Total Maximum Daily Loads for PCBs In the Houston Ship Channel

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Rev2 Project Plan, Monitoring Plan and 3rd Quarterly Report

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Introduction

Polychlorinated biphenyls (PCBs) are widespread organic contaminants that 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 the 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). 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.

The scope of the TMDL PCB project includes project administration, participation in stakeholder involvement, development of a project plan, development of a monitoring plan, and preparation of sampling and modeling Quality Assurance Project Plans (QAPPs).

This document is the draft PCB Project Plan and also serves as the third quarterly report for the project. The Project Plan includes the following elements:

- Compilation and Assessment of Existing Data
- Selection of Modeling Perspective and Tools
- Designing the Monitoring Plan
- Preparation of Cost Estimates for the Project Plan

These elements of the Project Plan will be described in more detail below:

Compilation and Assessment of Existing Data. A detailed literature review was undertaken in the first quarter of FY07 and the findings were summarized in the first quarterly report for the fiscal year (see Appendix A).

A compilation and analysis of data that were gathered by the PCB project team during summer 2002, fall 2002, and spring 2003 was prepared during the second quarter of the current fiscal year and presented in Chapter 2 of the second quarterly report. The analysis was updated during the third quarter and the updated Chapter 2 is included in Appendix B.

In addition, historical data from the SWQM database were downloaded and analyzed. The results from the analysis are included in Appendix C.

The PCB data gathered in summer 2002, fall 2002, and spring 2003 were analyzed during WO7 of the dioxin TMDL project to estimate bioaccumulation factors for PCBs in the Channel. The report is included for reference in Appendix D.

Based on the analyses completed and described in Appendices B and C, data gaps were identified and were incorporated into the monitoring plan design as will be discussed later in this document.

Lastly, the literature was also reviewed to determine potential sources of PCB into waterways and in particular into the Houston Ship Channel. The results from the literature review were summarized in the 1st quarterly report for FY07 (see Appendix A). Additional source information that has been gathered during the second and third quarters is being compiled and analyzed to develop a database of potential historical and current PCB sources to the Channel.

Selection of Modeling Perspective and Tools. The project team is currently developing an RMA2-WASP7 model for the Channel as well as a loading spreadsheet for the dioxin TMDL project. A similar approach will be used for the PCB TMDL. The RMA2-WASP7 models will be modified to represent sources and processes that are appropriate for PCBs.

It is noted, however, that while the models used for PCBs are the same as those for dioxins, the strategy guiding the PCB TMDL project is different. The strategy for PCBs is centered on the concept of defining PCB loading at the mouths of tributaries draining into the Houston Ship Channel and limiting the sources assessment to those sources that directly discharge into the Channel. PCB loading from runoff will be estimated for adjacent areas and tidal segments of the Channel that are not part of the tributary watersheds. Runoff from potential industrial sources and other facilities that directly discharge to the Channel will also be quantified.

Design Monitoring Plan. The literature review, analysis of historical and SWQM data, along with source data gathering and analyses were used to develop the following draft monitoring plan for PCBs:

Geographic Scope. In total, the consumption advisories for PCBs cover all or part of designated water quality segments 0901 Cedar Bayou Tidal, 1001 San Jacinto River Tidal, 1005 Houston Ship Channel/San Jacinto River Tidal, 1006 Houston Ship Channel Tidal, 1007 Houston Ship Channel/Buffalo Bayou Tidal, 2430 Burnett Bay, 2429 Scott Bay, 2428 Black Duck Bay, 2427 San Jacinto Bay, 2426 Tabbs Bay, 2436 Barbours Cut, 2438 Bayport Channel, and 2421 Upper Galveston Bay. All parts of those segments that are covered by the PCB consumption advisories will comprise the project area.

Media. Sediment, water, and fish would be sampled. Crab would not be sampled since previous data from summer, fall 2002, and spring 2003 indicated that levels were below standards for crabs in all segments. Air sampling and air deposition studies may be undertaken based on the results from the source assessment work that is on going at this time.

Target tissue species. Wherever possible, two fish species will be sampled at a single location: speckled seatrout (the species included in the advisory) and catfish (preferably hardhead). Each sample will consist of edible tissue from 3-5 individuals.

Congeners. All 209 PCB congeners will be quantified across the various media.

Parameters other than PCBs. For sediment: TOC, TPH. For water: TSS, DOC, POC, TPH, Salinity, Specific Conductivity, and Temperature. For fish: percent lipids.

Flow sampling will be undertaken at selected stations: 11347 (Buffalo Bayou at Main Street), 16873 (Patrick Bayou Upstream of WWTP), 11200 (San Jacinto River Tidal at US90), 11175 (or TBD99 – Upstream Carpenters Bayou) and 11272 (Carpenters Bayou at Sheldon Rd).

Data Gaps. A number of data gaps have been identified thus far and these have motivated some of the specifics of the monitoring plan:

- Boundary concentrations for the RMA2-WASP7 will be required so PCBs in water should be quantified at the non-tidal portions of the major tributaries preferably close to USGS gages that are used in the model.
- For deep channel locations, PCB concentrations in water would be measured as a vertical composite or as the average of deep and shallow samples for more meaningful comparisons to the two-dimensional vertically averaged RMA2-WASP7 modeling results.
- Flow measurements would be undertaken concurrently with water sample collection at the upstream boundaries (non-tidal segments) to allow estimation of the PCB loads entering the channel.
- To better estimate partitioning coefficients in WASP7, POC will be measured in addition to DOC.

Data Objectives. The objectives for sampling for PCBs for the three media in the Channel include:

- Address the data gaps listed above
- Provide a current snapshot of PCB concentrations in sediment, fish and water in the Channel.
- Minimize the number of sampled stations with non-detect concentrations.
- Maximize the number of sampled stations that have been sampled previously to obtain a temporal understanding of PCB behavior in the system.
- Sample stations that have historically exhibited high concentrations in any medium.
- Maximize the number of samples where all three media are sampled concurrently to allow comparisons among the media.
- Consider the presence of potential sources in station selection.
- Water concentrations at the mouth of major tributaries (non-tidal) would be measured to allow load estimation (using flow from USGS gage for the trib). The concentrations would be measured in dry and wet-weather conditions.

- Ambient concentrations in the channel for the three media would be sampled during warm and cold weather to assess temperature effects, if any.
- Undertake extensive localized surveys in sediment and water in areas that exhibit high PCB concentrations and in areas that might be experiencing precipitation of suspended or dissolved materials due to the fresh/saline interface between tidal and non-tidal conditions.

Sampling Sites. The selected sampling sites and frequency of sampling are presented in Table 1. Figure 1 shows the sediment and tissue station locations and Figure 2 shows the water sampling locations.

Intensive Surveys. In addition to the proposed sediment, tissue and water sampling proposed in Table 1, intensive sediment surveys in 1001 and 1006 in the vicinity of the observed hot spots in the 2002-03 dataset would be undertaken prior to water sampling to pinpoint the longitudinal extent of the hot spots and/or potential localized sources of PCBs. The exact location and number of samples have not yet been determined but the total number of samples is expected to be less than 40 from these intensive surveys.

Sediment studies to evaluate the validity of the high settling rates downstream of the hot spots in 1006. The project team is evaluating possible strategies for addressing this issue that arose during model development in the dioxin project. Possible studies include sediment traps, sediment samplers, grain size analysis of existing data and trends from upstream to downstream, obtaining and analyzing recent data from Corps of Engineers on sedimentation and maintenance/dredging, measuring TSS concentrations to determine areas of high deposition, measuring turbidity profiles to identify areas where re-suspension might be occurring, analyzing biomarkers such as sediment lipid content, isotropic C/N ratios, or chlorphyll-a, and laboratory studies of salinity effects on coagulation of colloids using HSC waters. Literature studies as well as the Superfund proposed efforts in Patrick Bayou will be reviewed to support the development of a final strategy. Dr. Kyle Strom from UH will assist in developing this component of the study.

Sources Sampling. Up to 20 facilities that directly discharge to the Channel would be sampled for PCB in their discharge as well as in their runoff.

Water Sample Volume. Sampled volumes will be between 200 and 400 L depending on historical levels.

Laboratory Methods. PCBs will be quantified as individual congeners using USEPA Method 1668A.

Detection Limits. Detection limits vary among congeners and among samples of a given media due to the presence of interferences.

Table 2 provides a summary of expected detection limit ranges that are based upon laboratory reports for the PCB samples collected in the HSC in 2002 and 2003.

Table 1. Sampling Stations by Media

Segment or Segment the Trib Flows Into	Segment	Station ID	Station Description - Locations From Upstream to Downstream	Water Normal Flows (Hot)	Water Normal Flows (Cold)	Water Storm Flow Conditions (2 storms ea.)	Sediment Normal Flows (Hot/Cool)	Fish Tissue Normal Flows (Hot/Cool)
1007	1014 Trib	11351	Buffalo Bayou at Sheppard Dr. (USGS 08074000)	1	1	2		
1007	1013 Trib	11387	Whiteoak Bayou at Heights Blvd	1	1	2		
1007	1013 Trib	11347	Buffalo Bayou Tidal at Main St.	1	1	0	2	2
1007	1007	11292	Houston Ship Channel/Buffalo Bayou in middle of Turning Basin	1	1	0	2	2
1007	1007 Trib	11139	Brays Bayou at South Main St.	1	1	2		
1007	1007 Trib	11132	Sims Bayou at Telephone Rd (USGS 08075500)	1	1	2	2	2
1007	1007	11287	Houston Ship Channel/Buffalo Bayou at Confluence with Sims Bayou	1	1	0	2	2
1007	1007 Trib	11171	Vince Bayou at W. Ellaine St. (USGS 08075730)	1	1	2		
1007	1007 Trib	11129	Hunting Bayou at North Loop East (IH 610) in Houston	1	1	2		
1007	1007 Trib	TBD-1	Small ditch discharging to Hunting Bayou			2		
1007	1007	11280	Houston Ship Channel/Buffalo Bayou at Armco Steel Corporation Intake Screens	1	1	0	2	2
1006	1016 Trib	11368	Greens Bayou at Brock Park	1	1	2		
1006	1016 Trib	11274 or 16981	Greens Bayou Tidal at Mechling Barge Lines, or Greens Bayou at ISK Biosciences Ditch	1	1	0	2	2
1006	1006	11270	Houston Ship Channel at CM 150	1	1	0	2	2
1006	1006	15979	Houston Ship Channel at Shell Barge Cut, 0.9 mi. downstream of Beltway 8	1	1	0	2	2
1006	1006 Trib	15936	HSC at OxyChem Ditch (005/004)	1	1			
1006	1006 Trib	11175 or TBD99	Carpenters Bayou Immediately Upstream of Loop 8 (Beltway) or TBD at Freshwater Locatior	1	1	2		
1006	1006 Trib	17149	Patrick Bayou 1	1	1	2		
1006	1006 Trib	17157	Patrick Bayou 2	1	1	2		
1006	1006	11264	Houston Ship Channel at at San Jacinto Park, West of Battleship Texas	1	1	0	2	2
1001	1001	16622	San Jacinto River Tidal at Banana Bend Road at end of pavement in Houston	1	1	0	2	2
1001	1001	11193	San Jacinto River Tidal IH 10 Bridge East of Channelview	1	1	0	2	2
1005	1005	15301	Old River Tidal/HSC at Old River Ship Building, Near Lakeside Dr and N Shore Dr	1	1	0	2	2
1005	1005	11262	HSC Between Lynchburg Ferry and IH-10, 121m S AND 1.27km W of Lynchburg Rd and Lakeview D	1	1	0	2	2
1005	1005	11261	Houston Ship Channel San Jacinto River at Lynchburg Ferry	1	1	0	2	2
1005	2430	13344	Burnett Bay at Mid-Bay	1	1	0	2	2
1005	1005	11258	Houston Ship Channel at CM 120	1	1	0	2	2
1005	2429	13342	Scott Bay at Mid-Bay	1	1	0	2	2
1005	1005	16618	Houston Ship Channel/San Jacinto River West of Exxon Docks and North of Alexander Island	1	1	0	2	2
1005	2427	16499	San Jacinto Bay 200 yds SW of CM25 (98GB007)	1	1	0	2	2
1005	2428	13340	Black Duck Bay at Mid-Bay	1	1			
1005	2426	13338	Tabbs Bay Midway Between Goose Creek and Upper Hog Island	1	1	0	2	2
1005	2436	13355	Barbours Cut mid-way between mouth And terminus	1	1	0	2	2
1005	1005	11252	Houston Ship Channel at CM 91, Morgan's Point	1	1	0	2	2
2421	901	TBD-2	Cedar Bayou non-tidal	1	1	2		
2421	2421	14560	Upper Galveston Bay at HSC Marker 75	1	1	0	2	2
2421	2438	13363	Bayport Channel mid-way between mouth and terminus	1	1	0	2	2
2421	2421	16213	Upper Galveston Bay at 97GB019, 5.25mi north of the HL&P P. H. Robinson Outfall	1	1	0	2	2
1006		TBD-3	Small ditch to obtain a direct runoff concentration in the eastern part of the channel			2		
1005		TBD-4	Small ditch to obtain a direct runoff concentration in the eastern part of the channel			2		
				37	**37**	**28**	**50**	**50**

Table 2. Method Detection Limits (MDL) by Media

Media	**Units**	**MDL Range**	**Reporting Limit**
Tissue	ng/g	0.011-0.067	0.06
Dissolved	ng	0.02-1	0.3
	ng/L[a]	0.0001-0.005	0.002
Suspended	ng	0.02-1	0.3
	ng/L[a]	0.0001-0.005	0.002
Bottom sediment	ng/g	0.05-0.25	0.25

[a] Based on a minimum sample size of 200 L

Equipment. The equipment previously used in the dioxin project will be used primarily for the PCB project. An equipment inventory analysis is currently underway to identify equipment needs for the PCB TMDL.

Data Management Roles and Personnel. Dr. Hanadi Rifai and Randy Palachek will be the project principal investigators from UH and Parsons, respectively. Monica Suarez, Dr. Kirk Dean, Jim Patek, Curt Burdorf and Nathan Howell will be key project scientists and engineers that will implement the Project Plan. Personnel from both UH and Parsons will be utilized to complete the Project Plan. Data management will be primarily a UH responsibility.

Quality Control Roles and Personnel. Field activities and quality control activities will be primarily a Parsons responsibility.

Public Participation. Members of the dioxin stakeholder group have been invited to serve as a technical advisory group for the PCB project. A number of public meetings will be held throughout the duration of the PCB project to encourage participation from the public (no more than twice per yr).

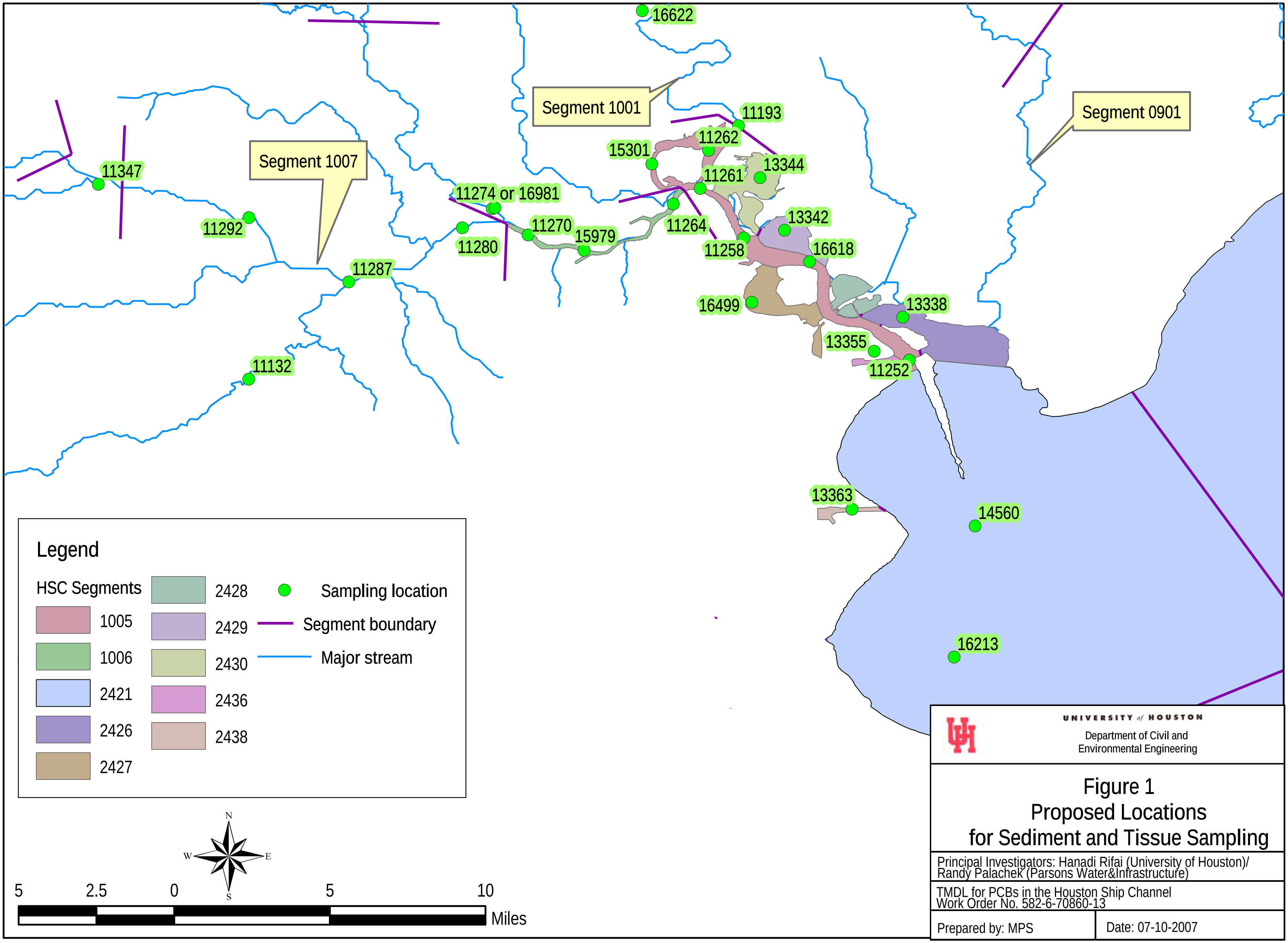
Timeline. The project plan calls for completing the PCB TMDL by FY 2010 as follows:

FY 2007 – Project Plan, Monitoring Plan and QAPP preparation
FY 2008 – Sampling and Analysis
FY 2009 – Sampling, Analysis and Modeling
FY 2010 – Estimating TMDL and Writing Report

Budget. The budget for the PCB Project Plan is $1,391,500. Details are shown below in Table 3.

Table 3. PCB Project Plan Budget

Category	**Cost**
Monitoring in Table 1	
Labor	$500,000
Analytical	$300,000
Supplies	$60,000
Intensive Surveys	$50,000
Sediment Settling Rate	$100,000
Modeling	$100,000
Public Meetings	$30,000
Load Allocation Spreadsheet	$20,000
TMDL Report	$50,000
Subtotal	**$1,210,000**
OH (15%)	**$181,500**
TOTAL	**$1,391,500**



UNIVERSITY of HOUSTON
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Figure 1
Proposed Locations
for Sediment and Tissue Sampling

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TMDL for PCBs in the Houston Ship Channel
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Prepared by: MPS
Date: 07-10-2007

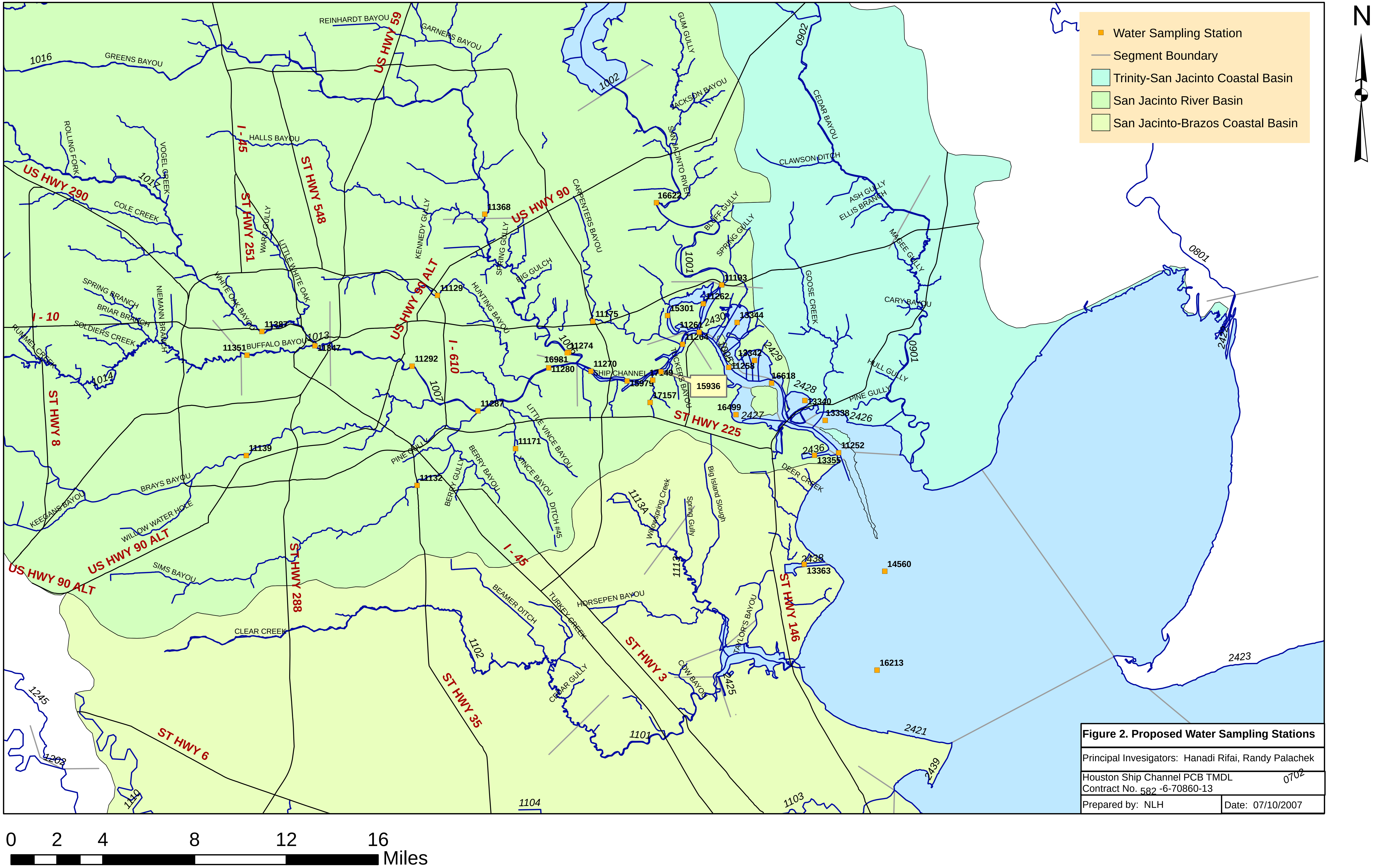

Figure 2. Proposed Water Sampling Stations

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Houston Ship Channel PCB TMDL
Contract No. 582 -6-70860-13

Prepared by: NLH
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APPENDIX A

PCB Literature Review

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2.4 MAJOR SOURCES OF PCBS

As was noted in the historical section of this report, PCBs have not been produced in the Unite States since 1977. An estimate of the amount of PCBs produced globally between 1929 and 1979 is 1.5 million metric tons. (De Voogt and Brinkman, 1989) Large–scale disposal continued for some time after the cessation of production, but at present there are few primary sources of PCBs to the environment. Most PCBs that enter a particular water body or biosphere are transported from another contaminated environment and are thus secondary sources.

2.4.1 Primary PCB Sources

The EPA states that "no significant release of newly formed dioxin-like PCBs is occurring in the United States." While the EPA acknowledges that waste combustion can yield small amounts of PCBs, they contend that these sources are not significant and that all significant sources of PCBs are from past production, use, and disposal. (USEPA, 2003) The EPA's statement is directed mostly towards the "dioxin-like" PCBs (which are nearly synonymous with the coplanar PCBs as discussed in a previous section), but since most of the historical primary sources released both coplanar and non-coplanar PCBs, it is reasonable to say that there are no significant releases of any newly formed PCBs (dioxin-like or not dioxin-like).

PCBs were once sourced to the environment by way of production, use, and disposal. Now disposal is likely the only they enter the environment. There are four main methods of disposal that still occur (USEPA, 2003):

- Large Amount PCB Disposal (>2 pounds): Dielectric fluids from transformers and large capacitors, which are disposed according to regulations.
- Small Amount PCB Disposal (<2 pounds): Disposal of small capacitors, light fixtures, and waste papers in municipal landfills.

- Leaks and spills from devices that still contain PCBs.
- Illegal PCB disposal

The EPA gives four quantified primary sources for PCBs as estimated in 1995 which are shown in Table 2.4. All are quite small in comparison to the total annual production of PCBs during any year between 1929 and 1977.

Table 2.1 Primary Source Quantities Listed by the EPA in 1995

Source Type	Receptor Media	Amount (g TEQ_P-WHO_{98}/yr)
Cigarettes	Air	0.016
Backyard Barrel Burning	Air	42.3
Municipal Sludge Disposal	Land	51.1
Municipal Sludge Disposal	Products	1.7

Source: (USEPA, 2003)

2.4.2 Recent Studies Concerning Primary Sources

Studies have shown that urban centers still supply an air source of PCBs by virtue of the difference in air concentrations of PCBs over time in urban areas as compared with rural areas. The specific increases are on the average around 7 times higher for urban areas over rural areas with greater emphasis placed on lighter weight PCB congeners. The cause of the urban source is believed to be domestic burning of coal and wood based on meteorological dependencies which followed the patterns of combustion-generated PCDD/Fs. (Lohmann et al., 2000) Urban sources were confirmed earlier by Halsall (1995), and they noted the additional detail that the strength of these urban sources varied with season. The summer source air concentration was shown to be greater than the winter source concentration by as much as 5 times due to previously deposited PCBs experiencing greater volatilization in warmer weather. When Blanchard et al. (2007) performed an air study on PCB sources in the Paris area, they considered those air sources to be volatilization from early 1970s buildings, cars, cement kilns, and sinter plants.

Some researchers have noted that what might be seen as a secondary source of PCB emissions is in fact a re-emission from water, soil, and sediment concentrations.

Temperature increases can volatize more old sources of PCBs and make them appear as new sources. (Breivik et al., 2004)

It should also be noted that PCB coproduction was at least considered a possibility for a new primary source after the production ban of PCBs. It was estimated in 1982 that the USA alone produced 50 tons of PCBs annually as byproducts in the production of other organic chemicals. The EPA in 1982 rated at least 80 chemicals (54 major classes shown in Table 2.5) with the potential of having PCB byproducts in them. (De Voogt and Brinkman, 1989) Byproduct PCBs were a large enough consideration that the EPA produced a report on the GC/MS analysis of PCBs in commercial products. (Erickson, 1982) Erickson et al. (1988) gives a list of potential chemical products that might contain PCB byproducts: chlorophenylsilane adhesives, technical tetrachlorobenzene, tear gas, phthalocyanine pigments, chlorinated paraffins, chlorinated phenols, and phenolic resins. Product waste examples that are given include chlorinated aromatic still bottoms, TCE production waste, asphaltenes, and used solvents.

Table 2.2 Potential PCB Coproduction Chemicals or Chemical Classes

Ally amines
Allyl alcohol
Aluminum chloride
Aminochlorobenzotrifluoride
Aminoethylethanolamine
Benzene phosphorous dichloride
Benzophenone
Benzotrichloride
Benzoyl peroxide
bis (2-chloroisopropyl) ether
Carbon tetrafluoride
Chlorendic acid/anhydride/esters
Chlorinated acetophenones
Chlorinated benzenes
Chlorinated benzotrichlorides
Chlorinated benzotrifluorides
Chlorinated benzylamines
Chlorinated ethanes
Chlorinated ethylenes
Chlorinated methanes
Chlorinated naphthalenes
Chlorinated pesticides
Chlorinated pigments/'dyes
Chlorinated, brominated methanes
Chlorinated, flourinated ethylenes
Chlorinated, flourinated methanes
Chlorinated, fluorinated ethanes
Chlorinated, unsaturated paraffins
Chlorobenzaldehyde
Chlorobenzyl hydroxyethyl sulfide
Chlorobenzyl mercaptan
Chlorobenzyl peroxide
Dimethoxy benzophenone
Dimethyl benzophenone
Diphenyl oxide
Epichloryhydrin
Ethylene diamine
Glycerol
Hexachlorobutadiene
Hexachlorocyclopentadiene
Linear alkyl benzenes
Methallyl chlorides
o-Phenylphenol
Pentachloronitrobenzene
Phenylchlorosilanes
Phosgene

Chlorinated propanediols	Propylene oxide
Chlorinated propanols	Tetrachloronaphthalic anhydride
Chlorinated propylenes	Tetramethylethylene diamine
Chlorinated, brominated ethylenes	Trichlorophenosy acetic acid

Further understanding of coproductive PCB sourcing relates less to products that are made alongside PCB and more to the disposal of waste by way of incineration. Ikonmou et al. (2002) presented the first study on municipal waste incinerators that examined all PCB congeners. They found that some incinerator conditions produce no PCBs, others actually generate new PCBs that are mostly lower level chlorinated PCBs, while still others generate high levels of non-ortho and mono-ortho highly toxic PCBs. Even more recent work was conducted in this area by Ishikawa et al. (2007). That group examined thermal waste treatment technology PCB-producing effects on Refuse-Derived Fuel (RFD) and Automobile Shredder Residue (ASR). ASR was especially interesting because it contains high amounts of catalytic iron and copper, the same types of catalysts used to intentionally produce chlorinated hydrocarbons. Their results showed that RDF produces more light congeners while ASR produces heavier congeners. At the outlet of these systems, an activated carbon adsorption tower removes most of the PCBs from the system, and so it is unclear how much of the products formed in incineration would actually be available in the environment.

Specific waste streams may also be a source of PCBs. Blanchard et al. (2007) made a comparison between air sources and waste water sludge. The sludge was what remained from treating waste streams that had small quantities of PCBs from other sources to water, but it was enriched in PCB and other bioaccumulative compounds then disposed of by land treating. Since PCBs are ubiquitous in the environment, any treatment process that involves separating PCBs from water or other media is potentially a source for concentrating them and should be considered as such.

In the discussion of contemporary primary PCB sources, it is important to remember that:

- The concentrations and variations in concentrations which are being measured to characterize a source are quite small and thus are easily invalidated by measurement errors.
- What might be seen as a secondary source of PCB emissions is in fact a re-emission from water, soil, and sediment concentrations. Temperature increases can volatize more old sources of PCBs and make them appear as new sources. (Breivik et al., 2004)

These considerations show that the current state of contemporary anthropogenic PCB emissions coming by unintentional means requires more study to understand and quantify how much might really be produced and which congeners are more likely from those production sources. (Breivik et al., 2004)

2.4.3 Secondary Sources

Secondary sources are more appropriately covered under the topic of environmental fate and transport, and that is where the details and mechanisms of those sources will be. In a general sense, however, it is useful to see how all of these secondary sources work in concert to transport PCBs even on a global scale.

Swackhamer (1996) developed a total mass balance on the Great Lakes PCB system in 1996 which shows a reasonable concept for secondary PCB sources in any large body of water. The balance showed that the Great Lakes were mostly in a steady state of total influx to out flux of PCBs, but the internal transport processes are the mechanisms by which that steady state is maintained. The major sources Swackhamer lists and discusses are atmospheric deposition (mainly to water in this case although it also occurs to land) and its reverse process, volatilization from water to air. The other "sources" which should be considered include the partitioning from water to sediment and sediment back to water. These would only be considered sources insofar as the reference sink is just the sediment or just the bulk water phase outside of the sediment pore spaces.

2.4.4 Hydroxylated PCBs

Hydroxylated PCBs (OH-PCBs) were recently studied at length for the first time by Ueno et al. (2007). OH-PCBs are metabolites when they are formed in biota, but they may also be formed abiotically mainly in the atmosphere through a reaction of PCBs with OH radicals. It is known that when hydroxylating the 209 possible PCB congeners that 837 monohydroxylated PCBs congeners are then possible. In terms of exposure, Ueno et al. were not certain whether or not OH-PCBs were a real exposure route to humans and biota when formed in the atmosphere and deposited to water. OH-PCBs could represent a loss of PCB from the environment since OH-PCBs may eventually be more easily broken down, and there are more OH-PCBs (as discovered in the study) under warmer conditions. This results from more volatilization generating more air-based PCBs and more OH radicals to react with air PCBs because of increased UV light.

2.5 ENVIRONMENTAL FATE AND TRANSPORT

2.5.1 Atmospheric Deposition and Air Transport

In general, transport of PCBs in air to water bodies happens via two sequential mechanisms. Once the PCBs have entered the air (via combustion, soil desorption, or water-air volatilization), they will be transported over the globe with distances depending on their half-life in the atmosphere. Within this mechanism, they will either move as free phase vapor or sorbed onto atmospheric particulates. If the PCBs make their way to a place where they can either be sorbed onto soil or dissolved into a body of water, they will either be wet deposited as rain or dry deposited via mass transfer across a water-air interface.

2.5.1.1 Air Transport

The general concept that one finds in atmospheric PCBs is that PCBs are partitioned between gas and particles phase. The partitioning between these phases depends generally on the amount of chlorines that are on the congener. More chlorination means that there is a greater tendency to remain in the particle phase. This translates to a lower vapor pressure. Therefore, it is also reasonable to say that lower vapor pressure leads to greater partitioning to the particle as well.

Another parameter to consider is temperature where a lower temperature is more favorable for congeners to remain on the particles. (Atkinson, 1996) This temperature dependency seems generally intuitive as one considers that increased temperature means that each particle has more energy. More energy means that more of the particles will be in the more energetic gaseous state over the particle bound state.

The quantification of PCB molecules as being particle-bound versus being in the gas phase is important in understanding atmospheric half-life. Atmospheric deposition to water or land can occur in either phase, but half-life is highly related to the phase. The only significant PCB degradation reaction that occurs in the atmosphere is the reaction with the OH radical (Atkinson, 1996), and this reaction is believed to occur primarily on gas-phase PCBs. Atkinson (1996) has documented this reaction rate thoroughly to yield general comparative half-lives of 0.8-3 days for air-phase PCBs and 5-50 day half-lives for particle-bound PCBs. These half-lives enable PCBs to travel great distances from an original primary or secondary source with the result that regions having little PCB contamination history can become a sink for them. But one should note that these half-life determinations are made without a strong body of quantitative kinetics understanding of the OH radical reaction with particle-bound PCBs. (Wania and Daly, 2002)

While the understanding of the fundamental kinetics of the OH radical reaction is helpful, atmospheric transport of PCBs cannot simply be predicted on the basis of the OH radical reaction. One also needs to consider the variability of OH radical concentration in the atmosphere as well as temperature, which affects the rate of the reaction and the amount of PCB which can easily react in the air due to gas/particle partitioning. (Wania and Daly, 2002)

Another factor to consider in time of transport is the volatility of the congener. More volatile PCBs travel farther than less volatile ones with the result that PCB mixture compositions will change with distance. (Agrell et al., 1999) In addition, Wania (2002) estimates that lighter PCB congeners remain in the atmosphere for 1 month while heavier congeners could spend more than a year in the atmosphere. These determinations are made based on modeling the combinatorial effects of OH radical degradation, air-particle partitioning, and relative congener volatilities. These factors and potentially others need always to be considered in PCB air transport. Another important conclusion from the differences in travel and half-life between congeners is that the composition of a PCB mixture will change throughout the transport. This compositional change makes the accurate analysis of an environmental sample all the more crucial in the area of resolving specific congeners, and it also means that tracing an air signature back to an original Aroclor is more difficult.

2.5.1.2 Deposition

The scale of travel distance for PCBs to places as remote as the arctic (Hung et al., 2001) shows that deposition from the atmosphere to water sources is a significant transport mechanism to understanding the temporal flux of PCBs to a region. In the case of these more remote areas, it is not only a significant source, but it is the only source of PCBs.

Some site-specific studies will convey some conceptual information about the nature of atmospheric PCB deposition. For example, PCBs were found in the Andes mountains in snow samples. This transport was likely by atmospheric transport and deposition processes, which in this case were wet deposition. PCB 52 was among the highest of the congeners present in the snow, which is similar to results found in Canadian snow (Barra et al., 2005)

The Andean snow example illustrates how precipitation can eventually get to water bodies by runoff and snowmelt (with some clear losses occurring on the way from PCBs sorbing to soils). Studies have been performed in the Baltic Sea that illustrate the dynamics of the volatilization-deposition balancing processes. In fact, gaseous air/sea exchange is one of the most important processes governing the fate of PCBs in the Baltic Sea. (Axelman, 2001) The general congener specific patterns of net volatilization to net deposition are that the higher chlorinated, more hydrophobic PCB congeners have much lower volatilization tendency, and thus they are more likely to remain transported in the surface water on particulate organic matter. (Bruhn et al., 2003) The opposite would obviously be true that lower chlorinated, less hydrophobic PCBs have a greater escaping tendency to the air. So from a depositional standpoint, water bodies should enrich in higher chlorinated congeners with time. And unfortunately for the state of the aquatic systems, these higher chlorinated congeners are also more recalcitrant and contain the greater toxicity coplanar PCBs.

Recently, Blanchard et al. (2007) found some interesting information concerning the degree of depositional flux of PCB. In both rural and urban areas, they found that the highest rain depths gave the highest depositional fluxes, which indicated that wet deposition was far more dominant over dry deposition. They also found that bulk deposition (the sum of wet and dry) was a greater source (13 times greater) to the Paris watershed than fluxes from sludge landfilling.

One final note on deposition to water bodies in the example of the Baltic Sea is that the determination of net direction of flux is difficult. Bruhn et al. note that the partitioning conditions in the surface water body, and the amount of PCB already present from other sources (such as sediment desorption to water) would determine if the surface water is a net PCB source or sink. One example of this is in the Baltic Sea where there is even disagreement about whether the surface water is a net sink or source based on parallel studies. (Bruhn et al., 2003) Thus the decision of whether the surface water system in question is in equilibrium, net PCB flux to water, or net PCB flux to atmosphere is highly dependent on local conditions and may not even be understood well enough in the environmental community to ascertain with certitude.

2.5.2 Water Transport

Characterizing PCB contaminant levels is complicated for at least two main reasons. Firstly, the levels of contaminant that one deals with are of a very small order due to low solubility of PCBs as well as high dilution amounts in large bodies of water. The second reason for the complication is that PCBs are distributed in the water column between a truly aqueous dissolved PCB phase and a PCB phase which is bound to suspended particles. This latter consideration becomes significant when PCB water concentrations are taken and reported since some sampling methods seek to get only the dissolved PCB concentration while others get an aggregate concentration that combines both PCB phases. Zhou et al. found that mass balances are extremely hampered by the distribution between solid particles and aqueous concentrations of PCBs. In that study, the concentrations did not follow a theoretical dilution line for different regions of the water body, and they speculate that the reason for this non-conservative behavior is that PCBs are often removed from the water column by partitioning to suspended particles. (Zhou et al., 2001)

The main transport and fate mechanisms within the water column itself are (Jurado et al., 2007):

- Volatilization
- Solids partioning
- Degradation of the dissolved phase (discussed in more detail in Section 2.5.3.3 Biodegradation)
- Incorporation into trophic chains (discussed in more detail in Section Biological Fate)
- Turbulent diffusion
- Vertical advection

2.5.2.1 Volatilization

Many studies have been performed to characterize the volatilization of PCBs all of which should be considered in their specific environmental context before being applied broadly.

As in the case of atmospheric deposition to water, the general state of the water body can be characterized as transient or steady-state. Data from the Wadden Sea in the Netherlands showed an equilibrium between the air and water PCB concentrations in time that varied over different seasons. Variations from equilibrium were very minor. (Booij and Van Drooge, 2001) This brings up the general issue of seasonal variations in volatilization rates, and these seasonal variations occur largely because of temperature changes with season.

PCB volatilization is a function of temperature, and it is a stronger function of temperature with the increasing level of chlorine on the congener. (Breivik et al., 2004) The presumable reason for the greater response of higher chlorinated PCBs to temperature is that these PCBs are in general less volatile than the lighter PCBs. Thus since a good portion of lower chlorinated PCBs will already volatize at many ambient air temperatures, the higher chlorinated PCBs will not volatize in more significant levels until the temperature is increased. Hence the greater response to temperature changes.

Lake Superior shows this trend in response to temperature change as the volatilization occurred at its highest rate in the fall when temperatures were higher and there was actually a net deposition in the spring when temperatures were colder. But the net yearly flux was a loss from the water due to volatilization, not a gain from deposition. (Hornbuckle et al., 1994) This could indicate that volatilization is more sensitive to temperature swings than deposition, but this has not been proven in a general sense. Recently, Blanchard et al. (2007) did show that deposition was in fact not seasonally effected in a study on a Parisian watershed.

Another Lake Superior study conducted showed PCB concentrations from 1978-1992 decreasing in time but that the loss from the water was heavily dominated by volatilization and not by sedimentation.(Jeremiason et al., 1994) The decrease in lake PCB concentrations from 1978-1992 was clearly related to the historical decrease in global industrial PCB production, but the study showed that even after those effects were removed, PCB levels were decreasing with volatilization as the main mechanism for the decrease.

The kinetics of degradation by volatilization were also available from two Great Lakes studies. One study showed that the decay of PCB concentrations in the water column was first order with a rate constant of 0.20 yr^{-1}. The main mechanism for this decay was volatilization even as atmospheric deposition was occurring. (Jeremiason et al., 1998) Pearson et al. reported a first order water PCB degradation rate in neighboring Lake Michigan of 0.078 yr^{-1} in the second study. (Pearson et al., 1996)

As is the case with many of these transport mechanisms, PCB mixture composition is important to ascertain as well as overall PCB levels. To that end, Dachs et al. found that in the Mediterranean, the higher chlorinated congeners were higher in relative proportion closer to the coast and that the lower chlorinated congeners were in higher proportion out in the open waters. The main reason given for this was the distance that lower chlorinated PCBs can travel in the atmosphere versus higher chlorinated PCBs. (Dachs et al., 1997)

2.5.2.2 Solids Partitioning

For suspended particles, the understanding of water to solid partitioning is crucial to predicting and quantifying sorbed PCB concentrations. One important consideration to keep in mind (as in the case of volatilization) is that temperature is a strong determinant of partitioning. (Burkhard et al., 1985)

PCB sorption onto suspended particles is also strongly correlated to levels of Particulate Organic Carbon (POC). A study in the Netherlands found that POC is the key factor to the concentration of PCBs in boundary layer water from particle sorbed with PCBs. They found their POC levels to be on the order of 7-16 g/L. (Booij et al., 2003) Marti et al. found the correlation of POC and PCB water concentrations particularly useful when combined with the variable of water depth. They noticed a general trend of decrease in PCB with increasing depth that correlated to a decrease in POC. The effect was particularly pronounced in the first 200 meters. (Marti et al., 2001)

Other researchers have made more detailed observations about the role of solid particles in PCB contaminant levels. Sobek (2004) found that the greatest source of POC (at least in total mass of particles) was from phytoplankton. They contend that POC is also believed to be a large source of deep water PCB concentrations, and more study is needed to understand the nature of this partitioning especially as it relates to phytoplankton as the biogenic source of POC.

Marti (2001)also considered biogenic POC by making the distinction in water-suspended particle partitioning between large and small-size particles. The small-size particle partitioning appears to be governed more by the physical partitioning process whereas as larger particles, generated more from biogenic processes, acquire sorbed PCBs from the food chain process. The latter process (which correlates to the phytoplankton source discussed by Sobek (2004)) would favor higher chlorinated congeners since these congeners are more bioaccumulative and would be present in higher proportion within an organism.

As depth increases in the water column, one needs to consider solid-aqueous partitioning in terms of deposited sediment as well as in suspended particles. The Booij et al. study in the Netherlands on “pore water” (water moving in and out of sediment beds) data showed aqueous PCB concentrations of 37 pg/L for the lower chlorinated congeners and as low as 0.01 pg/L for the higher chlorinated congeners. This was in an area near a former chlorobenzene waste discharge. (Booij et al., 2003) The difference in concentrations shows the greater affinity of the higher chlorinated congeners for sediment particles and leads to the conclusion that these congeners can accumulate and persist in sediment beds more than the lower chlorinated congeners.

2.5.2.3 Turbulent Diffusion

Diffusion that happens while water is in turbulent flow is turbulent diffusion. Jurado et al. (2007) performed a study of the phenomenon (specifically vertical turbulent diffusion) because historically this transport mechanism was not considered in much detail due to the difficulty of modeling it. Jurado et al. found that vertical turbulence creates two effects in the water column—the strengthening of upward diffusion of sediment entrained contaminants and an increase of atmospheric mixing of contaminants into the water column in the surface layer. These effects relate to the interaction of other media with water, sediment and air, and thus may be important considerations for conceptual understanding as well as quantitative modeling. The final vertical picture that resulted from the modeling study was a PCB-enriched surface zone followed by a depleted middle layer and finally an enriched benthic region.

2.5.2.4 Vertical Advection

Vertical advection can happen through upward and downward water currents, and it can also happen through gravity settling of suspended phase PCBs. Jurado et al. (2007) compared the vertical turbulent diffusion mechanism with vertical advection by settling in a 1-D model. They discovered what was often assumed by many modelers, that the most dominant effect is this settling process. Vertical turbulent diffusion was, however, not considered insignificant.

2.5.2.5 General Behavior in the Water Column

The less volatile, more lipophilic congeners can concentrate in the water column over time relative to the more volatile congeners. In a China study, all water samples contained most of the possible congeners, but three highly chlorinated congeners accounted for 94% of the total PCB concentration. (Zhou et al., 2001) The reasons for this enrichment include lower volatility, higher lipid solubility, more adsorption to sediments, and more resistance to microbial degradation. (Wan Ying and Mackay, 1986) This increased concentration of higher chlorinated congeners seen by Zhou et al. (2001) occurred in a scenario where runoff to the water column was a more major source than PCBs which could reenter the water column from sediments as was the case with Booij (2003).

2.5.3 Sediment Transport

2.5.3.1 Kinetics of Sediment Transport

PCB desorption/sorption processes from sediment are continually being characterized in the literature. Whereas many considered the process to be equilibrium controlled, that view of the process has changed in the last 10 years to be more kinetic based. Gong et al. (1998) stated that the standard toxic chemical fate and transport models for PCB desorption all assumed that PCBs desorbed by instantaneous equilibrium, and that this should no longer be a valid assumption. Cheng et al. (1995) rationalized this assertion further by stating that transport from resuspension of contaminated sediments needs to be considered kinetically especially for high K_{ow} contaminants of which PCBs are a prime example. Schneider et al. (2007) agree with the kinetic treatment of PCB desorption, but they found that, contrary to Cheng et al, that the percentage of PCBs transferred from the suspended to the dissolved phase actually was not correlated with congener molecular weight (i.e. direct relationship between level of chlorination and K_{ow}).

Some specifics of the kinetic understanding of PCB sediment desorption are presented here. A two stage kinetic model is accurate to describe PCB desorption from suspended sediments. The first stage is a fast release and the second stage is much slower. (Gong et al., 1998) Also, the rates at which individual congeners will desorb are based on their K_{ow} with the relationship being inverse. A higher K_{ow} has a lower rate of desorption due to the congener's hydrophobicity. (Wu and Gschwend, 1986) The general half-lives of PCBs are given by ASTDR as months to years with half-life increasing with the level of chlorination. (ATSDR, 2000)

More recent understanding of sediment resuspension processes was provided by Schneider et al. (2007) using Hudson River sediment samples in "STORM tanks" (purported to be more representative of real resuspension events). They confirmed the kinetic two-stage release model put forth by other authors calling the "quick release" PCBs "labile" PCBs. These labile PCBs are discharged quickly during resuspension and can be recharged once they have settled back to the benthic floor. They discovered that the recharge time is on the order of days with implications that tidally resuspended sediments (getting approximately 6 hours of recharge time) will not be able to recharge as much as sediments resuspended by infrequent storm events. If the labile PCBs are not recharged, then they will not have as much influence on the dissolved phase PCB concentrations. The sediments that are not the in the labile phase can take some time to reach equilibrium (when they would have their full PCB delivery effect to the dissolved phase) being on the order of 1-10 days minimum. (Cheng et al., 1995) Thus, time between resuspension events is important in considering PCB-delivery potential as well as total time the sediments are suspended. The quantitative significance of sediment resuspension events, as analyzed by Schneider et al. (2007), was that between three consecutive events 16-20% of the sediments were transferred from suspended to dissolved phase.

The Lake Superior study performed by Jeremiason et al. (1998) examined the time of suspension showed that PCBs on settling solids declined in a first order way with a rate constant of 0.26 yr^{-1} (presumably by way of release to the dissolved phase). The time trend data also showed that PCBs did not ultimately accumulate on the bottom lake sediment but instead recycled back into the water column at the bottom 5 m of the lake. This recycling is, of course, particular to Lake Superior and would not necessarily indicate sediment settling behavior in other water bodies.

2.5.3.2 General Behavior of Sediment Transport

The Hudson River system showed high concentrations of PCBs, which was mostly attributable to sediment. Model predictions show that increasing amounts of cohesive sediment deposition combined with PCB flux to the water column from noncohesive sediments from pore water will lower the overall PCB sediment concentrations. (Connolly et al., 2000) Thus, distinctions in sediment type between that which is cohesive and that which is non-cohesive increases the accuracy of PCB transport predictions.

In the Baltic Sea, the highest concentrations of PCB sediment were found in the areas of highest sedimentation, not in areas close to probable pollutant sources. (Konat and Kowalewska, 2001) So as in the case of the Hudson River, the sediment load was a significant source of PCBs to the system and should be focused on as much or more than historical waste PCB sources.

2.5.3.3 Total Organic Carbon (TOC) and PCB Sediment Concentration

It has been stated for a few decades that generally the sorption of PCBs and other hydrocarbons to sediments is directly related to the amount of organic matter in the sediment. (Karickhoff, 1981; Feng et al., 1998) While this relationship seems intuitively accurate based on simple concepts of the hydrophobicity of PCBs, some recent studies did not reproduce the correlation, and this effect brings further explanation to the TOC-PCB relationship.

Ouyang et al. (2006) found that in a Florida river basin that PCB and TOC were not correlated. They postulated that the reason for this was different source locations. TOC was sourced from a different watershed than PCBs because the two watersheds contributed a runoff that was land-use specific. The PCB-sourcing watershed was in an industrial area, and the TOC-sourcing was in a forested area.

Vane et al. (2007) also found no correlation between TOC and PCB in a Mersey Estuary near Liverpool. They state that “sorption of PCBs to organic matter is masked by other geochemical processes and local PCB inputs.” It is not clear exactly what geochemical processes are in view, but the “local PCB input” suggests that the authors are saying that the rate of PCB introduction into the sediment precludes any equilibrium concepts such as TOC-PCB correlation. Suggested sources in the area include shipping docks, chemical works, oil refineries, and general urban sources.

2.5.3.4 Relationship between TPH and PCB

In the 1970s, Dr. G. Fred Lee conducted studies involving the release of PCBs from resuspended sediments. Correlation analysis revealed that release from the sediments occurred more readily in sediment with low petroleum hydrocarbon content, and sediments with high petroleum hydrocarbon content held PCB more tightly. (Lee et al., 2002)

It has been suggested that this information may be a relevant matter of study for the HSC because the HSC, as part of a major historically industrial area, will have a certain quantity of TPH in the sediments. Also, Lee et al. specifically studied Total Petroleum Hydrocarbons (TPH) sediment from the HSC and Galveston when the study was conducted.

Fowler et al. (2007) conducted a study on several persistent organic pollutants (POPs) in benthic organisms (which can be related to sediment concentrations since the organisms are benthic) in the southern Oman port city of Sadh, far from oil related development. Since the study analyzed for both PCBs and TPH, relationships and comparisons could be drawn between the two. The study showed that over a 19-year span TPH did not show much change while total PCBs (based on Aroclor analysis) showed decreases in the organisms in factor decreases generally around 2.3. Thus, it appears that in this case TPH concentrations were not that temporally correlated to PCBs. It is speculated that the maintenance of TPH levels relates to the dumping of tanker ballasts while the PCB decrease is reflective of a general trend of decrease in PCB use since the early 1980s. These facts may be relevant to the HSC when considering that tanker ships also come into the Channel system and may influence TPH through ballast offloading or other means.

2.5.3.5 Grain Size Effects on PCB Concentration

Vane et al. (2007) suggest that total PCBs in their study were correlated with sediment grain size. Muddy sediments exhibited the maximum concentration and coarse sands exhibited the minimum concentration.

2.5.3.6 Volatilization from Sediment

Volatilization is not an impossibility as far as what could be considered a loss mechanism from sediment. Vane et al. (2007) considered it as a possibility for loss in estuarine sediment corings in the U.K. but ultimately concluded that it is not a major loss mechanism because the sediments do not have much exposure time to air during the tidal changes. Were sediments left exposed to the air due to tidal fluctuations, then volatilization would be a transport mechanism that needs considering.

2.5.4 Biological Fate

The three main PCB fate processes to be considered in aquatic life are bioconcentration, biomagnification, and bioaccumulation.

A mechanism called bioconcentration occurs when an aquatic organism absorbs the PCB from water through the skin or gills. It is a real mechanism when the concentration in the organism is greater than the concentration in the surrounding water. (Harrad, 2001) In other words, PCB uptake into fish may be occurring in many waters, but if that uptake does not result in a net increase in concentration within the organism, then the effect is not quantifiable and therefore only marginally useful in transport analysis.

Biomagnification occurs when the concentration of PCB in the organism exceeds the concentration of the PCB in the dietary uptake. This can be difficult to quantify within a certain aquatic organism since there is an uptake from water (bioconcentration) as well as diet. (Harrad, 2001) It should also be noted that within biomagnification a biotransformation of PCBs can occur whereby one PCB congener is transformed to another or eliminated, which will alter the relative congener proportions. This effect can especially be at issue if the proportional augmentation tends toward the increase of coplanar PCBs.

Bioaccumulation is the combined effect of biomagnification and bioconcentration. Strictly stated, it is when the concentration within an organism exceeds the concentration within the water when all routes of exposure are considered. (Harrad, 2001)

There is a distinction made for food-based bioaccumulation as a specific form of bioaccumulation that occurs when PCB concentration increases as one moves up the food chain. The reason that it occurs is because PCBs are transported through the food chain via the lipids that are consumed in the prey. When the lipid content within a predator is higher than the content in the prey, the new PCB concentration in the lipid of the predator will be increased. (Harrad, 2001)

One study illustrated this effect in Channel Catfish (a species found in the HSC) in the Clinch River/Watts Bar Reservoir. PCB levels in general were higher in Channel Catfish as compared with Largemouth Bass sampled in the study. The explanation the study gave was that the difference came from the "mode of benthic feeding" in the catfish and their higher body lipid content. Thus, higher body lipid content produces that bioaccumulative effect. (Adams et al., 1999)

One final note on metabolite biochemistry is that metabolism of PCBs can only happen when there is an adjacent pair of carbons that have no chlorine substitution. .This means that non-ortho and mono-ortho substituted PCBs (coplanar) that also have chlorine substitutions at the meta and para sites should be more resistant to metabolic breakdown. (Metcalfe and Haffner, 1995) Hence these compounds are more susceptible to biomagnification within an organism.

2.5.3.1 Biological Variables

The biological processes heretofore mentioned are all characterized by experimental factors. The definitions used here were all given by Harrad (2001).

Bioconcentration is characterized by the bioconcentration factor (BCF), which is most appropriately expressed as the ratio of the concentration of the PCB in the organism (C_B) to the concentration of freely dissolved PCB in the water (C_{WD}) (PCB not absorbed through food uptake.)

$$BCF = C_B / C_{WD}$$

Biomagnification is quantified by the biomagnification factor (BMF). It is the ratio of the chemical concentration in the organism (C_B) and the concentration found in the organism’s diet (C_D).

$$BMF = C_B / C_D$$

Bioaccumulation is measured with a bioaccumulation factor (BAF) and as stated previously attempts to take into account both of previous two factors. It is the ratio of chemical concentrations in the organism (C_B) and the water (C_W) and is usually a field-measured parameter.

$$BAF = C_B / C_W$$

The USEPA derives BAFs using this concept of bioaccumulation by defining a food-chain multiplier (FM) factor to quantify the bioaccumulation. The formula for the BAF in the EPA system is BAF=FM x BCF. (Harrad, 2001)

The BCF, BMF, and BAF are all experimentally measured factors that technically exist only in an accurately quantifiable way when equilibrium conditions are prevalent. It was noted in section 2.5.3.1 that a current understanding of sediment PCB adsorption and desorption is best described as kinetic rather than equilibrium controlled. The use of the biological variables needs then be considered in light of the kinetic processes occurring in the sediments at the base of the water column. The biological variables as described in this section may need to have their accuracy or application qualified, or they may need to be declared as erroneous altogether. One would need to characterize how kinetic the sediment transport is and then how much that transport affects the biological uptake being considered to justify the use of the equilibrium biological variables.

2.5.3.2 Factor Predictors

In trying to determine BAFs, which are the most useful in calculating the net transport of PCBs from the environment to aquatic organisms, it is important to note that a high K_{ow} will decrease the usefulness of any BCF (which is derived normally under laboratory conditions). This is because the BCF measures the uptake of the PCB from the water to the organism, and since PCBs have a high K_{ow}, most of the exposure of the organism to PCBs comes from food and not from water. (Harrad, 2001) So, a method of calculating BAF that does not take into account BCF is a better estimator in the case of PCBs.

Octanol-water partition coefficients have frequently been in use in the determination of suitable Bioaccumulation Factors (BAFs) for quite some time as they are well known, and the models that use them are fairly easy to employ. One study shows that K_{ow} consistently under predicts the bioaccumulative effect of PCBs in both kinds of lipids involved in biota. These two types are neutral triglycerides and phospholipids. The error in triglycerides is considerably smaller than in phospholipids. Thus the error in BAF using K_{ow}'s in a food web model will be greater in lower trophic level organisms, where phospholipids make up a greater percentage of the total lipid amount. The authors conclude that the use of K_{ow} for BAFs is only sometimes justifiable. (Jabusch and Swackhamer, 2005) Metcalfe and Haffner state that the uptake and elimination of non-ortho PCBs in aquatic biota cannot be predicted only from K_{ow}. (Metcalfe and Haffner, 1995)

In a general sense, the researcher must decide how much effort must be given to the accuracy of a BAF especially when considering that transport mechanism relative importance to all other transport mechanisms. This consideration is valid because there are empirical models, semi-empirical models, and theoretical models for calculating BAFs, and all of these models require different degrees of effort to be used. Empirical models usually involve the calculation of a BCF from the laboratory or a BAF from the field. With the current understanding of the mechanisms of bioaccumulation, especially that which results from metabolic means of food uptake, these models are usually the most accurate albeit often more difficult and time consuming. The understanding of mechanisms within the organism is growing, which renders theoretical models more and more useful. (Harrad, 2001)

2.5.3.3 Biodegradation

Reductive dechlorination is the mechanism by which PCB congeners are purported to be transformed from higher to lower chlorinated congeners. Borja et al. (2005) reviewed the literature up to that time concerning PCB biodegradation. They laid out two main pathways for biodegradation to occur: aerobic and anaerobic. The two processes work together in that higher chlorinated congeners are anaerobically dechlorinated to become lighter congeners that are then mineralized by aerobic means. In general, the anaerobic degradation selectively removes para and meta chlorines down to the potential level of mono- and dichloro PCBs. The ortho chlorines remain attached, but the PCB can be further degraded aerobically to such metabolites as chlorinated benzoic acids, hydroxybiphenyls, and polychloroacetophenones. Many studies have been performed to demonstrate the possibility of degradation in the laboratory

A recent study conducted by Vane et al. (2007) in Mersey Estuary using sediment core sampling looked at a 60 year span of PCB use. They discovered that there was no significant reduction in the amounts of the lighter chlorination congeners. This would rule out biodegradation at least from these particular sediments.

REFERENCES

Adams, S.M., Bevelhimer, M.S., Greeley Jr, M.S., Levine, D.A., Teh, S.J., 1999. Ecological risk assessment in a large river-reservoir: 6. Bioindicators of fish population health. Environ. Toxicol. Chem. 18, 628.

Agrell, C., Okla, L., Larsson, P., Backe, C., Wania, F., 1999. Evidence of latitudinal fractionation of polychlorinated biphenyl congeners along the Baltic Sea region. Environ. Sci. Technol. 33, 1149-1156.

Atkinson, R., 1996. Atmospheric Chemistry of PCBs, PCDDs and PCDFs. In: Hester, R.E., Harrison, R.M. (Eds.). Chlorinated Organic Micropollutants, Issues in Environmental Science and Technology, Number 6, Cambridge, UK, pp. 53-72.

ATSDR, 2000. Toxicological Profile for Polychlorinated Biphenyls (PCBs). Agency for Toxic Substances and Disease Registry.

Axelman, J., 2001. Biological, physico-chemical and biogeochemical dynamics of hydrophobic organic compounds. Zoology. Stockholm University, Stockholm.

Barra, R., Popp, P., Quiroz, R., Bauer, C., Cid, H., Tumpling, W.V., 2005. Persistent toxic substances in soils and waters along an altitudinal gradient in the Laja River Basin, Central Southern Chile. Chemosphere 58, 905.

Blanchard, M., Teil, M.J., Guigon, E., Larcher-Tiphagne, K., Ollivon, D., Garban, B., Chevreuil, M., 2007. Persistent toxic substance inputs to the river Seine basin (France) via atmospheric deposition and urban sludge application. Sci. Total Environ. 375, 232-243.

Booij, K., Hoedemaker, J.R., Bakker, J.F., 2003. Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. Environ. Sci. Technol. 37, 4213.

Booij, K., Van Drooge, B.L., 2001. Polychlorinated biphenyls and hexachlorobenzene in atmosphere, sea-surface microlayer, and water measured with semi-permeable membrane devices (SPMDs). Chemosphere 44, 91.

Borja, J., Taleon, D.M., Auresenia, J., Gallardo, S., 2005. Polychlorinated biphenyls and their biodegradation. Process Biochemistry 40, 1999-2013.

Breivik, K., Alcock, R., Li, Y.F., Bailey, R.E., Fiedler, H., Pacyna, J.M., 2004. Primary sources of selected POPs: regional and global scale emission inventories. Environ. Pollut. 128, 3-16.

Bruhn, R., Lakaschus, S., McLachlan, M.S., 2003. Air/sea gas exchange of PCBs in the southern Baltic Sea. Atmos. Environ. 37, 3445.

Burkhard, L.P., Armstrong, D.E., Andren, A.W., 1985. Henry Law Constants For The Polychlorinated-Biphenyls. Environ. Sci. Technol. 19, 590-596.

Cheng, C.Y., Atkinson, J.F., Depinto, J.V., 1995. Desorption During Resuspension Events - Kinetic V Equilibrium-Model. Mar. Freshw. Res. 46, 251-256.

Connolly, J.P., Zahakos, H.A., Benaman, J., Ziegler, C.K., Rhea, J.R., Russell, K., 2000. Model of PCB fate in the Upper Hudson River. Environ. Sci. Technol. 34, 4076.

Dachs, J., Bayona, J.M., Albaigés, J., 1997. Spatial distribution, vertical profiles and budget of organochlorine compounds in Western Mediterranean seawater. Marine Chemistry 57, 313-324.

De Voogt, P., Brinkman, U.A., 1989. Production, properties and usage of polychlorinated biphenyls. In: Kimbrough, R., Jensen, A.A. (Eds.). Halogenated biphenyls, terphenyls, napthalenes, dibenzodioxins and related products. Elsevier Science, New York, NY, p. 536.

Erickson, M.D., 1982. Methods of Analysis for By-Product PCBs - Literature Review and Preliminary Recommendations. USEPA, p. 137.

Erickson, M.D., Stanley, J.S., Turman, J.K., Going, J.E., Redford, D.P., Heggem, D.T., 1988. Determination of byproduct polychlorobiphenyls in commercial products and wastes by high-resolution gas chromatography/electron impact mass spectrometry Environ. Sci. Technol. 22, 71-76.

Feng, H., Cochran, J.K., Lwiza, H., Brownawell, B.J., Hirschberg, D.J., 1998. Distribution of heavy metal and PCB contaminants in the sediments of an urban estuary: The Hudson River. Mar. Environ. Res. 45, 69.

Fowler, S.W., Villeneuve, J.-P., Wyse, E., Jupp, B., de Mora, S., 2007. Temporal survey of petroleum hydrocarbons, organochlorinated compounds and heavy metals in benthic marine organisms from Dhofar, southern Oman. Marine Pollution Bulletin 54, 357-367.

Gong, Y., Depinto, J.V., Rhee, G.Y., Liu, X., 1998. Desorption rates of two PCB congeners from suspended sediments - I. Experimental results. Water Res. 32, 2507.

Halsall, C.J., Lee, R.G.M., Coleman, P.J., Burnett, V., Hardingjones, P., Jones, K.C., 1995. PCBs In UK Urban Air. Environ. Sci. Technol. 29, 2368-2376.

Harrad, S., 2001. Persistent Organic Pollutants: Environmental Behavior and Pathways of Human Exposure. Kluwer Academic Publishers, Norwell, MA, USA.

Hornbuckle, K.C., Jeremiason, J.D., Sweet, C.W., Eisenreich, S.J., 1994. Seasonal-Variations In Air-Water Exchange Of Polychlorinated-Biphenyls In Lake-Superior. Environ. Sci. Technol. 28, 1491-1501.

Hung, H., Halsall, C.J., Blanchard, P., Li, H.H., Fellin, P., Stern, G., Rosenberg, B., 2001. Are PCBs in the Canadian Arctic atmosphere declining? Evidence from 5 years of monitoring. Environ. Sci. Technol. 35, 1303-1311.

Ikonomou, M.G., Sather, P., Oh, J.-E., Choi, W.-Y., Chang, Y.-S., 2002. PCB levels and congener patterns from Korean municipal waste incinerator stack emissions. Chemosphere 49, 205-216.

Ishikawa, Y., Noma, Y., Yamamoto, T., Mori, Y., Sakai, S.-i., 2007. PCB decomposition and formation in thermal treatment plant equipment. Chemosphere 67, 1383-1393.

Jabusch, T.W., Swackhamer, D.L., 2005. Partitioning of polychlorinated biphenyls in octanol/water, triolein/water, and membrane/water systems. Chemosphere 60, 1270.

Jeremiason, J.D., Eisenreich, S.J., Baker, J.E., Eadie, B.J., 1998. PCB decline in settling particles and benthic recycling of PCBs and PAHs in Lake Superior. Environ. Sci. Technol. 32, 3249-3256.

Jeremiason, J.D., Hornbuckle, K.C., Eisenreich, S.J., 1994. PCBs In Lake-Superior, 1978-1992 - Decreases In Water Concentrations Reflect Loss By Volatilization. Environ. Sci. Technol. 28, 903-914.

Jurado, E., Zaldivar, J.-M., Marinov, D., Dachs, J., 2007. Fate of persistent organic pollutants in the water column: Does turbulent mixing matter? Mar. Pollut. Bull. 54, 441-451.

Karickhoff, S.W., 1981. Semiempirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils. Chemosphere 10, 833-846.

Konat, J., Kowalewska, G., 2001. Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea - Trends and fate. Sci. Total Environ. 280, 1.

Lee, G.F., Jones-Lee, A., Ogle, S., 2002. Preliminary Assessment of the Bioaccumulation of PCBs and Organochlorine Pesticides in Lumbriculus variegatus from City of Stockton Smith Canal Sediments and Toxicity of City of Stockton Smith Canal Sediments to Hyalella azteca. G. Fred Lee & Associates, El Macero, CA, p. 28.

Lohmann, R., Northcott, G.L., Jones, K.C., 2000. Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs, and PAHs to the UK atmosphere. Environ. Sci. Technol. 34, 2892-2899.

Marti, S., Bayona, J.M., Albaiges, J., 2001. A potential source of organic pollutants into the Northeastern Atlantic: The outflow of the Mediterranean deep-lying waters through the Gibraltar Strait. Environ. Sci. Technol. 35, 2682.

Metcalfe, C.D., Haffner, G.D., 1995. Ecotoxicology of coplanar polychlorinated biphenyls. Environmental Reviews 3, 171.

Ouyang, Y., Zhang, J.E., Ou, L.T., 2006. Temporal and spatial distributions of sediment total organic carbon in an estuary river. J. Environ. Qual. 35, 93-100.

Pearson, R.F., Hornbuckle, K.C., Eisenreich, S.J., Swackhamer, D.L., 1996. PCBs in Lake Michigan water revisited. Environ. Sci. Technol. 30, 1429-1436.

Schneider, A.R., Porter, E.T., Baker, J.E., 2007. Polychlorinated Biphenyl Release from Resuspended Hudson River Sediment. Environ. Sci. Technol. 41, 1097-1103.

Sobek, A., Gustafsson, O., Hajdu, S., Larsson, U., 2004. Particle-Water Partitioning of PCBs in the Photic Zone: A 25-Month Study in the Open Baltic Sea. Environ. Sci. Technol. 38, 1375.

Swackhamer, D.L., 1996. Studies of Polychlorinated Biphenyls in the Great Lakes. In: Hester, R.E., Harrison, R.M. (Eds.). Chlorinated Organic Micropollutants. Royal Society of Chemistry, Cambridge, p. 183.

Ueno, D., Darling, C., Alaee, M., Campbell, L., Pacepavicius, G., Teixeira, C., Muir, D., 2007. Detection of Hydroxylated Polychlorinated Biphenyls (OH-PCBs) in the

Abiotic Environment: Surface Water and Precipitation from Ontario, Canada. Environ. Sci. Technol. 41, 1841-1848.

USEPA, 2003. Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds National Academy Sciences (NAS) Review Draft. United States Environmental Protection Agency, Washington, D.C.

Vane, C.H., Harrison, I., Kim, A.W., 2007. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, U.K. Sci. Total Environ. 374, 112-126.

Wan Ying, S., Mackay, D., 1986. A critical review of aqueous solubilities, vapor pressures, Henry's law constants, and octanol-water partition coefficients of the polychlorinated biphenyls. Journal of Physical and Chemical Reference Data 15, 911.

Wania, F., Daly, G.L., 2002. Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs. Atmos. Environ. 36, 5581.

Wu, S.-c., Gschwend, P.M., 1986. SORPTION KINETICS OF HYDROPHOBIC ORGANIC COMPOUNDS TO NATURAL SEDIMENTS AND SOILS. Environ. Sci. Technol. 20, 717.

Zhou, J.L., Maskaoui, K., Qiu, Y.W., Hong, H.S., Wang, Z.D., 2001. Polychlorinated biphenyl congeners and organochlorine insecticides in the water column and sediments of Daya Bay, China. Environ. Pollut. 113, 373-384.

APPENDIX B

Compilation and Analysis of Summer 2002, Fall 2002, and Spring 2003 PCB Data

An Update of Chapter 2 of the Second Quarterly Report – FY07

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CHAPTER 2 - ANALYSIS OF PREVIOUS HSC PCB DATA

PCB water, sediment, fish, and crab samples were collected in the HSC in Summer, Fall, and Spring of 2002-2003. A fish sampling study conducted by TDH in 1999 revealed that PCBs posed a health risk requiring a TMDL just as had been the case with the already begun Dioxin TMDL Project. Thus, the scope of the dioxin project in 2002 was expanded to include a preliminary PCB assessment in anticipation of a separate PCB TMDL study. The resultant dataset was presented in the November 2005 Final Report for Work Order No. 5820-0-80121 of the Dioxin TMDL Project (Rifai et al., 2005). Figure 2.1 presents the HSC with the sampled station locations.

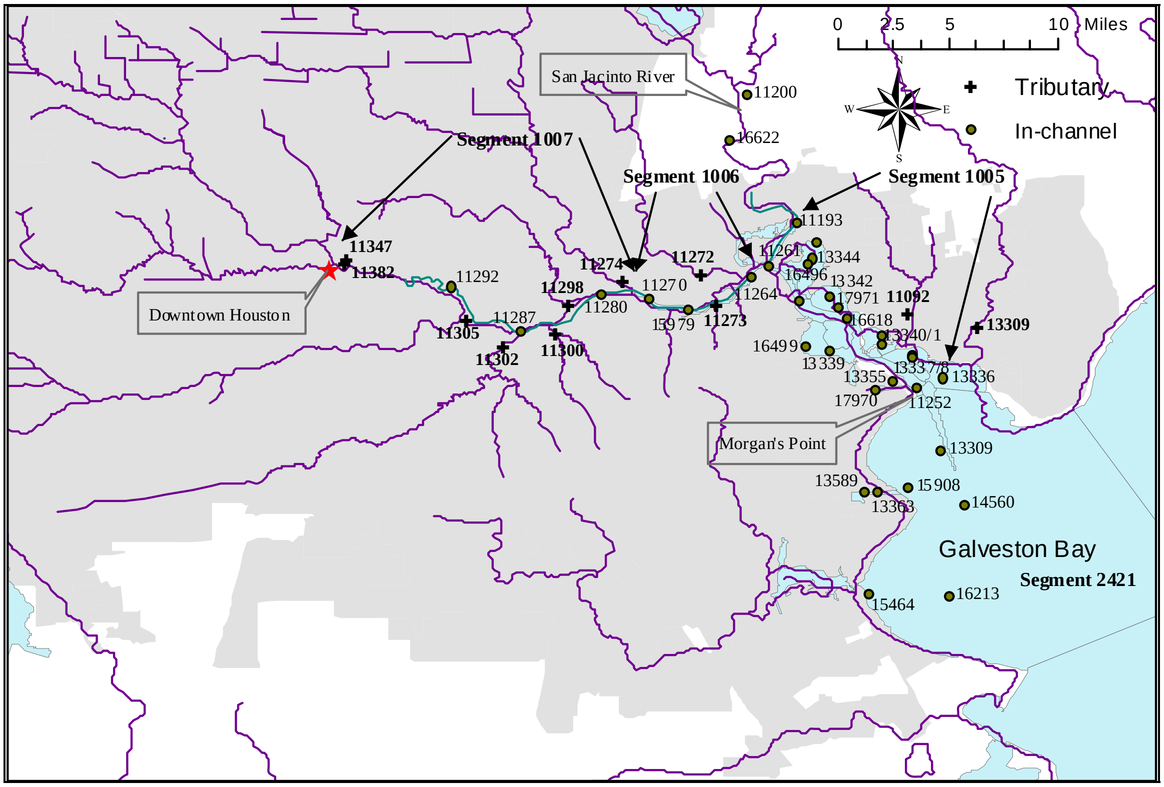


Figure 2.1 Stations sampled during the 2002-2003 PCB assessment

The concentration data were presented in the November 2005 report according to a congener summation method called NOAA EPA, which includes the 18 congeners shown in Table 2.1.

Table 2.1 NOAA total PCB concentration representative congener methods

Institution	**NOAA NS&T**	**NOAA NS&T**	**NOAA NS&T**	**NOAA EPA**
Year	**1984-1985**	**1986**	**1987**	**2000***
Congener Count	**Congener IDs**			
1	7	8	8	8
2	31	28	18	18
3	47	52	28	28
4	101	101	44	44
5	153	153	52	52
6	185	170	66	66
7	194	195	101	77
8	206	206	105	101
9	-	209	118	105
10	-	-	128	118
11	-	-	138	126
12	-	-	153	128
13	-	-	170	138
14	-	-	180	153
15	-	-	187	169
16	-	-	195	170
17	-	-	206	180
18	-	-	209	187
Total Count	*8*	*9*	*18*	*18*
∑PCB Multiplier	*NA*	*NA*	*2*	*1*

*The 2000 "NOAA EPA" method is referenced by EPA to a NOAA 1989 document which is most likely a mistaken reference. A document matching that title and edition could only be found for a NOAA MacLeod et al. (1985) document.

In addition to the concentration data, the November 2005 report also presented the following data analyses:

- Major congener contributors to concentration
- Bioaccumulation factors (BAFs) and biota to sediment factors (BSAFs)
- Dissolved-suspended phase partitioning relationships in water samples
- Spatial trend plots
- Aroclor results
- Principal component analysis (PCA) in sediment
- Hazard index (HI) calculation

The activities conducted in this quarter have expanded upon these analyses. The greatest departure from the 2005 data analysis is a recalculation of total PCB concentrations using all 209 congeners instead of any particular set of 18. There were two main reasons for the change:

1) Total PCB concentrations are more accurate when all of the congeners that were quantified by EPA Method 1668A are used.
2) PCB homolog profiles represent all homolog groups (mono- and deca-chlorinated homologs are not present in the NOAA EPA 18), and the homolog groups give a more accurate profile.

These alterations changed all of the values of the concentration data and provided insight into more analyses that could be performed. In addition to new concentration values, more analysis was done in the areas of:

- HSC comparison to other water bodies
- Correlations between different media types
- Calculation and use of dissolved phase-suspended phase distribution coefficients
- Spatial trends of total concentration and homolog profiles

- Tributary-main channel comparisons
- PCB quantification method evaluation

From these analyses, possible conclusions concerning transport and sources in the HSC were drawn. These conclusions will help direct the course of the project from here on out.

2.1 ADJUSTED TOTAL PCB CONCENTRATIONS

The statistics for total PCB concentrations under the all congener summation approach are given below in Table 2.2. Raw data concentrations for individual congeners were given in previous reports, but the new individual station totals were not presented previously and thus are given in Appendix A. Table 2.3 compares the national and state screening criteria for these media using these new calculated concentrations just as the November 2005 report did with the NOAA EPA 18.

Table 2.2 All congener method PCB concentration statistics

Media	Unit	Median	Min	Max	SD
Water	ng L^{-1}	1.85	0.49	12.5	2.17
Sediment	ng g^{-1}-dry wt	37	4.18	4,601	598
Fish	ng g^{-1}-wet wt	107	4.13	1,596	151
Crab	ng g^{-1}-wet wt	25.5	3.44	169	25.4

Table 2.3 Sample exceedances using both channel and tributary samples

Media	Unit	Screening Level	Total Exceedances[c]	Total Samples	Exceedance Percentage
Water	ng L^{-1}	0.885[a]	46	53	87%
Sediment	ng g^{-1}-dry wt	NA	NA	98	NA
Fish	ng g^{-1}-wet wt	47[b]	74	86	86%
Crab	ng g^{-1}-wet wt	47[b]	9	60	15%

[a] Texas Surface Water Quality Standard

[b] USEPA (1999)

[c] Exceedances taken from averaging duplicate concentrations for each station. These averages are not explicitly presented in this report due to lack of statistical analyses, but they are used here for the purposes of comparison with previous data.

A comparison between Table 2.2 and Table 2.3 reveals that the median concentration in water and fish exceeds the screening level criteria while the median crab concentration does not. Correspondingly, both water and fish show high percentages of exceedances while crab does not. Sediment had no screening value by which to compare.

When this data is compared with the data presented in November 2005 using the NOAA EPA 18 congeners, there are some differences in the results, which are summarized in Table 2.4.

Table 2.4 November 2005 PCB concentration summary using the NOAA EPA methodology

Media	Unit	Average[a]	Exceedances	Total	Exceedance Percentage	Percent Increase Using All Congeners[b]
Water	ng L^{-1}	0.665	12	53	23%	271%
Sediment	ng g^{-1}-dry wt	57	NA	98	NA	195%
Fish	ng g^{-1}-wet wt	86.1	59	84	70%	109%
Crab	ng g^{-1}-wet wt	16.6	1	58	2%	73%

[a] Average calculated from per station concentration values that average duplicate values.

[b] Represents the percentage increase in average apparent total PCB concentration when using an all congeners addition instead of the NOAA EPA 18 addition.

The concentration averages are higher in all media with increases greater than 100% in all media except for crab. As is expected, the percentage of exceedances is higher in the all congeners method of concentration calculation. The effect is especially pronounced in the water samples for reasons that will become clearer in later sections.

The obvious reason for these increases is simply that more congeners are added together to get the final value. Logically, summing all of the congeners as opposed to a representative few creates a more accurate result[1]. EPA’s recommendation of the use of fewer but representative congeners rests on the belief that most of the congeners that are not quantified in the total will not have a large effect or are possibly not as much of a health risk, which makes quantification of them irrelevant from a health perspective. What will be seen in the following additional analyses (all of which use the all congener method unless specifically stated otherwise) is that not only are the total PCB

---

[1] It is possible that some congeners are less accurately quantifiable than others. If this were the case, then a representative congener addition approach would be preferable because it would introduce less quantitative error to the resultant concentration. Current understanding in PCB detection by Method 1668A does not suggest such a scenario, but the assertion that summing all congeners is more accurate inexorably rests on the consistent level of accuracy with which each congener is quantified as compared with all of the other congeners in a sample. In other words, the accuracy of each individual congener measurement should be nearly the same.

concentrations significantly influenced by the use of every congener but the homolog profile as well. These changes are significant because of the greater conclusions that can be drawn concerning sources and transport.

2.2 EVALUATION OF ANALYSIS METHOD ASSUMPTIONS

At many points in the analysis, assumptions and arbitrary choices were made about how the data should be treated. Two of those assumptions were examined in light of the data to determine how the analysis and results should be different:

1) The use of a one half method detection limit to represent the value of non-detect results for each congener analyzed.
2) Sediment concentration normalization by dry weight of sediment rather than by organic carbon weight.

The first assumption was examined on a truly zero concentration non-detect level, and the second assumption was examined by an organic carbon weight basis rather than a dry weight basis.

In brief, the change of the first assumption created virtually no difference in any of the analyses shown. The change in sediment concentration weight basis, however, did provide some additional information. That information will be highlighted as necessary.

2.3 HSC PCB LEVELS AS COMPARED WITH OTHER WATER BODIES

The HSC is clearly not the only water body at risk from PCB contamination. Table 2.5 shows concentrations that were found in the HSC in comparison with other similar industrially located bays around the globe. These results illustrate that in general the HSC concentrations are higher than other sampling efforts conducted to date. One reason for this result may be that not all of the other studies use all congeners in their

PCB totals, but even with that consideration HSC concentrations are still high in an absolute sense.

The comparisons by media reveal information about where the HSC falls in terms of ranking the quantity and the range of PCB concentration. These comparisons show the following:

- Water: HSC had the greatest maximum concentration and the greatest range.
- Sediment: Maximum HSC concentration was the greatest, and the range was also the greatest.
- Fish: Maximum concentration was smaller only compared to the Hudson River with a range comparable to the Eman River.
- Crab: Sufficient comparison data for crab was not found.

These comparisons provide context to the HSC results, context which can help similarities to be drawn that may help in assessment and solution to the problem.

Table 2.5 Total PCB concentrations in water, sediment, fish from other studies

Location	*Water (ng L^{-1})*	*Sediment (ng g^{-1} d. wt.)*	*Fish (ng g^{-1} w. wt)*	*Aroclors Sed (x10^3 ng Kg^{-1}) Fish (ng g^{-1})*	*Year*	*Water Sample Collection*	*Reference*
Lake Michigan, US	0.34 – 1.74[d]				1991	Peristaltic pump (GFF/GLSE)	Pearson et al., 1996
Baltimore Harbor, MD, US	0.1 – 1.52[e]				1996 - 1997	18-L tanks (GFF/XAD-2)	Bamford et al., 2002
Palos Verdes Peninsula, CA, US	0.06 – 1.14[f]				1997	High-Vol (GFF/XAD-2)	Zeng et al., 1999
New York Harbor, NY, US	6.7 – 9.4[d]				1998	High-Vol (GFF/XAD-2)	Totten et al., 2001
San Diego Bay, CA, US	0.024 – 0.419[g]				1999	High-Vol (GFF/XAD-2)	Zeng et al., 2002
Delaware River, US	1.2 – 6.5[d]					20-L tanks (GFF/XAD-2)	Rowe et al., 2007
Chesapeake Bay, US		8 – 2,150[h]			1996		Ashley and Baker, 1999
Salton Sea Lake, CA, US		116 – 304[i]			2000		Sapozhnikova et al., 2004
Narragansett Bay, RI, US		20.8 – 1,760[j]			1997-1998		Hartmann et al., 2004.
Hanoi City, Vietnam		0.74 – 33.68[k]		0.79 – 45.8[a]	1997		Nhan et al., (2001)
Venice lagoon, Italy		2-2,049[l]		6 – 1590[a]	1996-1998		Frignani et al., 2001
Busan Bay, Korea		5.71 – 199[m]			2000		Hong et al., 2005
Bahrain coastal region		0.18 – 7.41[n]		0.30 – 12.2[a]	2000 - 2001		De Mora et al., 2005
Rio de la Plata estuary, Argentina		0.04 - 98.5[o]			2002 - 2003		Colombo et al., 2005
Singapore, Southwestern coast		1.4 – 329.6[p]			2003		Wurl and Obbard, 2005
Salton Sea Lake, CA, US			10.1 – 114.5[i]		2000		Sapozhnikova et al., 2004
Hudson River, NY, US			500 – 4,000[d]		1994 - 1995		Ashley et al., 2000
Hanoi City, Vietnam			5.45 – 58.12[b,k]	6.78 – 103.79[b,c]	1997		Nhan et al., (2001)
Los Padres Lake, Argentina			3.5 – 730.6[q]		2000		González-Sagrario et al., 2002
Eman River, Sweden			20.6 – 1,244[d]		1991		Bremle et al., 1995
Bahrain coastal region			2.39 – 40.1[b,n]	2.25 – 45[b,c]	2000 – 2001		De Mora et al., 2005
Houston Ship Channel, USA	**0.49-12.49[d]**	**4.18– 4,601[d]**	**4.13 – 1,596[d]**	**ND – 120** **ND – 480**	**2002-2003**	**High-Vol (GFF/XAD-2)**	**This study**

GFF, glass fiber filters; GLSE, liquid-liquid Goulden large-sample extractor.

[a] Aroclor 1254+Aroclor 1260; x10^3 ng Kg^{-1} d. wt; [b] Muscle; ng g^{-1} dry weight; [c] Aroclor 1254+Aroclor 1260; ND, non-detect; [d] 209 PCB congeners; [e] 24 individual PCB congeners + 21 chromatographically unresolved congener groups; [f] PCB-8, PCB-18, PCB-28, PCB-29, PCB-44, PCB-50, PCB-52, PCB-66, PCB-77, PCB-87, PCB-101, PCB-104, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138, PCB-153, PCB-154, PCB-170, PCB-180, PCB-187, PCB-188, PCB-195, PCB-200, PCB-206, PCB-209; [g] PCB-18, PCB-28, PCB-29, PCB-44, PCB-50, PCB-52, PCB-66, PCB-77, PCB-87, PCB-101, PCB-104, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138, PCB-153, PCB-154, PCB-170, PCB-180, PCB-187, PCB-188, PCB-195, PCB-200, PCB-206, PCB-209; [h] 113 PCB congeners; [i] 55 PCB congeners; [j] PCB-8, PCB-18, PCB-28, PCB-29, PCB-44, PCB-50, PCB-66/95, PCB-87, PCB-101/90, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138/163/164, PCB-170/190, PCB-180, PCB-187/182/159, PCB-188, PCB-195, PCB-200, PCB-206, PCB-209; [k] PCB-44, PCB-49, PCB-52, PCB-101, PCB-105, PCB-118, PCB-128, PCB-138, PCB-149, PCB-153, PCB-170, PCB-180, PCB-200; [l] PCB-18, PCB-28, PCB-52, PCB-77, PCB-101, PCB-118, PCB-126, PCB-153, PCB-138, PCB-169, PCB-180, PCB-194; [m] PCB-8, PCB-18, PCB-28, PCB-29, PCB-44, PCB-52, PCB-66, PCB-87, PCB-101, PCB-105, PCB-110, PCB-118, PCB-128, PCB-138, PCB-153, PCB-170, PCB-180, PCB-187, PCB-195, PCB-200, PCB-206, PCB-209; [n] PCB-44, PCB-49, PCB-52, PCB-87, PCB-101, PCB-105, PCB-118, PCB-128, PCB-138, PCB-149, PCB-153, PCB-170, PCB-180, PCB-187, PCB-201; [o] 41 PCB congeners; [p] PCB-18, PCB-28, PCB-31, PCB-33, PCB-44, PCB-49, PCB-53, PCB-70, PCB-74, PCB-82, PCB-87, PCB-95, PCB-99, PCB-101, PCB-105, PCB-118, PCB-128, PCB-132, PCB-138, PCB-153, PCB-156, PCB-169, PCB-170, PCB-171, PCB-177, PCB-180, PCB-183, PCB-187, PCB-190, PCB-194, PCB-195, PCB-199, PCB-205, PCB-206, PCB-208, PCB-209; [q] PCB-18, PCB-28, PCB-31, PCB-44, PCB-47, PCB-49, PCB-52, PCB-87, PCB-90, PCB-101, PCB-105, PCB-110, PCB-118, PCB-138, PCB-149, PCB-151, PCB-153, PCB-156, PCB-170, PCB-180, PCB-194, PCB-195, PCB-199;

2.4 CONGENER PROFILES

Total PCB concentrations are valuable in order to get a “one-value” type assessment of the level and distribution of PCBs in the channel. Yet PCBs are not a monolithic compound and their congener profiles can yield useful information.

Figure 2.2 presents the congener profile of PCBs in the HSC by season. The November 2005 presented some similar profiling except that the profiles at that time included only the NOAA EPA 18 congeners. This group of 18 left out some important homolog groups, the most notable of which is the deca-chlorinated homolog containing only PCB-209.

The largest difference between the various media is the water profile as compared with the other media profiles. The dominant homolog group in water in general is the tetra-chlorinated group while in the sediment, fish, and crab profiles the dominant homologs are five and six. This trend is not surprising since the chemical properties of PCBs render them hydrophobic and lipophilic. Thus, in sediment, the PCBs will have more affinity for the organic carbon content there, and in the biota, there is more affinity for the lipid content. Sediment TOC was correlated with total PCBs, and a positive but weak correlation was found ($p<0.05$; $r^2 = 0.13$, 3 outliers removed). A correlation was also run between catfish and crab and their lipid content with $p < 0.05$ and $p > 0.05$, respectively. Thus, catfish showed a positive correlation with lipid content while crab did not. One other major difference in the seasonal profiles is between the levels of PCB-209 in sediment as compared with the other media. In sediment, the average percentage across seasons was 6.9% while it was only 4.5, 3,and 2.5% in water, fish, and crab, respectively. This could indicate that PCB-209 has a final sink in sediment over the other media.

The only noticeable seasonal trend seen in the data is in the water sampling. The average PCB concentrations through summer 2002, fall 2002, and spring 2003 were 1.69 ng L^{-1}, 2.95 ng L^{-1}, and 6.58 ng L^{-1} respectively. Spring 2003 contained only four stations in its sample, which may have skewed the average for that season, but the twofold increase seen in concentrations from summer to fall could be indicative of volatilization losses in warmer conditions. Thus, later sampling results performed in different seasons should take this into account when assessing conditions in the channel.

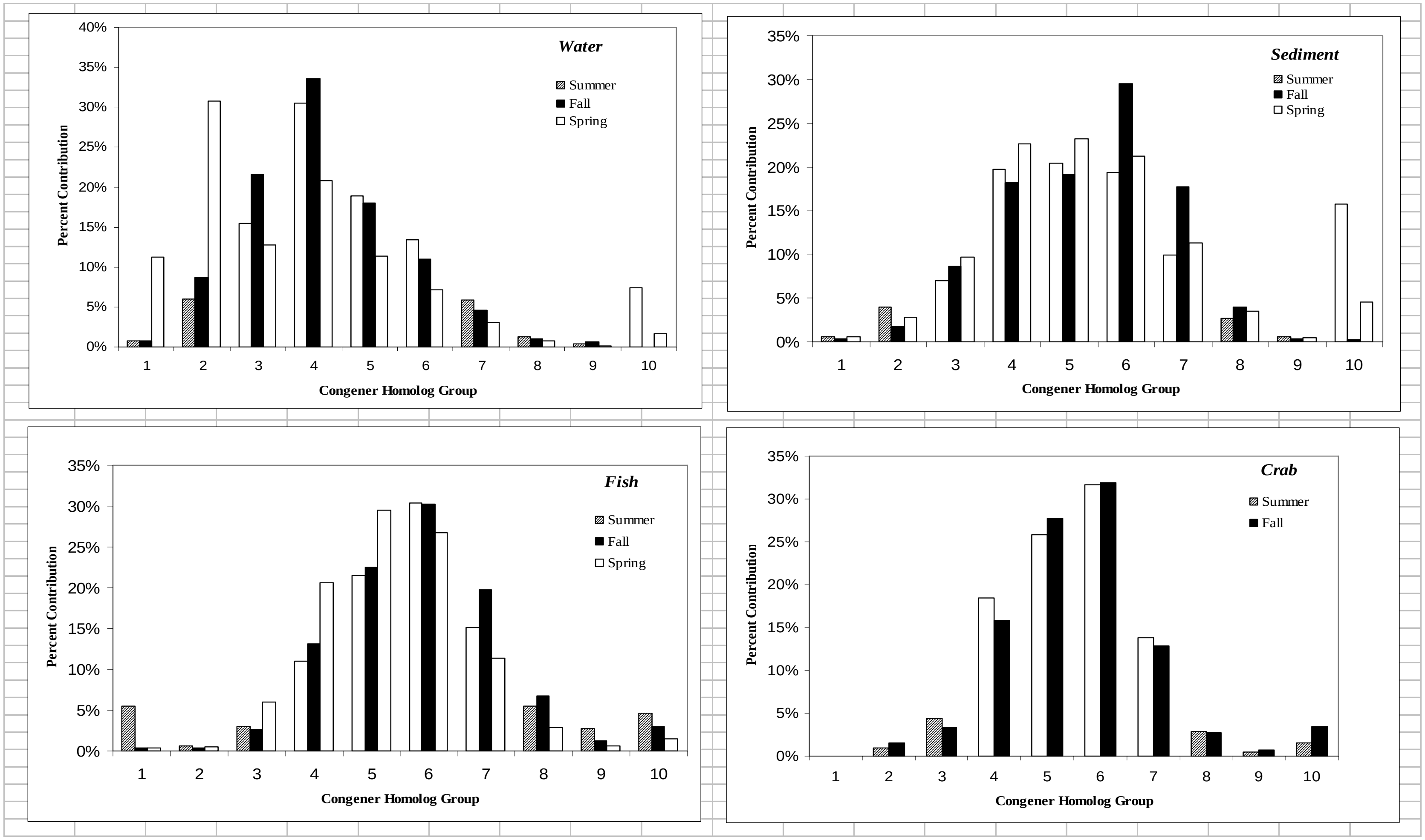


Figure 2.2 Seasonal variations in spatially averaged homolog profiles in water, channel sediment, catfish, and crab tissue samples. (Fall 2002 water PCB 209 erroneous results not included.)

2.5 INTER-MEDIA CORRELATIONS

It has been suggested that the recycling of PCB-contaminated sediment is one of the major potential sources of contamination to aquatic environments (Jeremiason et al., 1998; Zeng et al., 2002). Therefore, the observed PCB concentrations in water (dissolved and suspended phases) were correlated to the sediment concentrations. In a similar way, catfish and crab data can also be correlated to water concentrations. Table 2.6 provides the results of those correlations.

Table 2.6 Inter-media correlation statistics

Media Correlated	p < 0.05?	Station Outlier
Water-Sediment	Yes	NA
Water-Fish	Yes	16622
Water-Crab	Yes	16622
Sediment-Catfish	Yes	NA
Sediment-Crab	Yes	NA

2.6 DISSOLVED-SUSPENDED PHASE PARTITIONING

The dissolved phase-suspended phase relationship of PCB concentrations reveals some important information about transport pathways. In discussing the partitioning of dissolved-suspended phase PCBs, it is possible to discern if the dissolved phase is sourcing PCBs to the suspended phase or vice versa. Additionally, it might be valuable to know if there are different directions of transport for different congeners. An additional consideration in breaking down the two phases is the source of the suspended phase itself. At least three main sources have been described in the literature for this suspended phase. They are sediment scouring (Jeremiason et al., 1998; Schneider et al., 2007), particle deposition from air (Park et al., 2001; Totten et al., 2001), and waste and nutrients from planktonic organisms (Konat and Kowalewska, 2001; Sobek et al., 2004).

These suspended phase sources may act in combination as well as be single-sourced. They might also be a function of the vertical location within the water column. Sediment may be a greater contributor in the benthic zone, plankton in the pelagic, and deposition in the surficial.

More effort would be required to confirm the exact source of the suspended phase, but with the data that was available, the sediment to suspended phase transport of PCBs was considered. A look at the concentrations in the water showed that in 45 out of 53 station-season combinations, the dissolved phase PCB concentration was higher than the suspended phase. Moreover, segments 1006 and 1007 had the greatest deficit between the two phases. This trend suggests that PCBs are being sourced to the dissolved by way of a suspended phase that originates from scoured sediments. Zeng et al. (1999) and Gevao et al. (1997) have reported similar results.

Suspended-dissolved comparisons were also made by use of the distribution coefficient K_D defined as the concentration of suspended PCBs divided by the concentration in the dissolved (C_{susp}/C_{diss}). A more accurate way of looking at this relationship would be to normalize the C_{susp} by the particulate organic carbon (POC) level in the suspended particles. This information, however, was not taken at the time of the sampling. Figure 2.3 shows a distribution coefficient comparison of NOAA NST congeners between the in channel samples and the side bays, which only includes samples from Segment 1005. The top graph shows that spatially-averaged partitioning increases in favor of the suspended phase as the chlorination level increases, and the values themselves are not appreciably distinct from the side bays to the main channel. This trend is not surprising since chlorination and affinity for organic carbon are directly related. What is more surprising, however, is the trend in relative standard deviation (RSD) across all the samples as chlorination level is altered. The side bays show far more variation in distribution coefficient starting with PCB-8 that gradually decreases to a final congruency with the main channel from PCB-90/101/113 onward.

In general and assuming the POC is approximately the same for particles within the channel and side bays, the expectation would be to find distribution coefficients that are the same in space (i.e. K_D's though potentially different between the main channel and side bays should be relatively the same within these regions). For lighter congeners in the side bays, the variation in space is much greater than in the main channel. This difference in variability suggests greater conditions of non-equlibrium in the side bays as compared to the main channels, and these differences may likely result from different flow and mixing conditions in the side bays. The nature of this non-equilibrium points to a volatilization pathway because the greatest variation occurs in the lightest congeners. Park et al. (2001) showed that PCB deposition as well as net PCB exchange out of Galveston Bay is occurring, and further sampling activities may be able to confirm that this is happening in the channel as well as the side bays and in what way different flow regimes affect the mechanism and rate of the exchange.

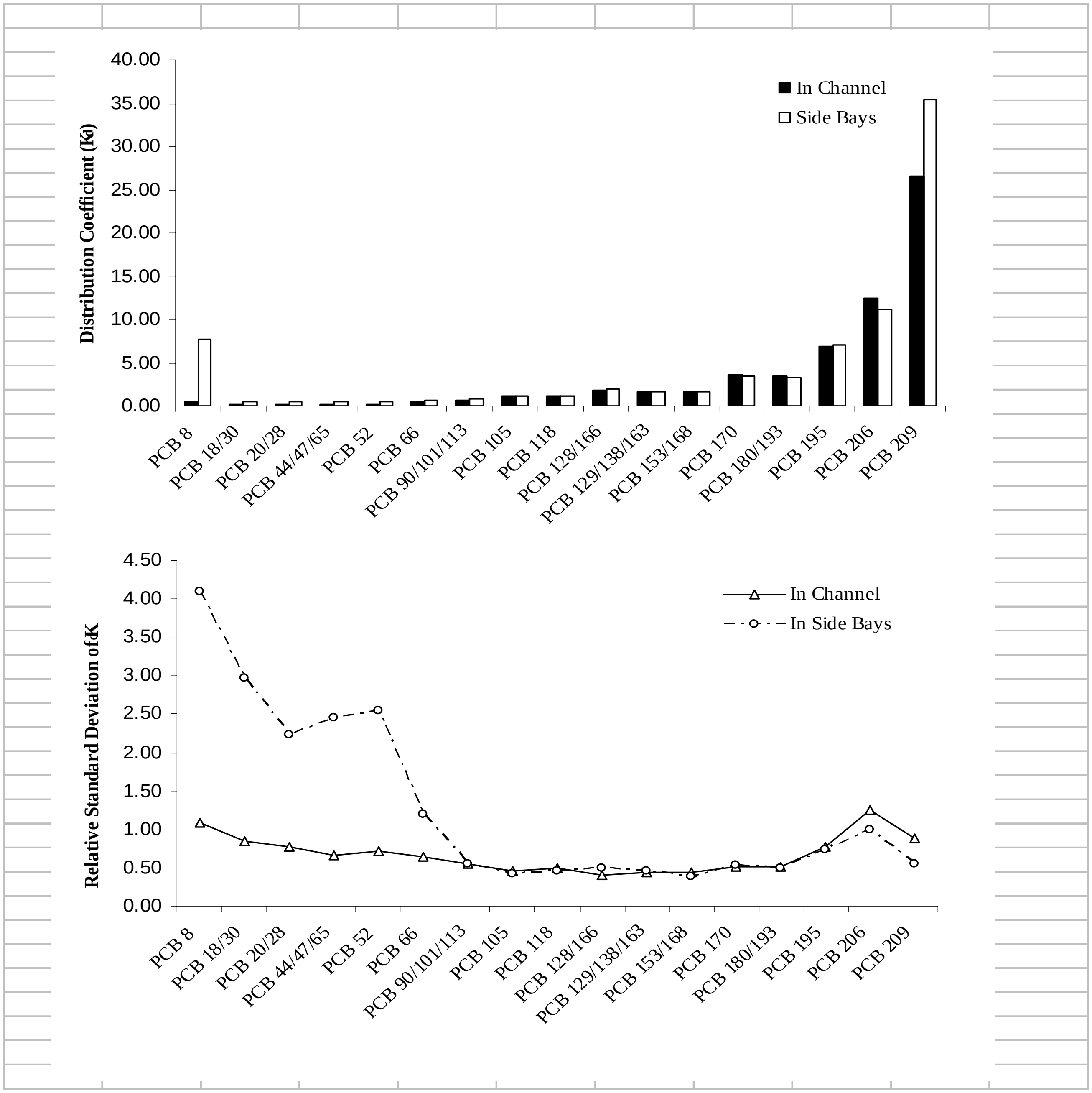


Figure 2.3 Suspended-dissolved phase distribution coefficient (C_{susp}/C_{diss}) average values and relative standard deviations in the channel and the side bays for the NOAA NST 18 congener set (PCB-187 excluded due to lack of data in the suspended phase)

2.7 PCB DEGRADATION IN SEDIMENT

The dataset gathered in the HSC suggested that total sediment PCBs in Galveston Bay have declined from their historical values at some locations. Santschi et al. (2001) found sediment concentrations in 1995 at a site slightly east of Segment 2421 to be 6.8 ng g^{-1} dry wt while they estimated average concentrations in the 1960s from that area to be 14 ng g^{-1} dry wt. Segment 2421 (sampled eight years later) showed average sediment concentration (using three stations closest to Santschi et al.'s sample 13309, 14560, and 16213) of 6.1 ng g^{-1} dry wt using the 18 representative congener set NOAA NST (see Table 2.1) that Santschi et al. used. This decrease yields an approximate first order rate constant of 0.013 yr^{-1} for the eight year period compared to the 0.045 yr^{-1} rate constant from Santschi et al. describing the decline between 1970 and 1990. The PCB sediment concentration dataset over time, however, is fairly limited and does not allow a more thorough analysis.

2.8 SPATIAL TRENDS

2.7.1 Total PCBs

Figure 2.4 displays spatial trending that was assessed in channel and tributary specific ways with the new total PCB concentration method. The trending was done by media as a distance from Morgan's Point.

Segments 1006 and 1007 clearly give the highest PCB concentrations in all media. Specifically, the maximum concentration of sediment, crab, and fish are in segment 1007 except for water, which has a maximum peak at Segment 1006. Thus, these two segments are the most likely candidates for "pockets" of historical sources, continuing contemporary sources, or both. These segments are closest in proximity to all of the refining, chemical production, petroleum distribution, catalyst processing, and waste treatment and disposal facilities that border the channel. Moreover, this portion of the channel is much thinner compared to downstream segments, which would allow sources in these segments to concentrate relative to their downstream counterparts. A look at other studies in literature finds that higher concentrations of PCBs in close proximity to industrial sources is not uncommon (Hong et al., 2005; Wurl and Obbard, 2005).

In addition to main channel analysis, it also proved useful to examine the spatial distribution of total PCBs in the tributaries. The highest observed concentrations in the tributaries for sediment, catfish, and crab were in Segment 1006 at station 11273 (19.5 km upstream from Morgan's Point), the entry point of Patrick Bayou into the HSC. Particular to sediment, there were two tributary concentrations above the main channel concentrations (Vince Bayou 31.5 km upstream and Patrick Bayou 19.5 km upstream), which indicated the possibility of tributary PCB sediment transport to the channel. The crab and sediment tributary profiles are more comparatively similar in that the large increase in 1006 is followed by (moving in the upstream direction) a large decrease in 1007 back to the tributary concentration levels seen in 1005 and 2421. The catfish profiles, however, remain at the 1006 concentration levels moving upstream to 1007. This difference in the catfish tributary spatial profile could suggest that the crabs' pathway of uptake relates more to the tributary sediments as a source while the catfish population may be influenced more by other sources such as lower trophic organisms consumed by the catfish.

The total PCB concentrations and their spatial trends all point to higher PCB impact in the upstream channel Segments 1007 and 1006. Thus, these segments were examined more closely at a congener homolog level to determine some linkages in the transport along the channel as well as to the sources that contribute to the PCB concentrations.

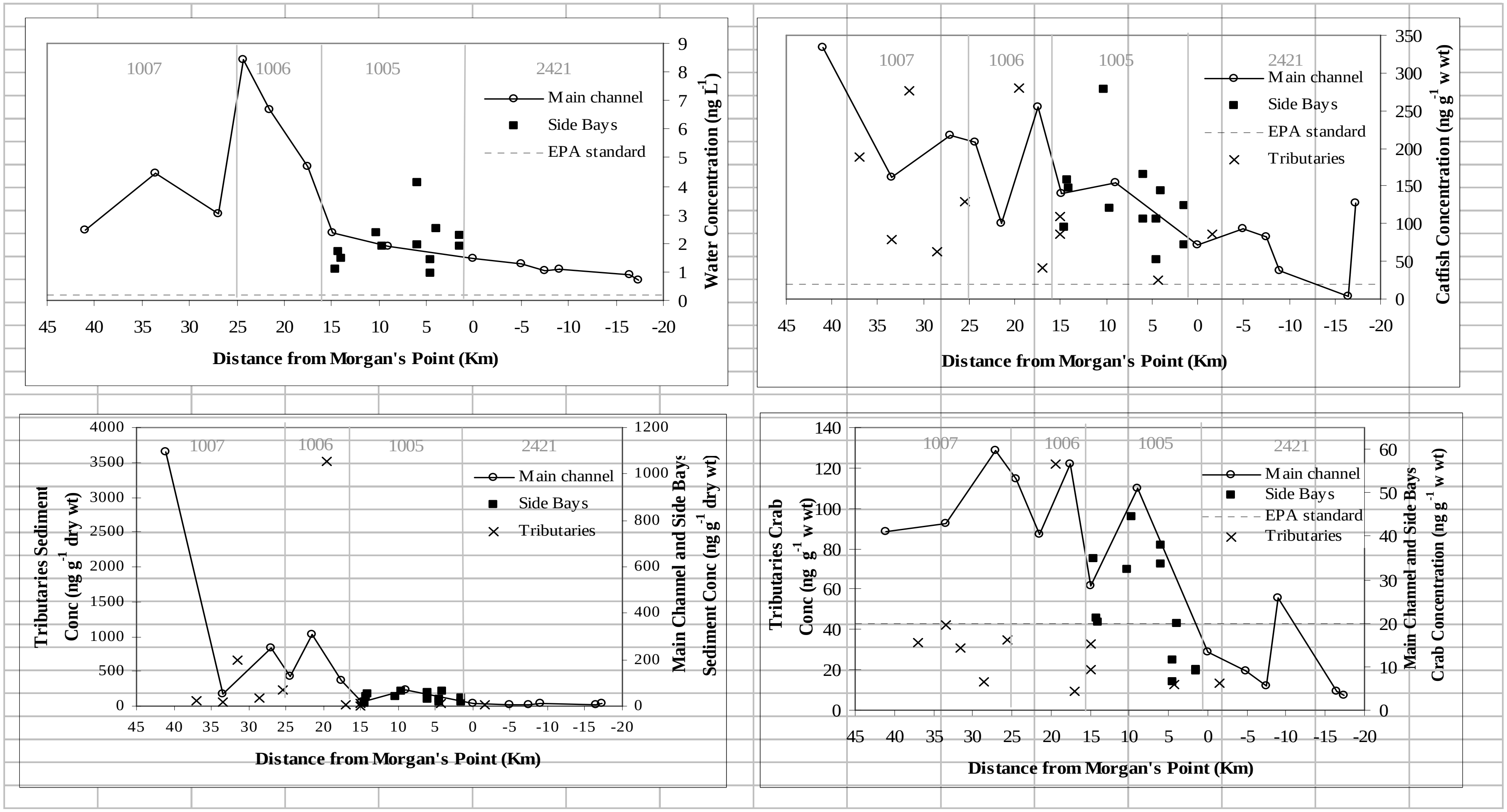


Figure 2.4 Total PCB concentration spatial distribution in water, sediment, catfish, and crab tissue in the HSC main channel, side bays, and tributaries

2.7.2 Sediment Total Organic Carbon

In analyzing the importance of a dry weight versus organic carbon weight basis, it is valuable to consider how total organic carbon (TOC) spatially varied through the HSC. Figure 2.5 presents this spatial analysis.

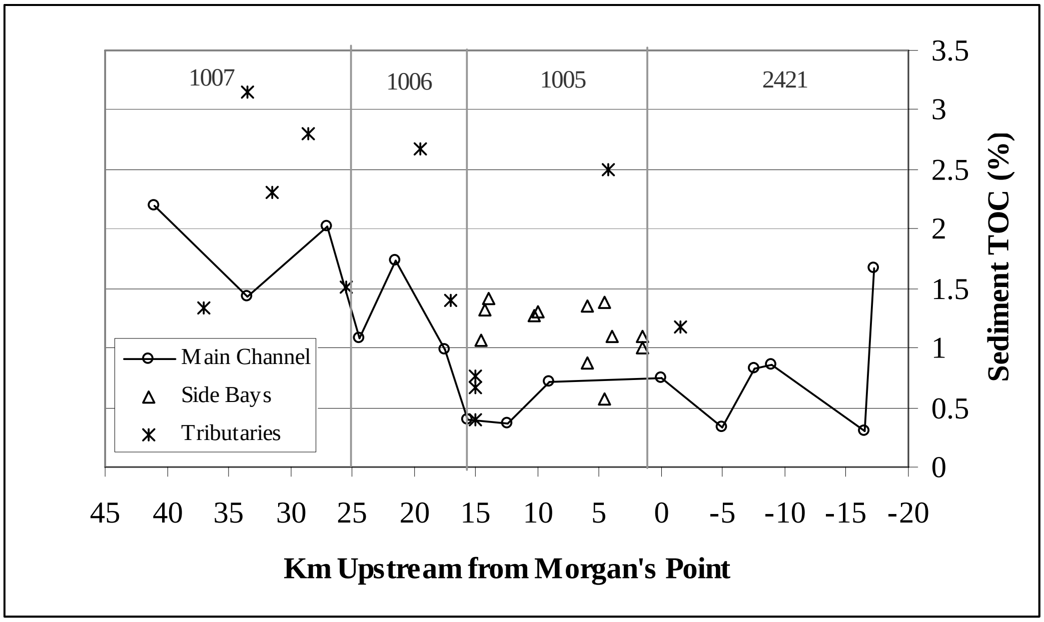


Figure 2.5 Spatial variation in time averaged total organic carbon profile in the HSC

This profile shows that in general, TOC was higher in sediments in 1007 and 1006 as compared with 1005 and 2421. TOC of sediment can be considered to be a load that results from nearby runoff just as PCB would be. Ouyang et al. (2006) found in a Florida watershed that TOC was not correlated with PCB concentrations in sediment as is commonly reported. The reason given was that most of the river TOC came from a different watershed than the PCB loading. Thus, if the two loading locations do not match, then the two may not be correlated. In the HSC system, the spatial trend of TOC and PCB seem to indicate similar sourcing (whether that sourcing be primary or secondary in the case of PCB is not yet certain), and the correlation between TOC and PCB is positive though a little weak ($p<0.05$, $r^2=0.13$,3 outliers).

Another interesting result in this profile is that the side bays have similar OC content as what is found in 1006. This means that bottom sediments in the side bays are more similar to 1006 than they are to 1005, at least in this one sediment characteristic. (The similarity could also just be related to similar TOC sourcing amounts in 1005 side bays and 1007-1006 main channel segments.) Higher TOC side bay sediments have more PCB-carrying capacity than the sediments in the 1005 main channel. The PCB spatial profiles in Figure 2.4 in fact show that by dry weight 1005 main channel and side bay sediment actually have similar PCB concentrations. This could be an indication of greater PCB sourcing to the main channel 1005 as compared to the side bays since the side bays have greater PCB-carrying capacity by virtue of their TOC content.

2.7.3 Homolog Groups

Figure 2.6 shows the in channel spatial congener trend of all samples averaged in time moving from segment to segment. The crab and fish profiles vary in similar ways showing a leaning towards heavier congeners in segment 1007 with almost no variation in the downstream segments immediately following 1007. The sediment spatial profile indicates that the PCB heavy Segment 1007 and 1006 have profiles which are quite similar to one another and are more dissimilar from the homolog profiles in Segments 1005 and 2421. When this analysis is performed on an OC instead of dry weight basis (Figure 2.7), it is shown that 1007, 1006, and 2421 are similar to one another with 1005 looking more different. Lastly, the relative abundance of the deca-chlorinated congener (PCB-209) has a large increase in Segment 1005 in both water and sediment that is diminished by Segment 2421, but it is still higher than in 1007 and 1006. The sediment PCB-209 peak occurs in 1006 under OC basis rather than in 1005. This result seems like a more accurate depiction of conditions because the total PCB-209 profile (Figure 2.12) spikes tremendously in 1006 as compared to all of the other segments. Tissue does not exhibit the PCB-209 increase in 1005, which may be a result of less efficient transfer of super-hydrophobic PCBs in the food web (Kannan et al., 1998).

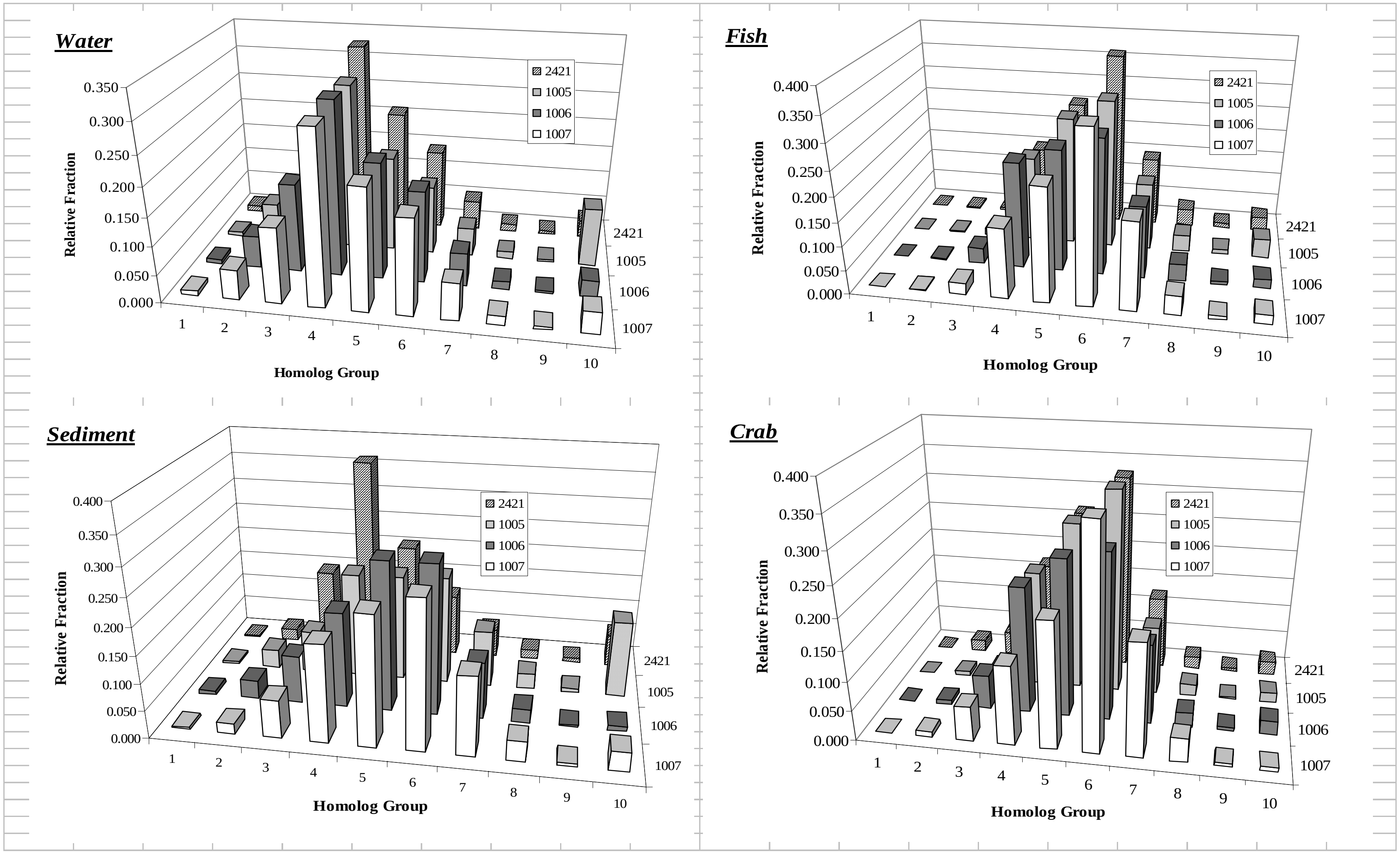
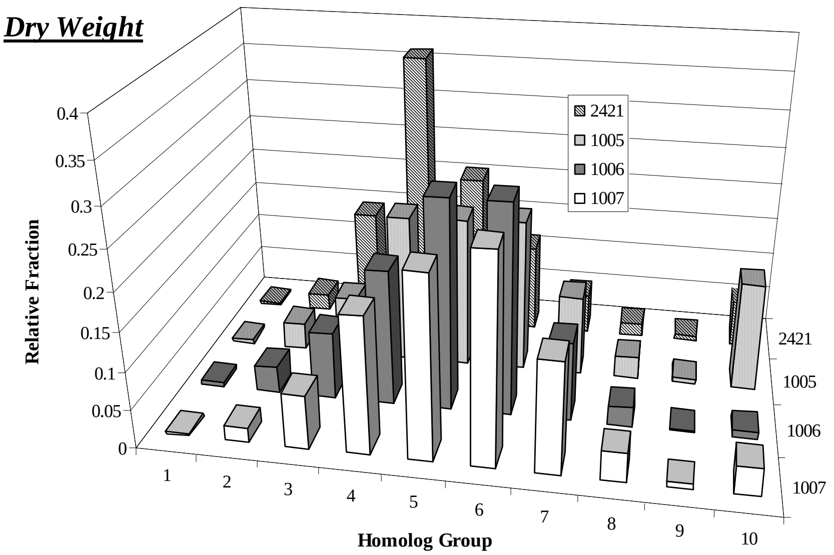


Figure 2.6 PCB main channel homolog profiles by segment

Dry Weight



Organic Carbon

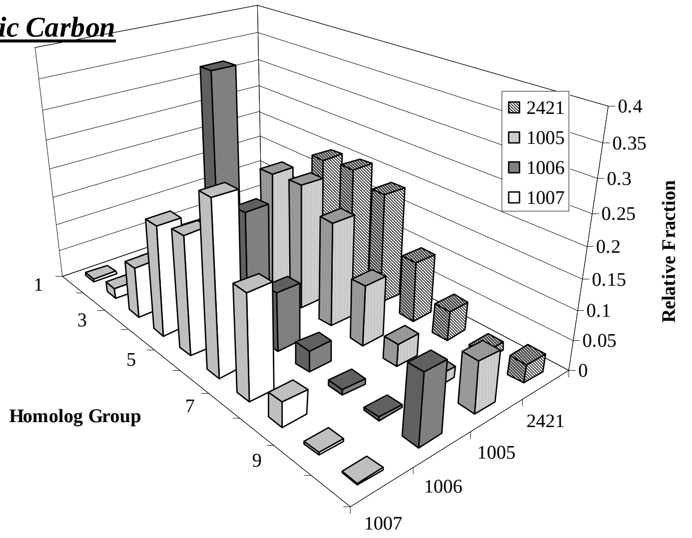


Figure 2.7. Main channel homolog profile sediment concentration comparisons between dry weight and organic carbon weight basis along the channel flow path. (Top figure is the same as the sediment profile shown in Figure 2.6)

Segments 1006 and 1007 were analyzed further because of the distinction in the sediment homolog fingerprints as compared to the other two segments. Figure 2.8 shows homolog profile comparisons between main channel and tributary sediments in 1006 and 1007.

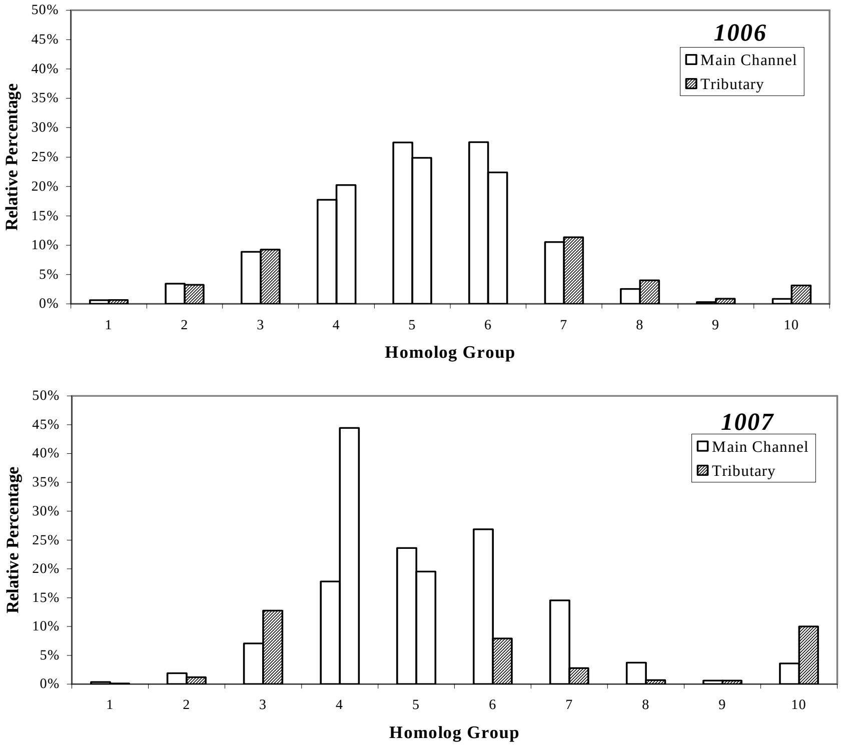


Figure 2.8 Main channel-tributary sediment profile comparisons in the high concentration segments

While it cannot be denied that high concentrations exist in 1007, 1006 shows a much closer sediment fingerprint between the tributaries and the channel. Further focus on Segment 1006 (Figure 2.9) from the various bayous that adjoin the channel there show that all three bayous show similar profiles to the overall in-channel 1006 profile.

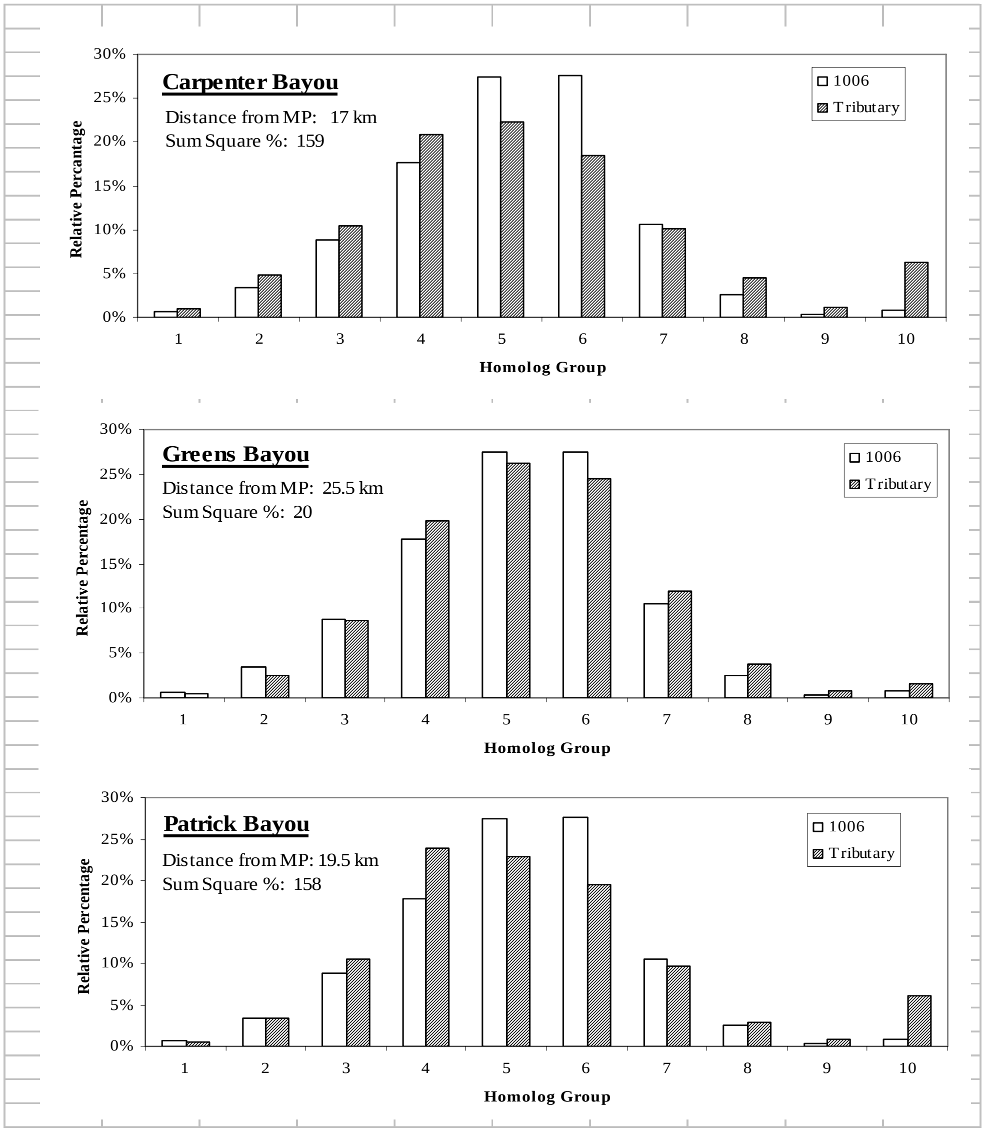


Figure 2.9 Comparative sediment congener profiles between the main channel and the tributaries in Segment 1006

The summed squared difference of the relative percentages for homologs between a tributary and the main channel was calculated as 159, 158, and 20 $\%^2$ (squared percents) for Carpenter, Patrick, and Greens Bayous respectively. This operation is analogous to a sum of squared error (SSE) in a regression analysis except in this instance a lower value does not indicate a better regression equation; it indicates a closer congener fingerprint match. Therefore, Greens Bayou, which is the farthest upstream tributary within 1006 (25.5 km from Morgan’s Point), appears to most closely resemble the fingerprint of the sediment within the channel. The water spatial profile shows that the maximum water total PCB concentration occurs just after this point though the sediment profile actually declines before peaking again just following Greens Bayou. So Greens Bayou sediment could be a sediment transport source to the main channel of segment 1006, but it is possible that other sources may exist from other sediment or from other media entirely as well. When this same tributary analysis is done for an OC basis, the greatest similarity in tributary to sediment profiles is in Patrick Bayou and not Greens. Thus, it seems that more samples per tributary would provide a more certain fingerprint by which to compare and confirm a sediment link between the tributaries and the main channel. Also, a standard weight basis should be chosen in order to facilitate analysis.

The presence of PCB-209 in Segment 1005 as noted previously is an important observation since Segment 1005 is the only segment that contains side bays. Figure 2.10 displays a comparison between side bay and main channel profiles for sediment and for water that indicates fairly similar profiles for most of the homolog groups, but both media show a greater relative fraction of PCB-209 in the main channel segment over what is found in the side bays. The comparison of the sediment and the suspended particles shown in Figure 2.11 profile in the main channel showed that PCB-209 dominated in the sediment phase over the suspended particles phase except in the case of Segment 1006. One would suppose that the higher concentration of PCB-209 media is sourcing to the lower concentration media. In this case, the sediment would be sourcing the suspended phase except in the case of 1006. If 1006 suspended particles are sourcing sediment in 1006, then this could relate to sediment transport links from 1006 tributaries (because many suspended particles are simply resuspended sediments from further upstream) as previously discussed and shown in Figure 2.8. The large sum squared percent value in Segment 1006 would support this idea in saying that the suspended sediments in 1006 are fairly dissimilar from bottom sediments. Though this logic seems plausible, it need be stressed that information is still not complete enough to certify this hypothesis at this time.

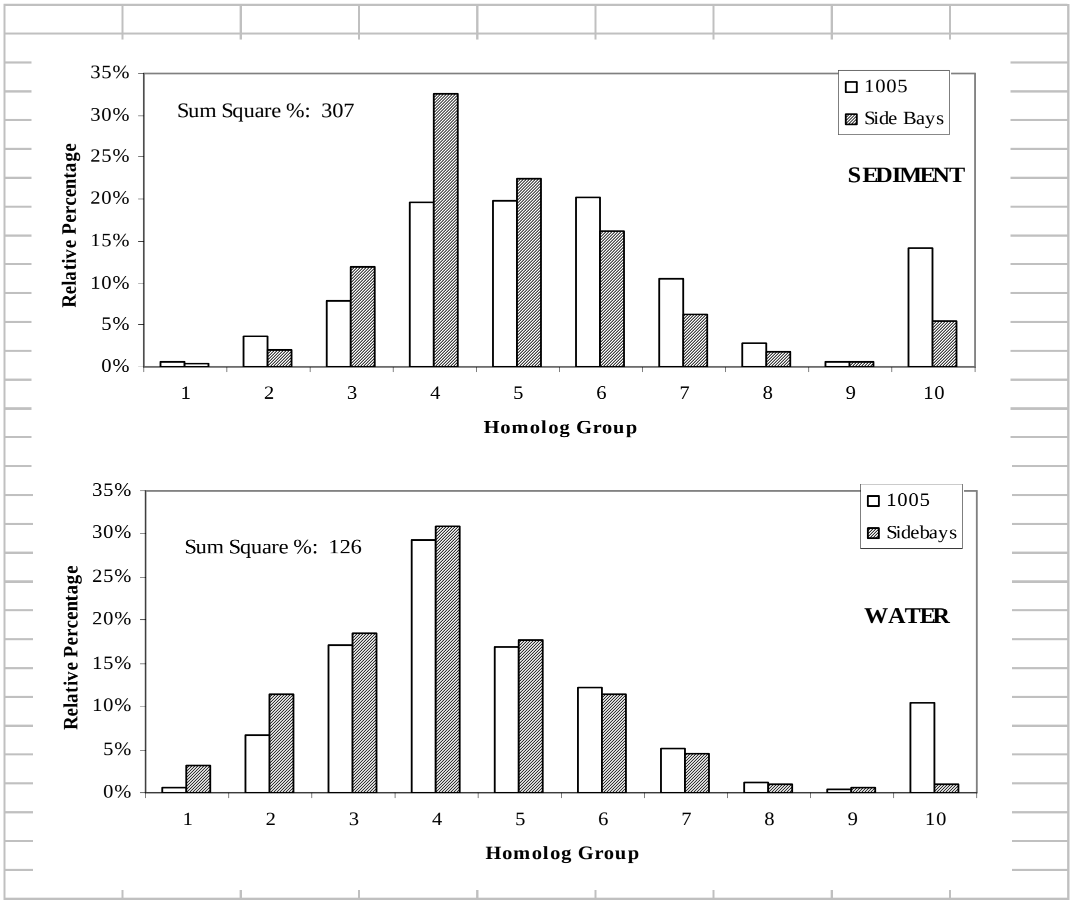


Figure 2.10 Main channel-side bay congener profile comparisons in water and sediment

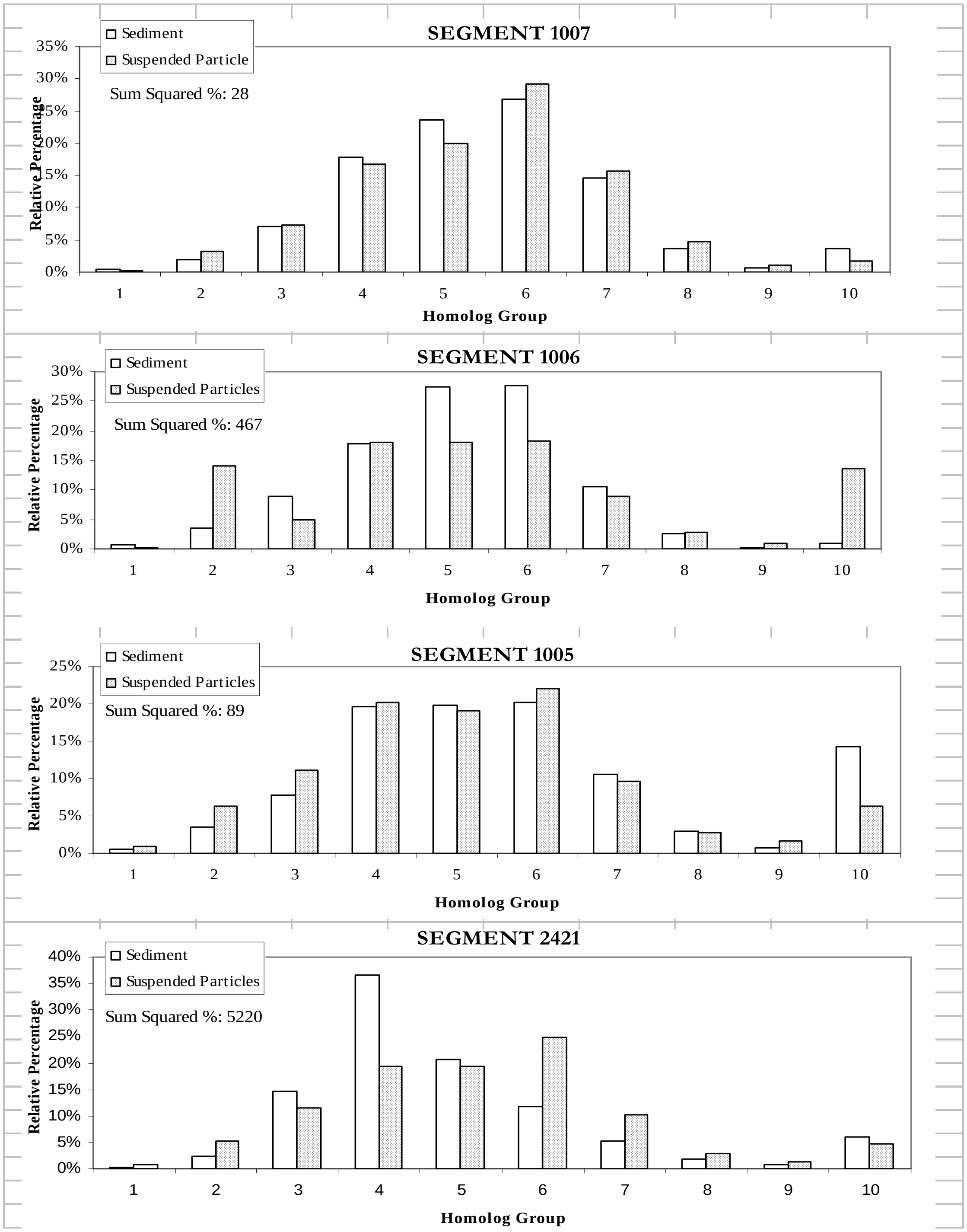


Figure 2.11 Sediment-suspended particle congener profile comparisons by main channel segment

It is important to remember that though Segment 1005 exhibits the highest relative fraction of PCB-209, Segment 1006 still contains the highest concentration of that individual congener by an order of magnitude in both water and sediment media as shown in Figure 2.12. Segment 1007 has PCB-209 concentrations that are on the same relatively low order of magnitude as PCB-209 in the downstream segments from 1006. The only difference in this profile under OC sediment weight basis is in the sediment profile at the 9 km sample point. Here in 1005 the PCB-209 has a small concentration increase before returning to what is seen. As shown previously in Figure 2.5, the TOC content is lower in 1005. So when moving from a dry weight basis to an OC basis, the apparent concentration of PCB-209 in 1005 would appear to increase. The baseline conclusion on this spatial profile is that the PCB-209 is far more prevalent in 1006 than anywhere else, which makes it more likely in terms of source considerations. Downstream fluctuations that occur under different weight bases relate more to the particulars of transport and the ability of sediment to retain PCB-209. These fluctuations may not be as important to understanding the role of PCB-209 in the HSC.

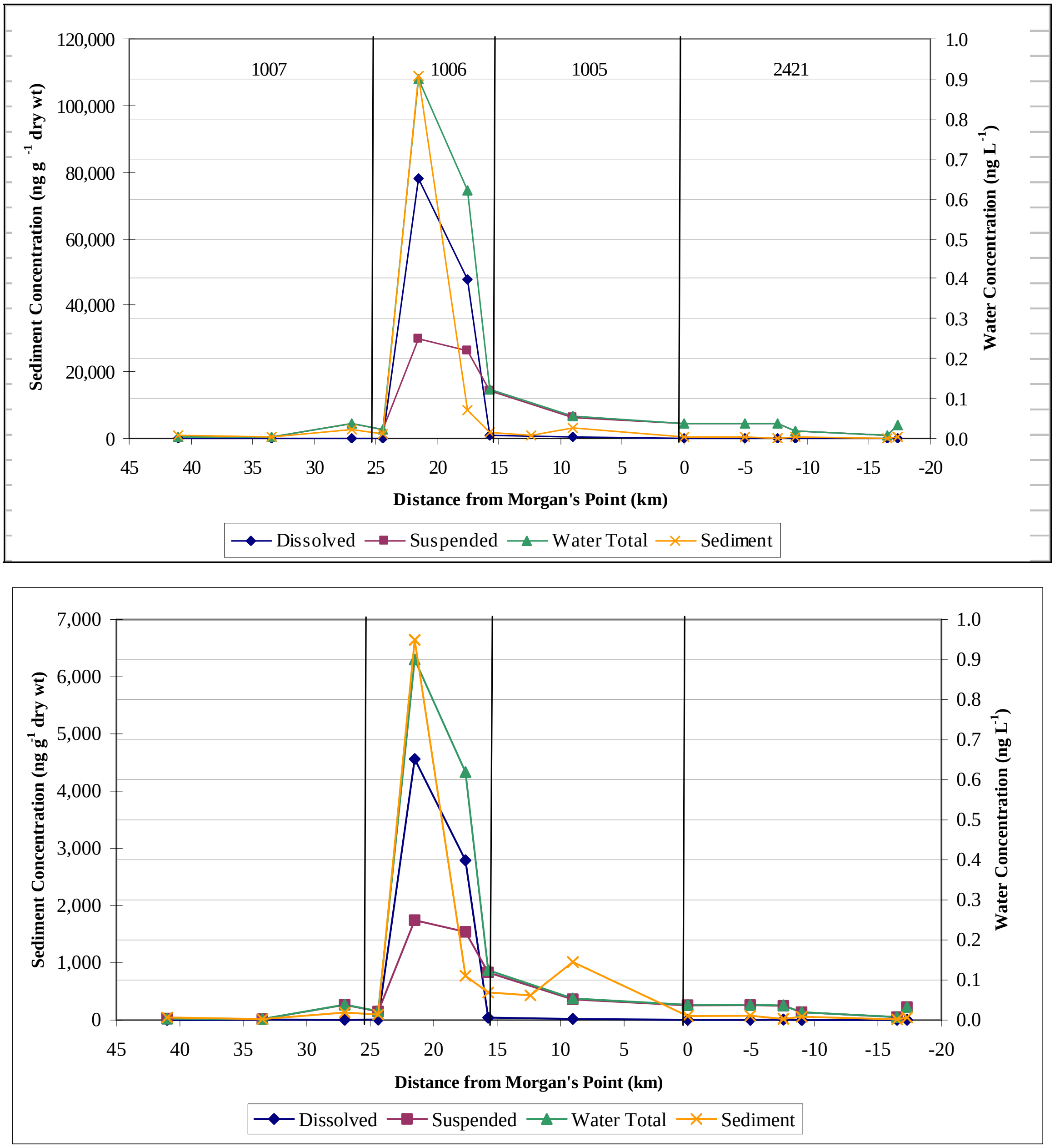


Figure 2.12 PCB-209 main channel spatial profiles by media type. Top figure is sediment under a dry weight basis while the bottom figure is sediment under an OC basis.

It is unusual to find PCB-209 in the environment, and many research studies do not give much consideration to PCB-209 presumably because it was not present in the most common Aroclor mixtures (Aroclors 1016, 1242, 1248, 1254, and 1260) that were industrially produced in the US. (Frame et al., 1996) Figure 2.13 presents these congener profiles as well as profiles from this study for comparison. In general, one can see how Aroclors are far more specific in their range of homologs that anything that is seen in the HSC. Distributions are much wider in the environment, which may point to multiple Aroclor sources as well as weathering effects. In reference to PCB-209, it is shown that out of the Aroclors, only 1268 contains PCB-209 to any measurable level. Yet PCB-209 has been reported in prior studies in the environment. Kannan et al. (1997) examined a site in coastal Georgia which was known to contain Aroclor 1268, the heavier technical mixture that contains PCB-209. Rowe et al. (2007) discovered PCB-209 in "unusually high concentrations in the suspended solids" in the Delaware river accompanied by significant concentrations of octa- and nona-chlorinated congeners and attributed the PCB-209 to a nearby titanium dioxide purification plant, and Ishikawa et al. (2007) demonstrated that PCB-209 can be generated in thermal waste treaters, especially those that are treating Automobile Shredder Residue (ASR). Park et al. (2001) found that PCB-209 was a "dominant" homolog which was deposited into Galveston Bay by way of wet and dry particulates.

In light of Park et al. (2001), it seems possible that air deposition might be sourcing PCB-209 to the channel. Yet the other studies by Kannan et al. and Rowe et al. demonstrate that it is possibly sourced as older Aroclors or even as coproducts in wastewater streams. The determination of the exact source requires more future sampling.

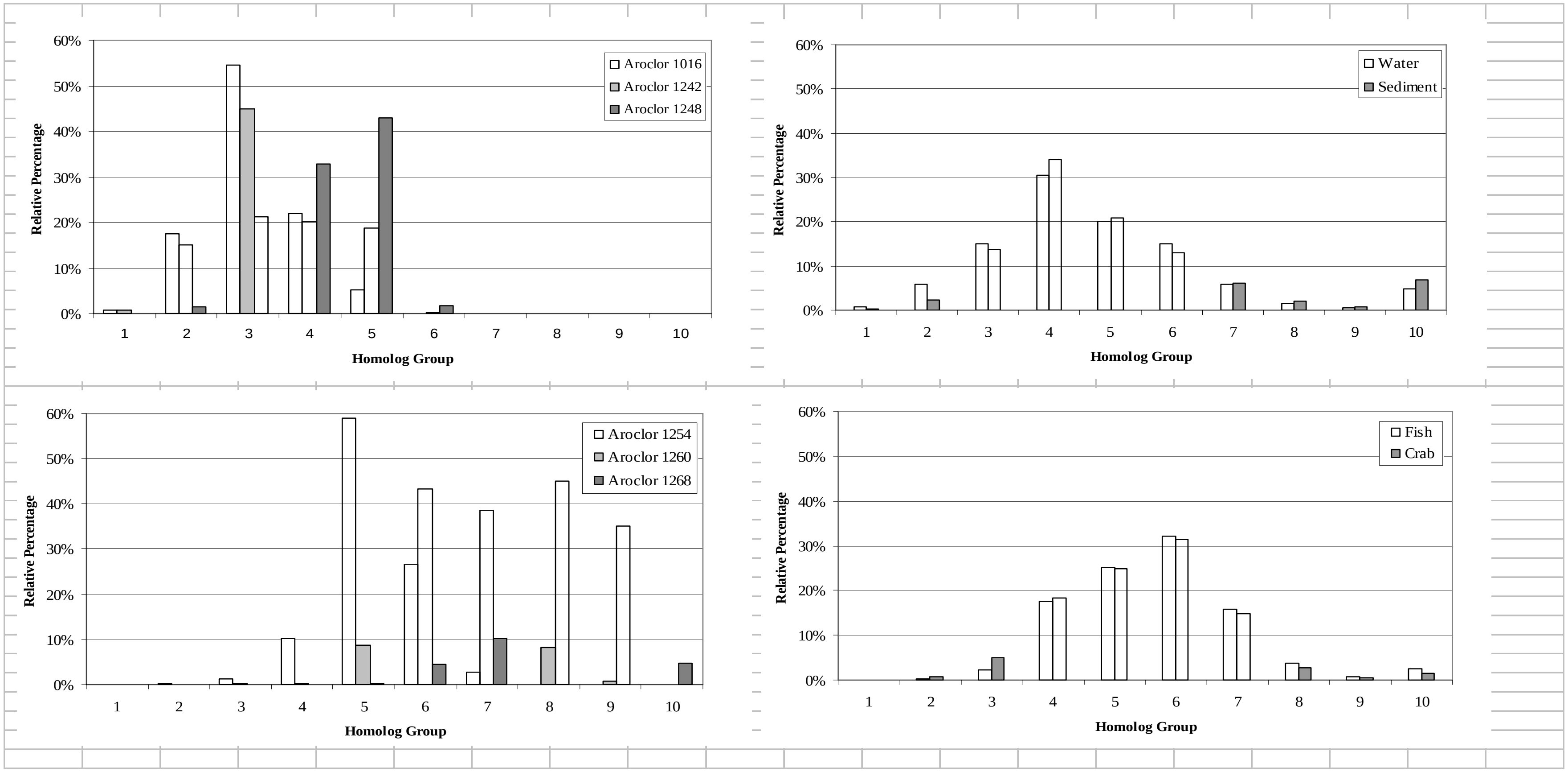


Figure 2.13 Aroclor profile comparison with main channel average congener profiles in different media. All Aroclor profiles are taken from Frame et al. (1996) except for Aroclor 1268, which was taken from Kannan et al. (1997).

2.9 PCB QUANTIFICATION METHODS

PCB quantification methods began with the use of Aroclor surrogates because it was understood that Aroclors were the original sources of PCBs at the time, and it was much simpler to correlate gas chromatographs with technical mixtures than individual congeners. This method has been suspect because it cannot account for Aroclor mixing, weathering in the environment, or PCBs that may not be originally Aroclors (e.g. incinerator emissions). A closer approximation to a complete congener profile is to use representative congener methods many examples of which are shown in Table 2.1. The large PCB sampling dataset of 2002-2003 was subjected to all of these analyses in an effort to determine levels of accuracy and usefulness between them.

2.8.1 Aroclor Method Evaluation

Aroclor analysis was conducted concurrently with full congener analysis in the summer and fall of 2002. Results indicated that the majority of the samples collected in the three media (> 90%) were non-detect. Aroclors were below the detection limit in all the water samples (n = 36), and Aroclor-1254 was the only species detected in one of the in-channel sediment samples collected (n = 44). For the water samples, it was clear that while the PCB-congener samples exhibited concentrations above the USEPA water standard of 0.17 ng L^{-1}, all of the Aroclors in all of the samples collected were found below the detection limit. This essentially indicated no relationship or correspondence between Aroclor data and total PCB in water and sediment, a finding that has been reported by Frignani et al. (2001).

Additionally, the USEPA assessment comparison value of 20 ng g^{-1} for catfish (n = 34) and crab (n = 40) was exceeded in 44 and 5% of the Aroclor collected samples, respectively as opposed to the 95 and 43% exceedances obtained using the total PCB data, also indicating that Aroclor data in tissue are not adequate to assess PCB contamination. It is noted that Aroclor-1254 and Aroclor-1260 were the most common mixtures detected in tissue samples in this study, and that may relate to the heavier overall weight of the samples from PCB-209.

Another factor that the Aroclor analysis loses is the ability to evaluate the health risk associated with the samples. The full congener profile analysis quantifies the 14 PCB congeners which are "PCDD-like" in the HSC, whereas the Aroclor analysis cannot provide this needed information. Thus, it was concluded that Aroclor analysis does not provide accurate total PCB concentrations or relevant health risk information and as such is not a suitable method of PCB characterization in the HSC.

2.8.2 Homolog Method Evaluation

The NOAA EPA and NOAA NST representative congener methods (Table 2.1) were compared with the complete 209 congener addition. The main differences between the two lists are that the NOAA NST list provides at least one representative congener from every homolog group while the NOAA EPA list includes coplanar PCBs 77 and 126, which are considered more toxicologically potent and "PCDD-like". The NOAA EPA method is used heavily in industry by virtue of its endorsement by the USEPA while at least two other studies conducted by Fikslin and Santoro (2003) and Lauenstein et al. (2002) used the NOAA NST list.

Figure 2.14[2] compares the accuracy of these two homolog methods against the all congeners standard in all media. As can be seen, the NOAA EPA method consistently under predicts the true total PCB concentration in all media. The NOAA NST method provided a much closer fit to the true total PCB concentration, with some under prediction in sediment and some over prediction[3] in tissue (occurs more drastically in crab as compared to fish). A comparison of the sum of squared error (SSE) shows that in water, sediment, catfish, and

---

[2] OC weight basis sediment concentrations were not considered separately for this analysis.

[3] Over prediction of the subset of congeners as compared to the total congener set because the total of congener surrogates in NOAA NST are multiplied by a standard factor two to adjust for representative deficiencies in the set. See Table 2.1.

crab, the NOAA EPA method has greater SSE over NOAA NST by factors of 3, 12, 27, and 2 respectively. Fikslin and Santoro (2003) used similar comparisons to evaluate the accuracy of the NOAA NST list against a sum of 81 congeners standard. They find significant inaccuracies in sediment and biota.

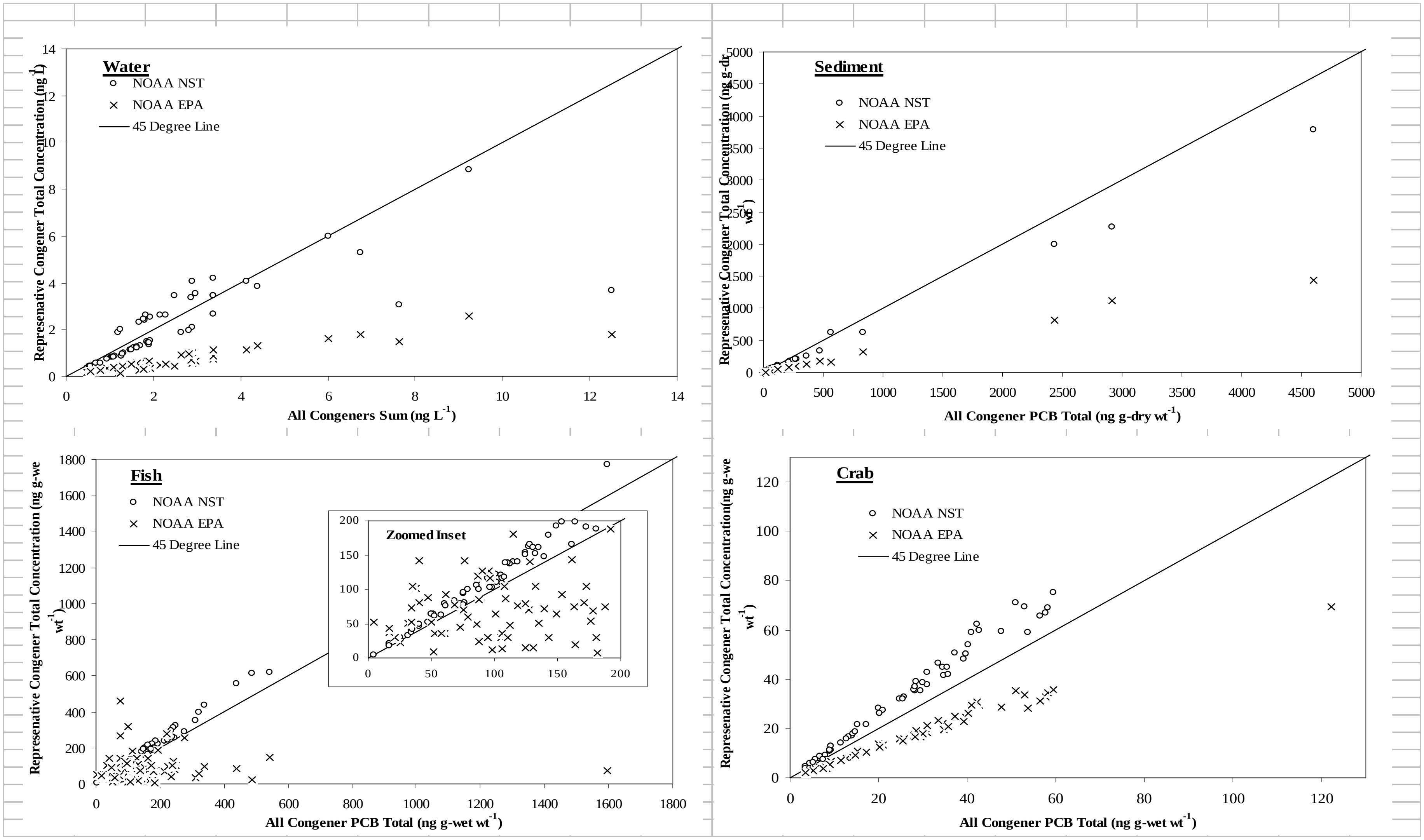


Figure 2.14 Comparison between representative congener and all congener methods in a total PCB calculation

A comparison was also made between the all congener, NOAA NST, and NOAA EPA approaches by way of the homolog profiles. These profiles generally showed agreement in the PCB signatures in all media with a few important exceptions. The mono-chlorinated group only appeared in the all congener profile for water and sediment. Moreover in the water samples, the di-chlorinated homolog group percentage was underrepresented by both the NOAA NST (3.1%) and NOAA EPA (3.5%) methods as compared with the all congener method (12.8%). The error in these lighter homologs could be important information to have if evaluating the degradation in higher chlorinated PCBs that occurs in the environment. The other exception particularly important to the HSC is the fact that the NOAA EPA method does not include the deca-chlorinated homolog group made up of PCB-209.

2.10 THOUGHTS ON SEDIMENT WEIGHT BASIS

Observations on sediment concentrations under dry weight basis versus organic carbon weight basis are

- Total PCB concentrations (sum of 209 congeners) did not exhibit much change.
- Homolog group profiling exhibited large changes that affected the overall spatial trend and tributary to channel sediment comparisons.
- The PCB-209 in-channel profiling changed slightly in favor of PCB-209 apparent concentration increases.

Many studies besides this one have used dry weight sediment determinations as can be seen from the number of sediment comparisons made in Table 2.5. In fact, every study reviewed thus far has used dry weight basis in reporting results rather than OC weight basis. While several studies have examined TOC-PCB correlations and found those correlations to be positive, they have not found it useful to look at concentrations on an OC weight basis.

Bases on the results presented here, however, it seems valuable to at least look at concentrations in terms of OC weight normalization. It may perhaps be useful to determine if the correlation between TOC and PCB is strong one before looking at concentrations on OC basis. If they are shown to be correlated, then the normalization would be by OC. If not, then the concentrations would be made on a dry weight basis.

REFERENCES

Fikslin, T.J., Santoro, E.D., 2003. PCB congener distribution in estuarine water, sediment and fish samples: Implications for monitoring programs. Environ. Monit. Assess. 87, 197-212.

Frame, G.M., Cochran, J.W., Bowadt, S.S., 1996. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. J. High Resolut. Chromatogr. 19, 657-668.

Frignani, M., Bellucci, L.G., Carraro, C., Raccanelli, S., 2001. Polychlorinated biphenyls in sediments of the Venice Lagoon. Chemosphere 43, 567-575.

Gevao, B., Hamilton-Taylor, J., Mubdoch, C., Jones, K.C., Kelly, M., Tabner, B.J., 1997. Depositional time trends and remobilization of PCBs in lake sediments. Environ. Sci. Technol. 31, 3274-3280.

Hong, S.H., Yim, U.H., Shim, W.J., Oh, J.R., 2005. Congener-specific survey for polychlorinated biphenlys in sediments of industrialized bays in Korea: Regional characteristics and pollution sources. Environ. Sci. Technol. 39, 7380.

Ishikawa, Y., Noma, Y., Yamamoto, T., Mori, Y., Sakai, S.-i., 2007. PCB decomposition and formation in thermal treatment plant equipment. Chemosphere 67, 1383-1393.

Jeremiason, J.D., Eisenreich, S.J., Baker, J.E., Eadie, B.J., 1998. PCB decline in settling particles and benthic recycling of PCBs and PAHs in Lake Superior. Environ. Sci. Technol. 32, 3249-3256.

Kannan, K., Maruya, K.A., Tanabe, S., 1997. Distribution and Characterization of Polychlorinated Biphenyl Congeners in Soil and Sediments from a Superfund Site Contaminated with Aroclor 1268. Environ. Sci. Technol. 31, 1483-1488.

Kannan, K., Nakata, H., Stafford, R., Masson, G.R., Tanabe, S., Giesy, J.P., 1998. Bioaccumulation and Toxic Potential of Extremely Hydrophobic Polychlorinated Biphenyl Congeners in Biota Collected at a Superfund Site Contaminated with Aroclor 1268. Environ. Sci. Technol. 32, 1214-1221.

Konat, J., Kowalewska, G., 2001. Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea - Trends and fate. Sci. Total Environ. 280, 1.

Lauenstein, G.G., Cantillo, A.Y., O'Connor, T.P., 2002. The status and trends of trace element and organic contaminants in oysters, Crassostrea virginica, in the waters of the Carolinas, USA. Sci. Total Environ. 285, 79-87.

MacLeod, W.D., Brown, D.W., Friedman, A.J., Burrows, D.G., Maynes, O., Pearce, R.W., Wigren, C.A., Bogar, R.G., 1985. Standard Analytical Procedures of the NOAA National Analytical Facility, 1985-1986, Extractable Toxic Organic Compounds, Second Edition. NOAA, Seattle, Washington.

Ouyang, Y., Zhang, J.E., Ou, L.T., 2006. Temporal and spatial distributions of sediment total organic carbon in an estuary river. J. Environ. Qual. 35, 93-100.

Park, J.S., Wade, T.L., Sweet, S., 2001. Atmospheric deposition of organochlorine contaminants to Galveston Bay, Texas. Atmos. Environ. 35, 3315-3324.

Rifai, H., Palachek, R., Jenden, P., 2005. Total Maximum Daily Loads for Dioxin in the Houston Ship Channel, Final Report, Work Order No. 582-0-80121-07. Texas Commission on Environmental Quality (TCEQ), Austin, p. 540.

Rowe, A.A., Totten, L.A., Xie, M., Fikslin, T.J., Eisenreich, S.J., 2007. Air-Water Exchange of Polychlorinated Biphenyls in the Delaware River. Environ. Sci. Technol. 41, 1152-1158.

Santschi, P.H., Presley, B.J., Wade, T.L., Garcia-Romero, B., Baskaran, M., 2001. Historical contamination of PAHs, PCBs, DDTs, and heavy metals in Mississippi River Delta, Galveston Bay and Tampa Bay sediment cores. Mar. Environ. Res. 52, 51-79.

Schneider, A.R., Porter, E.T., Baker, J.E., 2007. Polychlorinated Biphenyl Release from Resuspended Hudson River Sediment. pp. 1097-1103.

Sobek, A., Gustafsson, O., Hajdu, S., Larsson, U., 2004. Particle-Water Partitioning of PCBs in the Photic Zone: A 25-Month Study in the Open Baltic Sea. Environ. Sci. Technol. 38, 1375.

Totten, L.A., Brunciak, P.A., Gigliotti, C.L., Dachs, J., Glenn, T.R., Nelson, E.D., Eisenreich, S.J., 2001. Dynamic air-water exchange of polychlorinated biphenyls in the New York - New Jersey Harbor Estuary. Environ. Sci. Technol. 35, 3834-3840.

USEPA, 1999. Fact Sheet: Polychlorinated Biphenyls (PCBs) Update-Impact on Fish Advisories. USEPA, Office of Water, p. 7.

Wurl, O., Obbard, J.P., 2005. Organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in Singapore's coastal marine sediments. Chemosphere 58, 925-933.

Zeng, E.Y., Peng, J., Tsukada, D., Ku, T.L., 2002. In situ measurements of polychlorinated biphenyls in the waters of San Diego Bay, California. Environ. Sci. Technol. 36, 4975-4980.

Zeng, E.Y., Yu, C.C., Tran, K., 1999. In situ measurements of chlorinated hydrocarbons in the water column off the Palos Verdes Peninsula, California. Environ. Sci. Technol. 33, 392-398.

Appendic C

HSC PCB TMDL - SWQM Data Assessment

Assessment Purpose

This brief assessment of TCEQ SWQM data was performed to assist in selection of stations for sampling for the HSC PCB TMDL. The primary dataset for station selection is the comprehensive sampling data from the 2002 and 2003 PCB analysis performed in conjunction with HSC Dioxin TMDL sampling. The 2002-2003 data was collected under an approved TCEQ QAPP which ensures the quality of sample collection, analysis methods, and data verification. Review of the SWQM dataset was performed to verify the trends of the 2002-2003 data and to obtain wider temporal data and also wider spatial data.

Data Set

The SWQM data was downloaded from the TCEQ SWQM download website on April 9, 2006. Data from the 2002-2003 UH/Parsons sampling events was deleted from the SWQM dataset assessment, as this data was assessed separately. The following table summarizes the data obtained for the HSC area.

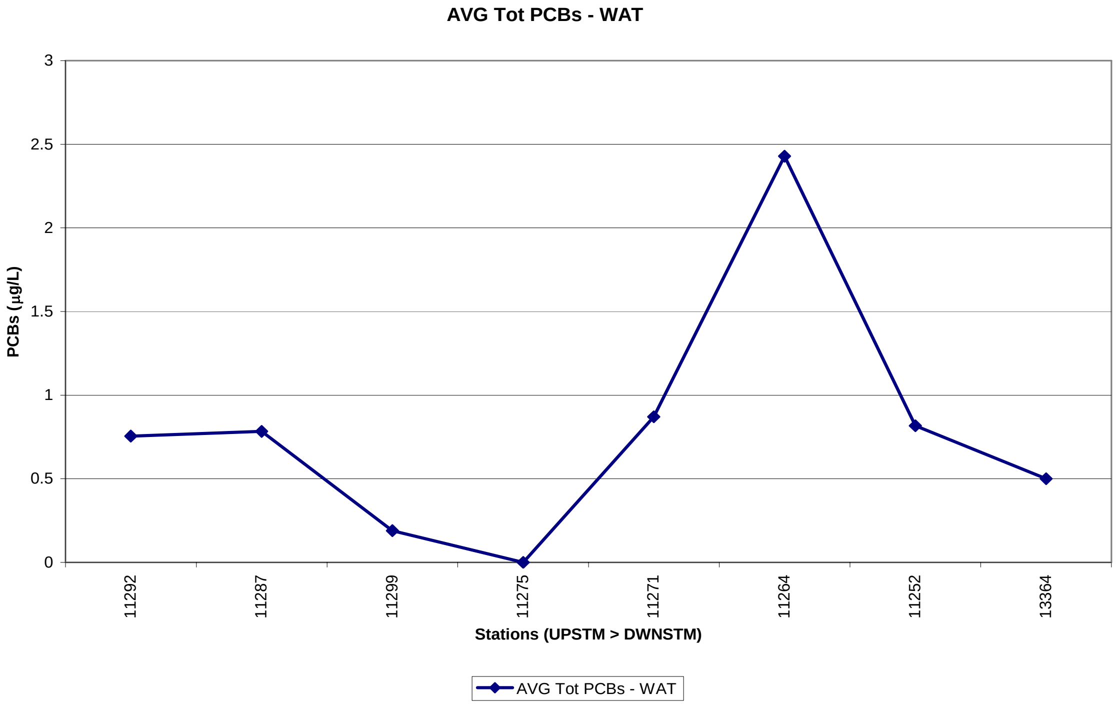
Media	Earliest Sample Date	Most Recent Sample Date	Total Records	Detects	Non-Detects
Fish	5/13/1975	8/19/2003	25	9	16
Sediment and Mud	5/7/1974	5/8/2006	417	69	348
Tissue	8/27/1992	8/19/2003	184	7	177
Water	5/7/1974	8/13/1991	72	3	69
Total			***698***	***88***	***610***

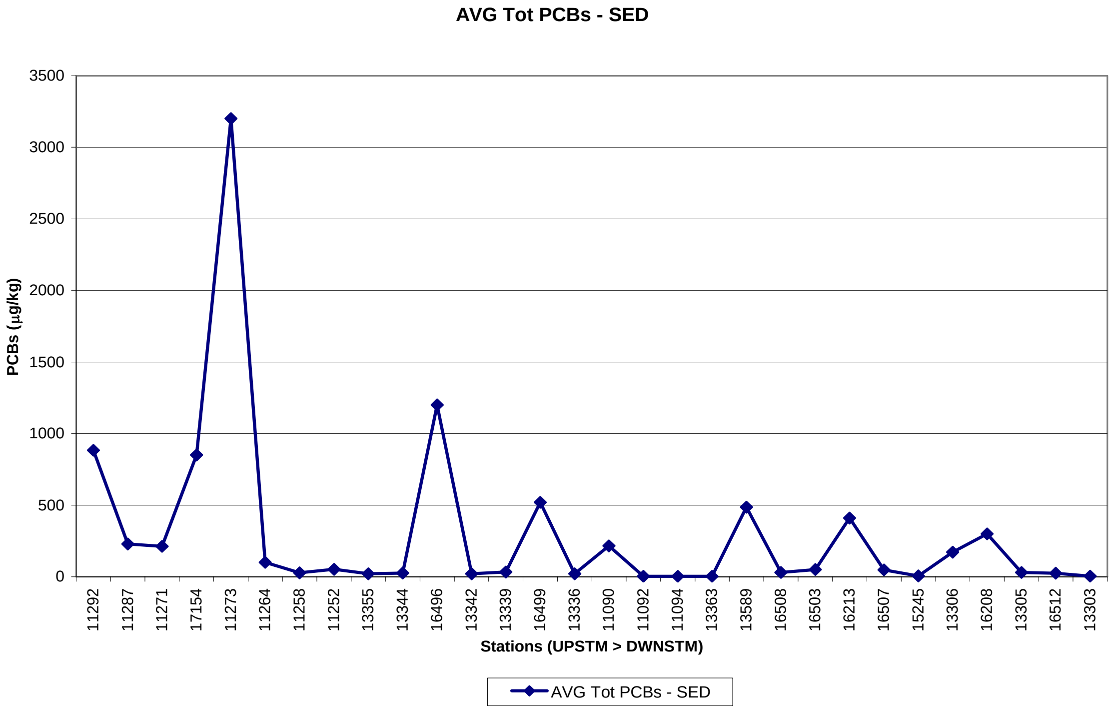
The above numbers include individual arochlors, total PCBs, and individual congeners. Uses and Possible Limitations with the SWQM dataset include the following:

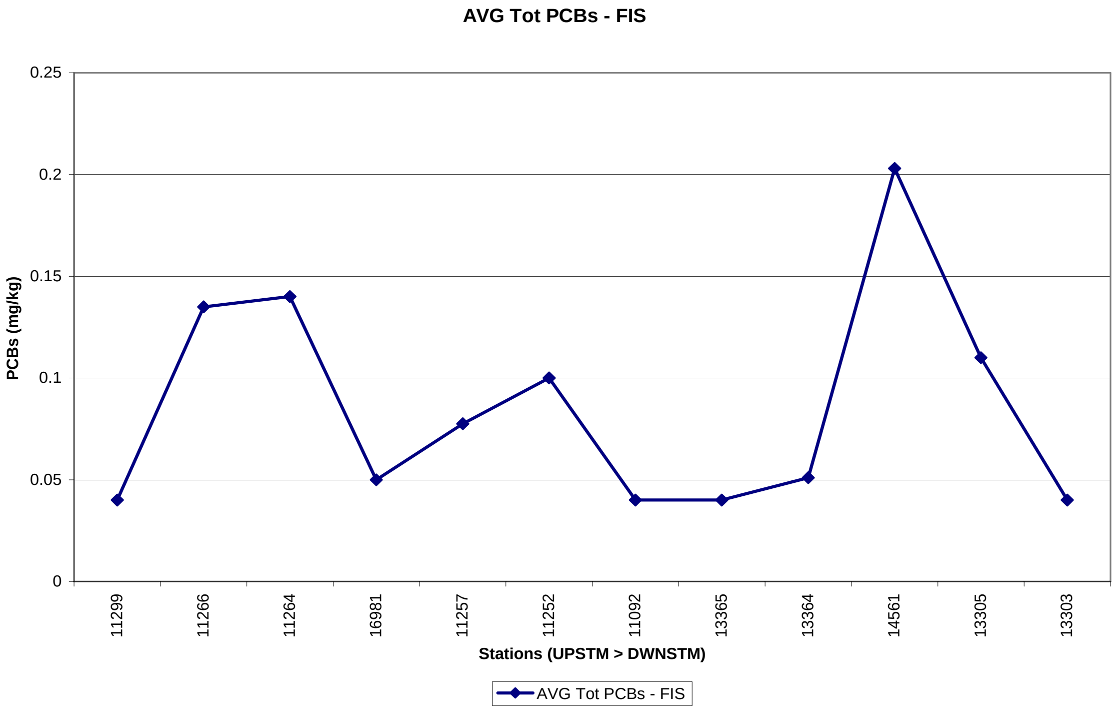
- Only total PCB results were utilized. Dropping arochlor results significantly reduces the number of records.
- Non-detects were given the value of the MDL.
- On some older data, data usability may not be fully comparable with more recent analysis method/capabilities, sampling methodology, and analysis QC.
- It should be noted that there are several stations with very few data points and some sampling stations have not been utilized in 30 years.
- There was no description of the media listed as “tissue”. This was thought to be either fish, crab, or a mix of both. As the primary data from 2002-2003 properly distinguishes between fish tissue and crab tissue results, this SWQM “tissue” data was used only as an overview.

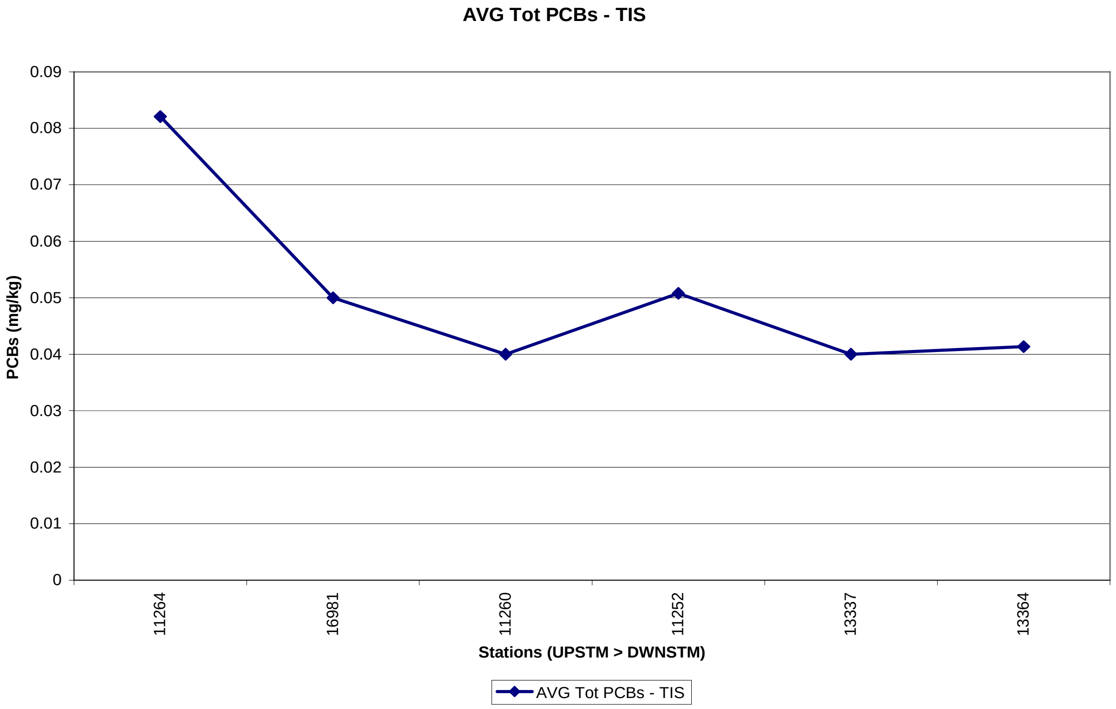
Spatial Assessment of Data

The following four charts depict the total PCB values (average of total PCB per location) spatially for the HSC area from upstream (left end of the x-axis) to downstream (right end of the x-axis). The charts are presented in sequence for the four media; water, sediment, fish tissue, and tissue.




AVG Tot PCBs - SED
PCBs (µg/kg)
3500
3000
2500
2000
1500
1000
500
0
11292
11287
11271
17154
11273
11264
11258
11252
13355
13344
16496
13342
13339
16499
13336
11090
11092
11094
13363
13589
16508
16503
16213
16507
15245
13306
16208
13305
16512
13303
Stations (UPSTM > DWNSTM)
AVG Tot PCBs - SED


AVG Tot PCBs - FIS
PCBs (mg/kg)
0.25
0.2
0.15
0.1
0.05
0
11299
11266
11264
16981
11257
11252
11092
13365
13364
14561
13305
13303
Stations (UPSTM > DWNSTM)
AVG Tot PCBs - FIS



The four charts indicate that the SWQM average total data do not show a distinct spatial trend through the HSC area (upstream to downstream). The limited and varying data reported in SWQM over the thirty year period for each of the four media proved difficult to make comparisons between media at all locations (several sediment sample locations, but few locations for water, fish, and tissue).

The charts do show frequent high PCB values at some stations. These are the same stations that the 2002-2003 HSC Dioxin/PCB data show as exhibiting high PCB values. Hence, this confirms the station selection based on the 2002-2003 results.

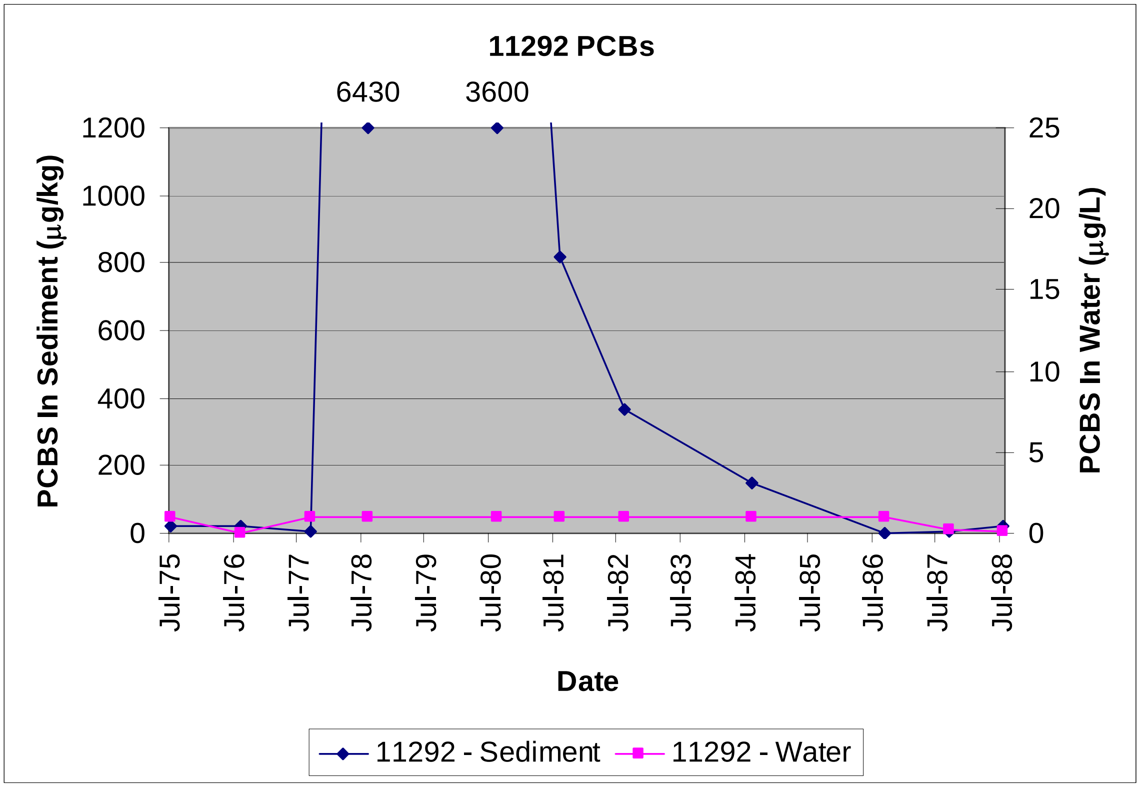
In addition to using total PCB values, results of individual arochlors with high values were assessed to verify that the SWQM data locations with total results and the locations selected from the 2002-2003 data covered the appropriate locations with high PCB results. This assessment of arochlor data and the PCB concentrations in sediment at station 11273 (second chart above) indicated high PCB values at the Patrick’s Bayou area. The Patrick’s Bayou area presents several challenges related to PCB sampling due to separate ongoing investigations and cleanup actions, around-the-clock operation of crucial petroleum industries, private ownership/land access issues, and hydrographic and infrastructure issues in and near the HSC area. This information is being addressed by the project team, including TCEQ representatives.

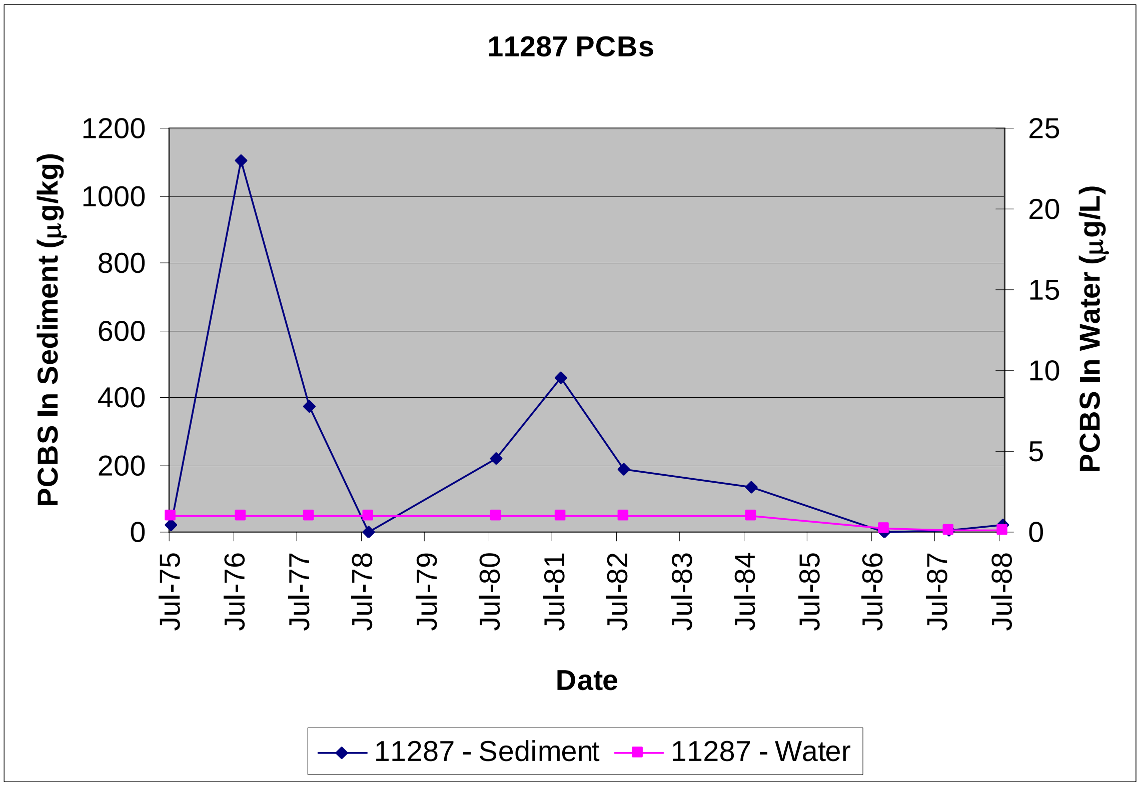
Temporal Assessment of Data

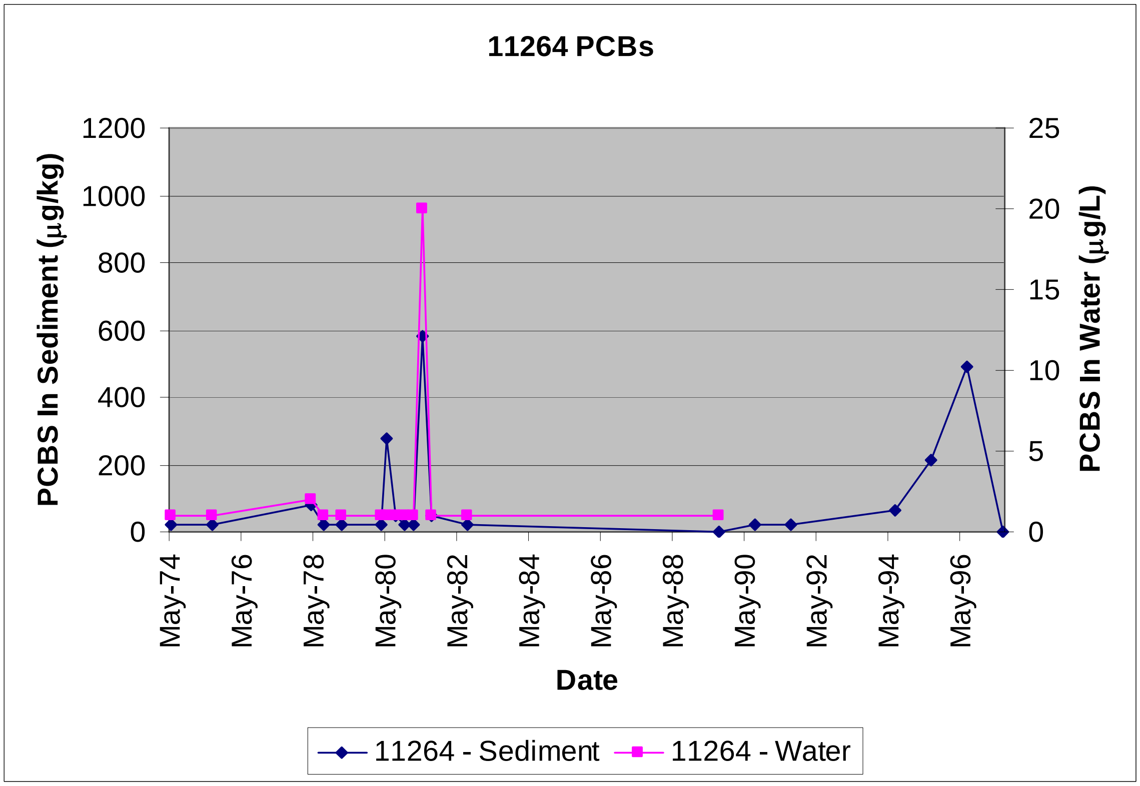
Charts are presented below showing the temporal results for total PCBs in water and sediment at the four stations which had enough data points to allow meaningful assessment.

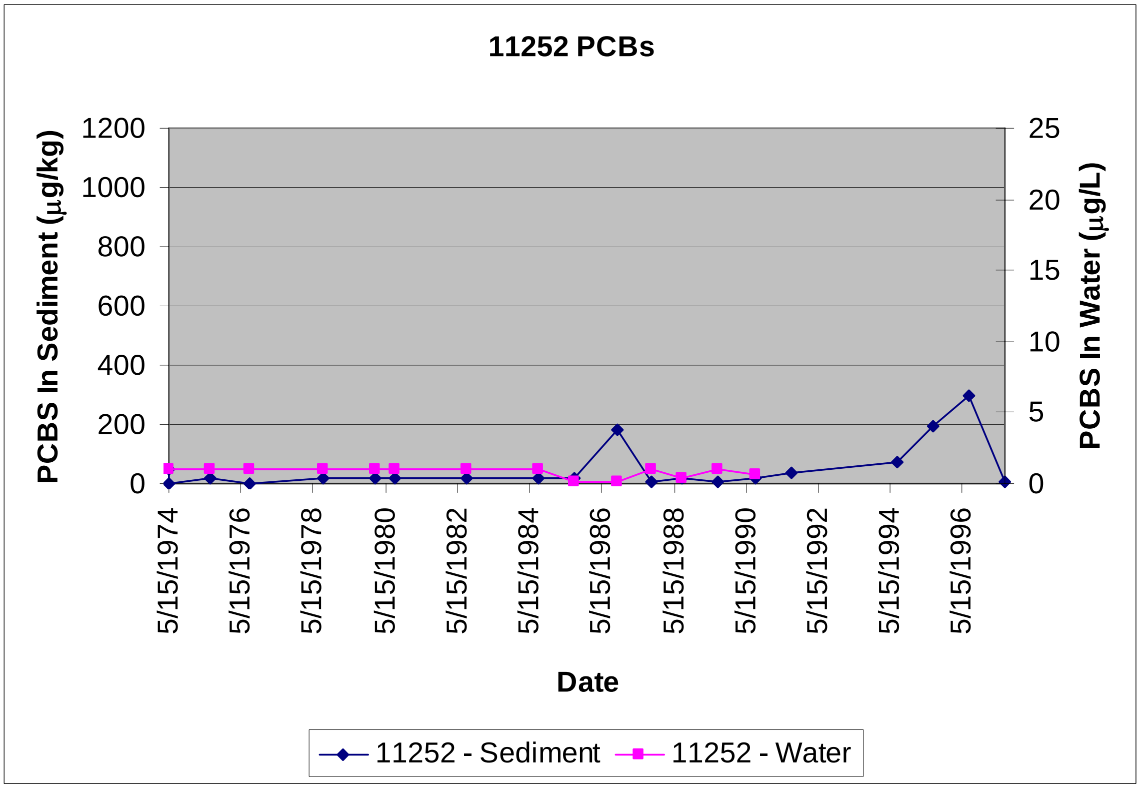
From upstream to downstream, station 11292 is the HSC at the Turning Basin, 11287 is the HSC at Simms Bayou, 11264 is the HSC at the Battleship Texas, and 11252 is the HSC at Morgan’s Point.

The water PCB results at each station indicated more stable values over time than the sediment results. An exception to this is a sample collected in 1981 at station 11264. This sample also exhibited a spike in sediment value.
In general, sediment results showed more variability at each station over time. Overall, no significant sediment result temporal trends could be determined from the limited dataset. The Turning Basin (11292) and Simms Bayou (11287) stations exhibited a few data points with higher sediment results than the two downstream locations.




11287 PCBs
PCBS In Sediment (µg/kg)
1200
1000
800
600
400
200
0
PCBS In Water (µg/L)
25
20
15
10
5
0
Jul-75
Jul-76
Jul-77
Jul-78
Jul-79
Jul-80
Jul-81
Jul-82
Jul-83
Jul-84
Jul-85
Jul-86
Jul-87
Jul-88
Date
11287 - Sediment
11287 - Water


11264 PCBs
PCBS In Sediment (µg/kg)
1200
1000
800
600
400
200
0
PCBS In Water (µg/L)
25
20
15
10
5
0
May-74
May-76
May-78
May-80
May-82
May-84
May-86
May-88
May-90
May-92
May-94
May-96
Date
11264 - Sediment
11264 - Water



Impacts of Assessment of SWQM Data on Sampling Station Selection
The results of this assessment verify that using the 2002-2003 HSC Dioxin/PCB results for sample station selection does well at representing PCB conditions in the HSC area well.

The single outlier identified in this study was that additional effort may need to be focused on the potential for sampling PCBs in the Patrick's Bayou area.

Appendix D

Bioaccumulation Calculations using summer 2002, fall 2002, and spring 2003 PCB Data

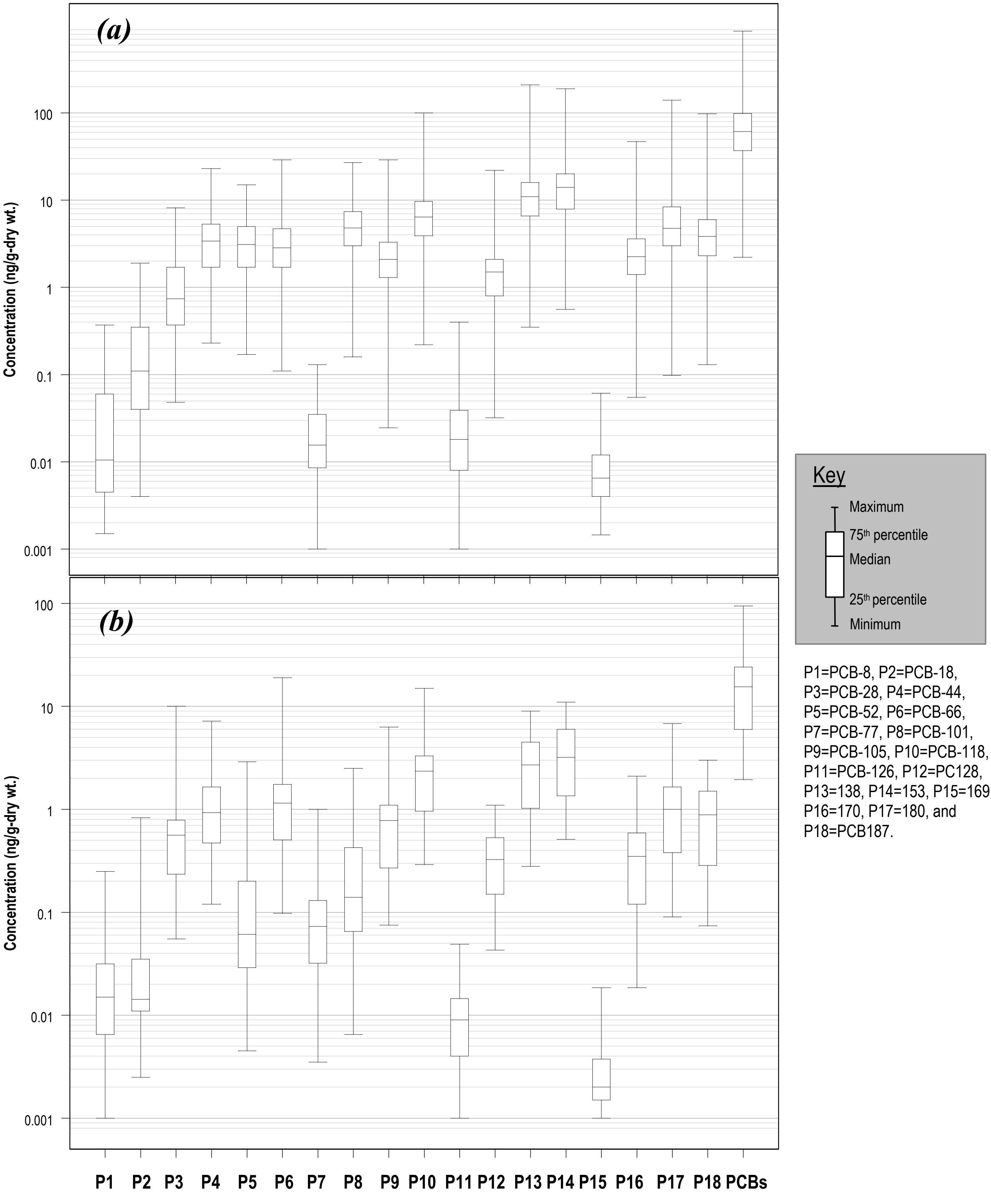
Figure 7.7 shows the concentration distribution for the 18 PCB congeners in catfish and crab samples. The concentrations for the individual PCBs ranged from 0.001 to 210 ng/g wet wt. for catfish and from 0.001 to 19 ng/g wet wt. for crabs. Most of the total PCB concentration in catfish can be attributed to PCB-138 and PCB-153 with average contributions of 20 and 21% to the total PCB sum, respectively. Similarly, the highest contributors to the total PCB concentration in crabs are also congeners PCB-138 and PCB-153, with average contributions of 18 and 23%, respectively. It is noted that congeners 138 and 153 are also the highest contributors to total PCB concentration in bottom sediments. PCB congeners 138 and 153 are not among the "dioxin-like" PCB congeners.

7.4 ANALYSIS OF PCB DATA IN THE HOUSTON SHIP CHANNEL

7.4.1 BAF/BSAF Calculations

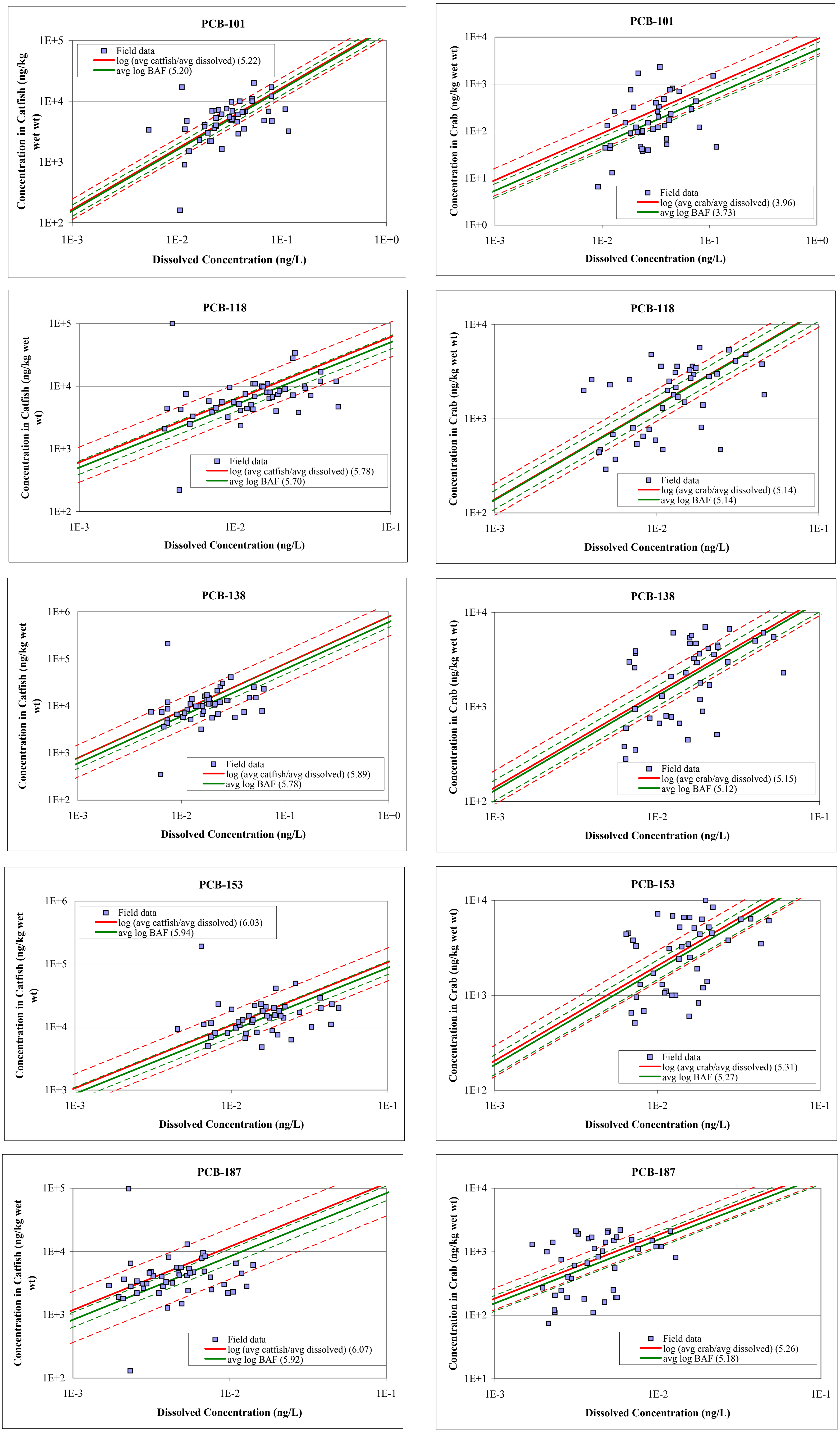
PCB data collected during WO4 were used to calculate congener-specific bioaccumulation factors (BAFs) and biota to sediment accumulation factors (BSAFs) for the entire Houston Ship Channel System. Two approaches for calculating BAFs were used. The first approach uses measures of central tendency (i.e. mean or median) of the ratios of tissue concentrations to dissolved concentrations and of the ratios of tissue concentrations to sediment concentrations. The second approach uses ratios of average concentrations for the different media (EPA, 2003).

Figure 7.8 shows dissolved and tissue dioxin data and BAF fitting lines for selected congeners using both approaches. Similarly, Figure 7.9 shows organic carbon-normalized sediment and tissue data and the BSAF fitting lines calculated using both approaches. The two approaches give similar results for BAFs, but not for BSAFs. As seen in Figure 7.9, the BSAFs



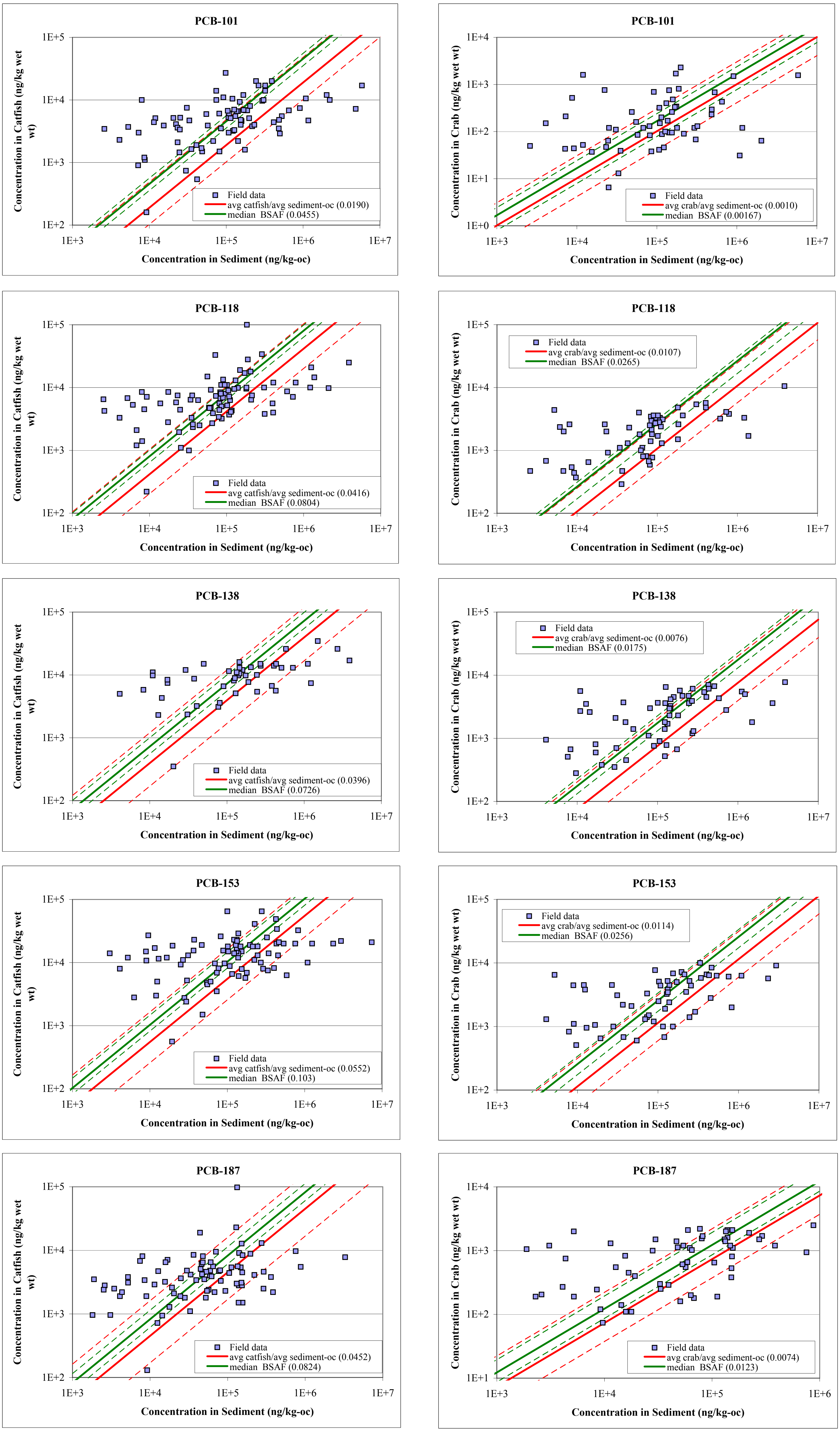
P1=PCB-8, P2=PCB-18, P3=PCB-28, P4=PCB-44, P5=PCB-52, P6=PCB-66, P7=PCB-77, P8=PCB-101, P9=PCB-105, P10=PCB-118, P11=PCB-126, P12=PC128, P13=138, P14=153, P15=169, P16=170, P17=180, and P18=PCB187.

Figure 7.7 Distribution of Individual PCB Congeners in Tissue Samples
(a) Catfish (b) Crab



Green dashed lines correspond to the 95% confidence intervals of average slope
Red dashed lines correspond to ratios of confidence interval limits for average tissue and dissolved

Figure 7.8 Line Fit Plots of BAF for Selected PCB Congeners in Tissue from the HSC



Green dashed lines correspond to the 95% confidence intervals of median slope
Red dashed lines correspond to ratios of confidence interval limits for average tissue and sediment-oc

Figure 7.9 Line Fit Plots of BSAF for Selected PCB Congeners in Tissue from the HSC

do not seem to fit the observed data very well, thus, a sediment-based water quality target was not calculated for PCBs.

Using the TDH screening value for PCBs (47 ng/g), a target concentration in water may be established using the following relationship:

$$WQ_{target,water} = TRC / BAF \qquad (7.1)$$

Each of the congeners contributing to the total PCB concentrations has different physical and chemical properties and different bioaccumulation potentials. Using the estimated bioaccumulation factors, the PCB concentration in tissue (PCB_b) can be calculated using:

$$PCB_b = \Sigma (C_{diss})_i * BAF_i \qquad (7.2)$$

Since the water quality criterion sets limits for the total equivalence of the mixture rather than the individual congeners and there are no guidelines to develop targets for mixtures of compounds that contribute to an exceedance of a WQ criterion, each congener was assigned a target concentration that corresponded to their associated fraction of the total PCB concentration that was observed historically (on average) in catfish and crab tissue in the system. This can be mathematically expressed as:

$$(C_{diss})_i = TRC*(PCB_b)_i/\Sigma PCB_b/BAF_i \qquad (7.3)$$

Using the BAFs estimated from both approaches, and Equations (7.2) and (7.3), the target concentrations for individual congeners were calculated (Tables 7.6a and b).

These BAF ratios were calculated from dissolved water concentrations, so this target applies to the dissolved PCB concentration in water. Based on the average log BAFs for catfish, the water quality target for total PCB dissolved in water would be 0.335 ng/L. Based on the log of the ratio of the average catfish concentration to the average dissolved concentration, the water

Table 7.6a Summary of Average log BAFs, log BAFs from Average Concentrations, and the Resulting Water Quality Targets for PCBs in Catfish from the HSC

Congener	avg log BAF	log BAF[1]	Average contribution to ΣPCB[2]	Water Quality Target - Diss (ng/L)[3]		Dissolved-Suspended Isotherm[4]		Water Quality Target - Susp (ng/L)[5]		Water Quality Target - Total (ng/L)	
				Value using avg log BAF	Value using log BAF[1]	K	1/n	Value using avg log BAF	Value using log BAF[1]	Value using avg log BAF	Value using log BAF[1]
PCB 8	3.006	3.165	0.1%	0.0477	0.0331	5256	0.1426	0.0885	0.0840	0.1362	0.1171
PCB 18	3.471	3.670	0.4%	0.0579	0.0366	5338	0.0934	0.1063	0.1019	0.1642	0.1385
PCB 28	4.328	4.363	1.8%	0.0406	0.0375	14546	0.2441	0.1730	0.1696	0.2137	0.2071
PCB 44	4.810	4.774	5.5%	0.0401	0.0436	43820	0.5330	0.2052	0.2144	0.2453	0.2580
PCB 52	4.634	4.629	5.2%	0.0565	0.0572	33834	0.4650	0.2312	0.2326	0.2877	0.2899
PCB 66	5.142	5.139	5.0%	0.0170	0.0171	80758	0.6480	0.1497	0.1504	0.1666	0.1675
PCB 77	4.074	4.066	0.0%	0.0015	0.0015	193085	0.8434	0.0207	0.0210	0.0222	0.0225
PCB 101	5.197	5.219	8.0%	0.0238	0.0226	249868	0.8130	0.3112	0.2984	0.3350	0.3210
PCB105	5.584	5.659	3.5%	0.0043	0.0037	384909	0.8682	0.0889	0.0766	0.0932	0.0802
PCB 118	5.702	5.786	10.7%	0.0100	0.0082	296062	0.7820	0.2093	0.1800	0.2192	0.1882
PCB 126	5.330	5.421	0.0%	0.0001	0.0001	31677	0.6364	0.0021	0.0019	0.0022	0.0019
PCB 128	5.797	5.882	2.3%	0.0017	0.0014	905371	0.9522	0.0540	0.0449	0.0557	0.0462
PCB 138	5.782	5.896	17.0%	0.0132	0.0101	846901	0.9302	0.3927	0.3075	0.4058	0.3176
PCB 153	5.941	6.030	21.1%	0.0114	0.0093	866810	0.9437	0.3296	0.2720	0.3410	0.2813
PCB 169	5.124	5.176	0.0%	0.0001	0.0000	2618	0.3961	0.0014	0.0013	0.0014	0.0014
PCB 170	5.979	6.088	4.0%	0.0020	0.0015	507217	0.7554	0.1196	0.0988	0.1216	0.1004
PCB 180	6.023	6.192	8.9%	0.0040	0.0027	968877	0.8479	0.2319	0.1665	0.2358	0.1692
PCB 187	5.921	6.075	6.5%	0.0037	0.0026	1000000	0.9428	0.1310	0.0938	0.1347	0.0963
Σ PCBs				0.3353	0.2887			2.8464	2.5155	3.1818	2.8042

[1] BAF calculated as ratio of average catfish concentration to average dissolved concentration

[2] Average contribution of each congener to total PCB in catfish

[3] WQ_{target} calculated using equation (7.3)

[4] From Figure 7.10

[5] average TSS 26

Table 7.6b Summary of Average log BAFs, log BAFs from Average Concentrations, and the Resulting Water Quality Targets for PCBs in Crabs from the HSC

Congener	avg log BAF	log BAF[1]	Average contribution to ΣPCB[2]	Water Quality Target - Diss (pg/L)[3]		Dissolved-Suspended Isotherm[4]		Water Quality Target - Susp (pg/L)[5]		Water Quality Target - Total (pg/L)	
				Value using avg log BAF	Value using log BAF[1]	K	1/n	Value using avg log BAF	Value using log BAF[1]	Value using avg log BAF	Value using log BAF[1]
PCB 8	3.211	3.074	0.3%	0.0979	0.1342	5256	0.1426	0.0981	0.1026	0.1960	0.2368
PCB 18	2.779	2.758	0.2%	0.1862	0.1953	5338	0.0934	0.1186	0.1191	0.3048	0.3144
PCB 28	4.120	4.067	4.2%	0.1505	0.1700	14546	0.2441	0.2382	0.2454	0.3887	0.4154
PCB 44	4.197	4.121	6.8%	0.2040	0.2428	43820	0.5330	0.4883	0.5358	0.6922	0.7785
PCB 52	3.034	3.330	1.1%	0.4747	0.2403	33834	0.4650	0.6221	0.4533	1.0968	0.6936
PCB 66	4.637	4.608	7.9%	0.0857	0.0917	80758	0.6480	0.4274	0.4465	0.5131	0.5383
PCB 77	4.592	4.585	0.5%	0.0063	0.0064	193085	0.8434	0.0702	0.0710	0.0765	0.0774
PCB 101	3.731	3.956	1.8%	0.1550	0.0922	249868	0.8130	1.4269	0.9354	1.5818	1.0276
PCB105	5.037	5.025	4.8%	0.0206	0.0211	384909	0.8682	0.3435	0.3514	0.3640	0.3725
PCB 118	5.138	5.145	14.7%	0.0503	0.0494	296062	0.7820	0.7432	0.7330	0.7935	0.7825
PCB 126	4.977	4.979	0.1%	0.0003	0.0003	31677	0.6364	0.0051	0.0051	0.0055	0.0054
PCB 128	5.103	5.108	2.1%	0.0079	0.0078	905371	0.9522	0.2332	0.2304	0.2411	0.2382
PCB 138	5.116	5.150	17.5%	0.0630	0.0583	846901	0.9302	1.6817	1.5658	1.7446	1.6241
PCB 153	5.267	5.310	22.9%	0.0583	0.0528	866810	0.9437	1.5413	1.4047	1.5995	1.4575
PCB 169	4.705	4.723	0.0%	0.0004	0.0004	2618	0.3961	0.0030	0.0029	0.0033	0.0033
PCB 170	5.084	5.134	2.4%	0.0092	0.0082	507217	0.7554	0.3831	0.3517	0.3923	0.3599
PCB 180	5.224	5.306	7.0%	0.0195	0.0162	968877	0.8479	0.8955	0.7641	0.9151	0.7803
PCB 187	5.188	5.263	5.6%	0.0170	0.0143	1000000	0.9428	0.5573	0.4740	0.5742	0.4883
Σ PCBs				1.6067	1.4018			9.8764	8.7922	11.4831	10.1940

[1] BAF calculated as ratio of average crab concentration to average dissolved concentration

[2] Average contribution of each congener to total PCB in crab

[3] WQ_{target} calculated using equation (7.3)

[4] From Figure 7.10

[5] average TSS 26

quality target for total PCBs dissolved in water would be 0.289 ng/L. Using dissolved-suspended partitioning relationships presented in Figure 7.10, the water quality target for total PCBs in water would be 3.182 and 2.804 ng/L for the first and second approach, respectively. These targets are higher than the Texas WQS of 0.885 ng/L for marine waters. Crab data yielded higher water quality targets with respective concentrations in whole water of 11.483 and 10.194 ng/L for the first and second approach.

Water data collected in WO4 were compared to the estimated congener-specific targets derived using both approaches to evaluate the current state of impairment of the Houston Ship Channel. Table 7.7 summarizes the percent target exceedances by congener in the entire system. Data in Table 7.7 indicate that the water quality targets calculated using site-specific BAFs are not exceeded for most congeners. The congeners with most exceedances are PCB-44 and PCB-52 with 4 out of 58 samples exceeding the WQ target. The water quality target for total PCB is not exceeded in the HSC samples.

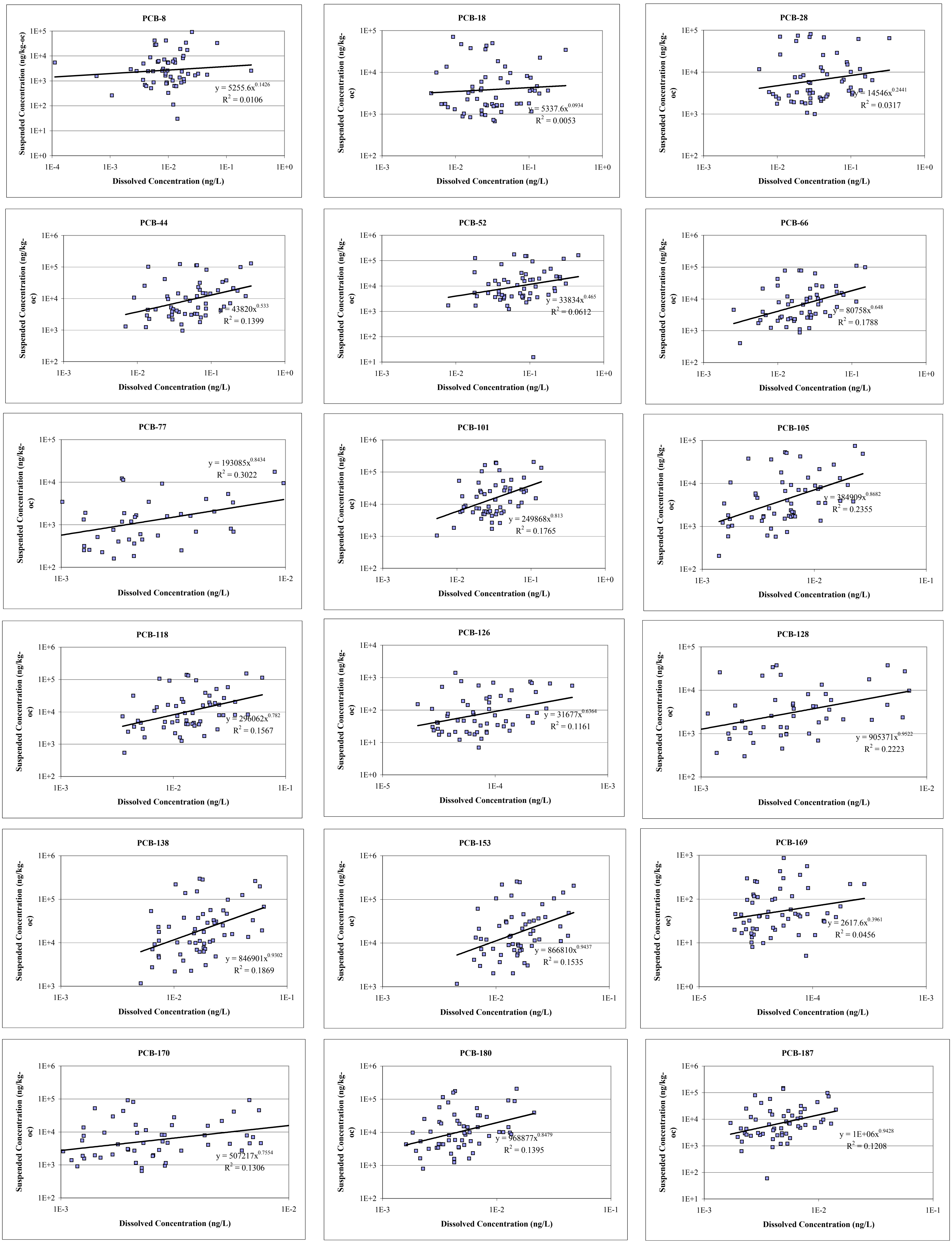


Figure 7.10 Partitioning of PCBs between Dissolved and Suspended Phases in the HSC

Table 7.7 Summary of Exceedances of the PCB Water Quality Criteria Estimated using Site-Specific BAFs

Congener	Using avg log BAF		Using log BAF[1]	
	# exceedances	%	% exceedances	%
PCB 8	1	1.7%	1	1.7%
PCB 18	2	3.4%	2	3.4%
PCB 28	2	3.4%	2	3.4%
PCB 44	4	6.9%	4	6.9%
PCB 52	4	6.9%	4	6.9%
PCB 66	1	1.7%	1	1.7%
PCB 77	0	0.0%	0	0.0%
PCB 101	0	0.0%	0	0.0%
PCB105	0	0.0%	0	0.0%
PCB 118	0	0.0%	0	0.0%
PCB 126	0	0.0%	0	0.0%
PCB 128	0	0.0%	0	0.0%
PCB 138	0	0.0%	0	0.0%
PCB 153	0	0.0%	0	0.0%
PCB 169	0	0.0%	0	0.0%
PCB 170	0	0.0%	0	0.0%
PCB 180	0	0.0%	0	0.0%
PCB 187	0	0.0%	0	0.0%
Σ PCBs	0	0.0%	0	0.0%

[1] BAF calculated as ratio of average catfish concentration to average dissolved concentration

samples=58