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

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

**Quarterly Report 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), which is shown according to TCEQ water quality segmentation in Figure 1.1. Two specific advisories have been issued recently for all finfish species based on concentrations of PCBs, organochlorine pesticides, and dioxins. ADV-20 was issued in October 2001 and includes the HSC upstream of the Lynchburg Ferry crossing and all contiguous waters, including the San Jacinto River Tidal below the U.S. Highway 90 bridge. ADV-28 was issued in January 2005 for Upper Galveston Bay (UGB) and the HSC and all contiguous waters north of a line drawn from Red Bluff Point to Five Mile Cut Marker to Houston Point. These two advisories represent a large surface water system for which TMDLs need to be developed and implemented.

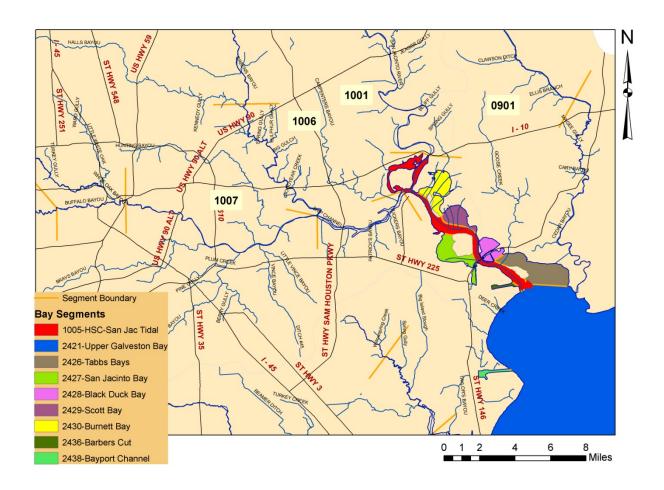


Figure 1.1. Houston Ship Channel water quality segmentation.

## 1.1 SCOPE OF THE PROJECT

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

#### 1.2 DESCRIPTION OF THE REPORT

This report summarizes the activities conducted by the University of Houston for the PCB TMDL Project under Work Order # 582-6-70680-19 for the 2nd quarter of 2008, which covers the period from December 1, 2007 to February 29,2008. The report contains a summary of efforts undertaken in the last quarter to gather dredging records from the Port of Houston Authority (PHA), and an analysis of velocity data obtained from the RMA2 hydrodynamic model for the HSC that was developed for the dioxin TMDL project. This analysis is intended to give an overall picture of the velocity distribution in the channel and to aid in understanding where sediment incipient motion conditions may be met. Lastly, the report contains a recommendation concerning the sampling and analysis of Particulate Organic Carbon (POC) and a detailed summary of the development of an intensive sediment sampling plan for segments 1006 and 1007 in the Channel.

## CHAPTER 2 - DATA GATHERING

The previous quarterly report mentioned the possibility of using dredging records to understand sedimentation rates and to perform a sediment balance on the HSC. This approach was pursued during this quarter although progress has been slow due to the time it has taken to gather the needed information. Permission to access the dredging information was requested from PHA and several trips were undertaken to PHA to gather the following data:

- Sediment Sampling Records The PHA had records from sampling events associated with companies that wished to use PHA disposal areas for their own dredged material pulled from their harbors. Also, the PHA dredges its own port areas, and sampling records are maintained for those. The records still need to be examined more exhaustively, but most sediment samples have non-detect results for PCBs though often those analyses were conducted with the less accurate Aroclor approach at a higher detection than would be used for this TMDL project.
- <u>Dredged Volumes</u> All dredged volume records related to actual disposal in PHA containment areas were provided to UH. These records are currently under study.
- <u>Dredging Narratives</u>: Though less frequent, some reports provided to UH contain information about the reason for dredging. For those cases where contamination is involved, this may be valuable in the sampling efforts for this project. For those cases where areas were continually dredged due to excessive sediment deposition, this information will be useful in understanding conceptually how sediment transport/accumulation might be occurring and will be useful as corroborative evidence to support the results from modeling.

The PHA data are currently being tabulated and will be presented in the next quarterly report. In terms of jurisdiction of dredging, the PHA only dredges in actual areas that are used as ports and receives dredge material from other ports along the HSC. The bulk of the dredged material comes from the navigational channel, but the actual dredging is completed by the Galveston District Army Corps of Engineers (COE). Their records will be requested and studied as well to determine their usefulness for this project.

## CHAPTER 3 - CHANNEL VELOCITY ANALYSIS

## 3.1 Background and Objectives

In considering the fate and transport of PCBs in the HSC, it is important to understand the velocity profile and the direction of velocity caused by the tidal influence along the Main channel and in the tributaries. The sign of the velocity indicates the direction of flow and the velocity magnitude indicates the flow rate at various points along the channel, which eventually helps in estimating the in stream PCB load at various segments in the Main channel and tributaries. Velocity is significant because it is a vital component of the conditions for sediment transport along with grain size and sediment cohesion. As part of the last quarterly report, calculations were made to understand the tidal influence along the channel based on the flow rate at various points in the channel. The results indicated some tidal influence on the channel and tributaries, but concrete conclusions could not be made with the flow analysis alone.

Velocity is a good measure of direction of flow because the loads into the streams as well as upstream loads and tributary loads will most often be high only when there is a positive velocity flow in the Main channel and the tributaries. The other effect is what has been deemed as the Segment 1007-1006 "bathtub effect." Segments 1006 and 1007 continue to remain abnormally high in water, sediment, and fish concentrations despite the likely cessation of large new sources in that area. One explanation for this is that the flow conditions in these upstream HSC segments discourages the downstream movement of sediment (suspected to be a major repository of PCBs) past the San Jacinto River (SJR) confluence due to a hydrodynamic "bathtub" whereby the combination of large SJR flows, tidal effects, and particle flocculation enhancement due to increasing salinity decreases net sediment velocity leading to increased sediment deposition rate. The result, if the effect exists, is that PCB contamination remains high in these segments and only in these segments as was found in the 2002-2003 dataset.

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

1. The velocity profile along the Main Channel and in San Jacinto River (SJR).

- 2. The velocity in the tributaries.
- 3. The tidal influence and thereby the direction of velocity in the Main channel, SJR and in the tributaries.

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

## 3.1.1 Velocity Calculations using Hydrodynamic Modeling Output

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

- Reliability
- Accuracy
- Temporal representativeness
- Spatial representativeness

The data source selected was the modeled velocities from the RMA2 hydrodynamic model\* used in the Dioxin TMDL project. The RMA2 model covered a three-year simulation period (07/20/2002 to 04/30/2005) that gave modeled velocities at various points in the channel and the tributaries. The output, however, was obtained from the WASP water quality model that gave velocities for each segment every 2 hours and 23 minutes on average. The measured data were not extensive enough to allow this analysis, but the modeled velocities were acceptable considering that the model flows, obtained from the velocities, are being used in the Dioxin TMDL. The data resolution in time was quite high with velocity being output every two hour and 23 minute intervals (on average) for any point throughout the channel. Data time resolution is critical in this analysis because a time step that averages a value over too large a period will

<sup>\*</sup> These velocities were not literally pulled from RMA2 modeling. The RMA hydrodynamic modeling results were entered into the WASP water quality model, and then the velocities were taken from the WASP output.

average out negative flow and negative velocity. The 2 hour and 23 minute interval should be sufficient because the tidal cycle from low to high is approximately 7.5 hours.<sup>†</sup>

The entire data set (all time steps) was analyzed for (1) the variation in the velocities along the Main Channel and in the tributaries and (2) percentage of time steps that the velocity was negative/positive along the Main Channel, SJR and in the tributaries. A brief overview of the WASP model segmentation is given below to understand the spatial grouping used in the analysis.

## 3.1.1.1 WASP Segmentation and Time Step

The WASP model segmentation had been developed by aggregating RMA2 elements to reaches maintaining the minimum segmentation required for water quality modeling. The WASP model for the HSC consists of 61 1-D water surface segments, 46 2-D water surface elements, and 107 benthic segments (one underlying each of the surface water segments) (Figure 3.1). Thirty-eight segments correspond to the main channel from Buffalo Bayou to the downstream boundary, twenty to the major tributaries, twenty-one to the San Jacinto River (including the Old River), and the remaining twenty-eight comprise the side bays, Barbour's Cut, Bayport Channel, Clear Lake, and Upper Galveston Bay.

<sup>†</sup> Based on averaging of NOAA tide data for January 2008 in Galveston Bay. http://tidesandcurrents.noaa.gov/get\_predictions.shtml?year=2008&stn=2310+Galveston

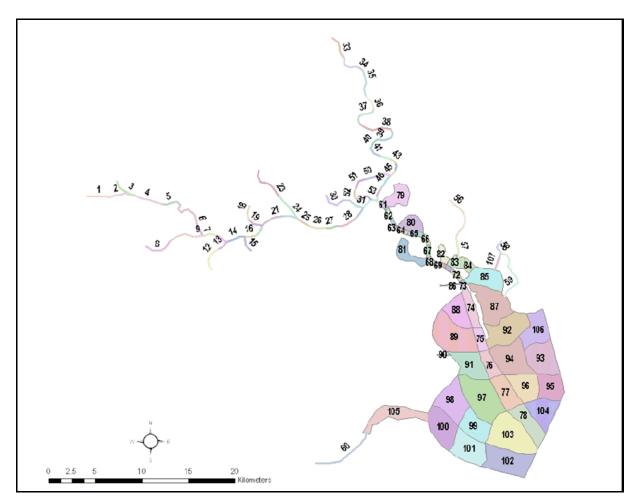


Figure 3.1. WASP model segmentation.

## 3.1.1.2 Segment Velocities and Negative-Positive Velocity Variations

The velocity data points obtained every 2 hour and 23 minutes were assessed to arrive at a fraction of the time that are negative and positive for segments of interest along the Main Channel and in the tributaries. Segments of interest are defined as:

• Main channel segments that are immediately upstream of major tributary confluences (i.e. tributaries that have a velocity that is a sizeable fraction of the main channel velocity at their confluence),

• Segments that were considered to be significantly impacted by tidal influence<sup>‡</sup>,

These segments were analyzed according (1) velocity comparisons between the Main Channel and tributaries, and (2) tidal influence in the channel as defined by flow reversals. Segments of interest were the tributary segments just before the confluence with the channel (Segment 9- Brays Bayou, Segment 13- Sims Bayou, Segment 15- Vince Bayou, Segment 19- Hunting Bayou, Segment 24- Greens Bayou, Segment 31- Carpenters Bayou, Segments in San Jacinto River (SJR) (segments 33, 39, 45, 51), the Main Channel segments before the confluence of the tributary and the channel segments after the confluence with the tributary down to Morgan's point (segments 1, 5, 7, 10, 14, 16, 20, 25, 29, 32, 61, 65, 68, 73). In addition, SJR segments were also selected from upstream of the river up until the confluence with Main channel. Finally, the tidal influence on the Main Channel and in the tributaries was interpreted by calculating the percentage of time steps where the velocity was negative or positive for each segment of interest.

#### 3.1.2 Results and Discussion

#### 3.1.2.1 Velocity in the Main Channel and the SJR over the simulation period

Figure 3.2 and Figure 3.3 show the average and median velocities in the main channel and in SJR respectively, over the entire course of the simulation period (07/20/2002 to 04/30/2005) for all time steps. The standard deviation is shown using error bars with respect to the mean.

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

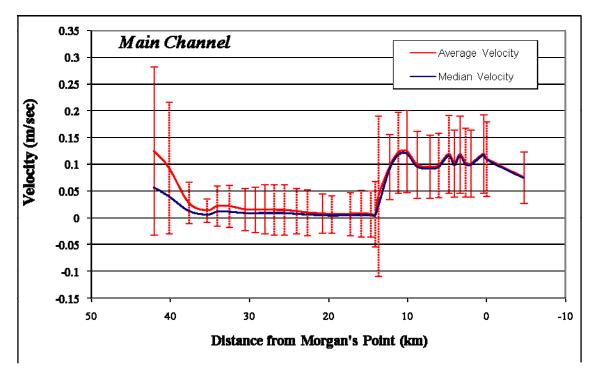


Figure 3.2. Average and Median velocities in the Main Channel. Error bars indicate standard deviations.

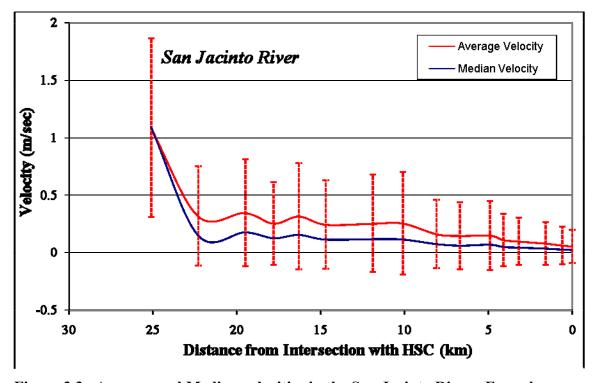


Figure 3.3. Average and Median velocities in the San Jacinto River. Error bars represent standard deviations.

Some important observations can be made from the data in Figure 3.2 and Figure 3.3:

- The average and median velocities<sup>§</sup> for the simulation period in the Main Channel and SJR were positive, thereby indicating a 100% net outflow. The median and average velocities from SJR were substantially higher when compared to the velocities in the Main channel.
- The upstream velocities both in the Main Channel (Buffalo Bayou) and SJR (Segment 33) were substantially high compared to the downstream velocities. This is because the tidal influence diminishes downstream velocities more than upstream velocities. The geometry of the channel downstream of the SJR confluence was also a factor because the channel cross-section increased, which results in lower velocities.
- The standard deviations were significantly high compared to the velocity average, both in the Main Channel and in SJR. This indicates highly variable velocity fluctuations over the simulation period. The large deviations in the channel and in the SJR are mainly due to the tidal influence though storm events also contribute to velocity variations.
- As can be seen from Figure 3.2, the average and median velocities significantly increased at about 15 km from Morgan's point, the confluence with SJR. The average velocities and the standard deviation associated with the mean were positive downstream of the confluence with SJR indicating a net positive velocity all the time. It is noted that the increase was more than a factor of 10, thereby indicating a significant contribution of velocity by SJR into the Main Channel. The velocity from SJR is so high that it prevents the tides from reversing the flow in the segments downstream of the confluence.

Figure 3.4 compares the average velocities along the Main Channel and the average velocities in the bayous. The solid line indicates the average velocity along the Main Channel, while the solid boxes indicate the average velocity in the tributaries just before the confluence with the Main Channel. The error bars along the boxes (averages) indicate the interquartile range (IQR), while the dashes above (green dash) and below (violet dash) the tributary averages indicate the upper and lower outlier boundaries.

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<sup>§</sup> Average and median velocities calculated with all the velocity data over the simulation period

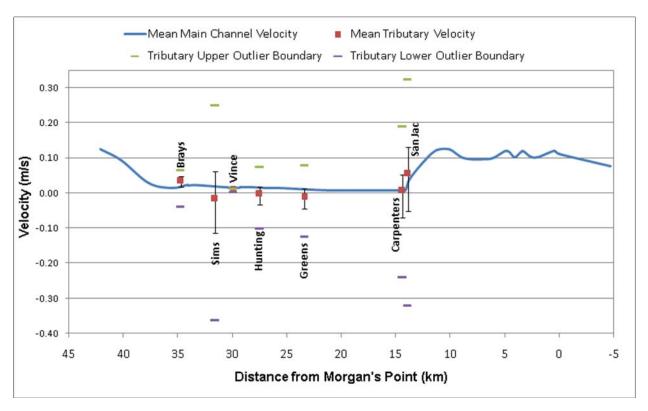


Figure 3.4. Average velocities in the tributaries compared to Main Channel velocity

The tributaries that were considered of importance were: Brays Bayou, Sims Bayou, Vince Bayou, Hunting Bayou, Greens Bayou, Carpenters Bayou, and San Jacinto River. Important observations can be made from the data:

- Except for a few outliers with negative velocity, Brays Bayou had an IQR that was always positive, indicating positive flow the majority of the time.
- The average velocity in Sims, Hunting, and Greens were negative indicating a significant backflow and tidal influence in those tributaries. While Hunting and Greens had a small IQR and a small outlier boundary range, Sims had one of the largest IQR and outlier boundary ranges. The large IQR in the case of Sims is due to the huge upper and lower outliers. Considering that the HSC itself is affected by tidal influence and has negative velocities, it is not surprising that the tributaries are affected and have average negative velocities over the three year period.

- The average velocity in Vince and Carpenters were positive over the course of simulation period. In the case of Vince, the IQR and outlier boundaries were positive and every time step in the simulation period had a net positive velocity. Even though Carpenters had a positive average velocity, the IQR and negative lower outlier boundary indicate the backward flow of water into Carpenters bayou during the simulation period.
- As mentioned previously, the San Jacinto River had the highest average velocity of all
  the tributaries and had a major impact on the Main Channel velocity downstream of the
  confluence of SJR. Even though SJR had a positive average velocity, the IQR
  encompassed negative values and had a large negative lower outlier boundary.

## 3.1.3 Velocity in the Tributaries and in the Main Channel

Appendix A shows the velocities in the Main Channel and tributaries over the simulation period. As can be observed from the figures, velocity fluctuations were significantly huge both in the tributaries and in the Main Channel, and the velocities were negative in some time steps indicating an observable tidal effect. The upstream segments in the Main Channel and SJR had velocity variations only on the positive side most of the time indicating minimum tidal observable effect. However the downstream segments had variations ranging from positive to negative velocity values. To observe the effects, four segments were selected which were representative of the velocity variations along the Main Channel: Segment 10-Upstream of the channel (Water Quality Segment 1007-upper), Segment 20 (Water Quality Segment 1007), Segment 25 (Water Quality Segment 1006), Segment 61- Confluence of SJR and Main channel (Water Quality Segment 1005-lower). Figure 3.5 shows the velocity profiles for the four segments for the simulation period. It can be seen that Segment 10 that is upstream of the channel had positive velocity  $3/4^{th}$  of the time, while Segment 20 and 25 had positive velocities only 60% of the time due to the segments being in the vicinity of the coastal area. As will be discussed later the % negative velocity timesteps increased as one moves from upstream to downstream of the channel. However the segments downstream of the confluence of SJR and Main channel had positive velocities 100% of the time (Segment 61 in Figure 3.5).

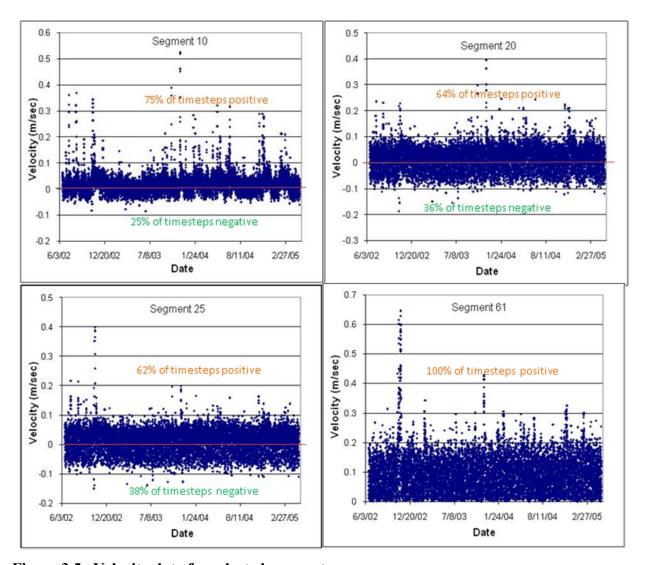


Figure 3.5. Velocity data for selected segments

The velocity data for the entire simulation period are shown as box plots in Figure 3.6. The figure shows the significant velocity variations in all the four segments. Segment 10, upstream of the channel has the least fluctuation of all the segments considered and had outliers mostly on the positive side and significantly less outliers than the other segments. Segments 20 and 25 had similar box plots and had huge IQR and large outliers both on the positive and negative side. In the case of Segment 61, the segment had huge outliers on the positive side and

no negative IQR or outliers, which confirms the positive net velocity downstream of the confluence of SJR during the simulation period.

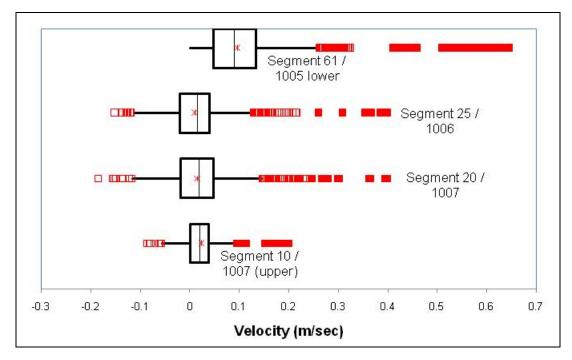


Figure 3.6. Box plots of absolute velocities along the Main Channel.

To better understand the velocity fluctuations, the velocity variations from the mean were normalized with respect to the mean ((Velocity- Mean Velocity)/Mean Velocity)) for the simulation period for the segments of interest, and the complete time series plots are given in Appendix B. The normalized velocity profiles and the box plots for Segments 10, 20, 25, and 61 are shown as Figure 3.7 and Figure 3.8, respectively. The normalized plots show the consistent change in water velocities from the mean, and the negative and positive variations from zero indicate the frequency of time steps with velocities less than or greater than the mean. It can be seen from Figure 3.7 that all the segments had approximately 50% of the time steps greater than or less than the mean. The magnitude of variation from the mean is observable from the box plots shown in Figure 3.8. The box plots for segments 20 and 25 indicate a huge IQR and significant number of outliers on both sides of the mean. This indicates a frequent velocity change in part due to the tidal influence. However in the case of Segment 10, the IQR and number of outliers are comparatively low partly due to less tidal influence. The segments downstream of the confluence of SJR (Segment 61) had low IQR and low number of outliers

only on the positive side which is understandable considering that the net velocities are positive downstream of the channel due to high velocities from SJR.

So considering the above segments along the Main Channel, the tidal influence along the Main channel can be classified into three major areas: Segments upstream of the channel which are less affected by the tidal influence, segments close to the coastal area which are significantly affected (half the time) by tidal influence, and segments downstream of the confluence of SJR which are likely affected by tidal influence, however had net positive outflows all the time.

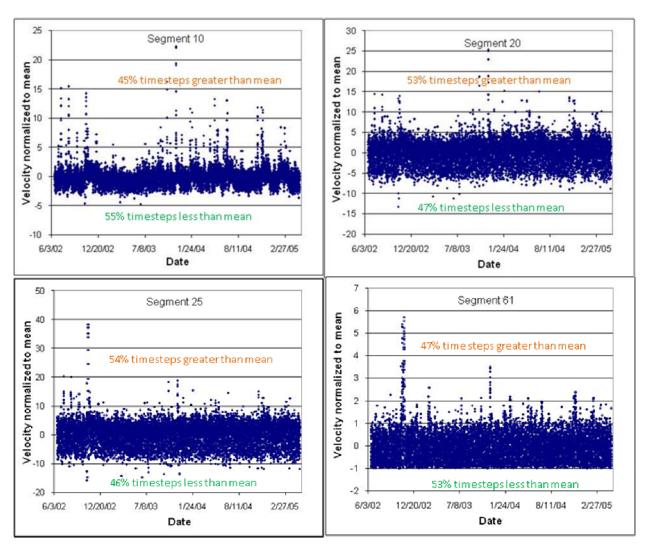


Figure 3.7. Velocity variations with respect to the mean along the Main Channel. Every value is the variation from the mean velocity and then divided by the mean.

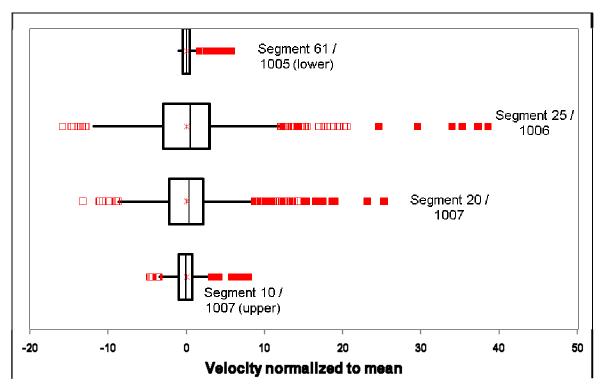


Figure 3.8. Box plots of velocities normalized to the mean along the Main Channel.

The summary statistics for the velocity in the tributaries (2 hour and 23 minute velocity data) over the simulation period are given in Table 3.1. It can be observed that SJR had the highest velocity of all the tributaries and thus had a major effect on the HSC compared to other tributaries. All the tributaries except Vince had a negative velocity time step at some point in the 3-year span of the simulation, indicating multidirectional flow due to tidal influence.

Table 3.1. Velocity (m/s) summary statistics in the tributaries.

	Brays	Sims	Vince	Hunting	Greens	Carpenters	SJR
Mean	0.0351	-0.0164	0.0126	-0.0024	-0.0109	0.0061	0.0564
Median	0.0216	-0.0011	0.0084	0.0036	-0.0044	0.0201	0.0627
Standard Deviation	0.0893	0.1248	0.0206	0.0352	0.0891	0.0755	0.1530
Minimum	-0.0629	-0.9046	0.0048	-0.4271	-1.1355	-0.2175	-0.3178
Maximum	1.9892	0.7021	0.4202	0.1294	2.1384	0.2809	1.4067

To better understand the negative and positive velocities in the tributaries and in the Main Channel, individual analysis was done by separating the time steps which had positive velocities from the negative velocity time steps over the period of simulation. The results are summarized in Table 3.2 through Table 3.4. The inferences from the analysis are as follows:

- Over the three year period, Brays had a positive velocity 81% of the time. This is understandable considering that Brays is located far upstream of the channel and the degree of tidal influence is expected to be less. Sims, Hunting, Greens, and Carpenters Bayou had a positive velocity 50%, 54%, 46%, and 58% of the time steps simulated. So more than half the time period, the velocity was negative, i.e., the flow was inwards towards the tributaries. Vince had a positive velocity 100% of the time and so according to the simulation indicated no observable tidal influence. The reason for no observable tidal influence in Vince could possibly be due to a higher elevation in the area or due to calculation of net velocities by the model and so the backward velocities were not observable. The percentage negative velocity time steps in the tributaries shown in Figure 3.9 gives a better understanding of the tidal influence on the various tributaries.
- The plot of percentage negative velocity time steps along SJR shown in Figure 3.10illustrates the degree of tidal influence being less far upstream from the coastal area. As can be seen segment 33 (25 km from the confluence with the HSC), which is farther away from the channel had a positive velocity 96% of the time, while segment 48 (just before the confluence of HSC) had a positive velocity 67% of the time. So it is clearly observable from the graph and from the summary statistics that tidal influence did affect the velocity in SJR. Even though SJR could be more affected by the tidal influence than

the numbers indicate due to its nearer vicinity to the channel, the substantially high stream power as indicated by high velocities in the SJR overpowered tidal effects and less observable negative velocity in SJR.

• Figure 3.11 illustrates the degree of tidal influence and the backflow occurring in the Main Channel. It can be observed from the figure that the observable tidal influence was minimal upstream of the channel (Buffalo Bayou), while the tidal influence constantly increased as the coastal area was approached. The segments after the confluence with SJR had positive velocities 100% of the time as discussed before. This is due to the higher washout velocities from SJR even though it experiences negative flow some percentage of the time.

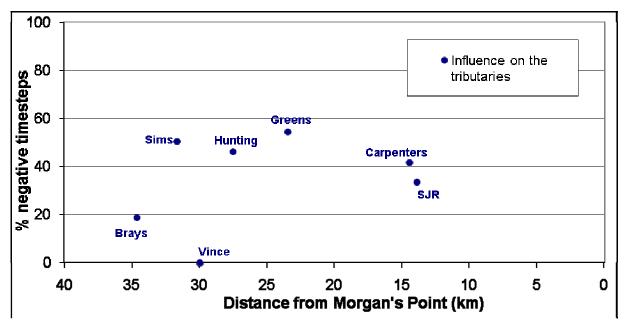


Figure 3.9. Tidal influence on the tributary velocities as determined by the presence of negative segment velocity changes with proximity to the mouth of the HSC.

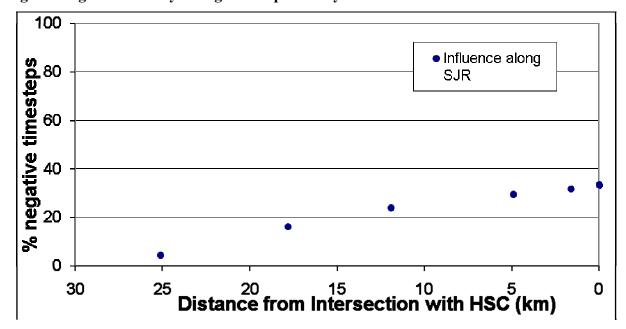


Figure 3.10. Tidal influence along San Jacinto River as determined by the presence of negative segment velocity changes with proximity to the mouth of the HSC.

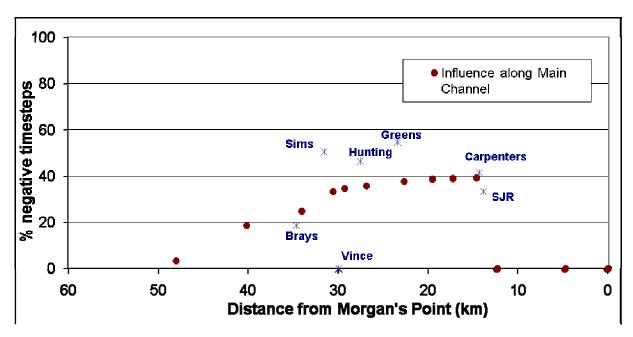


Figure 3.11. Tidal influence along the Main Channel segment velocities.

Table 3.2. Statistical summary for the negative and positive velocities in the tributaries.

Negative velocity	Brays	Sims	Vince	Hunting	Greens	Carpenters	SJR
% time steps the velocity was negative	19	50	0	46	54	42	33
Mean (m/s)	-0.0105	-0.1138	NA	-0.0324	-0.0500	-0.0706	-0.1010
Median (m/s)	-0.0093	-0.0990	NA	-0.0293	-0.0336	-0.0700	-0.0984
Standard Deviation (m/s)	0.0073	0.0936	NA	0.0276	0.0702	0.0424	0.0626
Minimum (m/s)	-0.0629	-0.9046	NA	-0.4271	-1.1355	-0.2175	-0.3178
Maximum (m/s)	-0.0001	-0.0001	NA	-0.0001	-0.0001	-0.0001	-0.0001
			•				
Positive velocity	Brays	Sims	Vince	Hunting	Greens	Carpenters	SJR
% time steps the velocity was positive	8	50	100	554	46	58	67
Mean (m/s)	0.0455	0.0822	0.0126	0.0233	0.0357	0.0608	0.1345
Median (m/s)	0.0264	0.0755	0.0084	0.0219	0.0235	0.0589	0.1130
Standard Deviation (m/s)	0.0960	0.0561	0.0206	0.0148	0.0869	0.0359	0.1212
Minimum (m/s)	0.0001	0.0001	0.0048	0.0001	0.0001	0.0001	0.0001
Maximum (m/s)	1.9892	0.7021	0.4202	0.1294	2.1384	0.2809	1.4067

Table 3.3. Statistical summary for the negative and positive velocities along San Jacinto River.

Negative velocity	Seg 33	Seg 36	Seg 39	Seg 43	Seg 46	Seg 48
% time steps the velocity was positive	4	16	24	29	32	33
Mean (m/s)	-0.009	-0.063	-0.140	-0.147	-0.118	-0.101
Median (m/s)	-0.008	-0.058	-0.133	-0.141	-0.115	-0.098
Standard Deviation (m/s)	0.006	0.043	0.088	0.091	0.073	0.063
Minimum (m/s)	-0.022	-0.215	-0.415	-0.544	-0.372	-0.318
Maximum (m/s)	-0.0001	-0.0001	-0.0001	-0.0005	-0.0002	-0.0001
Positive velocity	Seg 33	Seg 36	Seg 39	Seg 43	Seg 46	Seg 48
% time steps the velocity was positive	96	84	76	71	68	67
Mean (m/s)	1.13	0.32	0.38	0.28	0.17	0.13
Median (m/s)	1.13	0.19	0.25	0.21	0.14	0.11
Standard Deviation (m/s)	0.77	0.38	0.44	0.30	0.17	0.12
Minimum (m/s)	0.0002	0.0001	0.0002	0.0002	0.0001	0.0001
Maximum (m/s)	4.5	2.9	3.9	3.4	1.9	1.4

Table 3.4. Statistical summary for the negative and positive velocities in the Main Channel.

Negative velocity	Seg 1	Seg 5	Seg 10- after brays	Seg 14-after sims	Seg 16- after Vince	Seg 20- after Hunting	Seg 25- after Greens	Seg 27	Seg 28	Seg 32- after Carpenter	Seg 61- after SJR	Seg 67	Seg 73
% time steps the velocity was negative	3	19	25	33	35	36	38	38	39	39			
Mean (m/s)	-0.0072	-0.0249	-0.0169	-0.0264	-0.0306	-0.0354	-0.0343	-0.0298	-0.0352	-0.0381			
Median (m/s)	-0.006	-0.0227	-0.0155	-0.0237	-0.0278	-0.0331	-0.0325	-0.0286	-0.0339	-0.0369			
Standard Deviation (m/s)	0.0058	0.0175	0.0118	0.0184	0.021	0.024	0.0229	0.0196	0.023	0.0246			
Minimum (m/s)	-0.0298	-0.1109	-0.0847	-0.1505	-0.1668	-0.1857	-0.151	-0.1219	-0.143	-0.1527			
Maximum (m/s)	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001			
Positive velocity	Seg 1	Seg 5	Seg 10- after brays	Seg 14-after sims	Seg 16- after Vince	Seg 20- after Hunting	Seg 25- after Greens	Seg 27	Seg 28	Seg 32- after Carpenter	Seg 61- after SJR	Seg 67	Seg 73
% time steps the velocity was negative	97	81	75	67	65	64	62	62	61	61	100	100	100
Mean (m/s)	0.363	0.121	0.036	0.037	0.040	0.043	0.037	0.030	0.035	0.037	0.096	0.120	0.111
Median (m/s)	0.208	0.073	0.028	0.032	0.035	0.039	0.034	0.028	0.033	0.034	0.090	0.114	0.104
Standard Deviation (m/s)	0.343	0.122	0.036	0.030	0.030	0.031	0.027	0.021	0.023	0.024	0.063	0.075	0.071
Minimum (m/s)	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0006	0.0001	0.0006
Maximum (m/s)	1.8	1.3	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.6	0.7	0.6

Based on the above analyses using velocities and the analysis of flows presented in the previous quarterly report, it is likely that segment 1006 acts like a sediment "bath tub" due to tidal influence, which opposes the positive flow from Buffalo Bayou and limits the total outflow of sediment that comes from 1006 to the downstream segments of the HSC. If this is the case, it would affect the transport of PCBs and their total concentration attenuation in the Channel because 1006 has the highest concentrations in both water and sediment according to the data from 2002-2003. The fact that concentrations in 1006 and 1007 have remained high despite decades of PCB ban elicits hypotheses concerning the cause of persistent concentrations that are not flushed out downstream. It was observed that the downstream segments in the Main Channel before the confluence with SJR had positive velocities 60% of the time. So it is clear that there is a backflow from the coastal area 40% of the time. Segment 1006 had a negative velocity nearly 39% of the time (Segments 27 and 28 in WASP model). This indicates a large period of inward flow for this upstream segment. The constant backflow in the 1006 segment opposing the positive flow from Buffalo Bayou would result in stagnation in flow and so limit the total outflow of sediment that comes from 1006 to the downstream segments of the HSC.\*\*

#### 3.1.4 Conclusions

The important conclusions from the velocity analysis presented above are:

1. Tidal influence from the coastal area was found to affect the outflow in the tributaries and in the main channel. The calculations based on velocities rather than flow rates helped in better understanding the tidal influence in the main channel and in the tributaries. Based on the results, tide is expected to play a significant role in the fate and transport of PCBs (both in dissolved and suspended phases and in near bed sediment transport<sup>††</sup>).

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<sup>\*\*</sup> In addition to velocity direction, velocity magnitude is also important for two reasons. One is that suspended particles will have a greater chance of settling out and depositing on the sediment bed if the overall velocity is diminished. The second reason is that sediments that are on the bed require a critical velocity to get them to move. There has not yet been enough analysis to ascertain how much the diminished velocities are increasing sedimentation rates and decreasing the likelihood of initiating sediment bed motion.

<sup>&</sup>lt;sup>††</sup> The distinction between suspended phase sediments and near bed sediments is that suspended sediments actually move up into the water column due to their smaller size and weight. Near bed sediment move PCBs but only along

- 2. The tidal influence along the Main channel can be classified into three major areas: Segments upstream of the Main channel and SJR (farther away from the coastal area) are less affected by the tidal influence, segments closer to the coastal area are significantly affected (half the time) by tidal influence, and segments downstream of the confluence of SJR had net positive outflows all the time. Even though segments downstream of the confluence are likely to be affected by tidal influence, the significantly high positive velocities from SJR results in masking the tidal influence resulting in net positive velocities all the time.
- 3. Segment 1006 appears to act as a sediment "bath tub" at least some of the time and on the basis of velocity alone (i.e. not actually considering sediment grain size, channel bedforms, sediment cohesion, etc.). The velocity in the 1006 segment had a positive outflow 61% of the time, and so there is a backflow due to the coastal intrusion. The consistent backflow in the 1006 segment opposing the positive flow from Buffalo Bayou would result in limiting the total outflow of sediment that comes from 1006 to the downstream segments of the HSC.
- 4. All the tributaries except Vince were observably affected by tide and had negative velocities at some point during the simulation period. Brays was the least affected by the tide, while other tributaries (Sims, Hunting, Greens, and Carpenters) were observably affected nearly half the time period.
- 5. SJR was found to be the most influential tributary on the Main channel velocity. The tidal influence was minimal farther upstream of the SJR, while the effect increased as the coastal area was approached.
- 6. The Main Channel had similar velocity effects to what was seen in the SJR. The effect was minimal upstream of the Main Channel near Buffalo Bayou. However the observable tidal influence constantly increased as the flow approached the coastal area. After confluence with SJR, the Main channel had positive velocities 100% of the time. This is to be expected due to the higher washout velocities from SJR.

## CHAPTER 4 - FIELD SAMPLING PREPARATIONS

## 4.1 Particulate Organic Carbon (POC) Analysis

The previous quarterly report highlighted the issue of POC analysis both in areas of sample collection and sample analysis. Specifically the issues presented were the following:

- <u>Collection Methods</u>: There is a need to keep pressures low if a filter is used to ensure that small particles remain to be analyzed as POC while also achieving a large enough volume to get the larger and rarer particles.
- <u>Loss-On-Ignition (LOI) Method Detractions</u>: Accuracy suffers from mass subtractions before and after ignition, inorganic solids artificially increase the POC signal, and organic matter (OM) that combusts may be treated as OC when in fact it is not.

An additional issue that arose during the last quarter but had not been mentioned previously was that of NELAC accreditation. As of July 1, 2008 all data that are to be submitted to TCEQ must be performed under NELAC accreditation. So the issue involves finding a laboratory that can perform POC analysis and that is NELAC accredited for it.

The issue of collection method has been settled by the use of the pump filtration. Even in that method, there is still the issue of the operational definition of POC. POC is defined operationally as those particulates that remain on the filter during high volume sample collection. In the previous Dioxin TMDL project, the filters that were used were 1 micron filters, but filters that are at least as small as 0.7 micron exist. It may be more advantageous to truly understand the nature of POC to use a smaller size filter because the particulates between 0.7-1 micron behave more like POC than DOC, which is what they would be perceived as if a 1 micron filter was used[NLHI]. Regardless of the filter size, every high volume water sample will need to be taken with two high volume samplers run in parallel to yield two filters: one that will be analyzed for POC and on that will be analyzed for PCB. The sample volume of solids may not need to be as high for the POC as for PCB, and in fact it would be logistically simpler if not as much sample was needed and if the volumes did not need to be matched. All that is needed to link the PCB sample with the POC sample is take the sample from virtually the same location at

the same depth (or using the same depth compositing method) on the same filter size. If the POC analytical method is accurate given all of these conditions, then the two may be considered to be from the same sample.

Concerning the issues involved with POC sample analysis, the POC NELAC accredited laboratory, Applied Marine Sciences, Inc. has reported that they can perform the analysis for the amount of samples that would be generated in the project. Additionally they can work with the project team to make sure that a sufficient pre-treatment method for IC removal is employed. The low temperature combustion of IC before the high temperature used for OC analysis is preferred.

So in summary, there may be still some details requiring further consideration for the POC analysis, but the basic collection method and chemical analysis have been addressed.

## 4.2 Particle Size Analysis of Suspended Phase

The study on dioxins conducted by Yeager et al. (2007) in the Houston Ship Channel (HSC) was performed on sediment cores.<sup>‡‡</sup> In the study, sediment samples were analyzed for dioxin, TOC, and grain size as well as other constituents. Linear regressions showed that dioxin concentrations were not linearly related to TOC (in contrast to standard partitioning theory) but were linearly related to grain size. Howell et al. (2008) demonstrated that PCB sediment samples in the Channel were linearly related to TOC, and grain size correlations have not yet been assessed. POC deals with suspended particles, not sediment samples, but it is thought that PCB will be significantly related both to POC and grain size. Thus, it would be useful to get grain size data for the particulates (as well as the sediment samples, which are already set to be analyzed for grain size in the sample planning).

Determining grain size for particulates will be a somewhat time-intensive measurement. It would require getting an ambient water sample because GFFs and centrifuged samples will not be able to yield particles that can be assessed for grain size. If an ambient water sample were obtained, then it could be run through a particle size analyzer. The facilities at UH include a

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<sup>&</sup>lt;sup>‡‡</sup> The distinction should be made between suspended particulates, which may or may not be sourced from sediment beds, and sediment samples. The behavior of contaminant to sediment and contaminants to suspended particles may not be the same, but they are considered at least similar for this discussion.

Beckman Coulter Multisizer 3 Coulter Counter. This type of instrument is one of the best particle size counters available with the ability to analyze for distributions of particle number, mass, surface area, and size for particles in the size range of 0.4 – 1200 μm. The GFFs that were previously used for dioxins were 1 μm\*\*\*. The exact method that will be used for grain size analysis of particulates in a water sample has not yet been determined, but one method would be simply to use the high volume sampler to pump water from the desired depth into a holding vessel without the use of a filter. A much smaller volume than the PCB samples would be required since only a small volume size can actually be run on the particle counter.

## 4.3 Intensive Sediment Sampling Plan[NLH2]

A suspected source of PCBs to the entire HSC system is the sediment bed, which may contain either historical or contemporary PCBs. Irrespective of the age or the pathway that the PCBs took to get to the sediment, the sediment has sufficient concentrations of  $\Sigma$ PCB as indicated by the 2002-2003 sampling event to warrant a deeper investigation into the exact spatial nature of the sediment contamination.

## 4.3.1 Sampling Objectives

The overall strategy for the intensive sediment sampling is to understand the spatial variations in the most sediment contaminated area of the HSC, water quality segments 1006 and 1007. Previous sampling has indicated that these segments are high in PCBs in sediment and in water leading to the supposition that the one sources the other. Figure 4.1 plots the spatial extent of the contamination.

<sup>§§</sup> http://www.beckmancoulter.com/coultercounter/product multisizer.jsp

<sup>\*\*\*</sup> The minimum particle size that is analyzed should be the same as the filter size on the GFF. Previously 1 µm was used though smaller filter sizes are available. To use a cutoff for particle size that is smaller or larger than than the GFF filter size will misrepresent the particle size that is actually found in the PCB sample making inferences between particle size and PCB concentration more suspect.

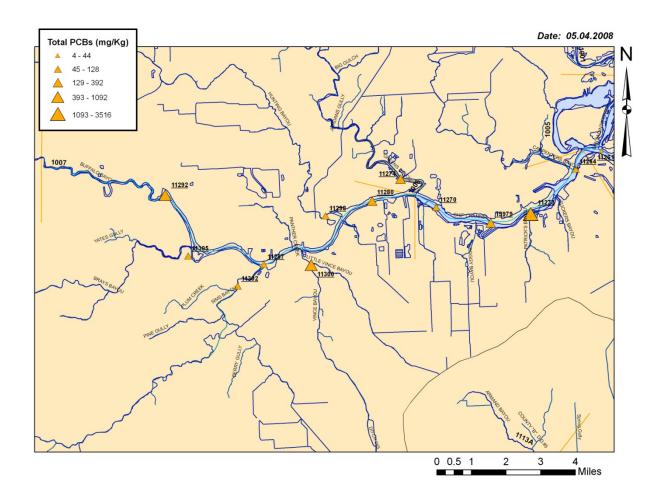


Figure 4.1. 2002-2003 Total PCB sediment concentrations averaged per station for the sediment intensive sampling area.

In general, the highest concentration points are in the Turning Basin, just upstream of Brays Bayou at station 11292, in Vince Bayou at 11300 (near N. Richey St), and at the confluence of Patrick Bayou and the HSC. Concentrations are high still all over this portion of the Channel. A background concentration consisting of the average of the first quartile from the sediment sampling conducted in 2002-2003 yields a value of 5.79 ng/g-dry. This background concentration is lower than every station averaged sediment value shown in Figure 4.1, and furthermore 29 of the 34 samples collected (85%) from this region in 2002-2003 were above the third quartile, which puts this region definitively in the highest zone of sediment concentrations in the whole HSC system.

Now that these concentrations define the region of highest PCB sediment influence, it is noted that this region contains both main channel and tributary portions. Most of the samples from 2002-2003 were taken from the main channel though 13 ((38%) were not. In previous analysis of the 2002-2003 dataset, Howell et al. (2008) supposed that sediment transport might be occurring from tributaries in the HSC. Therefore, it is a goal of this sediment study to gain understanding of the possible PCB contaminant transport by way of sediment transport through tributary sampling analysis.

Also the true mean of the more heavily contaminated region is also desired in sediment. The previous dataset allowed for a particular range of 95% confidence in the mean that gives a range of about 62% on either side of the mean (593  $\pm$  368 ng/g-dry). A new sediment study should be able to give the mean to a greater level of confidence.

Finally, a major objective of the study is to aid in the water quality modeling efforts. This modeling can be improved in two ways. The first is to provide a better understanding of sediment concentrations at more locations throughout the Channel by which to compare model results to actual results. Because there is high variation in the 1006-1007 portion of the HSC, more spatial resolution is needed to keep from interpolating concentrations that are spatially variable with large swings in concentration. The second way that modeling can be helped is by providing more physical sediment information in the form of grain size, which can be used to design a rigorous sediment transport model that will predict sediment loads moved in 1006-1007. Such a model would be a significant improvement to the Water Quality Simulation Program (WASP) because it would allow for a better handle on the suspended sediment settling rates that are currently assessed via calibration in the Dioxin TMDL.

The objectives then of the intensive sediment sampling study are:

- 1. Use tributary PCB concentrations along the HSC to ascertain the likelihood of sediment as a PCB transport vehicle from the tributaries to the main channel.
- 2. Get more certainty and precision on the range of the true mean of  $\Sigma$ PCB in the more heavily contaminated 1006-1007 region.
- 3. Gather more detailed sediment PCB spatial information to aid in water quality and sediment transport modeling in the HSC.

4. Determine to a greater extent what areas of the HSC are truly influenced by statistically significant contamination through the use of an established background PCB concentration in sediment.

## 4.3.2 Sample Design Stratification

The basic strategy employed in the selection of number, kind, and location of sediment samples is Stratified Systematic Sampling. The concept is first that the sampling area is broken down into smaller sections or strata. The method by which the strata are created is the stratification scheme. Once the stratification scheme has given a small number of strata (approximately 2-10 strata is usually appropriate), then points are chosen within each stratum according to a systematic approach. The systematic sample choosing approach usually involves gridding a stratum into regular sample location possibilities. Then the points are chosen according to a regular pattern in the sampling grid. The stratification scheme chosen for this sampling design is shown in Figure 4.2.

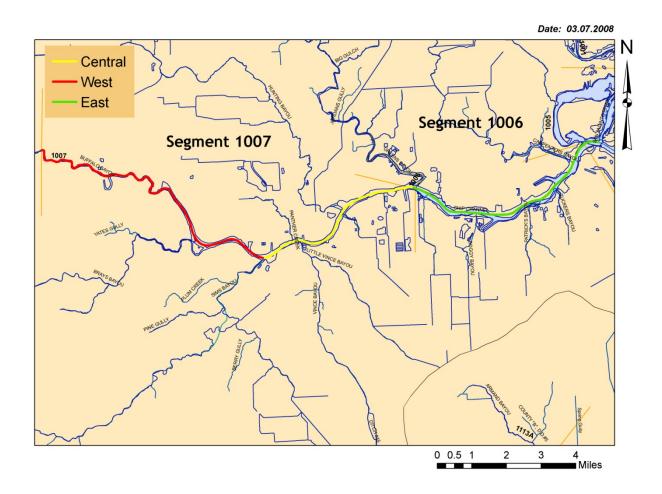


Figure 4.2. Sediment intensive sampling area stratification regions.

The figure shows that the 1006-1007 region was broken down into three strata according to location. The West stratum extends from upstream boundary of segment 1007 (100 meters upstream of Buffalo Bayou and US 59) until a point 290 meters upstream of Sims Bayou (just includes SWQM station 16620). The Central stratum extends from the point upstream of Sims Bayou to the downstream boundary of segment 1007 (immediately upstream of Greens Bayou). The East stratum covers the main channel portion of segment 1006 from the intersection of Greens Bayou with the HSC to Lynchburg ferry (includes all segment 1005 portions of the SJR-HSC confluence excluding Old River and the main SJR tidal sections). The strata that were chosen here were based on basic regional classification. Strata could just as easily have been picked based on TOC % regions, watershed boundaries, neighboring land use categories, or even

flow regimes<sup>†††</sup>. The geographic stratification is one of the simplest ways to stratify, and it is intuitive for this area of the channel because it experiences regions of "hotter" and "colder"  $\Sigma$ PCB concentrations that allow for good stratum-to-stratum comparisons.

The Stratified Systematic Sampling scheme can also be used as a way to conveniently break down the dataset so that it is easily analyzed. It is valid to perform this analysis because in addition to providing general information about contamination patterns, the analysis of each stratum will be used to determine how a total number of samples for the study area are apportioned between the various strata.

The analyses for the given strata are shown in Figure 4.3 and Figure 4.4. ΣPCB concentrations look fairly similar between strata whether using a dry weight or organic carbon (OC) based concentrations. The East stratum has the highest  $\Sigma$ PCB concentration when the means are compared to the other strata, but the 95% confidence ranges don't allow for a completely statistically different concentration between the East stratum and the other strata. ‡‡‡ The power of the 95% confidence statistic is not extremely high as the number of 2002-2003 samples between the West, Central, and East strata is only 12, 11, and 17, respectively. A greater number of samples in each stratum would lower the 95% confidence interval to increase precision around the mean and provide a better comparison between the strata. The TOC % was considered across the various strata, and it shows a more even distribution pattern. This result is not surprising, but TOC is being considered in this way because it is such a critical parameter in terms of the sediment's capacity to hold PCBs. In this case, since TOC is approximately equal across the strata, then the differences between strata are not consequential to differences seen in concentration. Comparisons to portions of the channel outside of the sediment intensive area might not have this picture since they experience different kinds of sediment loads in the form of runoff and other means of sediment delivery.

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<sup>†††</sup> The strata in this sampling plan were chosen only with regard to simple geography. There was no effort made to include the velocity analysis performed in the previous section as a means of stratification. The definition of flow regimes will be used to analyze data after sampling has been conducted and not for sampling design itself.

‡‡‡ Individual congener and congener distribution analysis was not performed between strata because this was not essential for sample planning, but it is likely that where statistical differences are not necessarily seen between the strata for ΣPCB, they would be seen more clearly in congener profiles as it is these congener profiles that reveal a different character between contamination at different locations.

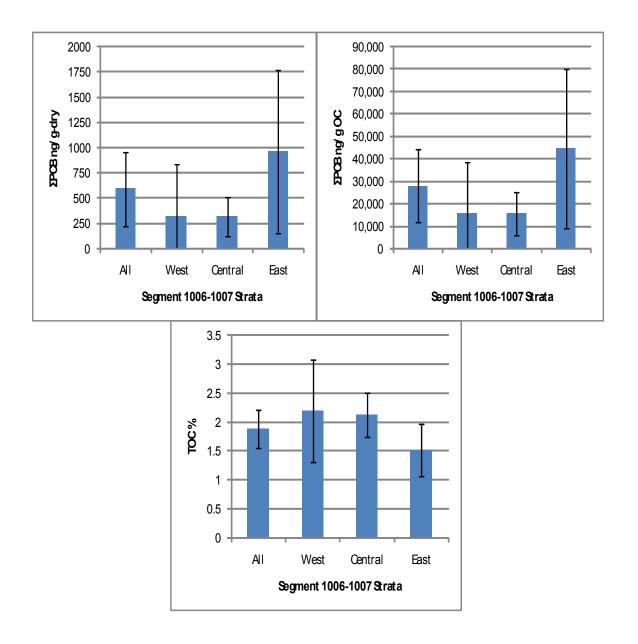


Figure 4.3. Mean PCB concentrations and TOC % per Channel stratum. Error bars indicated 95% confidence and are "clipped" so that they cannot yield negative values.

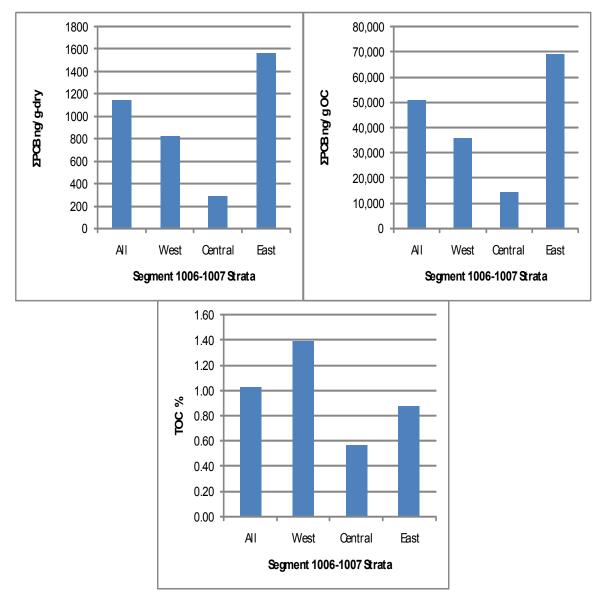


Figure 4.4. Standard deviation of PCB concentrations and TOC % per Channel stratum.

The comparison of standard deviation is more important for the sample design than the PCB concentrations. The reasons for this is that the Stratified Systematic sampling is powerful because it tries to apportion samples according to what will most effectively capture the variation in concentration across the region. Areas with higher standard deviation will eventually have more samples than areas of lower standard deviation. Figure 4.4 reveals that the greatest variation in PCB concentration is in the East stratum followed by the West and then the Central.

#### 4.3.3 Sample Size Selection

The total number of samples needed for the sediment intensive study area was generally determined according to Equation 1. Using the 2002-2003 PCB study data as a pilot study, the sample standard deviation, and the allowable range of 95% confidence ultimately desired helps to estimate how many samples are required in the sampling. This formulation is considered an estimate because it is based on a standard deviation taken from the 2002-2003 sample set. The only way to get an exact measure of sample size for a desired 95% confidence interval is to know the true standard deviation in the 1006-1007 HSC region. This "true" standard deviation is of course impossible to determine.

Equation 1. Sample size predictor given an initial standard deviation (s) and a desired 95% interval about the mean ( $I_{95\%}$ ).  $t_{0.05}$  is the t-statistic for a two-tailed t distribution at 95% confidence.

$$n = \frac{s}{I_{95\%}} t_{0.05}$$

In order to decide what 95% interval should be used in Equation 1, a quantitative measure of desired precision needs to be chosen. Equation 2 formulates the relative 95% confidence interval. This value simply gives the fractional precision on either side of the mean that the sample size should yield when all of the actual sampling has been conducted.

Equation 2. Relative 95% confidence interval about the sample mean  $(\bar{x})$ .

$$I_{95\%}^{rel} = \frac{I_{95\%}}{\bar{x}}$$

No external requirement was given by project goals to say what amount of 95% confidence interval was acceptable, and so Figure 4.5 shows the relationship between sample size and the relative 95% confidence interval. An efficient sample size will yield a fairly low

relative confidence interval without a high marginal increase in number of samples required. The figure gives the relationship per stratum as well as for the entire sampling region. The implications of this figure will become evident later in this report.

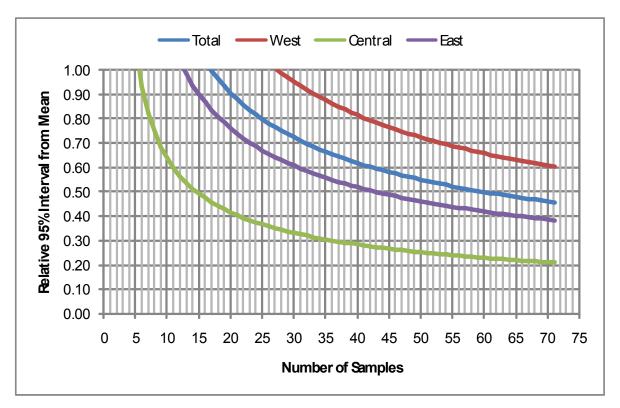


Figure 4.5. Relationship between 95% relative interval from the 2002-2003 sample means with varying sample sizes. Each interval represents either side of the mean. It is not from upper confidence to lower confidence. Dry weight PCB concentrations were used to govern the sample size selection because these concentrations (as compared to OC weight and TOC%) drove the sample size calculation to maximum values.

In addition to weighting the various strata according to their standard deviations relative to each other (Figure 4.4), the actual geographic area of each stratum was considered as calculated and presented in Table 4.1. The linear distance and areas were approximated using GIS, and two different strata weighting schemes were developed according to linear or area considerations. Linear weighting was chosen as the most appropriate weighting method because (1) the HSC is far more linear than area based, and (2) the manner in which sampling is performed along the HSC considers concentration in a primarily one dimensional fashion.

Table 4.1. Calculated linear and area weightings per stratum.
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Parameter	Unit	West	Central	East	Total
Linear Distance	km	14.4	8.3	10.6	33.3
Average Width	km	0.17	0.28	0.40	0.28
Area	km²	2.46	2.32	4.24	9.01
					1.00
					1.00

The previous analysis of standard deviations between strata examined the standard deviations of dry weight PCB, OC normalized PCB, and TOC. Figure 4.6 presents the weightings from dry weight PCB measurements, and it is this weighting that was ultimately chosen for the sediment sample apportioning between the strata.

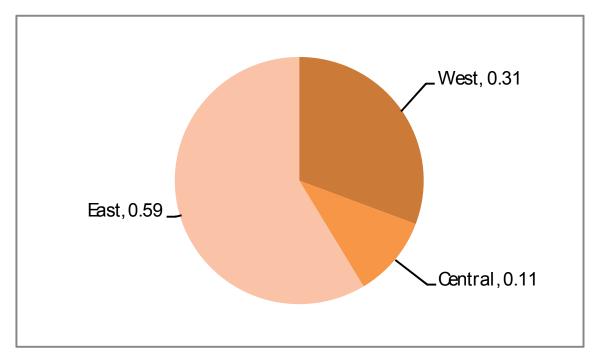


Figure 4.6. Standard deviation weightings per stratum based on dry weight PCB concentrations.

There were two weightings generated for the three strata in the Stratified Systematic sampling: standard deviation based and geographic based. To harmonize the effects of the two, they were simply multiplied together and renormalized according to the total of all three strata as formulated in Equation 3 and presented in Figure 4.7. As stated previously, it was the linear geographic weightings that were chosen over the area geographic weightings. The final weightings then were a combination of linear geographic and dry weight  $\Sigma$ PCB standard deviations.

Equation 3. Combined weight for sample selection per stratum.  $w_s$  is the weight based on standard deviation, and  $w_{geo}$  is the weight based on geographic parameter either line or area. The combined weight is renormalized by the total between all three strata to get a new total of unity.

$$W_{somblesd} = \frac{w_s w_{geo}}{\sum (w_s w_{geo})_t}$$

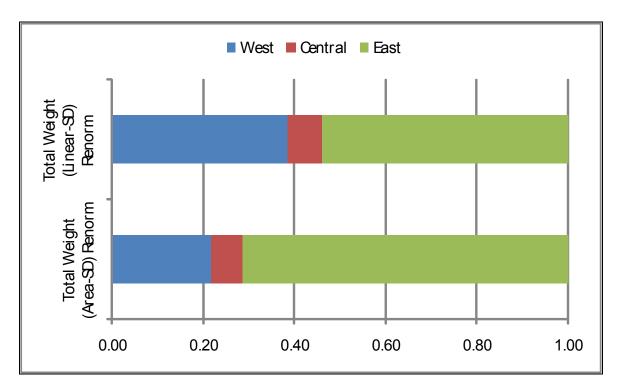


Figure 4.7. Combined weightings (linear/area and standard deviations) using dry weight  $\Sigma$ PCB concentrations.

Based on the effect of increasing 95% confidence precision with sample size described in Figure 4.5, the level of fractional relative 95% confidence chosen was 0.7. This level of confidence means that the final result of PCB concentration across the 1006-1007 region will be within 70% of the mean on either side of the estimated mean<sup>§§§</sup>. Considering the amount of variation that is expected in PCB concentrations as previously seen in the 2002-2003 sampling effort, 70% of the sample mean is considered reasonable.

Using this 70% level of precision, the sample size predicted according to the various constituents and in various strata are given in Table 4.2. The "Greatest" values (displayed graphically in Figure 4.8) are valuable because these values yield the estimate of sample size that will provide the greatest likelihood of achieving the 70% of the mean interval size.

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The final sample mean will be different in the full sediment intensive study as compared to the mean derived from the 2002-2003 PCB dataset. Thus, the fractional interval around the actual sample mean (after the sediment intensive sampling has taken place) will likely be slightly different from 70%.

Table 4.2 Predicted sample sizes between constituents and strata at a 0.7 relative 95% confidence level. The Greatest column contains the greatest sample size prediction predicted from each stratum.

	PCB Dry Wt	PCB OC	TOC	Greatest
Total	32	28	5	32
West	53	43	6	53
Central	9	9	3	9
East	23	21	5	23
Total (Strata Added)	85	73	14	85

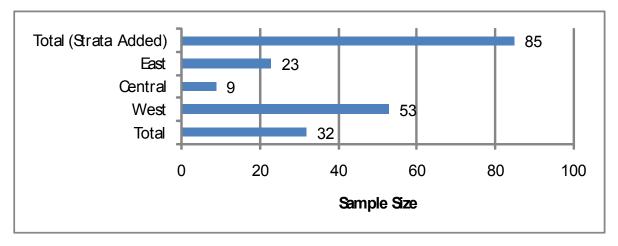


Figure 4.8. Comparison of predicted sample sizes by strata for the most number of samples predicted by a constituent. In this case, the greatest number of samples predicted was nearly always under the dry weight  $\Sigma$ PCB concentration. The one exception was with the Central stratum where the PCB Dry Wt and PCB OC predicted the same number of samples.

The stratification reveals that the three strata added together provide the largest sample size estimate 85. If this sample size were chosen, then the 70% precision would likely be present in each stratum after the sampling was conducted. The number of 85 samples, however, is an

extremely high number of samples for an area of this size. The objectives of the monitoring were to provide some better understanding into the spatial details of the "hot zone" of contamination and to aid in modeling. A number of 85 samples is excessive for these goals even though the 70% precision is not met for each stratum. Instead the efforts would be better spent on a fewer number of samples that achieves the sediment intensive objectives and at least gives a 70% precision (relative to the estimated mean) of the 95% confidence for  $\Sigma$ PCB concentration for all of segments 1006 and 1007. That 70% precision sample size estimate was 32. Therefore, a final sample size of 35 meets this estimate of 32 with a little conservatism\*\*\*\* built in with an extra three samples.

The final 35 sample size was apportioned amongst the strata according to the composite weightings of Figure 4.7 to yield the final sampling for each stratum according to what is seen in Table 4.3. This final sample design for the main channel was altered from the strict numerical determination to give the Central stratum slightly more than what the calculation alone predicted.

Table 4.3. Sample distribution between strata final selection process. Total final sample size is 35.

Stratum	Area-SD Wt	Line- SD Wt	Area-SD Samples	Line-SD Samples	Final Selection
West	0.22	0.38	8	13	10
Central	0.07	0.08	2	3	6
East	0.71	0.54	25	19	19

#### 4.3.4 Tributary Sampling Design

The tributaries may prove to be significant contributors to the PCB load in the HSC, but even if they do not, the hydrodynamics and sediment motion that does occur from them will likely be significant to any modeling efforts that are undertaken in the HSC. Additionally, since some of the tributaries contribute a significant amount of flow in the upper reaches of the

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<sup>\*\*\*\*</sup> The extra three samples are considered conservative because the standard deviations used in the sample size calculation are unknown without exhaustive sampling. If the standard deviations turns out to be greater than estimated, then the additional samples may still help provide a certainty of the true mean that is within 70% either side of the sample mean.

channel, they may themselves be considered to be an upper reach of the channel. The tributaries are quite long in some places, and it is thus impractical to attempt to sediment sample all portions of them or even to try and take representative samples from all areas. Thus, the following plan was adopted.

- 1. Find the tributaries that have large flows directly into the sampling area (based on experience as well as flow analysis done through RMA2 modeling).
- 2. Isolate the last four miles upstream of their confluence.
- 3. Decide on a sample size for the tributaries based on the 2002-2003 sampling information from the four-mile region of the tributary.

The tributaries that had the largest flows according to the three averages found from the RMA2 modeling effort (Rifai and Palachek, 2007) were Brays, Sims, and Greens Bayou. The lowest four-mile reaches and samples taken in those reaches in 2002-2003 were statistically analyzed and displayed in Table 4.4 and Figure 4.9. The calculations show (based on a very limited number of samples by which to derive a preliminary standard deviation that four samples will be sufficient in each tributary to achieve the same 0.7 precision that was desired in the case of the main channel.

how PCB concentration might vary with stream location, which will be vital for tributaries that contribute large PCB loads to the HSC.

Thus, it is likely that these standard deviations in fact underestimate the variability because much of the spatial variability is removed from the use of only co-located samples. Though the standard deviation is likely underestimated, it is thought that four samples will still provide a reasonable interval of 95% confidence. Because they will be spatially distributed for four miles rather than at one location, they should at least give an indication of

Table 4.4. Tributary sample size selection calculations.

	Brays	Sims	Greens
n <sub>2002-2003</sub>	3	4	7
Mean	78.3	52.8	233.4
SD	12.10	7.14	95.15
n <sub>plan</sub>	4	4	4
95% Relative Interval Actual	0.25	0.22	0.65
95% Relative Interval Goal	0.7	0.7	0.7
Relative Error Goal Met?	Yes	Yes	Yes

In addition to the tributary sample size strategy just used, Figure 4.1 shows that Vince Bayou has high concentrations of PCB in sediment. Though Vince Bayou does not have one of the highest flows, this sediment intensive sampling plan recommends that three stations be selected for sampling in the 4 miles closest to the Vince Bayou confluence with the HSC. With these two additional samples, the total number of tributary samples stands at 15.

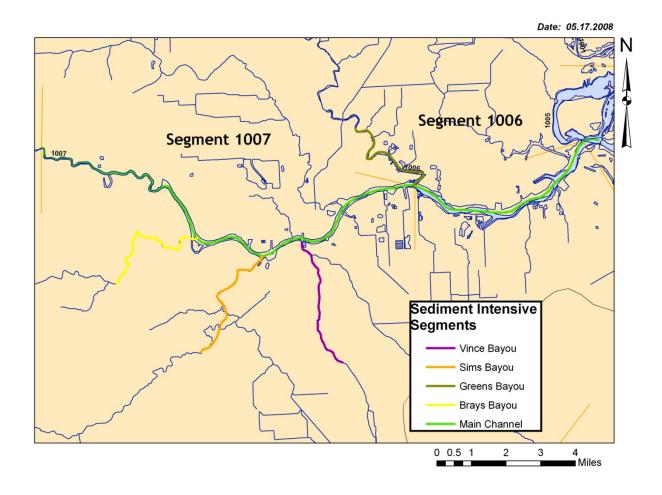


Figure 4.9. Tributary reaches considered for the sediment intensive sampling.

#### 4.3.5 Transect and Core Sample Design

The sampling design that has heretofore been described mainly considers how to sample to deal with linear variability along channel reaches. Three other kinds of variability need to be examined. These kinds are

- 1. Temporal Variability
- 2. River Width Variability
- 3. Sediment Bed Variability with Depth

The basic strategy for each of these three variabilities is to take a limited number of samples that will allow some general trends in variability to be made about the rest of the samples. For example, one might not expect to see much variability in surface sediment concentrations within a short time span because PCB samples taken in 2002-2003 did not show much variation. If this were proven during the intensive sampling study, then it could be assumed that most sample locations, though they were not sampled more than once, do not vary much in time.

The previous example shows how temporal variation could be examined. River width variability would be examined through the use of sample transects at certain locations in the study area. Conceptually one can imagine that the width variation could be fairly great since the environment from one side of the Channel to the other (especially at wider places) is different. If there were different historical sources of PCBs on different sides of the Channel (e.g. certain barges docked on one side of the Channel but not the other, different industries reside on opposite banks, etc.), PCB loads to sediment could be different. Certainly sediment motion and mixing would smooth out some of these PCB concentration profiles, but the differences may still exist. Also the presence of the navigational channel creates major depth changes along a transect that could represent PCB concentration differences. These differences could occur through transport rate variance due to geometry or may relate specifically to the motion of sediment and contaminant as a result of dredging and ship traffic.

Three transect sample locations were chosen so that the width variability would be examined in each of the three strata. Tributaries were considered to be too narrow to merit the use of transects. Each transect will have 5 samples in it regardless of the differing width. More may be gathered, but a detailed level of 5 should cover the Channel well without leaving any gaps.

Sediment bed depth variability is the third kind of variability that needs to be examined. The current sediment sampling protocol in the QAPP gathers sediment from the top 5 cm of the bed. One cannot expect that the concentration of PCB will be constant with depth, and it is important that the variation with depth be understood due to the implications of a future sediment transport model. More than 5 cm of sediment can be moved during anthropogenic resuspension events such as dredging and ship propellers, but even more worthy of note is the effect from large storm events. Whether it is increased flows coming from the upper watershed bayous that force more sediment down towards Upper Galveston Bay or whether it is wind-driven waves

from large storms moving sediments both upstream and downstream, it is highly likely that sediment can be moved even at depths of a foot or more depending on the consolidation in the Channel's cohesive sediment bed.

For these reasons, sediment coring is also proposed in this intensive sediment sampling study. One point about coring is that past efforts of coring in the HSC were somewhat frustrated due to the difficulty of finding undisturbed cores. Oftentimes cores were only marginally useful because they were used to help determine the history of, in previous TCEQ studies, dioxin. The use of coring here should be conceptualized slightly differently. An upcoming sediment transport model does not necessarily require an undisturbed core because all the core needs to do is to characterize the actual PCB profile in a few places within the channel so that a reasonable PCB profile can be imposed upon a model sediment bed. (i.e. If history did not lay down the core that way, it is of no consequence. For the modeling only cares about what is there and where it is going, not how it got there in the first place.) If an undisturbed core is gathered that yields historical source information is found, then it will certainly be used for that purpose, but all that is required is accurate quantitation of PCBs with sediment depth that may be representative of the Channel in general.

The types of locations chosen for coring can be grouped and selected according to many factors. Consider the following:

- Grain size distributions found in the current HSC region sediments. (See Figure 4.10)
- Types of development in the vicinity.
- Likely historical sourcing locations.

Three core samples should give a reasonable approximation of PCB concentration in the sediment bed if they are taken to a depth of at least one meter. Each one meter section will have a PCB sample taken at every 0.2 meters so that there are 5 samples per core. Three locations should be enough to cover the HSC. The main concern in coverage is the difference in sediment texture and PCB levels, and there are not more than three of these locations that represent different sediment texture-PCB level combinations.

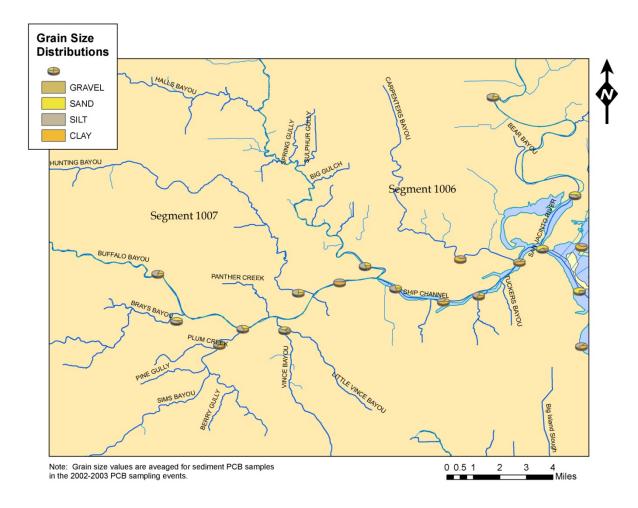


Figure 4.10. Grain Size Distribution in dry weight %.

#### 4.3.6 Sample Location Selection

The 15 tributary and 35 main channel sites had to be mapped to particular locations in the HSC. An effective way to do this was to place a linear grid on the HSC and systematically choose locations that followed a regular pattern. That grid was designed to create an even spacing over each stratum such that the number of sample locations was about the same as the number of samples allotted for each stratum as it was given in Table 4.3. This evenly spaced grid was slightly adjusted so that sample points would align with existing SWQM stations as well as avoid sediment sample points currently in the QAPP. The avoidance of current QAPP sediment stations ensures that the sample point gathered will be more unique. After the sample

locations were chosen, the remainders of the sample count for the three strata were made up by increasing the sampling frequency at certain locations.

The systematic sampling plan in its final state (Figure 4.11, Figure 4.12, Figure 4.14, and Table 4.5) satisfied the following goals:

- 1. Place 35 main channel sample locations in the three strata so that there are real and non-modeled data for PCB concentrations in all of the sampled area.
- 2. Delineate the main tributaries in the sampling site with four evenly spaced sample locations. Include additional sites for Vince Bayou due to its high 2002-2003 PCB concentrations.
- 3. Obtain a measure of temporal variance in the sediment concentrations using co-located samples taken during different sampling events.
- 4. Ascertain the width variability in the PCB data, especially that which results from ship traffic and dredging effort through the use of 5-sample transects.
- 5. Ascertain the sediment bed depth variability as well as total levels by taking sediment cores for PCB analysis to a depth of at least one meter. Figure 4.13 provides a comparison of grain size throughout the sample area as compared with sample locations in the Main Channel. This figure was used to help make the determinations for sediment core locations.
- 6. Background concentrations of PCB in sediment will be determined from the current sampling locations. It is hoped that the more upstream locations in the tributaries (mainly in Sims and Brays Bayous) will be able to be used as background. If this is not satisfactory, then further sampling may later be required or the lowest value in the study will be used.

In addition to simply giving the various sample locations and frequencies chosen, Table 4.5 provides lengthy explanations for the choice of various sample locations and the types of samples that were gathered there. The specific laboratory analysis that will be conducted on each kind of sample will be outlined more exactly on an upcoming Monitoring QAPP amendment.

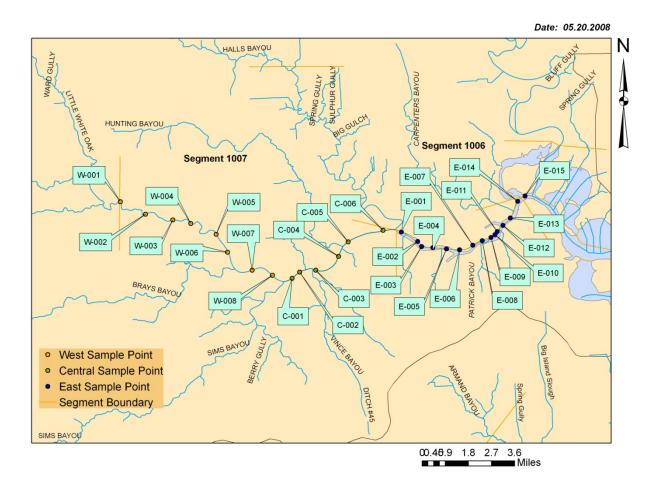


Figure 4.11. Intensive sediment sampling proposed stations in the Main Channel.

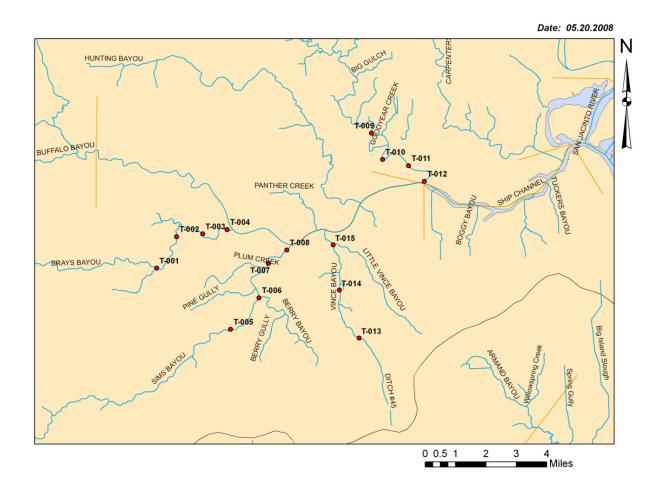


Figure 4.12. Proposed intensive sediment sampling locations in the tributaries.

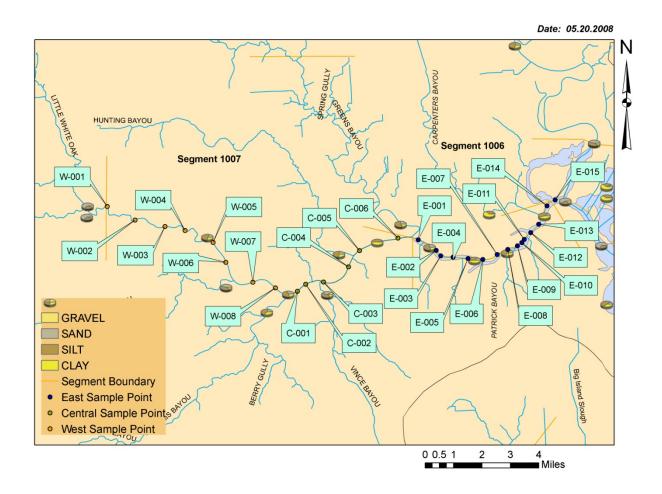


Figure 4.13. Sediment intensive sampling locations in the main channel compared with known grain size samples from 2002-2003 PCB sampling.

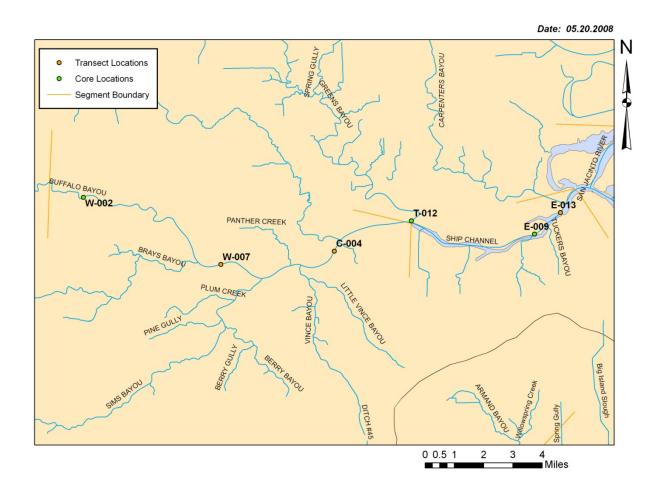


Figure 4.14. Transect and core locations. All locations presented have also been chosen for surface sediment sampling.

Table 4.5. Proposed intensive sediment station list with attributes.

Intensive ID	Stratum	Channel Type	Sample Type	SWQM Segment	SWQM Station ID	Latitude	Longitude	USGS Gauge	SWQM Description	Currently in QAPP?	Sampling Frequency	
W-001	West	Main Channel	Surface	1007	11297	29.76646	-95.34713	NA	BUFFALO BAYOU TIDAL AT US 59	No	1	Just ins
												Core samp
W-002	West	Main Channel	Surface, Core	1007	NEW STATION	29.75905	-95.33111	NA	TBD	No	1	upper Cha
												vertica
W-003	West	Main Channel		1007	NEW STATION	29.75542	-95.31366	NA	TBD	No	1	
W-004	West	Main Channel	Surface	1007	NEW STATION	29.75317	-95.30208	NA	TBD	No	1	
												Sample
												sedime
W-005	West	Main Channel	Surface	1007	NEW STATION	29.74672	-95.28581	NA	TBD	No	2	dry. Also will alrea
												exisitir
									HOUSTON SHIP CH			
W-006	West	Main Channel	Surface	1007	11290	29.73639	-95.27861	NA	ATWHARF 21/22	No	1	
			Surface,									Just dow
W-007	West	Main Channel	Transect	1007	NEW STATION	29.72588	-95.26317	NA	TBD	No	2	Brays Bay
												Thissam
W-008	West	Main Channel	Surface	1007	NEW STATION	29.72267	-95.25017	NA	TBD	No	1	will alrea
										TRATUM TOTAL	10	
C-001		Main Channel		1007	NEW STATION	29.72067	-95.23739	NA	TBD	No	11	
C-002	Central	Main Channel	Surface	1007	NEW STATION	29.72417	-95.23237	NA	TBD	No	1	This statio
												highest 2
												ng/ g dry
C-003	Central	Main Channel	Surface	1007	NEW STATION	29.72501	-95.22198	NA	TBD	No	1	(11300), j
												HSC (1000
												influence
												C-004 and
			0.1									of wha
C-004	Central	Main Channel	Surface, Transect	1007	NEW STATION	29.73249	-95.20710	NA	TBD	No	1	concent
			Hanseu									opposed
C-005	Central	Main Channel	Surface	1007	NEW STATION	29.74057	-95.20050	NA	TBD	No	1	0.00
C-006	Central	Main Channel	Surface	1007	18392	29.74642	-95.17773	NA	HSC 830M UPSTREAM GREENS	No	1	C-00 concentr
2 300	S. Itial	am aramici		1501	15002	20.1 1012	55.17776		BAYOU		•	
									CENTRALS	TRATUM TOTAL	6	
E-001	East	Main Channel	Surface	1006	NEW STATION	29.74533	-95.16599	NA	TBD	No	1	Thissan
									HSCUPSTREAM OF			Н
E-002	East	Main Channel	Surface	1006	15933	29.73981	-95.15553	NA	BELTWAY8	No	1	
									HSCBETWEEN			
E-003	East	Main Channel	Surface	1006	18391	29.73679	-95.15306	NA	CM150 AND	No	2	
									BELTWAY8 HOUSTON SHIP			
E-004	East	Main Channel	Surface	1006	11269	29.73583	-95.14584	NA	CHANNELAT	No	1	
									BELTWA			
E-005	East	Main Channel		1006	NEW STATION	29.73511	-95.13712	NA	TBD	No	1	
E-006	East	Main Channel	Surface	1006	NEW STATION	29.73439	-95.12861	NA	TBD	No	1	E-007 ar
												Patrick Ba
E-007	l E t	<sup>l</sup> MaiCh I	S f	1006	NEW STATION	29 73671	-95 12002	NA	TBD	l N	2	PtikB

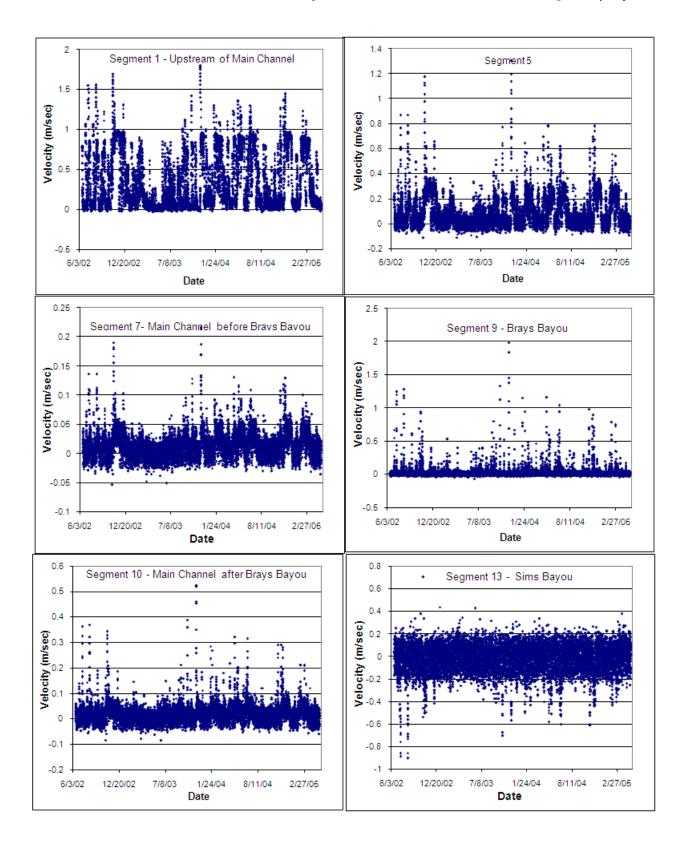
Intensive ID	Stratum	Channel Type	Sample Type	SWQM Segment	SWQM Station ID	Latitude	Longitude	USGS Gauge	SWQM Description	Currently in QAPP?	Sampling Frequency	
E-008	East	Main Channel	Surface	1006	16617	29.73908	-95.11384	NA	HSCAT CARGILL TERMINAL	No	1	
E-009	East	Main Channel	Surface, Core	1006	NEW STATION	29.74086	-95.10812	NA	TBD	No	2	A core s texture fro nearest to an idea o be
E-010	East	Main Channel	Surface	1006	NEW STATION	29.74242	-95.10553	NA	TBD	No	1	
E-011	East	Main Channel	Surface	1006	NEW STATION	29.74407	-95.10400	NA	TBD	No	1	
E-012	East	Main Channel	Surface	1006	NEW STATION	29.74745	-95.10016	NA	TBD	No	1	
E-013	East	Main Channel	Surface, Transect	1006	NEW STATION	29.75157	-95.09533	NA	TBD	No	1	This tran because i not a
E-014	East	Main Channel	Surface	1006	NEW STATION	29.76083	-95.09022	NA	TBD	No	1	
E-015	East	Main Channel	Surface	1005	NEW STATION	29.76377	-95.08539	NA	TBD	No	2	Sedim conflue here, whe will he Lynchbu (11261). high
									<i>EAST S</i>	TRATUM TOTAL	19	
T-001	Brays	Tributary	Surface	1007	15856	29.70936	-95.31645	NA	BRAYSBAYOUAT WAYSIDEDRIVE		1	
T-002	Brays	Tributary	Surface	1007	NEW STATION	29.72416	-95.30515	NA	TBD		1	
T-003	Brays	Tributary	Surface	1007	NEW STATION	29.72517	-95.29086	NA	TBD		1	
T-004	Brays	Tributary	Surface	1007	17037	29.72689	-95.27739	NA	BRAYSBAYOU TIDALMOUTH AT HSC		1	
T-005	Sms	Tributary	Surface	1007	15860	29.67931	-95.27692	NA	SIMSBAYOU AT BROADWAYST		1	
T-006	Sms	Tributary	Surface	1007	NEW STATION	29.69401	-95.26098	NA	TBD		1	
T-007	Sims	Tributary	Surface	1007	11302	29.71028	-95.25528	NA	SIMSBAYOUTIDAL ATLAWNDALE		1	
T-008	9ms	Tributary	Surface	1007	NEW STATION	29.71648	-95.24505	NA	TBD		1	
T-009	Greens	Tributary	Surface	1006	11275	29.77111	-95.19722	NA	GREENSBAYOU AT IH 10		1	
T-010	Greens	Tributary	Surface	1006	NEW STATION	29.75844	-95.19149	NA NA	TBD		1	
T-011	Greens	Tributary	Surface	1006	NEW STATION	29.75516	-95.17732	NA	TBD		1	
T-012	Greens	Tributary	Surface, Core	1006	NEW STATION	29.74749	-95.16898	NA	TBD		1	A core sam in a tribu and will
T-013	Vinœ	Tributary	Surface	1007	14370	29.67364	-95.20679	NA	VINŒBAYOUAT SOUTH SHAVER		1	
T-014	Vinœ	Tributary	Surface	1007	14369	29.69667	-95.21696	NA	VINCEBAYOU AT WESTHARRISAVE		1	
T-015	Vinœ	Tributary	Surface	1007	11300	29.71833	-95.21972	NA	VINCEBAYOUAT NORTH RICHEYST		1	
									TRIBUTARYS	TRATUM TOTAL	15	
									SURF	-ACE SAMPLES	50	
										SECT SAMPLES	15	
										ORE SAMPLES	15	
									GRAND TOTA	<i>LOFSAMPLES</i>	80	

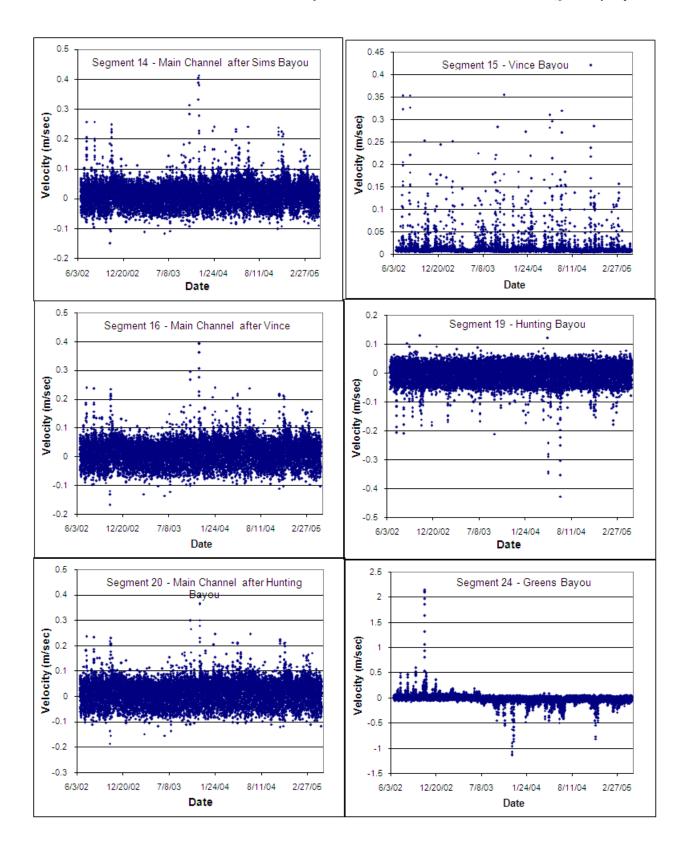
#### CHAPTER 5 - REFERENCES

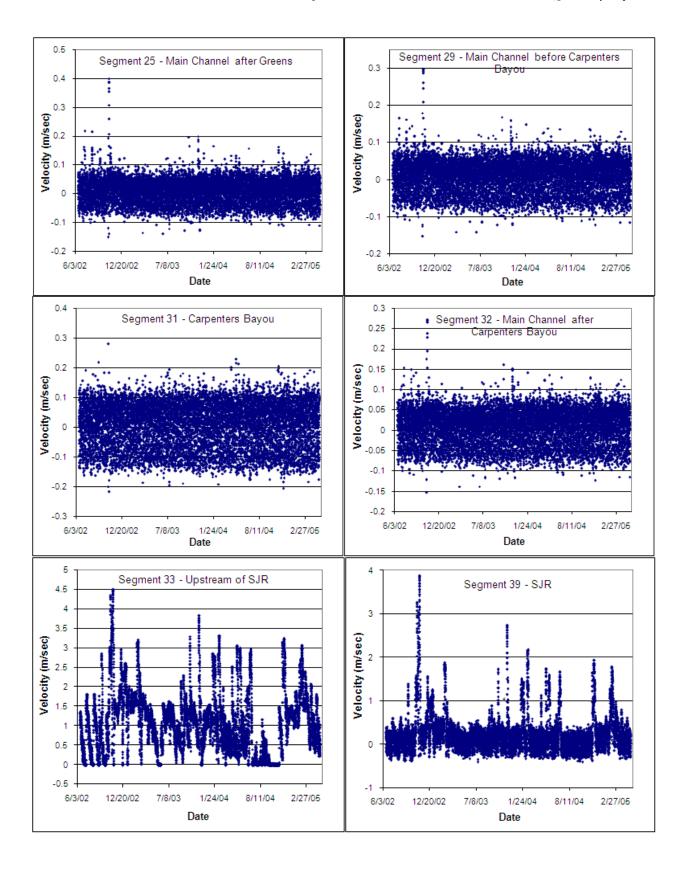
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- Yeager, K.M., Santschi, P.H., Rifai, H.S., Suarez, M.P., Brinkmeyer, R., Hung, C.C., Schindler, K.J., Andres, M.J., Weaver, E.A., 2007. Dioxin Chronology and Fluxes in Sediments of the Houston Ship Channel, Texas: Influences of Non-Steady-State Sediment Transport and Total Organic Carbon.

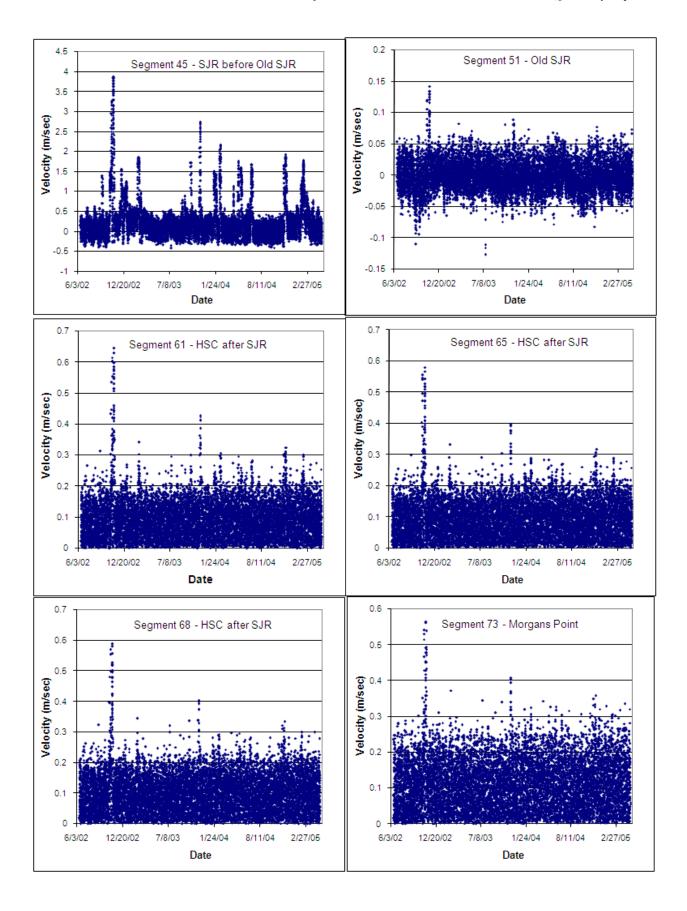
### CHAPTER 6 - APPENDICES

# APPENDIX A - WASP VELOCITY TIME SERIES PLOTS PER SEGMENT

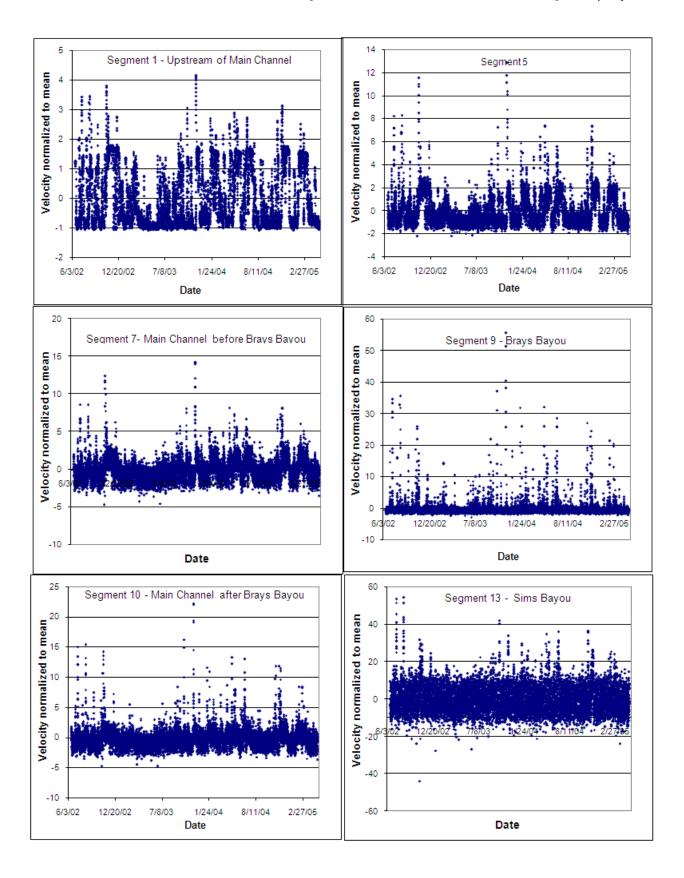


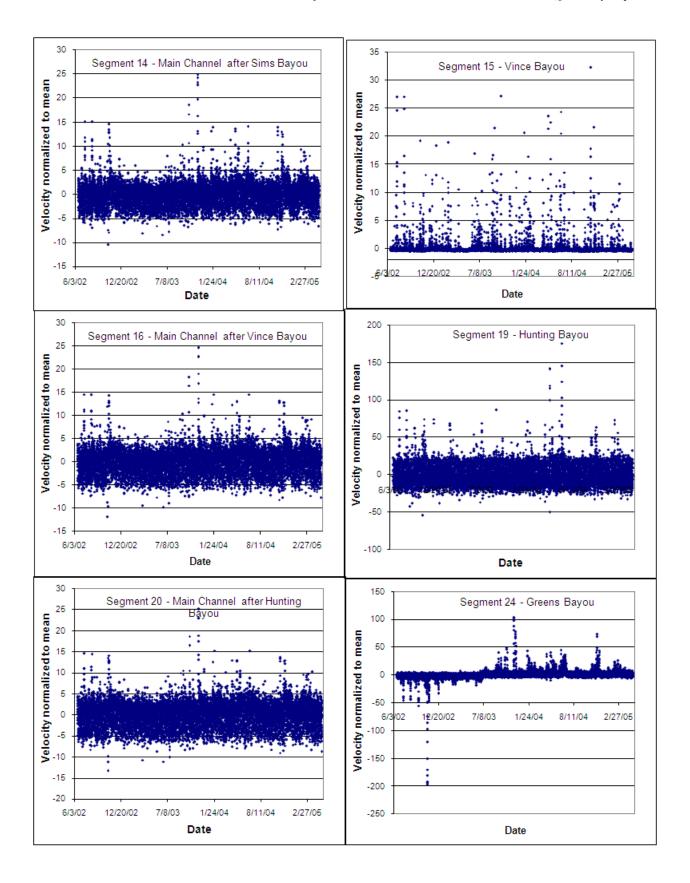


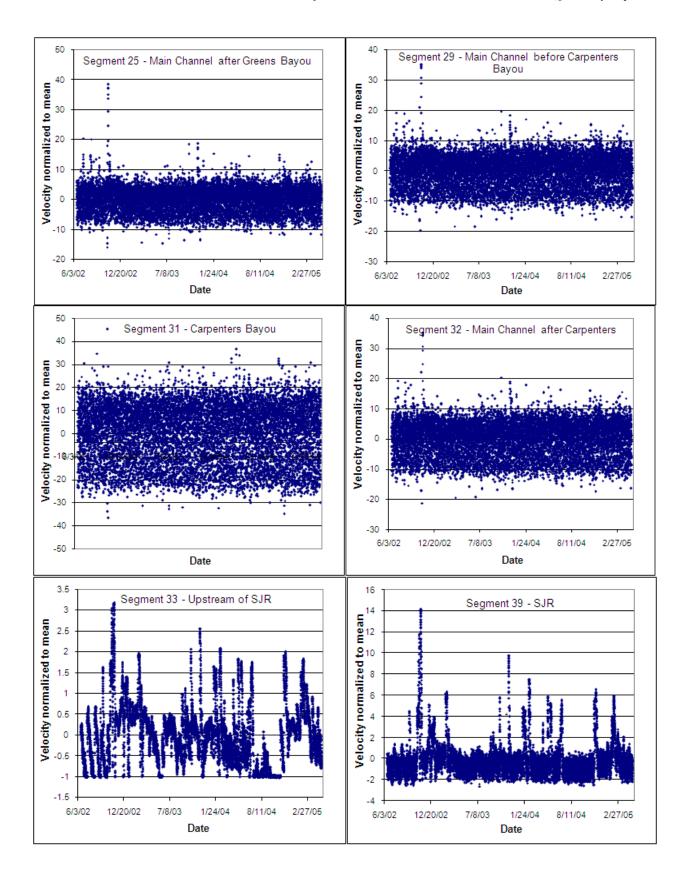


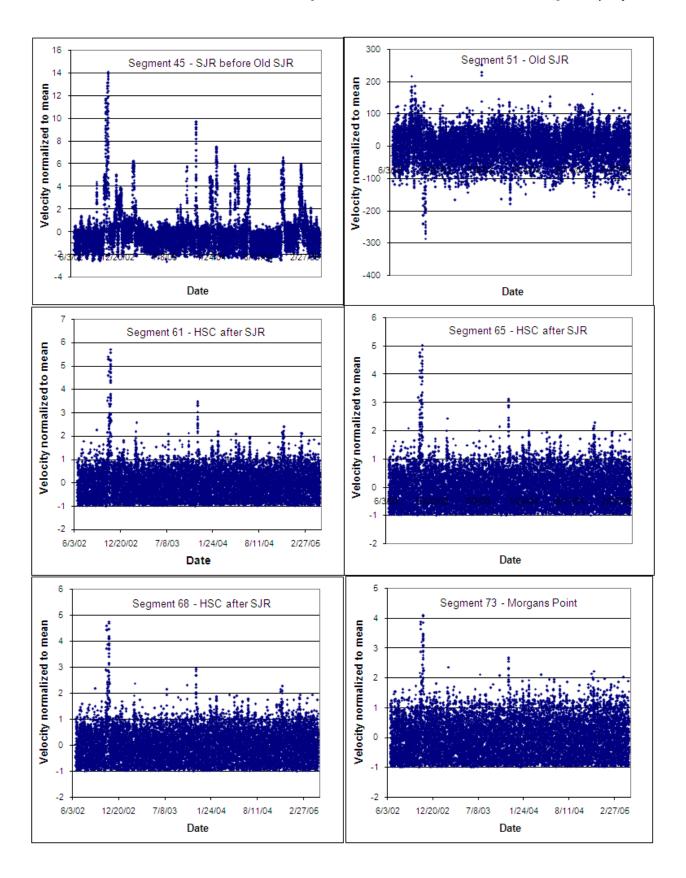


## APPENDIX B - NORMALIZED VELOCITY VARIATION PLOTS FROM WASP MODELING OUTPUT









### APPENDIX C -

## APPENDIX D - COMPLETE DATA USED IN THE SEDIMENT INTENSIVE SAMPLING DESIGN

## APPENDIX E - ADDITIONAL STATISTICS USED IN THE SEDIMENT INTENSIVE SAMPLING DESIGN

Table C.1. Sediment Intensive Sample Planning Analytical Results. Data data taken from the 2002-2003 PCB sample dataset.

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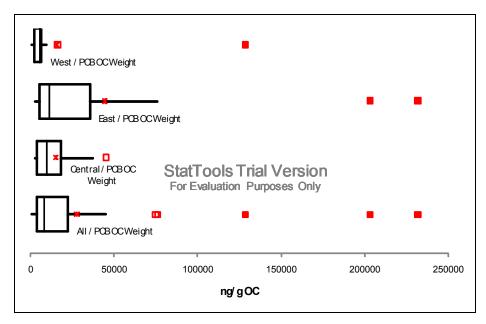


Figure D.1. Box plot distributions of dry weight PCB concentrations from 20022-2003 in the proposed sediment intensive sampling area.

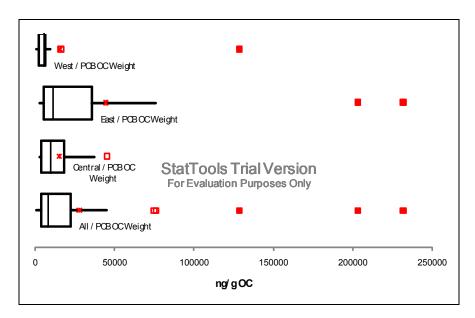


Figure D.2. Box plot distributions of OC normalized PCB concentrations from 20022-2003 in the proposed sediment intensive sampling area.

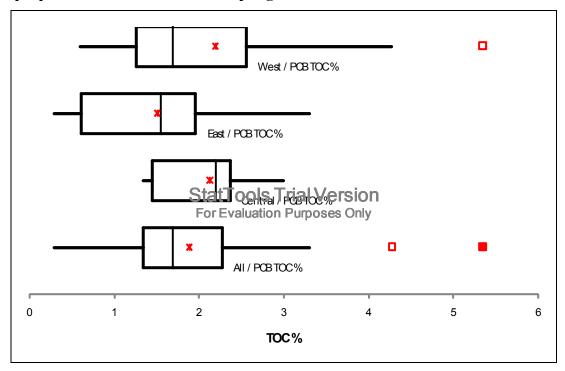


Figure D.3. Box plot distributions of TOC% concentrations from 20022-2003 in the proposed sediment intensive sampling area.

Table E.1. Complete summary statistics for the strata.

Constituent #	1		
Constituent	∑PCBdry wt	ng/g dry	
	West	Central	East

Wilderit	2 abony wi	rig/g ai y	
	West	Central	East
n	12	11	17
Mean	321	318	963
Median	71.5	232	126
SD	819	283	1567
Min	37	45	17
Max	2917	840	4669
CV	2.55	0.89	1.63
95% LCL	-199	128	158
95%UCL	842	509	1769
1st Quartile	115	48	54
3rd Quartile	397	527	102
IQR	282	479	48
True Low Outlier	-307	-670	-17
Lower Outlier Used	0	0	0
Upper Outlier	819	1246	173

Constituent	TOC%	%	
	West	Central	East
n	12	11	17
Mean	2.2	2.1	1.5
Median	1.9	2.2	1.6
SD	1.4	0.6	0.9
Min	0.6	1.3	0.3
Max	5.4	3.0	3.3
CV	0.63	0.27	0.58
95% LCL	1.3	1.7	1.1
95% UCL	3.1	2.5	2.0
1st Quartile	1.7	0.6	1.3
3rd Quartile	2.4	1.8	2.6
IQR	0.8	1.2	1.3
True Low Outlier	0.5	-1.2	-0.7
Lower Outlier Used	0.5	0.0	0.0
Upper Outlier	3.6	3.5	4.5

2

Constituent#

Constituent	∑POBOC .	ng/g OC	
	West	Central	East
n	12	11	17
Mean	1.6E+04	1.5E+04	4.5E+04
Median	5.6E+03	1.1E+04	1.4E+04
SD	3.6E+04	1.4E+04	6.9E+04
Min	7.9E+02	3.0E+03	2.7E+03
Max	1.3E+05	4.5E+04	2.3E+05
CV	2.26	0.93	1.55
95% LCL	-6.9E+03	5.9E+03	9.1E+03
95% UCL	3.9E+04	2.5E+04	8.0E+04
1st Quartile	4.4E+03	5.8E+03	2.4E+03
3rd Quartile	2.0E+04	3.3E+04	7.1E+03
IQR	1.6E+04	2.7E+04	4.8E+03
True Low Outlier	-2.0E+04	-3.5E+04	-4.8E+03
Lower Outlier Used	0	0	0
Upper Outlier	4.4E+04	7.4E+04	1.4E+04

3

Constituent#

## APPENDIX F - ORIGINAL RMA2 VELOCITY DATA SET INCLUDED AS IT IS AGGREGATED PER WASP SEGMENT

The data is included electronically on CD with this report.