Total Maximum Daily Loads for PCBs in the Houston Ship Channel

Contract No. 582-6-70860
Work Order No. 582-6-70860-29

Quarterly Report 4

Prepared by
University of Houston
Parsons Water & Infrastructure

Principal Investigators
Hanadi Rifai
Randy Palachek

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

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

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

September 2010

TABLE OF CONTENTS

1. 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 (TDSHS) to issue seafood consumption advisories, and some of these advisories have been issued for the Houston Ship Channel (HSC). Three 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 Morgan's Point. In addition to these two finfish advisories, the TDSHS issued ADV-35 (for PCBs and dioxins) that advises against consumption of gafftopsail Catfish and speckled trout in upper Galveston Bay, lower Galveston Bay, and Trinity Bay. These advisories represent a large surface water system for which a PCB TMDL needs to be developed and implemented. The overall purpose of this project is to develop a total maximum daily load (TMDL) allocation for PCBs in the Houston Ship Channel System, including upper Galveston Bay. Though ADV-35 covers surface water beyond upper Galveston Bay, the TMDL boundary is currently set for upper Galveston Bay. Chapter 2 presents the status of the QAPP for the project, while Chapter 3 presents the quality assurance activities. Chapter 4 presents the data analysis from the sampling activities undertaken in FY09.

2. QUALITY ASSURANCE PROJECT PLAN

Appendix A of this report includes the annual update of the Quality Assurance Project Plan (QAPP) for this fiscal year. The monitoring QAPP as it exists for the fiscal year 2009 is current for fiscal year 2010 without any substantive modification. Changes that have been made pertain to personnel names, organizational chart, and dates. The sampling that was performed in 2009 has also been updated. Runoff and Effluent sampling that remains to be completed has been updated. Potential sampling to obtain a snapshot post hurricane Ike was included in the QAPP update.

Based on the results from 2009 sampling, it was determined that increases in sediment, tissue, and water concentrations were observed in 2009 relative to 2002-2003 and 2008. These increases are possibly due to hurricane Ike and the dry weather patterns that were prevalent in summer 2009. As a result, a select number of sites sampled in 2008 and 2009 for sediment, tissue, and water may be resampled in FY11 to provide a second snapshot of PCB status beyond Ike and assess post Ike status and trends. Sediment and tissue sites (21 locations) selected for the snapshot include: 11132, 11292, 11287, 11298, 11280, 11274, 11270, 15979, 17157, 17149, 11272, 15936, 18322, 11265, 11264, 11197, 11193, 15301, 11261, 13344, and 13342. Alternate sites may be used depending on resources, access, and other considerations that emerge during sampling. Water sites (19) include: 11292, 11132, 11287, 11300, 11280, 20574, 11280, 11274, 15936, 15979, 11270, 17157, 17149, 11265, 11272, 11264, 11261, 16499, and 13355. Similar to sediment and tissue, alternate water sites may be used depending on resources, access, and other considerations that emerge during sampling.

3. QUALITY ASSURANCE/QUALITY CONTROL

3.1 QA/QC of sampling results

The quality assurance/quality control (QA/QC) tasks have been completed for sampling performed in 2009 that included monitoring/coordinating sample deliveries to the laboratories, verifying laboratory compliance with the QAPP, and verification of data packages. There were no major noncompliant issues encountered in the shipping and receiving of the samples collected. All samples were received from the sample site to the UH laboratory and from the UH laboratory to analytical laboratories without incident and were within the temperature range specified in the QAPP.

Once the sample results were obtained from the labs, UH/Parsons personnel using QA/QC criteria specified in the QAPP reviewed the results. The QA/QC requirements outlined in the QAPP included: holding times, method blanks, initial calibration curves, ambient water reporting limits (AWRL) verification, laboratory control sample (LCS), field duplicates, matrix spikes/matrix spike duplicates, laboratory duplicates, continuing calibration samples, surrogates, and internal standards. Table 3.1 lists the types and numbers of samples collected, data received and data reviewed from the Spring-Summer 2009 sampling. Table 3.2 shows the data flags that were used to designate the data as needed based on the QA/QC review.

Table 3.1 Percentage of sample results obtained and reviewed for QA/QC

Laboratory	Media	Analysis	Number of samples collected	Number of sample results obtained from laboratory	Number of sample results reviewed for QA/QC	% Results reviewed for QA/QC
Xenco/NWDL	Water	TSS, DOC, TOC	81	81	81	100%
Xenco/PTS	Sediment	Grain size and Solids content	42	42	*	*
Maxxam	Water	PCB (209 Congeners)	174	174	174	100%
Pace	Sediment	PCB (209 Congeners)	42	42	42	100%
Maxxam	Sediment	TOC	42	42	42	100%
Pace	Fish	PCB (209 Congeners), Lipid and Moisture content*	58	58	58	100%

* no specific QA/QC criterion.

Table 3.2 Standardized flags assigned to sample results

Flag	Description
B	Blank contamination (result is less than twenty times the amount found in the associated blank)
D	Surrogate/Internal Standard exceedance
E	Estimated
F	Field duplicate exceedance (%RPD of parent/duplicate sample > 50%)
H	Holding time exceedance
I	Ion ratio failure
J	Result is between the method detection limit (MDL) and the reporting level (RL) or the value is to be considered an estimate due to quality control issues involved in the analysis
L	Lab duplicate exceedance (%RPD of lab/lab duplicate sample > 50%)
M	Matrix spike exceedance
Q	Limit of Quantitation (LOQ) exceedance
R	Sample result is to be rejected and is considered unusable
S	Blank spike or lab control spike exceedance
U	Target analyte is not detected above the method detection level (MDL) in the sample

Table 3.3 below lists the percent of samples that have been flagged as a result of QA/QC analysis for all of 2009 sampling. As can be seen from Table 3.3, the majority of the flags were associated with the PCB results in water (46.4%) and fish (31.3%) for non-detects (“U” flag).

Table 3.3 Percentage sample results reviewed and flagged for QA/QC criteria

Analysis	Samples QA/QC reviewed/Samples collected*	Percentage results flagged for										
		U	B	J	E	H	F	M	Q	D	S	I
DOC-Water	81/81				6.17%			2.47%				
TOC-Water	81/81				6.17%							
TSS-Water	81/81	9.88%				6.17%	4.94%					
TOC-Sediment	42/42								1.23%			
PCB (209 Congeners) ¶ -Water	174	46.36%	0.34%	15.39%			0.47%		0.71%	0.31%	0.19%	0.01%
PCB (209 Congeners) ¶ -Sediment	42/42	0.44%	0.05%				2.94%	0.14%	1.08%			0.22%
PCB (209 Congeners) ¶-Fish	58/58	31.27%	0.14%						1.93%			0.17%

¶ Flagging Percentage based on individual congeners in the case of PCB.

4.41%

4. DATA ANALYSIS

4.1 Homolog Examination

Most of this section focuses on congener level analysis, but it is a valuable to consider the overall picture of the homologs before going into congener level detail. Figure 4.1 presents a statistical summary of the homolog profiles as wet weight of all fish samples from summer 2009 data collection as medians and means. In general, the plot shows that the highest contributors to the total PCB concentration in fish are at chlorinations 4-7. The trend of increasing concentrations is homologue 7 to homologue 4 using the mean and homologue 4 to homologue 6 using the median.

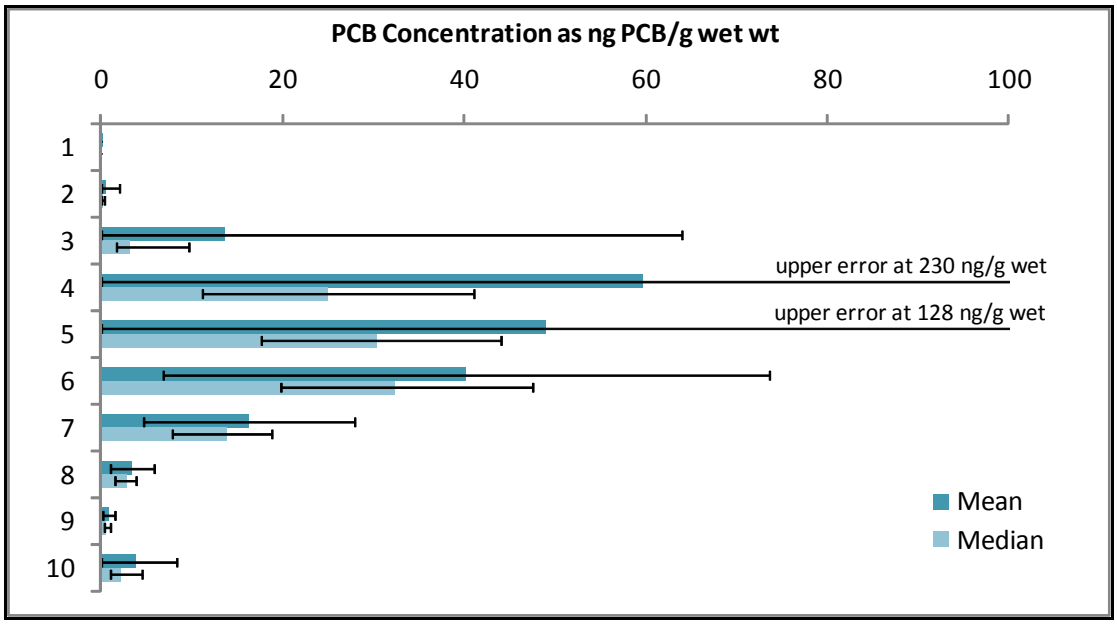


Figure 4.1 Median and mean homolog concentrations with first-third quartile and standard deviation error bars, respectively. Non-detects treated as analytical zeros on a total of 55 fish tissue samples not separated by species.

4.2 Congener Examination

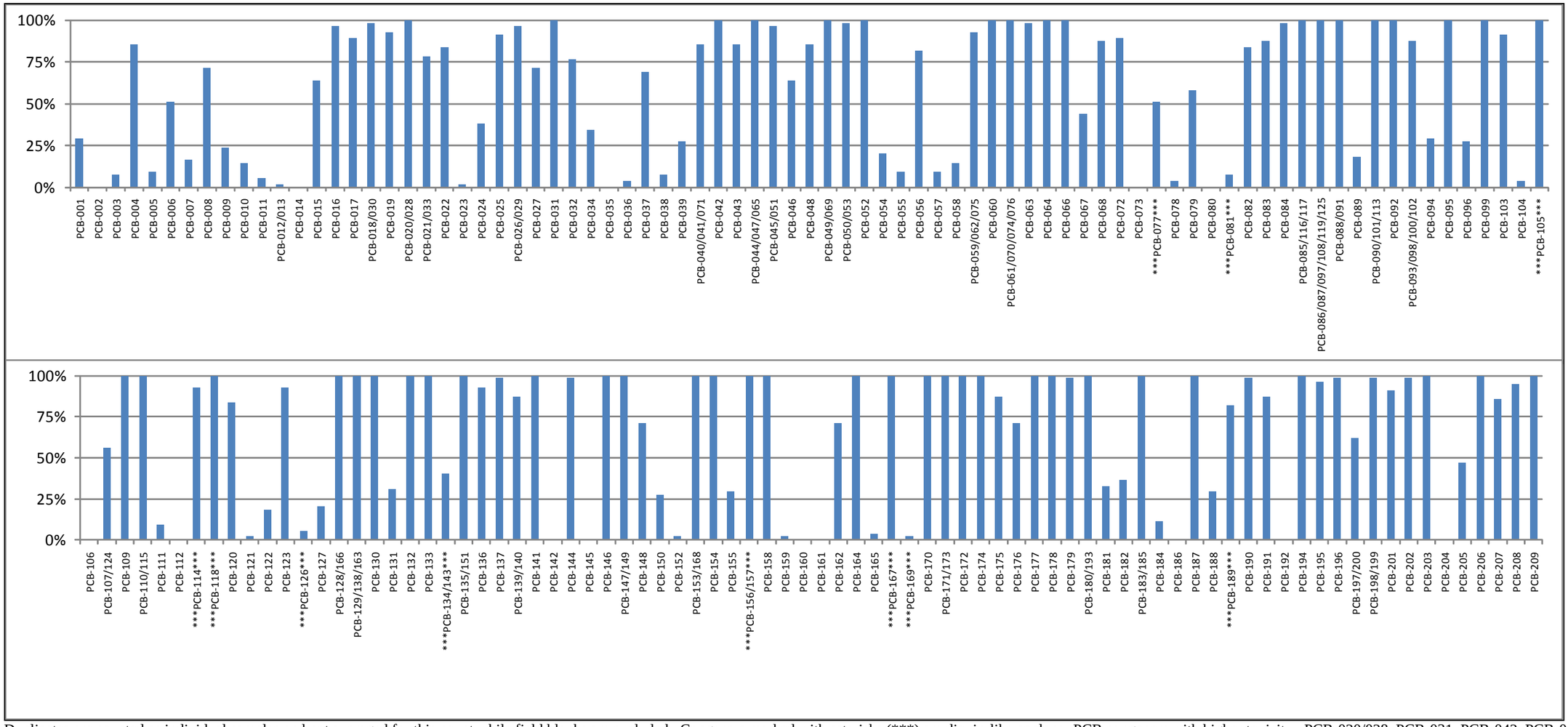
The examination of congener-specific data may at first seem daunting, but there are several considerations that lower the amount of relevant information and analysis. The first is what is built into the analytical chemistry process. Though there are 209 distinct PCB congeners, few if any laboratories can resolve them individually in samples that are at ultratrace or trace levels. Pace Analytial has been able to resolve 163 chemical analytes, some of which are individual congeners and some of which are coelutes, groups of congeners that leave the gas chromatogram (GC) at nearly the same time and thus mesh together into a single GC peak. The second data-limiting agent inherent in nearly all PCB data are non-detects. Non-detects are common in nearly all chemical and biological analysis of environmental samples, but with PCBs, non-detects are not always directly seen. PCBs are often viewed as congener sums for ease of

spatial-temporal understanding and risk. These are usually sums by chlorination, by according to dioxin-like and non-dioxin like identity, as a set more representative of the total such as the McFarland and Clarke (1989), or as all 209 congeners. It would be convenient if, in all media analyzed, the same congeners were detected and non-detected. This is not the case for many reasons, two of which are (1) that more lightly chlorinated congeners often volatilize before they can significantly and detectably associate with fish tissue and (2) that some congeners are more efficiently removed from biota or are biotransformed into another congener or a non-PCB species entirely.

Regardless of the reason for the change in detection between media, a detailed detection rate in the 2009 fish tissue samples was generated in Figure 4.2. The figure quickly provides a summary of congeners found in 2009 tissue samples and shows those that are only marginally present. There were 49 of the total 163 analytes detected 100% of the time. The exact list is given in the figure, but is important to note that out of 11 dioxin-like PCB analytes, only 4 (105, 118, 156/157, and 167) were detected 100% of the time. There were 14 of 163 congeners that were not detected in any fish tissue sample from 2009, and none of these were dioxin-like congeners. Out of the four100% detection rate dioxin-like congers, the Toxic Equivalency Factor (TEF) was 0.0005 or less. The two highest dioxin-like congeners with TEFs of 0.1 and 0.01 for PCB 126 and 169, respectively, exhibited detection rates of only 5 and 2%. For the practical purpose of eliminating congeners in this dataset, one can use a reasonable cutoff of 40% detection or greater and arrive at a PCB analyte list of 109 out of the original 163, a 33% reduction in the total dataset. A slightly less conservative cutoff of 50% gives 106 remaining analytes of the original 163, a 35% reduction. What would be removed is of no or mostly

marginal significance except in cases where the rare presence of an analyte is useful to characterize an abiotic transfer of PCB that is more unique to just a few fish samples.

The 50% detection rate PCB analyte reduction was applied to median statistic congener profiles of all 2009 fish tissue samples shown in Figure 4.3 (concentrations in wet weight) and Figure 4.4 (concentrations in lipid weight). Lipid variation is not excessively great amongst the fish samples, and so the statistical summary of medians as presented does not yield a visual profile that is different between concentration bases. Using the wet weight figure, it is fairly clear that there are a few dominant congeners over 2 ng PCB/g wet, which dominate a sum of 209 congeners concentration. The number of these congeners is 16, and when considering a "median sample", a statistically hypothetical sample consisting only of the medians, these 16 congeners make up 67% of the sample. Using a cutoff of 1 ng PCB/g wet give 25 congeners with a cumulative contribution of the median as sample as 79%. Finally, if an individual PCB congener concentration cutoff of 0.15 ng/g wet is used, then the result is 71 congeners that contain 96% of the median sample concentration. These 71 congeners would likely be the most useful and relevant PCB analyte subset for fish tissue concentrations and includes only four dioxin-like PCB congeners as shown with their median values in ng/g wet, PCB 118 (5.81), PCB 105 (1.83), PCB 156/157 (0.71), and PCB 167 (0.29). Not surprisingly, these significant (> 0.150 ng/g wet) concentration congeners are the same ones that had a high detection rate (78% or greater, 49 of 71 at 100%).



Duplicates are counted as individual samples and not averaged for this count while field blanks are excluded. Congeners marked with asterisks (***) are dioxin-like coplanar PCB congeners with higher toxicity. PCB-020/028, PCB-031, PCB-042, PCB-044/047/065, PCB-049/069, PCB-052, PCB-060, PCB-061/070/074/076, PCB-064, PCB-066, PCB-085/116/117, PCB-086/087/097/108/119/125, PCB-088/091, PCB-090/101/113, PCB-092, PCB-095, PCB-099, PCB-105, PCB-109, PCB-110/115, PCB-118, PCB-128/166, PCB-129/138/163, PCB-130, PCB-132, PCB-133, PCB-135/151, PCB-141, PCB-146, PCB-147/149, PCB-153/168, PCB-154, PCB-156/157, PCB-158, PCB-164, PCB-167, PCB-170, PCB-171/173, PCB-172, PCB-174, PCB-177, PCB-178, PCB-180/193, PCB-183/185, PCB-187, PCB-194, PCB-203, PCB-206, PCB-209 are congeners with 100% detection (49 of 163 possible congener/co-elutes), and PCB-002, PCB-014, PCB-035, PCB-073, PCB-080, PCB-106, PCB-112, PCB-142, PCB-145, PCB-160, PCB-161, PCB-186, PCB-192, PCB-204 (14 of 163) were not detected in a single tissue sample from summer 2009. All dioxin-like congeners were detected in at least one sample.

Figure 4.2 Detection percentages for the 55 fish tissue samples tested for PCB in the summer of 2009.

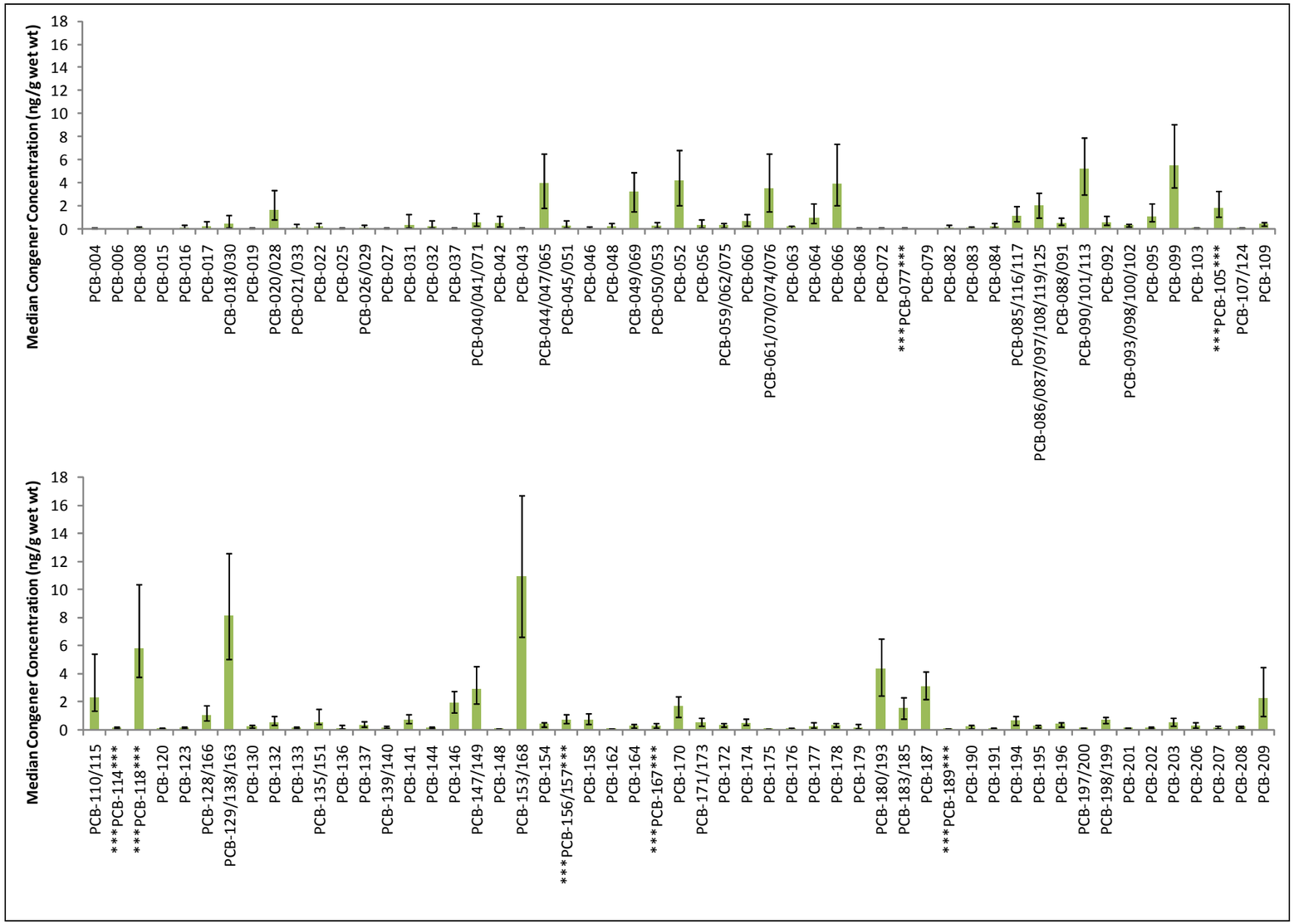


Figure 4.3 Median concentration values of individual PCB congeners in ng/g wet wt for all congeners with 50% or greater detection (lower detection rates excluded). Statistics were determined only by use of detected values, and error bars are the first and third quartiles. Dioxin-like PCB congeners are marked with triple asterisks (***).

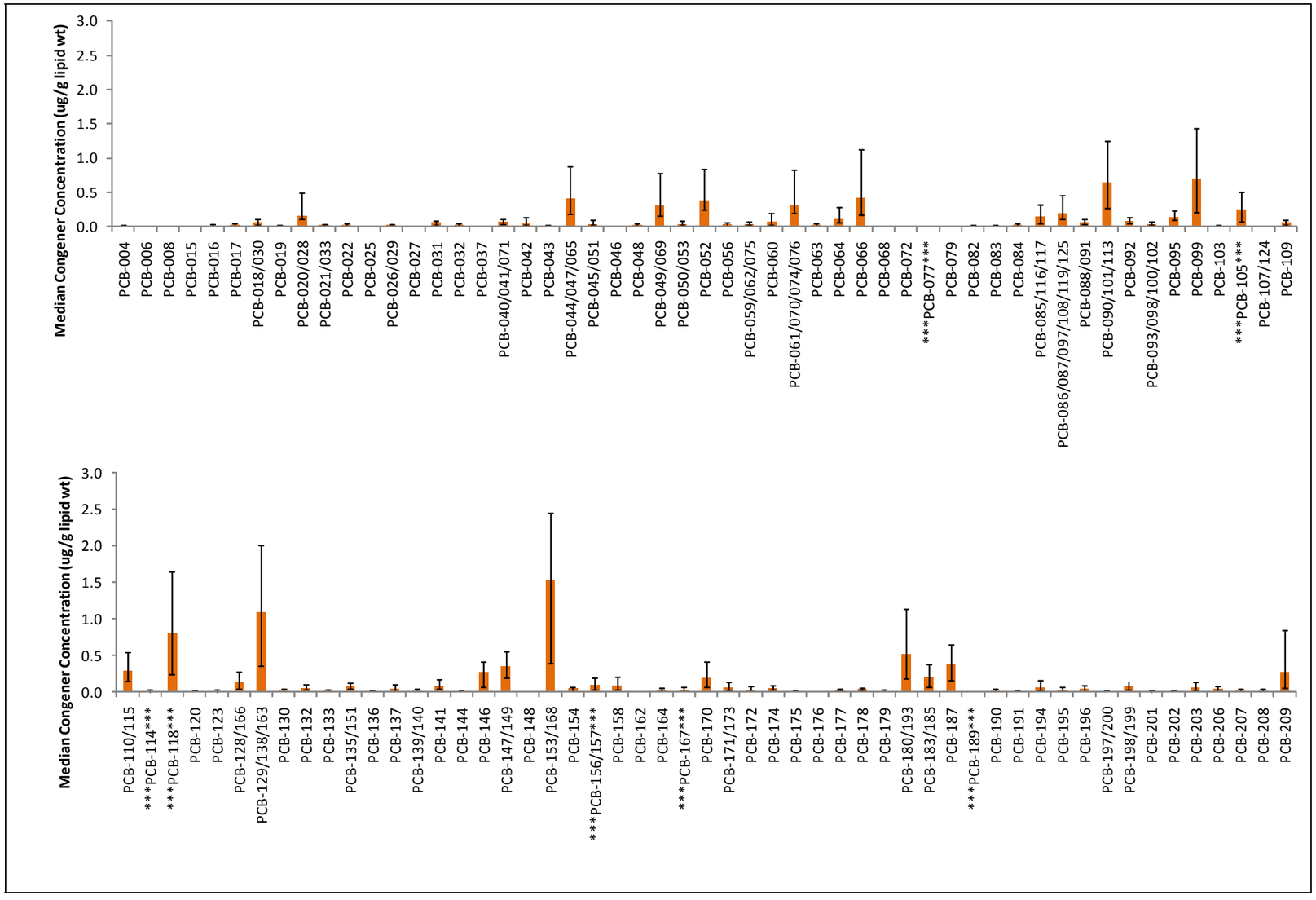


Figure 4.4 Median concentration values of individual PCB congeners in ng/g lipid wt for all congeners with 50% or greater detection (lower detection rates excluded). Statistics were determined only by use of detected values, and error bars are the first and third quartiles. Dioxin-like PCB congeners are marked with triple asterisks (***).

4.3 Spatial Trends

Statistical analyses were performed on individual PCB congener concentrations as lipid weight basis to ascertain the existence or non-existence of a linear parametric (Pearson R) or nonparametric rank-based trend (Spearman R) with river distance. Non-detect values were excluded to avoid detection limit-based sources of error, and some congeners that had a low amount of detects were not included. As a result, only 106 out of 163 congeners/coelute groups were spatially examined by correlation with distance. Analyses were performed on fish samples from all stations together including main channel, side bay, and tributary samples ("all locations") and main channel only.

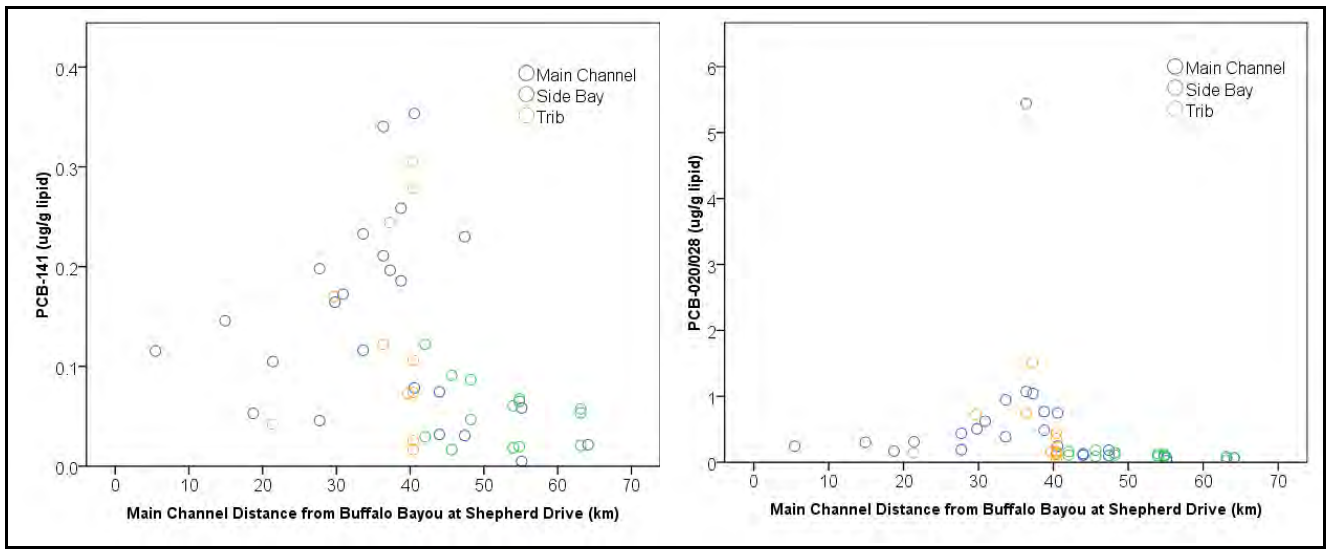
When all locations were considered, the Pearson correlations yielded statistically small value ($p < 0.05$) in a few congeners. These values were all at an absolute level of approximately 0.3 (exact range -0.284 to -0.335) and were negative (increasing distance downstream lowers the concentration of the congener). The significant Pearson correlation congeners for all locations together were PCB 68, PCB 93/98/100/102, PCB 141, PCB 158, PCB 170, PCB 174, and PCB 177. By Spearman rank-based spatial correlation, nearly all of the congeners/coelute groupings that met the suitable level of detection criterion (94 of 106) were significantly (at least $p < 0.05$, most at $p < 0.01$) correlated to river mile distance. All correlations were negative and in the range of -0.290 to -0.737.

Spatial correlation analysis of only Main channel locations yielded no significant Pearson correlations and a few significant and negative Spearman correlations. The congeners with significant ($p < 0.01$ in this case) Spearman correlations were PCB 42, PCB 135/151, and PCB 147/149 with values of -0.413, -0.483, and -0.465, respectively.

To help visualize the practical significance of these values, the best correlations are plotted in Figure 4.5 and Figure 4.6 as bivariate scatters. For all location correlations, the highest Pearson correlation was with congener PCB 141 while for Spearman it was for PCB 20/28 (Figure 4.5). For the main channel locations, the highest Spearman correlation (none of the Pearson correlations were significant) was with PCB 135/151 (Figure 4.6). As a general pattern, the plots (whether they include all types of locations or not) seem to show a large peak at around 38 km, right in the region between the Shell barge cut and the SJR-HSC confluence. Numerically, the correlations (parametric and rank-based) give a value that is negative. These plots are valuable because they give a sense of what a -0.7 Spearman correlation actually looks like. It would seem that even if the numerical value is high, data may scatter in such a way as to yield a visual trend that is neither consistently decreasing nor increasing.

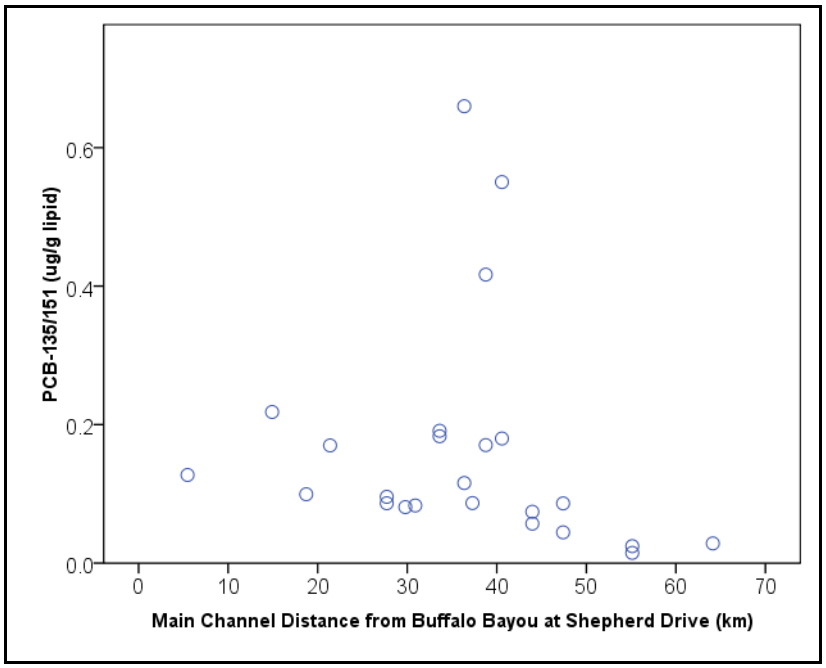
There is one extreme concentration sample that was collected at station 15936, Houston Ship Channel at the OxyChem ditch (seen as much higher than the rest in the spatial plot of PCB 020/028). It ranks highest out of all 2009 fish samples collected (123 ug/g lipid ΣPCB209). There was one sample collected in 2008 that was higher than this in an Atlantic Croaker sample. It was the highest of 2008 and also at 15936; a Hardhead Catfish sample at that location analyzed showed a value of 150 ug/g lipid. In the sampling conducted in 2002-2003, there is one sample higher than the 2009 Atlantic Croaker sample. It was at station 16622, San Jacinto River (SJR) at Banana Bend, with a ΣPCB209 value of 408 ug/g lipid. This value at SJR has been and remains the highest recorded ΣPCB209 concentration ever taken by UH. It is noted that this particular congener, PCB 209, is an odd congener to find in high abundance in surface waters. The source of this congener may be unusual Aroclor mixtures used in the history of the HSC or contemporary air sources from local industry. The 2009 Atlantic Croaker sample at 15936 is,

however, the highest concentration for a secondary species that has been found in 2008-2009, the time period at which UH began collecting the secondary species (Atlantic Croaker, Speckled Sea Trout, Red Drum). The next highest secondary species sample was also in Atlantic Croaker in the summer of 2009, but it was at 11264, HSC at the Battleship. The concentration here was much lower at 31.7 ng ΣPCB209/g lipid. The catch of secondary species was almost the furthest upstream for secondary species except for one sample collected in 2009 at 11280, HSC at Armco Steel, which had a much lower concentration of 6.52 ng ΣPCB209/g lipid. The locations at 11280 and 15936 are, due to salinity conditions, nearly the furthest upstream that one would expect to find Atlantic Croaker or other secondary priority species.



Distances are in reference to Buffalo Bayou at Shepherd Drive. Congeners chosen exhibited the highest lipid based concentration with channel distance as Pearson correlation (PCB 141, $R = -0.335$, $p < 0.05$) or highest Spearman correlation (PCB 020/028, $R=-0.737$, $p < 0.01$). The extreme value in the plot of PCB 020/028 is from an Atlantic Croaker sample collected at station 15936, Houston Ship Channel at the OxyChem ditch. The sample was composed of 4 individuals (3 male and 1 female).

Figure 4.5 PCB congener concentration in all fish samples regardless of species and location type versus distance along the main channel.



*Distances are in reference to Buffalo Bayou at Shepherd Drive. PCB 135/151 exhibited the highest lipid based concentration with channel distance as Spearman correlation ($R = -0.483$, $p < 0.05$). The highest value in the plot is from an Atlantic Croaker sample collected at station 15936, Houston Ship Channel at the OxyChem ditch. The sample was composed of 4 individuals (3 male and 1 female). It is the same high value as seen in the previous PCB 020/028 plot.

Figure 4.6 PCB congener concentrations in main channel only fish samples regardless of species versus distance along the main channel.

5. REFERENCES

McFarland, V.A., Clarke, J.U., 1989. Environmental Occurrence, Abundance, and Potential Toxicity of Polychlorinated Biphenyl Congeners: Considerations for a Congener-Specific Analysis. Environ. Health Perspect. 81, 225-239.

APPENDIX A

QUALITY ASSURANCE PROJECT PLAN