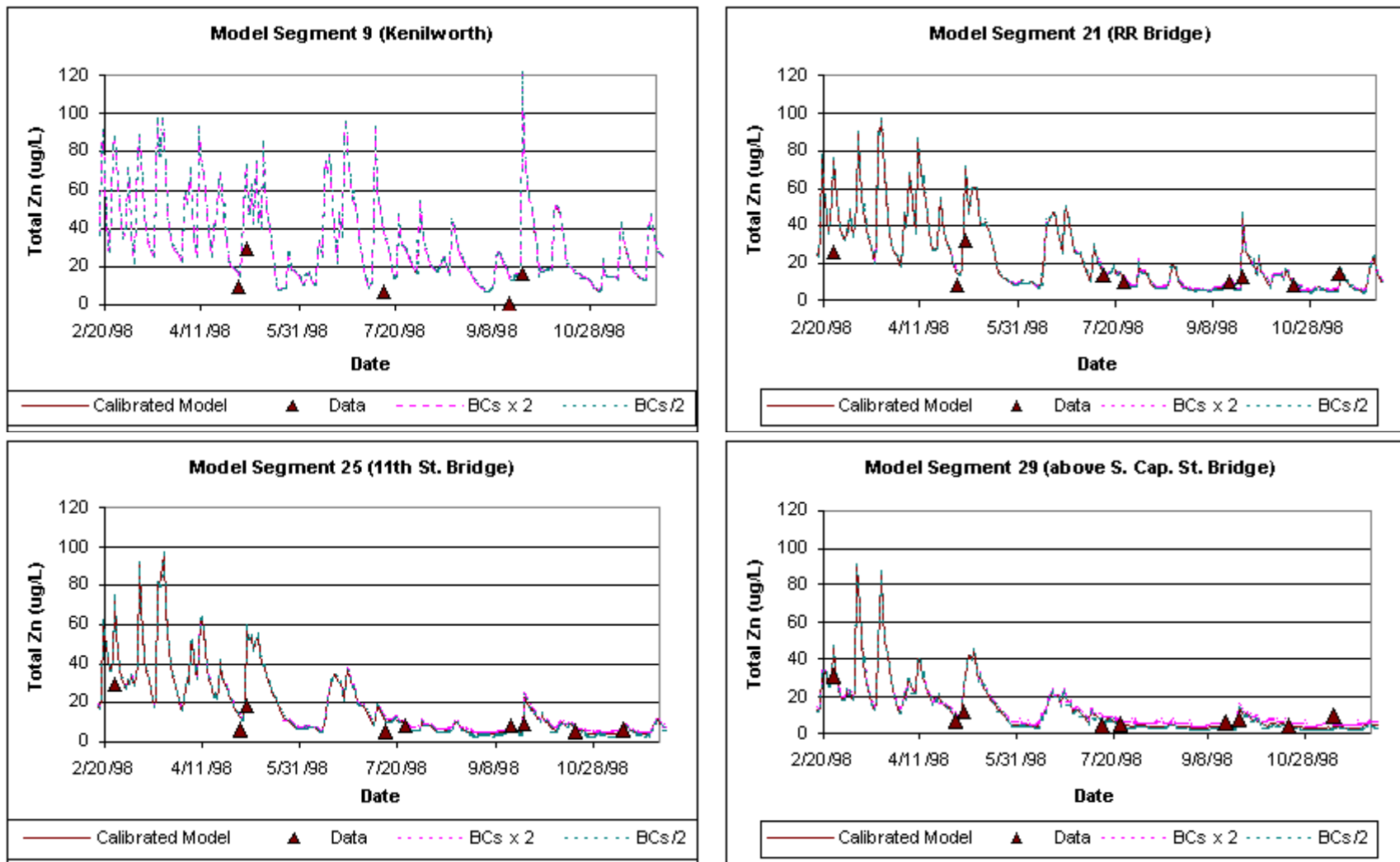


Figure 3-36. Total (Dissolv. + Partic.) Zinc Water Column Sensitivity Test Results: Potomac Boundary Conditions x 2; x 1/2

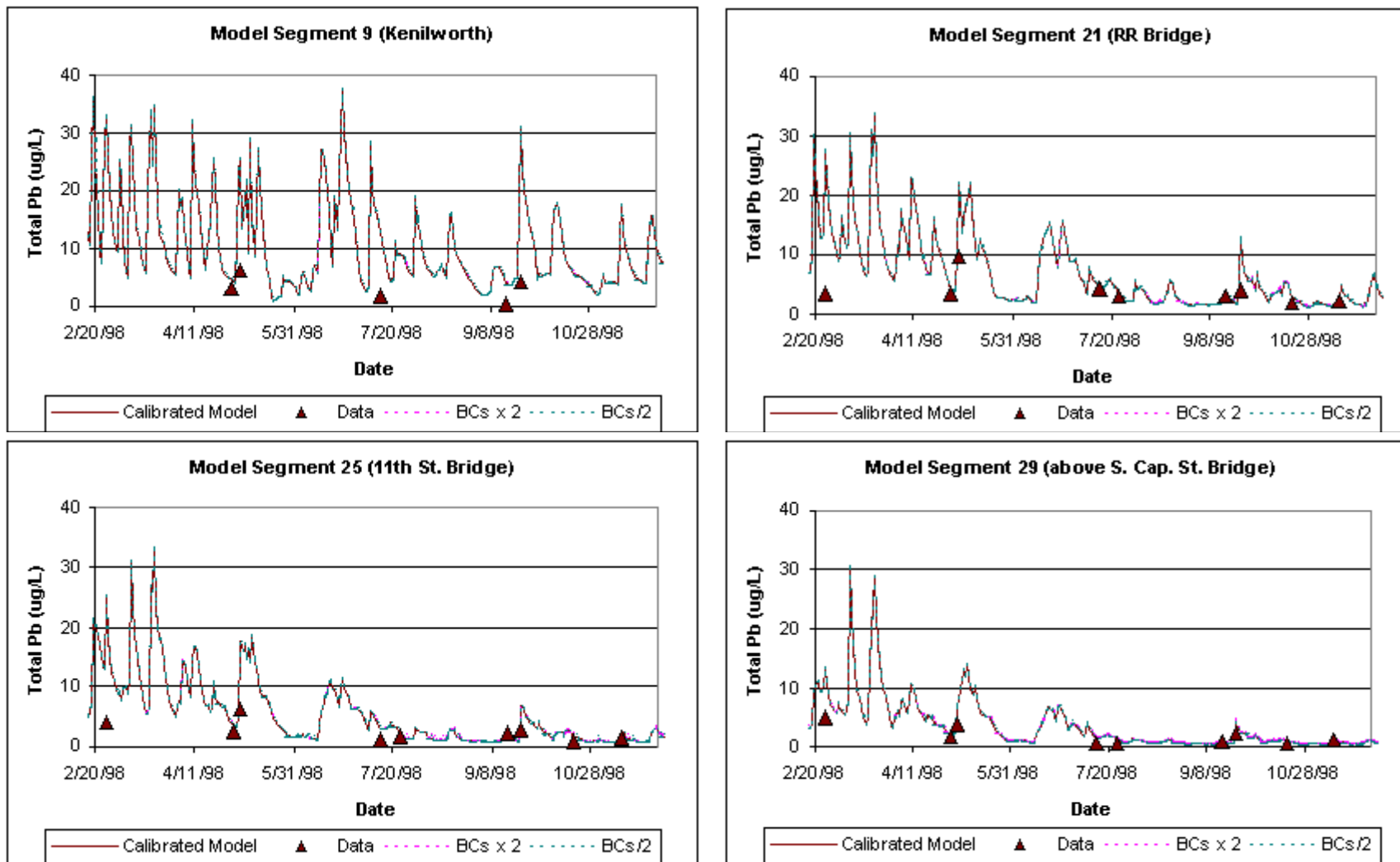


Figure 3-37. Total (Dissolv. + Partic.) Lead Water Column Sensitivity Test Results: Potomac Boundary Conditions x 2; x 1/2

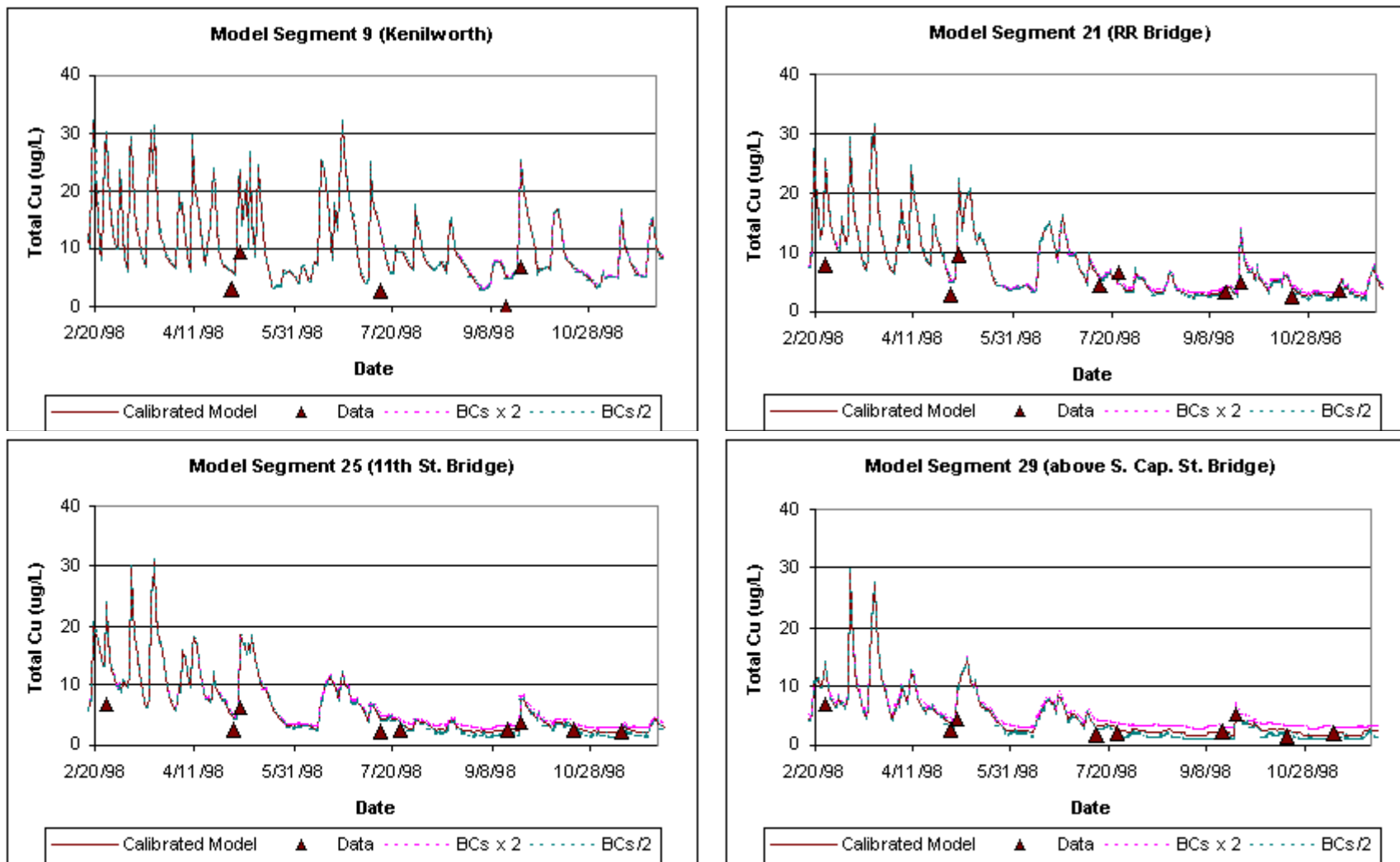


Figure 3-38. Total (Dissolv. + Partic.) Copper Water Column Sensitivity Test Results: Potomac Boundary Condition x 2; x 1/2

### 3.3.2. Arsenic (Metals2) Sub-Model

#### Model Description

A very simple model has been set up for total arsenic, with no speciation. The only fate and transport process simulated, in addition to advection and dispersion, is adsorption to the medium and fine-grained sediment fractions. ICPRB feels that this simple modeling framework is appropriate, given that data support for the arsenic model is limited. There is no data on arsenic in the Gruessner study of upstream loads (Gruessner et al., 1998), there is no arsenic data in the bed sediment study by Velinsky et al. (2001), and there is no data to compute site-specific partition coefficients. However, though data support is limited, the existing data exhibits little variability in either the water column or bed sediment.

#### Input Parameters

Input parameters for the arsenic sub-model are summarized in Tables 3-7 and 3-8. Upstream base flow concentrations are estimated at 0.2 ug/L, from a limited amount of data available in the water column sampling done by Velinsky in 1998 (Velinsky et al., 1999), which included two base flow arsenic concentrations for both the Northeast and Northwest Branches. Tidal sub-basin tributaries and separate storm sewer (SS) system arsenic concentrations are all estimated to be 1.4 ug/L, based on currently available MS4 monitoring data (20 samples with 15 non-detects, where non-detects were estimated to be ½ the detection limit). Bed sediment arsenic concentrations can be estimated from several historical data sets available in the AWTA/NOAA database, though coverage is limited, with most samples from locations near the west bank of the river directly adjacent to the Washington Navy Yard or the Washington Gas and Light facility, no samples below the S. Capitol Street Bridge and only a few samples above the Railroad Lift Bridge. Tidal sub-basin tributary base flow and groundwater concentrations are estimated to be 0.2 ug/L, based on the Northeast/Northwest Branches base flow results. Northeast/Northwest Branches storm flow concentrations and combined sewer system overflows (CSOs) concentrations are estimated to be 1.4 ug/L, based on the MS4 monitoring results.

No site-specific data were available to estimate partition coefficients for arsenic. Diamond et al. (1990; 1995) computed arsenic  $K_d$ 's of 30,000 - 60,000 and 150,000 L/kg using water column data from two Canadian lakes. Based on these literature values, the  $K_d$  was set at 100,000 L/kg for fine-grained material in the arsenic sub-model. A boundary condition for arsenic concentration at the Potomac confluence was set at 0.35 ug/L, equal to the mean of two pre-storm Potomac River concentrations reported in the Velinsky 1998 water column data set.

#### Model Results

Figure 3-39 shows a comparison of long-term model predictions (last day of 6 year run) versus empirical bed sediment concentration data. This comparison suggests that the arsenic model accounts reasonably well for arsenic mass inputs into the tidal portion of the Anacostia. (It should be noted that estimated average arsenic bed sediment concentrations for the first six and the last six model segments are just based on extrapolation because there were no samples located in these segments.) Likewise, predicted water column concentrations match the limited amount of available data reasonably well (Figure 3-40). Mass balance estimates for arsenic, given

in Table 3-9 and Figure 3-41, should be viewed as very preliminary, because no actual concentration data were available for most of the sources listed (see comments in Table 3-8).

**Summary**

The arsenic sub-model (Metals2) was constructed with very limited data support, with little bed sediment data, no data available for computation of site-specific  $K_d$ 's, and no data available on upstream storm concentrations. However, the data which does exist is fairly uniform, and the model appears to do a fairly good job in accounting for mass inputs into the tidal river. Available water column provides further model verification.

**Table 3-7. WASP Input Parameters for Metals2 Sub-Model**

Process	Parameter	Units	Arsenic	Source
<i>Adsorption:</i>				
	$K_d$ for fine-grained sediment	$L_w/kg_s$	100,000	Based on literature values.
	$K_d$ for coarse-grained sediment	$L_w/kg_s$	20,000	Based on literature values and best professional judgement.
<i>Downstream boundary condition:</i>				
	Typical Potomac concentration	ug/L	0.35	Computed from Velinsky et al. 1998 data from 2 pre-storm samples.
<i>Air/Water exchange:</i>				
	Wet deposition		0	No data has been found.
	Dry deposition		0	No data has been found.
	Volatilization input parameters		NA	Volatilization has not been included in the model.



**Table 3-8. Concentrations Used to Compute Metals2 Sub-Model Calibration Run Input Loads (ug/L)**

Source	Arsenic Orig	Suggested Arsenic Multiplier	Arsenic Final	Comment
NW Br Base	0.2	x 1	0.2	Concentration computed from Velinsky et al. 1998 data from 2 samples.
NW Br Storm	1.4	x 1	1.4	Assuming DC MS4 value.
NE Br Base	0.2	x 1	0.2	Concentration computed from Velinsky et al. 1998 data from 2 samples.
NE Br Storm	1.4	x 1	1.4	Assuming DC MS4 value.
SSTrib Base	0.2	x 1	0.2	Assuming Velinsky 1998 value.
SSTrib Storm	1.4	x 1	1.4	Concentration computed from available DC MS4 monitoring data, 20 samples with 15 NDs.
CSO	1.4	x 1	1.4	Assuming DC MS4 value.

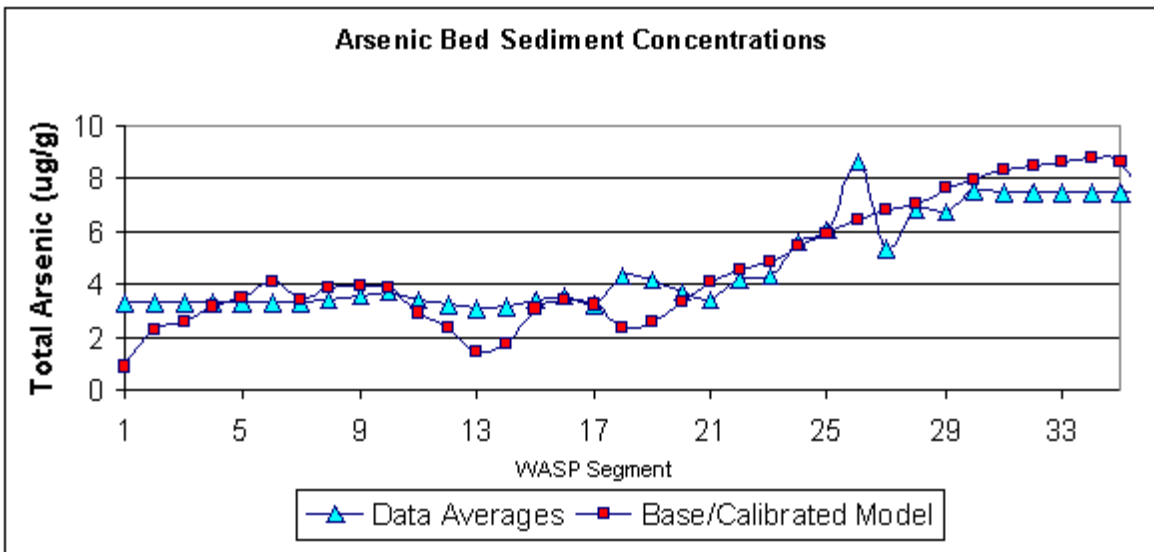


Figure 3-39. Arsenic Bed Sediment Results

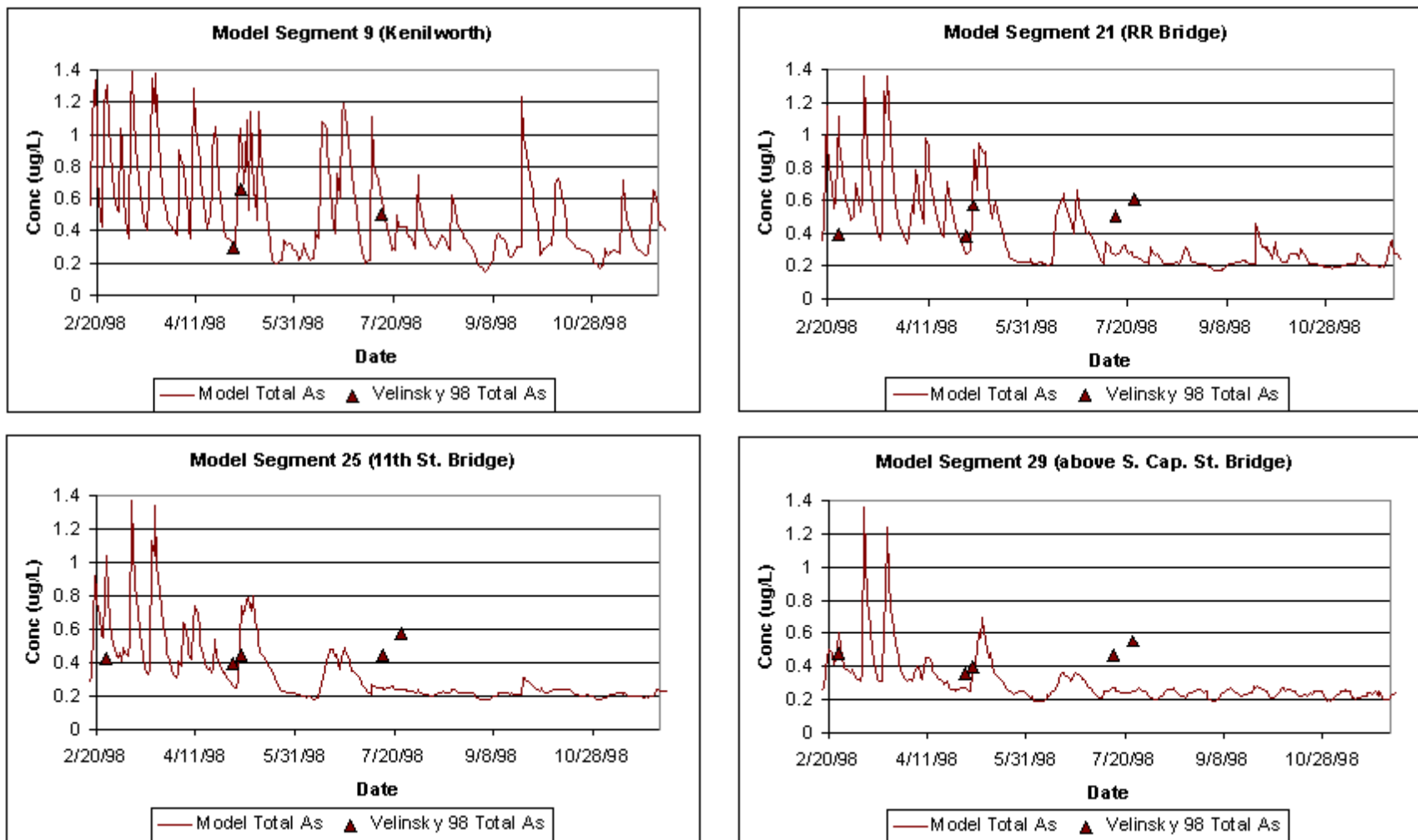


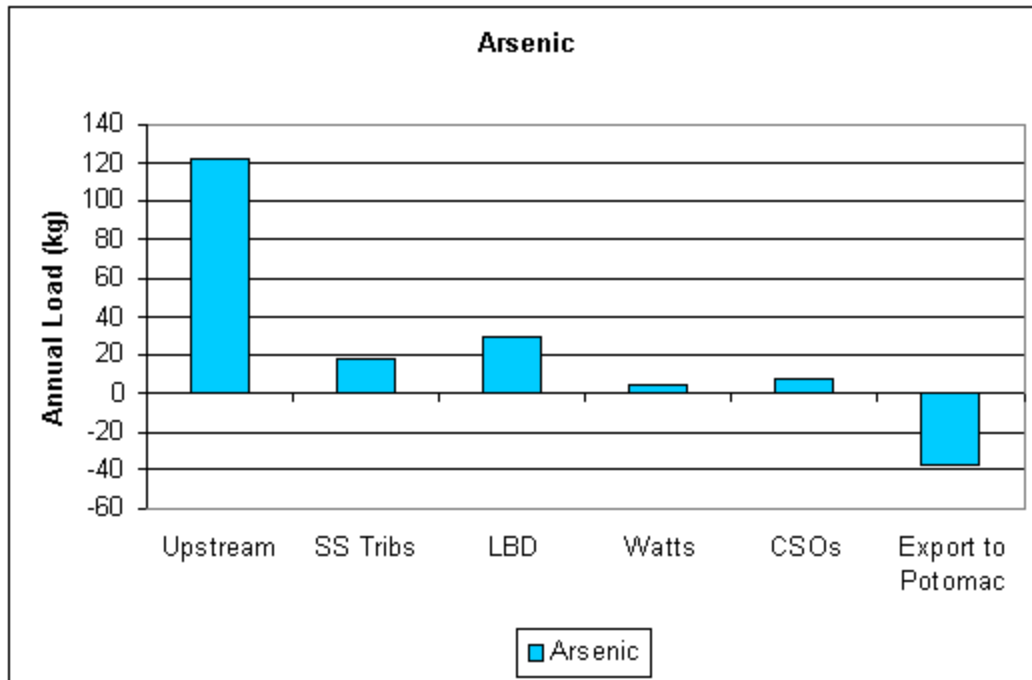
Figure 3-40. Predicted vs. Measured Water Column Concentrations for Total Arsenic (ug/L)

**Table 3-9. Average Annual Load Contributions and Losses by Source for Calibrated Metals2 Sub-Model**

	Arsenic	
Loads/Losses	kg	% <sup>2</sup>
Upstream	122	68
SS Tribs	18	10
LBD	29	16
Watts	4	2
CSOs	7	4
Total Input <sup>1</sup>	180	100
Export to Potomac	-37	-21

<sup>1</sup> Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

<sup>2</sup> % represents the percentage of total input (sum of all loads).



**Figure 3-41. Summary of Average Annual Loads and Losses for Arsenic (Metals2) Sub-Model**

### 3.3.3. PCB Sub-Model

#### Model Description

A TAM/WASP model has been set up for three groups of PCB homologs as shown in Table 1-2. The rationale for the groupings is based on similarities in molecular weights (MW), partition coefficients ( $K_d$ ), Henry's Law coefficients (HLC), and biodegradation potential (Table 1-3). Group PCB1 (di- and trichlorobiphenyls) consists of the less chlorinated, lower molecular weight congeners, which have a greater tendency to be found in the dissolved phase and less of a tendency to sorb onto sediment particles. Group PCB2 (tetra- through hexachlorobiphenyls) consists of mid-range molecular weight congeners. Group PCB3 (hepta- through nonachlorobiphenyls) consists of the most highly chlorinated and highest molecular weight congeners, which have the greatest tendency to be bound to sediment particles.

Probable fate processes for PCBs include sorption, volatilization, biodegradation, and bioaccumulation (TOXNET, U.S. ACE 1997). It is uncertain whether photolysis is a significant degradation process as little experimental data exists to determine its importance (TOXNET). Oxidation and hydrolysis are not deemed to be important fate processes for PCBs in an aquatic environment (TOXNET, U.S. ACE 1997).

Volatilization from water surfaces can be expected, but adsorption to suspended solids and sediments limits the rate of volatilization, especially in the case of higher chlorinated congeners (TOXNET). A study conducted by Bamford et al. from March 1997 to March 1998 found that the tri- through pentachlorobiphenyls contributed approximately 90% of the annual PCB volatilization fluxes for both the Baltimore Harbor and the northern Chesapeake Bay.

In the atmosphere, PCBs primarily exist in the vapor phase but may become associated with particles as the degree of chlorination increases (TOXNET, U.S. EPA). Physical removal of PCBs from the atmosphere can occur through wet and dry deposition.

In sediments, mono-, bi-, and trichlorobiphenyls may degrade rapidly and tetrachlorobiphenyls slowly by aerobic microbial dechlorination, depending on the position of the chlorine atoms on the biphenyl ring (TOXNET, U.S. EPA, Cho et al.). Higher chlorinated biphenyls are resistant to aerobic biodegradation, but may be degraded anaerobically, by reductive dechlorination, to lower chlorinated PCBs (IPCS 1992). The extent of PCB dechlorination by biotic processes in sediments, however, depends on the PCB concentration and the population size of the dechlorinating organisms. It has been reported that microbial dechlorination does not take place at concentrations below 40 ppm (Cho et al., Rhee 1999, TOXNET).

Based on the likely fate processes described above, the only transport and fate processes simulated are advection and dispersion, adsorption to the medium-grained and fine-grained sediment fractions, and volatilization.

Wet and dry deposition has not been included in the model because regional data for congeners or homologs is not available, and because ICPRB estimates, using non-site-specific data, indicate

that wet and dry deposition contribute an insignificant amount to the total PCB load to the Anacostia River (see Table 3-10). Furthermore, Foster et al. (1999) state that “the relative abundance of hexa- and heptachlorobiphenyls in PCB transport ... indicated that the major source to the river was land based erosion rather than from direct atmospheric deposition ...”

Although bioaccumulation is considered a significant fate process, it has not been included in the model framework due to a lack of data, and because WASP currently does not have the capability to simulate bioaccumulation. Biodegradation also has not been included in the model because, based on literature reviews, biodegradation in the sediment apparently does not take place below a concentration of 40 ppm total PCBs, but nowhere in the river has a sediment concentration been reported above this threshold.

### **Input Parameters**

Estimated base flow and storm flow concentrations used for the load estimates can be found in Table 3-11. Northeast and Northwest Branches base and storm flow values are means, assuming log normal distributions, of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin tributaries base flow values are estimated to be the averaged Northeast and Northwest Branches base flow concentrations. Tidal sub-basin tributaries storm flow, separate storm sewer (SS) system, and combined sewer overflows (CSO) estimates are based on data from the District’s MS4 monitoring activities (Nicoline Shelterbrandt, private communication), where non-detects (NDs) were estimated to be 0.00025 ug/L, which is about half the reported minimum detection limit (MDL) (Table 2-5). Upstream and downstream concentrations used in the load computations were increased based on sediment calibration results (Table 3-11) as discussed below.

Proposed input parameters for downstream boundary conditions, adsorption, and volatilization are listed in Table 3-12. Model boundary conditions at the confluence with the Potomac River are based on the average base and storm flow data of two stations reported in the Velinsky et al. (1999) water column data set. The proposed partition coefficients were calculated from site-specific Northeast and Northwest Branches base flow water column data reported by Velinsky et al. (1998). The proposed molecular weights for the three PCB groups are weighted means based on the percent occurrence of congeners in the Northeast and Northwest Branches data set. The Henry’s Law coefficients represent the average value of all congeners in a given PCB group (Source: Brunner et al., 1990). Atmospheric concentrations are based on average Baltimore Harbor concentrations for each PCB group (Source: Bamford et al.). A comparison of estimated atmospheric concentrations with other regional air studies is presented in Table 3-13.

### **Model Results**

The PCB model was run for two scenarios: a base scenario using loads calculated from storm flow and base flow PCB concentrations estimated from available monitoring data (see Section 2.4) and a scenario in which loads were adjusted to calibrate to the sediment data (Table 3-11). A comparison of model predictions (last day of six-year run) versus average bed sediment concentrations for each PCB group and scenario are presented in Figure 3-42. As can be seen in the figures, the base scenario underestimates sediment concentrations for all three PCB groups.

When the upstream and downstream loads are increased by a factor of three, which was judged to be within the likely limit of uncertainty, the model performs reasonably well, although it fails to predict the spike in the sediment data observed in segment 28. In this segment, sediment concentrations are elevated due to the inclusion of historic 1995 Navy Yard data, which was derived by disaggregating Aroclor 1260 sediment concentration data into homologs based on Aroclor composition data by Frame (1996).

Model predictions of water column concentrations versus water column data collected by Velinsky et al. (1999) for each PCB group and scenario are shown in Figures 3-44 to 3-49. The base scenario tends to underestimate water column concentrations (Figures 3-44 to 3-46), but when the loads are adjusted as described above to calibrate the sediment layer, the model performs reasonably well in predicting water column concentrations (Figures 3-47 to 3-49). The calibrated model's load adjustment factor of 3 is not unreasonable given the likely range of statistical uncertainty of current estimates of storm water concentrations. Also, because of the likely heterogeneous distribution of PCBs in the watershed, it is probable that PCB loads to the Anacostia are not well characterized because significant PCB source areas have not yet been identified. Finally, the PCB sub-model load estimates do not take into account any changes over time of PCB loads which may have occurred during the mid to late 1990's due to remedial activities at sites such as the Washington Navy Yard.

A mass balance for PCB loads by source, kinetic losses, and net export to the Potomac River is given in Table 3-14 and shown in Figure 3-43 for the loads adjusted scenario. According to predictions of the PCB sub-model, approximately one third of the total mass of PCBs entering the tidal portion of the Anacostia each year is eventually exported to the Potomac and approximately 5% is lost to the atmosphere due to volatilization. Because the results in Table 3-14 are based on only two storm water monitoring studies, the load estimates should be viewed as preliminary until more storm water data becomes available. For example, it can be seen from Table 3-11 that in PCB sub-model runs, all model separate sewer system sub-sheds, all CSO sub-sheds, as well as Lower Beaverdam Creek and Watts Branch, were assumed to have the same storm water concentrations of PCBs, based on the only data set available for the tidal sub-basin, the Districts MS4 monitoring data. When additional monitoring data becomes available, it is possible that different sub-shed areas will be found to have significantly different contributions of PCBs because of different historical patterns of PCB usage.

### **Sensitivity Runs**

$K_d$  estimates are subject to a high degree of uncertainty, and changes in  $K_d$  values affect model predictions concerning the amount of contaminants that accumulate in the bed sediment over time. Because the PCB sub-model base runs significantly under-predict the concentration of total PCBs in the bed sediment, two runs were done to investigate how sensitive the PCB sub-model is to changes in  $K_d$  values, and whether or not incorrect estimates of  $K_d$  values might account for the discrepancy in base run bed sediment predictions versus available data. In the first set of runs,  $K_d$  values for PCB1, PCB2, and PCB3 for both fine-grained and medium grained sediment fractions were all reduced by a factor of 1/4. In the second set of runs, all  $K_d$  values were increased by a factor of 10. Base loads (without the x 3 load multiplication factor) were used in

both sensitivity runs. Bed sediment results for these sensitivity tests are compared with base model runs in Figure 3-50. Results show that the increased  $K_d$ 's tend to increase long-term bed sediment concentration predictions, especially for the group PCB1. The increases were smaller for PCB2 and PCB3, however, and did not significantly change the model's long term predictions of total PCB bed sediment concentrations. The decreased  $K_d$ 's tend to decrease long-term bed sediment concentration predictions, with effects most pronounced for PCB1. Thus the 10-fold increase in  $K_d$ 's slightly increases, by about 4%, the amount of total PCB mass predicted to accumulate in the bed sediment after six years, and the factor of 1/4 somewhat decreases, by about 7%, the amount of mass predicted to accumulate in the bed sediment. Water column results for the two sensitivity tests are shown in Figures 3-51 to 3-56. It can be seen in these figures that the factor of 1/4 decrease in  $K_d$ 's increases and somewhat improves the model's predictions of dissolved PCB concentrations in the water column, but does not improve the predictions of (dissolved + particulate) PCBs in the water column. The 10-fold increase in  $K_d$ 's decreases the dissolved water column concentrations and seriously degrades the model's ability to predict dissolved concentrations of groups PCB1 and PCB2.

### **Summary**

The PCB sub-model predicts the fate and transport of three separate groups of PCB congeners, a low-chlorinated group (PCB1), a medium-chlorinated group (PCB2), and a high-chlorinated group (PCB3). The model is based on site-specific estimates of  $K_d$  values and two storm water monitoring data sets, the study of upstream loads by Gruessner et al. (1998) and the District's recent MS4 program monitoring results for the separate storm system. Initial model runs (base scenario) under-estimated bed sediment PCB concentrations by about a factor of three, so the model was "calibrated" by increasing all of the original PCB input load estimates by a factor of three. The calibrated model predicts water column PCB concentrations reasonably well when compared to the 1998 main channel water column data set of Velinsky et al. (1999). According to the predictions of the calibrated PCB sub-model, 33% of the PCBs entering the tidal portion of the Anacostia River are eventually exported to the Potomac and 5% volatilize to the atmosphere.



**Table 3-10. Estimated Annual Atmospheric Deposition of Total PCBs to the Anacostia River**

	Chesapeake Bay - Regional <sup>1</sup>		Chesapeake Bay - Urban <sup>1</sup>		Baltimore <sup>2</sup>	
	Wet	Dry	Wet	Dry	Wet	Dry
Deposition rate ( $\mu\text{g}/\text{m}^2\text{-yr}$ )	0.8	0.8	8.3	8	4.9 - 6.6	8.9 - 18
Deposition total <sup>3</sup> (kg/yr)	0.003	0.003	0.027	0.026	0.016 - 0.022	0.029 - 0.059

<sup>1</sup>CBP (1999) and

<sup>2</sup>From information provided by Joel Baker (private communication); Estimates assume a deposition velocity of 0.192 cm/sec.

<sup>3</sup> Calculations assume that the surface area of the Anacostia River with adjoining tidal embayments is 3,300,300 m<sup>2</sup>

**Table 3-11. Concentrations Used to Compute PCB Sub-Model Calibration Run Input Loads (ug/L)**

Source	PCB1 Orig	PCB1 Multiplier	PCB1 Final	PCB2 Orig	PCB2 Multiplier	PCB2 Final	PCB3 Orig	PCB3 Multiplier	PCB3 Final	Comment
NW Br Base	0.000597	x 3.0	0.00179	0.001897	x 3.0	0.005691	0.001058	x 3.0	0.003174	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.000409	x 3.0	0.00123	0.006127	x 3.0	0.018381	0.004584	x 3.0	0.013751	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
NE Br Base	0.000577	x 3.0	0.00173	0.002630	x 3.0	0.007891	0.000823	x 3.0	0.002468	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.000659	x 3.0	0.00198	0.008813	x 3.0	0.026439	0.007312	x 3.0	0.021937	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
SSTrib/LBD /Watts/CSO Non-storm	0.000585	x 3.0	0.00176	0.002337	x 3.0	0.007011	0.000917	x 3.0	0.002750	Estimated to be the averaged NE/NW Branches base flow (Gruessner et al., 1998)
SSTrib/LBD /Watts Storm	0.007796	x 3.0	0.02339	0.014971	x 3.0	0.044913	0.004082	x 3.0	0.012245	Estimated to be the averaged DC MS4 monitoring data, with NDs at ½ DL.
CSO Storm	0.007796	x 3.0	0.02339	0.014971	x 3.0	0.044913	0.004082	x 3.0	0.012245	Estimated to be the averaged DC MS4 monitoring data, with NDs at ½ DL.

**Table 3-12. WASP Input Parameters for PCB Sub-Model**

Process	Parameter	Units	PCB1	PCB2	PCB3	Source and Comment
<b><i>Downstream Boundary Condition:</i></b>						
	Potomac boundary concentration	ug/L	0.00031	0.00101	0.00080	Computed from Velinsky et al., (1999). Average base and storm flow concentrations of two sampling sites.
<b><i>Adsorption:</i></b>						
	K <sub>d</sub> for fine-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	50,000	172,000	554,000	Mean K <sub>d</sub> based on site-specific base flow data (Gruessner et al., 1998).
	K <sub>d</sub> for medium-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	13,000	43,000	139,000	Taken to be 1/4 of the fine-grained sediment K <sub>d</sub> . Based on best professional judgment.
<b><i>Volatilization:</i></b>						
	Molecular Weight	g/mole	253	327	412	Weighted mean of congeners.
	Henry's Law Coefficient	atm – m <sup>3</sup> /mole	2.04E-04	8.81E-05	1.42E-05	Mean of congeners. Adapted from Brunner et al., 1990.
	Atmospheric Concentration	mg/L	4.22E-10	2.86E-10	0.0	Average Baltimore Harbor conc. for group. Adapted from Bamford et al.

**Table 3-13. Measured Atmospheric Concentrations of PCB Homologs**

PCB Homologs	Gaseous Phase Concentration Range in pg/m <sup>3</sup>									
	Baltimore Harbor, MD <sup>1</sup>	Baltimore, MD <sup>2</sup>	Chesapeake Bay, MD <sup>2</sup>	Northern Chesapeake Bay <sup>3</sup>	Southern Chesapeake Bay <sup>3</sup>	New Brunswick, NJ <sup>3</sup>	Sandy Hook, NJ <sup>3</sup>	Jersey City, NJ <sup>3</sup>	Delaware River Estuary <sup>4</sup>	Galveston Bay, TX <sup>5</sup>
	Mar '97 - Mar '98	July '97	July '97	July '97	July '97	Oct. '97 - May '99	Feb. '98 - Feb '99	July '98, Oct. '98 - May '99		Feb. '95 - Aug '96
Mono									127 - 523 (est)	
Di	10 - 196								127 - 523 (est)	3.9 - 938
Tri	24 - 614	BDL - 188	BDL - 76	19.9 - 62.9	4.5 - 6.0	28.3 - 46.3	20.1 - 33.8	57.8 - 83.8	96 - 290	43.0 - 3428
Tetra	15 - 230	BDL - 279	1.3 - 122	15.8 - 19.3	5.2 - 7.7	9.1 - 30.9	9.6 - 30.6	21.8 - 56.0	65 - 288	44.3 - 1172
Penta	7.8 - 191	BDL - 68	3.8 - 55	6.8	4.8	16.1	13.5	26.5	45 - 195	5.1 - 210
Hexa	5.3 - 122	BDL - 50	6.6 - 38	4.4 - 10.1	5.9 - 10.2	5.4 - 6.0	5.0 - 5.2	9.9 - 10.4	9 - 37	4.4 - 159
Hepta		BDL - 8.5	0.9 - 6.8	1.8 - 2.3	1.7 - 2.7	0.9 - 2.0	0.7 - 2.1	1.7 - 2.6	4 - 9	ND - 305
Octa									0	ND - 4.7
Nona									0	ND - 3.2
Deca									0	ND - 13.3
Total PCB	64 - 1400	760 - 2220	290 - 990	510	210	526 ± 395	439 ± 303	960 ± 802	472 - 1865	207.8 - 4783.1

BDL - below detection limit

ND - not detected

<sup>1</sup> Bamford et al.

<sup>2</sup> Adapted from Brunciak et al., 2001

<sup>3</sup> Adapted from Brunciak et al., 2000

<sup>4</sup> Liao, 2001

<sup>5</sup> Park, 2000

**Table 3-14. Average Annual Load Contributions and Losses by Source for Calibrated PCB Sub-Model**

Loads / Losses	PCB1		PCB2		PCB3		Total PCBs	
	kg/yr	% <sup>2</sup>	kg/yr	%	kg/yr	%	kg/yr	%
Upstream	0.23	19%	2.25	54%	1.65	75%	4.13	55%
SS Tribs	0.29	25%	0.59	14%	0.17	8%	1.05	14%
LBD	0.48	41%	0.94	23%	0.26	12%	1.68	22%
Watts	0.07	6%	0.14	3%	0.04	2%	0.25	3%
CSOs	0.11	9%	0.23	6%	0.07	3%	0.41	5%
Total Load Input <sup>1</sup>	1.18	100%	4.15	100%	2.19	100%	7.52	100%
Kinetic Losses (volatilization)	-0.16	-14%	-0.17	-4%	-0.01	0%	-0.34	-5%
Export to Potomac	-0.48	-41%	-1.40	-34%	-0.62	-28%	-2.5	-33%

<sup>1</sup> Total load input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

<sup>2</sup> % represents the percentage of total load input.

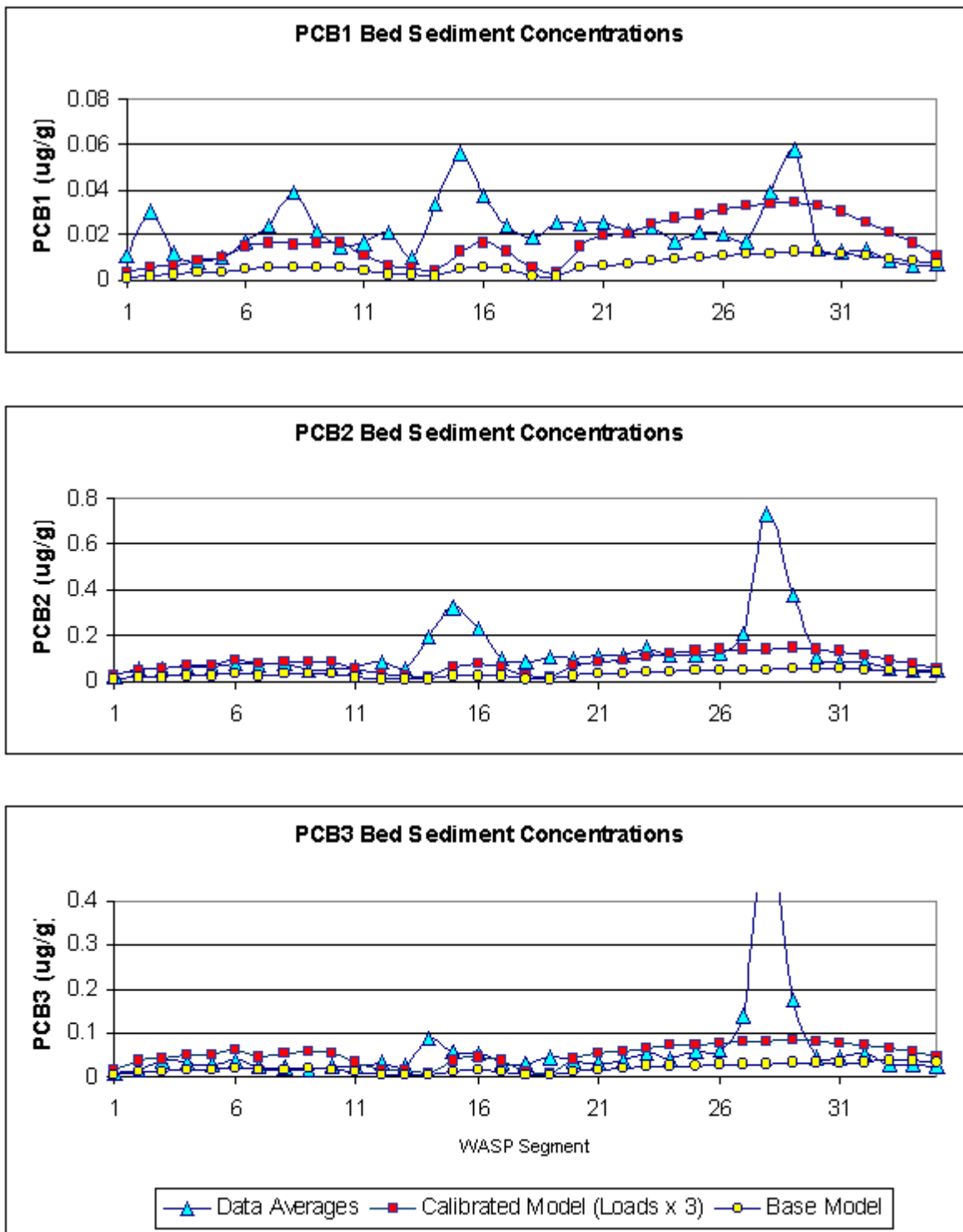


Figure 3-42. PCB Bed Sediment Results: Base Scenario and Calibrated Model (Loads x 3)

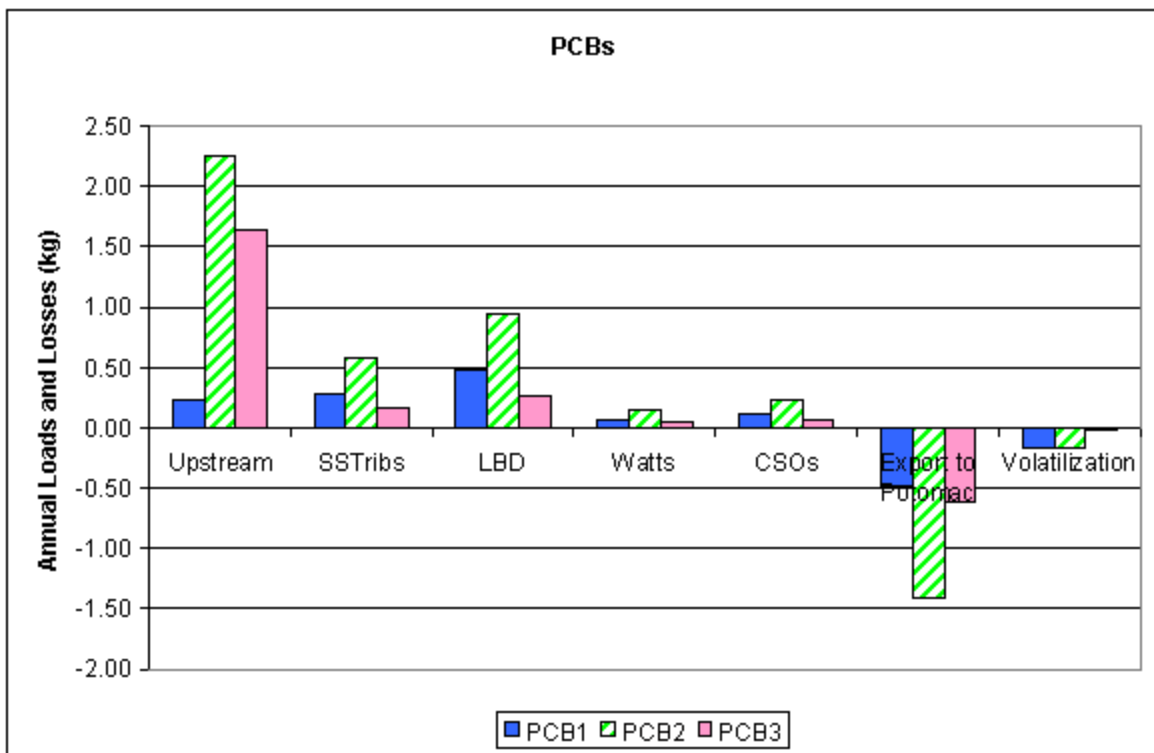


Figure 3-43. Summary of Average Annual Loads and Losses for the Calibrated PCB Sub-Model

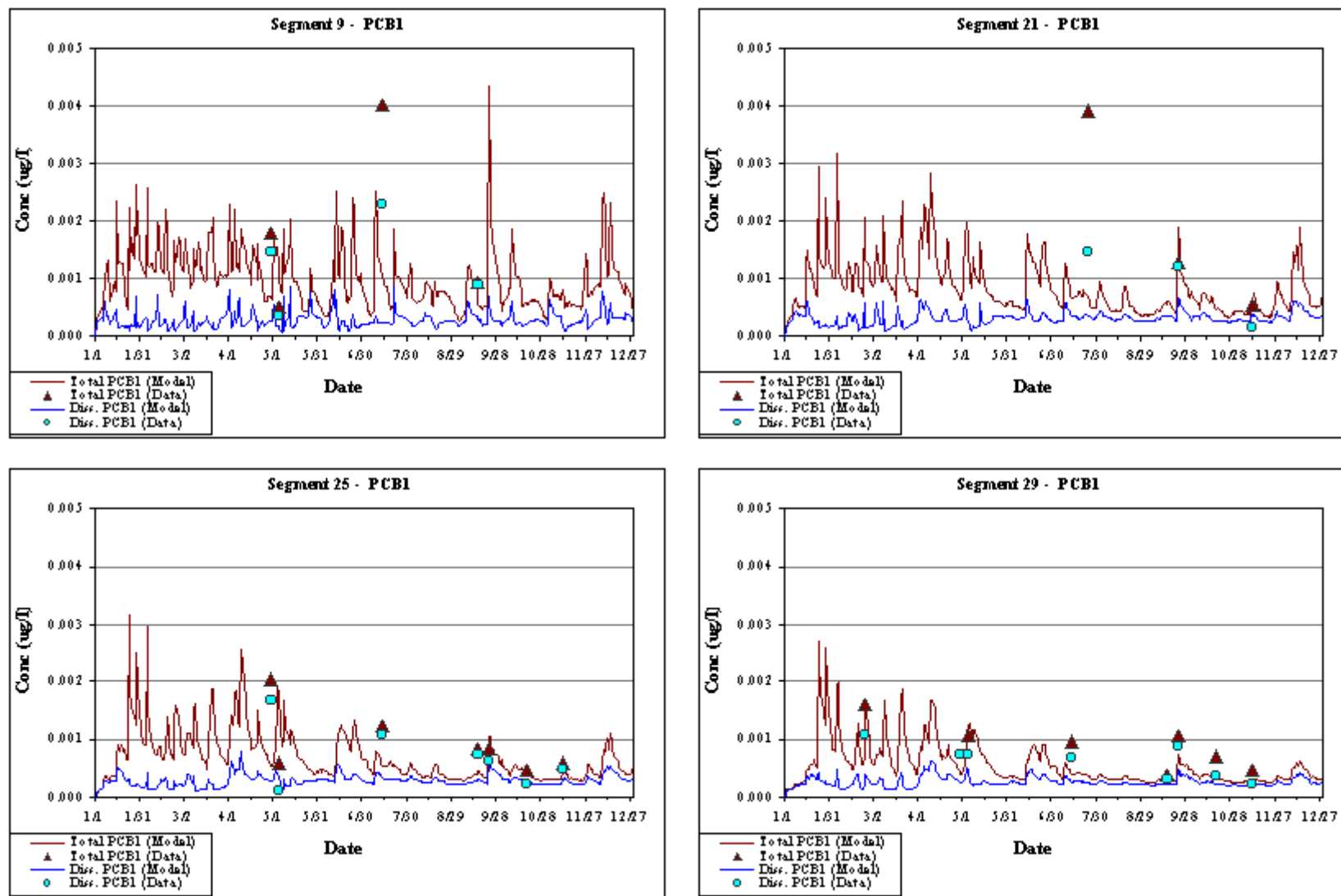


Figure 3-44. PCB1 Water Column Results for the Base Scenario



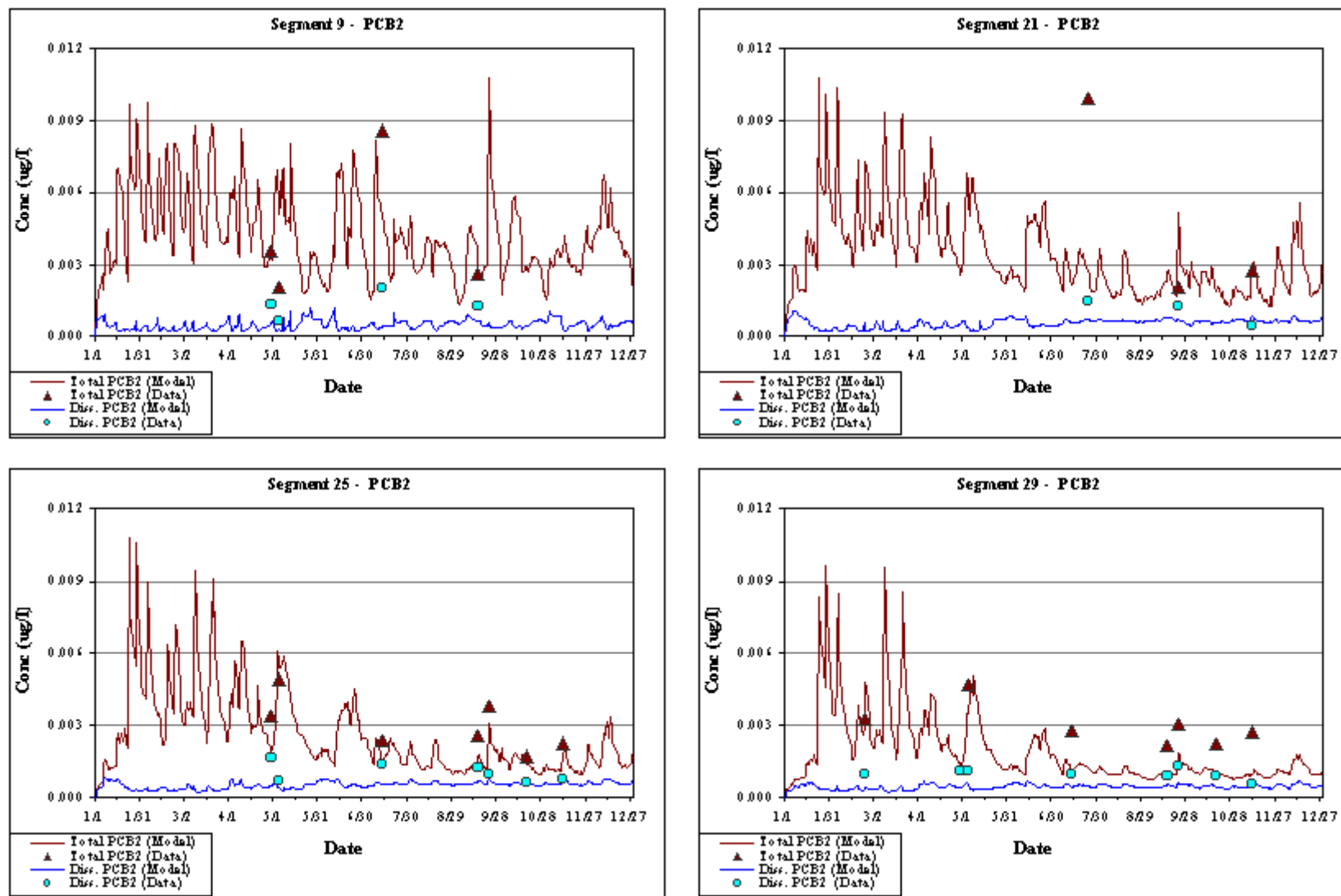


Figure 3-45. PCB2 Water Column Results for the Base Scenario

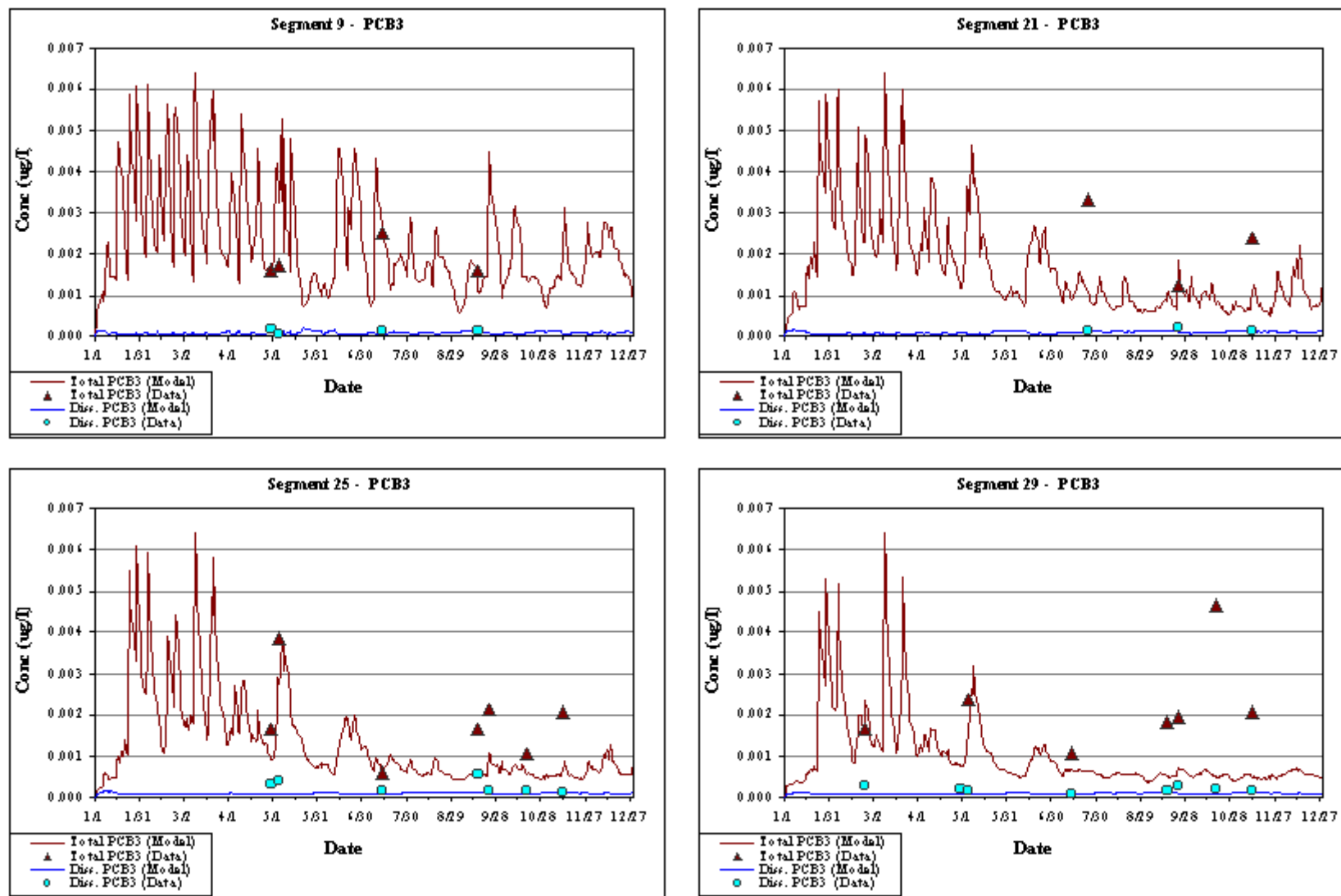


Figure 3-46. PCB3 Water Column Results for the Base Scenario

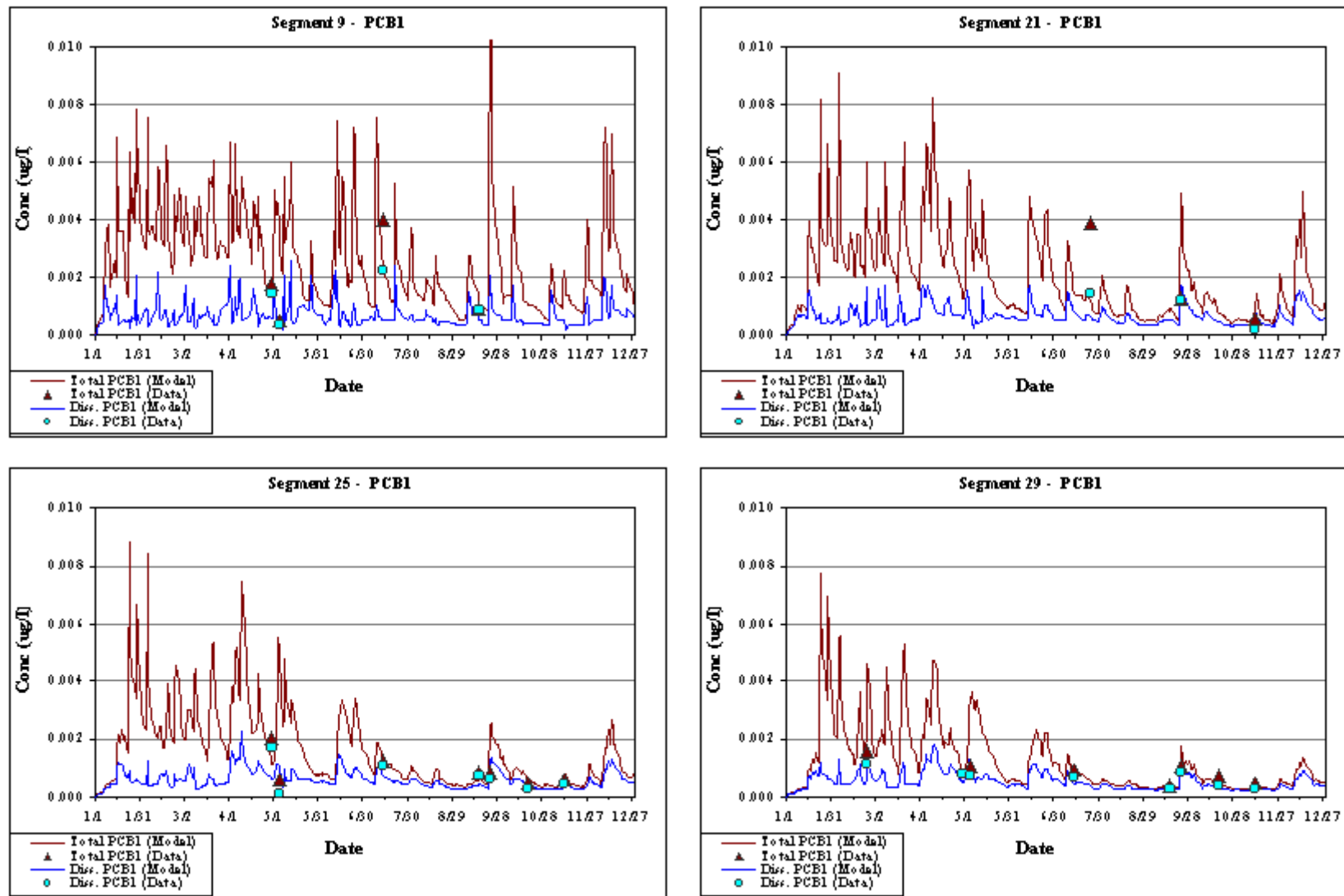


Figure 3-47. PCB1 Water Column Results for the Calibrated (3 x Loads) Scenario

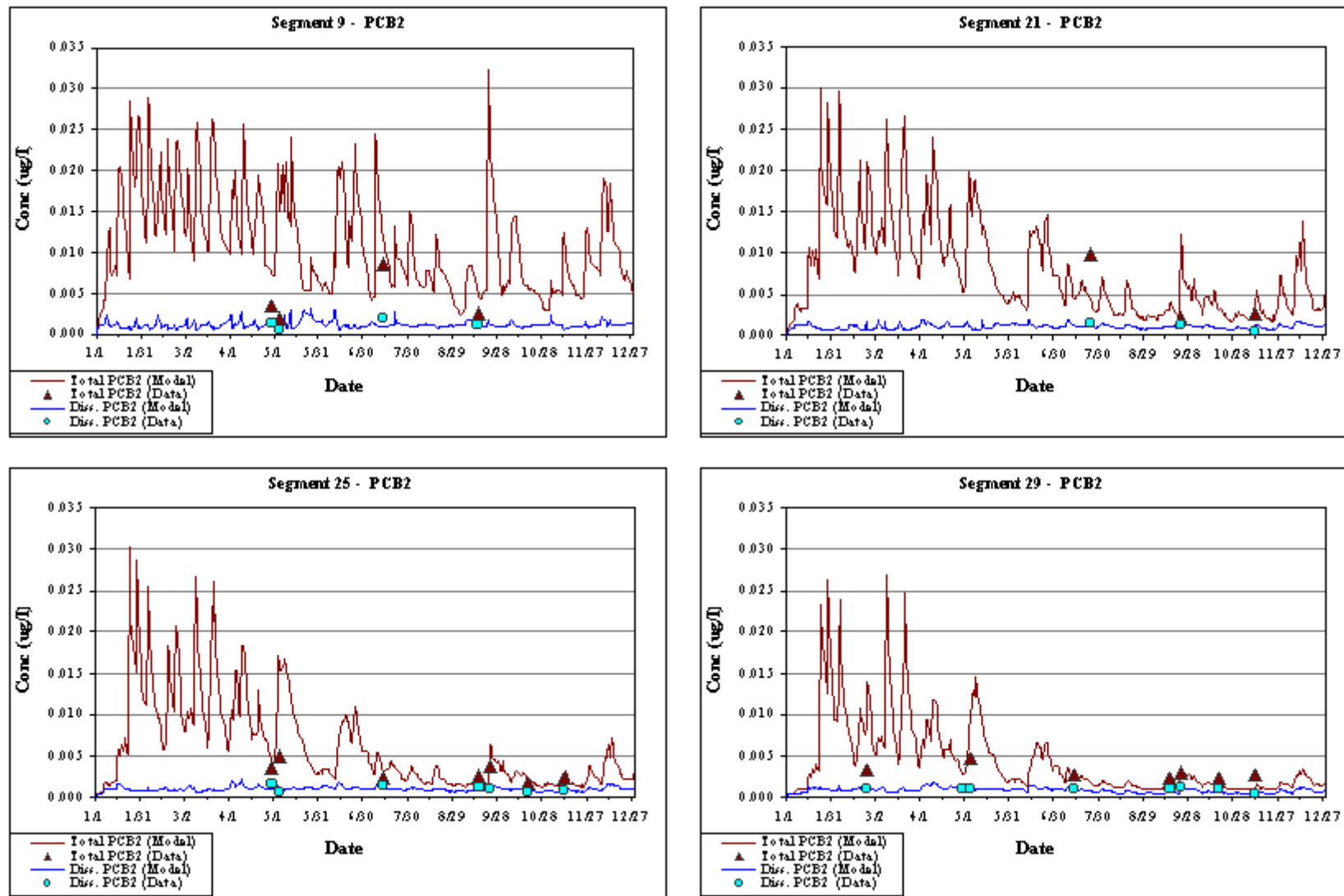


Figure 3-48. PCB2 Water Column Results for the Calibrated (3 x Loads) Scenario

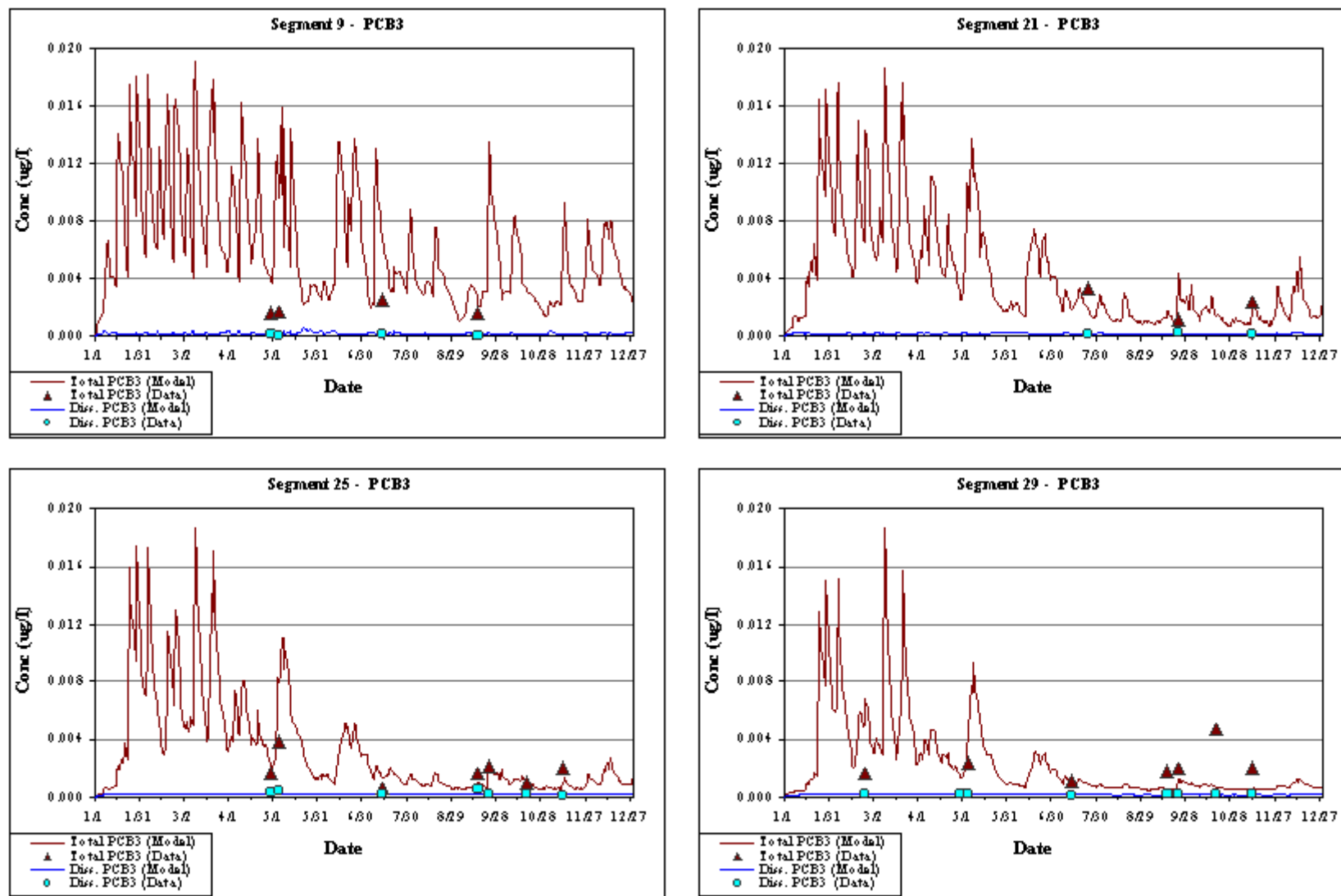


Figure 3-49. PCB3 Water Column Results for the Calibrated (3 x Loads) Scenario

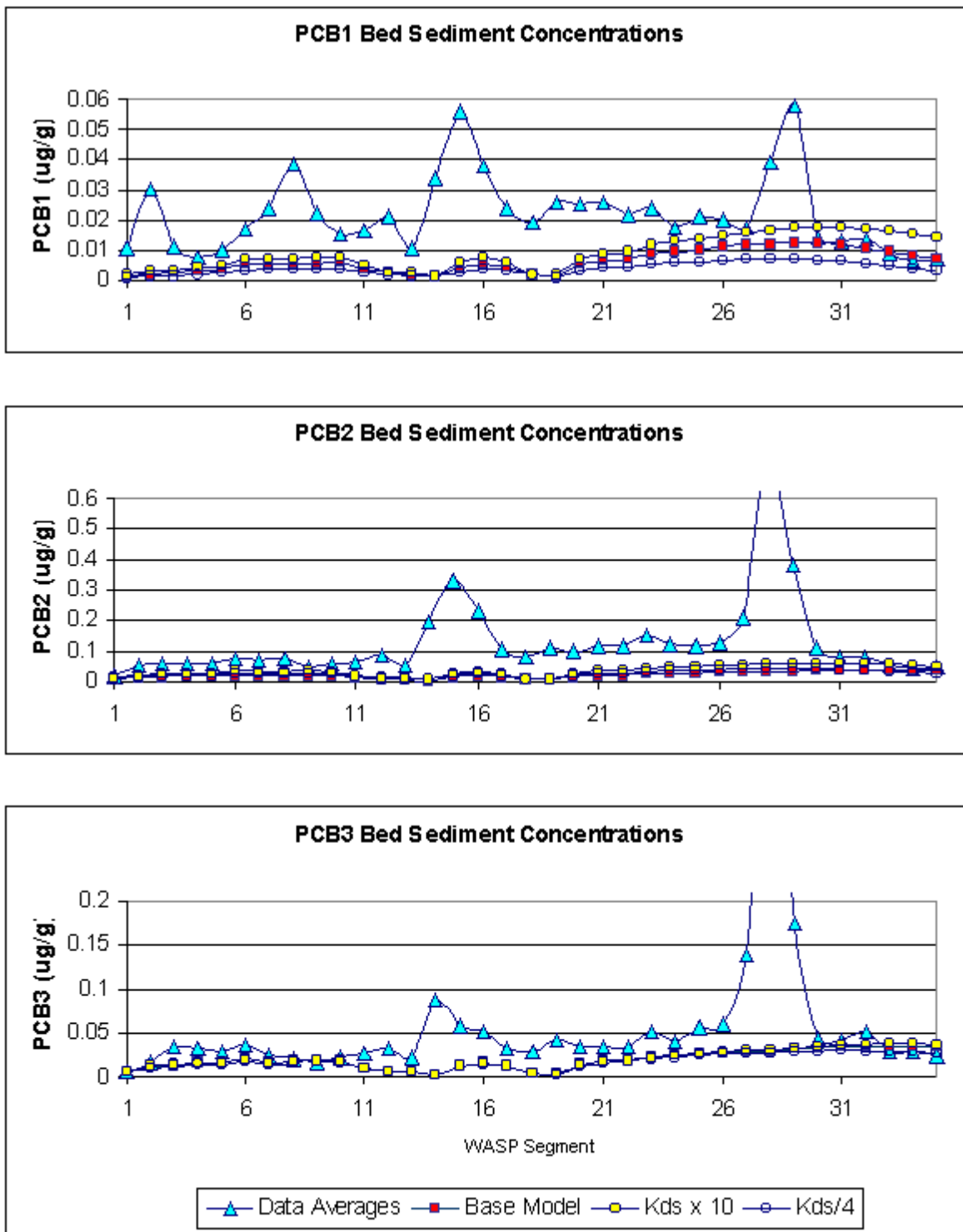


Figure 3-50. PCB Bed Sediment Sensitivity Test Results: All  $K_d$ 's x 10; All  $K_d$ 's x 1/4

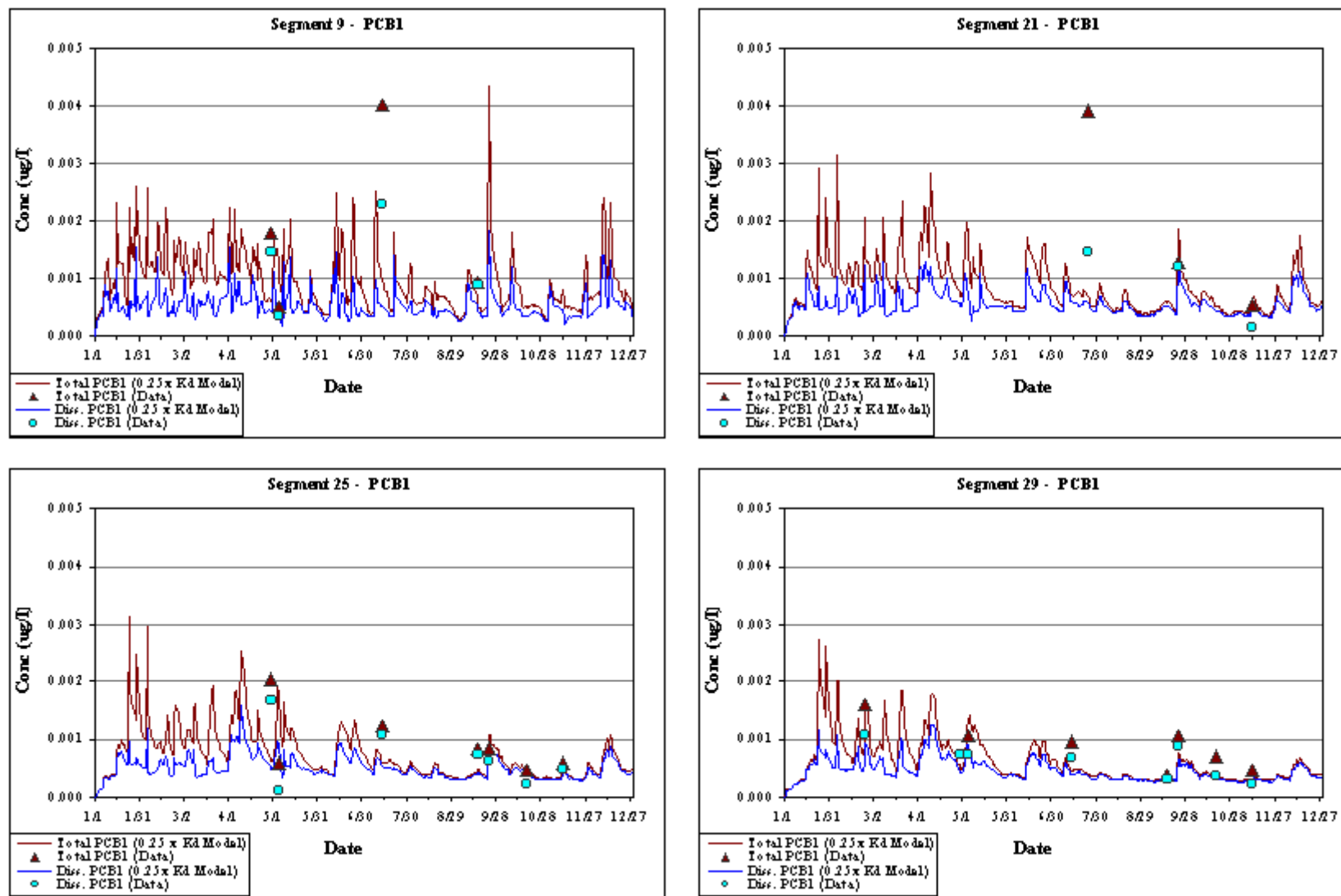


Figure 3-51. PCB1 Water Column Sensitivity Test Results: Both  $K_d$ 's x 1/4

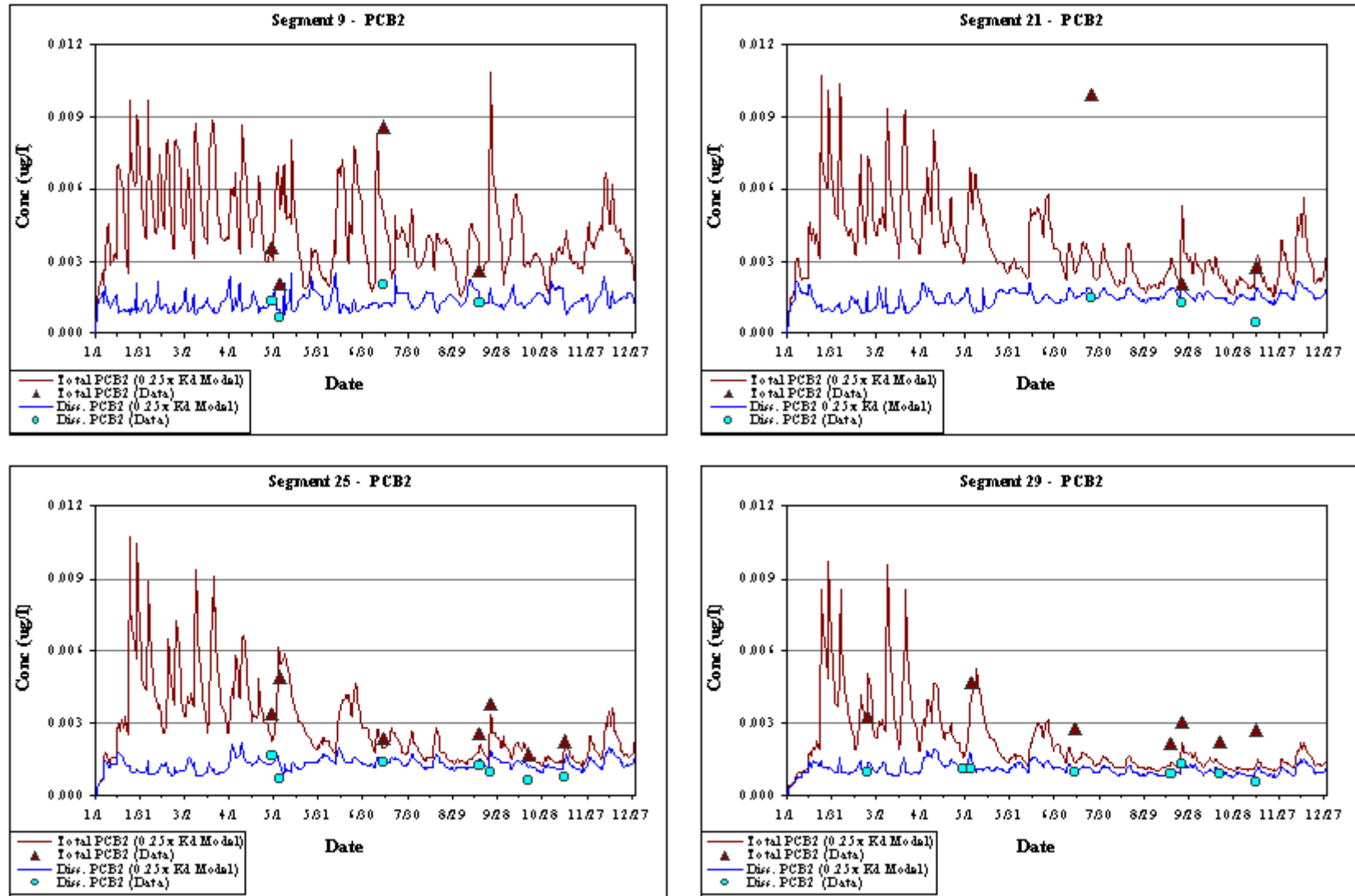


Figure 3-52. PCB2 Water Column Sensitivity Test Results: Both  $K_d$ 's x 1/4



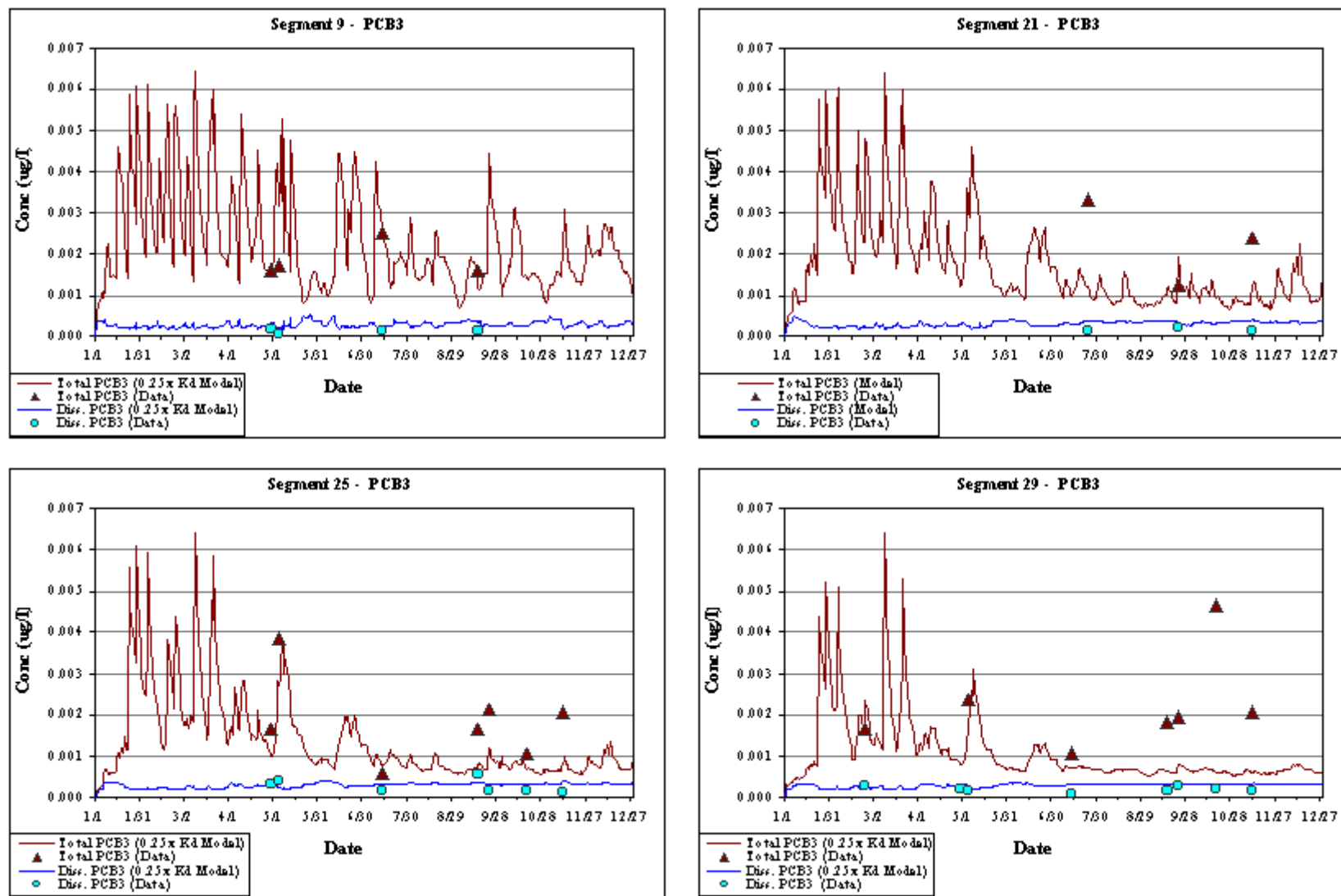


Figure 3-53. PCB3 Water Column Sensitivity Test Results: Both  $K_d$ 's x 1/4

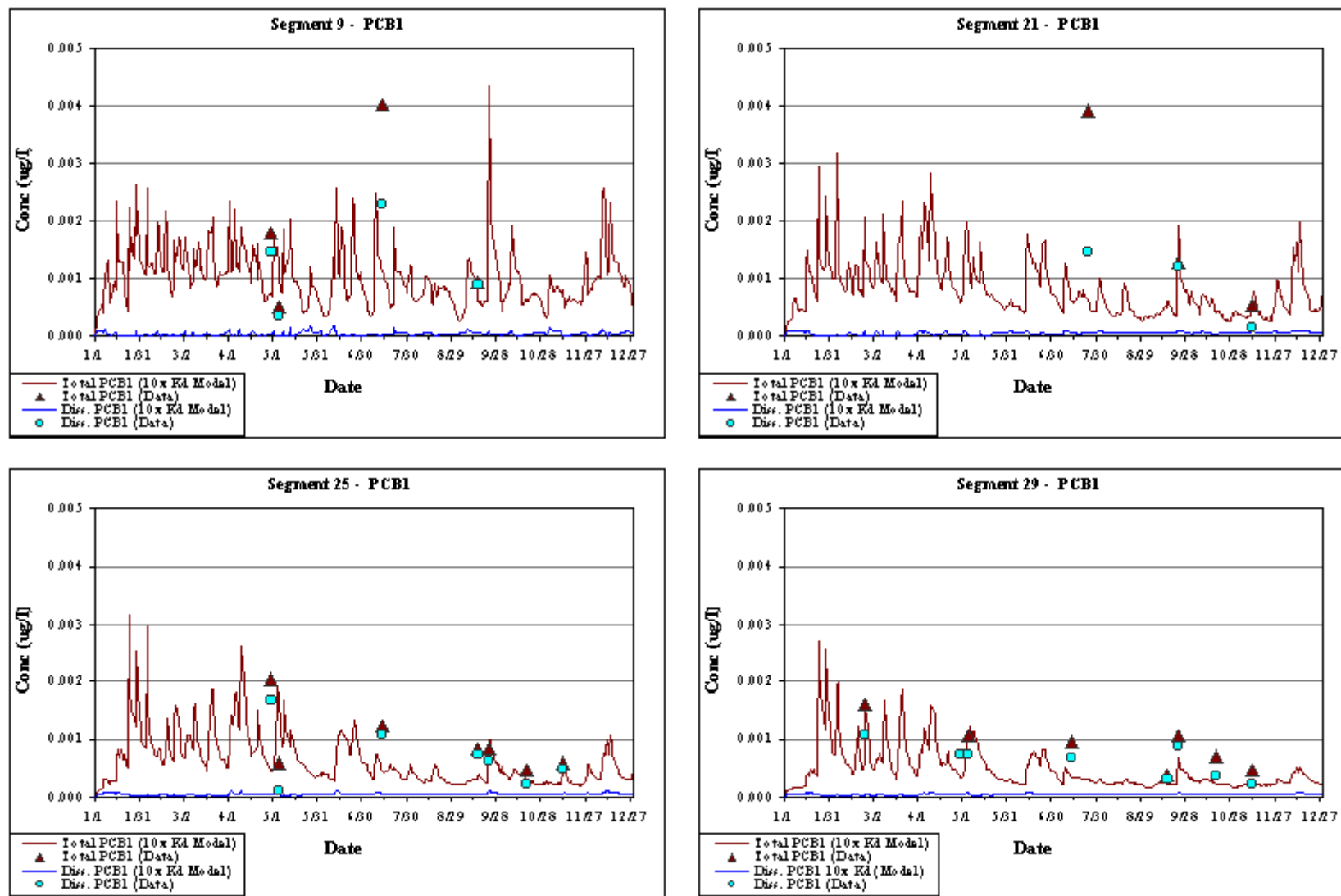


Figure 3-54. PCB1 Water Column Sensitivity Test Results: Both  $K_d$ 's x 10

TAM/WASP Toxic Screening Level Model for the Anacostia River - Final Report

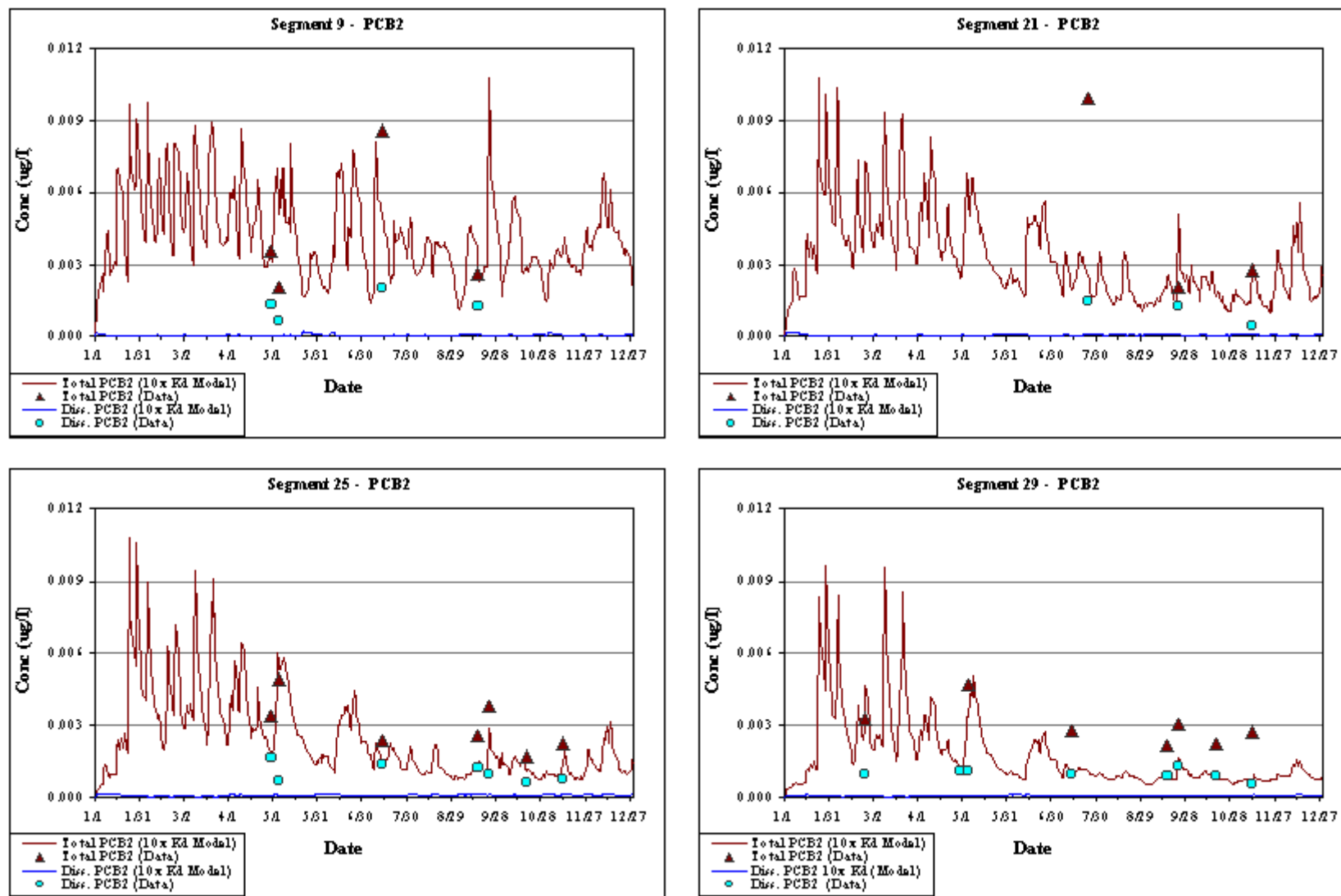


Figure 3-55. PCB2 Water Column Sensitivity Test Results: Both  $K_d$ 's x 10

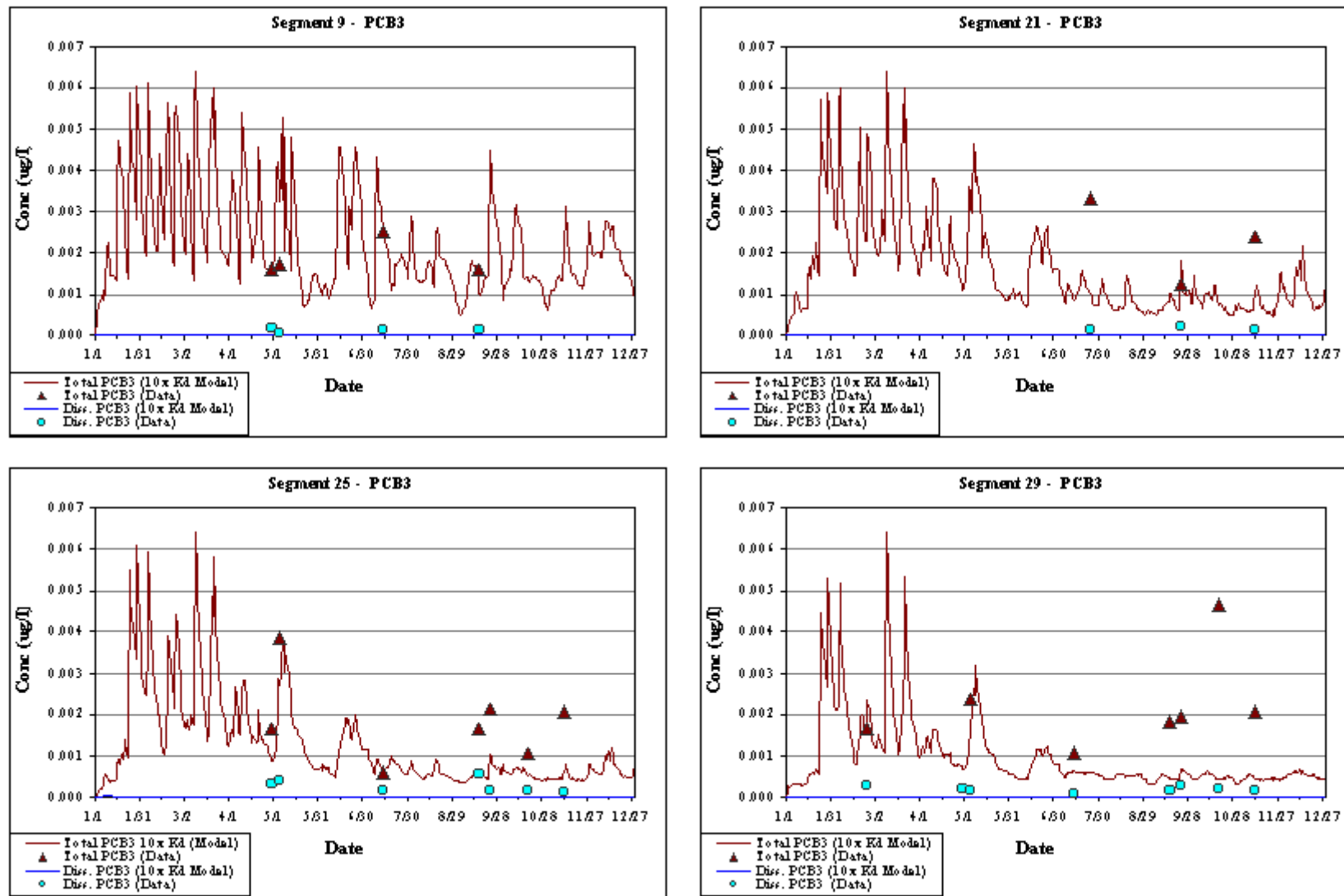


Figure 3-56. PCB3 Water Column Sensitivity Test Results: Both  $K_d$ 's x 10

### 3.3.4. PAH Sub-Model

#### Model Description

The TAM/WASP PAH sub-model has been set up to simulate the fate and transport of three groups of PAHs representing a total of 16 chemicals, distributed by number of benzenoid rings and molecular weight, as discussed in Chapter 1 (see Tables 1-2 and 1-4). The sixteen PAHs considered in the model were chosen for reasons of data consistency, because all 16 were included in both the study of Northeast/Northwest Branches loads by Gruessner et al. (1998) and the study on bed sediment concentrations by Velinsky and Ashley (2001). The transport and fate processes simulated include advection and dispersion, adsorption to the medium- and fine-grained sediment fractions, first-order degradation, and volatilization.

#### Input Parameters

Estimated base flow and storm flow concentrations are given in Table 3-15. Northeast and Northwest Branches values represent means (assuming log normal distributions) of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin tributaries and separate storm sewer (SS) system, and combined sewer overflows (CSO) values are estimates based on Northeast and Northwest Branches data because detection limits for available stormwater monitoring data from the District's MS4 monitoring program (Nicoline Shelterbrandt, private communication) were not sufficiently low enough to allow computation of loads.

Proposed input parameters for boundary conditions, adsorption, degradation, and volatilization are provided in Table 3-16. Values for the Potomac boundary concentrations are based on calibration results, because little water column data is available for PAHs. In addition, a boundary condition was specified for segment 60, the sediment segment underlying water column segment 24. This was done to simulate subsurface loading from the Washington Gas former manufactured gas plant site, located on the western shoreline at segment 24. Boundary condition PAH concentration estimates for this segment were based on average sediment concentrations of seven samples collected along the shoreline adjacent to the Washington Gas site during a 1995 Washington Gas study. This data was obtained by ICPRB from the AWT/NOAA database. A dispersive exchange coefficient of  $0.5 \times 10^{-6} \text{ m}^2/\text{sec}$  and an exchange length of 0.1 m were determined via calibration, by matching predicted versus observed average sediment PAH concentrations in segment 60. This simulated exchange represents mixing between river water and pore water in the very near shore subsurface due to tidal processes. The flux of PAHs from the Washington Gas site was also computed using the alternative and more traditional approach of multiplying estimated groundwater discharge from the site by estimated groundwater concentrations of PAHs. However, though groundwater concentration estimates for some PAHs at Washington Gas are available (Hydro-Terra, Inc., 1998), there are a significant number of non-detects in the data due to a high detection limit (10 ug/L) and several analytes in PAH group 3 were not included in the data set. Estimated yearly loads based on both approaches are presented in Table 3-17 and can be seen to be comparable (i.e. same order of magnitude), with an estimated load of 34 kg/yr from the sediment segment boundary condition method and an estimated load of 61 kg/yr from the ground water discharge method.

Proposed partition coefficients for the three PAH groups are shown in Table 3-16. These values were estimated from site-specific Northeast/Northwest Branches base flow data (see Section 2.3).

First-order lumped degradation rate constants were incorporated into the PAH model to represent the combined impacts of biodegradation and photolysis and were estimated based on reported literature values, as shown in Table 3-16 (Aronson et al., 1999 and Mackay et al., 1992). Degradation of PAHs was modeled as a first-order rate constant in the model primarily due to a lack of PAH water column data for calibration and lack of biodegradation and photolysis rate estimates for the Anacostia River. There is also little information available on degradation pathways. Literature review indicated a trend towards an increase in degradation with decreasing molecular weight and higher degradation rates in water than in sediment. Individual PAH biodegradation rates reported in literature cover a wide range (Aronson et al., 1999 and Mackay et al., 1992). For example, the range of reported rate constants for biodegradation of benzo[a]pyrene was  $6 \times 10^{-5}$  to  $5.7 \times 10^{-2} \text{ day}^{-1}$  (Aronson et al., 1999), a difference of approximately three orders of magnitude.

Parameters used by WASP to compute volatilization (i.e. air-water exchange) are shown in Table 3-16. Atmospheric PAH concentrations were not available for the Anacostia watershed. Therefore, atmospheric concentrations were estimated based on available regional data for urban watersheds as shown in Table 3-18 (Bamford et al., 1999, Gustafson and Dickhut, 1997).

Loads from wet and dry deposition have not been included in the model because they appear to be very small, and site-specific data on deposition rates for the Anacostia is not available. Table 3-19 contains estimates of PAH wet and dry deposition rates for the Chesapeake Bay watershed (CBP) and for Baltimore, Maryland, a comparable urban area (Offenberg and Baker, 1999). These data were used to estimate a likely range of annual loads of total PAHs to the river due to wet and dry deposition, based on an assumed surface area of 3,300,300 m<sup>2</sup>. It can be seen from Table 3-19 that wet and dry deposition loads are likely to be only a fraction of a percent of the total annual PAH loads to the river.

### **Model Results**

In order to compare model predictions with observed bed sediment PAH concentrations, six-year runs of the PAH sub-model were made for the following three scenarios: 1) load estimates based on available storm water monitoring data, without the Washington Gas exchange component; 2) load estimates based on available storm water monitoring data, with the Washington Gas exchange component (Base Model); and 3) original load estimates adjusted by a factor of 1.5, with the Washington Gas exchange component (Calibrated Model - Loads x 1.5). A review of results for scenario 1) indicated that the usual TAM/WASP model loading sources could not account for the high PAH concentrations in bed sediment segment 60, underlying water column segment 24, adjacent to the Washington Gas plant site. Figure 3-57 shows a comparison of model predictions (last day of 6-year run) versus segment averages of bed sediment concentration data for scenarios 2) and 3). It can be seen from this figure that though predictions of the base model for PAH2 were reasonable, base model results for all PAH groups were low in many portions of the river. Therefore, the final calibrated model includes a load adjustment factor of

1.5 (see Table 3-15) to provide a better fit to bed sediment data. This adjustment to the loads is within the likely uncertainty in load estimates computed from the Northeast/Northwest Branches monitoring data (see Section 2.5) and is not inconsistent with the detection limits for PAHs in the District's MS4 monitoring data (see Table 2-5). It is also not unlikely that there are some sources of PAHs in the tidal portion of the Anacostia that have not been well characterized by available data.

At this time, there are two water column data sets available to compare with predictions of the calibrated model. Katz et al. (2000) provided PAH water column estimates resulting from one sampling event (July 12, 2002) at several locations along the Anacostia. Results from this comparison are shown in Figure 3-58. In addition, there are data available for sorbed PAHs in the water column from Coffin et al. (1998) for several events during the November 1997 - May 1998 time frame. Results from this analysis are provided in Figures 3-59 to 3-61. Comparison of model predictions with the Katz et al. (2000) event data indicates that the model is overestimating PAH concentrations in the water column for this particular day, especially for PAH groups 2 and 3 (Figure 3-58). Comparison of model predictions of sorbed PAHs with Coffin et al. data generally indicates an overestimation of PAH water column concentrations. This could be explained, however, by uncertainties associated with the data. For example, there were two chemicals not included in the Coffin et al. analysis, 2-methyl naphthalene in PAH group 2 and perylene in PAH group 3. Also, exact sampling dates are not clear, and there were several gaps in the Coffin et al. data set for PAH groups 1 and 3 in which data was provided for a particular chemical during some sampling events but not for all events. It was assumed that these chemicals were not detected (although no detection limits were provided). It is also possible, however, that all samples were not measured for these chemicals. Additional water column data would allow better calibration and verification of the PAH sub-model.

A mass balance for the calibrated model (i.e. loads x 1.5) is presented in Tables 3-20 and 3-21, and shown graphically in Figure 3-62. Annual load estimates for each source category are given in units of kilograms and as a percentage of total load. However, because the load inputs from each of the first five source categories, the upstream tributaries, tidal basin minor tributaries and SS system, Lower Beaverdam Creek, Watts Branch, and CSOs, are all based on the upstream data collected by Gruessner et al. (see Table 3-15), these relative load estimates are really no more than a reflection of the corresponding relative drainage areas. Therefore, until additional storm water monitoring data becomes available to characterize storm water concentrations of PAHs in tidal basin minor tributaries and SS system, Lower Beaverdam Creek, Watts Branch, and CSOs, the relative importance of these sources is not well understood, and the results appearing in Table 3-20 should be viewed as preliminary.

According to the TAM/WASP model estimates given in Tables 3-20 and 3-21, over half of the annual load of total PAHs entering the tidal river leaves the system either via discharge to the Potomac or via kinetic processes. An estimated 28% are exported to the Potomac River, 22% are lost due to degradation processes which include biodegradation and photolysis, and 3% are lost due to volatilization (air/water exchange). A higher percentage of the PAHs in groups 2 and 3 are exported to the Potomac, because these compounds, with their higher partition coefficients,

have a greater tendency to be bound to suspended fine-grained sediments and to be carried out of the system via tidal and storm flows. Group PAH1 compounds are more volatile and have a greater tendency to be broken down into other compounds via degradation processes.

The estimated quantities of PAHs leaving the system due to losses, given in Tables 3-20 and 3-21, should be viewed as preliminary until more water column calibration data becomes available for PAHs. As discussed above, PAH degradation rates are highly uncertain, and a good set of calibration data, including a sufficient number of measurements to evaluate seasonal effects, would help improve the model's ability to simulate kinetic and other processes affecting the fate and transport of PAHs in the tidal Anacostia.

### **Model Sensitivity Analysis**

Model sensitivity to changes in degradation input parameters was investigated because, as discussed above, there is a great deal of uncertainty concerning the appropriate values for degradation rate constants in the PAH sub-model and little information available on degradation pathways.

The calibrated PAH sub-model simulates the processes of biodegradation and photolysis as lumped first-order decay reactions, where transformations to daughter products are not considered. There is little information available to reliably estimate the pathways or rates of degradation of individual PAHs into other PAHs. As a sensitivity test, the model was run to simulate degradation with interactions between PAH groups. Specifically, transformation yield coefficients were specified to simulate the decay of PAH3 into PAH2, the decay of PAH2 into PAH1. PAH1 is assumed to degrade out of the system. Results of this analysis are shown in Figure 3-63, in which the calibrated loads scenario was run with first-order degradation only (*Calibrated Model*) and with PAH decay interactions simulated (*Model w/ Decay Interactions*). Results indicate that there is not much change in the distribution or mass of PAH2 or PAH3 in the system. However, there is a significant increase in PAH1 when decay interactions are added, indicating that degradation of higher-molecular weight PAHs into PAH1 could be an explanation for the lack of PAH1 estimated by the model.

The sensitivity of the model to changes in degradation rate constants was also investigated. As mentioned, there is a wide range in reported decay rates for individual PAHs. The calibrated model (i.e. loads x 1.5) was run with degradation rate constants for all three groups increased by a factor of 10, and rate constants for all three groups reduced to 0. Results of this analysis are provided in Figure 3-64. Changes in degradation rate constants have the greatest impact on predicted concentrations of PAH1 and little impact on PAH3. It is evident that increasing the rate constants would decrease the predicted concentrations of PAHs in the bed sediment, producing a poorer match to observed values (unless load estimates are actually even higher than assumed in the calibrated model). Alternatively, reducing rate constants would lead to higher predicted concentration in the bed sediment. However, even if rate constants were reduced considerably, a load adjustment factor would still be necessary to match model predictions to observed PAH3 bed sediment concentrations. Because the uncertainties in PAH load estimates,



it is difficult to assess the appropriateness of the values of degradation rate constants used in the calibrated model.

**Table 3-15. Concentrations Used to Compute PAH Sub-Model Calibration Run Input Loads (ug/L)**

Source	PAH1 Orig	Suggested PAH1 Multiplier	PAH1 Draft Final	PAH2 Orig	Suggested PAH2 Multiplier	PAH2 Draft Final	PAH3 Orig	Suggested PAH3 Multiplier	PAH3 Draft Final	Comment
NW Br Base	0.056	x 1.5	0.084	0.193	x 1.5	0.2895	0.097	x 1.5	0.1455	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.607	x 1.5	0.9105	3.911	x 1.5	5.8665	2.631	x 1.5	3.9465	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 composite data
NE Br Base	0.054	x 1.5	0.081	0.099	x 1.5	0.1485	0.044	x 1.5	0.066	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.271	x 1.5	0.4065	1.634	x 1.5	2.451	0.945	x 1.5	1.4175	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 composite data
SSTrib/LBD /Watts/CSO Non-storm	0.055	x 1.5	0.0825	0.146	x 1.5	0.219	0.071	x 1.5	0.1065	Estimated to be the averaged NE/NW Branches base flow (Gruessner et al., 1998)
SSTrib/LBD /Watts Storm	0.439	x 1.5	0.6585	2.773	x 1.5	4.1595	1.788	x 1.5	2.682	Estimated to be the averaged NE/NW Branches storm flow (Gruessner et al., 1998)
CSO Storm	0.439	x 1.5	0.6585	2.773	x 1.5	4.1595	1.788	x 1.5	2.682	Estimated to be the averaged NE/NW Branches storm flow (Gruessner et al., 1998)

**Table 3-16. WASP Input Parameters for PAH Sub-Model**

Process/Parameter	Units	PAH1	PAH2	PAH3	Source
<i>Downstream Boundary Condition:</i>					
Potomac Boundary Concentration	ug/L	0.05	0.009	0.025	Calibration
<i>Sediment Segment 60 Boundary Condition:</i>					
Segment 60 Boundary Concentration	ug/g = mg/L	44.029	47.019	26.211	Washington Gas study sediment data
Dispersive exchange coefficient	m <sup>2</sup> /sec	0.50 x 10 <sup>-6</sup>			Calibration
Exchange length	m	0.1			Calibration
<i>Adsorption:</i>					
K <sub>d</sub> for fine-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	38,176	531,645	2,299,419	Mean K <sub>d</sub> based on site-specific base flow data
K <sub>d</sub> for medium-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	9,544	132,911	574,855	¼ of mean K <sub>d</sub>
<i>First-order Degradation:</i>					
Water Column Rate constant / half-life	day <sup>-1</sup> / years	1.0E-02 / 0.2	5.0E-03 / 0.4	5.0E-04 / 3.8	Estimated based on reported literature values (Aronson et al., 1999 and Mackay et al., 1992).
Sediment Rate constant / half-life	day <sup>-1</sup> / years	1.0E-03 / 1.9	5.0E-04 / 3.8	5.0E-05 / 38	Estimated based on reported literature values (Aronson et al., 1999 and Mackay et al., 1992).
<i>Volatilization:</i> (Using option 4 – transfer coefficients are computed by WASP assuming a flowing estuary)					
Molecular Weight	g/mole	154	215	265	average by type from several refs
Henry's Law Coefficient	atm – m <sup>3</sup> /mole	4.75E-04	1.03E-04	3.15E-06	average by type from several refs
Atmospheric Concentration	mg/L	8.80E-08	5.00E-09	4.40E-11	(Bamford et al., 1999, Gustafson and Dickhut, 1988)

**Table 3-17. Comparison of Washington Gas Annual PAH Load (kg/year) Estimates Based on Average PAH Concentrations in Groundwater and Sediment**

	<b>Groundwater Average Concentration (ug/L)</b>	<b>Groundwater Est. Load <sup>1</sup> (kg/year)</b>	<b>Average Sediment Concentration <sup>2</sup> (ng/g)</b>	<b>Pore Water Diffusion Est. Load <sup>2</sup> (kg/year)</b>
PAH1	2361	55	44029	12
PAH2	201	5	47019	14
PAH3	56	1.30 <sup>3</sup>	26211	8
Total	2619	61	117258	34

<sup>1</sup> Computed from average groundwater concentration and estimated total flow of 16,800 gpd (Hydro-Terra, Inc., 1998).

<sup>2</sup> Based on sediment concentration data from 1995 Washington Gas study (AWTA/NOAA database).

<sup>3</sup> Load may be underestimated because several analytes in PAH group 3 were not included in the groundwater analysis.

**Table 3-18. Measured Atmospheric Concentrations of PAHs**

	<b>Patapsco River<sup>1</sup></b> <b>(mg/L)</b>	<b>Elizabeth River<sup>2</sup></b> <b>(mg/L)</b>	<b>Hampton<sup>2</sup></b> <b>(mg/L)</b>	<b>Overall Average</b> <b>(mg/L)</b>
napthalene	NA	NA	NA	
2-methyl napthalene	1.81E-09	NA	NA	
acenapthylene	1.80E-10	NA	NA	
acenapthene	2.00E-10	NA	NA	
fluorene	1.60E-09	6.62E-09	1.71E-08	
phenanthrene	7.80E-09	1.47E-08	4.48E-08	
Sum PAH Group 1	1.39E-08	6.40E-08	1.86E-07	8.8E-08
fluoranthene	1.50E-09	2.51E-09	4.94E-09	
pyrene	1.10E-09	1.58E-09	1.99E-09	
benz[a]anthracene	NA	7.46E-11	1.51E-11	
chrysene	4.00E-11	3.62E-10	9.91E-11	
Sum PAH Group 2	3.52E-09	4.52E-09	7.05E-09	5.0E-09
benzo[k]fluoranthene	NA	6.72E-12	4.68E-12	
benzo[a]pyrene	NA	2.10E-11	3.12E-12	
perylene	NA	NA	NA	
indeno[1,2,3-c,d]pyrene	NA	6.06E-12	8.55E-12	
benzo[g,h,i]perylene	NA	9.77E-12	ND	
dibenz[a,h+ac]anthracene	NA	9.34E-12	4.02E-12	
Sum PAH Group 3	NA	6.34E-11	2.55E-11	4.4E-11

NA = not analyzed

ND = not detected

<sup>1</sup> Bamford et al., 1999<sup>2</sup> Gustafson and Dickhut, 1997**Table 3-19. Estimated Annual Atmospheric Deposition of Total PAHs to the Anacostia River**

	<b>Chesapeake Bay - Regional<sup>1</sup></b>		<b>Chesapeake Bay - Urban<sup>1</sup></b>		<b>Baltimore<sup>2</sup></b>	
	Wet	Dry	Wet	Dry	Wet	Dry
Deposition rate ( $\mu\text{g}/\text{m}^2\text{-yr}$ )	123 - 185	84 - 128	492 - 740	336 - 512	413 - 739	109 - 173
Deposition total <sup>3</sup> (kg/yr)	0.10 - 0.15	0.07 - 0.11	0.41 - 0.61	0.28 - 0.42	1.36 - 2.44	0.36 - 0.57

<sup>1</sup>CBP (1999)<sup>2</sup> Offenberg and Baker (1999)<sup>3</sup> Calculations assume that the surface area of the Anacostia River with adjoining tidal embayments is 3,300,300 m<sup>2</sup>

**Table 3-20. Average Annual Load Contributions and Losses by Source for Calibrated PAH Sub-Model**

	PAH1		PAH2		PAH3		Total PAHs	
	kg/yr	% <sup>2</sup>	kg/yr	%	kg/yr	%	kg/yr	%
Upstream	52	57%	306	63%	192	62%	549	62%
SS Tribs	8	9%	50	10%	32	10%	91	10%
LBD	14	15%	86	18%	55	18%	155	17%
Watts	2	2%	12	3%	8	3%	22	2%
CSOs	3	4%	20	4%	13	4%	36	4%
Wash Gas	12	13%	14	3%	8	3%	34	4%
Total Load Input <sup>1</sup>	91	100%	488	100%	308	100%	886	100%
Export to Potomac	-12	-13%	-142	-29%	-92	30%	-246	-28%
Kinetic Losses (volatilization and decay)	-51	-56%	-154	-32%	-13	4%	-218	-25%

<sup>1</sup> Total load input is the sum of loads from upstream, SS Tribs, LBD, Watts, CSOs, and Washington Gas.

<sup>2</sup> % represents the percentage of total load input

**Table 3-21. Comparison of Average Annual PAH Kinetic Losses**

	PAH1		PAH2		PAH3		Total PAHs	
	kg/yr	% <sup>1</sup>	kg/yr	%	kg/yr	%	kg/yr	%
Total Kinetic Losses (volatilization and decay)	-51	-56%	-154	-32%	-13	-4%	-219	-25%
Kinetic Losses with volatilization only	-17	-19%	-7	-1%	0	0%	-24	-3%
Kinetic Losses attributable to decay processes	-34	-37%	-147	-30%	-13	-4%	-195	-22%

<sup>1</sup> % represents the percentage of total load input.

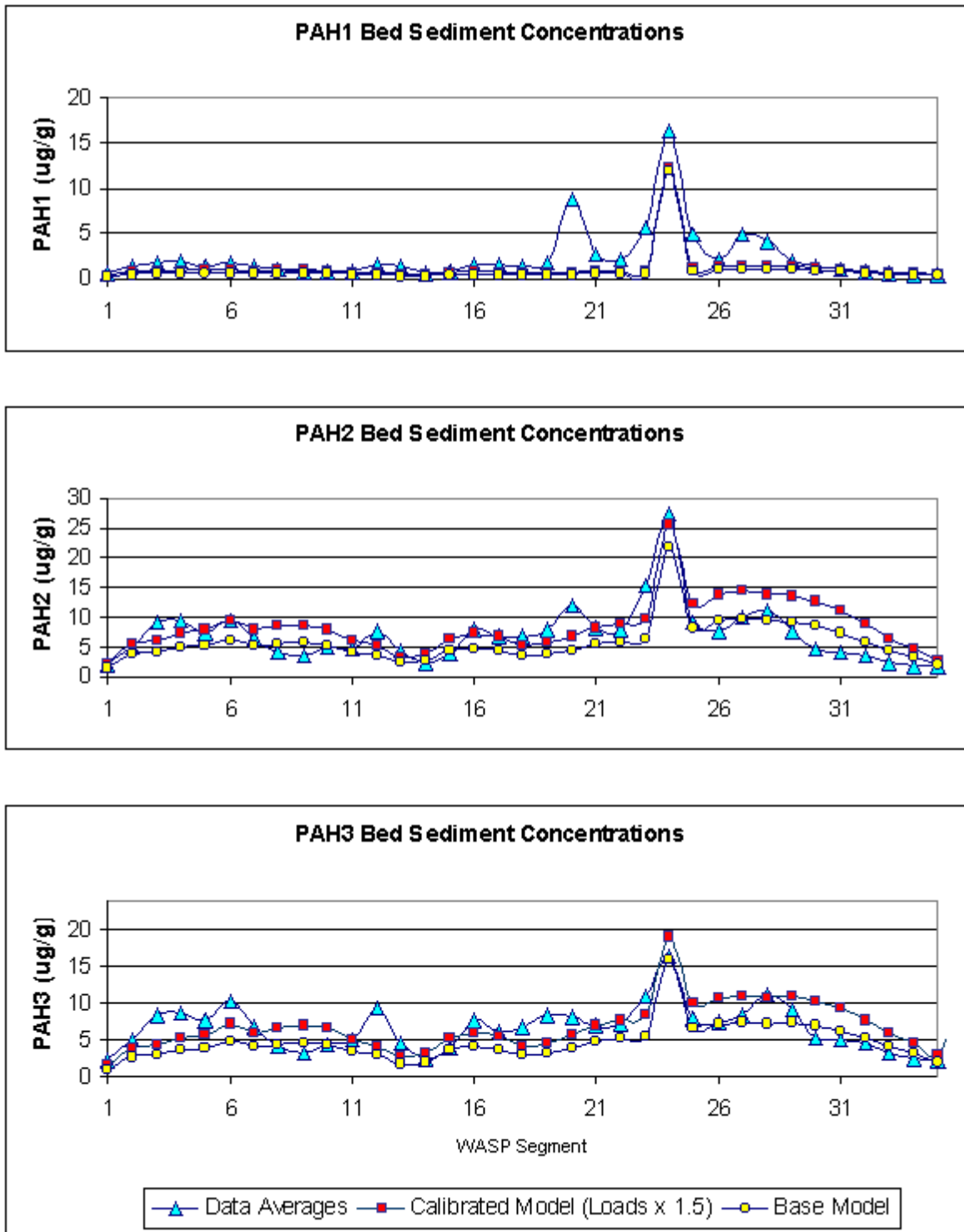


Figure 3-57. PAH Bed Sediment Results: Base Model and Calibrated model (Loads x 1.5)

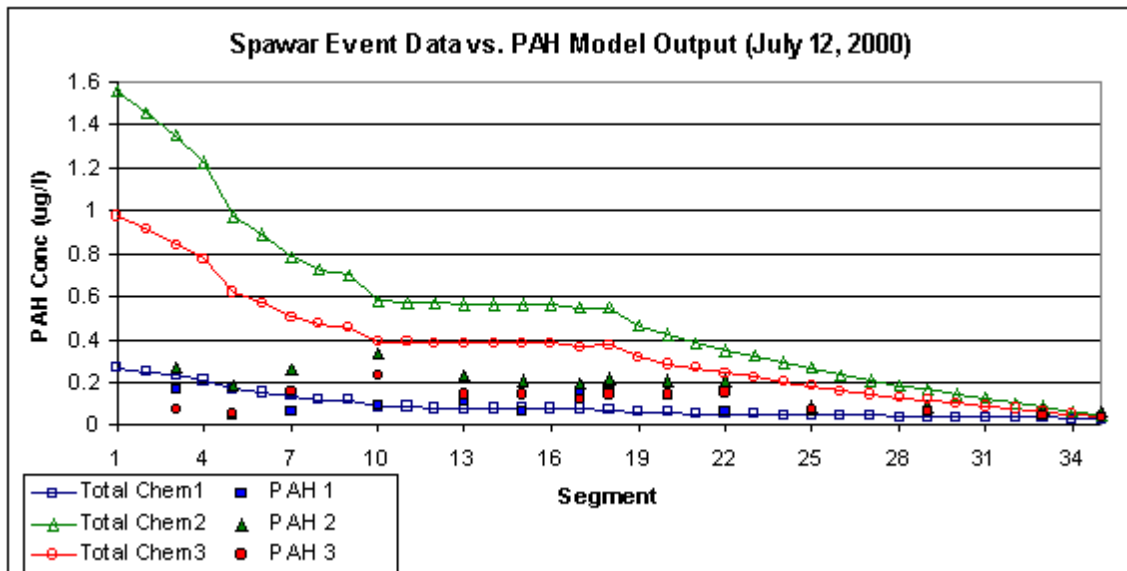


Figure 3-58. Total (Dissolv. + Partic.) PAH Water Column Results, Calibrated Model Versus Katz et al. (2000) Single Event Data



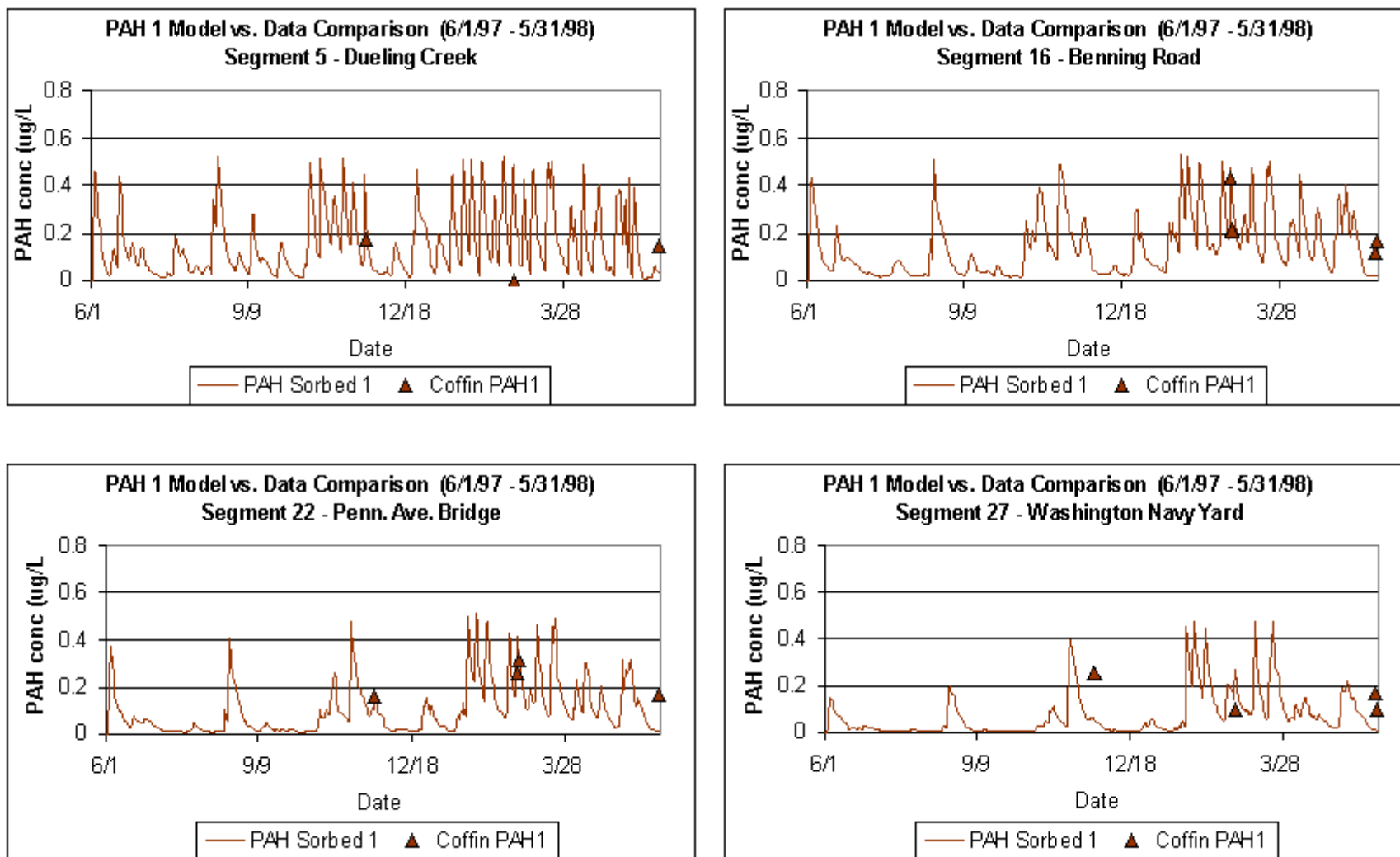


Figure 3-59. Particulate PAH1 Water Column Results, Calibrated Model Versus Coffin et al. (1998) Data

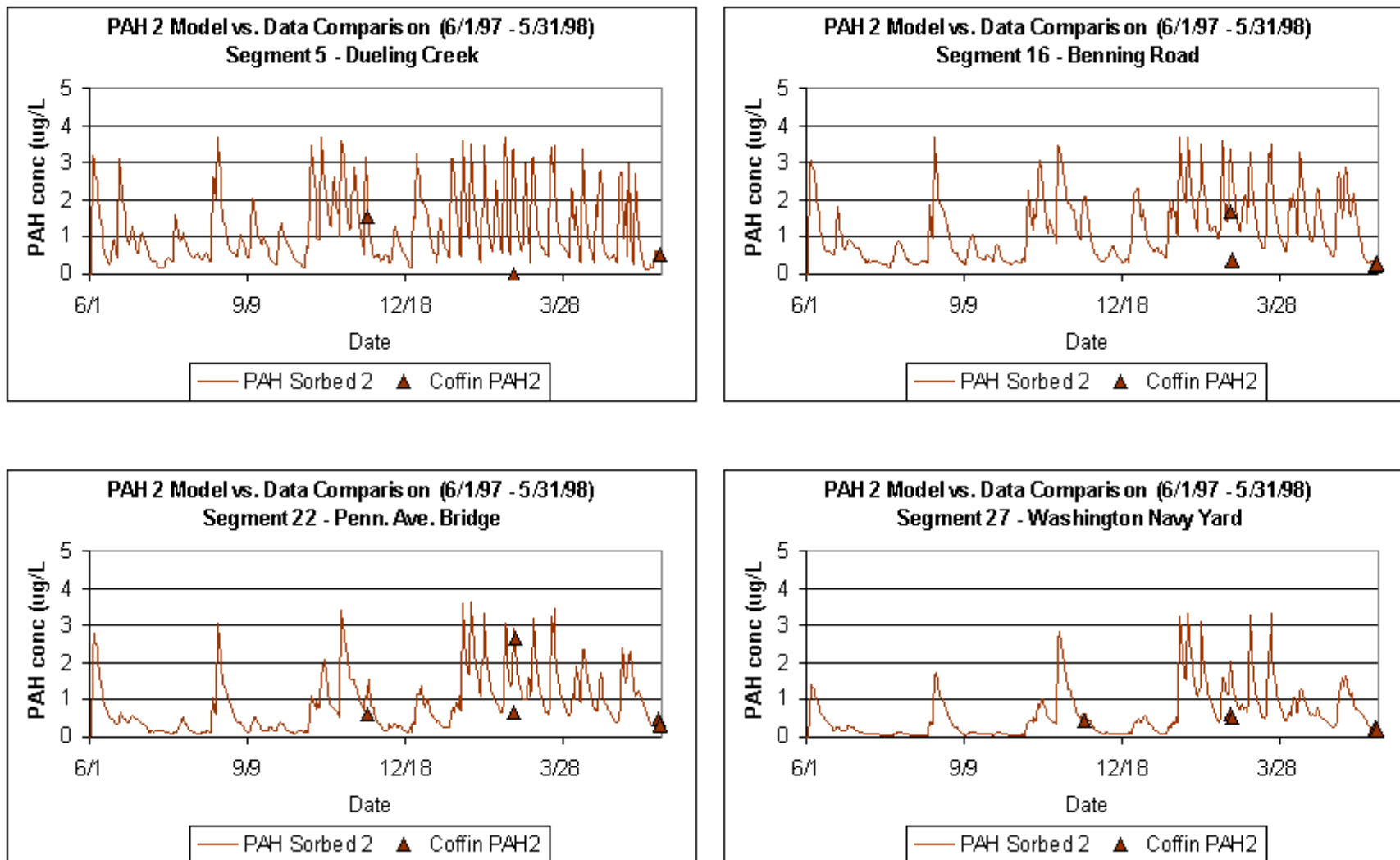


Figure 3-60. Particulate PAH2 Water Column Results, Calibrated Model Versus Coffin et al. (1998) Data

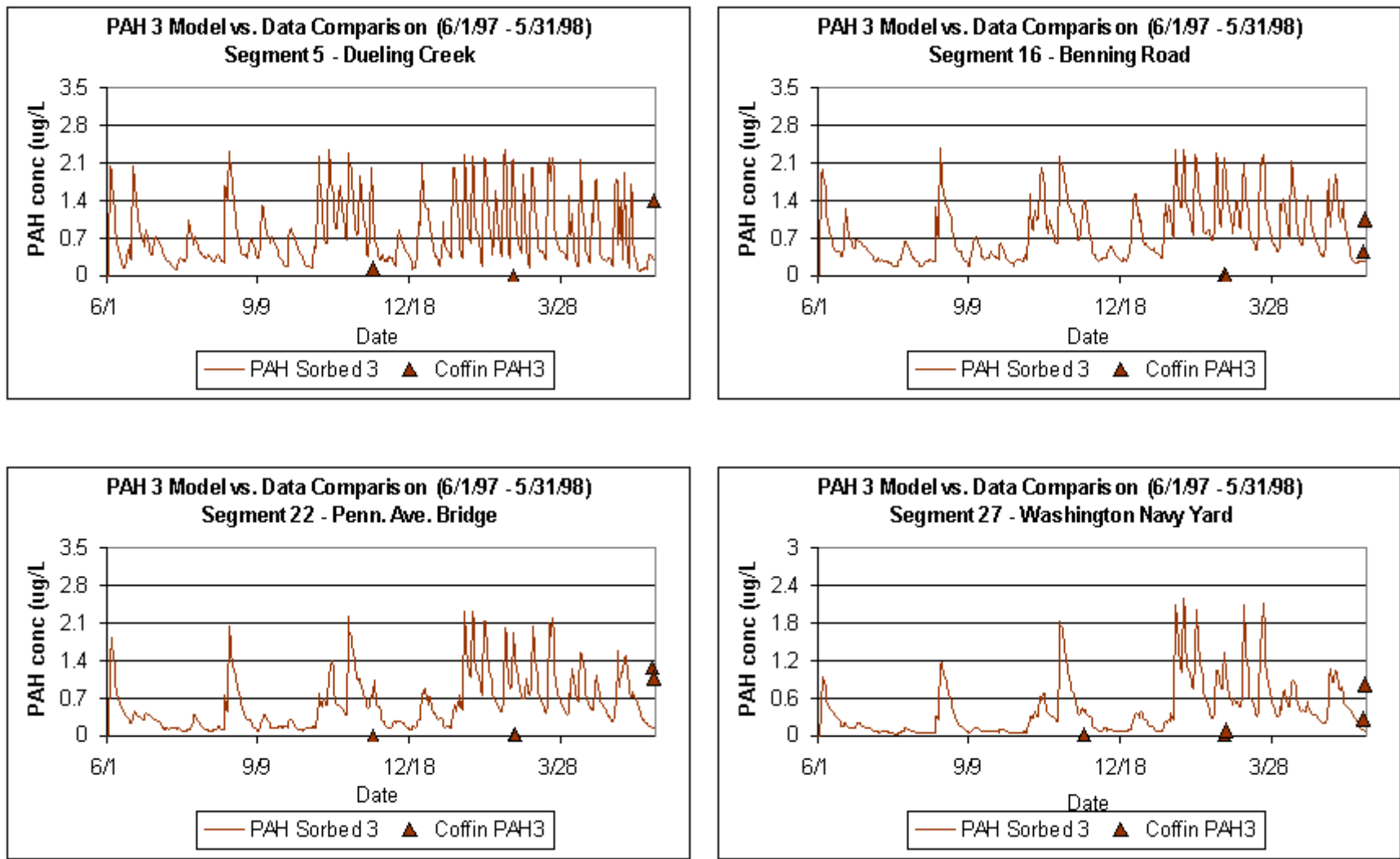


Figure 3-61. Particulate PAH3 Water Column Results, Calibrated Model Versus Coffin et al. (1998) Data

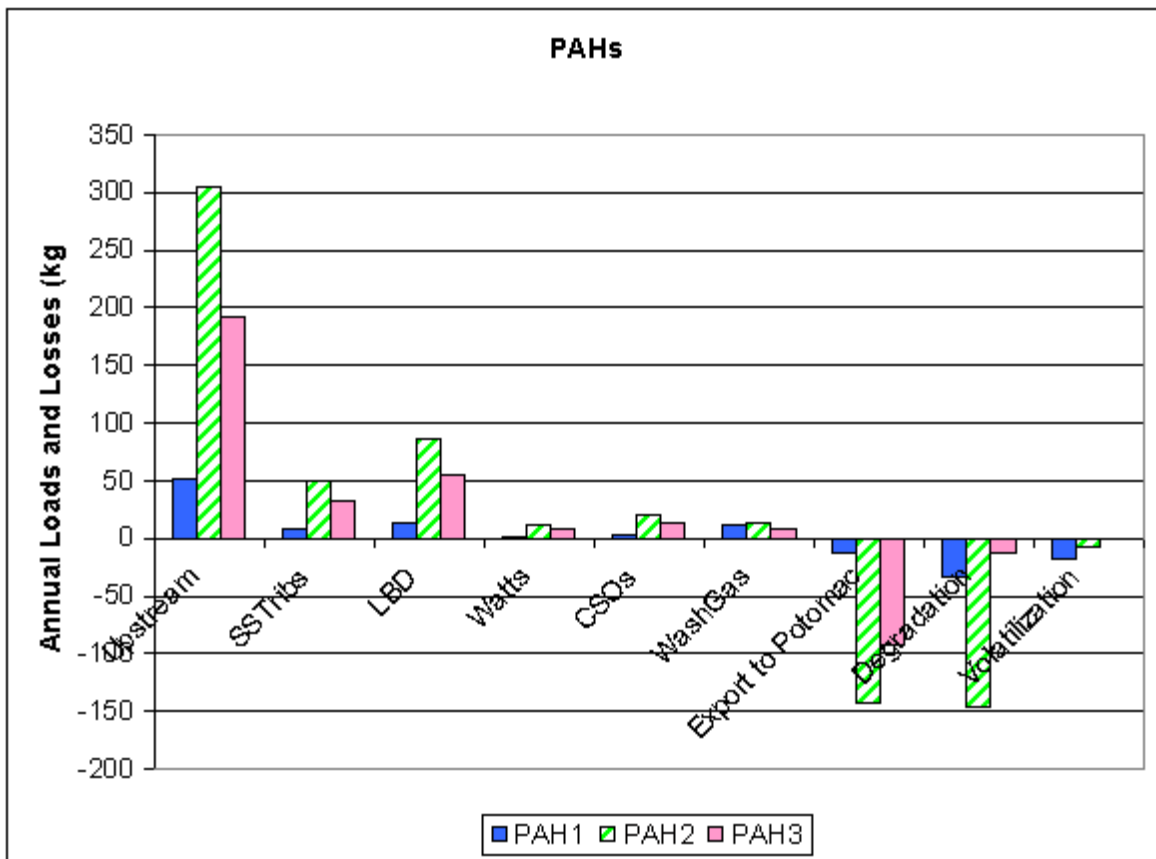


Figure 3-62. Summary of Average Annual Loads and Losses for the Calibrated PAH Sub-Model

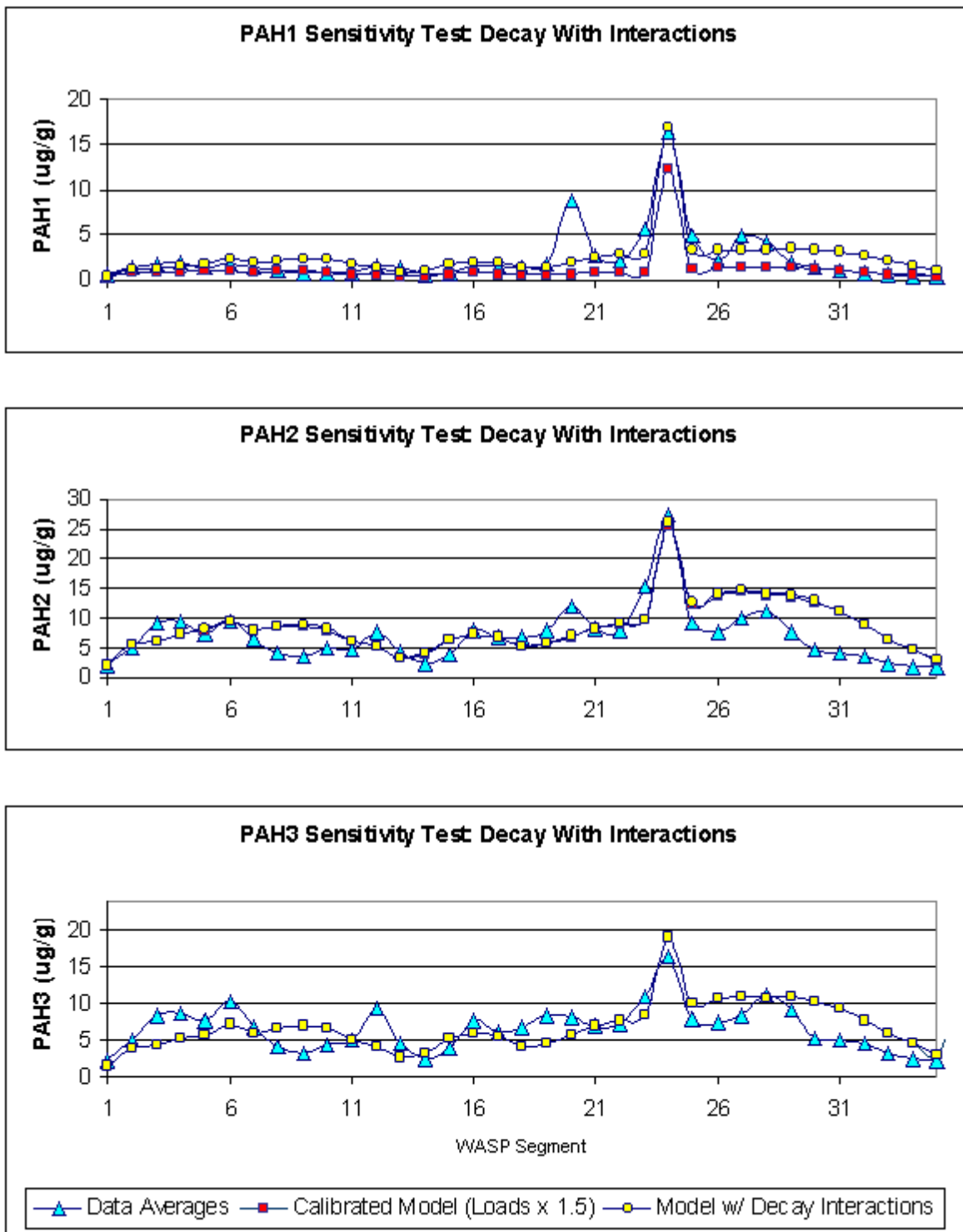


Figure 3-63. PAH Bed Sediment Sensitivity Test Results: Addition of Decay Interactions

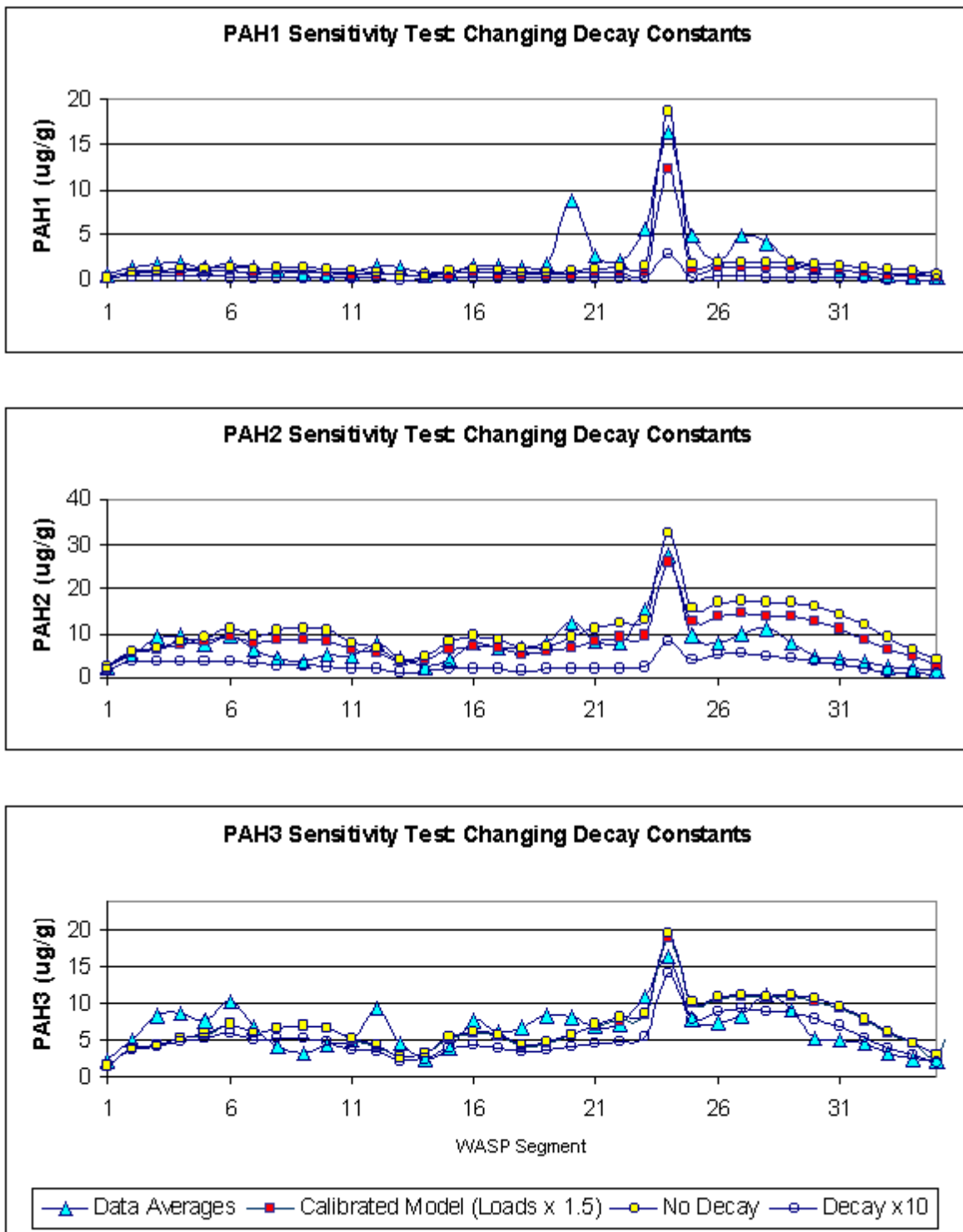


Figure 3-64. PAH Bed Sediment Sensitivity Test Results: Changes in Decay Constants

### 3.3.5. Chlordane and Heptachlor Epoxide (PEST1) Sub-Model

#### Model Description

The TAM/WASP sub-model PEST1 has been set up to simulate total chlordane (comprised of cis-chlordane, trans-nonachlor, and oxychlordane) and heptachlor epoxide (Table 1-2). Transport and fate processes simulated include advection and dispersion, adsorption to the medium- and fine-grained sediment fractions, and volatilization. Although the degradation processes of chlordane in the aquatic environment have not been extensively studied (ATSDR 1994b), it is believed that photolysis, hydrolysis, and biodegradation are not important fate processes (ATSDR 1994b, U.S. ACE 1997) and are therefore not included in the model framework. Heptachlor epoxide is also very resistant to biodegradation, but some loss due to photolysis may occur (TOXNET). It appears that sorption to sediment and particulates and to a lesser extent volatilization are the two major pathways for removal of chlordane and heptachlor epoxide from the water column.

Heptachlor epoxide is a breakdown product of the insecticide, heptachlor, and the source of the heptachlor epoxide present in the Anacostia basin is assumed to be heptachlor. In river water, heptachlor has been observed to decay into heptachlor epoxide and other compounds with a half life on the order of only several days (ATSDR, 1993). No heptachlor was detected in water samples in the Northeast/Northwest Branches study by Gruessner et al. (1999), but heptachlor was detected in bed sediment samples collected by Velinsky and Ashley (2001). Because there is no water column calibration data currently available for heptachlor epoxide and little information available on degradation processes, heptachlor was not included in the PEST1 model. It was felt that with available data support, inclusion of heptachlor as an additional source would not improve the predictive capabilities of the model, since PEST1 currently over-predicts concentrations of heptachlor epoxide (see below).

#### Input Parameters

Estimated base flow and storm flow concentrations used to compute daily load inputs are given in Table 3-22 for total chlordane (Chem1) and heptachlor epoxide (Chem2). Northeast and Northwest Branches values are means, assuming log normal distributions, of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). The Northeast/Northwest Branches storm and non-storm estimates are also used for the sub-sheds of the District's separate storm sewer (SS) system, Lower Beaverdam Creek (LBD), Watts Branch, and combined sewer overflows (CSO) because stormwater monitoring data for the tidal portion of the Anacostia River were not available and DC MS4 results for these contaminants are all non-detect.

Input parameters for downstream boundary conditions, adsorption, and volatilization are given in Table 3-23. The boundary concentrations for total chlordane and heptachlor epoxide at the confluence with the Potomac River are calibrated to 0.00015 ug/L and 0.000002 ug/L respectively because water column data was not available for this location. As ICPRB so far has been unable to find atmospheric concentrations for total chlordane and heptachlor epoxide for the Washington/Baltimore area, average air concentrations are estimates based on data reported by Jantunen et al. (2000) for Alabama.

### Model Results

A comparison of model predictions (last day of 6-year run) versus bed sediment concentration data averages suggests that the PEST1 sub-model accounts reasonably well for mass inputs of total chlordane into the tidal portion of the Anacostia River (Figure 3-65). Bed sediment concentrations for heptachlor epoxide (Figure 3-65) were over-estimated in the original model run (Base Run). Therefore the calibrated model incorporates a load reduction factor of 0.7 for heptachlor epoxide (see Table 3-22).

A mass balance for chlordane and heptachlor epoxide by source, kinetic losses, and net export to the Potomac River is shown in Figure 3-66. The relative contribution of the sources and losses compared to total river input (sum of all loads) is provided in Table 3-24. From this table, one sees that according to model predictions, 35% of total chlordane and 56% of heptachlor epoxide entering the tidal portion of the Anacostia river is eventually exported to the Potomac. Also, 9% of chlordane and 17% of heptachlor epoxide is exported to the atmosphere via volatilization. In both cases, more heptachlor epoxide is exported because this contaminant has a relatively low partition coefficient and hence a higher proportion is found in the dissolved phase, where it is more likely to be discharged to the Potomac or to volatilize. Results on relative loads appearing in Table 2-24 are very preliminary, because all storm and non-storm concentration estimates for chlordane and heptachlor epoxide are currently based on upstream data.

Model predictions of water column concentrations cannot be compared to measured water column concentrations, because water column data for total chlordane and heptachlor epoxide were not available. However, in Figure 3-67, a simulation of 1998 water column chlordane concentrations is compared to average Anacostia water column concentrations predicted by a bioaccumulation analysis based on fish tissue data (see Section 3.3.2). It is evident from this figure that the PEST1 sub-model predictions for chlordane are well below the average concentration predicted by fish tissue results.

### Sensitivity tests

The PEST1 sub-model over-predicts bed sediment concentrations of heptachlor epoxide, even after initial load estimates are reduced by a factor of 0.7. Because no site-specific data and little information in the literature was found on ambient air concentrations of heptachlor epoxide, a sensitivity run was done to investigate whether a reduction in the estimated air concentration would increase volatilization significantly and reduce predicted bed sediment concentrations. Results, shown in Figure 3-68, show no significant reduction of predicted bed sediment concentrations of either chlordane or heptachlor epoxide under the assumption that ambient air concentrations are zero. This sensitivity test indicates that, at least for the contaminants considered in the PEST1 sub-model, ambient air concentrations contribute a negligible load via the air/water exchange process.

Due to a lack of data on concentrations of chlordane and heptachlor epoxide in Potomac River water, the downstream boundary conditions for these contaminants were obtained by model calibration to bed sediment data, i.e. by adjusting the values of the boundary concentrations until model predictions matched observed bed sediment concentrations reasonably well. The



boundary condition values obtained in this manner for chlordane and heptachlor epoxide are rather low, with the boundary condition value for chlordane about 1/6 of the mean of the base flow concentrations observed in the upstream tributaries and the boundary condition value for heptachlor epoxide almost a factor of 1/500 less than the mean base flow tributary concentrations. Sensitivity runs were done to investigate how predicted bed sediment results would change if downstream boundary concentrations for both chlordane and heptachlor epoxide were increased by a factor of 10 and if the boundary concentration for heptachlor epoxide were increased by a factor of 100. In Figure 3-69, it is evident that the chlordane bed sediment results would deteriorate significantly if the chlordane downstream boundary condition was increased by a factor of 10. The heptachlor epoxide results would deteriorate significantly if the downstream boundary condition was increased by a factor of 100, but a 10-fold increase in the heptachlor epoxide boundary condition causes little change in bed sediment results. Therefore, more accurate determination of the downstream boundary conditions awaits the availability of main channel water column calibration data.

Finally, because partition coefficients computed from site-specific data are highly variable, a sensitivity test was done to see if the model's over-prediction of heptachlor epoxide could be reduced by a change in the  $K_d$  values used in the model. Results in Figure 3-70 show that if the fine/medium-grained  $K_d$ 's for heptachlor epoxide are reduced from 8300/2075 to 4150/1035 L/kg, the model no longer seriously over-predicts bed sediment concentrations. Though changes in  $K_d$  values were shown to have little effect on bed sediment concentration predictions for contaminants with large  $K_d$ 's, such as zinc, lead, and the more highly chlorinated PCBs, there is a significant effect when changes are made to smaller  $K_d$  values, as can be seen in this sensitivity test for heptachlor epoxide.

### **Summary**

The PEST1 sub-model was constructed with no data on input loads from areas other than the upstream portion of the watershed, and no water column data from the main channel of the Anacostia to assist in model calibration. None-the-less, the model does a reasonable job in predicting bed sediment concentrations of chlordane, though water column chlordane predictions are not consistent with predictions of a simple bioaccumulation model based on fish tissues data. The model significantly over-predicts heptachlor epoxide bed sediment concentrations, even after a 30% reduction in estimated load inputs. This over-estimation may be the result of inaccuracies in load estimates or inaccuracies in the value used for the partition coefficient. Alternatively, because it is known that photolysis of heptachlor epoxide probably occurs in the aquatic environment, though no information is available about rates (TOXNET), it is possible that photolysis, which is not currently included in PEST1, accounts for the discrepancy. Finally, a better determination of the Potomac boundary conditions for both contaminants, which have a significant effect on predicted water column concentrations in downstream segments of the model, can be made once main channel water column calibration data becomes available.

**Table 3-22 Concentrations Used to Compute PEST1 Sub-Model Calibration Run Input Loads (ug/L)**

Source	Chem1 Original	Suggested Multiplier	Chem1 Final	Chem2 Original	Suggested Multiplier	Chem2 Final	Comment
NW Br Base	0.001186	x 1	0.001186	0.001211	x 0.7	0.000848	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.018928	x 1	0.018928	0.001456	x 0.7	0.001019	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
NE Br Base	0.000813	x 1	0.000813	0.000719	x 0.7	0.000503	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.003751	x 1	0.003751	0.001314	x 0.7	0.00092	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
SSTrib/LBD/Watts/CSO Non-storm	0.000963	x 1	0.000963	0.000916	x 0.7	0.000641	Estimated to be the averaged NE/NW Branches base flow (Gruessner et al., 1998)
SSTrib/LBD/Watts Storm	0.009829	x 1	0.009829	0.001367	x 0.7	0.000957	Estimated to be the averaged NE/NW Branches storm flow (Gruessner et al., 1998)
CSO Storm	0.009829	x 1	0.009829	0.001367	x 0.7	0.000957	Estimated to be the averaged NE/NW Branches storm flow (Gruessner et al., 1998)

**Table 3-23. WASP Input Parameters for PEST1 Sub-Model**

Process	Parameter	Units	CHEM1	CHEM2	Source
<i>Downstream Boundary Condition:</i>					
	Potomac Boundary Concentration	ug/L	0.00015	0.000002	Calibration
<i>Adsorption:</i>					
	K <sub>d</sub> for fine-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	83,600	8,300	K <sub>d</sub> based on site- specific base flow data (Gruessner et al., 1998)
	K <sub>d</sub> for medium-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	20,900	2,075	Taken to be ¼ of the fine-grained sediment K <sub>d</sub> . Based on best professional judgment.
<i>Volatilization:</i> (Using option 4 – transfer coefficients are computed by WASP assuming a flowing estuary)					
	Molecular Weight	g/mole	430	389	Estimated to reflect group.
	Henry's Law Coefficient	atm – m <sup>3</sup> /mole	2.9E-04	3.2E-05	ATSDR, 1994
	Atmospheric Concentration	mg/L	5.45E-11	1.6E-11	Mean concentration in Alabama (based on Jantunen et al., 2000)

**Table 3-24. Average Annual Load Contributions and Losses by Source for Calibrated PEST1 Sub-Model**

	Total Chlordane		Heptachlor Epoxide	
	kg/yr	% <sup>2</sup>	kg/yr	%
Upstream	0.834	67%	0.112	70%
SS Tribs	0.123	10%	0.017	11%
LBD	0.204	16%	0.021	13%
Watts	0.030	2%	0.004	2%
CSOs	0.052	4%	0.007	4%
Total Load Input <sup>1</sup>	1.243	100%	0.161	100%
Kinetic Losses (volatilization)	-0.113	-9%	-0.027	-17%
Export to Potomac	-0.436	-35%	-0.090	-56%

<sup>1</sup> Total load nput is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

<sup>2</sup> % represents the percentage of total load input.

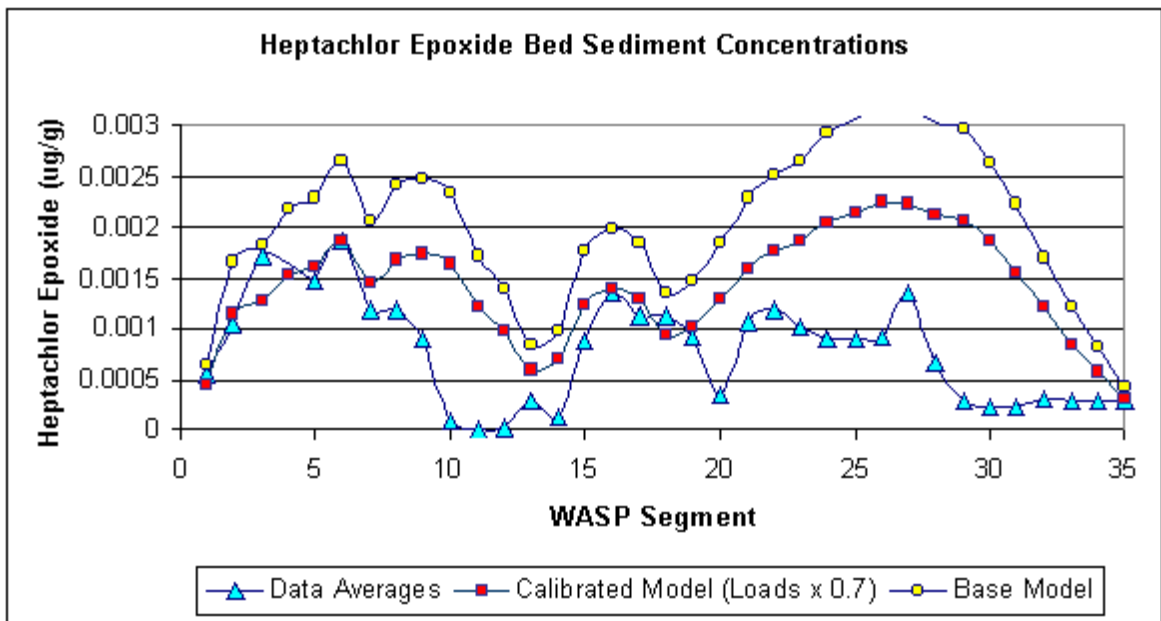
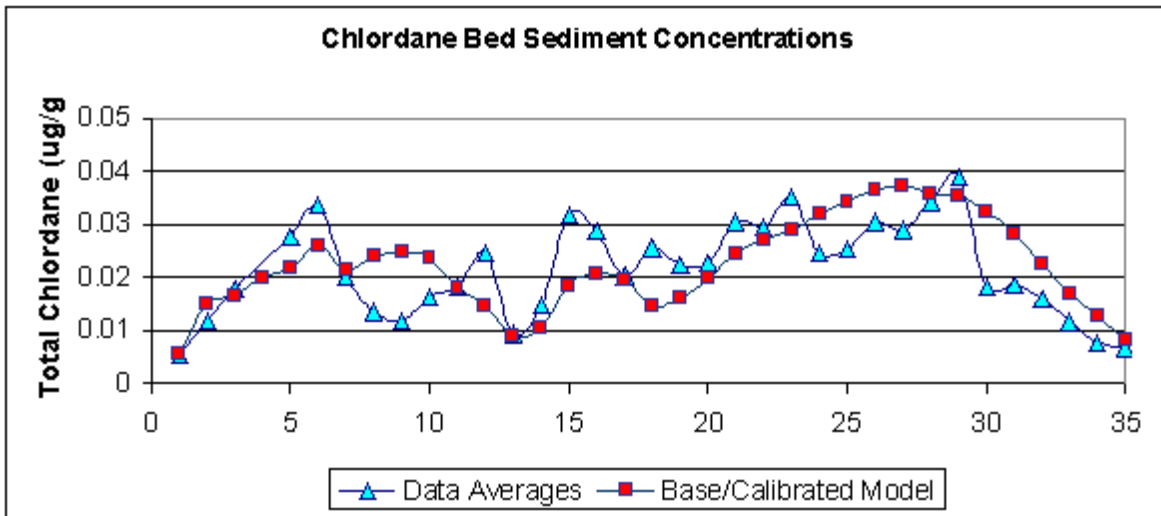
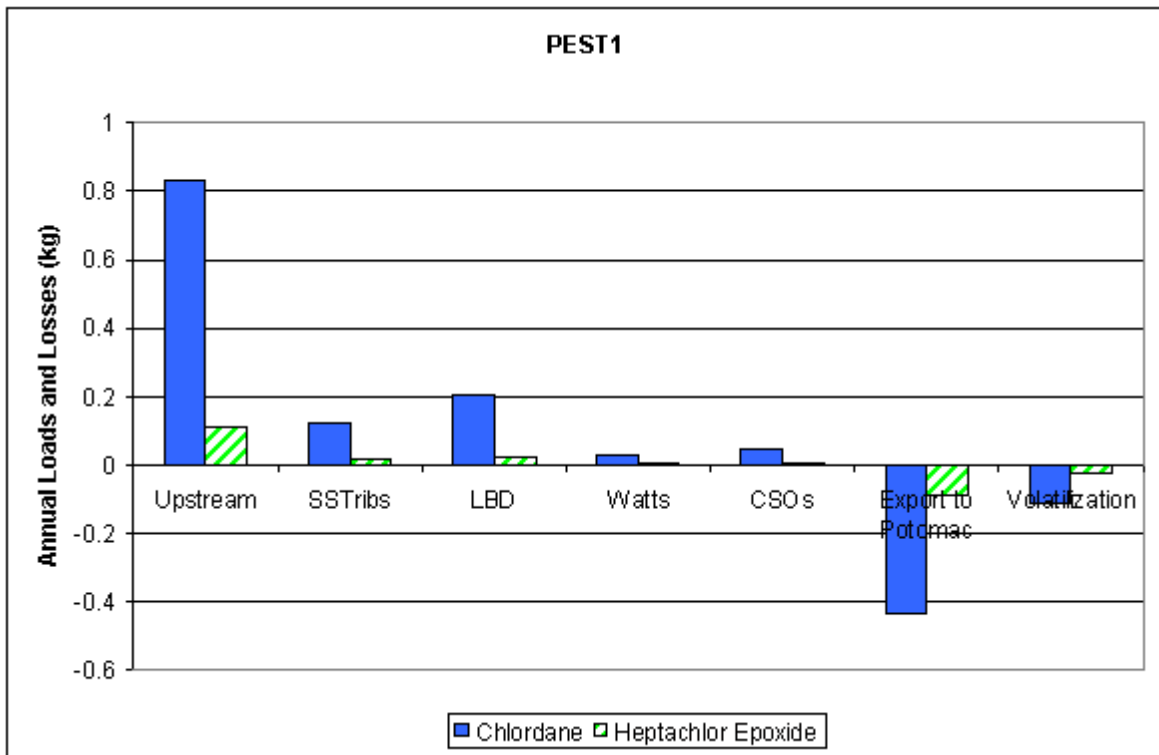


Figure 3-65. Chlordane/Heptachlor Epoxide Bed Sediment Results: Base Model and Calibrated Model (Loads x 0.7) Predictions



**Figure 3-66. Summary of Average Annual Loads and Losses for the Calibrated PEST1 Sub-Model**

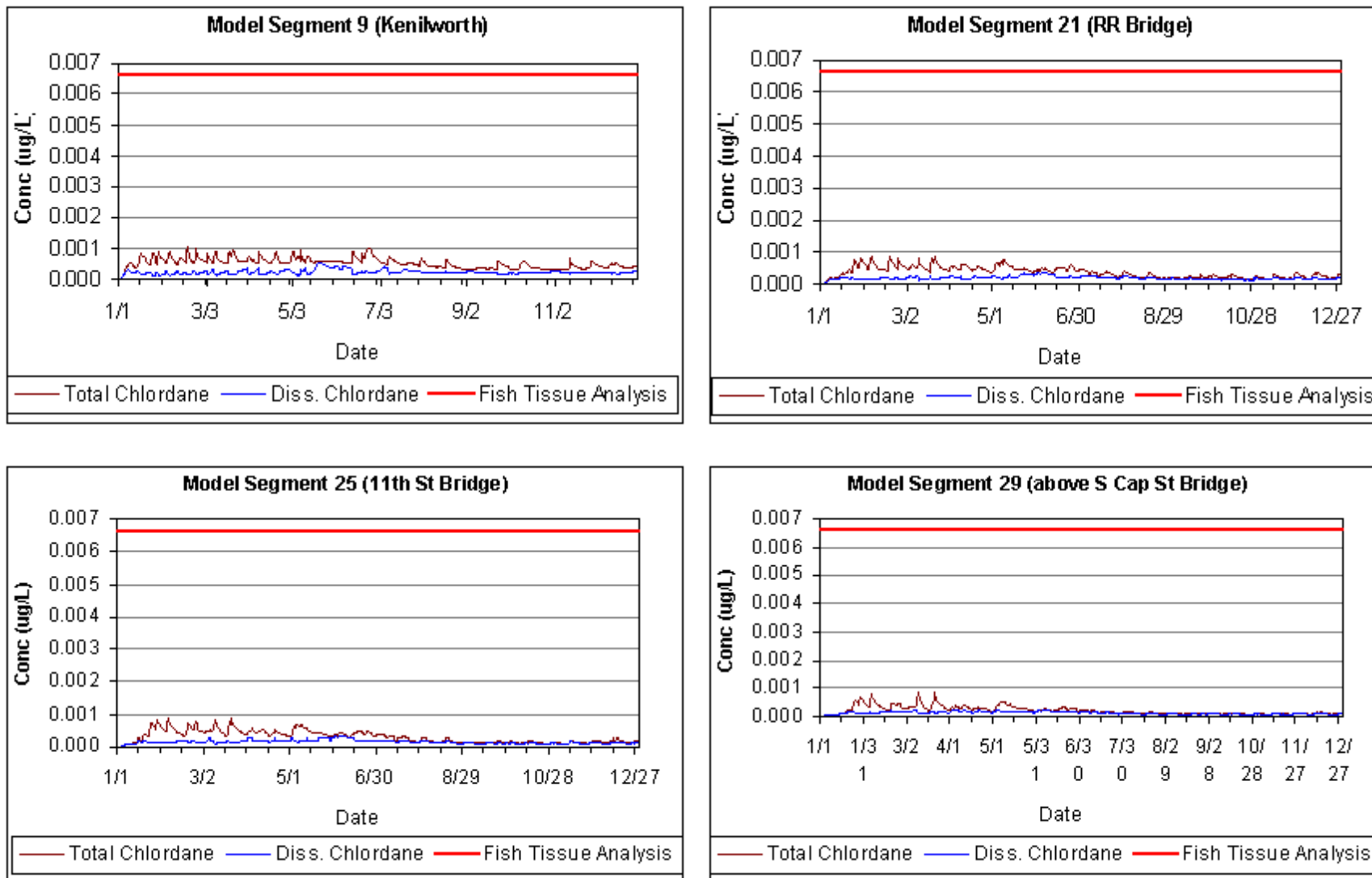


Figure 3-67. Chlordane Water Column Results for Base/Calibrated Model

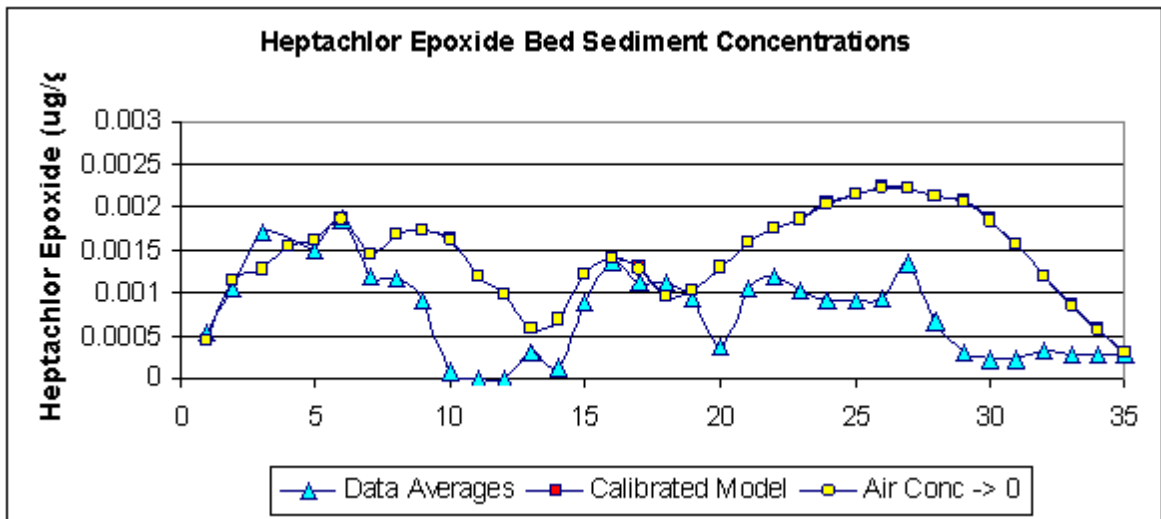
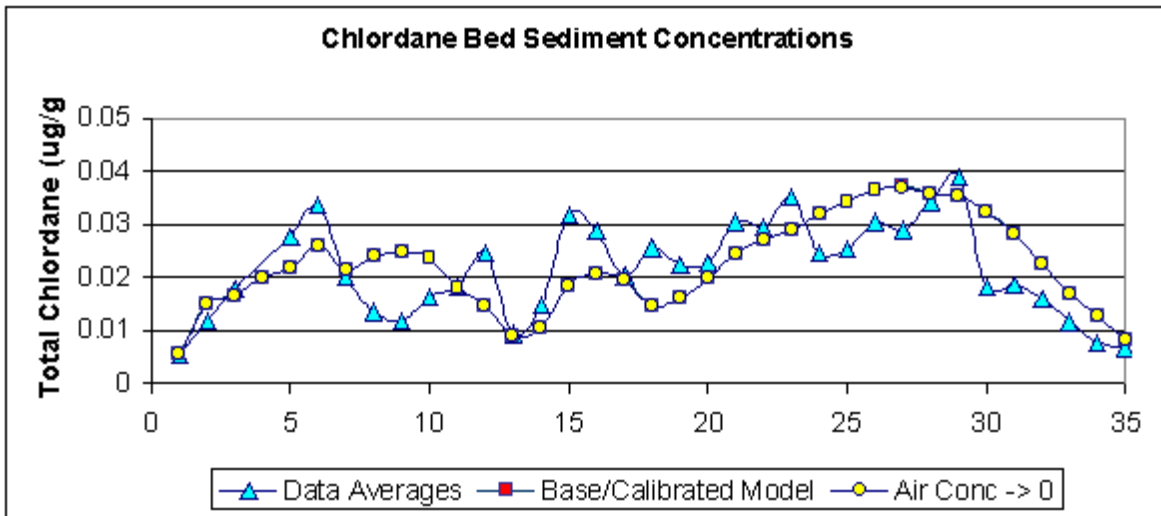


Figure 3-68. Chlordane/Heptachlor Epoxide Bed Sediment Sensitivity Test Results: Calibrated Model Predictions with Air Concentrations Reduced to 0.



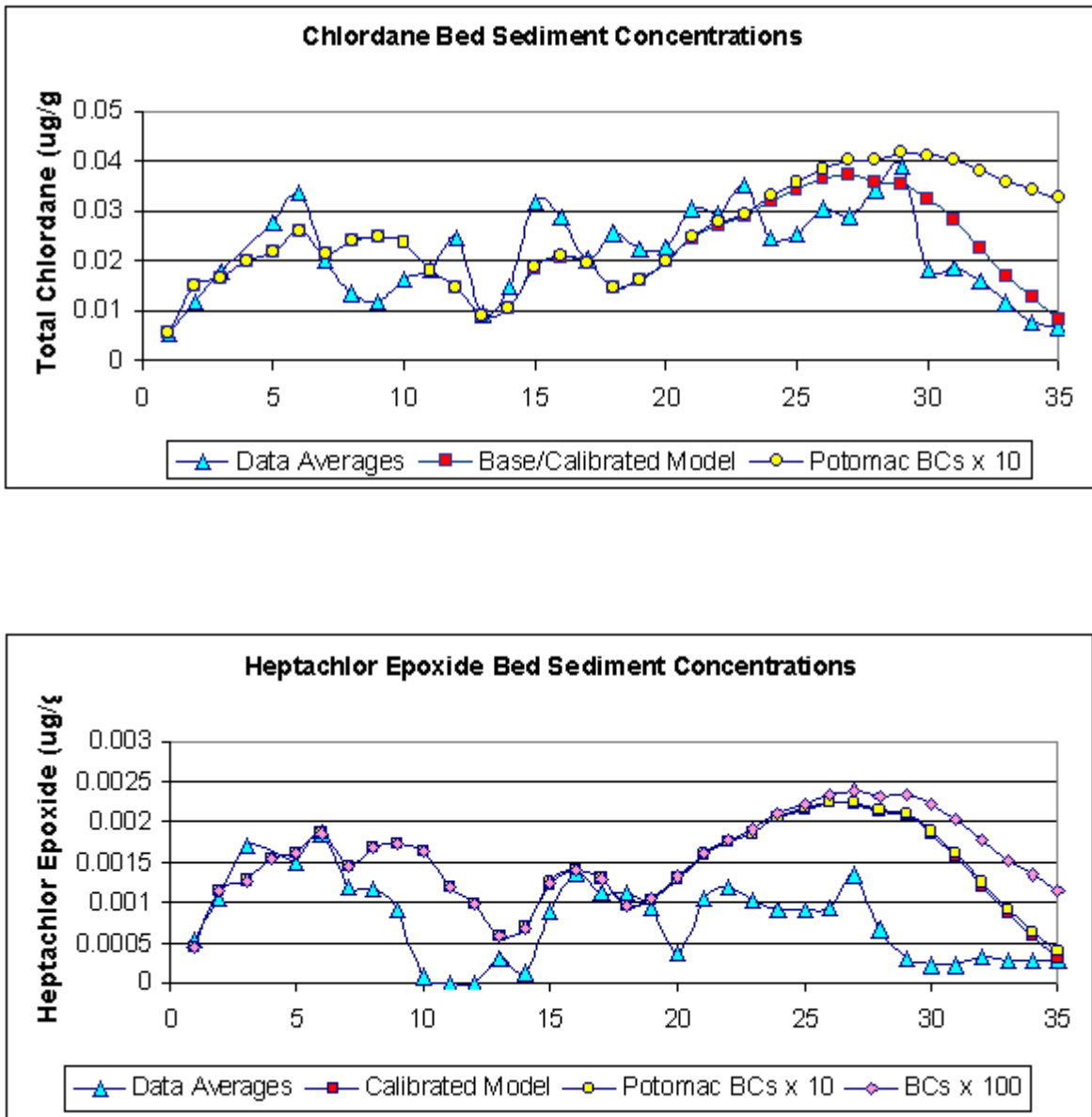


Figure 3-69. Chlordane/Heptachlor Epoxide Bed Sediment Sensitivity Test Results: Potomac Boundary Concentrations x 10, x 100.

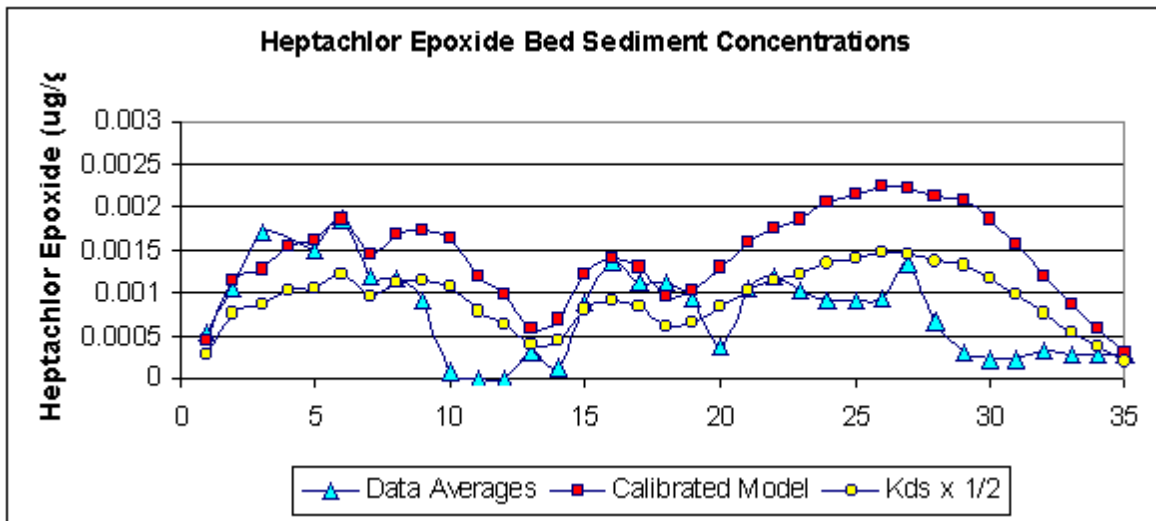


Figure 3-70. Heptachlor Epoxide Bed Sediment Sensitivity Test Results:  $K_d \rightarrow K_d/2$

### 3.3.6. Dieldrin (PEST2) Sub-Model

#### Model Description

The TAM/WASP model PEST2 (Table 1-2) has been set up for dieldrin. Transport and fate processes simulated include advection and dispersion, adsorption to the medium-grained and fine-grained sediment fractions, and volatilization. Although dieldrin may rearrange via photolysis into its stereoisomer photodieldrin (Spectrum Laboratories), ATSDR (2000c) reports that “it is unlikely ... that photodieldrin occurs widely in the environment”, and therefore, this fate process has not been included in the model. Likewise, hydrolysis and biodegradation have not been included because dieldrin is resistant to biodegradation in an aquatic environment and undergoes hydrolysis only slowly, with a half-life of greater than four years (TOXNET).

Wet and dry deposition has not been included in the model because regional data has not been found, although concentration data for stations in the Great Lakes region is available from the Integrated Atmospheric Deposition Network (IADN). However based on our experience with other chemicals, it is unlikely that wet and dry deposition contributes significant loads due to the relative small surface area of the tidal river.

Aldrin has been found in a few of the historical sediment sample data sets (AWTA/NOAA database: 1995 PEPCO and 1997 Sediment Core Analysis). Aldrin could be viewed as a source for dieldrin because it reportedly degrades readily into dieldrin in aerobic, biologically active soils and under anaerobic conditions in aquatic environments (TOXNET), albeit the exact pathways for these reactions are not clear. In water, photodieldrin may be formed via photolysis from aldrin (ATSDR 2000c). It is questionable, however, whether this is a likely process in the Anacostia River, as photolysis takes place near the water surface, and aldrin has only been found once, as particulate in a storm sample, in Anacostia River water column data. Because aldrin was below the detection limit in all Northeast/Northwest Branches monitoring data and all sediment samples in the Velinsky and Ashley 2001 data set, it appears that it does not play an important role in determining dieldrin concentrations in the Anacostia and therefore, was not included as a constituent in the dieldrin model.

#### Input Parameters

Estimated base flow and storm flow concentrations used for load estimates can be found in Table 3-25. Northeast and Northwest Branches values are means, assuming log normal distributions, of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin tributaries and separate storm sewer (SS) system concentrations are estimated at 0.00029 ug/L, based on MS4 monitoring data (Nicoline Shelterbrandt, private communication) of 20 samples with 18 non-detects, where non-detects were estimated  $\frac{1}{2}$  the detection limit (Table 2-5). Tidal sub-basin tributary base flow concentrations are estimated to be 0.000641 ug/L, based on the Northeast/Northwest Branches base flow results. Lower Beaverdam Creek (LBD) and Watts Branch storm flow concentrations and combined sewer system overflows (CSOs) concentrations are estimated to be 0.00029 ug/L, based on the MS4 monitoring results.

Proposed input parameters for downstream boundary conditions, adsorption, and volatilization are listed in Table 3-26. Because ICPRB has so far been unable to find atmospheric concentrations of dieldrin in the Washington/Baltimore area, the mean air concentration of dieldrin reported by Jantunen et al. (2000) for Alabama is used in the model.

### **Model Results**

A comparison of the model predictions (last day of six-year run) versus bed sediment data concentration averages suggests that the model accounts reasonably well for dieldrin mass inputs into the tidal portion of the Anacostia River as shown in Figure 3-71. A mass balance analysis for dieldrin by sources, kinetic losses, and net export to the Potomac River is shown in Figure 3-72 and given in Table 3-27. Results on relative loads appearing in Table 2-27 are preliminary, because storm and non-storm concentration estimates for dieldrin are currently based on just two data sets.

Model predictions of water column concentrations cannot be compared to measured water column concentrations because water column data for dieldrin were not available.

### **Sensitivity Runs**

Because of lack of data on concentrations of dieldrin in Potomac River water, the downstream boundary conditions for these contaminants were obtained by model calibration to bed sediment data. The boundary condition value obtained in this manner is rather low, about a factor of 1/10 less than the mean base flow tributary concentrations. A sensitivity run was done to investigate how predicted bed sediment results would change if the downstream boundary concentration was increased by a factor of 10. In Figure 3-73, it is evident that the dieldrin bed sediment results deteriorate significantly when this change is made. A more accurate determination of the downstream boundary condition for dieldrin awaits the availability of main channel water column calibration data.

### **Summary**

The sub-model for dieldrin, PEST2, does a fairly good job of predicting bed sediment concentrations, but no water column data is available for further model calibration/verification. Additionally, when main channel water column data becomes available, it will be possible to better determine the Potomac River boundary concentration, which can have a significant effect on predicted water column concentrations in downstream segments of the model. This value was determined for the current version of PEST2 via calibration to bed sediment data.

**Table 3-25. Concentrations Used to Compute PEST2 Sub-Model Calibration Run Input Loads (ug/L)**

Source	Chem1 Original	Suggested Multiplier	Chem1 Final	Data Source/Comment
NW Br Base	0.000784	x 1	0.000784	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.001697	x 1	0.001697	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
NE Br Base	0.000546	x 1	0.000546	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.000650	x 1	0.000650	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
SSTrib/LBD/Watts/CSO Non-storm	0.000641	x 1	0.000641	Estimated to be the averaged NE/NW Branches base flow (Gruessner et al., 1998)
SSTrib/LBD/Watts Storm	0.00029	x 1	0.00029	DC MS4 monitoring data, 20 samples with 18 NDs
CSO Storm	0.00029	x 1	0.00029	Assuming DC MS4 value

**Table 3-26. WASP Input Parameters for PEST2 Sub-Model**

Process	Parameter	Units	CHEM1	Source/Comments
<b><i>Downstream Boundary Condition:</i></b>				
	Potomac boundary concentration	ug/L	0.00005	Bed sediment calibration
<b><i>Adsorption:</i></b>				
	K <sub>d</sub> for fine-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	24,700	Based on 1998 water column data (Velinsky et al., 1999)
	K <sub>d</sub> for medium-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	6,175	Taken to be ¼ of the fine-grained sediment K <sub>d</sub> , based on best professional judgment
<b><i>Volatilization:</i></b>				
	Molecular Weight	g/mole	381	
	Henry's Law Coefficient <sup>a</sup>	atm – m <sup>3</sup> /mole	5.2E-06	ATSDR, 2000c
	Atmospheric Concentration	mg/L	3.8E-11	Mean concentration in Alabama (Jantunen et al. 2000)

<sup>a</sup> Literature values of Henry's law coefficient for dieldrin range from 5.2E-06 (ATSDR 2000c) to 1.51E-05 (U.S. EPA 1996).

**Table 3-27. Average Annual Load Contributions and Losses by Source for Calibrated PEST2 Sub-Model**

	Dieldrin	
	kg	% <sup>2</sup>
Upstream	0.119	84%
SS Tribs	0.009	6%
LBD	0.008	6%
Watts	0.002	1%
CSOs	0.004	3%
Total Load Input <sup>1</sup>	0.142	100%
Kinetic Losses (volatilization)	-0.001	-1%
Export to Potomac	-0.059	-42%

<sup>1</sup> Total load input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

<sup>2</sup> % represents the percentage of total load input.

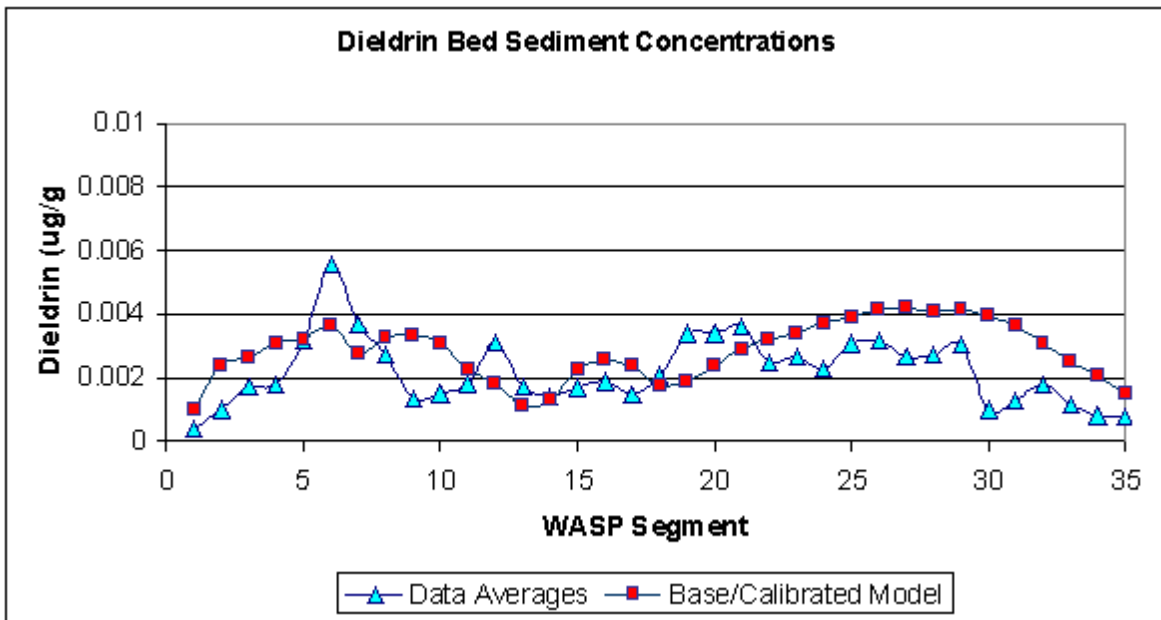
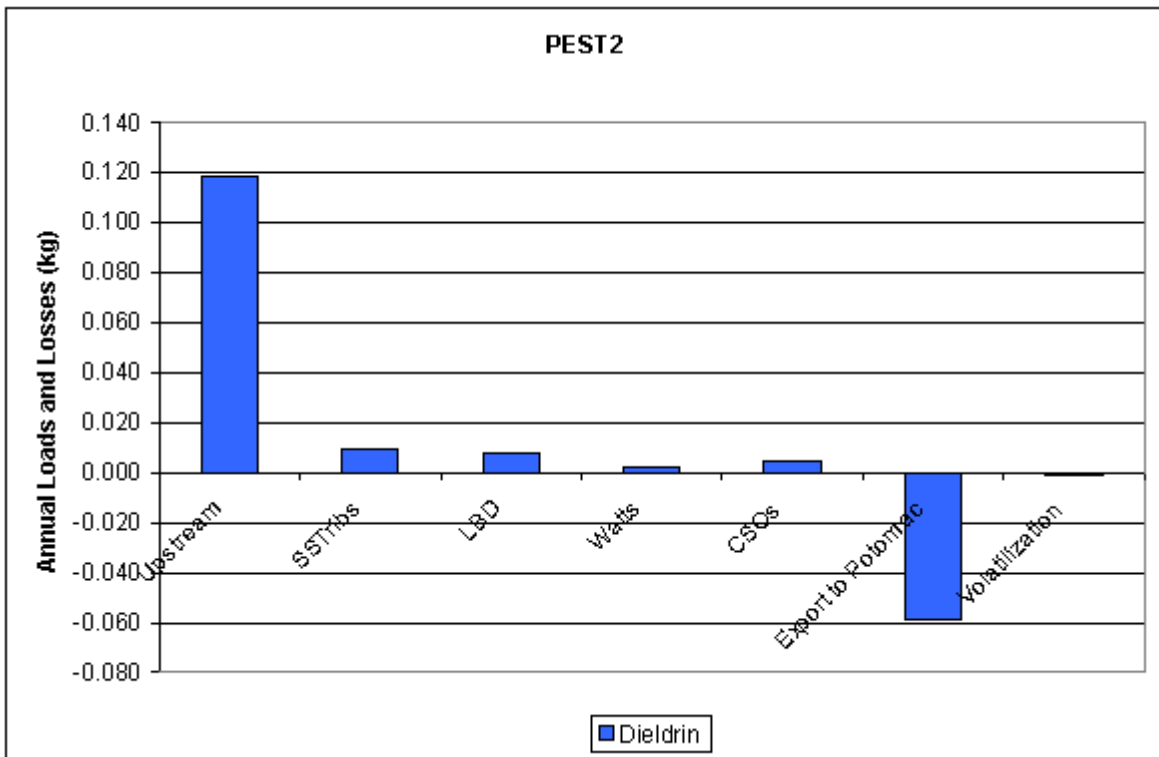


Figure 3-71. Dieldrin Bed Sediment Results for Base/Calibrated Model





**Figure 3-72. Summary of Average Annual Loads and Losses for the Calibrated Dieldrin (PEST2) Sub-Model**

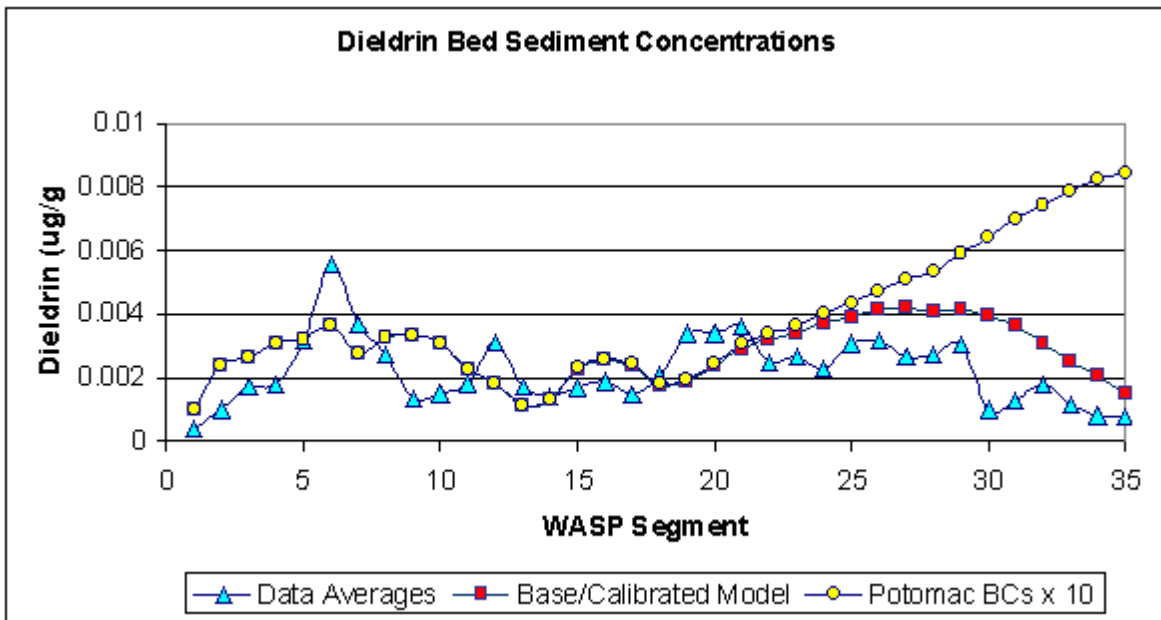


Figure 3-73. Dieldrin Bed Sediment Sensitivity Test Results - Potomac Boundary Concentration x 10

### 3.3.7. DDT Sub-Model

#### Model Description

The TAM/WASP DDT model simulates the fate and transport of the following three DDT isomers/metabolites: p,p DDD, p,p DDE, and p,p DDT (Table 1-2). The decision to model these three constituents was based on data availability. The only fate and transport process simulated, in addition to advection and dispersion, is adsorption to the medium and fine-grained sediment fractions. Volatilization is not included in the kinetic transport of DDT in the model due to a lack of data. Furthermore, although volatilization from water surfaces can be expected, this fate process is severely attenuated by adsorption to suspended solids and sediment. For example, the DDT volatilization half-life from a model pond is about 129 years when adsorption is considered (TOXNET). The US Army Corps of Engineers' Riverine Emergency Management Model and TOXNET lists other kinetic processes such as photolysis and biodegradation as "probably not important" and were not incorporated into the model framework (TOXNET, U.S. ACE 1997).

Biotransformation is considered a significant fate process for DDTs (TOXNET, U.S. ACE 1997). However, the biotransformation of DDTs is currently not included as a fate process in the model because no data are available to reliably assess the rate of DDT transformation in aquatic environments (TOXNET).

Wet and dry deposition has not been included in the model because regional data has not been found. However, based on our experience with other chemicals, it is unlikely that wet and dry deposition contributes significant loads due to the relative small surface area of the tidal river.

#### Input Parameters

Estimated base flow and storm flow concentrations are given in Table 3-28. Northeast and Northwest Branches values represent means (assuming log normal distributions) of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin estimates, including separate storm sewer (SS) system, and combined sewer overflows (CSO) are based on data from the District's MS4 storm water monitoring program, with an average minimum detection limit of 3E-04 ug/L (Nicoline Shelterbrandt, private communication). Upstream and tidal sub-basin concentrations used in load computations were increased based on calibration results (Table 3-28), as discussed below. It should be noted that for DDE and DDT, average upstream base flow concentrations were found to be higher than average storm flow concentrations. Because of the very low concentrations of these constituents and the high numbers of non-detects in the data set (with an average minimum detection limit of 2E-05 ug/L), it is not clear if this result is meaningful, indicating that ground water may be a significant source of DDXs to the system, or if the result is merely due to high variability and uncertainty in reported values. Also, in Table 3-28, note that the estimated load of DDE from the Northwest Branch is zero for both base flow and storm flow conditions. This is because DDE was listed as "ND" (not detected) in all samples analyzed from the Northwest Branch in the Gruessner data set. ICPRB assigned a value of zero to all ND notations based on private communication with David Velinsky.

Bed sediment concentrations of DDXs in the tidal sub-basin are based on the Velinsky and Ashley (2001) data set and several historical data sets available in the AWT/NOAA database, yielding 187, 168, and 185 stations for p,p DDD, p,p DDE, and p,p DDT respectively.

Proposed input parameters for downstream boundary conditions and adsorption are provided in Table 3-29. Model boundary conditions at the Potomac confluence, also given in Table 3-29, were set for p,p DDE and p,p DDT using the results of one pre-storm Potomac river sampling reported in the Velinsky et al. (1999) water column data set. Boundary conditions for p,p DDD were set through calibration as p,p DDD was not analyzed in the Velinsky study.

Proposed partition coefficients are also shown in Table 3-29. These values are based on an analysis of water column data available in Velinsky et al. (1999) for p,p DDE and p,p DDT and Northeast/Northwest Branches base flow data for p,p DDD.

### **Model Results**

The DDT model was run for 2 scenarios: a base scenario using loads calculated from measured storm and non-storm concentration means (Table 3-28) and a scenario in which loads were adjusted to calibrate to bed sediment data. A comparison of model predictions (last day of 6-year run) versus bed sediment concentration data is presented for each chemical and scenario in Figure 3-74. Model predictions of water column concentrations (total = dissolved + particulate, and dissolved) for p,p DDE and p,p DDT were compared to measured water column concentrations from Velinsky et al. (1999). Results of water column comparisons are shown in Figures 3-75 - 3-78. The predicted water column concentrations based on fish tissue analysis (see section 3.2.2) are also shown in Figures 3-75 to 3-78 for comparison. Total loads by source and net export for the calibration loads adjustment scenario are presented in Figure 3-79. The relative contribution of each source and loss compared to total river input (sum of all loads) is provided in Table 3-30, though these results should be viewed as preliminary because they are based on a very limited set of storm water monitoring data.

Model results for both scenarios suggest that DDT sources of loading to the tidal Anacostia River are currently not well characterized. In the load adjustment scenario, upstream and downstream loadings of DDTs were altered (multiplication factors presented in Table 3-28) in an effort to calibrate the model. Model results in this scenario account reasonably well for mass inputs of DDT into the tidal portion of the Anacostia River, but only after increasing upstream loads by up to a factor of 4 and downstream loads by up to a factor of 20. Though the load uncertainty analysis in Section 2.5 shows that confidence intervals for mean concentrations may produce this degree of error, it is also possible that important sources of DDTs, particularly downstream, have not been captured by the available data.

Comparison of predicted versus measured water column concentrations for p,p DDE and p,p DDT indicate that calculated loads used in the base scenario account fairly well for water column concentrations of p,p DDE and p,p DDT, as shown in Figures 3-75 and 3-76 respectively. In general, increasing loads by the magnitude necessary to calibrate the sediment layer caused an

over-estimation of water column concentrations for p,p DDT (Figures 3-77 and 3-78), and, to a lesser extent, for p,p DDE.

### **Summary**

The initial runs of the DDT sub-model seriously under-predicted bed sediment concentrations, and significant adjustments had to be made to initial load estimates in order to calibrate the model to bed sediment data. These results point to the limitations of currently available data and suggest that the sources and loads for DDT may not yet be well characterized. It should be pointed out that detected concentrations of p,p DDD, p,p DDE, and p,p DDT are some of the lowest found in the studies considered, ranging from just a fraction of a nanogram per liter to approximately one nanogram per liter in water samples (part per trillion). These low concentrations and the corresponding number of non-detects, even for the very precise analytical techniques used by the Gruessner study of Northeast/Northwest Branches loads, suggest that available data is of low precision and accuracy and highly variable.

**Table 3-28. Concentrations Used to Compute DDT Sub-Model Calibration Run Input Loads (ug/L)**

Source	CHEM1 Orig	Suggested CHEM1 Multiplier	CHEM1 Draft Final	CHEM2 Orig	Suggested CHEM2 Multiplier	CHEM2 Draft Final	CHEM3 Orig	Suggested CHEM3 Multiplier	CHEM3 Draft Final	Comment
NW Br Base	0.00023	x 4.0	0.00091	0.00000	x 4.0	0.00000	0.00060	x 1.0	0.00060	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.00125	x 4.0	0.00500	0.00000	x 4.0	0.00000	0.00015	x 1.0	0.00015	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
NE Br Base	0.00023	x 4.0	0.00093	0.00052	x 4.0	0.00210	0.00063	x 1.0	0.00063	Concentration computed from 6 base flow samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.00104	x 4.0	0.00416	0.00007	x 4.0	0.00028	0.00025	x 1.0	0.00025	Concentration computed from 4 composite storm samples of Gruessner et al. (1998) 1995-96 data
SSTrib Base	0.00023	x 20.0	0.00462	0.00026	x 15.0	0.00393	0.00061	x 20.0	0.01230	Estimated to be the averaged NE/NW Branches base flow (Gruessner et al., 1998)
SS Trib Storm	0.00015	x 20.0	0.00300	0.00089	x 15.0	0.01330	0.00171	x 20.0	0.03420	From available DC MS4 monitoring data, 20 samples with 15 NDs.
Watts/LBD Base	0.00023	x 20.0	0.00462	0.00026	x 15.0	0.00393	0.00061	x 1.0	0.00061	Estimated to be the averaged NE/NW Branches base flow (Gruessner et al., 1998)
Watts/LBD Storm	0.00015	x 20.0	0.00300	0.00089	x 15.0	0.01330	0.00171	x 1.0	0.00171	From available DC MS4 monitoring data, 20 samples with 15 NDs.
CSO Storm	0.00015	x 20.0	0.00300	0.00089	x 15.0	0.01330	0.00171	x 20.0	0.03420	From available DC MS4 monitoring data, 20 samples with 15 NDs.
CSO Non-storm	0.00023	x 20.0	0.00462	0.00026	x 15.0	0.00393	0.00061	x 20.0	0.01230	Estimated to be the averaged NE/NW Branches base flow (Gruessner et al., 1998)

**Table 3-29. WASP Input Parameters for DDT Sub-Model**

Process	Parameter	Units	CHEM1	CHEM2	CHEM3	Source
<i>Downstream Boundary Condition:</i>						
	Potomac Boundary Concentration	ug/L	2.30E-05	5.27E-05	3.35E-05	DDE, DDT: Velinsky et al. (1999) DDD: calibration
<i>Adsorption:</i>						
	K <sub>d</sub> for fine-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	80,000	100,401	2,602,545	Mean K <sub>d</sub> based on site- specific base flow data
	K <sub>d</sub> for medium-grained sediment	L <sub>w</sub> /kg <sub>s</sub>	20,000	25,100	650,636	¼ of mean K <sub>d</sub>

**Table 3-30. Average Annual Load Contributions and Losses by Source for Calibrated DDT Sub-Model**

	p,p DDD		p,p DDE		p,p DDT	
	kg/yr	% <sup>2</sup>	kg/yr	%	kg/yr	%
Upstream	0.406	66%	0.087	13%	0.052	6%
SS Tribs	0.078	13%	0.191	28%	0.511	62%
LBD	0.075	12%	0.284	41%	0.037	5%
Watts	0.018	3%	0.046	7%	0.006	1%
CSOs	0.034	6%	0.078	11%	0.210	26%
Total Load Input <sup>1</sup>	0.611	100%	0.69	100%	0.82	100%
Export to Potomac	-0.247	-40%	-0.30	-43%	-0.349	-43%

<sup>1</sup> Total load input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

<sup>2</sup> % represents the percentage of total load input.

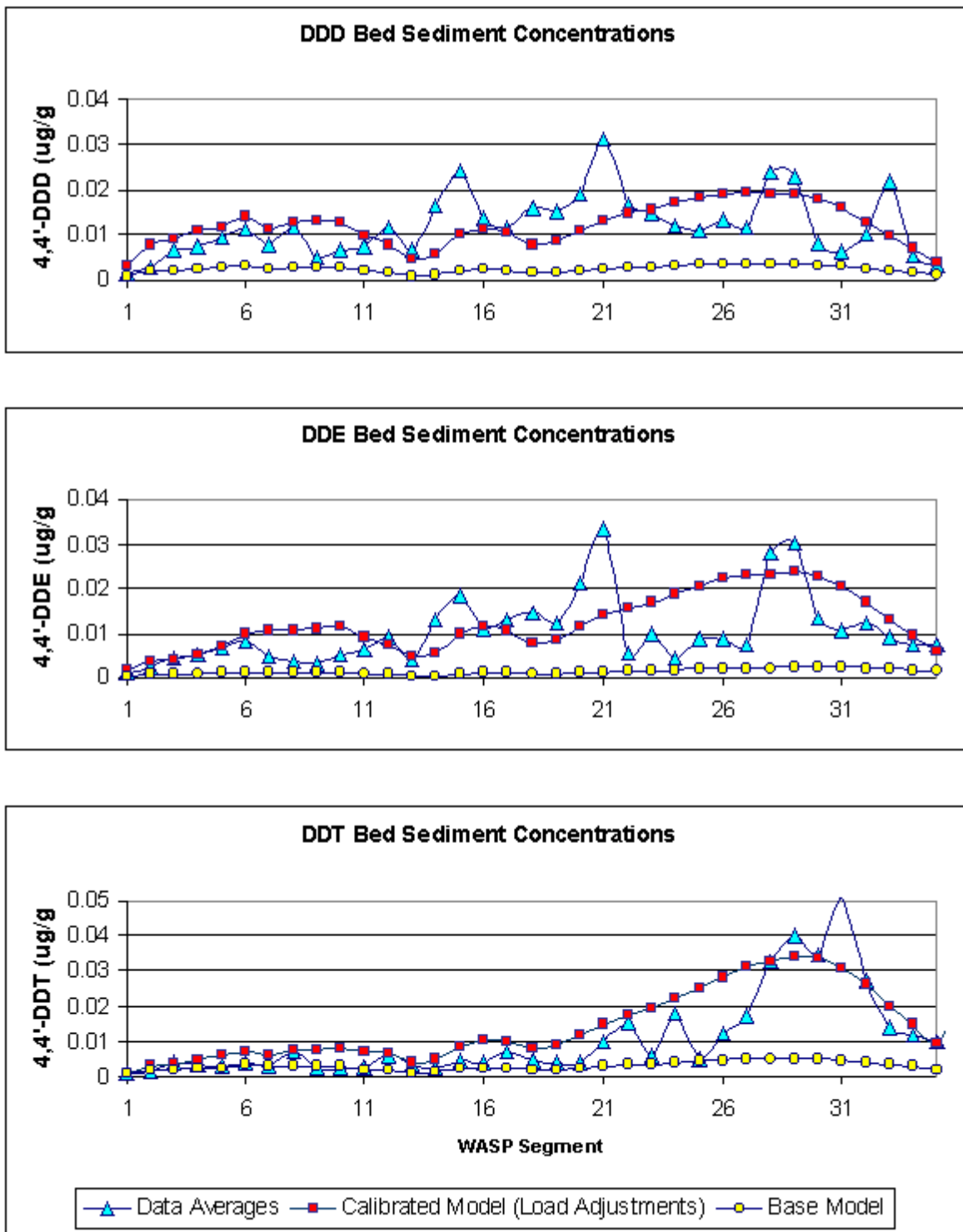


Figure 3-74. DDT Bed Sediment Results: Base and Calibrated (with Load Adjustments) Models



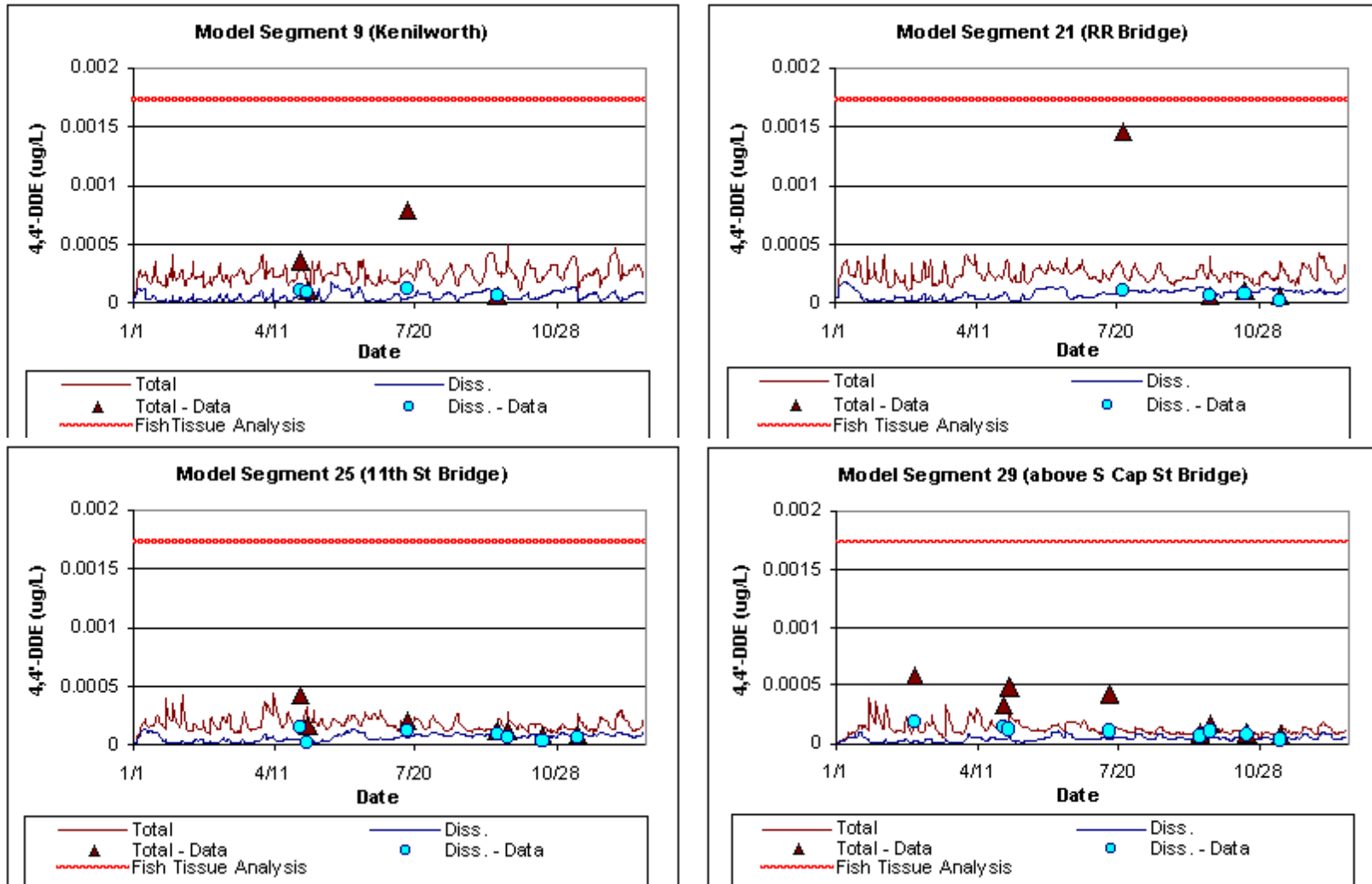


Figure 3-75. DDE Base Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data

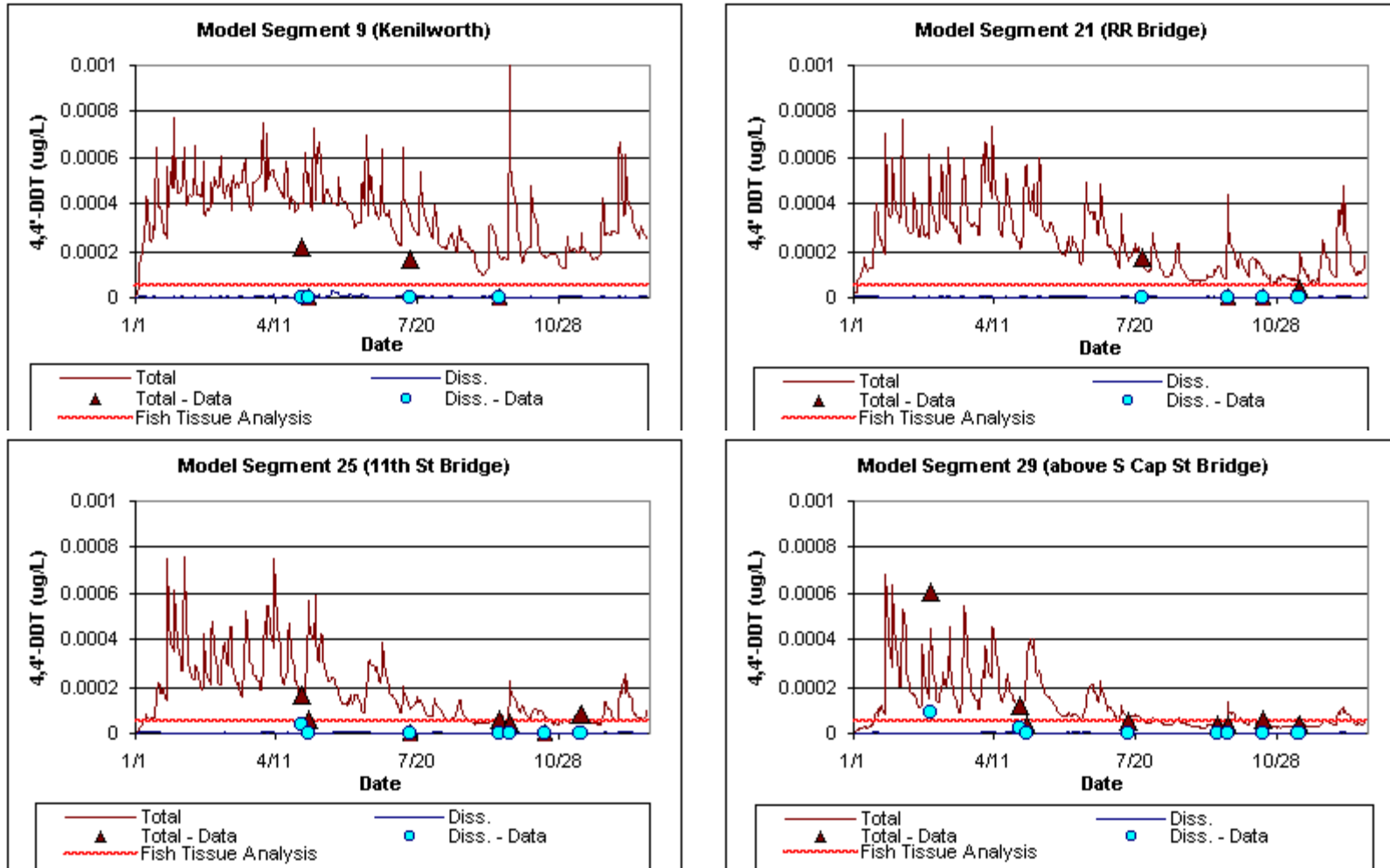


Figure 3-76. DDT Base Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data

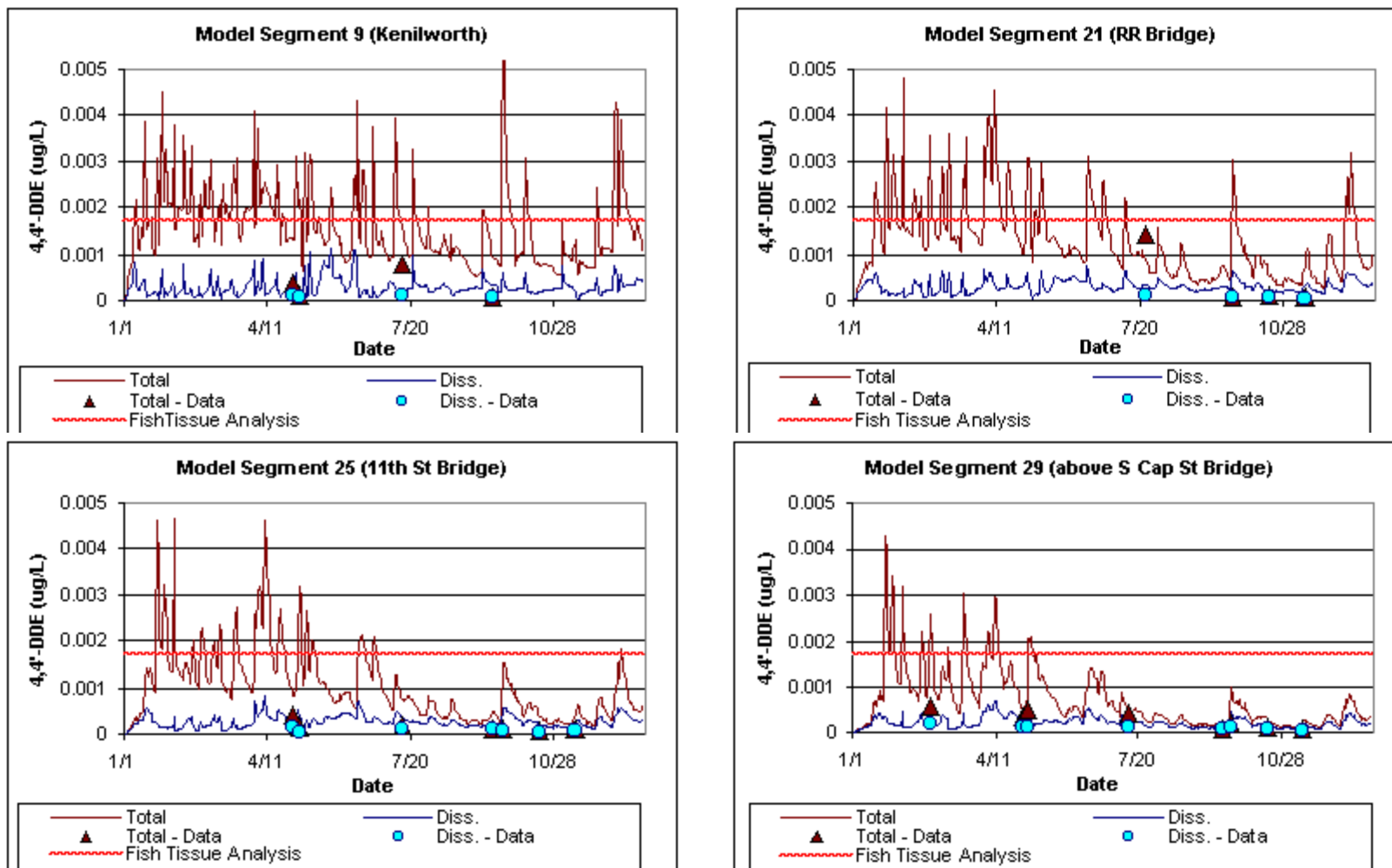


Figure 3-77. DDE Calibrated Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data

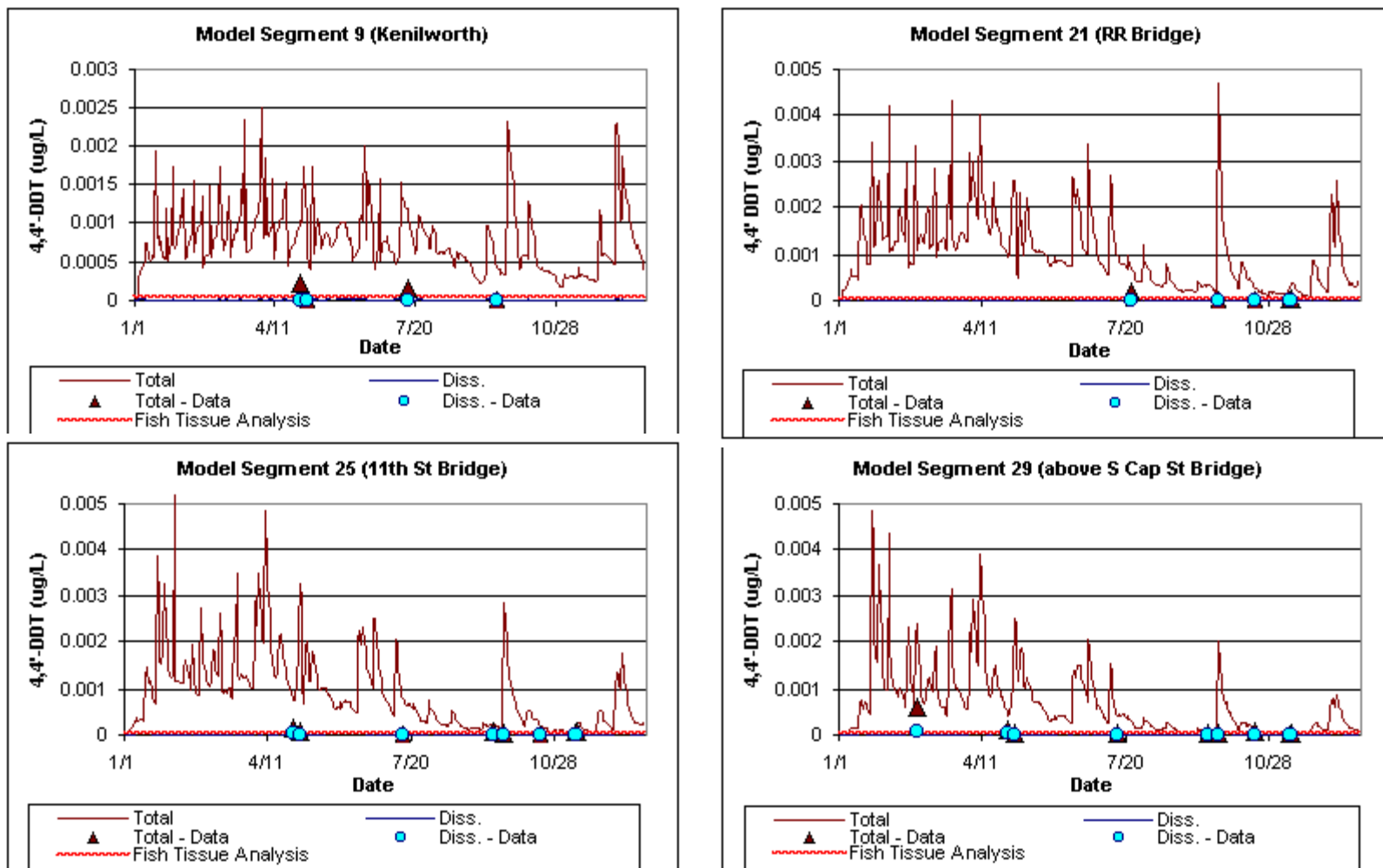


Figure 3-78. DDT Calibrated Model Water Column Results: Model Predictions vs. 1998 Data Vs. Bioaccumulation Analysis Prediction Based on Fish Tissue Data

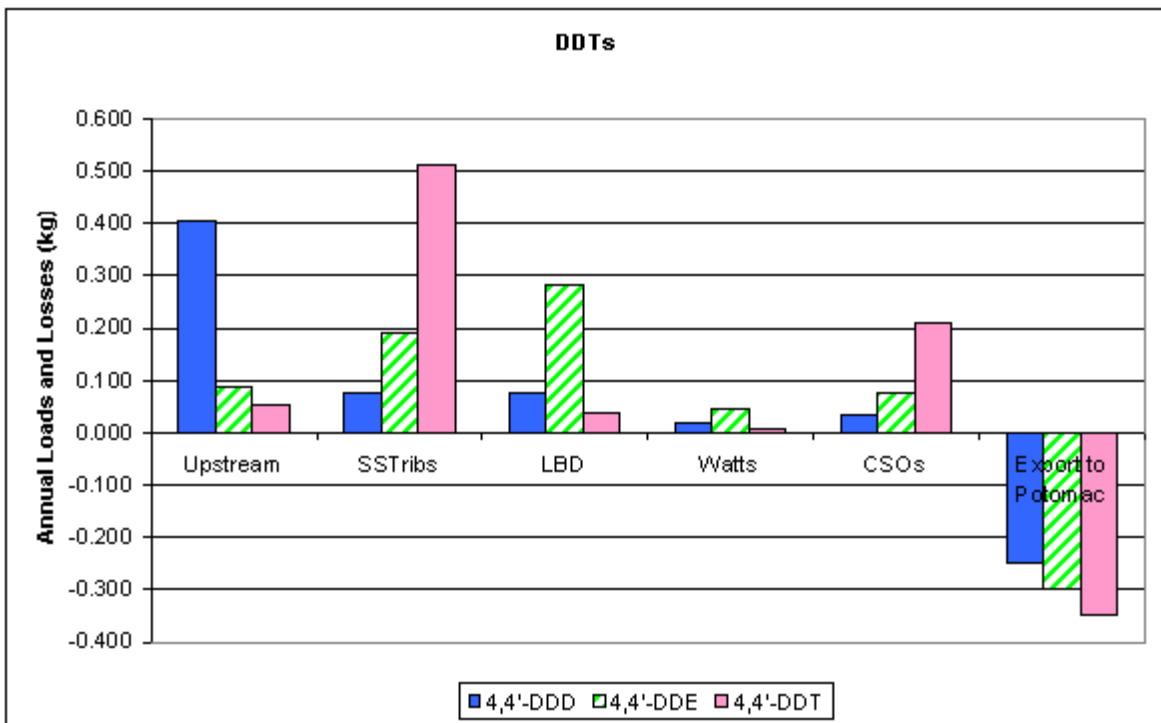


Figure 3-79. Summary of Average Annual Loads and Losses for the Calibrated DDT Sub-Model

## CHAPTER 4: CONCLUSION

### 4.1. Summary of Model Results

The TAM/WASP Toxics Screening Level Model consists of seven sub-models which simulate the loading, fate, and transport of zinc, lead, copper, arsenic, PCBs, PAHs, chlordane, heptachlor epoxide, dieldrin, and DDTs in the tidal portion of the Anacostia River. The model can be used to provide daily estimates of concentrations of these chemicals in both the river's water column and surficial bed sediment under current loading conditions and under potential load reduction scenarios. This one-dimensional model incorporates a 36 segment version of the TAM hydrodynamic model and a version of the EPA's WASP-TOXI5 water quality model, modified by ICPRB to simulate settling and resuspension of sediment based on local, time-varying hydrodynamic conditions. The underlying sediment transport model is the same as that which was used, with only very minor changes, for development of the District's sediment TMDL for the Anacostia. It simulates the loading and transport of three classes of sediment grain sizes ( $< 30 \mu\text{m}$ ,  $> 30 \mu\text{m}$  and  $< 120 \mu\text{m}$ ,  $> 120 \mu\text{m}$ ), and quite successfully predicts the observed spatial pattern of grain-size distribution in the river bed sediment.

The seven sub-models were calibrated individually with varying amounts of data support, and only a few changes were made to model input parameters during the calibration process. For all constituents but arsenic, site-specific data was available to estimate values for  $K_d$ 's, the parameters which govern partitioning between the dissolved and solid phases. During the calibration process,  $K_d$ 's for some constituents were adjusted in order to improve model predictions of water column dissolved concentrations. Also, for constituents for which there was no data on Potomac River concentrations, downstream boundary condition concentrations were estimated via calibration to bed sediment data. Finally, when long-term predictions of model segment bed sediment concentrations (last day of six-year run) were very different from segment averages computed from available data, calibration adjustments were made to initial constituent load estimates. Calibration load adjustments were made for lead, heptachlor epoxide, PCBs, PAHs, and DDTs.

Overall, the TAM/WASP Screening Level Toxics Model does a good job in accounting for load inputs of toxic chemicals to the tidal Anacostia. As shown in Table 4-1 and Figure 4-1, though the total mass of various contaminants residing in the surficial bed sediment (upper 1 cm) varies over five orders of magnitude, from about 0.02 kg for heptachlor epoxide to almost 8,000 kg for zinc, model predictions of total mass vary from 13% to 252% of observed mass, before calibration load adjustments are made. After calibration load adjustments, model predictions of sediment mass range from 49% to 182% of observed mass.

In cases in which data is available, predictions of the calibrated model match observed water column concentrations reasonably well. Also, the model is able to reproduce to some extent the spatial pattern of contaminant concentrations observed in the bed sediment, with concentrations generally highest in the wider, slower moving downstream portion of the river from segments 24 to 32.

From the error analysis of upstream storm concentration estimates (Section 2.5) and the various sensitivity test runs, it appears that model errors are dominated by uncertainties in the load estimates, with load confidence intervals likely in the range of -50% to +300%. The use of the calibration load adjustment factors was an effort to use information from contaminant bed sediment data to reduce this error. There is also a great deal of uncertainty in the  $K_d$  values used as model inputs because of the high variability of  $K_d$ 's computed from site-specific data. However, sensitivity test runs for metals and PCBs indicate that changes in  $K_d$ 's have little effect on bed sediment concentration predictions for many of the contaminants modeled, though they do have a significant effect on dissolved water column concentration predictions. An analysis presented in Section 3.3.1 supports this finding by showing that, for constituents with relatively large  $K_d$ 's (say  $> 200$  L/g), particulate concentrations are relatively insensitive to changes in  $K_d$ 's, while dissolved concentrations are approximately proportional to  $1/K_d$ .

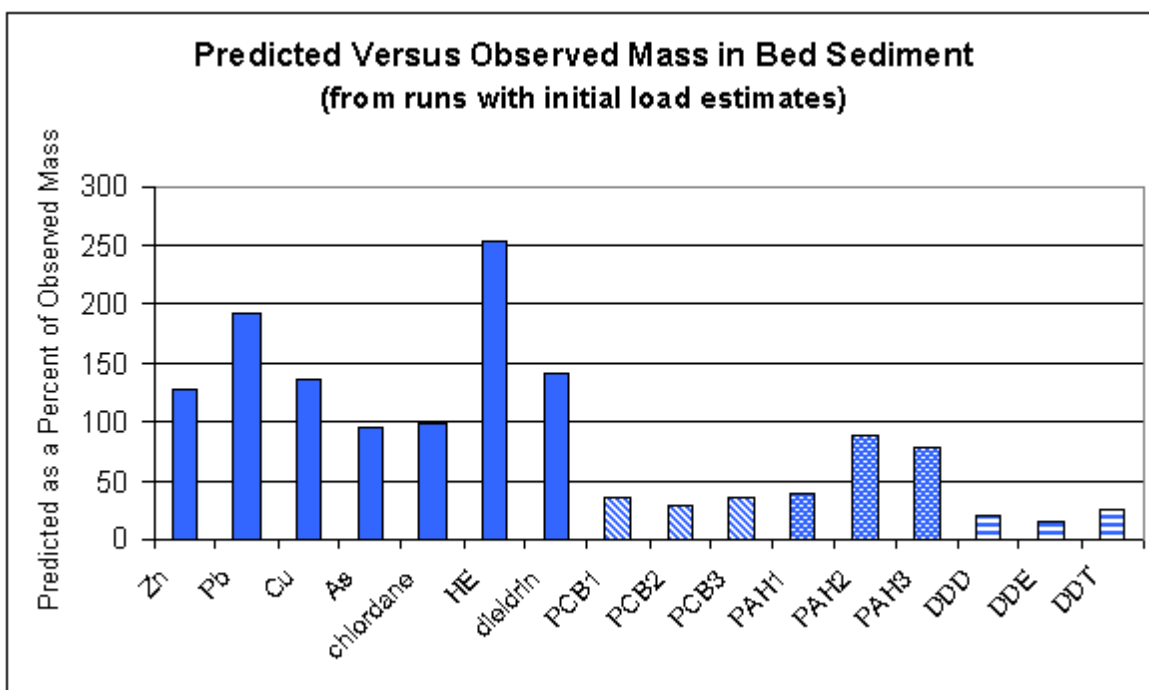
Additional data support is necessary to address the current limitations of the TAM/WASP Screening Level Model. Key data gaps and corresponding model uncertainties include:

- Uncertainties in chemical load estimates, currently probably in the range of about -50% to +300%, could be reduced by additional storm water monitoring data for the upstream tributaries, Lower Beaverdam Creek, and the SS and CS systems, especially from outfalls in the vicinity of apparent sediment “contaminant hot spots”. In order to support quantification of toxic chemical loads, it is necessary to use analytical techniques with sufficiently low detection limits.
- Uncertainty concerning the importance of ground water load inputs could be improved by the collection of ground water monitoring data at several locations adjacent to the river, again, using sufficiently low analytical detection limits. Currently, the model uses upstream base flow monitoring results to estimate chemical concentrations in ground water inputs.
- Lack of information concerning decay processes, such as biodegradation and photolysis, for chemicals such as PAHs, could be addressed by collection of a comprehensive water column calibration data set, including data to assess seasonal variations in concentrations. Decay rate coefficients are currently estimated by using values found in the published literature, which often vary by several orders of magnitude.
- Lack of understanding of the importance of potential mixing processes, such as bioturbation, methane gas bubble generation, and tidal pumping effects, could be addressed by the collection of radioisotope and other types of data to characterize vertical mixing in the sediment bed. At this time it is not possible to assess the potential for recontamination of recently deposited sediments by underlying sediments due to these processes, and sediment bed mixing processes are not currently simulated by the model.

At the time of preparation of this report, a number of studies, funded by the DC DOH, AWT, and other groups, are being conducted to begin filling in some of these data gaps. A better understanding of some of the issues listed above will lead to improvements in the predictive capabilities of the TAM/WASP Screening Level Toxics Model.

**Table 4-1. Model Predictions of Total Accumulated Mass in Bed Sediment (upper 1 cm)**

	Data	Base Model		Calibrated Model	
	kg	kg	% Data	kg	% Data
<b>Zinc</b>	7,972	10,122	127%	10,122	127%
<b>Lead</b>	2,489	4,767	192%	2,897	116%
<b>Copper</b>	2,162	2,903	134%	2,903	134%
<b>Arsenic</b>	174	149	86%	149	86%
<b>Chlordane</b>	0.67	0.68	102%	0.68	102%
<b>Heptachlor Epoxide</b>	0.02	0.06	252%	0.04	182%
<b>Dieldrin</b>	0.06	0.09	142%	0.09	142%
<b>PCB1 (homologs 2 - 4)</b>	0.67	0.24	36%	0.66	98%
<b>PCB2 (homologs 5 - 6)</b>	4.18	1.14	27%	3.03	73%
<b>PCB3 (homologs 7 - 9)</b>	2.05	0.73	36%	1.82	89%
<b>PAH1 (2 and 3 rings)</b>	74	29	39%	37	49%
<b>PAH2 (4 rings)</b>	209	182	87%	265	127%
<b>PAH3 (5 and 6 rings)</b>	189	147	78%	214	113%
<b>DDD</b>	0.36	0.07	20%	0.37	101%
<b>DDE</b>	0.33	0.04	13%	0.41	124%
<b>DDT</b>	0.41	0.10	24%	0.51	125%



**Figure 4-1. TAM/WASP Toxic Screening Level Model Predictions of Total Accumulated Mass in Bed Sediment (upper 1 cm; before load adjustments)**



## LIST OF ACRONYMS AND ABBREVIATIONS

AWTA	Anacostia Watershed Toxics Alliance
BC	Boundary condition
CS	Combined sewer
CSO	Combined Sewer Overflow
DDD	dichloro-diphenyl-dichloroethane
DDE	dichloro-diphenyl-ethane
DDT	dichloro-diphenyl-trichloroethane
DDXs	DDT and its metabolites, DDD and DDE
EMC	Event mean concentration
EPA	United States Environmental Protection Administration
ICPRB	Interstate Commission on the Potomac River Basin
LTCP	Long Term Control Plan
NOAA	National Oceanographic and Atmospheric Administration
PCB	polychlorinated biphenyl
PAH	polycyclic aromatic hydrocarbon
ppm	parts per million
ppb	parts per billion
SS	Separate sewer
TAM	Tidal Anacostia Model
TSS	Total suspended solids
USGS	United States Geological Survey
WASA	District of Columbia Water and Sewer Authority
WASP	Water Analysis Simulation Program

### Abbreviations for metric units:

cm	centimeter = 1/100 of a meter
g	gram
kg	kilogram = 1000 grams
mg	milligram = $10^{-3}$ of a gram
m	meter
L	liter
ng	nanogram = $10^{-9}$ of a gram
pg	picogram = $10^{-12}$ of a gram
$\mu$ g	microgram = $10^{-6}$ of a gram

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