

**Total Maximum Daily Loads for PCBs
in the Houston Ship Channel**

**Contract No. 582-6-70860
Work Order No. 582-6-70860-13**

Quarterly Report No. 2

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CHAPTER 1 - INTRODUCTION

Polychlorinated biphenyls (PCBs) are widespread organic contaminants which are environmentally persistent and can be harmful to human health even at low concentrations. A major route of exposure for PCBs worldwide is through food consumption, and this route is especially significant in seafood. The discovery of PCBs in seafood tissue has led Texas Department of State Health Services to issue seafood consumption advisories, and some of these advisories have been issued for the Houston Ship Channel (HSC). 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.

1.1 SCOPE OF THE PROJECT

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

1.2 DESCRIPTION OF THE REPORT

This document comprises the second quarterly report of the TMDL PCB project and summarizes the results of the activities undertaken by the University of Houston for Work Order No.582-6-70860-13 during the period from December 1, 2006 to February 31, 2007.

This report reflects the progress made towards task 3.1 of the Work Order, “Compile and Assess Existing Data”. Chapter 2 presents a detailed analysis of previously sampled HSC PCB data in water, sediment, catfish, and crab that occurred in the three sampling events Summer 2002, Fall 2002, and Spring 2003. This data has already been presented in the November 2005 Dioxin TMDL final report, but greater analysis detail has been performed in order to arrive at conclusions useful in planning this project. Chapter 3 presents a preliminary analysis of sources of PCBs in the HSC based on the information that is presented in Chapter 2. Information from current scientific literature was assessed to see what might apply to the HSC PCB situation. Chapter 4 presents a summary of activities in this quarter and a preview of what is expected in the coming quarter.

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.

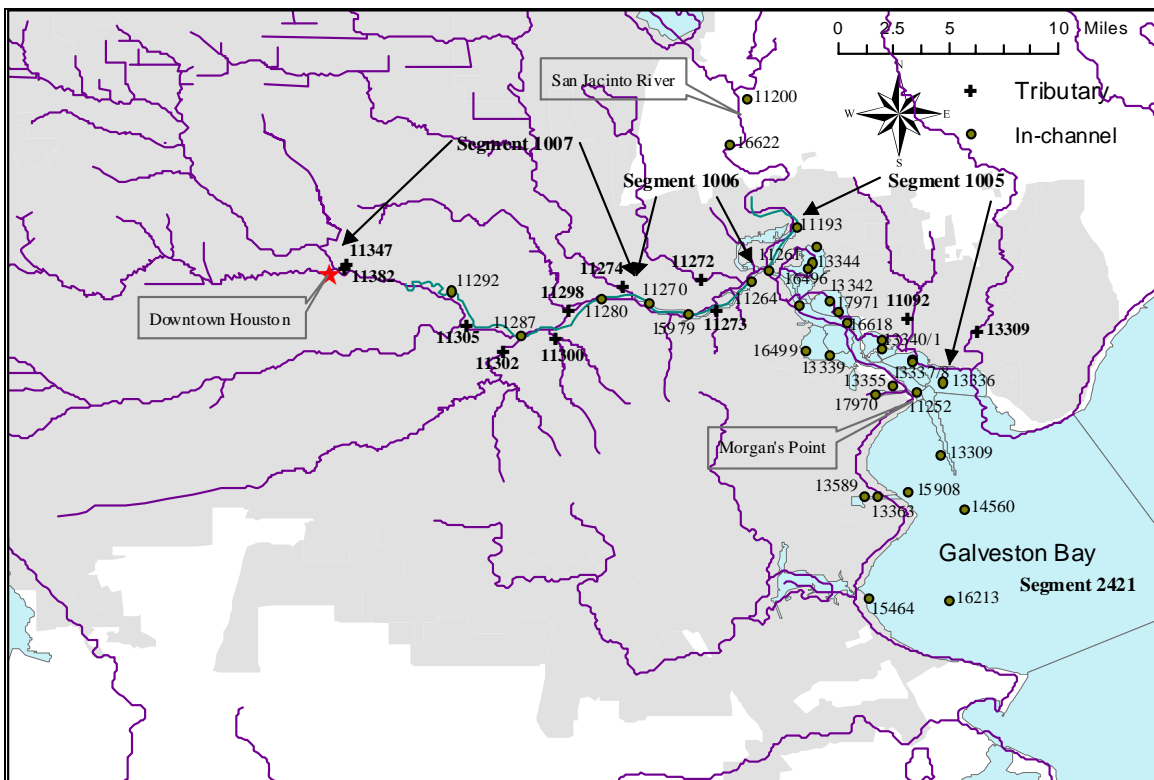


Figure 2.1 Stations sampled during the 2002-2003 PCB assessment

The concentration data was 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
<i>Total Count</i>	<i>8</i>	<i>9</i>	<i>18</i>	<i>18</i>
<i>∑PCB Multiplier</i>	<i>NA</i>	<i>NA</i>	<i>2</i>	<i>1</i>

*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%

^aTexas Surface Water Quality Standard

^bUSEPA (1999)

^cExceedances 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%

^aAverage calculated from per station concentration values that average duplicate values.

^bRepresents 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*. 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

* 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 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 of PCB concentration as well as the range of that concentration. Those 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

<i>Location</i>	<i>Water (ng L⁻¹)</i>	<i>Sediment (ng g⁻¹ d. wt.)</i>	<i>Fish (ng g⁻¹ w. wt)</i>	<i>Aroclors Sed (x10³ ng Kg⁻¹) Fish (ng g⁻¹)</i>	<i>Year</i>	<i>Water Sample Collection</i>	<i>Reference</i>
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; x10³ 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;

2.3 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 the difference seen 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 two-

fold 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.

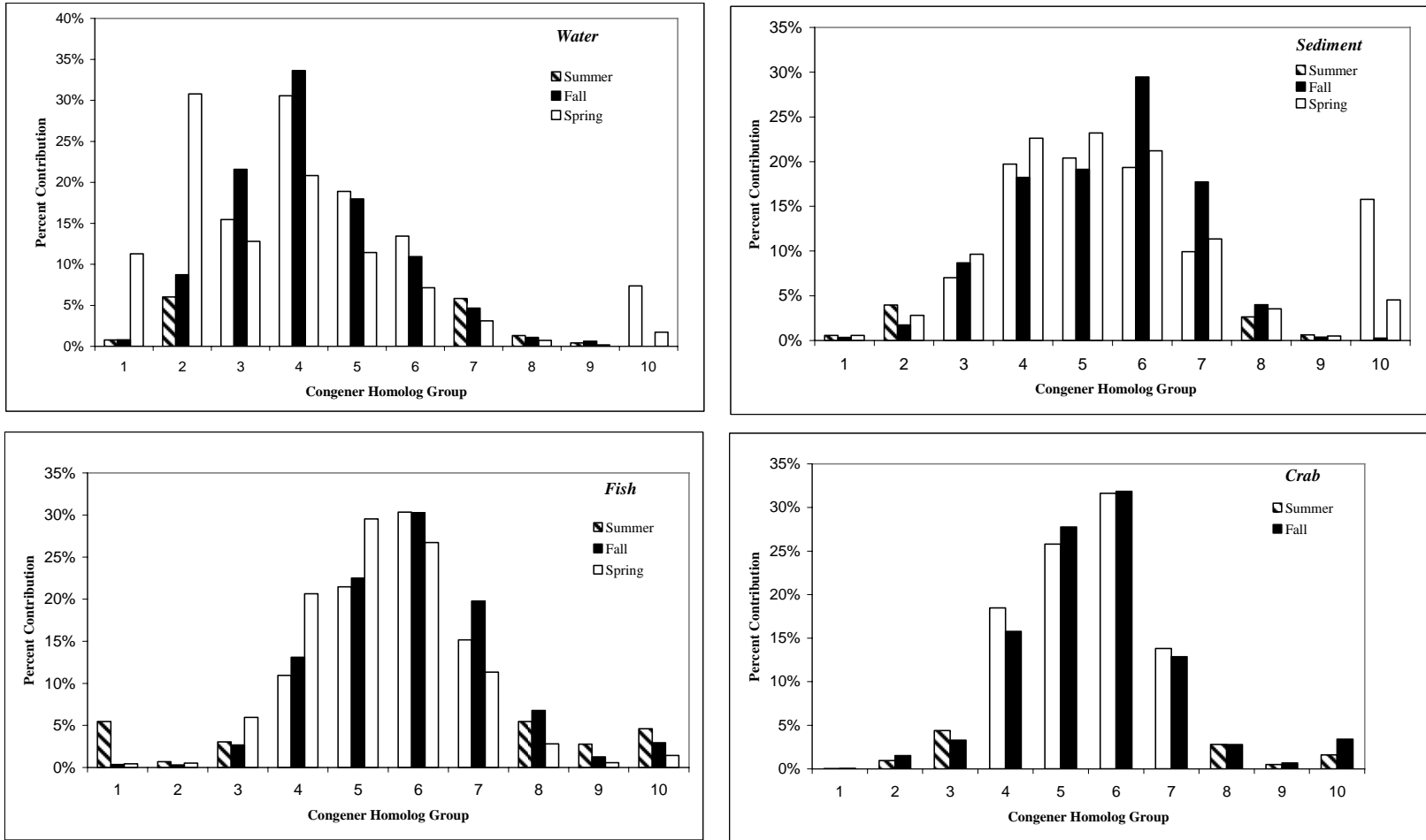


Figure 2.2 Seasonal variations in spatially averaged homolog profiles in water, channel sediment, catfish, and crab tissue samples. (Fall 2002 water PCB 209 erroneous results not included.)

2.4 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

2.5 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 is sourcing PCBs to the suspended 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 Gevaio 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 ($C_{\text{susp}}/C_{\text{diss}}$). 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-equilibrium 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.

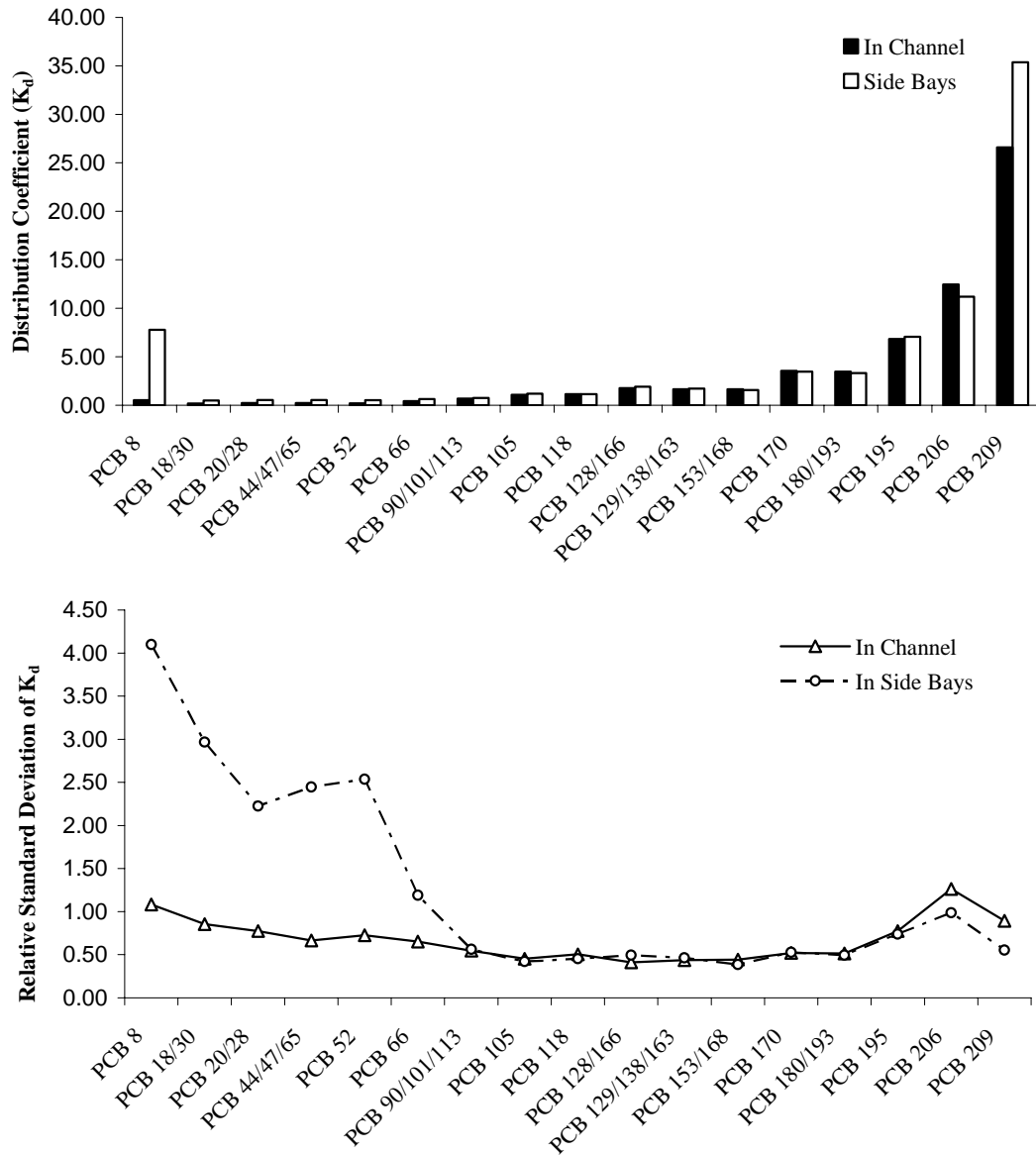


Figure 2.3 Suspended-dissolved phase distribution coefficient (C_{susp}/C_{diss}) average values and relative standard deviations in the channel and the side bays for the NOAA NST 18 congener set (PCB-187 excluded due to lack of data in the suspended phase)

2.6 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 an 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.

2.7 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 closet 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.

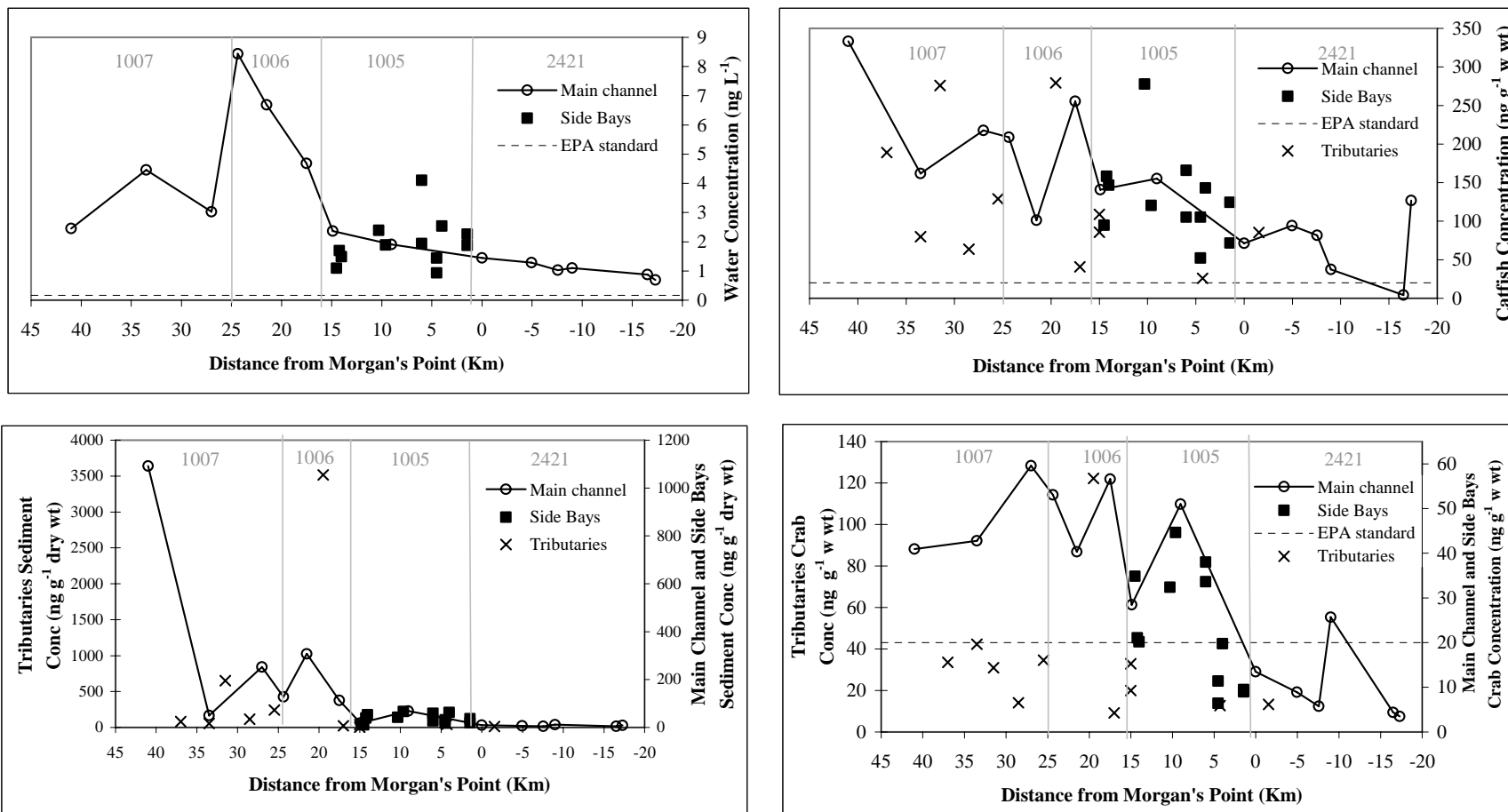
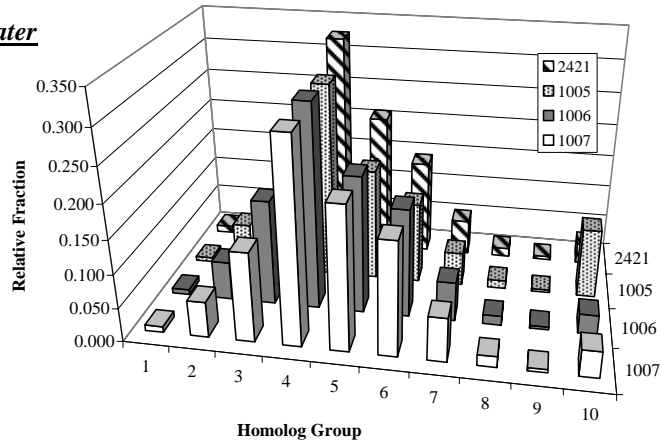


Figure 2.4 Total PCB concentration spatial distribution in water, sediment, catfish, and crab tissue in the HSC main channel, side bays, and tributaries

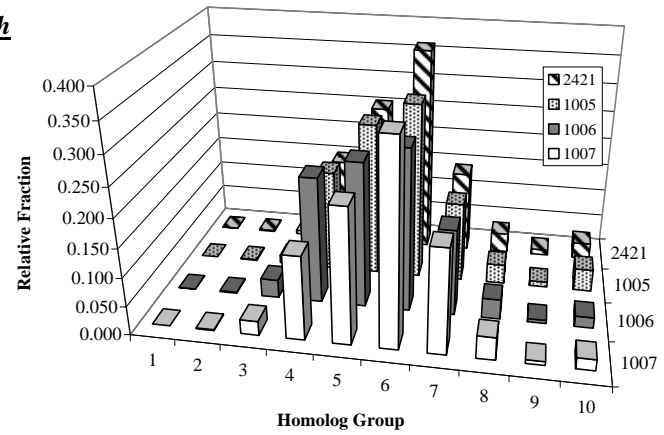
2.7.2 Homolog Groups

Figure 2.5 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. 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. 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).

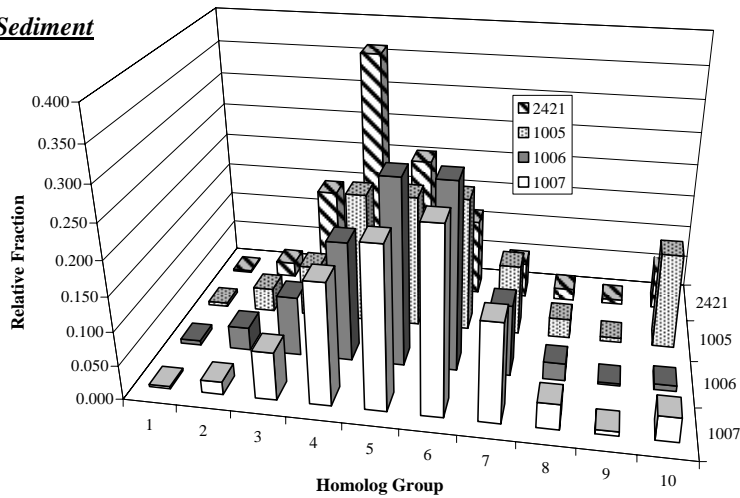
Water



Fish



Sediment



Crab

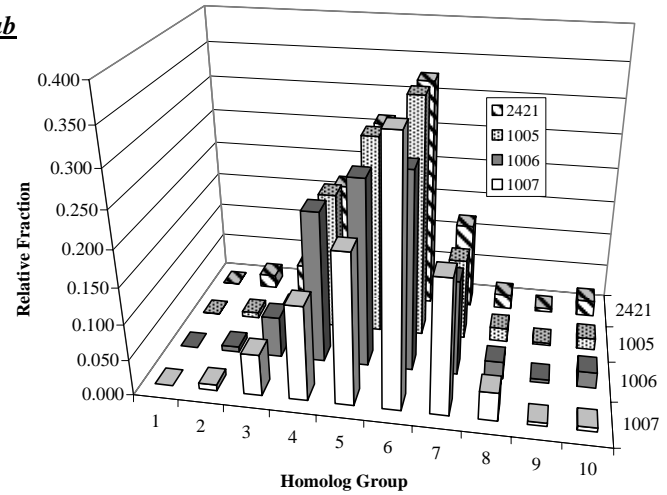


Figure 2.5 PCB main channel homolog profiles by segment

Segments 1006 and 1007 were analyzed further because of the distinction in the sediment homolog fingerprints as compared to the other two segments. Figure 2.6 shows homolog profile comparisons between main channel and tributary sediments in 1006 and 1007.

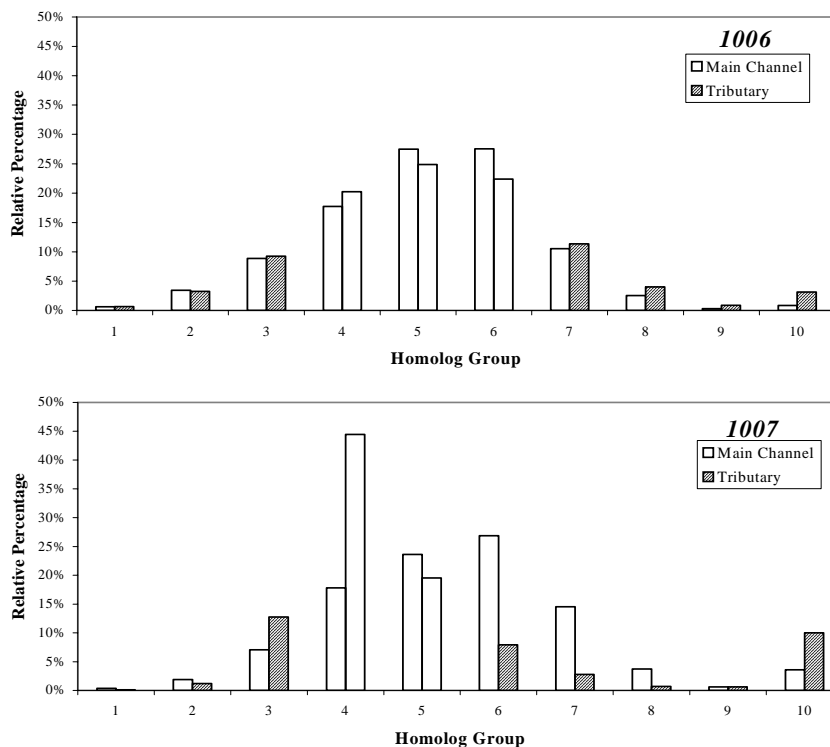


Figure 2.6 Main channel-tributary sediment profile comparisons in the high concentration segments

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 2.7) from the various bayous that adjoin the channel there show that all three bayous show similar profiles to the overall in-channel 1006 profile.

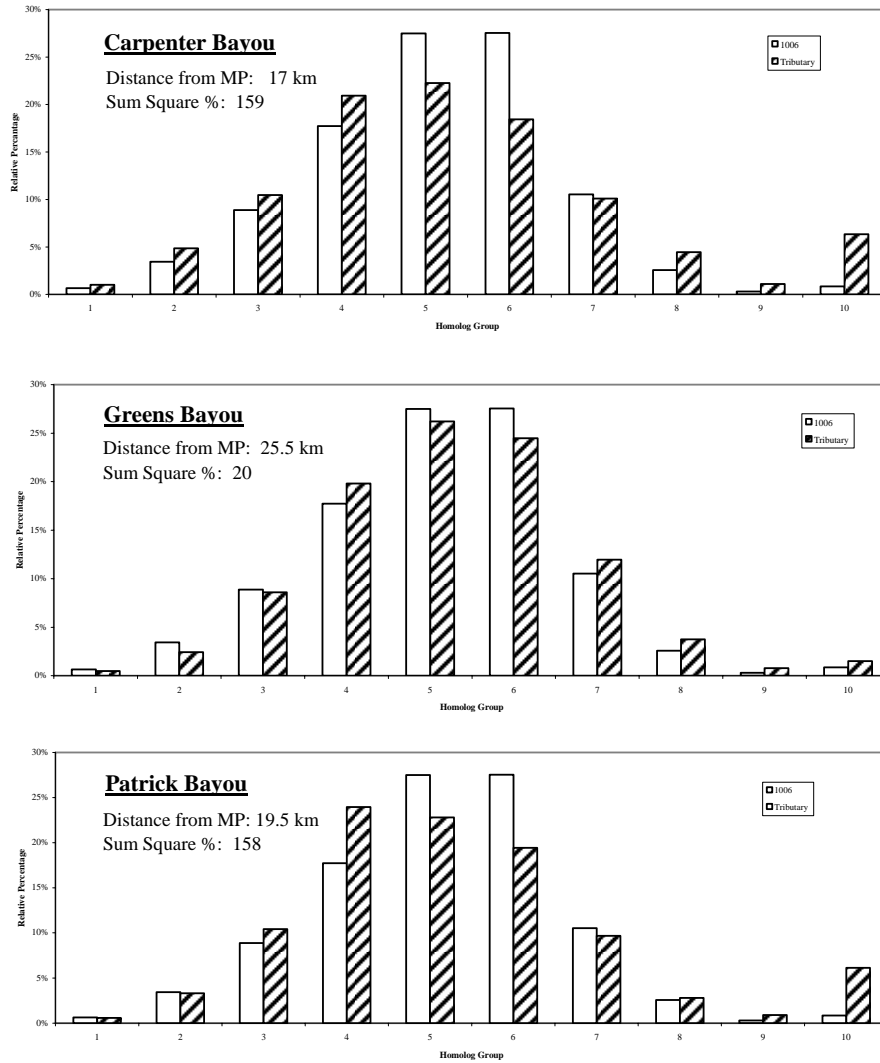


Figure 2.7 Comparative sediment congener profiles between the main channel and the tributaries in Segment 1006

The summed squared difference of the relative percentages for homologs between a tributary and the main channel was calculated as 159, 158, and 20 (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. 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.

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 2.8 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 2.9 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 2.6. 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.

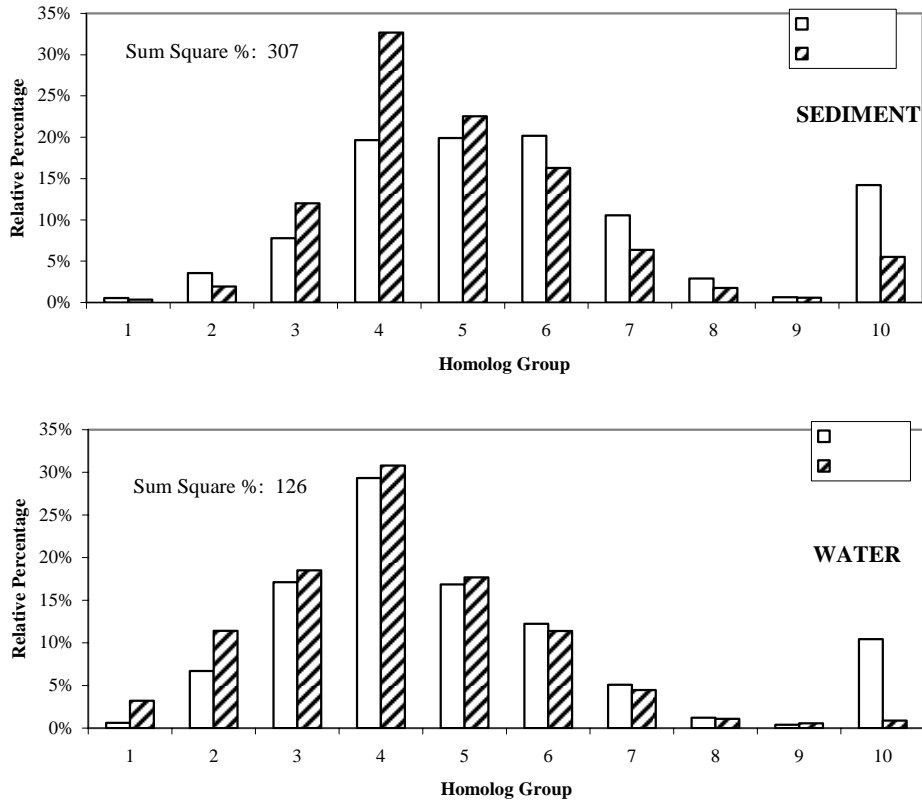


Figure 2.8 Main channel-side bay congener profile comparisons in water and sediment

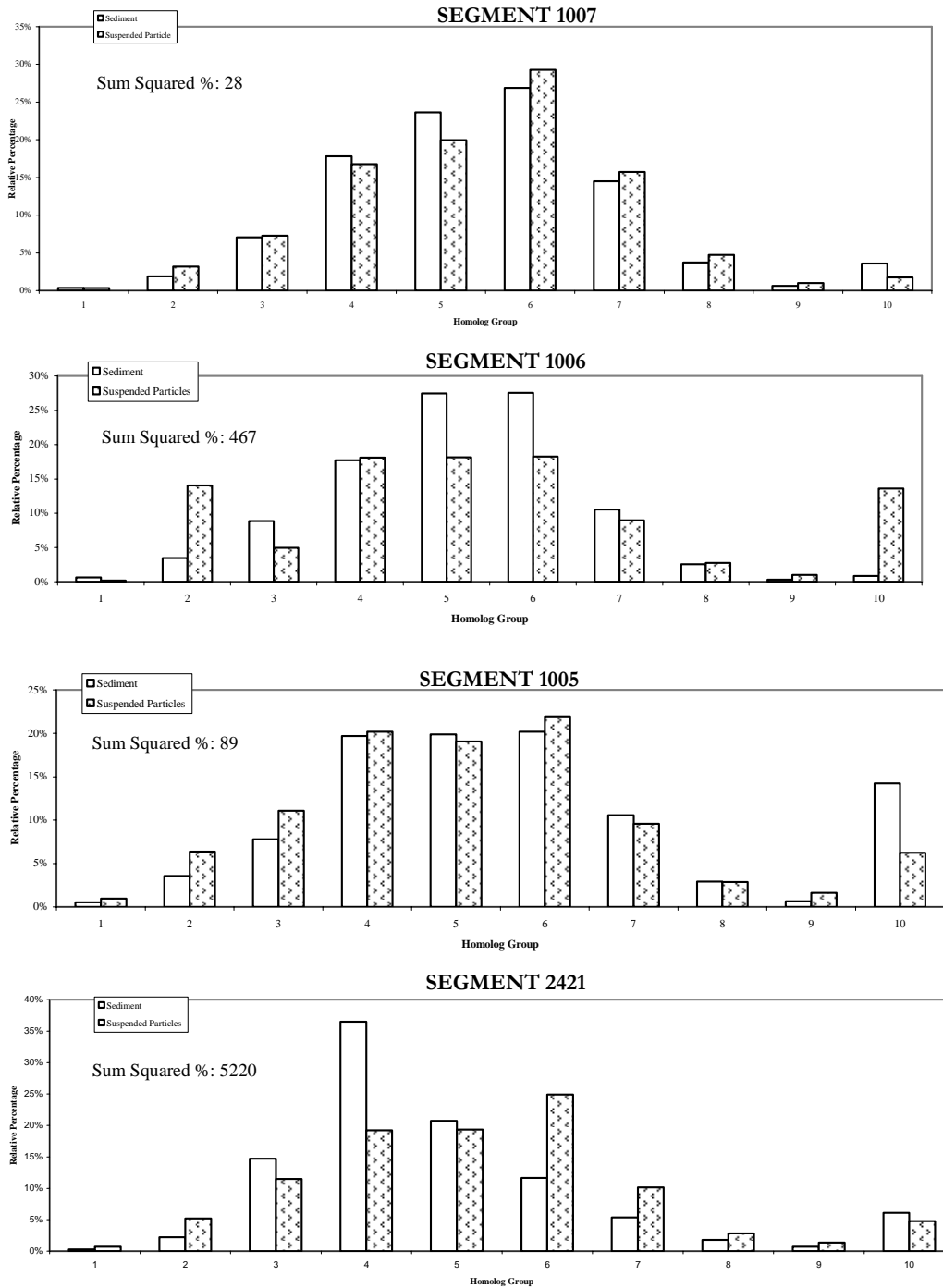


Figure 2.9 Sediment-suspended particle congener profile comparisons by main channel segment

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 (Figure 2.10). 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.

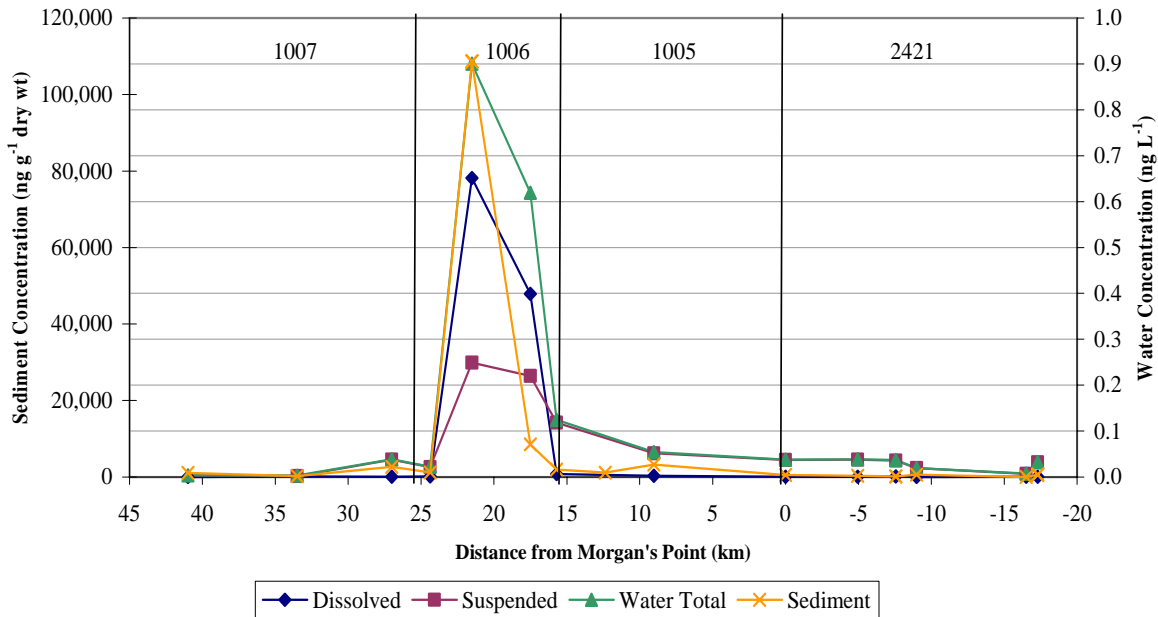


Figure 2.10 PCB-209 main channel spatial profiles by media type

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 2.11 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. 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. So, if air is assumed to be a source for the HSC, as the PCB-209 deposits in particulates to the surface, those particulates in water still retain much of the congener from that transfer.

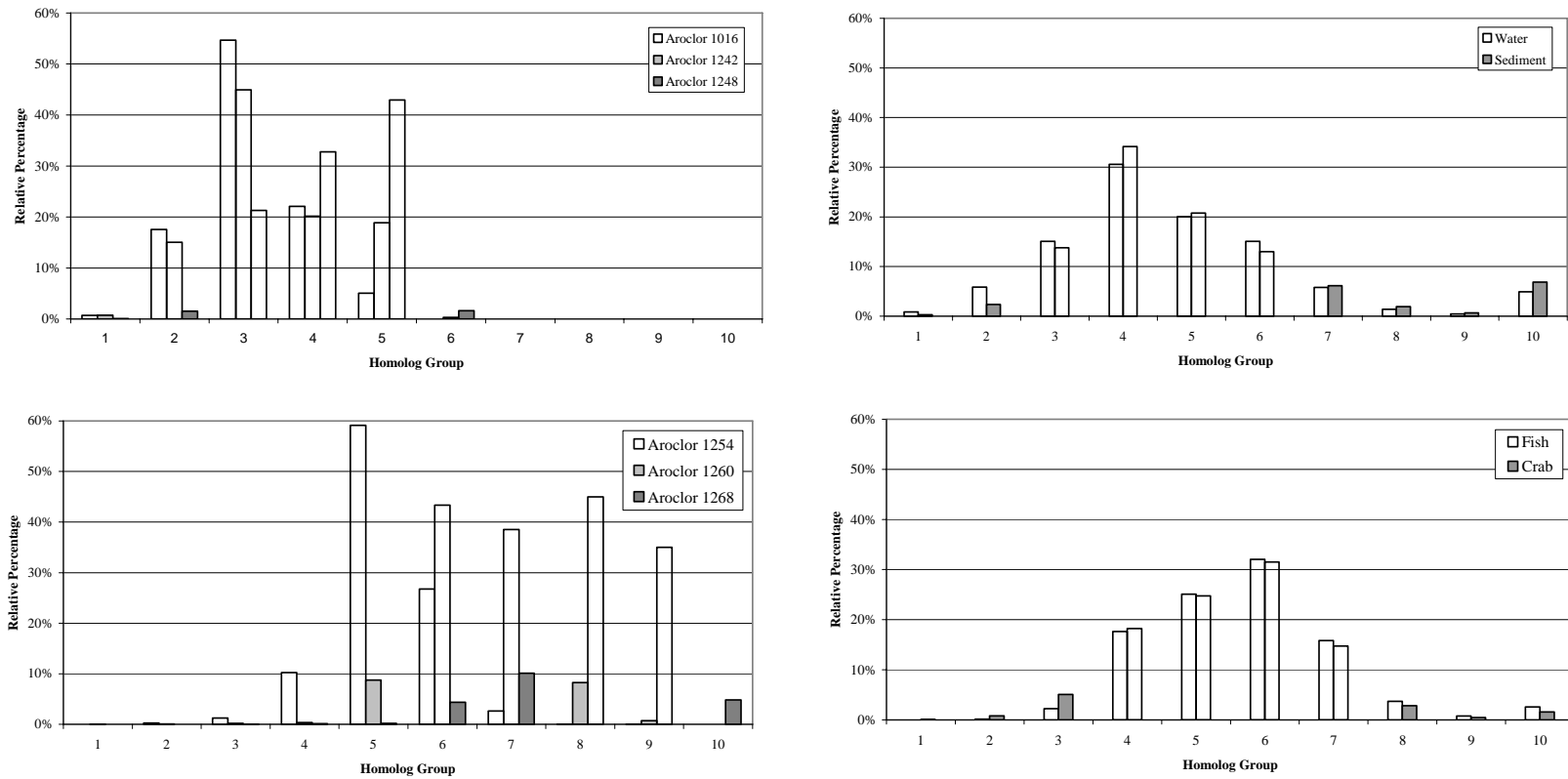


Figure 2.11 Aroclor profile comparison with main channel average congener profiles in different media. All Aroclor profiles are taken from Frame et al. (1996) except for Aroclor 1268, which was taken from Kannan et al. (1997).

2.8 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 were 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 2.12 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[†] 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 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

[†] 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.

the NOAA NST list against a sum of 81 congeners standard. They find significant inaccuracies in sediment and biota.

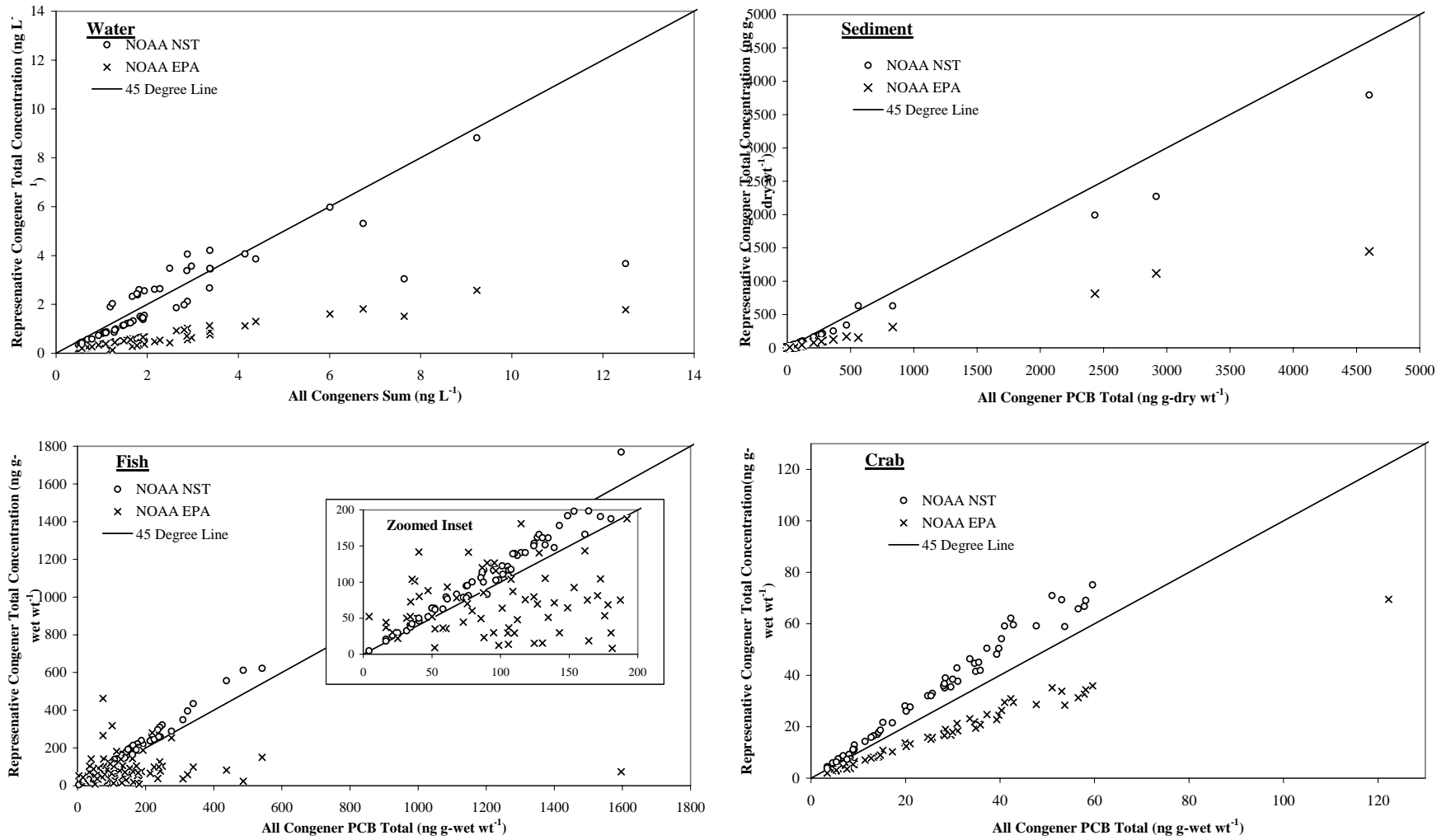


Figure 2.12 Comparison between representative congener and all congener methods in a total PCB calculation

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.

CHAPTER 3 - POTENTIAL PCB SOURCES IN THE HSC

In last quarter's report, PCB sources were discussed as a matter of generality and what might be important to the HSC. In this last quarter, the previous analysis presented in CHAPTER 2 was used to further explore potential sources.

3.1 ATMOSPHERIC

The analysis of the previous PCB data revealed a few salient points about atmospheric sources. They are the following:

- Potential volatilization trends exist seasonally from Summer 2002 to Spring 2003. (Figure 2.2)
- The presence of PCB-209 in all media, especially in suspended particles which may have come from the atmosphere, correlates with PCB-209 found in air samples by Park et al. (2001).

The HSC as an overall water body should be a net source or sink of PCBs. Park et al. (2001) found that Galveston Bay was probably a net atmospheric source meaning that volatilization dominated over deposition. There are a few complications in simply using that study to characterize the HSC.

- The HSC may be hydraulically unique from the rest of Galveston Bay. Park et al. (2001) found that prevailing winds blowing from industrial Houston increased air concentrations. Since the HSC is closer to this industry than Galveston Bay, it is possible that it may be a net sink of PCBs due to greater fluxes.
- The Park et al. study believed that their analysis needed to be confirmed with further sampling.

- Even when it is discovered if total PCBs are a net source or sink, this still does not speak to the issue of individual congeners or homolog groups being a net source or sink.

To these points, it is fair to say that more work will need to be done to resolve them. The hydraulic linkage of Galveston Bay to the rest of the channel is probably discernible through what was learned in the Dioxin project as well as through further modeling. Park et al.'s comment of confirmation of source direction may already have been resolved through further studies conducted by the group. Even if they are, however, this is no guarantee that the same source conditions exist in the HSC versus Galveston Bay.

Congener fluxes in and out of the channel are important because these relate to particular health risks and ultimate accumulation. Firstly, the reason that congener fluxes differ is that volatilization from the channel is affected by two chemical interactions. The first is the ability of congeners to partition from either suspended particles to water or from sediment to water. The second is the ability of a truly dissolved congener to volatilize at the air-water interface. Both of these are related to level of chlorination in the same way. Heavier congeners have more affinity for suspended particles/sediment. They also require more energy to volatilize from solution by virtue of increased size and weight. These two factors together mean that more chlorination decreases volatilization flux to the preference of depositional flux. The opposite is true for lighter congeners.

Congener flux relates to health risk because some congeners (e.g. coplanar “dioxin-like” congeners, etc.) are more detrimental to health than others. Thus, even if total concentrations of PCBs are decreasing in time due to net overall PCB loss from to the air, most of those congeners may be more benign to human and ecological health, which in the end leaves relatively the same health risk in the system. Ultimate accumulation matters here because it must be considered what the ultimate source of some of these congeners may be. Some heavier congeners that enter the HSC may never leave if volatilization is the main pathway by which they leave. With the example of PCB-209, it is clear from Figure 2.3 that the partitioning is heavily preferential towards the suspended phase. This means that PCB-

209 which may come from atmospheric deposition (Park et al., 2001) or PCB that is in sediment, and even scoured sediment that reenters the water column may remain in the channel with the continuing potential to accumulate in aquatic biota.

3.2 SAN JACINTO RIVER “LOST” WASTE PITS

The submerged waste pits in the San Jacinto River discovered in the course of the Dioxin Project need be considered as a potential source. Though they have not been totally characterized to this point, it is known that they contained paper mill waste. Resolute PCB data has not yet been taken to definitively determine that the waste pits are a source. A literature review of paper mill sites that involve PCB will help to define the possibility before it is investigated via sampling.

3.2.1 Paper Mill Waste Composition

Paper mill wastes result from processing and storage of timber, conversion of wood to pulp, and bleaching operations. All of these operations can occur in the vicinity of the mills, and they may result in various organic waste products including wood extracted natural products, paper-making additives including biocides, surfactants, phenolic compounds, and by-products from the bleaching process such as PCDD/F (Lacorte et al., 2003)

3.2.2 Paper Mill Related Studies

Some studies have linked PCBs in a general way to paper mill operations. Bettiol et al. (2005) conducted simultaneous river and atmospheric samples in the Venice Lagoon to discover that PCBs were coming in nearly equally amounts to the lagoon from deposition and river advection. They also determined using fingerprint of dioxins that paper mill contaminant contribution to the lagoon happened primarily by atmospheric deposition. Champoux (1996) discovered PCBs in Merganser eggs and fledgling downstream from the

historically largest pulp and paper mill in Quebec. These studies showed a definite linkage of paper mill wastes to PCB residence in water and biota. Petreas et al. (1992) attempted to find links between proximity to a bleached pulp and paper mill operation in Northern California and PCBs in bivalves and sediment to no avail.

Other paper mill studies have known ahead of time that certain PCB-type sources were definitely present. The most prevalent source in the literature is PCB self-copying paper. PCBs were used in self-copying paper until such paper was banned and replaced by carbon copy. That PCB paper was, however, recycled into new paper which was recycled again in later uses. The process of recycling would have generated waste from paper mills containing PCBs, and it would have perpetuated further use of PCBs in recycled papers still in use. Statistically significant increases of PCBs from PCB paper was reported in Sweden by Axelman and Broman (1999) and in Finland by Herve et al. (2002). A significant source of 1100 kg of PCBs from PCB paper was found from pre-1975 paper recycling activities along the Baltic Coast as well (Sundberg et al., 2005)

Merilainen et al. (2003) linked PCB concentrations found in sediment cores dating back as far as 200 years to Aroclor 1260. A primary source of effluent to the lake in the study was a paper mill that had been operating since 1872. This is significant because Aroclor 1260 is one of the higher chlorinated Aroclors. Aroclor 1260 was mainly used in electric transfers, condensers, and hydraulic oils.

3.2.3 *Likelihood of Paper Mill Related Waste in HSC*

It is not yet clear what the details of the paper mill operations were that produced the waste pits in SJR. If these pits were known to have dealt in paper recycling before the PCB ban of 1977, then they would be likely candidates for PCB sourcing. They would also be a source possibility if Aroclor fluids were specifically used at the facility in operations. One final possibility of PCB sourcing in the pits is through coproduction wastes from the paper making process itself. This particular possibility has not been seen in the current literature that has been reviewed, but it may still remain a possibility if for no other reason than the

production chemistry used in paper mills is not yet understood well enough to predict the presence of PCBs as byproducts.

3.3 SEDIMENT MOVEMENT

Figure 2.6 suggested the possibility of tributary sediment transport into the main channel. This transport may not be limited to the three tributaries that were examined nor to tributary to channel transport alone. PCB-laden sediment could also be transported down the channel directly or from the side bays. If indeed sediments do prove to be a large repository of PCBs and especially highly chlorinated PCBs, then the conceptual and quantitative understanding of their transport in sediment is significant.

3.3.1 *Mechanism of Transport*

As it relates to PCBs, the concern in sediment transport is the deposition and resuspension of sediments that could carry PCB down a channel network. The factors that can influence this behavior in the environment include particle size, particle cohesion, turbulent stress at the water-sediment interface, benthic organisms, water velocity, river hydraulics, and consolidation time (Gailani et al., 1991) Particle size and cohesion is important in sediment transport as it relates to storm events in a flowing water body. Nelson and Benedict (1950) showed that flood events can increase flows to such a degree that 50% of the sediment may be transported in some way whereas at lower flow conditions only the fine-grained sediments are easily resuspended and transported downstream (Gailani et al., 1991).

One method of measuring sediment transport is through naturally-occurring and artificial radioactive tracers. Naturally-occurring tracers include ^{234}Pb , ^{210}Th , and ^7Be while an artificial tracer present in the environment since nuclear weapons testing is ^{137}Cs (Olmez et al., 1994). Knowledge of half lives of the tracer used can be used to quantify sediment

deposition rates and transport rates if a long enough observation time is used. Sediment coring may also be required to observe larger time scales.

3.3.2 *Studies of PCB Transport in Sediment*

It is known the Hudson River's large PCB source is mainly contained in sediments, and the disturbing of those sediments through dredging operations is particularly treacherous because of PCB present in the bed. Sediment PCBs are often exchanging with water, which transports PCBs, but the sediments themselves may also have been carried downstream as hypothesized by Olsen et al. (1993). They determined that the riverine and estuarine systems in the Hudson have contaminant profiles that maintain dynamic equilibrium against the sometimes opposing forces of freshwater discharge and tidal activity. This equilibrium determines accumulation rates and distributions of the contaminant. Thus, in a tidally influenced system such as the HSC, sediment transport of PCBs will be influenced by both the freshwater flows that relate to upstream wastewater discharges and storm events as well as downstream effects of tide. Feng et al. (1998) acknowledged this wastewater effect in the Hudson by finding a correlation between water quality from PCBs and waste water discharges, especially at low flows. And intuitively and experimentally, they determined that higher surficial sediment concentrations were related to more recent sediment transport from upstream sources.

A study in a Korean harbor conducted by Kim et al. (2000) highlights further information concerning tidal effects, sediment transport, and congener profiles. They made the distinction between sediment that was tidal and subtidal (sometimes exposed to air) in the correlative discovery that subtidal sediments concentrate PCBs more than tidal sediments. In looking at congener profiles, they found a positive link between sediment, a wastewater storage reservoir, and suspended solids. This correlation leads to the real possibility of tidally driven horizontal sediment transport. And finally, they made the important comparison of kinetic weathering processes of PCBs and the rate of tidal sedimentation. At least in that harbor, deposition happened at a significantly higher rate such that congener profiles would not be significantly altered in the journey from sediment source to sediment deposition

location. This means that sediment source fingerprints remain intact at their new location, which facilitates comparison.

Bzudusek et al. (2005) studied PCB profiles in sediment cores in the Sheboygan River, and they found that PCB sediment transport occurred primarily in fine grain suspended sediments. They stated that larger-grained PCB sediment only happened during large storm events historically. PCBs are present in sediment particles of many sizes, but their transport by actual sediment movement may only occur through smaller particles. Larger and especially more cohesive agglomerating particles would then contribute PCBs to downstream locations only via partitioning to water.

These studies point lead to some fundamental conclusions that can serve as recommendations for the HSC:

1. Knowledge of sediment particle size distribution, historical flood events, and dredging operations in the HSC would all be important considerations to link fingerprinting evidence with the real possibility of sediment transport.
2. Considering the freshwater flow-tidal flow interaction in various regions of the channel and its tributaries is important to understanding sediment transport behavior.
3. The distinction between subtidal and tidal sediments in the HSC and tributaries may be an important way of contextualizing PCB concentrations.
4. As long as it can be determined that weathering is slower than sediment deposition and resuspension, congener profile comparisons to determine sediment sourcing is a valid activity.

3.4 COPRODUCTION

Coproduction sources of PCBs were discussed in the previous quarterly report with the qualification that not much information had yet been found to help ascertain the likelihood

of coproduction in the HSC. This quarter has yielded some more information from the literature, and further information will need to be more HSC-specific.

Coproduction in the HSC would be possible by two possible means:

- Waste and product streams from chemical production that could be released in wastewater
- Waste incineration that could enter the channel via atmospheric deposition

Both issues have been discussed in the literature.

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. With the variety of chemical production facilities adjacent to the channel (especially those that involve chlorination processes), the possibility of contemporary or historical sources from coproduction is apparent.

In addition to the suggestion of coproduction sources, Erickson et al. (1988) analyzed some halocarbon products and waste. Halocarbon product and process samples used were non-detect for PCBs while three out of five vinyl chloride waste samples contained PCBs, and a TCE still bottoms sample contained PCBs with 94% of that signal attributable to PCB-209. The presence of PCB-209 in the still bottoms waste is an interesting find for the HSC since PCB-209 has been found in measurable quantities.

One other point of note about this kind of coproduction is the absence of literature discussion of the topic beginning in the mid-1990s. The absence may be indicative of at least two possibilities. One is that coproduction from process product and waste streams is not a significant PCB source. The other is that the coproduction has not been as much of a topic because of analytical chemistry advances. Much of the original interest in coproduction was a result of the need for different analytical methods to be developed to deal with coproduction media. It was difficult to do the standard Aroclor surrogate analysis on these alternate media.

Yet as Aroclor surrogates have given way to congener-specific analyses, the coproduction analytical challenge has not been as great. Thus, the analytical chemistry motivation for coproduction studies has been removed, and no one else has taken up the source side of the issue. The latter possibility seems more likely since no paper has yet been found that convincingly confirms that PCBs are not formed as industrial byproducts.

The incineration side of coproduction has only begun to be more intensely studied in the last few years when Ikonomou 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. Research continues in this area, but it appears that incineration of at least municipal waste is a real source of atmospheric PCBs.

Confirmation of either or both of these source possibilities in the HSC would require more information about the industries that are currently operating in the channel and potential sampling of wastewater and incinerator stack emission streams from those industries.

CHAPTER 4 – SUMMARY AND FURTHER ACTIVITIES

This report presented some detailed analyses of previously sampled PCB data taken from the HSC. The strength of the dataset as it was presented in November 2005 was improved primarily from a larger scope of congeners, which included all 209 possible PCBs. The greater scope yielded a more accurate concentration in all media that showed higher concentrations in the channel than what had previously been reported. Additionally, the use of more congeners allowed the examination of congener profiles, which gave more insight into environmental weathering, source possibilities, and transport linkages from various parts of the channel (e.g. side bay – main channel comparisons, tributary – main channel comparison, upstream influence of downstream concentrations, etc.). More research into different total PCB quantification methods revealed what kind of information is lost in using fewer congeners.

The source research section of this report provided some background into potential areas of further sampling and correlation. Knowing how sediment is transported, what kinds of PCB behavior one can expect from paper mill wastes, how the atmosphere may contribute to channel concentrations, and the role of chemical byproducts in unintentional PCB production should yield some leads for further investigation into sources. Much speculation can be made in regards to these and other potential sources, and so more analysis and data collection will be required in conjunction with modeling to determine the most likely sources.

The first and second quarterly reports together provide a fair amount of background information in terms of literature research and previous data analysis. It is the aim of the project to develop more project specific plans to carry through into sampling and modeling activities that will eventually lead to assessment of PCB source and fate in the HSC. To that end, the activities of the next quarter will at least include the following:

1. A review and possible selection of the modeling tools
2. Design of a monitoring plan
3. More detail of sampling needs and methods by which they will be carried out

In addition to these more “action-oriented” goals, supporting background research will continue to be conducted as is necessary. Possible topics of that research include further study in biodegradation, sampling technology and theory, forensic analysis methods, and physical-chemical parameters.

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APPENDIX A - ALL CONGENER TOTAL PCB CONCENTRATIONS FROM 2002-2003 SAMPLING EVENTS

Table A.1 Dissolved, suspended, and total water concentrations

Tag ID	Station ID	Sample Date:	Unit	Dissolved	Suspended	Total
UHDW001	11193	09/11/2002	ng/L	0.58	0.73	1.31
UHDW002	11200	09/02/2002	ng/L	0.25	0.24	0.49
UHDW003	16622	09/02/2002	ng/L	0.38	0.26	0.64
UHDW004	11252	08/30/2002	ng/L	0.74	0.37	1.11
UHDW005	11261	09/12/2002	ng/L	1.18	0.67	1.85
UHDW006	16618	08/26/2002	ng/L	1.35	0.56	1.91
UHDW007	11270	08/28/2002	ng/L	3.43	0.95	4.38
UHDW008	11264	08/27/2002	ng/L	4.92	1.09	6.01
UHDW009	15979	08/27/2002	ng/L	3.20	0.94	4.15
UHDW010	11287	09/12/2002	ng/L	0.85	0.43	1.28
UHDW011	11292	09/03/2002	ng/L	1.26	0.92	2.18
UHDW012	11292	09/03/2002	ng/L	2.23	0.87	3.10
UHDW013	11280	09/04/2002	ng/L	2.22	0.66	2.88
UHDW014	13309	08/25/2002	ng/L	0.63	0.66	1.29
UHDW015	14560	09/04/2002	ng/L	0.30	0.24	0.54
UHDW016	15908	08/29/2002	ng/L	0.62	0.41	1.03
UHDW017	16213	09/10/2002	ng/L	0.29	0.40	0.69
UHDW018	13337	08/24/2002	ng/L	1.12	0.76	1.88
UHDW019	13338	08/26/2002	ng/L	0.96	0.74	1.69
UHDW020	13336	08/29/2002	ng/L	0.84	0.72	1.56
UHDW021	13339	09/06/2002	ng/L	1.16	0.78	1.94
UHDW022	16499	09/13/2002	ng/L	0.94	0.51	1.45
UHDW023	16499	09/13/2002	ng/L	0.97	0.51	1.48
UHDW024	13340	09/06/2002	ng/L	0.52	0.41	0.93
UHDW025	13341	09/05/2002	ng/L	0.57	0.50	1.06
UHDW026	13342	08/23/2002	ng/L	1.30	0.60	1.91
UHDW027	17971	08/31/2002	ng/L	1.18	0.44	1.62
UHDW028	13343	08/20/2002	ng/L	0.50	0.59	1.09
UHDW029	15464	09/11/2002	ng/L	0.26	0.30	0.56
UHDW030	13344	08/21/2002	ng/L	1.21	0.42	1.63
UHDW031	16496	08/22/2002	ng/L	0.97	0.52	1.49
UHDW032	13355	11/11/2002	ng/L	1.38	1.11	2.49
UHDW033	13363	08/31/2002	ng/L	0.47	0.32	0.79
UHDW034	13589	09/10/2002	ng/L	0.31	0.26	0.57
UHDW035	11193	11/20/2002	ng/L	1.06	0.88	1.94
UHDW036	11252	11/14/2002	ng/L	1.16	0.69	1.85
UHDW037	11252	11/14/2002	ng/L	1.13	0.60	1.73
UHDW038	11261	10/21/2002	ng/L	1.75	1.13	2.88
UHDW039	15979	11/01/2002	ng/L	6.53	2.70	9.23
UHDW040	11280	11/06/2002	ng/L	2.24	1.14	3.39

Table A.1 Dissolved, suspended, and total water concentrations (continued)

Tag ID	Station ID	Sample Date:	Unit	Dissolved	Suspended	Total
UHDW041	14560	11/13/2002	ng/L	1.03	0.64	1.67
UHDW042	15464	11/19/2002	ng/L	0.68	0.51	1.19
UHDW043	13338	11/12/2002	ng/L	1.86	1.51	3.37
UHDW044	13336	11/05/2002	ng/L	1.81	1.15	2.97
UHDW045	13341	10/24/2002	ng/L	0.92	0.90	1.82
UHDW046	13342	10/29/2002	ng/L	0.99	1.88	2.87
UHDW047	17971	11/18/2002	ng/L	1.42	0.75	2.17
UHDW048	17971	11/18/2002	ng/L	1.43	0.72	2.15
UHDW049	13344	11/08/2002	ng/L	1.17	0.60	1.77
UHDW050	13363	10/31/2002	ng/L	2.55	0.83	3.37
UHDW051	11280	06/11/2003	ng/L	2.21	0.60	2.81
UHDW052	11287	06/17/2003	ng/L	6.37	1.27	7.64
UHDW053	11270	06/18/2003	ng/L	3.45	9.05	12.49
UHDW054	11264	06/02/2003	ng/L	2.65	0.81	3.47
UHDW055	11264	06/02/2003	ng/L	2.41	0.86	3.27
UHDW056	11200	11/21/2002	ng/L	0.61	0.63	1.24
UHDW057	16499	10/30/2002	ng/L	5.30	1.44	6.74
UHDW058	11292	11/07/2002	ng/L	1.39	0.89	2.28

Table A.2 Sediment concentrations

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPS001	13343	08/20/2002	ng/Kg,dry	9.20E+03
UHPS002	16496	08/21/2002	ng/Kg,dry	4.14E+04
UHPS003	13363	08/16/2002	ng/Kg,dry	4.27E+03
UHPS004	13589	08/16/2002	ng/Kg,dry	5.24E+03
UHPS005	15464	08/16/2002	ng/Kg,dry	4.46E+03
UHPS006	11092	08/01/2002	ng/Kg,dry	4.59E+04
UHPS007	11258	08/01/2002	ng/Kg,dry	4.38E+03
UHPS009	13340	08/06/2002	ng/Kg,dry	3.35E+04
UHPS010	13341	08/06/2002	ng/Kg,dry	2.97E+04
UHPS011	11305	08/13/2002	ng/Kg,dry	6.87E+04
UHPS012	11305	08/13/2002	ng/Kg,dry	7.42E+04
UHPS013	13337	08/14/2002	ng/Kg,dry	3.14E+04
UHPS014	11193	08/08/2002	ng/Kg,dry	2.31E+04
UHPS015	11347	08/12/2002	ng/Kg,dry	9.97E+04
UHPS016	11382	08/12/2002	ng/Kg,dry	5.58E+04
UHPS017	11302	08/21/2002	ng/Kg,dry	4.93E+04
UHPS018	11252	08/27/2002	ng/Kg,dry	7.20E+03
UHPS019	11252	08/27/2002	ng/Kg,dry	4.50E+03
UHPS020	11287	08/26/2002	ng/Kg,dry	5.55E+04
UHPS021	17970	08/18/2002	ng/Kg,dry	4.80E+03
UHPS022	13355	08/18/2002	ng/Kg,dry	4.69E+03
UHPS023	11273	08/28/2002	ng/Kg,dry	4.53E+06
UHPS024	11273	08/28/2002	ng/Kg,dry	4.67E+06
UHPS025	13338	08/22/2002	ng/Kg,dry	1.03E+05
UHPS026	13338	08/21/2002	ng/Kg,dry	9.89E+04
UHPS027	13342	08/21/2002	ng/Kg,dry	4.65E+04
UHPS028	13344	08/21/2002	ng/Kg,dry	3.81E+04
UHPS029	11111	07/31/2002	ng/Kg,dry	1.27E+04
UHPS030	11272	07/25/2002	ng/Kg,dry	9.27E+03
UHPS031	11274	07/30/2002	ng/Kg,dry	3.64E+05
UHPS032	11298	07/29/2002	ng/Kg,dry	1.23E+05
UHPS033	11270	08/28/2002	ng/Kg,dry	2.22E+05
UHPS034	11292	09/05/2002	ng/Kg,dry	2.52E+05
UHPS035	11300	09/05/2002	ng/Kg,dry	8.28E+05
UHPS036	11300	09/05/2002	ng/Kg,dry	8.40E+05
UHPS038	15908	09/11/2002	ng/Kg,dry	5.88E+03
UHPS039	15979	09/04/2002	ng/Kg,dry	6.30E+05
UHPS040	15979	09/04/2002	ng/Kg,dry	4.93E+05
UHPS041	16213	09/11/2002	ng/Kg,dry	1.19E+04
UHPS042	16622	09/03/2002	ng/Kg,dry	1.87E+04
UHPS043	11264	08/20/2002	ng/Kg,dry	1.05E+05
UHPS044	11261	08/19/2002	ng/Kg,dry	1.72E+04
UHPS045	16618	08/20/2002	ng/Kg,dry	2.06E+04

Table A.2 Sediment concentrations (continued)

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPS047	11200	09/03/2002	ng/Kg,dry	4.34E+03
UHPS048	11200	09/03/2002	ng/Kg,dry	4.45E+03
UHPS049	13309	08/30/2002	ng/Kg,dry	8.64E+03
UHPS050	14560	08/30/2002	ng/Kg,dry	1.83E+04
UHPS051	13336	08/27/2002	ng/Kg,dry	1.42E+04
UHPS052	13336	08/27/2002	ng/Kg,dry	1.46E+04
UHPS053	13339	08/22/2002	ng/Kg,dry	4.42E+04
UHPS054	16499	08/22/2002	ng/Kg,dry	6.49E+04
UHPS055	17971	08/24/2002	ng/Kg,dry	9.26E+04
UHPS056	17971	08/24/2002	ng/Kg,dry	1.00E+05
UHPS057	11252	10/24/2002	ng/Kg,dry	1.20E+04
UHPS058	11261	10/26/2002	ng/Kg,dry	1.80E+04
UHPS059	13342	10/30/2002	ng/Kg,dry	4.30E+04
UHPS060	13344	10/27/2002	ng/Kg,dry	4.06E+04
UHPS061	17971	10/28/2002	ng/Kg,dry	3.67E+04
UHPS064	17970	10/24/2002	ng/Kg,dry	7.05E+03
UHPS065	13340	10/23/2002	ng/Kg,dry	3.40E+04
UHPS066	16499	10/24/2002	ng/Kg,dry	5.28E+04
UHPS067	11280	12/02/2002	ng/Kg,dry	2.32E+05
UHPS068	11280	12/02/2002	ng/Kg,dry	3.25E+05
UHPS069	11292	12/10/2002	ng/Kg,dry	2.92E+06
UHPS070	13363	11/06/2002	ng/Kg,dry	5.38E+03
UHPS071	15464	11/06/2002	ng/Kg,dry	4.47E+03
UHPS072	11200	11/21/2002	ng/Kg,dry	4.38E+03
UHPS073	11193	10/31/2002	ng/Kg,dry	3.06E+04
UHPS075	13338	10/22/2002	ng/Kg,dry	2.36E+04
UHPS076	13336	10/22/2002	ng/Kg,dry	2.39E+04
UHPS077	11092	04/30/2003	ng/Kg,dry	4.22E+04
UHPS078	11274	05/01/2003	ng/Kg,dry	1.09E+05
UHPS079	11252	05/28/2003	ng/Kg,dry	9.75E+03
UHPS081	11280	08/29/2002	ng/Kg,dry	2.69E+05
UHPS088	11111	05/01/2003	ng/Kg,dry	1.05E+04
UHPS089	11193	05/13/2003	ng/Kg,dry	6.46E+04
UHPS090	11252	05/28/2003	ng/Kg,dry	1.08E+04
UHPS092	11258	04/30/2003	ng/Kg,dry	2.44E+04
UHPS093	11261	05/11/2003	ng/Kg,dry	2.09E+04
UHPS094	11264	05/29/2003	ng/Kg,dry	1.21E+05
UHPS095	11270	05/06/2003	ng/Kg,dry	3.35E+04
UHPS096	11272	04/30/2003	ng/Kg,dry	3.58E+04
UHPS097	11273	05/03/2003	ng/Kg,dry	2.37E+06
UHPS098	11273	05/03/2003	ng/Kg,dry	2.49E+06
UHPS099	11274	05/01/2003	ng/Kg,dry	1.26E+05
UHPS100	11280	05/06/2003	ng/Kg,dry	2.09E+05
UHPS101	11287	05/05/2003	ng/Kg,dry	4.48E+04
UHPS102	11292	05/06/2003	ng/Kg,dry	1.07E+05
UHPS103	11298	05/02/2003	ng/Kg,dry	1.07E+05
UHPS104	11300	05/29/2003	ng/Kg,dry	4.68E+05
UHPS105	11302	05/01/2003	ng/Kg,dry	6.10E+04
UHPS106	11305	05/04/2003	ng/Kg,dry	9.17E+04
UHPS107	11347	05/04/2003	ng/Kg,dry	3.74E+04
UHPS108	11382	05/05/2003	ng/Kg,dry	4.23E+04

Table A.2 Sediment concentrations (continued)

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPS110	13309	05/12/2003	ng/Kg,dry	4.25E+03
UHPS111	13337	05/28/2003	ng/Kg,dry	4.12E+04
UHPS112	13339	05/04/2003	ng/Kg,dry	1.05E+04
UHPS113	13340	05/28/2003	ng/Kg,dry	2.64E+04
UHPS115	13341	05/28/2003	ng/Kg,dry	5.11E+03
UHPS116	13342	05/11/2003	ng/Kg,dry	3.73E+04
UHPS117	13343	05/11/2003	ng/Kg,dry	1.29E+04
UHPS118	13355	05/28/2003	ng/Kg,dry	4.18E+03
UHPS119	13589	05/22/2003	ng/Kg,dry	9.07E+03
UHPS120	14560	05/12/2003	ng/Kg,dry	5.44E+03
UHPS121	15464	05/12/2003	ng/Kg,dry	5.36E+03
UHPS122	15908	05/28/2003	ng/Kg,dry	4.73E+03
UHPS123	15979	05/29/2003	ng/Kg,dry	5.31E+04
UHPS124	16213	05/12/2003	ng/Kg,dry	5.93E+03
UHPS125	16496	05/11/2003	ng/Kg,dry	6.55E+04
UHPS126	16618	05/06/2003	ng/Kg,dry	1.16E+05

Table A.3 Catfish concentrations

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPF001	11111	08/01/02	ng/g wet	1.31E+02
UHPF002	11193	08/09/02	ng/g wet	1.64E+02
UHPF003	11200	09/03/02	ng/g wet	4.07E+01
UHPF004	16622	09/04/02	ng/g wet	1.60E+03
UHPF005	11252	08/26/02	ng/g wet	7.93E+01
UHPF006	11258	08/01/02	ng/g wet	1.05E+02
UHPF007	11261	08/23/02	ng/g wet	1.10E+02
UHPF008	16618	08/19/02	ng/g wet	6.13E+01
UHPF009	11273	08/30/02	ng/g wet	3.23E+02
UHPF010	11270	08/28/02	ng/g wet	1.76E+02
UHPF011	11264	08/20/02	ng/g wet	1.71E+02
UHPF012	15979	09/05/02	ng/g wet	1.01E+02
UHPF013	11292	09/11/02	ng/g wet	2.44E+02
UHPF014	11298	08/29/02	ng/g wet	5.23E+01
UHPF015	11300	09/06/02	ng/g wet	2.76E+02
UHPF016	11302	08/26/02	ng/g wet	1.02E+02
UHPF017	11305	08/13/02	ng/g wet	1.57E+02
UHPF018	11305	08/13/02	ng/g wet	1.21E+02
UHPF019	11280	08/28/02	ng/g wet	1.43E+02
UHPF020	11347	08/13/02	ng/g wet	1.45E+02
UHPF021	11347	08/13/02	ng/g wet	6.62E+01
UHPF022	11347	08/13/02	ng/g wet	4.59E+02
UHPF023	11347	08/13/02	ng/g wet	5.68E+02
UHPF024	11382	08/11/02	ng/g wet	1.06E+02
UHPF025	13309	08/30/02	ng/g wet	6.04E+01
UHPF026	14560	08/30/02	ng/g wet	3.74E+01
UHPF027	15464	08/18/02	ng/g wet	4.13E+00
UHPF028	15908	09/11/02	ng/g wet	8.67E+01
UHPF029	15908	09/11/02	ng/g wet	4.94E+01
UHPF030	16213	09/11/02	ng/g wet	1.27E+02
UHPF031	13337	08/14/02	ng/g wet	1.40E+02
UHPF032	13337	08/14/02	ng/g wet	1.09E+02
UHPF033	13338	08/23/02	ng/g wet	1.78E+02
UHPF034	13336	08/27/02	ng/g wet	1.71E+01
UHPF035	13336	08/27/02	ng/g wet	5.13E+01
UHPF036	11092	08/02/02	ng/g wet	3.55E+01
UHPF037	13339	08/23/02	ng/g wet	1.21E+02
UHPF038	13339	08/23/02	ng/g wet	1.04E+02
UHPF039	16499	08/23/02	ng/g wet	7.89E+01
UHPF040	16499	08/23/02	ng/g wet	1.90E+02
UHPF041	13340	08/07/02	ng/g wet	5.21E+01
UHPF042	13341	08/09/02	ng/g wet	1.05E+02
UHPF043	13342	08/22/02	ng/g wet	1.33E+02

Table A.3 Catfish concentrations (continued)

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPF044	17971	08/24/02	ng/g wet	8.75E+01
UHPF045	13343	08/20/02	ng/g wet	9.49E+01
UHPF046	13344	08/21/02	ng/g wet	1.92E+02
UHPF047	16496	08/21/02	ng/g wet	1.06E+02
UHPF048	13355	08/18/02	ng/g wet	8.79E+01
UHPF049	17970	08/18/02	ng/g wet	2.51E+01
UHPF050	13589	08/17/02	ng/g wet	8.02E+01
UHPF051	13589	08/17/02	ng/g wet	7.00E+01
UHPF052	11193	11/20/02	ng/g wet	7.66E+01
UHPF053	11200	11/21/02	ng/g wet	9.03E+01
UHPF054	11200	11/19/02	ng/g wet	3.17E+01
UHPF055	11200	11/21/02	ng/g wet	1.81E+02
UHPF056	11252	10/24/02	ng/g wet	1.18E+02
UHPF057	11261	10/26/02	ng/g wet	1.49E+02
UHPF058	11272	07/26/02	ng/g wet	3.13E+01
UHPF059	11272	07/26/02	ng/g wet	3.75E+01
UHPF060	11292	12/02/02	ng/g wet	2.14E+02
UHPF061	11280	12/05/02	ng/g wet	7.28E+01
UHPF062	13338	10/22/02	ng/g wet	1.14E+02
UHPF063	13338	10/22/02	ng/g wet	1.39E+02
UHPF064	13336	10/22/02	ng/g wet	1.09E+02
UHPF065	16499	10/24/02	ng/g wet	7.58E+01
UHPF067	13342	10/28/02	ng/g wet	6.80E+01
UHPF068	17971	10/28/02	ng/g wet	1.54E+02
UHPF069	13344	10/27/02	ng/g wet	1.25E+02
UHPF074	11273	04/29/03	ng/g wet	2.35E+02
UHPF075	11092	04/30/03	ng/g wet	1.62E+01
UHPF076	11272	04/30/03	ng/g wet	4.71E+01
UHPF077	11274	05/01/03	ng/g wet	9.66E+01
UHPF078	11302	05/01/03	ng/g wet	5.80E+01
UHPF079	11111	05/01/03	ng/g wet	4.04E+01
UHPF080	11382	05/02/03	ng/g wet	1.93E+02
UHPF081	11347	05/02/03	ng/g wet	1.81E+02
UHPF082	13342	05/11/03	ng/g wet	4.87E+02
UHPF083	13309	05/12/03	ng/g wet	1.74E+02
UHPF084	11193	05/14/03	ng/g wet	8.57E+01
UHPF085	11252	05/16/03	ng/g wet	1.65E+01
UHPF086	13589	05/16/03	ng/g wet	2.12E+01
UHPF087	11287	05/05/03	ng/g wet	2.25E+02
UHPF088	16618	05/05/03	ng/g wet	2.49E+02
UHPF089	11280	05/06/03	ng/g wet	4.37E+02
UHPF090	11270	05/06/03	ng/g wet	2.41E+02
UHPF091	15908	05/28/03	ng/g wet	9.56E+01
UHPF092	13355	05/28/03	ng/g wet	8.65E+01

Table A.3 Catfish concentrations (continued)

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPF093	11292	05/30/03	ng/g wet	5.42E+02
UHPF094	11298	05/01/03	ng/g wet	7.51E+01
UHPF095	11305	05/03/03	ng/g wet	2.39E+02
UHPF096	13339	05/04/03	ng/g wet	2.19E+02
UHPF097	11261	05/10/03	ng/g wet	1.63E+02
UHPF098	16496	05/11/03	ng/g wet	1.28E+02
UHPF099	11264	05/15/03	ng/g wet	3.40E+02
UHPF100	11092	04/30/03	ng/g wet	1.68E+01
UHPF101	11382	05/02/03	ng/g wet	1.53E+02
UHPF102	16496	05/11/03	ng/g wet	2.47E+02
UHPF103	11287	08/25/02	ng/g wet	9.87E+01
UHPF104	13363	08/17/02	ng/g wet	5.01E+01
UHPF105	17970	10/24/02	ng/g wet	1.05E+02
UHPF106	17970	10/24/02	ng/g wet	1.25E+02
UHPF107	11274	07/30/02	ng/g wet	1.61E+02

Table A.4 Crab concentrations

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPC001	11111	07/31/02	ng/g wet	13.2
UHPC002	11193	08/09/02	ng/g wet	58.2
UHPC003	11200	09/02/02	ng/g wet	19.9
UHPC004	16622	09/02/02	ng/g wet	28.4
UHPC005	11252	08/29/02	ng/g wet	5.7
UHPC006	11252	08/29/02	ng/g wet	7.8
UHPC007	11258	08/01/02	ng/g wet	57.8
UHPC008	11261	08/20/02	ng/g wet	39.8
UHPC009	16618	08/20/02	ng/g wet	51.0
UHPC010	11273	08/28/02	ng/g wet	74.9
UHPC011	11273	08/28/02	ng/g wet	169.5
UHPC012	11270	08/28/02	ng/g wet	53.1
UHPC013	11264	08/20/02	ng/g wet	56.6
UHPC014	15979	09/05/02	ng/g wet	40.3
UHPC015	11287	08/25/02	ng/g wet	68.6
UHPC016	11287	08/25/02	ng/g wet	17.1
UHPC017	11292	09/11/02	ng/g wet	41.0
UHPC018	11300	09/09/02	ng/g wet	30.9
UHPC019	11302	08/26/02	ng/g wet	42.3
UHPC020	11305	08/14/02	ng/g wet	33.6
UHPC021	11280	08/28/02	ng/g wet	81.2
UHPC022	11280	08/28/02	ng/g wet	38.0
UHPC023	11347	08/12/02	ng/g wet	15.2
UHPC024	11382	08/13/02	ng/g wet	9.2
UHPC025	13309	09/11/02	ng/g wet	8.9
UHPC026	14560	08/30/02	ng/g wet	25.7
UHPC027	15464	08/17/02	ng/g wet	5.3
UHPC028	15908	09/11/02	ng/g wet	5.7
UHPC029	16213	09/10/02	ng/g wet	3.4
UHPC033	13337	08/14/02	ng/g wet	9.0
UHPC034	13338	08/23/02	ng/g wet	11.4
UHPC035	13336	08/27/02	ng/g wet	4.6
UHPC036	11092	08/02/02	ng/g wet	12.7
UHPC037	13339	08/25/02	ng/g wet	28.3
UHPC038	13339	08/23/02	ng/g wet	47.7
UHPC039	16499	08/23/02	ng/g wet	37.2
UHPC040	13340	08/07/02	ng/g wet	8.0
UHPC041	13341	08/16/02	ng/g wet	6.4
UHPC042	13342	08/24/02	ng/g wet	39.3
UHPC043	17971	08/24/02	ng/g wet	53.7
UHPC044	13343	09/04/02	ng/g wet	34.9
UHPC045	13344	08/23/02	ng/g wet	21.4
UHPC046	13344	08/23/02	ng/g wet	37.8
UHPC047	16496	08/24/02	ng/g wet	20.2

Table A.4 Crab concentrations (continued)

Tag ID	Station ID	Sample Date	Unit	Concentration
UHPC048	13355	08/18/02	ng/g wet	33.0
UHPC049	13355	08/18/02	ng/g wet	16.4
UHPC050	17970	08/18/02	ng/g wet	31.1
UHPC051	13363	08/17/02	ng/g wet	9.1
UHPC052	13589	08/17/02	ng/g wet	11.9
UHPC053	13589	08/17/02	ng/g wet	4.9
UHPC056	11252	11/13/02	ng/g wet	20.2
UHPC057	11261	10/25/02	ng/g wet	17.2
UHPC058	11272	07/26/02	ng/g wet	9.2
UHPC059	13338	10/22/02	ng/g wet	28.1
UHPC060	13336	10/22/02	ng/g wet	14.4
UHPC062	16499	10/24/02	ng/g wet	30.0
UHPC063	13342	10/28/02	ng/g wet	25.4
UHPC064	17971	10/28/02	ng/g wet	32.1
UHPC065	17971	10/28/02	ng/g wet	38.9
UHPC066	13344	11/14/02	ng/g wet	28.2
UHPC068	13344	10/27/02	ng/g wet	5.4
UHPC080	13363	11/16/02	ng/g wet	35.8
UHPC081	11274	07/30/02	ng/g wet	34.6
UHPC082	11298	07/29/02	ng/g wet	14.0
UHPC083	11193	10/21/02	ng/g wet	7.6
UHPC084	13340	10/22/02	ng/g wet	14.7
UHPC085	17970	10/24/02	ng/g wet	21.0
UHPC086	15464	11/13/02	ng/g wet	3.4