Total Maximum Daily Loads for PCBs in the Houston Ship Channel

Contract No. 582-6-70860 Work Order No. 582-6-70860-19

Quarterly Report 1

Prepared by
University of Houston
Parsons Water & Infrastructure

Principal Investigators

Hanadi Rifai

Randy Palachek

PREPARED IN COOPERATION WITH THE TEXAS COMMISSION ON ENVIRONMENTAL QUALITY AND U.S. ENVIRONMENTAL PROTECTION AGENCY

The preparation of this report was financed through grants from the U.S. Environmental Protection Agency through the Texas Commission on Environmental Quality

TCEQ Contact:
Larry Koenig
TMDL Team
P.O. Box 13087, MC - 203
Austin, Texas 78711-3087
lkoenig@tceq.state.tx.us

December 2007

TABLE OF CONTENTS

TABI	LE OF (CON	TENTS	2
CHA	PTER 1	l -	INTRODUCTION	5
1.1	SC	OPE	OF THE PROJECT	6
1.2	DE	ESCR	IPTION OF THE REPORT	7
CHA	PTER 2	2 -	LITERATURE REVIEW	8
2.1	Mo	ODEL	REVIEW, WASP MODELING APPLICATIONS REVIEW, AND SELECTION OF MOD	EL
AP	PLICAB	LE FO	R PCB TMDL STUDIES IN THE HOUSTON SHIP CHANNEL	8
	2.1.1	Back	kground	8
	2.1.2	In-S	tream Models	9
	2.1	.2.1	Analytical Models	11
	2.1	.2.2	Steady State Models	11
	2.1	.2.3	Dynamic Models	14
	2.1.3	Run	off Models	15
	2.1	.3.1	Simple Methods	18
	2.1	.3.2	Mid-range Models	18
	2.1	.3.3	Detailed Models	19
2	2.1.4	Air	Dispersion Models	21
	2.1	.4.1	Industrial Source Complex Short Term Model (ISCST3)	21
	2.1	.4.2	Regional Lagrangian Model of Air Pollution (RELMAP):	22
	2.1	.4.3	Models - 3 Community Multi-Scale Air Quality (CMAQ) Modeling System	23
	2.1	.4.4	Regulatory Modeling System for Aerosols and Deposition (REMSAD)	24
	2.1	.4.5	Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT)	24
	2.1	.4.6	Regional Atmospheric Modeling System (RAMS)	25
	2.1.5	Hyd	lrodynamic Models	26
	2.1	.5.1	One-Dimensional Models	27
	2.1	.5.2	Two-Dimensional Models	29
	2.1	.5.3	Three-Dimensional Models	29
2	2.1.6	Sedi	ment Transport	30
2	2.1.7	Sele	ction of Models	31

	2.1.8	In-st	ream Quality Model to Estimate the Transport and Fate of PCB Compounds in ti	he
	Housto	n Ship	Channel	31
	2.1.9	Selec	tion of Hydrodynamic Model as Input to WASP	33
	2.1.10	Н	SCREAD Interface	35
	2.1.11	F	inal Selection of Models for the HSC Modeling Framework	36
	2.1.12	R	ecord of Previous Application of WASP in PCB/Dioxin Studies	37
	2.1	.12.1	The Lake Michigan Mass Balance Project (USEPA, 2006)	37
	2.1	.12.2	Transport of polychlorinated biphenyls (PCB) in the Scheldt Estuary simulated w	vith
	the	e wate	quality model WASP (Vuksanovic et al., 1995)	38
	2.1	.12.3	Total Maximum Daily Loads in Anacostia River Watershed for Organics and Metals	
	(U	SEPA,	2003a, b)	39
	2.1	.12.4	Country Club Lake Phase One Total Maximum Daily Load for Dioxin and	
	Pe	ntachl	orophenol (PCP) (MDEQ, 2000)	41
	2.1	.12.5	Total Maximum Daily Loads of PCBs for Tidal Portions of the Potomac and Anac	costia
	Ri	vers in	the District of Columbia, Maryland, and Virginia Draft report (DCDE, 2007)	42
	2.1	.12.6	PCB TMDL Model for Potomac River Estuary (USEPA, 1997)	43
	2.1	.12.7	PCB Water Quality Model for Delaware Estuary (DRBC, 2003, 2006)	44
	2.1	.12.8	Importance of DOC in Sediments for Contaminant Transport Modeling (Hwang	et al.,
	19	98)	46	
	2.1.13	U	se of WASP in Other Studies	46
	2.1.14	S	ummary	48
2.	2 PA	ARTICU	ILATE ORGANIC CARBON CONSIDERATIONS	48
	2.2.1	Sam	pling Methods	49
	2.2	2.1.1	Conventional Methods	50
	2.2	2.1.2	More Rarely Used Sampling Methods	51
	2.2.2	Ana	lysis Methods	52
	2.2	2.2.1	Loss-On-Ignition (LOI) Method	53
	2.2	2.2.2	CHN Analysis Method	54
	2.2	2.2.3	TOC-DOC Difference Method	55
	2.2.3	POC	Recommendations	56
CHA	APTER	3 -	DATA ANALYSIS	57
3.	1 20	02-20	03 PCB Dataset Grain Size Analysis	57
	3.1.1	Grai	n Size Spatial Distribution	58
3.	2 H	SC GR	OUNDWATER CONSIDERATION CALCULATION	63

	3.2.1	Intro	oduction	63
	3.2.2	Ove	rview	64
	3.2.3	Арр	roach	65
	3.2.4	Resi	ılts and Discussion	69
	3	3.2.4.1	Groundwater PCB Scenario	69
	3	3.2.4.2	Sensitivity Analysis Scenarios	71
	3.2.5	Con	clusions and Further Considerations	73
3	.3 I	HSC Tr	IBUTARY FLOW SIGNIFICANCE ANALYSIS	74
	3.3.1	Back	ground and Objectives	74
	3.3.2	Flou	v Calculations using Hydrodynamic Modeling Output	75
	3	3.3.2.1	WASP Segmentation and Time Step	76
	3	3.3.2.2	Net Segment Flows	77
	3	3.3.2.3	Average Daily Flow with Negative-Positive Flow Considerations	78
	3.3.3	Resi	ılts and Discussion	78
	3	3.3.3.1	Flow in the Main Channel and the SJR over the simulation period	78
	3.3.4	Flou	o in the Tributaries and their Influence on Main Channel Flow	82
	3.3.5	Con	clusions	85
CH	APTER	R4 C	CURRENT AND ONGOING ACTIVITIES	87
4	.1 (Chann:	EL DREDGING ANALYSIS	87
	4.1.1	Drea	dging Data Retrieval	87
	4.1.2	Pote	ntial Dredging Data Calculations and Uses	90
4	.2	CONTIN	UING GRAIN SIZE ANALYSIS	93
4	.3 (QAPP F	PROGRESS	93
	4.3.1	POC	C Method Selection	94
	4.3.2	Inte	nsive Sediment Survey	94
CH	APTER	R5 -	REFERENCES	98
CH	APTER	R6 -	APPENDICES	103
APP	PENDIX	A -	2002-2003 PCB SAMPLING GRAIN SIZE RAW DATA	104
APP	PENDIX	В -	DAILY FLOW AVERAGES IN THE MAIN CHANNEL AND TRIE	BUTARIES 108
APPENDIX C -		C -	PORT OF HOUSTON AUTHORITY DREDGE SEDIMENT CORE	SAMPLING
GUI	DELIN	Е	109	
APP	PENDIX	D -	REVISION 0 MONITORING QAPP	110
APP	PENDIX	E -	REVISION 0 MODELING QAPP	111

CHAPTER 1 - INTRODUCTION

Polychlorinated biphenyls (PCBs) are widespread organic contaminants which are environmentally persistent and can be harmful to human health even at low concentrations. A major route of exposure for PCBs worldwide is through food consumption, and this route is especially significant in seafood. The discovery of PCBs in seafood tissue has led Texas Department of State Health Services to issue seafood consumption advisories, and some of these advisories have been issued for the Houston Ship Channel (HSC), which is shown according to TCEQ water quality segmentation in Figure 1.1. Two specific advisories have been issued recently for all finfish species based on concentrations of PCBs, organochlorine pesticides, and dioxins. ADV-20 was issued in October 2001 and includes the HSC upstream of the Lynchburg Ferry crossing and all contiguous waters, including the San Jacinto River Tidal below the U.S. Highway 90 bridge. ADV-28 was issued in January 2005 for Upper Galveston Bay (UGB) and the HSC and all contiguous waters north of a line drawn from Red Bluff Point to Five Mile Cut Marker to Houston Point. These two advisories represent a large surface water system for which TMDLs need to be developed and implemented.

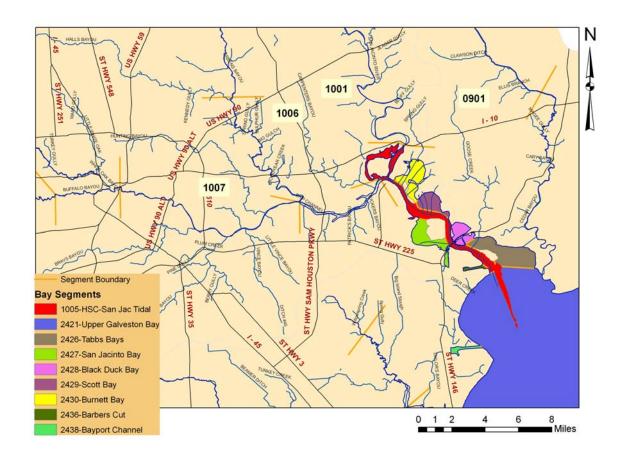


Figure 1.1. Houston Ship Channel water quality segmentation.

1.1 SCOPE OF THE PROJECT

The scope of the PCB TMDL project includes studies and implementations related only to PCBs in the HSC System including Upper Galveston Bay. The work included in the scope currently includes project administration, participation in stakeholder involvement, development of a monitoring plan, preparation of sampling and modeling Quality Assurance Project Plans (QAPPs), and actual monitoring data collection.

1.2 DESCRIPTION OF THE REPORT

This report summarize the activities conducted by the University of Houston on the PCB TMDL Project under Work Order # 582-6-70680-19 for the 1st Quarter, which spans from September 1, 2007 to November 31, 2007.

CHAPTER 2 - LITERATURE REVIEW

2.1 Model Review, WASP Modeling Applications Review, and Selection of Model Applicable for PCB TMDL Studies in the Houston Ship Channel

The main objective of this task is to evaluate existing models that can assist in understanding the impact of environmental process on Persistent Organic Pollutants (POPs)*, elucidating the effects of various sources, determining the effects of control measures, and identifying the maximum permissible total loading.

The modeling framework was developed specifically to address each of the objectives of the HSC PCB fate and transport modeling effort, as well as the requirements identified in the development of the conceptual model. In this section, the principal components of the modeling framework are described, including:

- Criteria used to evaluate the alternative models and to guide model selection.
- Summary of the model selected to represent the HSC watershed system.
- Spatial domain of each model.
- Manner in which the models will be linked for simulations.

2.1.1 Background

Readily available models were inventoried to identify those that could be used as credible tools to develop a quantitative understanding of PCB transport in the HSC. The

^{*} The current project focuses on polychlorinated biphenyls (PCBs), and the previous TMDL study focused on dioxins. Both of these are part of a family of compounds called Persistent Organic Pollutants (POPs). These compounds, while they do not all have the same chemical and physical behaviors are all organic and persistent in the environment and are often grouped in the same class of environmental issue. For purposes of model selection, and since the project team will consider modeling in terms of both dioxin and PCBs, it is convenient to refer to the contaminant of concern in this context as POPs.

purpose of this section is to identify, evaluate, and select candidate models for the HSC modeling framework. The modeling framework that will be used to evaluate the transport and fate of PCBs in the HSC could require any or all of the following types of model formulations:

- 1. In-stream models
- 2. Watershed runoff
- 3. Air Dispersion
- 4. Hydrodynamics
- 5. Sediment transport

2.1.2 In-Stream Models

There is a diverse range of analytical tools or models that simulate the resulting concentration of a compound that derives from some external load. These models vary widely in both approach and complexity. The more simple models tend to either lump together various processes or ignore them, based upon the assumption that the process is relatively insignificant to the fate of the modeled compound. The more complex models may have many more processes and pathways accounted for in the model, but rely upon rates, kinetics and other parameters that may be immeasurable and only approachable in a theoretical basis. The selection of an appropriate model to analyze a given situation is a function of site characteristics, available data and resources and, perhaps most importantly, the objective that the model is intended to achieve. The clear definition of the question the model is expected to resolve then dictates the physical process and kinetics requiring simulation and, ultimately, the selection of the model to be employed.

For example, in the POP studies, the main decisions to be made are whether to simulate bulk concentrations in the water column, dissolved and particulate phase concentrations, sediment concentrations and movement, body burdens in various organisms, or some combination of these. Since the ultimate goal of the TMDL is the

reduction of fish tissue concentrations of dioxins and PCB to levels that would allow the Texas Department of Health to remove the seafood consumption advisory, it must be determined whether it is necessary to model these fish tissue concentrations directly or whether it is appropriate to model an analog such as water column or sediment concentrations.

A number of models have been employed in the simulation of the movement of contaminants such as dioxin and PCBs in the environment. These models range from simple mass balance "box" models to deterministic multidimensional dynamic models. Some of the important water quality in-stream models considered are summarized in Table 2.1.

Table 2.1 Water quality in-stream models

Steady-state water quality models	Dynamic water quality models	Mixing zone models
EPA Screening Procedures	DYNTOX	CORMIX
EUTROMOD	WASP5	PLUME
PHOSMOD	CE-QUAL-RIVI	
BATHTUB	CE-QUAL-W2	
QUAL2E	CE-QUAL-ICM	
EXAMS II	HSPF	
TOXMOD		
SMPTOX3		

2.1.2.1 Analytical Models

For the dioxin TMDL of the Kanawha River, Pocatalico River, and Armour Creek in West Virginia, a simple spreadsheet based analytical dilution model was chosen based upon the assumption that loss processes are insignificant (USEPA, 2000). This model is basically a mass balance that considers neither variations over time or over space and that assumes all losses (degradation, loss to sedimentation, etc.) to be small relative to the overall mass in the system. Often, this type of simple analytical model is used as a screening tool before a more complex model is applied.

2.1.2.2 Steady State Models

In a steady state model all flows, loadings and other inputs are assumed to be constant over time. In addition, all kinetics in the model are also assumed to be constant over time. Most steady state models allow variation over space (upstream, downstream, etc.) for both inputs and kinetics and calculate variation of concentration with distance in the system. However, most steady state models are one dimensional with respect to space. In other words, they predict variations in concentrations in only one dimension, usually upstream to downstream, and assume complete mixing across the cross section. A brief description of some steady state models is discussed below:

SMPTOX4 (Simplified Method Program – Variable-Complexity Stream Toxics Model): This is a steady-state 1-D model that simulates dilution, advection, dispersion, first-order decay and sediment exchange processes for conservative and non-conservative substances (USEPA, 1997). The model is based on an EPA-recommended technique (USEPA, 1990b) for calculating water column and streambed toxic substance concentrations caused by point source discharges into streams and rivers. The model allows the prediction of pollutant concentrations in dissolved and particulate phases for the water column and bed sediments, as well as the total suspended solids concentrations

(USEPA, 1997). However, nonpoint source loadings cannot be simulated, nor can process kinetics be modeled. This model was successfully used for assessing a TMDL for 2,3,7,8-TCDD in the Ohio River (ORVWSC, 2000). Input requirements include stream geometry, flow, total pollutant and suspended solids concentrations, physical/chemical coefficients and rates (USEPA, 1997). The model does not allow reversing flows and, therefore, is not able to simulate tidal flows, which limits its applicability to the Houston Ship Channel for dioxin and PCB TMDL studies.

TOXMOD (Long-Term Trends of Toxic Organics in Lakes): TOXMOD is a steady-state model developed to assess the impact of toxic organic compounds on lakes and impoundments on a long-term basis. The system is idealized as a well-mixed reactor (water layer) overlying a well-mixed sediment layer. The model computes a mass balance for solids and toxics, with toxics being partitioned into dissolved and particulate forms (USEPA, 1997). The model is capable of simulating burial and resuspension for both dissolved and particulate forms and diffusion from the dissolved fraction. This model does not have the capability to simulate reversing flows which limits again its applicability for the dioxin/PCB TMDL studies in the HSC. Input requirements include lake depth and surface area, sediment thickness, settling and burial rates, sorption and volatilization coefficients, decay rates, time series of flow and inflow concentrations of contaminant of concern (USEPA, 1997).

QUAL2E (Enhanced Stream Water Quality Model): QUAL2E is a one-dimensional steady-state water quality model that allows simulation of diurnal variations in temperature (USEPA, 1997). The model includes the effects of advection, dispersion, dilution, constituent reactions and interactions, and sources and sinks (Brown and Barnwell, 1987). The stream is represented as a system of reaches of variable length, which are subdivided into computational elements of the same length for all reaches. A mass and heat balance is applied to each element. QUAL2E does not include a hydrodynamic component, and the flows must be supplied by the user. Since the flow

regime is assumed to be steady state, the flow in the stream channel is equal to the (algebraic) sum of flows across the water-surface boundaries, predominantly the flows through the upstream and downstream ends. An important feature of this model is that it can be applied to estuaries and bays and, therefore, is capable of simulating both seawater and freshwater influxes, and, specifically tidal movement. QUAL2E, however, does not have a capability for modeling sediment and sedimentary processes, which are very important in dioxin/PCB transport and fate. It is possible, though, to include settling and resuspension by calculating net loss rates and inputs for each calculation element. Input requirements include physical, chemical and biological properties for each reach, climate, river geometry, stream network, flow, boundary conditions, inflows/withdrawals (USEPA, 1997).

QUAL-TX (Stream Water Quality Model, Texas): This model is a one-dimensional steady-state model that is very similar to QUAL2E. As is the case with QUAL2E, QUALTX represents a stream as a series of computational "elements," which are grouped into "reaches" to facilitate input of constant parameters. Constituent concentrations at each element are computed using a finite difference solution of the advection-dispersion equation with various source and sink terms (Ward and Benaman, 1999). QUAL-TX provides for multiple pollutant inputs, withdrawals, tributary flows and incremental inflow and outflow. Similar to QUAL2E, this model is capable of simulating reversing flows in tidal areas. However, since both QUAL-TX and QUAL2E are steady-state models, they are applicable only to tidal-mean conditions in an estuary under steady inflow and loadings (Ward and Benaman, 1999). The model could be used only if the dioxin/PCB concentrations in the Houston Ship Channel are estimated by including net loss rates and inputs for settling and resuspension for each calculation element. Input requirements include parameters same as said for the QUAL2E model above.

2.1.2.3 <u>Dynamic Models</u>

A dynamic model allows variations in input and sometimes kinetics over time as well as spatially. The results from a dynamic model also vary in both space and time. There are a number of different types of dynamic models that each has associated advantages and disadvantages. Often dynamic models are utilized to simulate episodic events such as high flow storm water events. Generally, dynamic models are very resource intensive from the standpoint of data requirements, effort to develop, and computer resource requirements. In addition, dynamic models are often two or three dimensional with respect to space, allowing variation in simulated results longitudinally, laterally and with depth.

WASP (Water Quality Analysis Simulation Program): WASP is a dynamic model that can be applied in 1-, 2-, or 3-D and can be linked with simulated hydrodynamics. It simulates advective and dispersive transport and considers resuspension/deposition and benthic exchange (USEPA, 1997). WASP includes two submodels for water quality and toxics referred to as EUTRO and TOXI. It is important to note that zooplankton dynamics are not simulated in this model. Input requirements include water body geometry, climate, water body segmentation, flow (or input from hydrodynamic model), boundary conditions, initial conditions, benthic flux, external loadings, spatially variable and time-variable functions, rate constants. The reason for use of WASP for modeling the dioxin/PCB concentrations in the Houston Ship Channel is discussed in detail later. The WASP model has been used to evaluate dioxin bioaccumulation in Lake Ontario (USEPA, 1990a). WASP traces each water quality constituent from the point of spatial and temporal input to its final point of export, conserving mass in space and time. To perform these mass balance computations, the user must supply WASP with input data defining seven important characteristics:

- Simulation and output control
- Model segmentation

- Advective and dispersive transport
- Boundary concentrations
- Point and diffuse source waste loads
- Kinetic parameters, constants, and time functions
- Initial concentrations

EcoFate: The EcoFate model is an example of dynamic model that was utilized for simulation of dioxin fate and transport in the Fraser River Watershed (Gobas et al., 1998). This is a 3-D model that uses compartments to represent spatial differences in an ecosystem. These compartments consist of sub compartments that can be subdivided horizontally to represent thermoclines or surface flow processes. The model includes suspended sediments and a bed-sediment compartment. EcoFate is a dynamic model capable of simulating seasonal variations in concentrations. The model integrates all the environmental media (water, sediments, benthos, vegetation, and fish). However, it requires knowledge of the uptake and elimination routes of dioxins/PCBs in fish and their corresponding rates, which may make it an impractical model for the HSC TMDL study. The model has the strength of being capable of including point source discharges, atmospheric inputs, and runoff.

2.1.3 Runoff Models

In order to assess a watershed or to develop a TMDL, the effects of land uses and practices on pollutant loading to water bodies need to be evaluated. A common tool to perform such evaluation is the use of watershed-scale loading models. These models vary widely in both approach and complexity. As with in-stream models, the more simple models tend to either lump together various processes or ignore them, based upon the assumption that the process is relatively insignificant to the fate of the modeled compound. The more complex models may have many more processes and pathways

accounted for in the model, but rely upon rates, kinetics and other parameters that may be more difficult to measure. Watershed runoff models are designed to link precipitation, climatological factors, basin topography, surface and subsurface infiltration characteristics, and land uses to develop a basin scale water balance to simulate time-varying stream flow and groundwater inflow. Erosion characteristics of the various land uses are then coupled with surface runoff and empirical formulations to estimate non-point loads of sediment yield, nutrients, chemicals, and organic matter within a watershed.

Table 2.2 presents an inventory of watershed runoff models available for the modeling framework depending on the usage area. In a watershed model, the spatial resolution of drainage basin properties is described using either: (1) zero-dimensional, sub-watershed scale "lumped" parameters; or (2) two-dimensional, physically based spatially distributed parameters. HSPF is an example of a "lumped" parameter watershed model. MODFLOW-HMS is an example of physically based, spatially distributed watershed models. Watershed runoff models have been developed to represent limited land use categories such as urban land uses (SWMM) or agricultural and rural land uses (AGNPS; SWAT; GWLF). In addition to these types of limited land uses, watershed models (HSPF) have also been developed to represent a mix of urban, rural, forested, and agricultural land uses. Runoff models were also developed to target specific contaminants such as agricultural pesticides, suspended sediment, nutrients, or heavy metals. These models have the capability to simulate stream flow and runoff over time scales ranging from an hour to a year or longer. Watershed-scale loading models can be grouped into three categories: simple methods, mid-range models, and detailed models (USEPA, 1997). The level of application of each model depends upon the objectives of the analysis.

Table 2.2 Inventory of Watershed Runoff Models

Model	Type of Model	Source
AGNPS	Agriculture/rural	USDA-ARS
BASINS	Urban/non-urban	EPA OS&T
GWLF	Agriculture/urban	EPA OWOW
HSPF	Urban/non-urban	EPA OS&T
SWAT	Agriculture/rural	USDA-ARS
SWMM	Urban	EPA CEAM
MODFLOW-HMS	Two-dimensional	Hydro Geologic

2.1.3.1 Simple Methods

Simple methods can be used to support an assessment of the relative significance of different sources. They provide a rapid means for identifying critical areas and data requirements. They are typically derived from empirical relationships between physiographic characteristics of the watershed and pollutant export (USEPA, 1997). They provide rough estimates of sediment and pollutant loadings and, therefore, have limited predictive capacity. For this reason, this category of runoff models may not be useful for TMDL studies in the HSC.

2.1.3.2 Mid-range Models

Mid-range models simulate multiple pollution sources and impacts over a broad geographic area and, thus, they are useful in defining target areas for pollution mitigation programs within a watershed. These models, however, use simplifying assumptions that can limit the accuracy of their predictions (USEPA, 1997). A mid-range model such as SLAMM is a candidate to assess dioxin/PCB loading to the HSC via runoff.

Source Loading and Management Model (SLAMM) identifies pollutant sources and evaluates the effect of different stormwater control practices on runoff (USEPA, 1997). SLAMM computes continuous mass balances for particulate and dissolved pollutants and runoff volumes. Runoff, which is calculated using a method developed by Pitt (1987), is calculated for both pervious and impervious areas. Pollutant loadings are estimated using exponential buildup and rain wash-off and wind removal functions. The model was found to be representative of Texas hydrological systems and Texas hydroclimates (Ward and Benaman, 1999). The basin to be modeled must be subdivided into elemental "lumped" watersheds by the user. The runoff and contaminant loads from each such area are determined by empirical relations, and then accumulated.

2.1.3.3 Detailed Models

Detailed models provide relatively accurate predictions of variable flows and water quality at any point in a watershed. However, these models require considerable time and resource expenditure for data collection and model setup (USEPA, 1997). Candidates for this task include SWMM and HSPF. Depending on the effect of runoff on fate and transport of dioxin/PCB in the HSC for a period following the rainy events, the modeling might include runoff simulations and dynamic models may be required. An additional requirement is the capability of the model to represent data sets collected along the HSC over a time span following a wide range of antecedent moisture conditions. To achieve this goal efficiently, a continuous model is a practical necessity. Ward and Benaman (1999) have conducted a survey and review of models for TMDL application in Texas. They concluded that the following are the most appropriate existing models for watershed simulation:

 Hydrologic Simulation Program – FORTRAN (HSPF) by the U.S. Environmental Protection Agency.

- Soil and Water Assessment Tool (SWAT) by the Agricultural Research Service of the U.S. Department of Agriculture.
- Precipitation-Runoff Modeling System (PRMS) by the U.S. Geological Survey.

They noted that while these were recommended, each has significant weaknesses and limitations for Texas applications. They also identified the EPA Storm Water Management Model (SWMM) as a specialized model that may be applicable for some TMDL problems in urban areas. Since PRMS does not include a water-quality capability, it was not further considered in their evaluation. Ward and Benaman commented that the greatest weakness of SWAT is its reliance on the empirical formulations of the curve number method and the universal soil loss equation. Between SWAT and HSPF, the deterministic basis of HSPF hydrology and sediment loading is preferred. SWMM simulates storm events with rainfall input, other meteorological inputs and system characterization to predict runoff water quantity and quality. It is capable of modeling the rainfall/runoff process, including surface and subsurface flows, runoff water quality, transport routing through the drainage networks or channel systems, and through a set of storage and treatment units. HSPF simulates the hydrologic and water quality processes on pervious and impervious land surfaces as well as streams. It uses a conceptual framework to account for the fluxes and storage involved in interception, infiltration, overland flow, interflow, groundwater and evapotranspiration. The model performs fate and transport of water quality constituents in one-dimensional channels. Both SWMM and HSPF are capable of modeling the following processes that are relevant in the TMDL study:

- Build-up and washoff of water quality constituents in the watershed.
- Water quality routing by means of advection and mixing in the stream.
- In-stream first-order decay of water quality constituents.
- Scour and deposition of sediments in the stream.

SWMM was originally developed for a particular event simulation. A continuous simulation capability has been added in a later version. In order to perform continuous simulation, the model needs to account explicitly for antecedent moisture conditions. In contrast, HSPF was developed as a continuous model. It computes a continuous moisture balance within a watershed, taking into account evapotranspiration and other long-term hydrologic abstractions that are responsible for the change in moisture during dry periods. It appears that HSPF is the better choice for continuous simulation. Input requirements for SWMM include metereologic and hydrologic data, land use distribution, accumulation and washoff parameters, and decay coefficients. Input requirements for HSPF include metereologic and hydrologic data, land use distribution, loading factors and washoff parameters, receiving water characteristics, decay coefficients.

2.1.4 Air Dispersion Models

2.1.4.1 Industrial Source Complex Short Term Model (ISCST3)

ISCST3 is a Gaussian plume model, which computes ambient air concentrations and surface deposition rates at specified receptor points. The model accepts a variety of source geometries and schedules. This short-term model uses hourly wind speed, wind direction, and stability for describing dispersion. The ISCST3 model was used by EPA for its Dioxin Reassessment Document (USEPA, 2000) and its performance in predicting dioxin concentrations was examined using data from the Columbus Municipal Waste-to-Energy Facility in Columbus, OH (Lorber et al., 1999). The default modeling options of the ISCT models include the use of stack-tip downwash, buoyancy-induced dispersion, final plume rise (except for sources with building downwash), a routine for processing averages when calm winds occur, default values for wind profile exponents and for the vertical potential temperature gradients, and the use of upper bound estimates for buildings having an influence on the lateral dispersion of the plume. The model can use either rural or urban dispersion parameters, depending on the characteristics of the source

location. The model also has the option of calculating concentration values or deposition values for a particular run.

The model is capable of handling multiple sources, including point, volume, area and open pit source types. Line sources may also be modeled as a string of volume sources or as elongated area sources. Several source groups may be specified in a single run, with the source contributions combined for each group.

The Short Term model also contains an algorithm for modeling the effects of precipitation scavenging for gases or particulates. For the Short Term model, the user may specify for the model to output dry deposition, wet deposition and/or total deposition. Source emission rates can be treated as constant throughout the modeling period, or may be varied by month, season, hour-of-day, or other optional periods of variation. These variable emission rate factors may be specified for a single source or for a group of sources. For the Short Term model, the user may also specify a separate file of hourly emission rates for some or all of the sources included in a particular model run.

2.1.4.2 <u>Regional Lagrangian Model of Air Pollution (RELMAP):</u>

The Regional Lagrangian Model of Air Pollution (RELMAP) is used to simulate the emission, transport and diffusion, chemical transformation, and wet and dry deposition of various chemicals. This model was used for the analysis of atmospheric deposition of mercury to the Savannah River Watershed and to determine the relative contributions of clusters of several thousands of emission sources, as well as the spatial patterns of mean air concentrations and wet and dry deposition amounts. Comments from the Dioxin Workshop on Deposition and Reservoir Sources held in Washington, D.C., in July 1996 indicated that the RELMAP model was doing an accurate job of simulating the spatial patterns of deposition of dioxins, given the levels of scientific uncertainty that still exist regarding the semi-volatile behavior of the various dioxin/furan compounds modeled. However, the magnitude of the simulated deposition appeared to be much smaller than experimental monitoring studies would suggest.

2.1.4.3 Models – 3 Community Multi-Scale Air Quality (CMAQ) Modeling System

This model is a third generation air quality model and assessment system, which combines Models 3 and CMAQ. Models-3 allows the building of a modeling system to suit the needs of the project. It can assist the developer with creating, testing, and performing comparative analysis of new versions of air quality models. It allows the user to execute models and visualize the results. CMAQ allows for modeling of urban to regional-scale air quality, which can include tropospheric ozone, acid deposition, visibility, toxics, and fine particles.

Models-3/CMAQ is a system of compatible atmospheric transport models and data analysis tools. CMAQ can model acid precipitation, photochemical oxidant, and aerosol chemical and physical processes for up to five days after emission event (an "event" model) over areas ranging from 100 to 5000 km. It uses a workstation, is easy for people with moderate technical expertise to operate, and can be run at different grid sizes.

Models-3 and Community Multi-scale Air Quality (CMAQ) software in combination form a powerful air quality modeling and assessment system that enables users to execute air quality simulation models for their specific problem domain and visualize the results. The primary goals for the system are to improve 1) the environmental management community's ability to evaluate the impact of air quality management practices for multiple pollutants at multiple scales and 2) the scientist's ability to better probe, understand, and simulate chemical and physical interactions in the atmosphere.

The Models-3 release contains two types of environmental modeling systems, emission, and chemistry transport, and a visualization and analysis system. Emissions Modeling System simulates trace gas and particle emissions into the atmosphere depending on surrounding meteorological conditions and socioeconomic activities. Chemistry/Transport Modeling System simulates various chemical and physical processes that are thought to be important for understanding atmospheric trace gas

transformations and distributions. Visualization and Analysis System plots and graphs data that have been created by one of the Models-3 modeling systems or that have been imported into Models-3.

2.1.4.4 Regulatory Modeling System for Aerosols and Deposition (REMSAD)

REMSAD can model mercury, cadmium, dioxin, polycyclic organic matter, atrazine, primary and secondary particles, and nitrate, and can be run on a workstation or high-end PC. It includes a nested grid system (grids can vary in size from 60 to 4 km) and can be run for an entire year's worth of meteorological data for the entire country or specific areas. REMSAD has been used to estimate wet and dry deposition rates for mercury over the United States on a variable grid size, with fine resolution (12-20 kilometers) over the Great Lakes, Northeastern US, and South Florida, among others, and a coarser (36-60 kilometers) resolution over the remainder of the U.S.

2.1.4.5 Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT)

This computer model has been chosen to simulate the atmospheric fate and transport of pollutants from sources in the United States and Canada to the Great Lakes. HYSPLIT was originally developed at the U.S. National Oceanic and Atmospheric Administration (NOAA) for medium and long-range transport modeling of accidental releases of radioactive materials. It is currently used operationally for emergency response at NOAA. HYSPLIT is a Lagrangian model, in which puffs of pollutant are emitted from user-specified locations, and are then advected, dispersed, and subjected to destruction and deposition phenomena throughout the model domain. It has been used to simulate many different atmospheric processes, including sulfur transport and deposition in the U.S. (Rolph et al., 1992, 1993) and dispersion of pollutants from Persian Gulf oil fires (Draxler et al., 1994). A modified version of the NOAA HYSPLIT model was used

to simulate the atmospheric fate and transport of dioxin from sources in the United States and Canada to the Great Lakes. Modeling of the atmospheric fate of dioxin performed using this model includes simulation of vapor/particle partitioning, wet and dry deposition, reaction with the hydroxyl radical, and photolysis. The methodology involves simulations of the fate and transport of specific dioxin congeners from unit-source-strength sources at a range of different source locations.

2.1.4.6 <u>Regional Atmospheric Modeling System (RAMS)</u>

The Regional Atmospheric Modeling System (RAMS), developed at Colorado State University, is a mesoscale model. RAMS is a primitive, nonhydrostatic model based on a terrain following coordinate system. Subgrid-scale turbulent diffusion is parameterized using a 2.5-level turbulence closure with prognostic turbulent kinetic energy equation. Shortwave and long wave parameterizations are used to determine the heating or cooling due to radiative fluxes. Prognostic soil-vegetation relationships are used to calculate the diurnal variation of temperature and moisture at the groundatmosphere interface. Turbulence sensible heat, latent heat, and momentum fluxes in the surface layer are based on similarity equations. RAMS also contains cumulus and explicit microphysics parameterizations. The model can be configured to cover an area as large as a hemisphere to simulate synoptic-scale atmospheric systems. Two-way interactive grid nesting allows fine mesh grids to resolve mesoscale atmospheric systems using a grid spacing as small as 1 km, while simultaneously simulating the large-scale environment on a coarser grid. A nudging four-dimensional data assimilation technique has been incorporated into the model so that mesoscale analyses, which combine predicted and observed variables, can be produced if needed.

2.1.5 Hydrodynamic Models

Hydrodynamic models account for the movement of surface water using equations for fluid motion. The level of detail used to solve these equations is driven by the availability of computer technology and numerical methods to perform the necessary calculations. Improvements in computer technology and advanced numerical methods have enabled the development of physically realistic representations with very few simplifying assumptions. The fundamental principle behind modeling flow in surface water is conservation of momentum, as well as mass and energy. All flow models are based on, at a minimum, conservation of momentum and are classified as either hydraulic or hydrodynamic models. Hydraulic models, developed only for one-dimensional applications for streams and rivers, generally require many simplifying approximations to the equations of motion. In some cases, hydraulic models have evolved from empirical approximations such as Manning's relationship for steady-state open channel flow. Even this simplified method is based on conservation of momentum and the elimination of all the acceleration terms in the equations of motion, except for the balance of forces governed by bottom slope and bottom friction.

Hydrodynamic models are more complex than hydraulic models because they use fewer approximations to the equations of motion. Hydrodynamic models, constructed to represent realistic geometry of shorelines and bathymetry with two-dimensional and three-dimensional grids, require advanced numerical methods to solve the time-dependent equations for the horizontal and vertical distributions of water surface elevation, salinity, water temperature, and velocity. Vertical stratification, and its influence on the vertical flux of horizontal momentum in a water body, is represented in some hydrodynamic models. The complexity of methods used to represent closure of turbulent mixing processes also differentiates hydrodynamic models. Brief overviews of several of these models are presented below with the discussion organized as one-dimensional, two-dimensional, and three dimensional models. The inventory of hydraulic and hydrodynamic models available for modeling framework is listed in Table 3.3.

Table 2.3 Inventory of Watershed Runoff Models

Model	Type of Model	Source
HEC-2	1D	USACE Hydrologic Engineering Center
CE-QUAL-RIV1	1D	USACE/WES
FLDWAV2.0	1D	NOAA
RIVMOD	1D	EPA CEAM
MIKE11	1D	DHI Water & Environment
EFDC-1D	1D	EPA Region IV; Tetra Tech
MODFLOW-HMS	2D	Hydro Geologic
TABS-2	2D	USACE/WES
HSCTM-2D	2D	EPA CEAM
RMA-2	2D	Resource Management Assoc.
FESWMS-2D	2D	USGS
POM	3D	OAA Geophysical
ECOM-3D	3D	HydroQual
CH3D-WES	3D	USACE/WES
EFDC	3D	EPA OS&T/Tetra Tech

2.1.5.1 One-Dimensional Models

For steady-state, uniform flow conditions, Chezy and/or Manning's equations are used to describe the interactions of flow, cross-sectional area, bottom friction, water

surface elevation, and velocity within a spatially homogeneous reach. The Manning equation, for example, is used to determine water depth and velocity in QUAL2E, a widely used one-dimensional, steady-state, water quality model supported by EPA. For steady flow conditions where changes in flow depths of the water surface along the length of a river channel result from reaches characterized by different bottom slope and varying cross-sectional geometries, steady flow, non-uniform hydraulic models have been developed, for example, the USACE HEC-2 Water Surface Profile model. The HEC-2 model is used to provide flow and velocity data for HEC-6, a USACE sediment transport model.

In developing one-dimensional, steady, non-uniform hydraulic models, the model equations are simplified by assuming that lateral and vertical variations in velocity have a negligible effect on kinematic energy or velocity head. Many one-dimensional numerical models have been developed for a complete dynamic solution of the conservation of momentum and mass equations. In contrast to the kinematic wave model, a dynamic model of flow in a moderate gradient river requires specification of both upstream and downstream boundary conditions for either flow and/or water surface elevation to allow for the representation of both kinematic and dynamic waves. The practical implication of this hydraulic condition is that downstream conditions can exert a considerable influence on upstream velocity and depth through the backwater effects of a dam, impoundment, or some other blockage (such as debris) to flow in a moderate gradient river.

The "pseudo two-dimensional" link-node model, DYNHYD, available with WASP water quality model, is an example of a one dimensional dynamic model that uses an explicit solution scheme to simulate velocity and water surface elevation. Examples of implicit one-dimensional dynamic models include: CE-QUAL-RIV1 developed by the USACE WES; FLDWAV, DWOPER, and DAMBRK developed by the National Weather Service; BRANCH developed by USGS; RIVMOD developed by Hosseinipour and Martin for EPA; and MIKE11 developed by the Danish Hydraulic Institute. EFDC-1D, a modified version of EFDC, developed for EPA, also uses an implicit solution

technique to provide an advanced hydrodynamic model for simulations of transport in branched networks of one-dimensional, variable cross-section streams and rivers.

2.1.5.2 Two-Dimensional Models

Two-dimensional, depth-averaged hydrodynamic models have been developed using both finite difference and finite element solution techniques for application to rivers, estuaries, coastal waters, and shallow lakes and reservoirs. MODFLOW-HMS, developed by HydroGeologic, Inc., is an integrated two-dimensional model applied for overland flow and one dimensional river channel hydraulics. MIKE21 is a twodimensional model developed by DHI Water & Environment. The USACE WES has developed the WES Implicit Flooding Model, constituent transport finite difference model (WIFM-SAL), and TABS-2 modeling system for two-dimensional hydrodynamics and sediment transport (Thomas and McNally, 1985). The Hydrodynamics, Sediment and Contaminant Transport Model (HSCTM-2D) is a two-dimensional, finite element, hydrodynamic sediment transport, and contaminant transport model developed by Hayter et al. (1999) for EPA. RMA-2, a two-dimensional finite element hydrodynamic model developed by Resource Management Associates, is included as the hydrodynamic component of both the TABS-2 modeling system and the HSCTM-2D sediment transport model. The Finite Element Surface Water Modeling System is a two-dimensional depthaveraged model available from USGS.

2.1.5.3 Three-Dimensional Models

Since the mid-1980s, three-dimensional hydrodynamic models, which can also be applied for one- and two-dimensional problems, have become an indispensable tool for advanced sediment transport, water quality, eutrophication, and contaminant transport and fate modeling studies. More recent three-dimensional hydrodynamic models employ

turbulence closure schemes to simulate horizontal and vertical mixing. These models can also represent complex shorelines and bathymetry with Cartesian or boundary-fitted curvilinear coordinates to define the horizontal plane and bottom-following sigma-stretched coordinates to define the vertical plane. Although three-dimensional models were originally developed for estuarine and coastal ocean applications, these models are now increasingly being used to simulate hydrodynamics for water quality studies of rivers, lakes, reservoirs, and wetlands. With the appropriate spatial resolution, the use of a three-dimensional grid scheme for a river model can allow for a realistic dynamic simulation of meander-induced secondary currents, lateral gradients in bottom stresses, and resulting cross-channel gradients of sediment deposition and erosion and contaminant transport and fate.

2.1.6 Sediment Transport

Suspended solids and sediment bed solids in surface waters are derived from natural geomorphologic processes related to external weathering, erosion and surface runoff of solids in a drainage basin, and in situ deposition and resuspension of solids between the water column and sediment. Erosion processes in a watershed can be greatly altered by industrial, residential, and urban land use activities that change the timing of runoff and increase the input of solids to a water body. The deposition and resuspension of solids defines an important pathway for the transfer of a contaminant among the water column, sediment bed, and aquatic food web. Because of the known contamination of the river sediment and floodplain, and the affinity of PCBs to adsorb to solids, a sediment transport model, coupled with the hydrodynamic model, could be a necessary component of the HSC modeling framework. A sediment transport model represents the movement of inorganic solids both as suspended load and bed load within the water column, the exchange of solids between the water column and the surficial sediment bed, and the exchange of solids within the sediment bed. Solids are transported in the water column by advection, turbulent mixing, and settling. Solids are exchanged between the water column

and sediment bed by deposition and resuspension. Brief overviews of the sediment transport models available and their applicability for the HSC will be discussed in the next quarterly report.

2.1.7 Selection of Models

The availability of an established, well-documented model in the public domain is a primary criterion for incorporation in the modeling framework. Many watershed runoff, hydrodynamic, sediment transport, contaminant fate, water quality, and ecosystem models, although technically excellent models possessing a high degree of scientific credibility, are either proprietary or are not widely available. Therefore, proprietary models are not advisable unless deemed necessary for the modeling framework. Models that are considered should have at least the following initial criteria: (1) Public domain with source code availability, (2) Ability to be linked to other interlinked models, (3) User documentation and support, (4) Record of previous application history, and (5) Deterministic/mechanistic and mass-balance-based.

2.1.8 In-stream Quality Model to Estimate the Transport and Fate of PCB Compounds in the Houston Ship Channel

Water Quality Analysis Simulation Program (WASP) model: The Water Quality Analysis Simulation Program (WASP) is a dynamic compartment model that can be used to simulate contaminant fate and transport in surface water. WASP consists of a main program, WASP, and three subprograms: EUTRO, TOXI, and DYNHYD. EUTRO is used to model BOD/DO eutrophication, TOXI to simulate toxic chemicals (tracers, organics, metals), and DYNHYD to simulate hydrodynamics. WASP can be applied in 1-, 2-, or 3-D and can be linked to simulated hydrodynamics and sediment transport models. The model includes both the surface water column and the underlying benthic

sediment layer. WASP simulates the varying processes of advection, dispersion, point and non-point mass loading, deposition/resuspension, and boundary exchange. Input requirements include water body geometry, climate, water body segmentation, flow (or input from hydrodynamic model), boundary conditions, initial conditions, benthic flux, external loadings, spatially variable and time-variable functions, and rate constants.

The basic principle of both the hydrodynamics and water-quality program is the conservation of mass. The water volume and water-quality constituent masses being studied are tracked and accounted for over time and space using a series of mass balancing equations. The hydrodynamics program also conserves momentum, or energy, throughout time and space. As said above, the WASP system consists of two stand-alone computer programs, DYNHYD and WASP, which can be run in conjunction or separately. The hydrodynamics program, DYNHYD, simulates the movement of water while the water quality program, WASP, simulates the movement and interaction of pollutants within the water. While DYNHYD is delivered with WASP, other hydrodynamic programs have also been linked with WASP. RIVMOD handles unsteady flow in one-dimensional rivers, while SED3D handles unsteady, three-dimensional flow in lakes and estuaries. An advantage of WASP in many modeling strategies is its ability to link to other models through input and output formatting. Although DYNHYD is set up to be read directly into WASP, it is fairly easy to use different hydrodynamic models such as RMA, and format their output for input to WASP. RMA2 was used as the hydrodynamic model in the dioxin TMDL project due to the DNYHYD model inability to model the hydrodynamic characteristics more accurately in the HSC for the dioxin study, details discussed later. The hydrodynamic results from RMA were then linked to the WASP water quality program through use of an interface.

Key steps in the in-stream modeling include the following:

 Modification of the numerical model to reflect the kinetics of dioxin/PCB adsorption and desorption on sediments and the bioavailability of dioxin/PCB in sediments to aquatic organisms in the study area.

- Compilation and preparation of water quality, fish tissue, deposition, and other data on dioxin/PCB.
- Model calibration to existing conditions using the collected data.
- Sensitivity analyses to show the extent of variation or uncertainty in the model to changes in various parameters in the model.

2.1.9 Selection of Hydrodynamic Model as Input to WASP

Hydrodynamic Model (DYNHYD): As said above, WASP modeling program in whole consists of two stand-alone computer programs, DYNHYD and WASP, which can be run in conjunction or separately. The Hydrodynamic Program (DYNHYD) is a simple link-node hydrodynamic program capable of simulating variable tidal cycles, wind, and unsteady flows. It produces an output file that supplies flows, volumes, velocities, and depths (time averaged) for the WASP modeling system. The WASP hydrodynamics model DYNHYD is an enhancement of the Potomac Estuary hydrodynamic model which was a component of the Dynamic Estuary Model. DYNHYD solves the one-dimensional equations of continuity and momentum for a branching or channel-junction (link-node), computational network. Driven by variable upstream flows and downstream heads, simulations typically proceed at one- to five-minute intervals.

The hydrodynamic model solves one-dimensional equations describing the propagation of a long wave through a shallow water system while conserving both momentum (energy) and volume (mass). The equation of motion, based on the conservation of momentum, predicts water velocities and flows. The equation of continuity, based on the conservation of volume, predicts water heights (heads) and volumes. This approach assumes that flow is predominantly one-dimensional, Coriolis and other accelerations normal to the direction of flow are negligible, channels can be adequately represented by a constant top width with a variable hydraulic depth, i.e., rectangular, the wave length is significantly greater than the depth, and bottom slopes are

moderate. The resulting unsteady hydrodynamics are averaged over larger time intervals and stored for later use by the water quality program.

The DYNHYD model was the initial hydrodynamic model selected for dioxin study because of its relatively easy interface with WASP, model used for in-stream modeling. However the hydrodynamic model had the following limitations:

- It can treat fairly complex branching flow patterns but it cannot handle stratified water bodies.
- DYNHYD only allows up to 5 variable inputs (inflows).
- The variable inflow only allows up to 100 breaks in the flow series.

It was determined that the model does not predict reverse flows for the reaches upstream of the San Jacinto river even though they were observed via flow sampling. In an attempt to find the cause of this, the freshwater flows were eliminated and the model rerun. The model predicted some negative flows for the reaches upstream of the San Jacinto River but did not seem to represent the flow reversal magnitude observed. Furthermore, exclusion of the freshwater flows from the input cannot be justified which suggests problem with using DYNHYD for the HSC projects. Therefore, in order to continue with model development and to meet TMDL objectives, possible alternative hydrodynamic models were used. So RMA2 was chose to model the hydrodynamics of the HSC system.

Resource Management Associates-2 (RMA2): RMA2 is a two-dimensional depth averaged finite element hydrodynamic numerical model. It computes water surface elevations and horizontal velocity components for subcritical, free-surface two-dimensional flow fields. The program has been applied to calculate water levels and flow distribution around islands, flow at bridges having one or more relief openings, in contracting and expanding reaches, into and out of off-channel hydropower plants, at river junctions, and into and out of pumping plant channels, circulation and transport in

water bodies with wetlands, and general water levels and flow patterns in rivers, reservoirs, and estuaries.

The initial version of the Houston Ship Channel RMA2 model presented a few problems and to address the issues the following changes were made to the model:

- The geometry of 1-D elements at some junctions was modified to eliminate water leaks,
- Upstream reaches with bottom elevations above -0.5 m mean sea level (msl) were eliminated and the associated volume replaced using off-channel storage,
- The RMA2 model segmentation was refined (from 1032 to 3356 elements) to minimize mass balance problems,
- Continuity lines were specified so that at least two RMA2 elements were on each side of the continuity line.

2.1.10 HSCREAD Interface

Once the hydrodynamic model was completed with RMA2, it was necessary to organize the RMA2 output in a format that could be read by WASP. In addition, because the model segmentation for WASP differed from that of RMA2 (the WASP segments are coarser than the RMA2 elements), it was necessary to "aggregate" the RMA2 results for all the elements that composed a WASP segment. These two operations were accomplished using an interface (HSCREAD) written for this project using Fortran 90. Briefly, HSCREAD reads the output and geometry files from RMA2 and processes 1-D and 2-D segments. Because there was a small difference in the volume of WASP elements calculated using the two methods described, flows were corrected to eliminate any potential errors with the water quality model. When all the calculations are completed, HSCREAD formats a "HYD" file, which is the hydrodynamic file that can be read by WASP. Five records comprise the external hydrodynamic file.

2.1.11 Final Selection of Models for the HSC Modeling Framework

The hydrodynamic model RMA2 was successful in simulating the tidal flows during the dioxin TMDL project and so will be continued with. Once the hydrodynamic model was completed with RMA2, the interface HSCREAD would be used to organize the RMA2 output in a format that could be read by the water quality model. As part of the modeling studies, the important step is to develop an in-stream quality model to estimate the transport and fate of PCB compounds in the Houston Ship Channel. So a dynamic model which allows variations in input-kinetics over time as well as spatially is necessary. Due to its advantages over other models in modeling HSC (tidal wave effects) and the fact that WASP has been successfully used in modeling organic and inorganic compounds and in TMDL projects (discussed in detail below), WASP was chose as the in-stream quality model. The relative significance of PCB loading via runoff and deposition will be evaluated if the results show that the two sources are very important. From the current dioxin results runoff and deposition were found to be insignificant dioxin sources to the HSC and so runoff and deposition models did not seem necessary. Similar results are also expected in the case of PCB TMDL study, however if results warrant appropriate models will be chosen at that point of time. In regards to sediment transport model, its importance and the models that are available will be researched in the literature.

Similar to the dioxin TMDL modeling, RMA2 was used for hydrodynamic modeling followed by WASP for mass transport in a modeling study of tidal wetlands and was successfully applied (Yang et al., 2007). The water quality and ecosystem model was developed to simulate nutrients, heavy metals, and aquatic plants in the Erh-Chung Flood Way wetland in Taiwan. A sediment system was incorporated into the model. The RMA2 and WASP/EUTRO5 models were adopted as the basic framework with modifications and enhancement of kinetics to incorporate ecosystem dynamics and sediment-water interactions. Hydrodynamic results from the RMA2 model were used to quantify mass transport for the EUTRO5 model. The major effort in this study was

adding four water quality variables; macrophyte biomass, suspended solids, heavy metals in macrophytes, and heavy metals in the water column and sediment were incorporated into EUTRO5 to form the water quality and ecosystem model. Site-specific water quality data were collected to support the model calibration and verification analyses.

2.1.12 Record of Previous Application of WASP in PCB/Dioxin Studies

2.1.12.1 The Lake Michigan Mass Balance Project (USEPA, 2006)

The first models of toxic chemical transport and fate were developed for the Great Lakes by Thomann and Di Toro (1983). This framework was also applied to Saginaw Bay (Richardson et al., 1983) which was the first attempt to calibrate a model to a collected dataset for PCBs. The basic WASP transport and fate framework was revised to include more detailed processes involving particulate fractions (Bierman et al., 1992; DePinto et al., 1993). This model was referred to as GBTOX. In the same project, WASP4 was also modified to improve the simulation of sediment transport, based upon process research and modeling of settling and especially resuspension processes in the Fox River (Velleux and Endicott, 1994). This model was named IPX. Each of these models was developed to simulate the transport and fate of PCBs. Results showed that the greatest, external gross input of PCBs to the system was atmospheric vapor phase absorption followed by tributary inputs and atmospheric deposition, respectively. The greatest gross losses from the system were volatilization and deep burial in sediments. Internal PCBs loading from sediment resuspension was found to be substantial.

2.1.12.2 <u>Transport of polychlorinated biphenyls (PCB) in the Scheldt Estuary simulated</u> with the water quality model WASP (Vuksanovic et al., 1995)

The Scheldt Estuary is situated in the northwest of Belgium and the southwest of the Netherlands. Domestic and industrial activities were found to significantly disturb the natural balance in the estuary, causing serious pollution problems. The industrial compounds known as polychlorinated biphenyls (PCB) were, among many other toxic substances, present in the Scheldt Estuary. According to investigations concentration levels of PCB in the Scheldt river were much higher than in any other river draining to the North Sea and the total annual riverine input of PCB into the estuary was estimated at 400 kg. Because PCB was stored in estuarine sediment, only a small fraction of this input was transported to the sea, increasing ecotoxicological risks in the estuary.

The behavior of PCB in the Scheldt Estuary was governed by dynamic transport of water and sediment, while hydrophobic sorption was the most important physicochemical reaction. In order to analyze and quantify the present distribution of these micro-pollutants in the estuary, a modeling study was conducted. The water quality model WASP was selected for this. The water quality model WASP was applied to simulate the spatial distribution of 12 selected PCB isomers (PCB 26, 28, 31, 44, 49, 52, 101, 118, 138, 153, 170, and 180). The simulations were performed under average hydrodynamic and suspended sediment transport regimes. The hydrodynamic module of WASP was based on one-dimensional unsteady flow in an open channel.

Generally, as reported observations agreed with simulation results for hydrodynamic, salinity and suspended sediment transport. Hydrophobic sorption was determined to be an important process which distributes PCB between sediment and water. Simulations performed using WASP suggested that the model was capable of satisfactorily simulating evolution profiles of dissolved and sorbed PCB. The results indicated a strong accumulation of the PCB in the zone of high turbidity at the head of the salt water intrusion, and little transport to the sea. However, the conclusion was made

that more measurements were needed in order to verify the predictability of the simulations.

2.1.12.3 <u>Total Maximum Daily Loads in Anacostia River Watershed for Organics and</u> Metals (USEPA, 2003a, b)

The Anacostia River runs through the heart of Washington, D.C. 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-diphenyltrichloroethane (DDT) have been detected in the river's bed sediments.

To assist in the TMDL allocation process, 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 was developed. 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:

- A hydrodynamic component, based on the Tidal Anacostia Model (TAM). This
 component simulated 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, constructed using Microsoft Access. Water containing sediment and chemicals flows into the river every day from a variety

of sources, including the upstream tributaries, the tidal basin tributaries, the combined sewer system overflows, the DC separate storm sewer system, and ground water. The 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 was enhanced to more realistically simulate sediment erosion and deposition processes based on hydrodynamic conditions.

The TAM/WASP Toxics Model consisted of seven sub-models which simulated the loading, fate, and transport of zinc, lead, copper, arsenic, PCBs, PAHs, chlordane, heptachlor, dieldrin, and DDTs in the tidal portion of the Anacostia River. 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. Overall, the TAM/WASP Toxics Model was reported to have done a good job in accounting for load inputs of toxic chemicals to the tidal Anacostia. From the error analysis of upstream storm concentration estimates and the various sensitivity test runs, it appeared that model errors were dominated by uncertainties in the load estimates, with load confidence intervals likely in the range of -50% to +300%. However, sensitivity test runs for metals and PCBs indicated that changes in distribution coefficient had 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.

In the TAM/WASP PCB sub-model, PCB congeners were grouped into three classes by PCB homolog. The first group, PCB1, consisted of di- and tri-chlorobiphenyls (homologs 2 and 3), the second group, PCB2, consisted of tetra-, penta-, and hexa-chlorobiphenyls (homologs 4, 5, and 6), and the third group, PCB3, consisted of hepta-,

octa-, and nonachlorobiphenyls (homologs 7, 8, and 9). The PCB model was run for two scenarios: (a) a base scenario using loads calculated from storm flow and base flow PCB concentrations estimated from available monitoring data and (b) a scenario in which loads were adjusted to calibrate to the sediment data. The PCB sub-model predicted the fate and transport of the three separate groups of PCB congeners. 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 predicted water column PCB concentrations reasonably well.

2.1.12.4 <u>Country Club Lake Phase One Total Maximum Daily Load for Dioxin and</u> Pentachlorophenol (PCP) (MDEQ, 2000)

Mississippi's 1998 Section 303(d) list identified Country Club Lake near Hattiesburg, MS as impaired for the use of fish consumption due to elevated levels of dioxin and PCP in fish tissue samples. The source of dioxin and PCP to Country Club Lake is from an abandoned wood preservative site that closed in the early 1990s and is currently being investigated by the Superfund program. Past operations at the site have contaminated soil, surface water, and groundwater.

WASP5 was used to determine water column concentrations for Country Club Lake. The model was used to estimate the impacts of loads of PCP and dioxin in the lake sediments, water quality, and biota. The settling and re-suspension of sediments was expected to play an important role in the water column PCP and dioxin concentrations and WASP/TOXI was able to consider the movement of sediment between the overlying water column and the benthos. Because of the lack of data and full understanding of the sources of dioxin and PCP, this Phase One TMDL computer modeling effort only considered the chemical contamination that was found to be in the lake sediments. The WASP model estimated the overlying water column concentrations given the current sediment concentrations and estimates of flow and sediment re-suspension and settling.

2.1.12.5 Total Maximum Daily Loads of PCBs for Tidal Portions of the Potomac and Anacostia Rivers in the District of Columbia, Maryland, and Virginia Draft report (DCDE, 2007)

The Potomac PCB Model (POTPCB), developed for this TMDL was a coupled, hydrodynamic and PCB mass balance model for the tidal portions of the Potomac and Anacostia rivers. Hydrodynamic simulation was based on a version of the DYNHYD model and sorbent dynamics and PCB mass balance were simulated with a version of the WASP5/TOXI5 model.

To achieve the objective:

- (1) PCB sources were identified and current loads estimated by analysis of observed data and various models;
- (2) A linked hydrodynamic and PCB transport and fate model, POTPCB, was built and calibrated to existing data; and
- (3) The POTPCB model was run with a series of loading scenarios that identified the impact of individual sources, and then the model was run with an iterative series of adjustments to input loads until a set of loads (the TMDL scenario) that met the water target in all model segments was achieved.

A Potomac PCB, POTPCB, model was developed to simulate transport and fate of PCBs in the estuary. The model simulated PCB homologs 3 through 10, to reduce uncertainty and overcome gaps in the historical data. Model output was converted back to total PCBs during post-processing. Model scenarios were run for a representative hydrologic design year. An analysis of the data led to new estimates of water and sediment target concentrations necessary to be protective of PCB levels in fish.

2.1.12.6 PCB TMDL Model for Potomac River Estuary (USEPA, 1997)

The overall conceptual approach was an integrated modeling framework that included hydrodynamics, sorbent dynamics and PCB transport and fate. The underlying premise was that the transport and fate of toxic chemicals, especially hydrophobic organic chemicals (HOCs) like PCBs, are strongly influenced by sorption to organic carbon and interactions between the water column and bedded sediments. In this framework, separate balances were conducted in series for water, sorbents (as organic carbon) and PCBs. The first operational step was calibration of the hydrodynamic model to data for tidal heights and confirmation using the computed hydrodynamics to drive a mass balance model for salinity. The computed hydrodynamics, in terms of flows and tidal mixing coefficients, were then used as a "hydraulic chassis" to drive a mass balance model for sorbent dynamics. The sorbent dynamics model was calibrated to data for two different forms of particulate organic carbon (biotic carbon (BC) and particulate detrital carbon (PDC)), and the computed sorbent dynamics, in terms of settling, resuspension and net burial, were then used as a "sorbent dynamics chassis" to drive a mass balance model for PCBs

The conceptual framework for the PCB model was built upon the organic carbon sorbents model. Using equilibrium partitioning relationships, total PCB concentration was separated into four components, a truly dissolved aqueous phase and components sorbed on to three types of organic carbon: biotic carbon (BIC), particulate detrital carbon (PDC) and dissolved organic carbon (DOC).

Hydrodynamics was implemented for the tidal Potomac and Anacostia Rivers using a 1D branched version of DYNHYD5 coupled to a modified version of WASP5/TOXI5. To represent organic carbon sorbent dynamics, the three solids state variables in WASP5/TOXI5 were converted to represent BIC, PDC and inorganic solid (IS). The WASP5 variable volume option was used for the surface sediment layer to maintain constant porosity. The principal goals of this modeling effort was to gain an understanding of the principal environmental processes influencing the transport and fate

of PCBs in the tidal portions of the Potomac and Anacostia rivers and assessment of various PCB load reduction scenarios to determine the external PCB loads that can enter the system and still meet the applicable TMDL targets.

Results from these simulations helped to inform the design of the TMDL forecast scenarios. Given the model assumptions and the available data for model inputs and ambient water quality conditions, the model results were said to be a reasonable representation of seasonal magnitudes and spatial distributions for water surface elevation, salinity, organic carbon sorbents, and PCBs in the tidal Potomac and Anacostia Rivers. In consideration of the overall objective, the model was judged to be scientifically credible and acceptable for use in developing the PCB TMDL.

2.1.12.7 PCB Water Quality Model for Delaware Estuary (DRBC, 2003, 2006)

WASP5 was selected as the water quality model as per recommendation from PCB modeling expert panel. The results from DRBC's monitoring programs indicated that the major PCB sources to the Delaware River Estuary were mainly from the external loads (point, nonpoint discharges, and air influxes) instead of those from the sediment. Upon examining the algorithms of standard WASP5/ TOXI5, its three types of "solids" the state variables were conservative, which indicated that no existing kinetics functions were available or applicable between solids. As per recommendation/guidance from PCB modeling expert panel, the scope of enhancement to TOXI5 included:

(1) OC decay in both water column and sediment; (2) constantly maintained particulate detrital carbon (PDC) to inorganic solid (IS) ratio and porosity during the surface sediment burying process; (3) spatial and temporal varying dissolved organic carbon (DOC) concentrations; (4) independent values between PCB partitioning coefficients to DOC and dissolved organic carbon (OC); (5) temperature dependent Henry's Law constant; (6) spatial and temporal varying gaseous PCB, and air-water flux conversions; and (7) new formulation for volatilization mass transfer coefficient.

The overall objective of the model calibration was to assess the predictive capability of the water quality model in representing the principal environmental processes that influence the transport and fate of penta-PCBs in the Delaware River Estuary. These processes include hydrodynamics, sorbent dynamics and partitioning of PCBs to organic carbon in the water column and bedded sediments. The model was calibrated to ambient data for biotic carbon (BIC) and PDC in the water column, and to available data for net solids burial in the sediments. Finally, the calibrated sorbent dynamics model was used to drive a mass balance model of penta-PCBs in the water column and sediments. Due to the time constraint for the TMDLs, the model calibration concentrates on one homolog: penta-PCB was done due to its representativeness for each zone. No adjustment of parameters for PCBs was performed following the calibration of the organic carbon model.

The model simulated spatial and temporal distributions of organic carbon and penta-PCB utilizing biotic carbon and particulate detrital carbon state variables as well as one inorganic solid as a pseudo-state variable. The model treated the two OC sorbents as non-conservative state variables that are advected and dispersed among water segments, settle to and erode from benthic segments, move between benthic segments through net sedimentation or erosion, and decay at user specified rates. The Delaware Estuary Polychlorinated Biphenyl Water Quality Model (DELPCB) simulated tidal flows, and spatial and temporal distributions of organic carbon (OC) and penta-PCB. Comparisons of simulated to measured water quality concentrations were reported to indicate a generally good agreement and low bias of the estimate for organic carbon and penta PCB. The mass balance tracking in standard WASP5 was enhanced in order to track mass fluxes of PCBs through every model segment including water column and sediment segments, and to track individual processes that would normally be aggregated. The approach implemented within the model code demonstrated that the model does properly track mass transport fluxes and transformations. The mass balance results for the shortterm calibration showed that the for the water quality zones of interest for the PCB TMDL study there were three ultimate fate pathways for Penta PCB which included transport to the bay (53%), volatilization (44%), and net burial (3%).

2.1.12.8 <u>Importance of DOC in Sediments for Contaminant Transport Modeling (Hwang</u> et al., 1998)

A three phase portioning model that consisted of free dissolved, DOC-bound, particulate-bound components of the chemicals involved was used for the contaminant transport model in order to include the effects of DOC on the partition coefficient. The contaminant model was linked to WASP modeling framework to predict mobilization of PCBs in sediments and the fate and transport of the contaminant in overlying waters of the New Bedford Harbor manufacturers. A good agreement was reported between the model result and the observed data indicating that the estimation of toxicant loading was reasonable and that key parameters controlling the physical-chemical processes were appropriately quantified. It was concluded that as long as the sediment remains contaminated, the water column PCB concentrations will not be reduced. Sediment concentrations in the HSC are quite high, and the same conclusion may be so for those water column PCB concentrations as well.

2.1.13 Use of WASP in Other Studies

WASP has been used for about twenty years and is a well-established water quality model, supported by the USEPA. It has been in use since the mid-nineties and has been applied in Texas, and as well in many other states and countries. Examples of modeling projects according to their use are:

WASP was used for (a) DO/BOD studies in the Houston Ship Channel (Benaman, 1996), (b) low DO problems of the Black River, a tributary of the Chehalis River

- (Picket, 1994, 1997), (c) studying DO in a tidal reach of the Johor River, Malaysia, impacted by agro-industrial waste (Koh et al., 1995).
- WASP was used to (a) determine daily phytoplankton and nutrient dynamics in perturbed microcosms (Hernandez et al., 1997), (b) simulate the DO and algal levels within TMDL-listed stream reaches to support EPA TMDL development in Hillsborough River Basin near Tampa, Florida (Bottcher, 2005), (c) simulate the water hydrodynamics and coliform concentrations within the North Fork (Scarlatos, 2001).
- WASP was used (a) to simulate CBOD, nutrients, chlorophyll, salinity and oxygen (Morton et al., 1989) (b) to evaluate the impact of biosolids on agricultural lands in a watershed (Zhou, 1998), (c) as a water quality planning tool to perform the water quality evaluation and carrying capacity calculation in the Love River basin (Chao et al., 2006).
- WASP has also been used to examine eutrophication of Tampa Bay, Neuse River and estuary, Potomac Estuary (Thomann and Fitzpatrick, 1982), Great Lakes, and in Lake Okeechobee (Jin et al., 1998),
- WASP was used to model phosphorus loading to Lake Okeechobee, simulate phosphorous loading in the Carson River of Nevada (Warwick et al., 1997) and in wetland of Ontario (Lopezivich et al., 1996).
- WASP was used to model kepone pollution of the James River Estuary (O'Connor et al., 1983), volatile organic pollution of the Delaware Estuary (Ambrose, 1987), transportation and transformation of nitrobenzene, spill due to an industrial accident, in the Songhua River, northeast of China (Wang et al., 2007).
- WASP has been applied to modeling toxics and organics (Vuksanovic et al., 1995; De Smedt et al., 1998), heavy metals in the Scheldt estuary (De Smedt et al., 1998), and heavy metal pollution of the Deep River, North Carolina (JRB, 1984),
- WASP has been used for modeling of non-point source nutrients in the Milwaukee River (Hajda and Novotny, 1996) and simulating nutrients and synthetic organics in a Russian River (Hosseinipour and Yereschukova, 1993).

• WASP has been used to model and evaluate TMDLs for several heavy metals in Tenmile Creek, a mountain stream supplying drinking water to the City of Helena, Mont (Caruso, 2005) and also in a USEPA TMDL Case Study in Delaware(Morton, 1993).

2.1.14 *Summary*

From the research on the various models, it was found that the two basic models needed initially are the hydrodynamic and water quality models. WASP has been the preferred choice in contaminant transport of POPs and in TMDL studies on dioxins and PCB. So WASP was chosen as the model for dioxin TMDL study and the results have been comparable with real data. The same model is preferred for modeling during PCB TMDL studies. In the studies where WASP was used, DNYHYD was the preferred choice as the hydrodynamic model. However with respect to the HSC, DYNHYD had a few limitations and so alternative model, RMA2 had to be used and successful during dioxin TMDL study. Use of a RMA2 as hydrodynamic model along with WASP water quality model is the first of its kind used for PCB-TMDL studies.

2.2 Particulate Organic Carbon Considerations

There are two main forms of organic carbon that exist in the water column—Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC). DOC is the organic carbon associated with the dissolved phase and POC is the organic carbon associated with the suspended phase. PCBs, due to their large hydrophobicity, preferentially reside in the suspended phase rather than the dissolved phase. Within that preference the degree to which they partition from other nearby sources (e.g. sediments and air) is strongly a function of organic carbon on the suspended particles. So it is

valuable to know the POC in connection with a PCB concentration from a suspended phase sample.

The previous Dioxin TMDL study did not assess POC in connection with sampling, but it is valuable to make POC an analyte in this study. Literature review was conducted during this quarter to understand some of the methodologies and considerations in measuring POC. Neither sampling for POC nor analyzing for it are straightforward issues.

2.2.1 Sampling Methods

The sampling for POC is the more difficult part of the sampling-analysis process for POC. The reason for this is that particulates are present in the water column and must be removed to be separately analyzed from the rest of the water sample. If the removal does not occur, then any analysis done on the sample is a TOC measurement rather than a POC measurement because it combines DOC with the POC. The removal is not an easy task because of two large issues.

- 1. Large Particles Sizes: POC in a sample can be significantly affected by large particles that can contain a large amount of organic carbon. These particles, however, are rarer. Thus, the size that is chosen for the POC sample must be large enough to get the larger particles if they are present.
- 2. Small Particle Sizes: What is defined as a "suspended particle" is for the most part arbitrary because what it effectively means is "whatever is filtered". So filter size is important if filtration is the method chosen for the separation of the suspended phase. Different methods may separate to different minimum particle sizes and ultimately end up with different POC results.

2.2.1.1 Conventional Methods

There are two main methods[†] of sample collection for POC--sample bottles and pump filtration. Sample bottles require less volume and have lower pressure differential across the separation filter while pump filtration has greater pressure differential and larger total volume sampled. A major functional difference between the two methods is that sample bottles are filtered back at the laboratory while pump filtration happens insitu in the field.

There have not been many studies comparing the two, but a notable study was performed by Gardner et al. (2003). They found that POC concentrations were consistently higher when using bottle POC sampling as compared to a pump filtration method. At temperate climates, such as can be found in the HSC, the difference was consistently 1.2-5 times greater in bottle sampling methods. The reasons they gave for these were:

- Greater pressure differentials across the filter for pump filtration systems pull fine particles through the filter that should remain on it to be counted as POC.
- Larger sample volumes in the case of pump filtration systems yielded a better representative sample that can collect the more rare large particles. (Note that this would actually offset the previous effect created by the pressure differential, but it is not enough of an offset.)

The ultimate solution that they gave was to use filtration pumps because of their utility in getting larger sample volumes but to **change the operating conditions** to lower the pressure differential across the filter.

used in a new sampling environment without extensive calibration. It may be worth using in this project as secondary measure of POC (Bishop, 1999).

[†] A third method of POC analysis is to calibrate POC concentrations to transmissometer readings. The slope between these two readouts is commonly called a beam attenuation coefficient. The method could be extremely useful if it was calibrated to the Channel water because it would yield potentially a rapid field method of POC detection without any additional water samples being taken. Beam attenuation coefficients are the subject of much research, and the variability of the coefficient is being studied such that it could be

It is recommended for now then that the PCB sampling conducted in conjunction with the TMDL test for POCs use a pump filtration method. The practical application of this plan will be that a second filter will be necessary during sampling that is separate from the one used to get suspended phase PCB concentrations. Common analysis techniques preclude the use of the same filter for both PCB and POC analyses. In addition to the use of two filters, it will be valuable to consider at least in some cases what the pressure differential is across the filter as Gardner et al. (2003) suggests. The flow rate used on the pump may need to be adjusted if POC results will be significantly influenced by harder pumping rates.

2.2.1.2 More Rarely Used Sampling Methods

Though it would seem that the conventional pump filtration method will suffice for POC sample collection in this project, it may be useful to get a secondary collection method to compare by. The following sampling methods may be helpful to run on a subset of all of the POC samples to check the consistency and accuracy of the POC result insofar as it influenced by the collection method. Since the POC parameters is likely to be a critical parameter for the modeling PCBs in the water column as well as for general conceptual understanding, it is beneficial to consider an alternative "check method" for POC sample collection.

POC has been successfully correlated to light transmission analytical equipment such as the transmissometer. This principal is the basis for another kind of POC analysis that can be rapidly conducted, even in the field without extensive chemical analysis. The method works by continually drawing water from the field and running it through a transmissometer to get transmission readings nearly in real time. The transmission reading must be correlated through a dual POC chemical analysis conducted at in the same sampling event. The correlation slope between these two readouts is commonly called a beam attenuation coefficient. The method could be extremely useful if it was calibrated to the Channel water because it would yield a rapid field method of POC

detection without any additional water samples being taken. It is also an interesting alternative because it essentially combines POC sample collection and analysis in one step once an accurate beam coefficient has been determined. Beam attenuation coefficients are the subject of much research, and the variability of the coefficient is being studied such that it could be used in a new sampling environment without extensive calibration (Bishop, 1999). It may be worth using in this project as secondary measure of POC.

A second method used for POC sample collection is to collect the particulate fraction through a continuous centrifugation technique as in the case of Dean (1994). This method completely bypasses any kind of filter whether in-situ (as in a pumping method) or ex-situ (as a sample collection bottle). Instead, the water sample is pumped on board through a continuous centrifugation system that spins the particulate matter into pellets that can be freeze-dried for later laboratory analysis. The use of this method in the project would require the likely purchase of a continuous flow centrifuge, but the method does not require filters that must later be disposed of.

2.2.2 Analysis Methods

Analysis methods should be grouped into two main classes. There are methods that analyze the particulate fraction of a water sample directly to get a Total Organic Carbon (TOC) value on the particulate, which is a POC. Then there is the more indirect difference method. This method analyzes for TOC of a water sample and Dissolved Organic Carbon (DOC) of the same sample. The difference is taken to be the POC.

The general issue in any kind of organic carbon analysis is separating the organic carbon from the inorganic carbon. Most of these methods deal with that separation first and then analyze the remaining carbon content as "organic carbon".

2.2.2.1 Loss-On-Ignition (LOI) Method

The general LOI methodology is to weigh some sample on a medium (e.g. Glass Fiber Filter (GFF), bottle filter, etc.) prior to ignition, ignite the sample, reweigh the sample after the ignition, and then take the weight difference as the organic carbon content. The weight difference divided by the weight of the original sample yields a value of OC that is given unit of Mass OC/Total Mass (e.g. g-OC/g-total). When this analysis is run on a particulate sample from the water column, it is the POC.

LOI presents certain challenges when making decisions on how it should be done. Two of these critical factors are ignition time and temperature. Smith (2003) noted that there are significant differences in exposures given in the literature and in standard methods that often range from 1-4 hours. Their experiment, conducted on clay rich sediments, found that 2.5 hours was a reasonable time to ignite sediments. The reason given for an increase in exposure time from the common hour that many labs use is that there often exists a surface crust on the sediment particles, and this surface crust is greatest in high clay content particles. This surface crust requires a longer exposure time to be cracked so that the ignition temperature can be achieved inside the sample as well as on the surface. Their studies on ignition temperature showed that there is nearly an insignificant difference on loss when 1000°C was used versus 550°C. This particular example applies to the HSC system because many of the sediment and suspended phase particles have high clay content, and thus the use of LOI to determine either POC or TOC in sediments would require a longer ignition time.

Heiri et al. (2001) conducted a similar LOI study that showed that the main factors contributing to LOI variability were sample ignition time, location in the ignition furnace, and sample size. They noted that there was greater variability in samples with higher OC content. Some of the previous samples in the HSC also exhibited a higher OC content in sediment; therefore it is likely that the particulates also exhibited this high content of OC.

The main detractions of the LOI are many and significant. As stated by Dean (2007) they are:

- 1. <u>Small Mass Differential</u>: The difference between a crucible or filter weight before and after combustion is very small. The mathematical fallout from this is that two very large numbers are subtracted from one another to get a small difference. Accuracy in this kind of differencing always suffers.
- 2. <u>Inorganic Solid Volatility</u>: While most inorganic solids remain in the sample at ambient temperatures, upon heating these solids can volatilize and be counted as POC when in fact they are not.
- 3. <u>Organic Matter Metric</u>: When the sample is ignited, what burns is any matter that is organic, not just carbon. So the true value that results is organic *matter* rather than organic *carbon*. Ratios between the two can be used to convert the one to other, but these ratios are variable.

2.2.2.2 CHN Analysis Method

CHN analysis (commonly called the Lloyd Kahn method when it refers to organic carbon analysis) occurs via combustion that then submits the gases to an elemental analyzer. Assuming that all of the carbon in the combustion has evolved from organic sources in the sample, then the resultant carbon quantitation is the POC of the sample. This method sometimes requires chemical prep work before being combusted (to remove inorganic carbon) and sent to the analyzer (Schumacher, 2002). There are several methods of combustion before the gases go into the analyzer, and these include high temperature combustion, persulfate, ultraviolet, and low temperature combustion. High temperature combustion is preferable for this project because any other combustion method will likely result in incomplete combustion of the organic carbon on in the sample (Dean, 2007).

The Lloyd Kahn method is preferable to LOI methodology because it does not require a larger sample mass to mitigate the weight subtraction problem, but both of these methods require destruction of the sample on the filter or whatever sample medium is used.

2.2.2.3 TOC-DOC Difference Method

The TOC-DOC difference method was described in brief by Gardner et al. (2003). Two simultaneous water samples are taken--a high volume filtered sample of sea water and a high volume sample of unfiltered sea water. The two samples were both analyzed for OC via High Temperature Combustion (HTC), though another combustion method could have been used. The unfiltered sample result represent TOC, and the filter sample result represents DOC. The difference should be the POC. Some detractions from this method include

- The addition of the analysis uncertainties since two independent quantitative results are used—TOC and DOC. A single measurement as in a direct POC method would have only one uncertainty.
- The role of colloids and smaller non-filterable particles is slightly more confusing than a direct POC method because the OC in those forms will be quantified in DOC though it is not actually dissolved. If, however, POC is only an operational definition dependent on the filter size that is chosen, then this is less of a concern.

This method may seem less accurate or less rigorous because it relies on subtraction of other analyses rather than a more direct form of analysis, but is used by the U.S. Joint Global Ocean Flux Study (http://www1.whoi.edu/), a major U.S. research effort to understand the global movement or carbon in the oceans (Gardner et al., 2003).

2.2.3 POC Recommendations

For the sampling portion of POC quantification, it is recommended that the high volume pump filtration method be used. This method is more established than other methods with acceptable accuracy (assuming that the definition of a particulate is operationally dependent on filter size). It is also fairly easy to implement in this project because high volume sampling of PCBs will already be conducted. Modifications to the sampling process will be required because the particulate fraction of the sample will need to have a portion that can be destroyed for this analysis. The amount of sample required for all congener PCB quantification needs to be weighed against how much sample is required for POC analysis. If more sample is required because of the POC analysis, then a splitter line may need to be put in place to run the sample onto two filter, one that can be use for PCB and one for PCB. The ultimate solution to this issue is not yet clear.

Once the sample has been collected on a GFF, it is recommended that the sample be analyzed by the Lloyd Kahn method of OC analysis because the method is both accurate and available in commercial laboratories. Specific instructions may need to be given to a lab, but the equipment is already there. In addition to this direct method of POC analysis, the POC should be quantified (with uncertainty) through the TOC-DOC subtraction method for some samples. Since DOC is going to be analyzed for already, it would be possible to take a few samples of unfiltered sea water by which to get a TOC value from which to subtract.

CHAPTER 3 - DATA ANALYSIS

3.1 2002-2003 PCB Dataset Grain Size Analysis

Grain size analysis was performed on the whole sediment PCB data set[‡] for the 2002-2003 sampling during the Dioxin TMDL project. The PCB TMDL project will involve an understanding of sediment, and so some further analyses were conducted to describe the general spatial patterns of sediment in the HSC as well as their correlation with PCB concentrations.

[‡] The PCB dataset is not the only dataset that would provide useful grain size spatial analysis in the HSC. All of the dioxin-only samples taken throughout all sampling events would be useful as well. Those data points will be added in the future to increase the power of the averages used.

3.1.1 Grain Size Spatial Distribution

Figure 3.1 shows the sediment sampling locations in the previous PCB dataset. These locations generally cover the HSC in reasonable detail with only a few representative point in SJR and the side bays. Each tributary only had one sediment sample if it was sampled at all. All of the grain size percentages were averaged together according to sample location to arrive at sediment grain size breakdown at every SWQM station used in the study. That averaging and spatial linking is shown on a station basis in Figure 3.2 and Table 3.1.

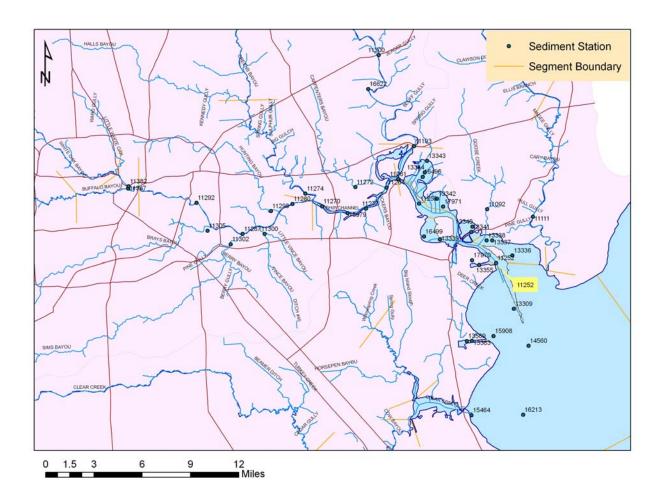


Figure 3.1. Sediment sampling locations in the HSC for the 2002-2003 PCB sampling.

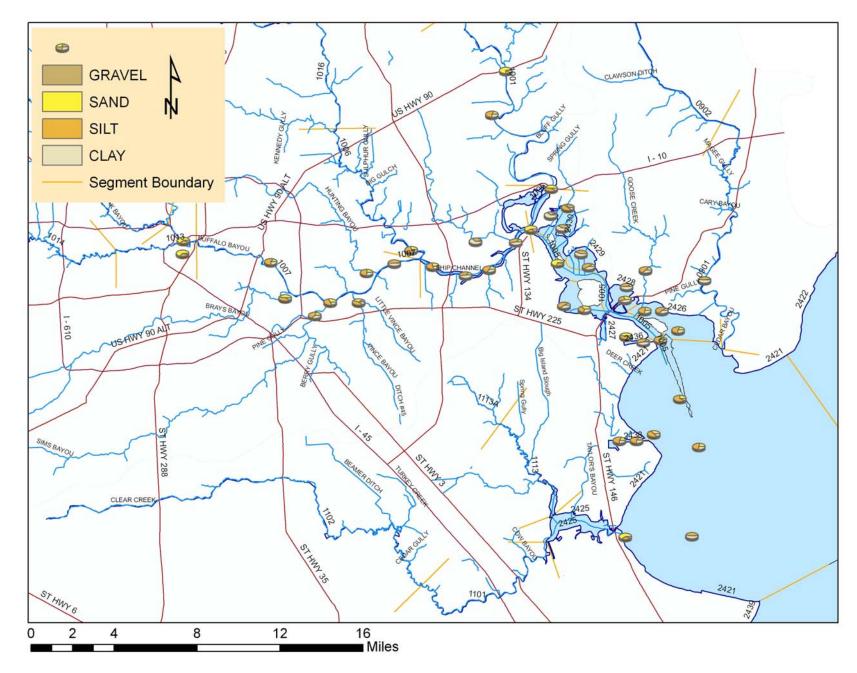


Figure 3.2. Grain Size Distribution in dry weight %. All 2002-2003 dry weight percentages for every sample were averaged and renormalized to 100%.

The map shows that coarse sediment (> 50% sand or > 25% gravel) exists in a few choice locations. These locations are

- Upstream Buffalo Bayou near the confluence with White Oak Bayou
- Upstream SJR where the river crosses US 90
- HSC at Lynchburg Ferry where the SJR meets the HSC
- Upper Galveston Bay at Kemah just outside Clear Lake
- Back of Burnett Bay (Large gravel content)

Being that the natural soils in the Houston area are more small-grained in general, it is thought that areas of high large particle size may be influenced by runoff and especially urban runoff. The reason urban runoff is especially likely is that if the natural soils are more fine-grained, then coarse-grain material would more likely come from anthropogenic means, and there is more of this development in urban areas where construction requires outside materials to be brought in. Further analysis in the form of actual runoff sampling that measures entrained sediments is required to confirm this, but all of the areas listed do conform to a reasonable spatial requirements to receive coarse grain runoff—proximity to the HSC side boundaries and proximity to urban development¹.

Since 1006 and 1007 are the "hot spot" segments, and this increased concentration of PCB critically occurs in the sediment, it bears mention of the grain size distribution found in those segments in the main channel. This distribution, in consideration of only main channel samples, contains high concentrations of fine-grained sediment with the silt and clay content totaling 73% and 82% by weight for 1007 and 1006, respectively. So the "hot spot" regions are high in fine-grained sediments. Implications of this result have not been fully considered but the following considerations are observed.

1. **Particle Size Motion Effects**: Lighter particles are easier to move at lower Channel velocities. Thus, the sources of sediment to 1006 and 1007 can get sediment there easily,

_

¹ It may seem redundant to imply that there are areas of the Channel that are urban influenced while other areas are not urban influenced. While the Houston-Galveston metropolitan area has a high level of development, there are still regions along the Channel with lower urban development.

- but it may also leave easily and be suspended in the water column. Increased suspension time can allow for greater PCB transfer from suspended phase to dissolved phase.
- 2. **Particle Cohesion**: Clays are known to have high cohesion. This will offset the small particle size enhancement towards sediment transport by way of increasing sediment fall velocity and the force required to scour sediments from the bed. It is also known that suspended sediment concentration tends to drop with increased salinity (due to ionic effects in the sediments leading to flocculation), and salinity increases with proximity to the mouth of the Channel (Ferreira et al., 2003). The effect of salinity on the ability of suspended sediments to coalesce and form flocs that will settle more quickly is still being researched. In general, cohesive sediments are also less well understood in terms of sediment transport, which may complicate sediment transport modeling if it is ever needed in the project (Je et al., 2007).
- 3. **TOC Content**: As TOC may or may not be correlated with grain size, a preferential grain size in 1006-1007 may indicate an expected level of TOC that can sorb PCBs.

The last analysis conducted was an averaging of all of the grain size distributions per segment. These results are given in Figure 3.3 according to the four grain size classes. As can be seen, there is a majority amount of clays and silts in nearly every segment. If fines are defined as silts and clays and coarses defined as gravel and sand, then there is only one segment that has a majority of coarse—segment 1013, Buffalo Bayou. This segment contains the two highly sandy sediment samples mentioned earlier. Segments 1001 and 1005 also have a high percentage of coarse material (43% and 45% respectively), but other than these exceptions every segment is dominated by at least 68% fines. It not yet certain how the specific makeup of grain size in a location will combine with the other sediment factors to influence how data analysis, modeling, and decision making are performed.

61

¹ Please note that while the sediment cohesion effect is a factor in the fall velocity of sediments and the rate of sedimentation, the advective water velocity is an even larger influence. As will be discussed later in this report, the advective velocity has not yet been examined but will be in the next quarter.

Table 3.1. Grain size distribution in dry weight % averaged by segment. Averages were renormalized to yield 100%.

Segment	GRAVEL	SAND	SILT	CLAY	Total
901	0.00	3.20	45.10	51.70	100.00
1001	0.15	42.55	42.10	15.21	100.00
1005	0.23	44.98	37.64	17.15	100.00
1006	0.13	17.97	45.65	36.25	100.00
1007	2.07	25.19	48.31	24.43	100.00
1013	0.20	64.12	30.14	5.54	100.00
2421	0.23	32.21	47.27	20.29	100.00
2426	0.23	20.39	46.17	33.22	100.00
2427	0.00	23.95	42.63	33.43	100.00
2428	0.10	9.50	40.37	50.03	100.00
2429	0.18	6.60	44.29	48.94	100.00
2430	11.90	4.68	38.21	45.20	100.00
2436	1.85	27.61	42.72	27.81	100.00
2438	1.01	16.54	57.28	25.17	100.00



Segment	Name	Segment	Name
1013	Buffalo Bayou	2426	Tabbs Bay
1005	Lower HSC	1006	HSC
1001	SJR	2438	Bayport Channel
2421	UGB	2430	Burnett Bay
2436	Barbours Cut	2428	Black Duck Bay
1007	HSC	2429	Scott Bay
2427	San Jacinto Bay	901	Cedar Bayou

Figure 3.3. Grain size distributions in dry weight % by HSC segment. All values renormalized to 100% after averaging. Segment are sorted according to increasing percentage of fines (silt + clay). Percentages for gravel are intentionally unlabeled.

3.2 HSC Groundwater Consideration Calculation

3.2.1 Introduction

It is necessary to at some level consider every load type that could possibly deliver PCBs to the Houston Ship Channel (HSC). Some of these load types are clearly major contributors to the total load in the project while some could be insignificant. Air deposition and groundwater mass loadings are generally considered insignificant compared to other loadings (e.g. sediment,

point source, upstream). The air deposition calculation was done as part of the last quarterly report and it was found that the air deposition load insignificant compared to the in-stream load. In the next part of the study, it is necessary to know the amount of load possible into the HSC through groundwater sources in order to evaluate the potential significance. The calculation of groundwater mass flux will help determine the (1) possible total load through groundwater contamination, and (2) the percentage groundwater load to the in-stream load. The emphasis in these calculations is on a preliminary approximation of the total load determination from groundwater sources by way of typical aquifer values and conservative contamination scenarios.

3.2.2 Overview

Describing flow and contaminant transport within river systems requires estimates of mass transfer through the river's surface water – groundwater interface. For any particular stretch of river, the question that arises is does the groundwater flow into the river and if so what is the contaminant load. Calculation of mass flux across the interface is difficult due to the lack of data describing groundwater movement in the vicinity of the river. The calculation is based on observations of river stage, water table elevations, and soil samples within the surrounding groundwater system. Using Darcy's Law the specific discharge (q_i, cm/sec), is expressed as:

$$q_i = -K \times i$$

where K = hydraulic conductivity (cm/sec)

i = hydraulic gradient (cm/cm)

The groundwater mass flux passing through the surface water – groundwater interface is then calculated by multiplying the specific discharge by the product of the surface area of the boundary and the constituent concentration, i.e., PCB concentration in our study. So the total mass flux (Kg/sec) from source zone also called groundwater mass discharge/loading is given by:

64

$$w = q_i \times A_i \times C_i \times CF$$

where A_i = Area associated with the interface (m²)

 C_i = Concentration of constituent (g/L)

CF = Conversion factor

Detailed aquifer and plume characterization in the vicinity of the groundwater-surface water interface¹ (transect) is necessary to ensure validity of the mass flux measurements. Aquifer characterization must be sufficiently detailed to identify localized vertical and horizontal variations in specific discharge (hydraulic conductivity and hydraulic head) within the transect, which can have a significant effect on total mass flux across the transect. Investigative techniques to evaluate specific discharge variations include down-hole geophysical gamma logs, grain size analyses, permeameter analysis, pumping tests, slug tests and monitoring of nested piezometers. However in this report, the objective was to derive the possible groundwater mass loading in the study area with theoretical values under different scenarios. If preliminary calculations show a significant possible groundwater mass loading to the in-stream load, more precise values of the mass flux will be necessary and measurements of conductivity, head, and groundwater total PCB (ΣPCB) concentrations will have to be made in the study area later.

3.2.3 Approach

As mentioned above, the exact calculation of PCB discharge into the HSC requires knowledge of groundwater contaminant zones in the study area and also requires knowledge on physical and chemical characteristics of the aquifer. The preliminary calculation was done to know the extent of Σ PCB mass discharge based on parameter estimates made and values taken from the literature. The steps associated with the calculation are:

1. *Hydraulic conductivity:* Hydraulic conductivity is the proportionality constant in Darcy's law, which relates the amount of water that will flow through a unit cross-sectional area

¹ Transect is used to refer to the interface area between groundwater and the surface water.

65

of aquifer under a unit gradient of hydraulic head. The typical values of hydraulic conductivity associated with different kinds of soils are given in Table 3.2. The Houston-Galveston study area of interest is typically considered to be clay-sand type and so the hydraulic conductivity was assumed to be 1×10^{-4} cm/sec for the base case scenario. Similar values of hydraulic conductivity were reported in the Carrizo-Wilcox aquifer study in which the K values ranged typically ranged between 1×10^{-4} and 1×10^{-3} cm/sec in counties nearer to Houston area (TWDB, 1999).

Table 3.2 Typical input values of hydraulic conductivity (API, 2003)

K (Clays)	$< 1 \times 10^{-6} \text{ cm/sec}$
K (Silts)	$1 \times 10^{-6} \text{ to } 1 \times 10^{-3} \text{ cm/sec}$
K (Silty sands)	1×10^{-5} to 1×10^{-3} cm/sec
K (Clean sands)	1× 10 ⁻³ to 1 cm/sec
K (Gravel)	> 1 cm/sec

- 2. Hydraulic gradient: It's not possible to calculate the exact hydraulic gradient due to data limitations. A rough estimate was made based on aquifer data that was available for the Houston and Galveston counties from the Texas Water Development Board (TWDB) database. The calculations gave a hydraulic gradient value of ≈ 0.001 cm/cm which is within typical range value for hydraulic gradient (0.0001 to 0.01 cm/cm).
- 3. Segment Areas: The channel lengths of all segments in the study area were determined using GIS. The deep draft channel survey (USACE, 2007) showed the approximate depth of the channel and typically was 40-50 ft for deep water channels and 10-15 ft for shallow water channels. Therefore, for calculation of groundwater flow areas for each segment, the thickness of the aquifer was considered to be 10 ft for shallow channels and 20 ft for deep channel. All HSC boundaries were assumed to be contaminated by PCB groundwater of the same concentration i.e., 100% contamination all along the channel length and at all segments. This is not typically possible; however calculations were made for the worst case scenario. Table 3.3 summarizes the area along the groundwater-surface water interface associated with each segment.

Table 3.3 Area of the groundwater-surface water interface by segment

SWQM segment	Segment name	Area (km²)
1007	Upper HSC	0.144
1006	Lower HSC (not including Greens Bayou)	0.185
1005	San Jac Tidal	0.295
1001	SJR	0.17
2426	Tabbs Bay	0.069
2427	San Jacinto Bay	0.07
2428	Black Duck Bay	0.073
2429	Scott Bay	0.037
2430	Burnett Bay	0.110
2436	Barbours Cut	0.029

4. *Groundwater PCB Concentrations:* A summary of the ΣPCB concentration typically observed in groundwater is shown in Table 3.4. It can be observed that the method of PCB determination ranged from measuring specific Aroclors to measurement of all PCB congeners. Typically the PCB concentration in the contaminated groundwater was close to the MCL of 0.5 μg/L. The PCB concentration in groundwater was significantly lower (< 1.1 μg/L) in one of EPA superfund sites in the study area (Geneva Industries). So for calculating mass flux, the PCB concentration in the aquifer was assumed to be ten times the MCL limit (5 μg/L), which will give a conservative load estimate.

Table 3.4 Typical PCB concentrations in groundwater

Site Information	No of stations sampled	PCB conc.	Average PCB conc.	Source
Landfill (Rasslebygd, Sweeden) ^a	9	0.28-37 ng/L	5.16 ng/L	Persson et. al., 2004
Commonwealth of Pennsylvania ^b	1	3.4±0.5 - 6.6±0.6 μg/L	4.9±1.7 μg/L	Meadows et al., 1998
Dump site at Villie Mercier, Quebac ^c	4	0.2 -17.2 μg/L	5.65 μg/L	Lesage et. al., 1992
Geneva Industries ^d	Monitoring well (11)	<0.153 - < 1.1 μg/L	-	EPA-Superfund Report 2003
	Recovery well (8)	8.1-193 μg/L	61.13 μg/L	•

^aCongeners 18, 15, 17, 31, 33/20, 52, 49, 41/64, 70/76, 66,95, 90/101, 99, 97, 115/87, 110, 149, 118, 132/153, 105, 138, 156, 157, 180, 170, 196/203, 194

- 5. Flow Determination in HSC for In-Stream Load Calculation: Flows from the HSC RMA2 hydrodynamic model were used for the calculation. This is the RMA2 model used for the dioxin TMDL, and it should be applicable to PCBs. These flows were time-averaged for the RMA2 2002-2005 three year run. The resultant time-averaged flows were then spatially averaged together to get a representative flow for the entire SWQM segment. Flows were not used for the side bays since calculation of side bay in-stream load was more complicated than what is needed for this preliminary calculation.
- 6. *Final Calculation:* Groundwater loads and in-stream loads were calculated using all of the previously mentioned datasets on an annual basis.

^bAll 209 congeners

^cSum of Aroclors 1242, 1254, and 1260

^dSum of Aroclors 1016, 1221, 1232, 1242, 1254, 1260

3.2.4 Results and Discussion

3.2.4.1 Groundwater PCB Scenario

The calculation of the total mass flux for each segment was calculated with the following input parameters:

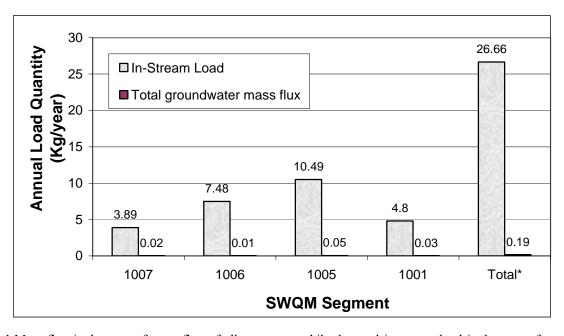
- Hydraulic conductivity = 1×10^{-4} cm/sec
- Hydraulic gradient = 0.001 cm/cm
- Segment areas as presented in Table 3.3
- PCB concentration in the groundwater = $5 \mu g/L$

Table 3.5 shows the various loads calculated by groundwater mass flux and in-stream for the four main HSC segments. The comparison of the in-stream loads to mass flux load is shown in Figure 3.4. From the figure, it can be observed that the groundwater mass loadings were significantly lower compared to the in-stream load for all segments compared. In general, all segments compared were at a low percentage of groundwater mass loads relative to in-stream load as shown in Figure 3.5. The total in-stream segment loads include only segments 1005, 1006, 1007, and 1001 while the total groundwater mass flux load includes all segments (1007, 1006, 1005, 1001, 2426, 2427, 2428, 2429, 2430, and 2436). Thus, the comparison is biased conservatively towards giving the groundwater load as much significance as possible. Yet even in that bias, the ratio of total mass flux to in-stream is less than 1%.

Table 3.5 Resultant values of the groundwater mass flux and in-stream load calculation

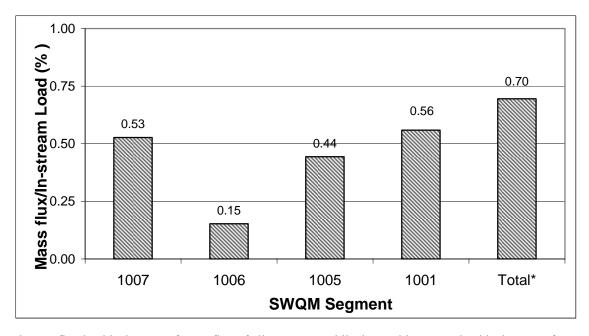
Segment	Area	Total groundwater mass flux	In-stream load	Groundwater mass Flux to in-stream load
	m ²	kg/yr	kg/yr	
1007	1.30E+05	0.02	3.89	0.53%
1006	7.25E+04	0.01	7.48	0.15%
1005	2.95E+05	0.05	10.49	0.44%
1001	1.70E+05	0.03	4.8	0.56%
Total*	1.18E+06	0.19	26.66	0.70%

^{*}Total Mass flux load is the sum of mass flux of all segments, while the total in-stream load is the sum of segments 1007, 1006, 1005, 1001.



^{*} Total Mass flux is the sum of mass flux of all segments, while the total in-stream load is the sum of segments 1007, 1006, 1005, 1001

Figure 3.4 Comparison of total groundwater mass load and in-stream PCB load



^{*} Total Mass flux load is the sum of mass flux of all segments, while the total in-stream load is the sum of segments 1007, 1006, 1005, 1001

Figure 3.5 Comparison of total groundwater mass load to in-stream PCB load

3.2.4.2 <u>Sensitivity Analysis Scenarios</u>

The calculation of mass flux was done based on assumptions and literature values rather than actual measurements in each specific segments. Sensitivity analysis was therefore performed to quantify the importance of parameters and their influence on groundwater mass flux. Sensitivity scenarios are summarized in Table 3.6.

Table 3.6 Summary of mass flux calculation scenarios

Case No.	Description
Base Case	Hydraulic conductivity = 1×10^{-4} cm/sec
	Hydraulic gradient = 0.001 cm/cm
	PCB concentration in the groundwater = $5 \mu g/L$
Case 1	Hydraulic conductivity/2 OR
(Base Case/2)	Hydraulic gradient/2 OR
(Base Case/2)	ΣPCB concentration/2
Case 2	Hydraulic conductivity/5 OR
(Base Case/5)	Hydraulic gradient/5 OR
(Base Case/3)	ΣPCB concentration/5
Case 3	Hydraulic conductivity/10 OR
(Base Case/10)	Hydraulic gradient/10 OR
(Base Case/10)	ΣPCB concentration/10
Case 4	Hydraulic conductivityx2 OR
(Base Casex2)	Hydraulic gradientx2 OR
(Buse CuseA2)	ΣPCB concentrationx2
Case 5	Hydraulic conductivityx5 OR
(Base Casex5)	Hydraulic gradientx5 OR
(Base Casexs)	ΣPCB concentrationx5
Case 6	Hydraulic conductivityx10 OR
(Base Casex10)	Hydraulic gradientx10 OR
(Dasc CascX10)	ΣPCB concentrationx10

Results for all the six cases are presented along with the base case in Figure 3.6. The comparison of the mass flux to in-stream loads shows that the mass fluxes were lower compared to the in-stream load in all cases. As expected, highest percentage mass flux to in-stream load was observed with a tenfold increase in base condition. However, even with a tenfold increase, the mass flux load was less than 10 % of the in-stream load.

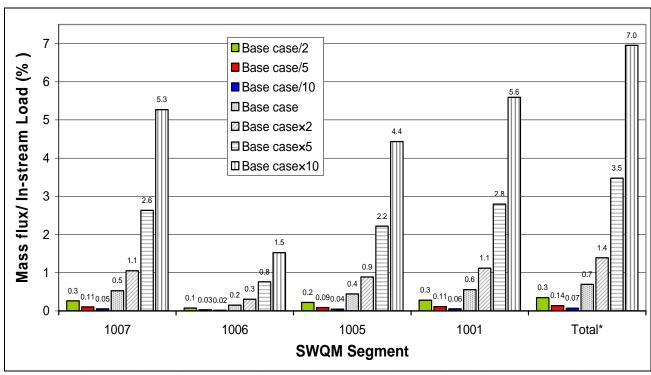


Figure 3.6 Comparison of total mass flux to in-stream PCB load for different scenarios

3.2.5 Conclusions and Further Considerations

The foremost conclusion from this calculation is that under all conditions evaluated the mass flux load is not very large relative to the entire in-stream loads on a per segment comparison. A 10% cutoff of significance seems reasonable given the sizes of the other loads that will be measured more directly in the project: sediment, runoff, and point sources. Since this estimation was extremely conservative, it is reasonable on the basis of total groundwater mass flux to not seek out more detailed measurements of PCBs in groundwater. The calculations performed in this report, were thorough but not rigorously exact as the calculations were to the most part based on broad assumptions. At this point the result from this calculation and previous studies in the literature does not seem strong enough to consider groundwater contamination as a significant contributor to the in-stream load. Literature should still be continuously monitored to see what is valuable to the project and groundwater may need to be revisited if data results warrant in the future. Yet the current understanding of the groundwater loads is that it is not significant.

3.3 HSC Tributary Flow Significance Analysis

3.3.1 Background and Objectives

In considering the fate and transport of PCBs in the HSC, it is important to understand the flow rates at various points along the channel and the change caused by the tidal influence and tributary flows on the overall flow. The overall flow rate determines the total PCB mass inload at any point along the channel.

Two very specific considerations are in view here. One is the need to discern the significance of a tributary versus another along the channel banks. Flow rates are a good measure of tributary significance because the runoff loads into these streams as well as upstream tributary loads and tributary point source loads will most often be high only at higher total tributary flow rates. The other effect is what has been deemed as the Segment 1007-1006 "bathtub effect." Segments 1006 and 1007 continue to remain abnormally high in water, sediment, and fish concentrations despite the likely cessation of large new sources in that area (Rifai and Palachek, 2007). One explanation for this is that the flow conditions in these upstream HSC segments discourages the downstream movement of sediment past the San Jacinto River (SJR) confluence due to a hydrodynamic "bathtub" whereby the combination of large SJR flows and tidal effects decreases net sediment velocity leading to increased sediment deposition time. The result, if the effect exists, is that PCB contamination remains high in these segments and only in these segments as was found in the 2002-2003 dataset.

These background ideas led to the following specific objectives for this analysis of HSC flows, which were to evaluate

- 1. The average flow in the channel at various segments.
- 2. The contribution of flow by the tributaries.
- 3. The tidal influence and thereby multidirection of flow in the channel and in the tributaries.

With the understanding of the above three concepts for the channel system, important conclusions can be made concerning how flows affect the current PCB situation in the HSC as well as what future mitigation strategies are viable.

3.3.2 Flow Calculations using Hydrodynamic Modeling Output

Before any flow comparisons could be performed, there needed to be a source of flow data meeting the following criteria.

- Reliability
- Accuracy
- Temporal Representativeness
- Spatial Representativeness

Many sources were considered including USGS stage and flow stations and NOAA tide stations. These sources, although quite accurate, did not have enough data to represent the channel flows in the Main Channel and the tributaries. So the final data source selected was the modeled flows from the RMA2 hydrodynamic model used in the Dioxin TMDL project. The RMA2 model covered a three year simulation period (07/20/2002 to 04/30/2005) that gave modeled flows at various points in the channel and the tributaries. The output however was obtained from WASP water quality model, which gave flows for each segment every 2 hours and 23 minutes on average. The measured data was lacking in the areas of temporal and spatial representativeness, but the modeled flows were still acceptable considering that the model flows were used during the Dioxin TMDL studies. The data resolution was quite high with flow rate model output at two hour intervals for any point throughout the channel.

The model dataset was a large amount of data, and so it had to be averaged and grouped in meaningful ways for analysis purposes. Two methods were chosen to group data -- (1) Net Segment Flows and (2) Average Daily Flow with Negative-Positive Flow Considerations. A brief overview of the WASP model segmentation will first help explain the spatial grouping.

75

¹ These flows were not literally pulled from RMA2 modeling. That modeling was fed through the WASP water quality model, and then the flows were taken from that model output though the flows themselves were not altered in the water quality modeling.

3.3.2.1 WASP Segmentation and Time Step

The WASP model segmentation was developed by aggregating RMA2 elements to reaches maintaining the minimum segmentation required for water quality modeling. The WASP model for the HSC consists of 61 1-D water surface segments, 46 2-D water surface elements, and 107 benthic segments (one underlying each of the surface water segments). Figure 3.7 illustrates this segmentation of the WASP model for the Houston Ship Channel. Thirty-eight segments correspond to the main channel from Buffalo Bayou to the downstream boundary, twenty to the major tributaries, twenty-one to San Jacinto River (including the Old River), and the remaining twenty-eight comprise the side bays, Barbour's Cut, Bayport Channel, Clear Lake, and Upper Galveston Bay.

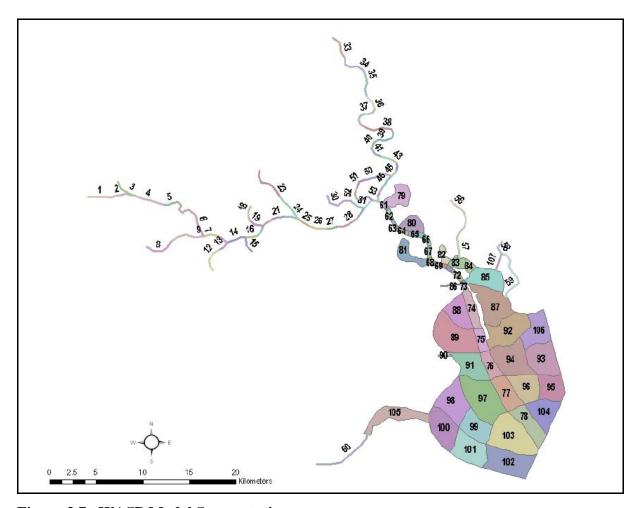


Figure 3.7. WASP Model Segmentation

3.3.2.2 Net Segment Flows

The net flow was estimated as the average of all the flow rates (model flows every 2 hours and 23 minutes) at the downstream end of each water quality segment. The calculations were done over the entire channel to ensure that flow rates at various segments are modeled for the same time period to be compared. However the flow averages over the entire simulation period did not disclose the details of positive and negative flow that occur on a daily basis. So the WASP output flows were analyzed for daily average flows to obtain a net flow at each segment on a daily basis.

3.3.2.3 Average Daily Flow with Negative-Positive Flow Considerations

Flows were averaged from the 2.23 hour flow data points to be daily flows per WASP segments, only for the segments of interest. The segments of interest were chosen according to the following criteria:

- Segments that were considered to be affected by the flow from tributaries,
- Segments that were considered to be significantly affected by the tidal influence¹,
 and
- Segments that were considered to affect the Main Channel flow.

These criteria were important to understand the contribution of flow by the tributaries and the tidal influence and thereby reversal of flow in the channel and in the tributaries. So the segments that were considered important were the tributary segments just before the confluence with the channel (Segment 9- Brays Bayou, Segment 13- Sims Bayou, Segment 15- Vince Bayou, Segment 19- Hunting Bayou, Segment 24- Greens Bayou, Segment 31- Carpenters Bayou, Segments in San Jacinto River (SJR)), the Main Channel segments before the confluence of the tributary and the channel segments after the confluence with the tributary down to Morgan's point.

3.3.3 Results and Discussion

3.3.3.1 Flow in the Main Channel and the SJR over the simulation period

Figures 3.8 and 3.9 show the average and median flows in the main channel and in SJR respectively, over the whole course of simulation period (07/20/2002 to 04/30/2005) for all time steps (i.e. not the daily mean flows).

-

¹ All segments are influenced by tide to some degree since this is an estuarine system. Most of the analysis in this section is concerned with the more observable tidal influence where the net flow of a segment is changing directions. Smaller degrees tidal influence only serve to attenuate the flow and though affected by tide, are easier to analyze since the direction of flow does not change.

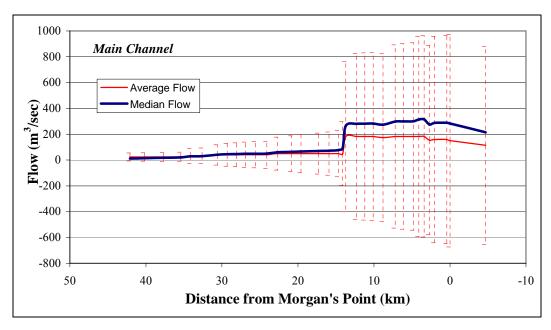


Figure 3.8. Average and Median flows in the Main Channel

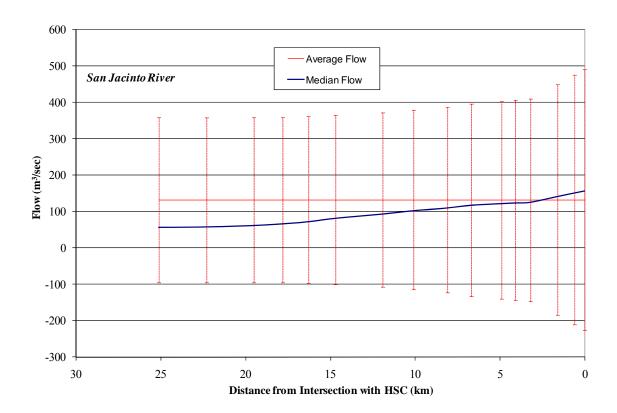


Figure 3.9. Average and Median flows in the San Jacinto River

The important observations were as follows:

- The average and median flows¹ over all of the simulation period in the Main Channel and SJR were positive, thereby indicating a net outflow.
- The median and average flows from SJR were significantly high compared to the flows upstream of Buffalo Bayou.
- The standard deviations were significantly high compared to the flow average, both in the Main Channel and in SJR. This indicates that the flow was not constant over the simulation period and had significant variation.
- The standard deviations in the Channel were low upstream (Buffalo Bayou) in comparison to downstream of the Channel. SJR also had huge standard deviations.
- The large deviations downstream in the channel and in the SJR are due to the tidal influence, which increases the variability associated with the flow.
- As can be seen from Figure 3.8, both the average and mean flows significantly increased
 at about 15 km from the Morgan's point. This is due to the confluence of SJR to the Main
 Channel. It can be seen that the increase was more than 50 %, thereby indicating a
 significant contribution of flow by SJR into the Main Channel.
- The median flow for SJR increases as it approaches the confluence with the HSC while the average flow remains constant. There are two potential findings from this:
 - 1. The runoff and tributaries that feed SJR as it moves south towards the HSC increases the flow enough to see a measurable increase.
 - 2. SJR does not experience much backflow because if it does, this increase near the confluence would not be observable. The negative flows would average it down to a more constant flow or even an apparent decreasing flow.

Figure 3.10 shows the increase in flow along the Main Channel caused due to the inflow of bayous and the SJR. The solid line indicates the average flow along the Main Channel and the bars indicate the average flow of the tributaries at the confluence of the Main Channel.

_

¹ Average and median flows calculated with all the flow data over the simulation period

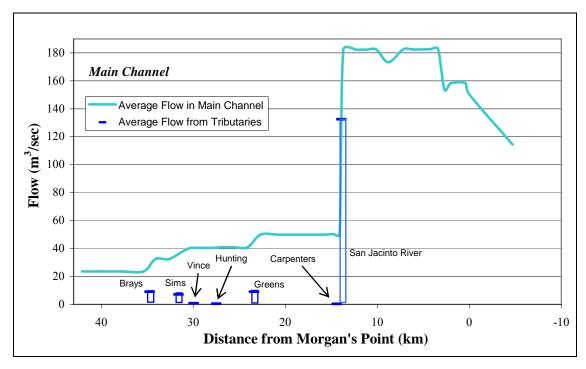


Figure 3.10. Average flows in the tributaries and their influence on Main Channel flow

The tributaries that were considered of importance as said above were: Brays Bayou, Sims Bayou, Vincent Bayou, Hunting Bayou, Greens Bayou, Carpenters Bayou, and San Jacinto River. The important observations made were as follows:

- Vince, Hunting, and Carpenters Bayou did not significantly influence the Main Channel flow.
- Brays, Sims, and Greens had a minor effect on the Main Channel flow.
- San Jacinto River had the major impact on the Main Channel flow which accounted for more than 50% of the flow.
- The increase in flow in the Main channel at the intersection of tributaries and Main Channel correlated well with the average flows from the tributaries.
- The flow starts to decrease at about 3.5 km and downstream of Morgan's Point probably because of an increase in areas adjacent to the channel (i.e. Galveston Bay).

3.3.4 Flow in the Tributaries and their Influence on Main Channel Flow

The summary statistics¹ of the flow in the tributaries (daily mean flows) over the simulation period are given in Table 3.7. It can be observed that SJR had the significantly highest flow and thus was the main contributor of flow to the HSC compared to other tributaries. It could also be seen that except for Brays, all other tributaries and SJR had a negative minimum flow which indicates multidirectional flow due to tidal influence. It can be seen that the average and median flows in all the tributaries were greater than zero, which represents a net positive outflow from the tributaries. All the tributaries except Brays had a negative flow day at some point in the 3-year span of the simulation. This analysis, however, does not indicate the amount of time the flow was negative or positive within each day to better understand the periods of greater tidal influence and their effect on each tributary.

Table 3.7. Daily-averaged flow summary statistics over the simulation period in the tributaries

	Brays	Sims	Vince	Hunting	Greens	Carpenters	SJR
Mean	9.16	7.27	0.79	0.42	9.01	0.33	135.04
Median	4.09	4.41	0.59	0.17	4.10	0.18	62.08
Standard Deviation	17.06	9.98	1.16	1.12	18.81	1.56	249.22
Minimum	0.70	-3.22	-1.27	-1.39	-1.38	-3.98	-63.47
Maximum	197.16	84.81	11.29	12.21	426.22	10.22	3091.75

So to better understand the negative and positive flows in the tributaries, individual analysis was done on the flows in the tributaries by separating the positive flow days from negative flow days over the period of simulation. The results are summarized in Table 3.8. The inferences from the analysis of daily flow means per tributary are as follows:

• Over the three year period and on a daily mean basis, Brays, Sims, and Vince Bayou had positive net flow 100%, 96%, and 88% of the time. This is understandable considering

¹ See Appendix B for all of the mean segment flows. Generally, the net flow was positive indicating discharge from the upstream end of the segment to the downstream end of the segment. It can also be seen that the flow had a significantly huge range in some segments, and the flow negative in some days, indicating greater tidal influence.

82

- that these tributaries are located in the upstream Channel and the degree of tidal influence is less as one moves farther upstream from the coastal area.
- Hunting and Carpenters Bayou had a positive outflow 67% and 57% of the days simulated. So there was considerable amount of days when the flow was negative, i.e., the flow was inwards towards the tributaries. In the case of Greens Bayou, the net flow was positive nearly 100% of the time.
- The reason behind the negative flow being higher in Hunting and Carpenters compared to Greens is partially due to the daily average flow magnitude in the tributaries. Greens Bayou has an average flow of 9.01 m³/sec in comparison to 0.42 and 0.33 m³/sec in Hunting and Carpenters Bayous, respectively. The lower flow tributaries (Hunting and Carpenters Bayous) could more easily be overcome by tidal influence to generate net negative flows as compared with higher flow tributaries (Greens Bayou) where it was more difficult to do more than merely diminish the positive outflow.
- In the case of SJR, the net flow was positive 90% of the time. Even though SJR could be more affected by the tidal influence due to its nearer vicinity to the channel, the significantly higher positive average flows prevented a negative inflow most of the time.
- SJR has positive flow 90% of the time, and at the same time had the highest mean and median negative flow values. If we consider the energy needed for sediment transport out of the tributary and into the main channel, it requires high velocities, which are often directly related to higher flows. So SJR might be a tributary with higher outwash velocities even it experiences negative flow some percentage of the time.

Table 3.8. Statistical summary on the negative and positive flows in the tributaries

Negative flow	Brays	Sims	Vince	Hunting	Greens	Carpenters	SJR
% days the flow was negative	0	4.00	12.20	32.60	0.76	42.71	12.01
Mean		-1.11	-0.32	-0.28	-0.42	-0.87	-15.05
Median		-0.89	-0.23	-0.23	-0.22	-0.68	-13.16
Standard Deviation		0.87	0.29	0.24	0.42	0.74	12.31
Minimum		-3.22	-1.27	-1.39	-1.38	-3.98	-63.47
Maximum		-0.01	0.00	0.00	-0.12	0.00	-0.08
					•		
Positive flow	Brays	Sims	Vince	Hunting	Greens	Carpenters	SJR
% days the flow was positive	100.00	96.00	87.70	67.30	99.24	57.20	87.99
Mean	9.16	7.62	0.95	0.76	9.09	1.23	155.53
Median	4.09	4.58	0.67	0.37	4.12	0.82	75.23
Standard Deviation	17.06	10.03	1.15	1.22	18.87	1.40	259.00
Minimum	0.70	0.05	0.00	0.00	0.01	0.00	0.08
Maximum	197.16	84.81	11.29	12.21	426.22	10.22	3091.75

To understand the contribution of flow from each tributary into the channel, calculations were made for the percentage flow from the tributary into the Main channel at the same period of our simulation period. The results are summarized in Table 3.9. As expected SJR was the main contributor of flow into the Channel (\approx 60%). This was followed by Sims, Brays and Greens Bayou. Vince, Hunting, and Carpenters Bayou were minor contributors to the Channel flow.

It was speculated whether segment 1006 acts as a sediment "bath tub" due to tidal influence, which opposes the positive flow from Buffalo Bayou and limits the total outflow of sediment that comes from 1006 to the downstream segments of the HSC. Were this to be true, it would affect the transport of PCBs and their attenuation in the Channel because 1006 has the highest concentrations in both water and sediment according to the data from 2002-2003 (Rifai and Palachek, 2007). The fact that concentrations in 1006 and 1007 have remained high despite

decades of PCB ban elicits hypotheses concerning the cause of persistent concentrations that are not flushed out downstream.

Table 3.9. Contribution by the Tributaries into the Main Channel using Mean Daily Flows

	% Brays	% Sims	% Vince	% Hunting	% Greens	% Carpenter	% SJR
Mean	16.03	22.30	4.98	2.72	14.34	4.27	58.59
Median	19.53	25.55	4.74	3.00	8.95	4.34	50.22

3.3.5 Conclusions

So the important conclusions from this flow analysis are:

- 1. Tidal influence was expected on the tributaries and in the main channel. The calculations presented here do not provide the best understanding of the influence because the tide is not often significantly strong enough to cause a negative flow in the main channel and in the tributaries. We still believe, however, that tide does play a significant role in the fate and transport of PCBs (both in the dissolved and suspended phases). Its role is better seen in terms of diminishing flows and velocities, and that effect will be researched more thoroughly in the next quarter.
- 2. It was speculated whether segment 1006 acts as a sediment "bath tub". However the speculation of bathtub was not provable from the flow calculations. The flow calculations gave a net positive outflow 90% of the time in Segment 1006, which might lead one to conclude that sediments usually do continue moving past the SJR confluence and further downstream. There are other more direct factors to sediment transport that need be considered such as water velocity (average as well as a function of depth), sediment cohesion, and the relation of grain size and grain type with all of the other sediment transport factors.
- 3. SJR was found to be the most influential tributary since it contributed more than 50% of the flow into the Main Channel.

4. Vince, Hunting, and Carpenters Bayou did not significantly influence the Main Channel flow, while Brays, Sims, and Greens had a minor effect on the Main Channel flow.

CHAPTER 4 CURRENT AND ONGOING ACTIVITIES

4.1 Channel Dredging Analysis

The 2002-2003 PCB sampling analysis revealed that sediments, as in the case with the Dioxin TMDL, look to be extremely high source areas for of PCB to the water column and thus present a large human health risk (Rifai and Palachek, 2007). The locations of the "hot" sediment zones are slightly different than what was seen in the Dioxin TMDL, but sediments still prove to be a large repository and significant factor in understanding what an effective PCB TMDL will be.

Because of the significance of sediment as a source, the project team decided initiated analysis and background research on many aspects of sediment distribution (see Section 3.1), sediment transport, and Channel activities related to sediment. These activities can be natural or anthropogenic, and dredging is one of the anthropogenic activities on which analysis has begun¹. The mid-way results of that analysis are as follows.

4.1.1 Dredging Data Retrieval

The HSC is dredged periodically to maintain the proper draft depth for large shipments. The dredging is performed essentially as an "as needed" basis under the joint authority of the Galveston District Army Corps of Engineers (COE) and the Port of Houston Authority (PHA). The COE is the main body over the HSC dredging efforts, and it is responsible for keeping the Channel at navigable depths. Practically, however, the dredging activities are administered jointly between COE and PHA according to locations within the Channel. PHA is responsible for the dredging of the HSC as far downstream as Morgan's Point. At Morgan's Point, the HSC fans out into Upper Galveston Bay. It sheds all semblance of a natural channel at this point and

_

87

¹ A dredge data analysis was conducted as part of the Dioxin TMDL study in a December 2005 quarterly report (Rifai et al., 2005). That report is now incomplete because it does not include dredging activities since that time. Additionally, however, that report is not as intelligible as is needed for the understanding in this project nor has the original data for it been discovered. So efforts are being made to get to the original data so that a larger dataset may be considered than what was covered in December 2005 and so that the analysis better meets the needs of this project.

is only a channel because of shallow water dredging as it crosses the bay. It is this section of the channel for which COE has dredging responsibility (Campbell, 2007).

Dredging activities are contracted out by both organizations to independent private organizations that dredge the amount, the frequency, and the ultimate depth of dredging according to contracts made with PHA or COE. These organizations keep records of these contracts as well as database entries of amounts dredged. The team's activities from this quarter consisted of attempting to procure these records from both organizations, and that procurement still continues. Once the dredge depth, yardage, and contract records have been attained, further analysis of the dredging may be performed, which will be explained shortly.

In addition to sediment removal activities conducted by PHA, it was discovered that PHA (PHA, 2007) also requires that sediment analysis be conducted from the dredge spoils in order to analyze for contaminants of concern. Figure 4.1 shows the locations of the dredge spoils in relation to the entire HSC (including out to Galveston Island). The requirements for sampling frequency are "approximately every 500 linear feet over the dredge prism and represent a maximum sediment volume of 5,000 cubic yards". Moreover, the dredging conducted near outfalls is required to have a sample that is representative of sediment from the corresponding outfall. The contaminant of concern included parameters that are useful to this project including TOC, Grain Size, and Total PCBs. The full list of contaminants is given in Appendix C. These parameters are also analyzed for in elutriate from the sediment samples. Elutriate analysis may give a somewhat similar surrogate to pore water though it would depend on how the analysis is conducted. PHA has been contacted with regards to obtaining these sampling records, which should be available to the public yet may require retrieval time and cost. It is not known at this time how long the sediment sampling from dredge cores has been conducted, but it is fairly certain that the data would be useful for more spatial but especially temporal analysis of PCB distribution in the HSC.

⁻

¹ Note that nothing in the dredge sediment analysis document states how often sampling should be conducted. The document gives guidance on how it should be done however often the sampling is conducted, but it does not specific if sampling should done every time dredging occurs whether it is annual, biannual, or any other temporal frequency.

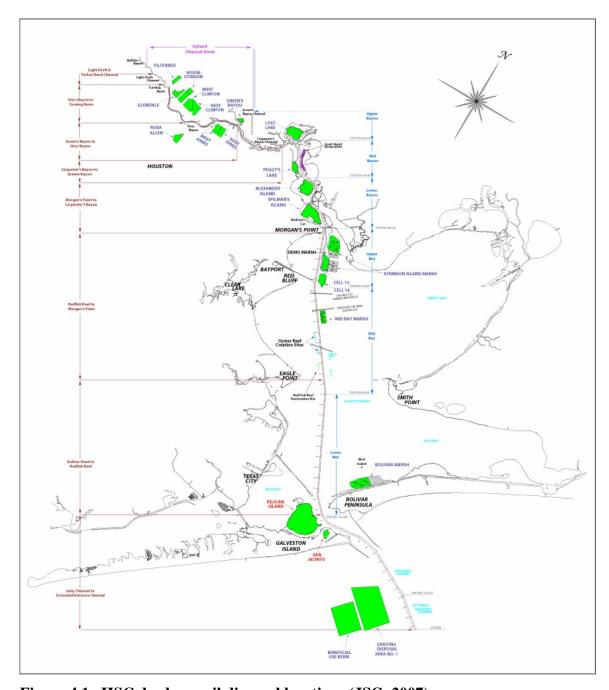


Figure 4.1. HSC dredge spoil disposal locations.(JSG, 2007)

4.1.2 Potential Dredging Data Calculations and Uses

The summary of the dredging data¹ that is eventually expected is as follows:

- Dredging Activity Records: Date of dredging, time span of dredging, location of dredging, and dredging company.
- 2) Dredging Amounts: Depths and yardage of sediment dredged for every contract that was dredged upstream of Morgan's Point including the Light Draft Channel (the HSC upstream of the Turning Basin) and the Greens Bayou Channel.
- 3) Sediment Core Analysis: The full suite of analytes (POHA, 2007) for dredged sediments.
- 4) Dredge Disposal Locations: The particular disposal locations for dredge spoils from particular locations in the Channel

This dataset was gathered for the following applications, but other applications may become apparent as the data received and used.

Sedimentation Rates should be able to be calculated via the dredge volumes that are summed together and annualized for the period of record. The idea is that sedimentation is linked to dredged volumes because it is the desire of COE and PHA to maintain a certain depth in the dredge prism. At whatever annualized rate the dredge spoils are removed, this should be an estimate of local sedimentation. This is a much less rigorous means of quantifying sedimentation in the Channel, but it may be a valuable first estimate that may later be combined with better estimation methods. The Dioxin TMDL used the WASP model, which requires estimates of sedimentation rates. That modeling effort used sediment settling as a completely calibratable parameter. It would be helpful to have an understanding of what a reasonable settling rate would be from an independent means outside of the modeling efforts unless those modeling efforts also include some sediment transport modeling. Sediment transport modeling is still an option for this project in terms of coordinating that with water quality modeling or

-

¹ Most if not all dredging data will be for dredging activities upstream of Morgan's Point. It is certainly possible that the project team may receive data for dredging south of Morgan's Point, and that data would be used. It is currently believed that the data upstream of Morgan's Point is the most useful.

simply using it as another tool for understanding. If the sediment transport modeling takes place, it is valuable to gather as much information regarding sediment settling as possible.

Temporal Sediment PCB Records can be generated from a large set of PCB-analyzed sediment core data. Accurate and useful temporal records of sediment PCBs have not existed for the HSC until the 2002-2003 PCB sampling was conducted. Previous sampling efforts used an Aroclor based analysis method for nearly all of that sampling, which has been determined to be incomparable to all congener or representative congener datasets such as what is found in the 2002-2003 sampling (Howell et al., 2008). Thus, if the sampling conducted by PHA in the sediment coring uses some method of PCB quantification that is closer to congener-specific quantification, then a temporal-spatial picture of sediment PCB concentrations will result to provide better understanding of sources and conditions in the Channel past and that will indicate what degree of attenuation in sediment concentrations may be expected in the Channel future. The preliminary data that has been received from COE does not seem indicate that any non-Aroclor analysis was done, but more may be received.

Dredge Spoil Runoff Loads are a concern as a specific kind of runoff load into the HSC. As stated previously, sediments, in comparison to other media in the HSC, contain the highest concentrations of PCBs. From a completely environmental standpoint, if those sediments were going to be removed from the Channel bottom, then it would be most prudent to make sure they have no influence on the Channel after their removal. Yet these dredge spoils are placed all along the Channel banks¹ in the areas for this TMDL, as shown in Figure 4.1 and Figure 4.2, where the PCBs contained in the sediment can be reintroduced to the HSC by runoff dissolution of PCBs or by spoil particle entrainment that becomes suspended phase in the water column or eventually sediment in the Channel bed again.

91

¹ Inquiries have been made as to the containment procedures used for the dredge spoils to assess what the risk the spoils have to reintroduce PCBs in runoff. The nature of the spoil containments still is not clear.

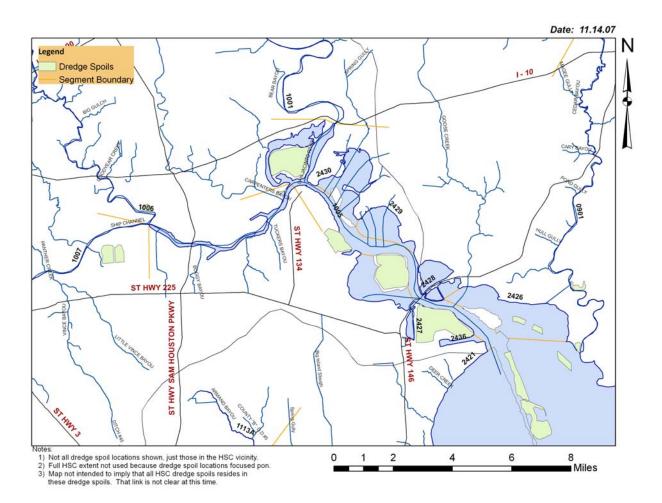


Figure 4.2. Locations of dredge spoils in the vicinity of the TMDL study area.

An Enlarged PCB Sampling Dataset is a possible result for the gathered results on the sediment cores. If the PCB data comparable, then there are several benefits that may be had from an enlarged PCB dataset beyond the ability to have better temporal understanding as stated above:

- More sediment data that can be used for modeling. While sediment concentrations do not enter into the WASP model as it currently stands, sediment concentrations can be used to predict water concentrations near the benthic layer, and they certainly can be used in any kind of sediment modeling that occurs.
- Better understanding of spatial trends for PCB, TOC, and grain size. Since these three are all important parameters for understanding PCB transport, a better spatial assessment in these parameters should benefit all areas of the project.

Better field data on PCB partitioning from sediment to pore water. TOC is often the
critical factor that needs to be known on sediments in order to best predict
partitioning behavior. More TOC data will help yield better global and segmentspecific values for partitioning.

Early into this coming quarter, these datasets should begin arriving, and these analyses will begin to be included in later quarterly reports, to aid in field sampling, and to improve modeling efforts.

4.2 Continuing Grain Size Analysis

As can be seen from the data analysis section on grain size (Section 3.1), there is more work that can and should be done to understand the role of grain size in PCB fate and transport in the HSC. Planned for the coming quarter are linear regression analyses to assess the effects that grain size has on Σ PCB concentration (and possibly on significant PCB congeners as well) and the effects that grain size has on TOC. It is likely that grain size is only one factor that helps to explain the high concentrations of PCB in Segments 1006 and 1007, but a better understanding of its role will help to understand how big a role it plays and how that role interacts with other factors such as TOC, closeness to potential industrial sources, sediment transport (both upstream and tributary), and flow velocity.

4.3 QAPP Progress

This quarter saw further development of both the monitoring and modeling QAPPs in terms of the team being asked to respond to initial comments from TCEQ. Those comments have been significantly addressed, and thus the updated versions of the QAPPs are being reviewed by TCEQ at this time. What follows is a description of the major issues discussed in those QAPPs and how they have been or are being addressed.

4.3.1 POC Method Selection

Section 2.2 presented a POC method and literature review as well as some analysis of what sampling and analysis methods will be appropriate for the PCB TMDL study. The monitoring QAPP (Appendix D) currently refers to the chosen POC analysis method as the Lloyd Kahn method. This method is likely the method that will be used. What has not yet been addressed in the Monitoring QAPP is what kind of special sampling considerations will need to be made to get a usable suspended particulate solids sample for POC apart from that which will be used for PCB. This issue will be resolved before sampling begins next quarter. The considerations given in the method review of Section 2.2 will be part of that discussion.

4.3.2 Intensive Sediment Survey

The first PCB sampling conducted in 2002-2003 provided a good spatial overview of ΣPCB in water, sediment, fish, and crab. In all of those media, the highest concentrations were found in Segments 1006 and 1007, which are believed to have continually high concentrations due to the benthic source beneath the water column. Hwang et al. (1998) found, through modeling efforts in New Bedford Harbor, Massachusetts, that as long as sediments in that harbor remained contaminated with PCB, that water quality would not be improved. A similar situation is likely in the HSC, and it has been suggested that the team pursue a more detailed sediment sampling effort to understand the full range of "hot spot" sediment concentrations, distributions, and sourcing.

In addition to these general assessment specificity goals, the detailed sediment sampling would also be able to look some specific effects in the high PCB zone. These effects include

- 1. Tributary to Channel interactions and the possibility of contaminated transport from the tributaries to the Channel.
- 2. Suspended particle phase dropout to the sediment bed when the saline wedge in the water meets a greater freshwater zone.

The most likely candidate tributaries (Greens Bayou, Carpenter Bayou, and Patrick Bayou) for such sediment transport were chosen based on sediment PCB homolog fingerprints as discussed previously in Quarterly Report 2 (Rifai and Palachek, 2007) and Howell et al. (2008). The chemical fingerprint evidence is suggestive of PCB sourcing to 1006 and 1007 via tributary sediment transport, but more sampling information is needed to confirm this.

Suspended particle phase dropout arose as a possible phenomenon that needed to be examined through WASP model development during the Dioxin TMDL. The settling rates in the model had to be manually increased to high levels compared to surrounding model segments in order to fit the calibration and verification PCB concentration datasets. It is not known whether this high suspended particle settling actually exists, and direct settling measurements (e.g. sediment traps) would confirm or deny the effect. If this dropout hypothesis were falsified, then an alternative explanation would be hypothesized and pursued.

The current Monitoring QAPP does not include any section on a detailed sediment survey, and it is expected that this sediment survey would take the form of a later amendment. Some of the analysis to choose sites for the sampling was begun this quarter, and this analysis was performed by GIS mapping. Figure 4.3 and Figure 4.4 show concentrations of Σ PCB in water and sediment from 2002-2003 sampling dataset in Segments 1006 and Segment 1007. These figures will be combined with others to make more complete analysis, but it is possible to see that there are some significant concentrations of PCB in the segments that are bounded upstream and downstream often by much smaller concentrations. The sediment survey should be assigned to if nothing else

- Address what the trend in concentration is between large concentration differences.
- Determine what lateral trend of PCBs is in the "hot" segments. Lateral trending may be
 able to assess what effects the dredging has on sediment PCB concentrations since
 dredging is normally conducted only in the center of the HSC.

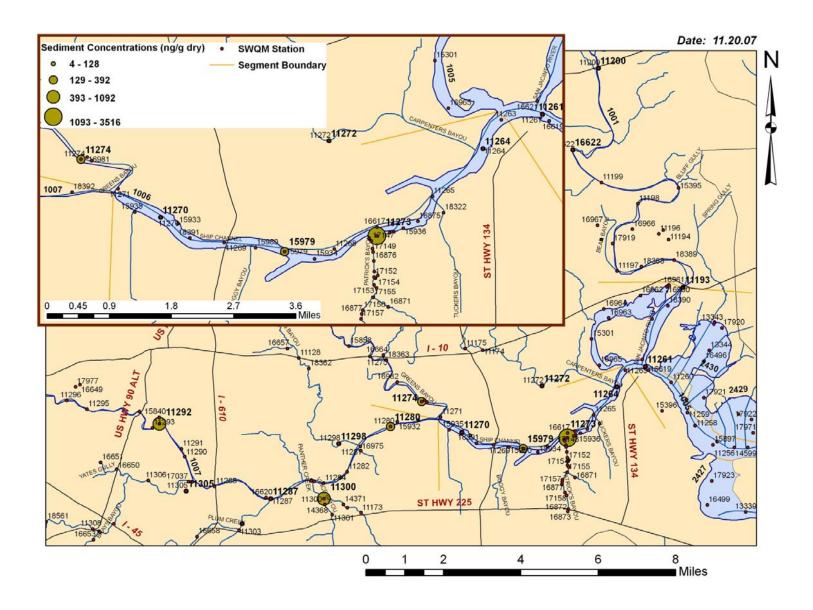


Figure 4.3. Hot spot sediment concentrations in the HSC.

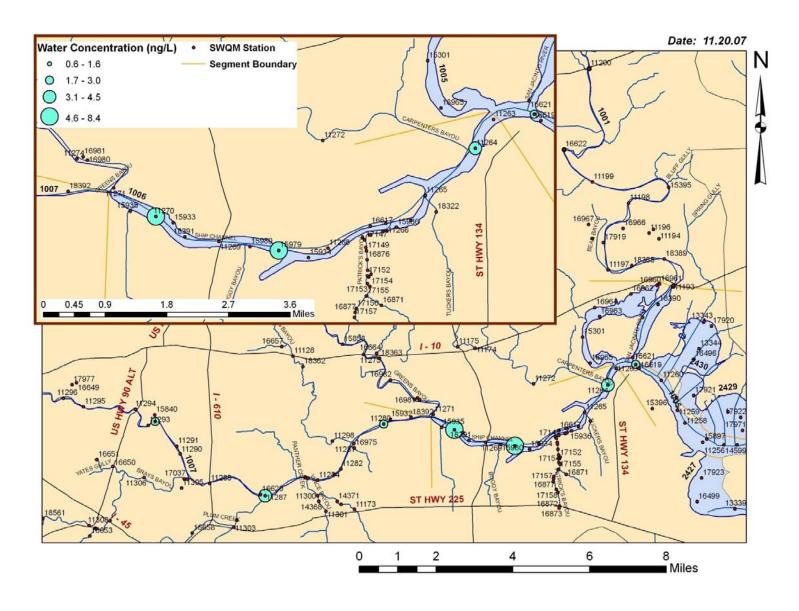


Figure 4.4. Hot spot water concentrations in the HSC.

CHAPTER 5 - REFERENCES

- Ambrose, R.B., 1987. Modeling Volatile Organics in the Delaware Estuary. Journal of Environmental Engineering 113, 703-721.
- API, 2003. Groundwater Remediation Strategies Tool.
- Benaman, J., 1996. Modeling of Dissolved Oxygen in the Houston Ship Channel using WASP5 and Geographic Information Systems. Department of Civil, Architectural, and Environmental Engineering. The University of Texas at Austin, Austin.
- Bierman, V.J., Jr., DePino, J.V., Young, T.C., Rodgers, P.W., Martin, S.C., Raghunathan, R., United States Environmental Protection Agency (USEPA), Office of Research and Development, ERL-Duluth, Large Lakes Research Station, 1992. Development and Validation of an Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan, Final Report. Grosse Ile, Michigan, p. 381.
- Bishop, J.K.B., 1999. Transmissometer measurement of POC. Deep-Sea Res. Part I-Oceanogr. Res. Pap. 46, 353-369.
- Bottcher, A.B.J., B.M.; Hiscock, J.G., 2005. TMDL assessment using WAM/WASP. 3rd Conference on Watershed Management to Meet Water Quality Standards and Emerging TMDL. American Society of Agricultural Engineers Atlanta, GA, pp. 478-488.
- Brown, L.C., Barnwell, T.O., U.S. Environmental Protection Agency (USEPA), Environmental Research Laboratory, 1987. The Enhanced Stream and Water Quality Models QUAL2E and OUAL2E-UNCAS: Documentation and Users Manual.
- Campbell, T.C., 2007. Personal Communication. In: Lakshmanan, D. (Ed.). Galveston District Army Corps of Engineers (GDACOE), Houston, TX.
- Caruso, B.S., 2005. Simulation of metals total maximum daily loads and remediation in a mining-impacted stream. Journal of Environmental Engineering 131, 777-789.
- Chao, A.C., Chen, S.W., Chen, T.Y., Kao, C.M., Lai, Y.C., Lin, C.E., 2006. Application of water quality modeling on river basin management. WSEAS Transactions on Mathematics 5, 1078-1082.
- DCDE, District of Columbia Department of the Environment (DCDE), 2007. Total Maximum Daily Loads of Polychlorinated Biphenyls (PCBs) for Tidal Portions of the Potomac and Anacostia Rivers in the District of Columbia, Maryland, and Virginia.
- De Smedt, F., Vuksanovic, V., Van Meerbeeck, S., Reyns, D., 1998. A time-dependent flow model for heavy metals in the Scheldt estuary. Hydrobiologia 366, 143-155.
- Dean, K., 1994. Phase Partitioning And Fate Of Hydrophobic Organic Contaminants In Lake Michigan. Water Chemistry. University of Wisconsin-Madison, Madison, Wisconsin, p. 169.

- Dean, K., 2007. Re: Alternate TOC Method. In: Suarez, M.P. (Ed.), Austin, TX.
- DePinto, J.V., Raghunathan, R., Sierzenga, P., Zhang, X., Bierman, V.J., Jr., Rodgers, P.W., Young, T.C., United States Environmental Protection Agency (USEPA), Office of Research and Development, 1993. Recalibration of GBTOX: An Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan, Final Report., ERL-Duluth, Large Lakes Research Station, Grosse Ile, Michigan, p. 132.
- Draxler, R.R., McQueen, J.T., Stunder, B.J.B., 1994. An Evaluation fo Air Pollutant Exposures due to the 1991 Kuwait Oil Fires using a Lagrangian Model. Atmos. Environ. 28, 2197-2210.
- DRBC, Delware River Basin Commission, 2003. PCB Water Quality Model for Delaware Estuary (DELPCB). West Trenton, New Jersey.
- DRBC, Delaware River Basin Commission, 2006. Revised Calibration of the Water Quality Model for the Delaware Estuary for Penta-PCBs and Carbon. West Trenton, New Jersey.
- Ferreira, A.M., Martins, M., Vale, C., 2003. Influence of diffuse sources on levels and distribution of polychlorinated biphenyls in the Guadiana River estuary, Portugal. Mar. Chem. 83, 175-184.
- Gardner, W.D., Richardson, M.J., Carlson, C.A., Hansell, D., Mishonov, A.V., 2003. Determining true particulate organic carbon: Bottles, pumps and methodologies. Deep-Sea Research Part II: Topical Studies in Oceanography 50, 655-674.
- Gobas, F., Pasternak, J.P., Lien, K., Duncan, R.K., 1998. Development and field validation of a multimedia exposure assessment model for waste load allocation in aquatic ecosystems: Application to 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzo-furan in the Fraser River watershed. Environmental Science & Technology 32, 2442-2449.
- Hajda, P., Novotny, V., 1996. Modelling impact of urban and upstream nonpoint sources on eutrophication of the Milwaukee River. Water Sci. Technol. 33, 153-158.
- Hayter, E.J., Bergs, M., Gu, R., McCutcheon, S., Smith, S.J., Whiteley, H.J., USEPA, 1999. HSCTM-2D, a Finite Element Model for Depth-Averaged Hydrodynamics, Sediment, and Contaminant Transport. Technical Report. Athens, GA.
- Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of Paleolimnology 25, 101-110.
- Hernandez, P., Ambrose, R.B., Prats, D., Ferrandis, E., Asensi, J.C., 1997. Modeling eutrophication kinetics in reservoir microcosms. Water Res. 31, 2511-2519.
- Hosseinipour, E.Z., Yereschukova, M.G., 1993. Water Quality Modeling of a Major Russian River, the Data Dilemma. Water Environment Federation, Alexandria, VA.
- Howell, N.L., Suarez, M.P., Rifai, H.S., Koenig, L., 2008. Concentrations of polychlorinated biphenyls (PCBs) in water, sediment, and aquatic biota in the Houston Ship Channel, Texas. Chemosphere 70, 593-606.

- Hwang, B.-G., Jun, K.-S., Lee, Y.-D., Lung, W.-S., 1998. Importance of DOC in sediments for contaminant transport modelling. Water Sci. Technol. 38, 193-199.
- Je, C.-h., Hayes, D.F., Kim, K.-s., 2007. Simulation of resuspended sediments resulting from dredging operations by a numerical flocculent transport model. Chemosphere 70, 187-195.
- Jin, K.R., James, R.T., Lung, W.S., Loucks, D.P., Park, R.A., Tisdale, T.S., 1998. Assessing Lake Okeechobee eutrophication with water-quality models. J. Water Resour. Plan. Manage.-ASCE 124, 22-30.
- JRB, JRB Associates, 1984. Development of Heavy Metal Waste Load Allocations for the Deep River, North Carolina. McLean, VA.
- JSG, 2007. J. Simmons Group Website. Houston, TX.
- Koh, H.-L., Lim, P.-E., Lee, H.-L., 1995. Water quality modeling for an estuary in Johore. Water Qual. Res. J. Can. 30, 45-52.
- Lopezivich, K.T., James, W., Heathcote, I.W., Fitzgibbon, J., 1996. Feasibility of Modeling Phosphorus Dynamics in Stormwater Wetlands. In: Bathala, C. (Ed.). North American Water and Environment Congress '96, Anaheim, CA.
- Lorber, M., Robinson, R., Eschenroeder, A., 1999. An Evaluation of EPA's ISCST -Version 3 Model. Part 2 Deposition and Soil Concentration of Dioxins. Dioxin'99, the 19th International Symposium on Halogenated Environmental Organic Pollutants and POPs, September 12-17, Venice, Italy, pp. 541-545.
- MDEQ, Mississippi Departement of Environmental Quality, 2000. Country Club Lake Phase One Total Maximum Daily Load For Dioxin and Pentachlorophenol (PCP). Jackson, MS.
- Morton, M., United States Environmental Protection Agency (USEPA), 1993. TMDL Case Study: Modeling the Appoquinimink River. Case Study Number 9. EPA841-F-94-004. http://www.epa.gov/OWOW/tmdl/cs12/cs12.htm
- Morton, M., Stoddard, A., Pagenkopf, J., 1989. Eutrophication and nutrient enrichment in Peconic Bays. Numerical model of historical conditions of the Mid-1970s. Estuarine and Coastal Modeling Proceedings of the Conference, Waterway, Port, Coastal and Ocean Div, ASCE, pp. 351-360.
- O'Connor, D.J., Mueller, J.A., Farley, K.J., 1983. Distribution of Kepone in the James River Estuary. J. Environ. Eng.-ASCE 109, 396-413.
- ORVWSC, Ohio River Valley Water Sanitation Commission (ORVWSC), 2000. Development of a Total Maximum Daily Load for Dioxin on the Ohio River. Cincinatti, OH.
- PHA, Port of Houston Authority (PHA), 2007. Port of Houston Authority: Sediment Sampling Requirements. Houston, TX. http://www.portofhouston.com/pdf/channel/PHASedimentProcedures.pdf
- Picket, P.J., Washington State Department of Ecology, 1994. Upper Chehalis River Dry Season Total Maximum Daily Load Study. Olympia, WA. http://www.wa/gov/ECOLOGY/eils/biblio/ abstracts/94-126_abs.html

- Picket, P.J., 1997. Pollutant loading capacity for the Black River, Chehalis River system, Washington. Journal of the American Water Resources Association 33, 465-480.
- Pitt, R., 1987. Small Storm Urban Flow and Particulate Washoff Contributions to Outfall Discharges. University of Wisconsin, Madison, WI, Madison, WI.
- POHA, Port of Houston Authority (POHA), 2007. Port of Houston Authority: Sediment Sampling Requirements. Houston, TX.
- Richardson, W.L., Smith, V.E., Wethington, R., 1983. Dynamic Mass Balance of PCB and Suspended Solids in Saginaw Bay A Case Study. Physical Behavior of PCBs in the Great Lakes. Ann Arbor Science Publishers, Ann Arbor, Michigan, pp. 329-366.
- Rifai, H., Palachek, R., Jensen, P., Texas Commission on Environmental Quality (TCEQ), 2005. Total Maximum Daily Loads for Dioxin in the Houston Ship Channel, Final Report, Work Order No. 582-0-80121-07. Austin, p. 540.
- Rifai, H.S., Palachek, R., The University of Houston, 2007. Total Maximum Daily Loads for PCBs in the Houston Ship Channel: Quarterly Report No. 2. Houston, TX, p. 59.
- Rolph, G.D., Draxler, R.R., Depena, R.G., 1992. Modeling Sulfur Concentrations And Depositions In The United-States During ANATEX. Atmospheric Environment Part a-General Topics 26, 73-93.
- Rolph, G.D., Draxler, R.R., Depena, R.G., 1993. The Use of Model-Derived and Observed Precipitation in Long-Term Sulfur Concentration and Deposition Modeling. Atmospheric Environment Part a-General Topics 27, 2017-2037.
- Scarlatos, P.D., 2001. Computer modeling of fecal coliform contamination of an urban estuarine system. Water Sci. Technol. 44, 9-16.
- Schumacher, B.A., 2002. Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments. In: USEPA, E.S.D., National Exposure Research Laboratory (Ed.), Las Vegas, Nevada, p. 25.
- Smith, J.G., 2003. Aspects of the Loss-On-Ignition (LOI) Technique in the Context of Clay-Rich, Glaciocustrine Sediments. Geografiska Annaler: Series A, Physical Geography 85, 91-97.
- Thomann, R.V., Di Toro, D.M., 1983. Physicochemical Model of Toxic Substances in the Great Lakes. Journal of Great Lakes Research 9, 474-496.
- Thomann, R.V., Fitzpatrick, J.P., HydroQual, Inc., 1982. Calibration and verification of amathematical model of the eutrophication of the Potomac estuary. Washington, D.C.
- Thomas, W.A., McNally, W.H., U.S. Army Corps of Engineers, 1985. User's Manual for the Generalized Computer ProgramSystem-Open Channel Flow and Sedimentation TABS-2. Vicksburg, MS.
- TWDB, Texas Water Development Board, 1999. Transmissivity, Hydraulic Conductivity, and Storativity of the Carrizo-Wilcox Aquifer in Texas. Draft Technical Report. TWDB Contract No. 99-483-279, Part 1.

- USACE, 2007. Galveston District Surveys. U.S. Army Corps of Engineers, Houston.
- USEPA, 1990a. Lake Ontario TCDD Bioaccumulation Study Final Report.
- USEPA, Office of Water Regulations and Standards, Monitoring and Data Support Division, 1990b. Simplified Analytical Method for Determining NPDES Effluent Limitations for PTOWs Discharging into Low-flow Streams. Washington, D.C.
- USEPA, Office of Wetlands, Oceans, and Watershed, 1997. Compendium of Tools for Watershed Assessment and TMDL Development, EPA-841-B-97-006. Washington, D.C.
- USEPA, Region III, 2000. Dioxin TMDL Development for Kanawha River, Pocalitico River, and Armour Creek, West Virginia. Philadelphia, PA.
- USEPA, 2003a. Amended Decision Rationale Total Maximum Daily Loads Anacostia River Watershed For Organics and Metals. Philadelphia, PA.
- USEPA, 2003b. TAM/WASP Toxics Screening Level Model for the Tidal Portion of the Anacostia River Final Report. Philadelphia, PA.
- USEPA, Great Lakes National Program Office, 2006. Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyls Modeling Report, EPA-600/R-04/167. Chicago, IL.
- Velleux, M., Endicott, D., 1994. Development of a Mass-Balance Model for Estimating PCB Export from the Lower Fox River to Green Bay. Journal of Great Lakes Research 20, 416-434
- Vuksanovic, V., De Smedt, F., Van Meerbeeck, S., 1995. Transport of polychlorinated biphenyls (PCB) in the Scheldt Estuary simulated with the water quality model WASP. Journal of Hydrology 174, 1.
- Wang, A.J., Li, Z., Yin, L.L., Lee, D.J., Wang, F., Xin, L., Zhao, L.J., He, Z.Y., Feng, Y.J., Han, H.J., Hong, Y., 2007. Modeling the nitrobenzene spill in the Songhua River. Water Science and Technology: Water Supply 7, 115-123.
- Ward, G., Benaman, J., University of Texas at Austin, Center for Research in Water Resources, 1999. A Survey and Review of Modeling for TMDL Application in Texas Watercourses (Draft Report). Austin, TX.
- Warwick, J.J., Cockrum, D., Horvath, M., 1997. Estimating non-point-source loads and associated water quality impacts. J. Water Resour. Plan. Manage.-ASCE 123, 302-310.
- Yang, C.P., Kuo, J.T., Lung, W.S., Lai, J.S., Wu, J.T., 2007. Water Quality and Ecosystem Modeling of Tidal Wetlands. J. Environ. Eng.-ASCE 133, 711-721.
- Zhou, J., 1998. Water quality modeling of reservoir using WASP. ASCE 1998 International Water Resources Engineering Conference, Part 2, pp. 1458-1463.

CHAPTER 6 - APPENDICES

APPENDIX A - 2002-2003 PCB SAMPLING GRAIN SIZE RAW DATA

 $\begin{tabular}{ll} Table A.1 Sediment sample sediment distributions in dry weight \%. Duplicates have been averaged together. \end{tabular}$

Station	Season	Gravel	Sand	Silt	Clay	Total
11092	Spring	0.6	19	49.8	29.9	99.3
11092	Summer	0	8.6	49.5	41.9	100
11111	Spring	0	4.6	44.6	50.9	100.1
11111	Summer	0	1.8	45.6	52.5	99.9
11193	Fall	0.7	45.6	45.7	8	100
11193	Spring	0	54.5	34	11.6	100.1
11193	Summer	0.1	42.2	46.7	11	100
11200	Summer	0	75.05	14.65	10.05	99.75
11252	Fall	0.1	5.5	45.3	49.1	100
11252	Spring	0.95	14.25	51.05	33.65	99.9
11252	Summer	1	42.9	48.8	7.3	100
11258	Spring	0	73.6	24.1	2.3	100
11258	Summer	0	68	29.3	2.7	100
11261	Fall	0	58.9	32.1	9	100
11261	Spring	0	43.7	43.1	13.2	100
11261	Summer	0	76.2	13.9	9.9	100
11264	Spring	0.3	12.3	41.1	46.3	100
11270	Spring	0	38.5	50.6	10.9	100
11270	Summer	0	16.3	53.4	30.3	100
11272	Spring	0	5.8	35.5	58.7	100
11272	Summer	0	0.8	30.4	68.7	99.9
11273	Spring	0	17.2	49.3	33.5	100
11273	Summer	1	21.8	44.5	32.6	99.9
11274	Spring	0	40.9	50	9.1	100
11274	Summer	0	12.8	63	24.1	99.9
11280	Spring	0	4.7	39	56.3	100
11280	Summer	0	3.3	50.6	46	99.9
11287	Spring	0.7	23.5	57.3	17.5	99
11287	Summer	0	38.5	41.5	20	100
11292	Spring	0.8	26.1	55	18.1	100
11292	Summer	0	6.8	64.2	28.7	99.7

11298	Spring	1.8	34.8	40.1	23.3	100
11298	Summer	0	12.2	62.3	25.5	100
11300	Spring	20.2	37.8	33.6	8.5	100.1
11300	Summer	1.55	28.85	51.6	16.7	98.7
11302	Spring	1.5	19	43.2	36.2	99.9
11305	Spring	0.3	60.6	33.2	5.5	99.6
11305	Summer	0	30.55	54.95	14.55	100.05
11347	Spring	0.3	58.7	36.7	4.2	99.9
11347	Summer	0	70.8	23.3	5.9	100
11382	Summer	0.3	62.8	30.4	6.5	100
13309	Spring	0	33.4	55.9	10.7	100
13309	Summer	0	17.2	76.7	6.1	100
13336	Fall	0	19.7	52.8	27.4	99.9
13337	Spring	0	13.3	51.4	35.3	100
13337	Summer	0	7.5	56.8	35.2	99.5
13338	Fall	0	40.3	45.7	14	100
13338	Summer	0	5.1	54.9	40	100
13339	Spring	0	63.9	33.3	2.8	100
13339	Summer	0	10	34.8	55.2	100
13340	Fall	0.2	11.9	39.2	48.6	99.9
13340	Summer	0	7.1	41.5	51.4	100
13341	Spring	1.6	81.7	0	0	83.3
13341	Summer	0	2	36.1	61.9	100
13342	Spring	0.7	0.7	53.4	45.2	100
13342	Summer	0	1.1	31.9	67	100
13343	Spring	56.9	3.2	30.4	9.5	100
13343	Summer	0	14.4	70.9	14.5	99.8
13344	Fall	3.5	4.9	35.6	56	100
13344	Summer	10.5	1.7	18.9	68.9	100
13355	Spring	3.7	7.8	42.4	46.1	100
13363	Fall	3.7	15	52.8	28.5	100
13363	Summer	0	12.9	64.5	19.8	97.2
13589	Spring	0.3	14	58.7	26.9	99.9
13589	Summer	0	23.4	50.2	24.2	97.8
14560	Spring	1.3	41.8	33.7	19.1	95.9
14560	Summer	0	3.3	61.6	35	99.9
15464	Fall	0	59.2	36.3	4.4	99.9
15464	Spring	0	51.8	39	9.2	100
15464	Summer	0	74.5	16.3	8.5	99.3
15908	Spring	0	35.7	50.5	13.8	100
15908	Summer	1.2	32.5	52.6	12.9	99.2
15979	Spring	0	13.2	38.6	48.2	100
16213	Spring	0	1.3	56.6	42.1	100

16213	Summer	0	1.7	38	60.2	99.9
16496	Spring	0	1	42.1	56.9	100
16496	Summer	0.5	2.9	31.3	65.3	100
16499	Fall	0	7.2	57.9	34.9	100
16499	Summer	0	14.7	44.5	40.8	100
16622	Spring	0.1	10.1	47.5	41.9	99.6
16622	Summer	0	27.6	63.8	8.6	100
17970	Fall	0	47.4	43	9.5	99.9
17971	Fall	0	21.5	47.1	31.4	100
17971	Summer	0	3.1	44.7	52.1	99.9

Table A.6.1. Average sample station grain size distributions averaged over all seasons by dry weight %.

Station	Lat	Long	Station Description	GRAVEL	SAND	SILT	CLAY	Total
11092	29.7318	-94.9887	GOOSE CREEK AT MARKET STREET	0.3	13.8	49.65	35.9	99.65
11111	29.72306	-94.9417	CEDAR BAYOU AT ROSELAND PARK	0	3.2	45.1	51.7	100
11193	29.79195	-95.0614	SAN JACINTO RIVER AT IH 10	0.266667	47.43333	42.13333	10.2	100.0333
11200	29.87583	-95.0936	SAN JACINTO RIV TIDAL AT US 90	0	75.05	14.65	10.05	99.75
11252	29.68278	-94.9819	HOUSTON SHIP CH MORGANS POINT	0.683333	20.88333	48.38333	30.01666667	99.96667
11258	29.73972	-95.0589	HOUSTON SHIP CHANNEL AT CM 120	0	70.8	26.7	2.5	100
11261	29.76278	-95.0792	HOUSTON SHIP CH LYNCHBURG FERR	0	59.6	29.7	10.7	100
11264	29.75556	-95.0917	HOUSTON SC AT SAN JACINTO PARK	0.3	12.3	41.1	46.3	100
11270	29.74111	-95.1592	HOUSTON SHIP CHANNEL UPSTRM OF	0	27.4	52	20.6	100
11272	29.75722	-95.1239	CARPENTERS BAYOU AT SHELDON RD	0	3.3	32.95	63.7	99.95
11273	29.73722	-95.1139	PATRICK BAYOU AT TIDAL ROAD	0.5	19.5	46.9	33.05	99.95
11274	29.75333	-95.1758	GREENS BAYOU AT MECHLING BARGE	0	26.85	56.5	16.6	99.95
11280	29.74444	-95.1897	HOUSTON SHIP CHANNEL AT ARMCO	0	4	44.8	51.15	99.95
11287	29.71917	-95.2425	HSC AT CONFL WITH SIMS BAYOU	0.35	31	49.4	18.75	99.5
11292	29.74917	-95.2889	HSC IN TURNING BASIN	0.4	16.45	59.6	23.4	99.85
11298	29.73879	-95.2123	HUNTING BAYOU AT FEDERAL ROAD	0.9	23.5	51.2	24.4	100
11300	29.71833	-95.2197	VINCE BAYOU AT NORTH RICHEY ST	10.875	33.325	42.6	12.6	99.4
11302	29.71028	-95.2553	SIMS BAYOU TIDAL AT LAWNDALE	1.5	19	43.2	36.2	99.9
11305	29.72342	-95.2786	BRAYS BAYOU AT BROADWAY ST	0.15	45.575	44.075	10.025	99.825
11347	29.76472	-95.3589	BUFFALO BAYOU AT MAIN STREET	0.15	64.75	30	5.05	99.95
11382	29.76667	-95.3583	WHITEOAK BAYOU AT N MAIN ST	0.3	62.8	30.4	6.5	100
13309	29.64083	-94.9658	UPPER GALVESTON BAY AT CM 83	0	25.3	66.3	8.4	100
13336	29.68889	-94.9647	TABBS BAY AT CM 14	0	19.7	52.8	27.4	99.9
13337	29.70333	-94.985	TABBS BAY AT RUINED BRIDGE	0	10.4	54.1	35.25	99.75
13338	29.70354	-94.9906	TABBS BAY NEAR GOOSE CREEK	0	22.7	50.3	27	100
13339	29.70639	-95.0389	SAN JACINTO BAY AT BUOY 15	0	36.95	34.05	29	100
13340	29.71667	-95.0047	BLACK DUCK BAY AT MID-BAY	0.1	9.5	40.35	50	99.95
13341	29.71186	-95.0062	BLACK DUCK BAY AT SH 146	0.8	41.85	36.1	61.9	140.65
13342	29.74333	-95.04	SCOTT BAY AT MID BAY	0.35	0.9	42.65	56.1	100
13343	29.77806	-95.0486	BURNETT BAY NEAR SPRING GULLY	28.45	8.8	50.65	12	99.9
13344	29.76778	-95.0514	BURNETT BAY AT MID BAY	7	3.3	27.25	62.45	100
13355	29.68186	-94.9995	BARBOURS CUT MID CUT	3.7	7.8	42.4	46.1	100
13363	29.61339	-95.0106	BAYPORT CHANNEL MIDPOINT	1.85	13.95	58.65	24.15	98.6
13589	29.61354	-95.0157	BAYPORT CHANNEL AT TURNING BAS	0.15	18.7	54.45	25.55	98.85
14560	29.60666	-94.9523	UGB AT HSC MARKER 75	0.65	22.55	47.65	27.05	97.9
15464	29.54611	-95.0144	UPPER GALVESTON BAY AT KEMAH	0	61.83333	30.53333	7.366666667	99.73333
15908	29.61697	-94.988	UPPER GALVESTON BAY AT 96GB013	0.6	34.1	51.55	13.35	99.6
15979	29.73394	-95.1332	HSC AT SHELL BARGE CUT	0	13.2	38.6	48.2	100
16213	29.5445	-94.9612	UPPER GALVESTON BAY AT 97GB019	0	1.5	47.3	51.15	99.95
16496	29.76386	-95.0538	BURNET BAY (98GB004)	0.25	1.95	36.7	61.1	100
16499	29.70969	-95.0552	SAN JACINTO BAY (98GB007)	0	10.95	51.2	37.85	100
16622	29.84556	-95.1061	SJR TIDAL AT BANANA BEND ROAD	0.05	18.85	55.65	25.25	99.8
17970	29.68622	-95.0066	BARBOURS CUT AT TERMINUS	0	47.4	43	9.5	99.9

APPENDIX B - DAILY FLOW AVERAGES IN THE MAIN CHANNEL AND TRIBUTARIES

APPENDIX C - PORT OF HOUSTON AUTHORITY DREDGE SEDIMENT CORE SAMPLING GUIDELINE

Can be found at http://www.portofhouston.com/pdf/channel/PHASedimentProcedures.pdf

APPENDIX D - REVISION 0 MONITORING QAPP

APPENDIX E - REVISION 0 MODELING QAPP