Total Maximum Daily Loads for PCBs in the Houston Ship Channel

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Quarterly Report 4

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PREPARED IN COOPERATION WITH THE
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September 2009

TABLE OF CONTENTS

TABLE OF CONTENTS 2

1. INTRODUCTION 3

2. MONITORING AND DATA COLLECTION 4

2.1 ASSESSMENT OF CURRENT LEVELS AND TRENDS OF PCBS IN THE HOUSTON SHIP CHANNEL 4

2.1.1 In-stream Water Quality Sampling 5

2.1.2 Sediment Sampling 11

2.1.3 Tissue Sampling 11

2.2 RUNOFF SAMPLING 12

2.3 EFFLUENT SAMPLING ACTIVITIES 15

2.3.1 Effluent Site Selection and Methodology 15

2.3.2 Summer 2009 Effluent Sampling 18

3. PLANNED ACTIVITIES FOR THE NEXT QUARTER 24

Appendix A - Slides from Stakeholder/Public Participation Meeting

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 to issue seafood consumption advisories. Two specific advisories have been issued recently for the Houston Ship Channel (HSC) 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 (Total Maximum Daily Loads) need to be developed and implemented. The overall purpose of this project is to develop TMDL allocations for PCBs in the Houston Ship Channel System, including upper Galveston Bay, and establish a plan for managing PCBs to correct existing water quality impairments and maintain good water quality in the future. This report is the fourth quarterly report for FY09 and describes progress during the months June through August 2009. The main task that was the focus of effort in this quarter was the monitoring and data collection task. One stakeholder/public involvement meeting was held on July 14, 2009. The project team attended the meeting and made a presentation about the project. The slides for the presentation are attached in Appendix A.

2. MONITORING AND DATA COLLECTION

This task encompasses monitoring and sampling activities to assess current levels of PCBs in the Houston Ship Channel (HSC) system. Runoff sampling was conducted in the few wet days that occurred during the quarter and 7 stations have been sampled thus far for this fiscal year. Dry weather reconnaissance and sampling activities were initiated in May 2009, and all the sampling activities discussed in the QAPP have been completed except for one site. To date, a total of 47 water locations, 35 sediment locations, and 30 locations for fish tissue, have been sampled. Additionally 16 effluent locations were sampled. These activities will be described in more detail below.

2.1 Assessment of Current Levels and Trends of PCBs in the Houston Ship Channel

The main purpose of the sampling task is to assess the severity, spatial and temporal extent of the PCBs and determine whether water quality is improving or deteriorating for the segments of interest. The goals are: (i) to use the data results to verify whether PCB concentrations are above the criteria and where, and/or how much PCB levels must decline to meet the criteria, (ii) to identify historical increases and declines in PCB levels that may be related to changes in sources over time, and (iii) to characterize other segments/waterbodies, such as the side bays, where PCB levels have not been previously measured.

As mentioned above, 35 locations have been sampled for sediment, 47 locations for ambient water, and 30 locations for fish tissue. Table 1 includes a summary of the total number of samples collected in 2009.

Table 1 Summary of samples collected during 2009 sampling event

Matrix		2009 Dry sampling		
		# of samples	**QC samples***	**Total # of samples**
Water	XAD column	47	8	55
	GFF	47	7	54
In-stream sediment		35	7	42
Fish tissue	Cat fish	31	5	36
	Trout/Croaker	18	4	22

* QC samples include field duplicates, field blanks and recovery columns specified in the QAPP.

2.1.1 In-stream Water Quality Sampling

Since PCB concentrations in water are significantly lower than the analytical detection limit, water sampling was conducted using the high-volume technique. Using this technique allows concentrating PCBs from large volumes of water to obtain measureable quantities. The high-volume system uses a stainless steel column packed with hydrophobic polymeric resin beads through which large volumes of water can be passed. Because PCBs are very hydrophobic, they rapidly sorb to the resin, making it possible to completely collect the dissolved PCBs from the sampled water. The PCBs can then be recovered from the resin by extraction with a nonpolar organic solvent in the laboratory. PCBs associated with suspended particulates are collected on a 1-μm filter that is also extracted in the laboratory. For this TMDL, an Infiltrex 300 high-volume sampling system is used. The Infiltrex 300 system is primarily comprised of the following components:

• An in-line pre-filter (140 μm) to remove debris and plankton larger than 140 μm that has the capability to foul the system and damage the pump head;

• a stainless steel positive displacement pump;

- Glass fiber filter cartridges (1 μm effective pore size);
- a pressure gauge on the filter cartridge to help in preventing the filter from clogging;
- XAD-2 resin column; and
- a digital display unit displaying the pumping rate.

Water sampling was conducted at three different depths (2 ft from bottom, middle, and 1ft from top), to form a composite water column sample for analysis. A pumping rate of 1.1 ± 0.1 L/min was selected so that the target volume of 200 L could be attained in 3 hours. Figure 1 shows the locations of the stations sampled and Table 2 includes a description of the sites. In addition to collecting the glass filter and XAD resin at each location, water samples composited by depth were collected for TSS, DOC, and TOC analyses. Field probe parameters (i.e., pH, temperature, conductivity, and salinity) were also obtained using an YSI sonde (YSI 600-XLM).

The water sampling activities went without major concerns except at station 11171. Due to construction work at that site, a new location about 1500 ft upstream of station 11171 had to be selected for water sampling. The only site that was not sampled during the event was 16872 (Patrick Bayou at SH 225) due to access issues.

Table 2 Summary of water, sediment, and tissue sampling

					Samples collected as of August 31, 2009				
									Fish (F3)
									√ (HH) (Dup)

					Samples collected as of August 31, 2009				
									Fish (F3)
									√ (ST)
									√ (ST) (Dup)

					Samples collected as of August 31, 2009				
									Fish (F3)

Notes:

1) Δ indicates samples that were to be collected as specified in the QAPP.
2) √ indicates successful sample collection; * indicates yet to be sampled; × indicates unsuccessful sample collection (i.e., no fish present)
3) Red color indicates that the station was replaced with a new station due to access issues.
4) Dup indicates duplicate collected on the sampling day.
5) HH = Hardhead Catfish, BC = Blue Catfish, AC = Atlantic Croaker, ST = Speckled Trout, CC = Channel Catfish.

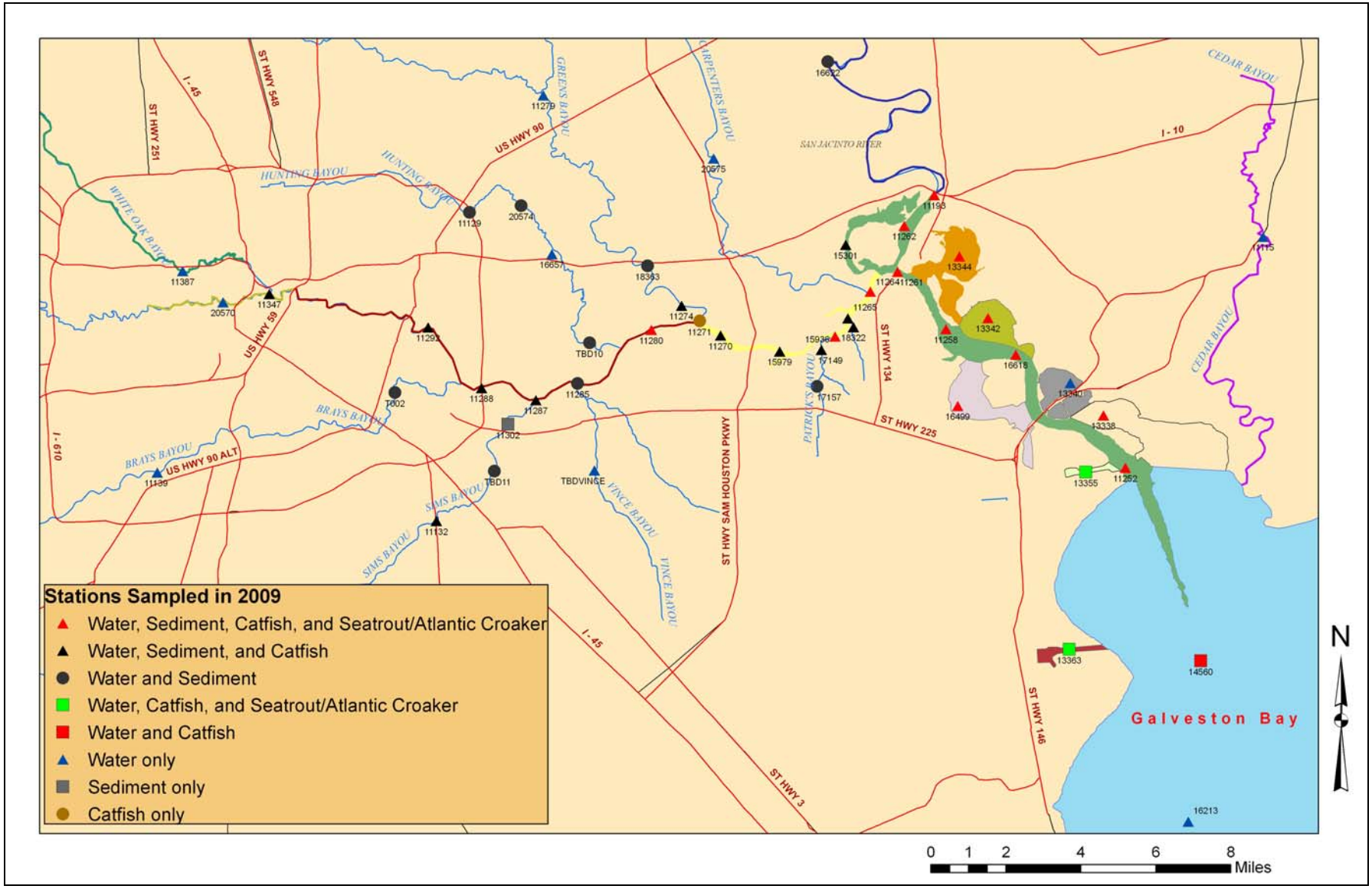


Figure 1 Locations of stations sampled for water, sediment and fish in 2009

2.1.2 Sediment Sampling

Sediment samples were collected using a steel Ponar dredge. Prior to collection at each sample site, the dredge, stainless steel spoon/trowel, and stainless steel bucket were rinsed with deionized water, then ambient water. Samples were collected and deposited into a stainless bucket. A minimum of three grab samples along a channel transect were composited using the top 5 centimeters of sediment, mixed thoroughly with a clean stainless steel trowel, and deposited into appropriate labeled, pre-cleaned glass jars as necessary for analysis.

A total of 35 locations have been sampled for sediment in the main channel, San Jacinto River, Upper Galveston Bay, and side bays during the 2009 event. Figure 1 shows the locations of the stations. Table 2 includes a summary of the sampling activities at the stations.

2.1.3 Tissue Sampling

Tissue was sampled along with the sediment samples to obtain data on accumulation and/or transport of PCBs. For this sampling component, fish were collected, processed, and analyzed. Species that were sampled include Hardhead catfish (*Arius felis*), Blue catfish (*Ictalurus furcatus*), Speckled trout (*Cynoscion nebulosus*), and Atlantic croaker (*Micropogonias undulates*). For fish tissue collection, gill nets or fishing lines were used with bait (shrimp or chicken) to catch enough fish (catfish, trout, croaker) to obtain the appropriate mass of muscle tissue. Fish with a total length of 300 mm or greater were the target length for collection. After each station collection, fish were placed into a labeled Ziploc plastic bag, and placed into a cooler with ice. Once all fish samples were collected, the samples were taken to the U of H laboratory, measured, weighed, and then processed. Collected fish were then filleted with a clean stainless steel knife, packed in clean

aluminum foil with the dull side facing the tissue and placed into individual Ziploc bags. Fillets were taken from the left side of the fish and, in most cases; the right side was used as a duplicate sample. All Ziploc bags were labeled, and frozen until shipment was made to the analytical laboratory. The fish tissue samples of a single species collected at a single station were composited into a single sample for analysis.

All 38 locations specified in the QAPP were sampled for fish, however successful collection was only possible for 30 locations for catfish and 16 locations for Seatrout/Atlantic Croaker (see Table 2 and Figure 1).

2.2 Runoff Sampling

For runoff sampling, 12 sites were selected and visited to ascertain access and identify safety issues. During the year, seven locations have been sampled for runoff using a high-volume unit (Infiltrex 300). It is noted that very few wet weather opportunities for sampling occurred during the quarter and it appears that the region is in a drought cycle. The stations that have been sampled and those yet to be sampled for runoff are shown in Figure 2. Sampling typically proceeded in the following manner:

First, using radar images and weather reports, a sampling team mobilized to a preselected sampling site in advance of the storm. Upon arrival at the sampling site, the booster pump and discharge line were placed in the stream and sampling begun using the high-volume equipment located in a suitable location on the bank. The gear pump on the Infiltrex drew from the stainless steel reservoir while the booster pump continuously pumped runoff water from the channel. This arrangement was necessary due to the low suction lift capability of the Infiltrex unit gear pump.

The team continued sampling until the desired sample size (i.e. 200 L) was achieved. The standard high-volume equipment was supplemented with extractable 40 micron pre-filters installed before the standard 1 micron filters to extend filter run times under heavy solids loading and minimize primary filter changes. All filters and pre-filters used during the processing of a sample were collected for PCB analysis.

During sample volume collection, grab samples were collected at equal intervals. Equal amounts of all samples were combined into one large container and stored on ice. The composite volume was used to obtain sub-samples for TSS, TOC, and DOC.

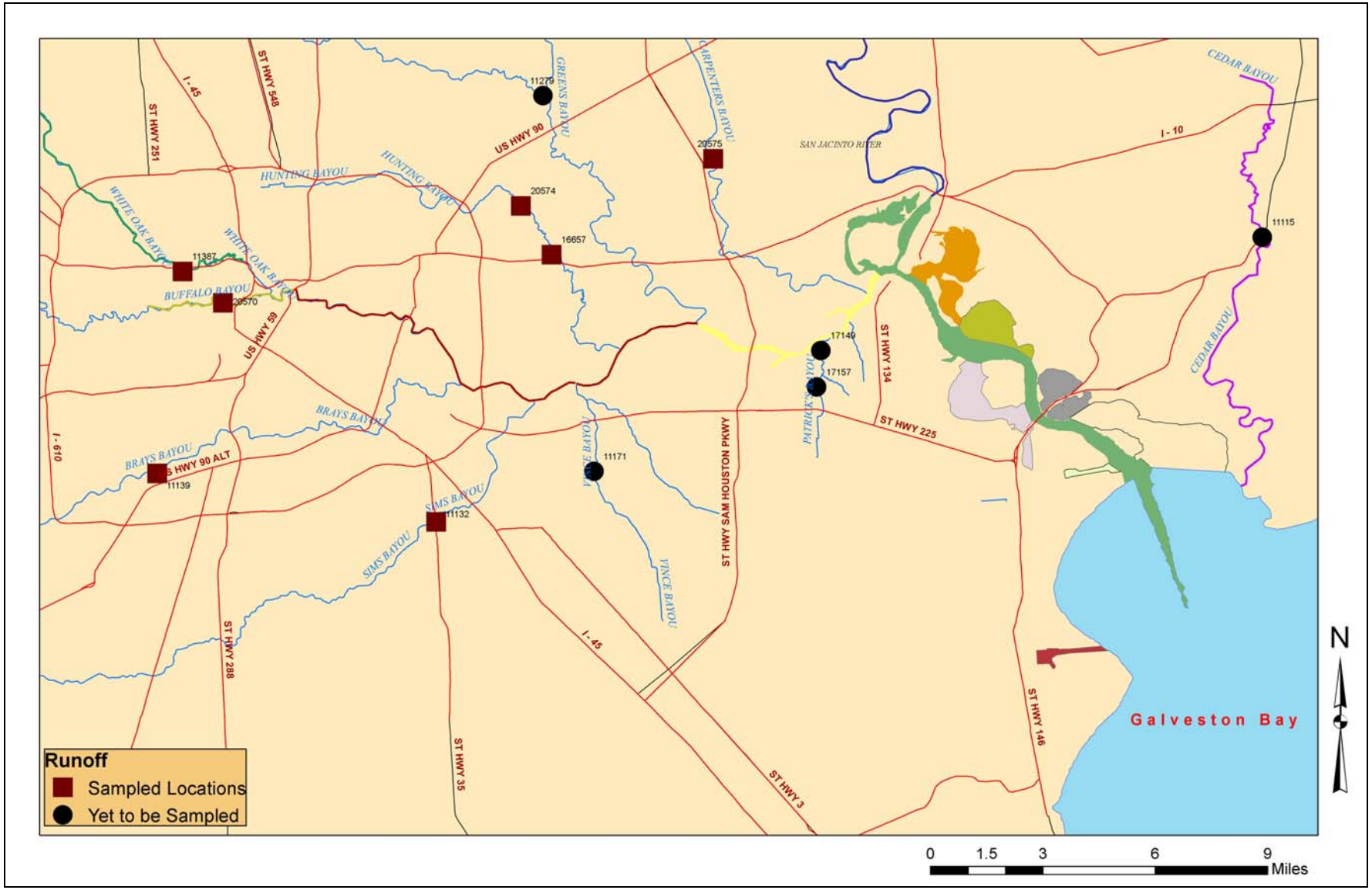


Figure 2 Locations of stations sampled/ yet to be sampled for runoff

2.3 Effluent Sampling Activities

Effluent site selection and sampling were also conducted in this quarter. The following section presents the site selection methodology and a summary of the field activities related to effluent sampling.

2.3.1 Effluent Site Selection and Methodology

There were specific goals that drove the development of criteria for effluent sampling locations. These goals were.

1. *Geospatial Variability*: Since the overall goal of this project is to generate a TMDL for PCBs and not every outfall may be sampled, it was important to be able to have samples that would be representative of different areas in the HSC.

2. *Industry Diversity*: Current research in industrial PCB sourcing often focuses on trying to understand the fingerprint of particular industry types. While it is true that particular outfalls from different facilities of the same industry type will differ, there should be some similar contamination signatures that may be used for source tracking and modeling outfalls that could not be sampled directly.

3. *Positive Results*: If there are any significant PCB sources, the sampling design should set out to identify them. Outfalls that yield a large percentage of non-detects may not be as representative or useful.

The outfall selection process (Figure 3) was progressively selective. At various points, a smaller and smaller funnel was used. The starting point was to gather information on all of the

outfalls in the HSC area. The EPA Envirofacts[1] database was used according to three counties that encompass the HSC—Chambers, Harris, and Galveston. Rather than search by facility, outfalls drove the process. Thus, there were many cases were multiple outfalls within a facility had to be searched according to their individual characteristics. Once the information for the outfalls was gathered, the list was narrowed down by limiting the search to outfalls that were within 2-3 miles of the HSC.

The narrowed down list represented all industrial outfalls that could hydrologically be relevant to the ship channel. It contained different kinds of industries within it. The outfall information was combined with facility information including the Standard Industrial Classification (SIC) code and then further combined with permit information that includes a listing of specific constituents that were included on the NPDES Permit. From this combined information, a final list of 25 facilities was chosen according to following criteria.

1. *Chlorinated Organic Contaminant Regulation*: Only one facility in all of Harris, Chambers, and Montgomery counties is explicitly regulated for PCBs. It is likely, however, that facilities that are on record for making and wasting chlorinated substances in their effluent may incidentally produce PCBs. Therefore, a large portion of facilities where access was requested were regulated for chlorinated contaminants and had a high potential load of chlorinated contaminants as determined by the recorded monthly outfall data.

2. *Large and Current Flows*: Generally, outfalls were only chosen if they had relatively large flows, and those flows were current and consistent. It is unlikely that a facility that has very low flows (even if it produces PCBs) would be a significant source of PCBs.

[1] http://www.epa.gov/enviro/

3. *Industry Diversity*: A look at the industry profile given by facilities that are regulated for chlorinated organic yields almost completely chemical plants and refineries. Other industry types such as storage facilities, municipal wastewater treatment plants, and power plants were added to the list to increase the number and diversity of industry types.

4. *Geospatial Considerations*: Outfalls were chosen to allow good spatial coverage in the HSC and to try and get at least one facility that discharges to the major bayous along the upper Houston Ship Channel[2] whenever possible.

[2] Brays, Sims, Vince, Hunting, Patrick, Greens, and Carpenters Bayous

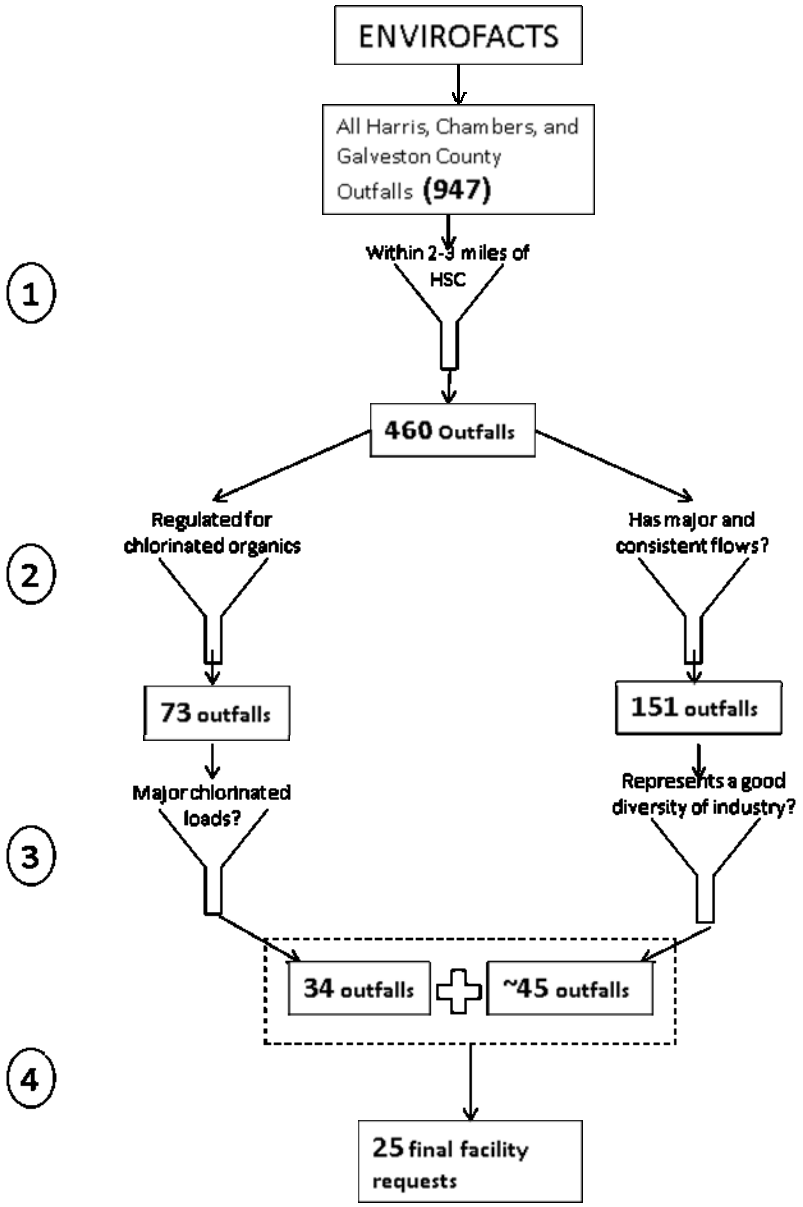


Figure 3 Effluent site location selection process

2.3.2 Summer 2009 Effluent Sampling

The final list of effluent facilities selected for possible sampling is shown in Table 3. Twenty total effluent samples were specified in the QAPP, however, and anticipating some difficulty in obtaining permissions, a total of twenty-six facility access requests were made. Of the

twenty-six, only sixteen were requests were granted (2 additional facilities granted access for October 2009).

All effluent sites were sampled for PCBs in both suspended and dissolved phases, Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Total Suspended Solids (TSS), and standard water quality parameters. One effluent location was used as a field duplicate (Almeda-Sims Bayou WWTP), and two facilities requested that a split sample be taken for their own separate analysis (Rohm & Haas, Ineos Polyethylene). It is not clear at this time if the plants that have the split sample are going to analyze them or not to compare with the results from the parent sample.

Table 3 List of facilities where effluent sampling access was requested

NPDES Permit	TCEQ Permit	Entity Name	Facility Name	City	Industry Type	Response to Effluent Sampling Request	Sampling Status
TX0007412	WQ0000305-000	Oxy Vinyls LP	Deer Park Plant	Deer Park	ALKALIES AND CHLORINE	Access delayed until later date	Delayed access prevented sampling
TX0124303	WQ0004344-000	Deer Park Energy Center LP	Deer Park Energy Center	Deer Park	ELECTRICAL SERVICES	Access delayed until later date	Delayed access prevented sampling
TX0002798	WQ0001499-000	Bayer Material Science LLC	Bayer WWTP	Baytown	INDUST. ORGANIC CHEMICALS NEC	Access denied	Not sampled
TX0003531	WQ0000391-000	Equistar Chemicals L.P.	Channelview Complex	Houston	INDUST. ORGANIC CHEMICALS NEC	Access denied	Not sampled
TX0119792	WQ0004013-000	Equistar Chemicals L.P.	Polyethylene Plant	Deer Park	PLSTC MAT./SYN RESINS/NV ELAST	Access denied	Not sampled
TX0007552	WQ0000815-000	Chevron Phillips Chemical Co.	Pasadena Plastics Complex	Pasadena	PLSTC MAT./SYN RESINS/NV ELAST	Access denied	Not sampled
TX0069493	WQ0002927-000	Lyondell Chemical Company	Channelview Facility	Channelvie w	CYCLIC CRUDES INTERM. DYES	Access denied	Not sampled
TX0005380	WQ0001054-000	Gulf Coast Waste Disposal Authority	Bayport Faciltiy	Pasadena	SEWERAGE SYSTEMS	Access granted	Sampled
TX0052591	WQ0001740-000	Gulf Coast Waste Disposal Authority	Washburn Tunnel Facility	Pasadena	SEWERAGE SYSTEMS	Access granted	Sampled

NPDES Permit	TCEQ Permit	Entity Name	Facility Name	City	Industry Type	Response to Effluent Sampling Request	Sampling Status
TX0006033	WQ0000544-000	Ineos Polyethylene North America	La Porte Plant	La Porte	PLSTC MAT./SYN RESINS/NV ELAST	Access granted	Sampled
TX0004863	WQ0000402-000	Shell Oil Company	Deer Park Chemical Plant	Deer Park	PLSTC MAT./SYN RESINS/NV ELAST	Access granted	Sampled
TX0004731	WQ0000492-000	Albemarle Corporation	Pasadena Plant	Pasadena	INDUST. ORGANIC CHEMICALS NEC	Access granted	Sampled
TX0006084	WQ0000458-000	Rohm & Haas Texas Incorporate	Rohm & Hass Texas Inc.	Deer Park	INDUST. ORGANIC CHEMICALS NEC	Access granted	Sampled
TX0004961	WQ0000587-000	Texas Petrochemicals LP and Kemira Water Solutions	Texas Petrochemicals LP and Kemira Water Solutions	Houston	INDUST. ORGANIC CHEMICALS NEC	Access granted	Sampled
TX0007439	WQ0000749-000	GB Biosciences Corporation	Greens Bayou Plant	Houston	PESTICIDES & AGRICULTURAL CHEM	Access granted	Sampled
TX0068349	WQ0001984-000	Intercontinental Terminals Co.	ITC	Deer Park	SPECIAL WAREHOUSING & STORAGE	Access granted	Sampled
TX0005941	WQ0001429-000	Clean Harbors Deer Park L.P.	Clean Harbors Deer Park WWTP	Deer Park	REFUSE SYSTEMS	Access granted	Sampled
TX0072834	WQ0010395-008	City of Baytown	General District Plant	Baytown	SEWERAGE SYSTEMS	Access granted	Sampled

NPDES Permit	TCEQ Permit	Entity Name	Facility Name	City	Industry Type	Response to Effluent Sampling Request	Sampling Status
TX0025062	WQ0010032-001	Harris County FWSD 51	Harris County FWSD NO. 51-WWTP	Houston	SEWERAGE SYSTEMS	Access granted	Sampled
TX0034924	WQ0010495-003	City of Houston	Almeda-Sims WWTP	Houston	SEWERAGE SYSTEMS	Access granted	Sampled
TX0096172	WQ0010495-090	City of Houston	69th Street WWTP	Houston	SEWERAGE SYSTEMS	Access granted	Sampled
TX0063061	WQ0010495-009	City of Houston	Chocolate Bayou WWTP	Houston	SEWERAGE SYSTEMS	Access granted	Sampled
TX0022799	WQ0010206-001	City of La Porte	Little Cedar Bayou WWTP	La Porte	SEWERAGE SYSTEMS	Access granted	Sampled
TX0002976	WQ0000535-000	Valero Refining - Texas L.P.	Valero Refining - Texas L.P.	Houston	PETROLEUM REFINING	No response	Not sampled
TX0006378	WQ0001031-000	Reliant Energy Incorporated	NRG Texas Power LLC	La Porte	ELECTRICAL SERVICES	No response	Not sampled
TX0053970	WQ0010195-001	City of Jacinto City	City of Jacinto City WWTP	Jacinto City	SEWERAGE SYSTEMS	No response	Not sampled

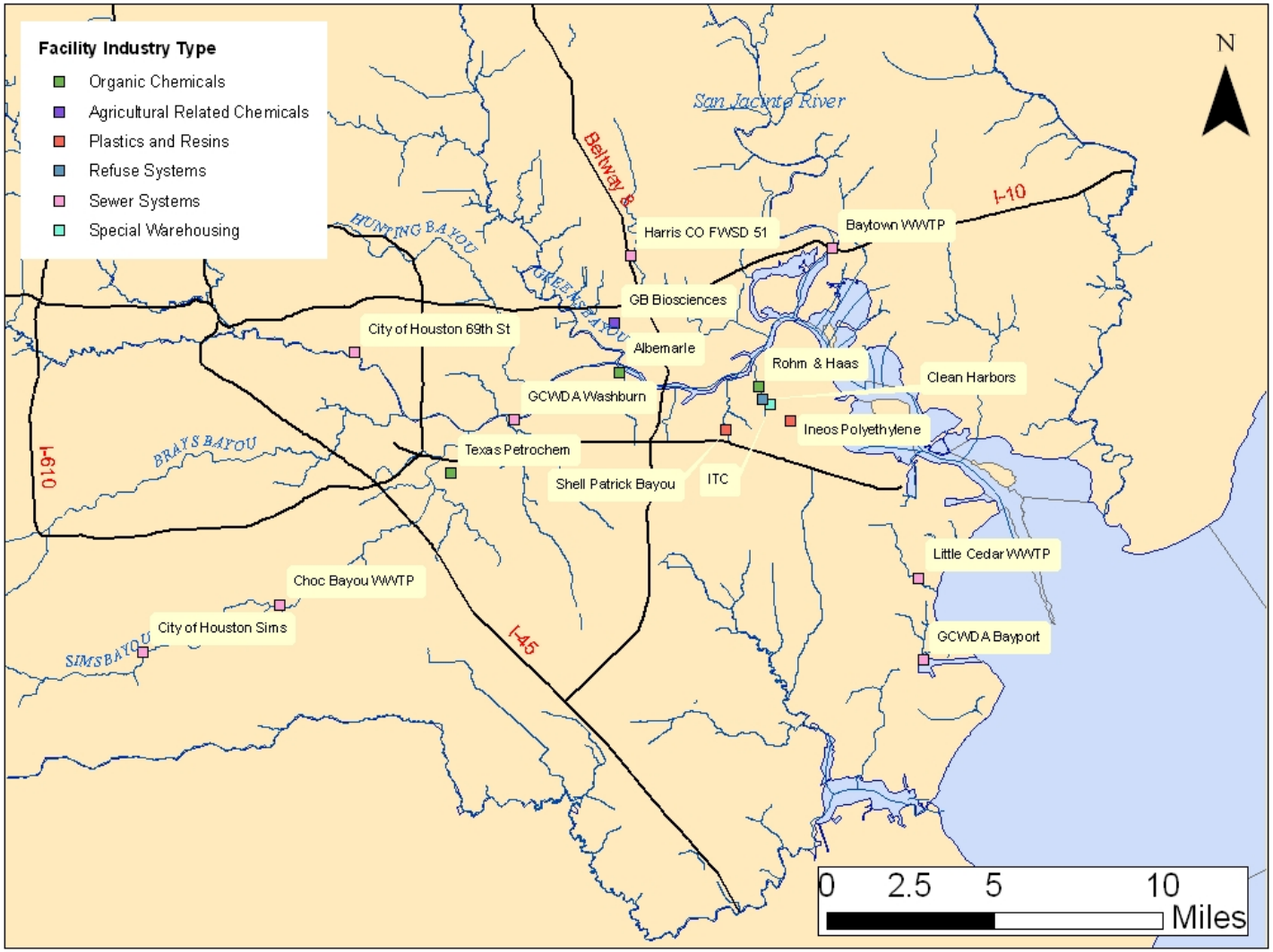


Figure 3 Locations of stations sampled for effluent

3. PLANNED ACTIVITIES FOR THE NEXT QUARTER

During the period from September 1, 2009 to November 31, 2009, the project team will focus on the following activities:

1) The runoff sampling activities for this fiscal year in support of the assessment of current levels and trends of PCBs in the Houston Ship Channel will be continued.
2) The quality assurance/quality control (QA/QC) tasks will be conducted including monitoring/coordinating sample deliveries to the laboratories, laboratory compliance with the QAPP, and verification of data packages.
3) The results from the 2009 event will be analyzed and compared with previous datasets.

Appendix A

Slides for Stakeholder Presentation on July 14, 2009

Total Maximum Daily Load for PCBs in the Houston Ship Channel

University of Houston
Parsons

July 14, 2009

Outline

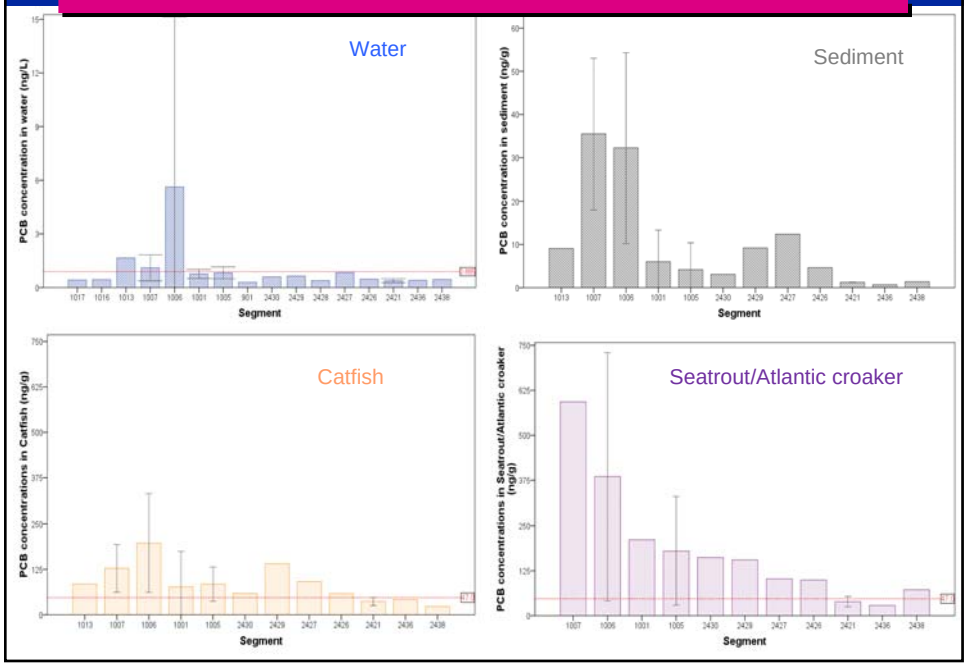
- **FY 2008 PCB results**
- **2009 PCB sampling status**
- **PCB concentration over time**

FY 2008 PCB Results

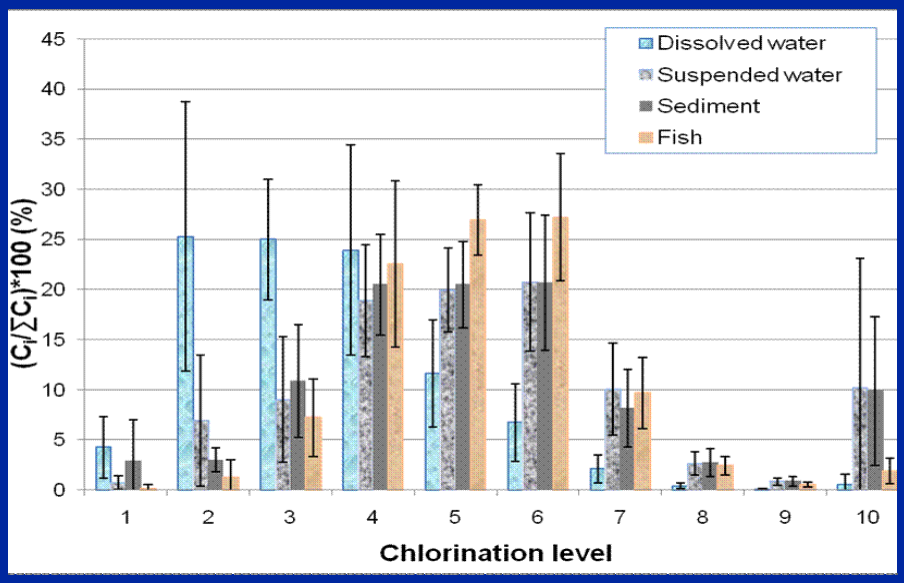
FY 2008 PCB Sampling

- 37 sites sampled for water (dissolved & suspended)
- 25 sites sampled for sediment
- 26 sites sampled for catfish and 19 sites sampled for seatrout or atlantic croaker
- Additional sediment samples collected as part of intensive sediment sampling
- Total PCB calculated as sum of 43 congeners (McFarland and Clarke, 1989); non-detects assumed as ½ MDL

PCB Concentrations by Segment (2008)

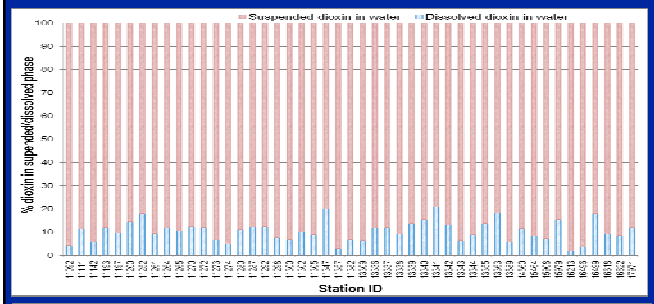


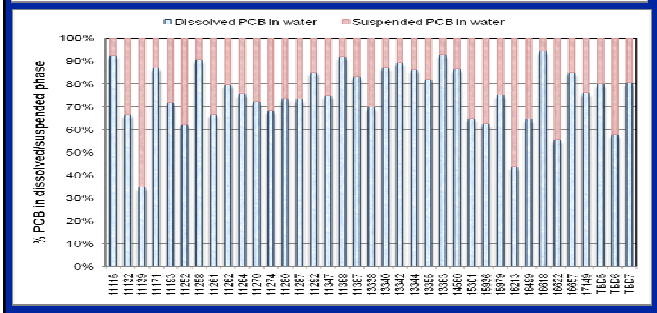
PCB Homologue Distribution in Water, Sediment, and Fish



* Fish results include average of catfish and seatrout/atlantic croaker results

Suspended vs Dissolved Dioxin/PCB in Water





- Dioxin concentrations = ∑17 congeners;
- PCB concentrations = ∑ 43 congeners (McFarland and Clarke, 1989)

Water bodies reported to have PCB higher in dissolved phase

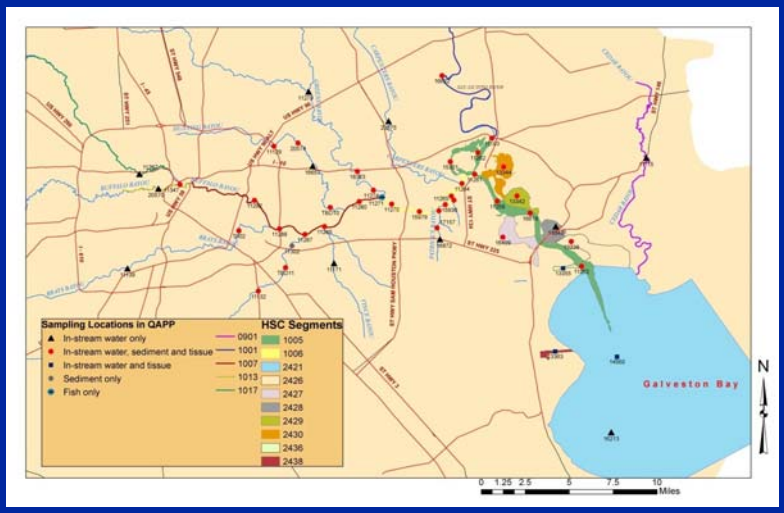
Location	Reference
Coastal locations in Hong Kong, China	Wurl et al., 2006
Yangtse river, China	Jiang et al., 2000
Singapore	Wurl et al., 2006a
Delaware River	Rowe et al., 2007
Barcelona, Spain	Garcıa-Flor et al., 2005
Banyuls-sur-Mer, France	Garcıa-Flor et al., 2005
Lake Michigan	Swackhamer et al., 1987
Green Bay	Swackhamer et al., 1987
Ebro River, Spain	Dachs et al., 1997
Danube Estuary, Romania	Maldonado and Bayona, 2002

Summary 2008 PCB results

- Water quality criteria exceeded in 41% of the samples
- More than 70% of the fish samples exceeded DSHS Health Assessment Comparison Value.
- Dissolved PCB concentration higher than suspended PCB concentration, contrary to what was observed during dioxin study.

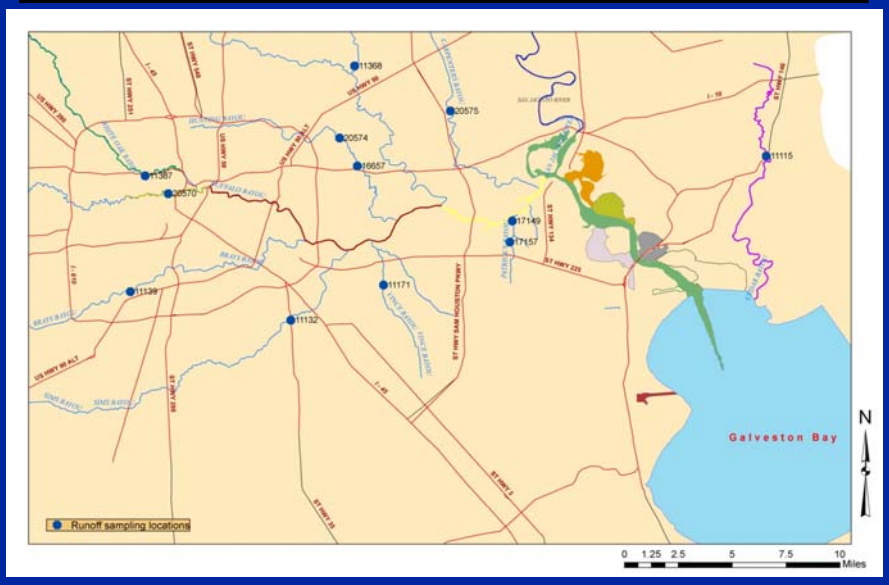
2009 PCB Sampling Status

PCB Ambient Sampling - 2009



- 45 sites sampled for water (dissolved & suspended); 3 sites remain.
- 33 sites sampled for sediment ; 2 sites remain.
- Catfish and Seatrout/Atlantic croaker caught at 28 and 15 sites respectively, out of 36 sampled; 2 sites remain.

Runoff Sampling - 2009

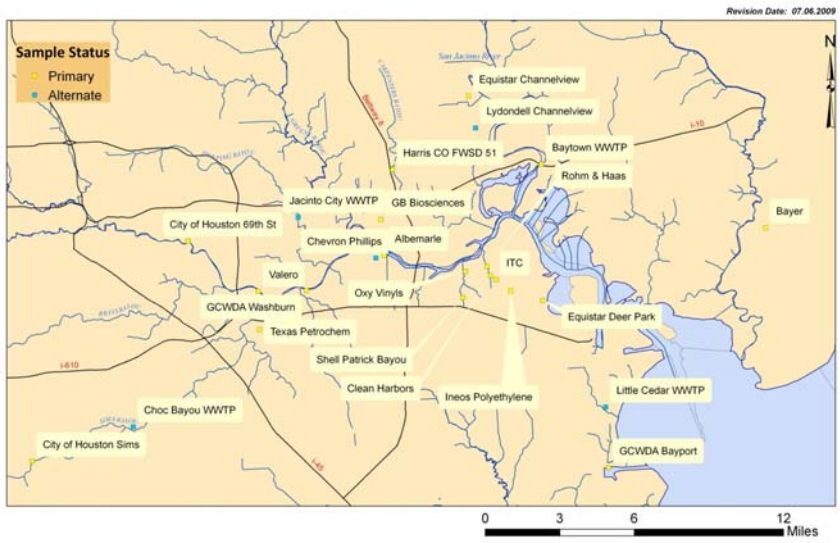


- 4 sites sampled (dissolved & suspended); 8 sites remain
- 2 sites to be determined for small ditch to obtain a direct runoff concentration

Effluent Facility Selection Criteria

- Presence of chlorinated organic compounds on the NPDES permit
- Flow magnitude
- Flow frequency: regular monthly flows required
- Diversity of industry types
- Location of outfalls to known PCB hot spots
- Good spatial coverage of the entire HSC

Effluent Sampling - 2009



- **Sampling planned once permissions received**
- **1 power plant facility under selection and not included in the figure**

Industry Types to be Sampled for Effluent

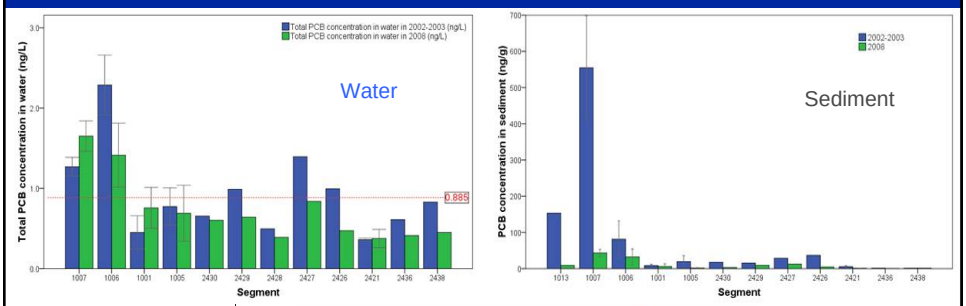
- 20 Main Sampling Facilities (one still to be determined)
- 5 Alternate Facilities

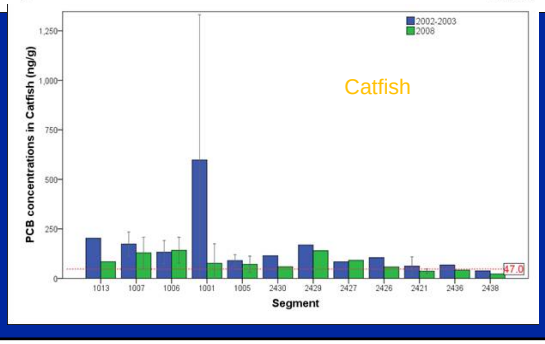
SIC	SIC Expansion	Primary	Alternate
2812	Alkalies and Chlorine	1	0
2821	Plstc Mat./Syn Resins/NV Elast	3	1
2869	Indust. Organic Chemicals NEC	5	0
2879	Pesticides & Ag Chemicals	1	0
2911	Petroleum Refining	1	0
4226	Special warehousing and storage	1	0
4911	Electrical Services	1	0
4952	Sewerage Systems	6	3
4953	Refuse Systems	1	0
2865	Cyclic Crude Intermediate Dyes	0	1

Summary FY 2009 PCB Sampling

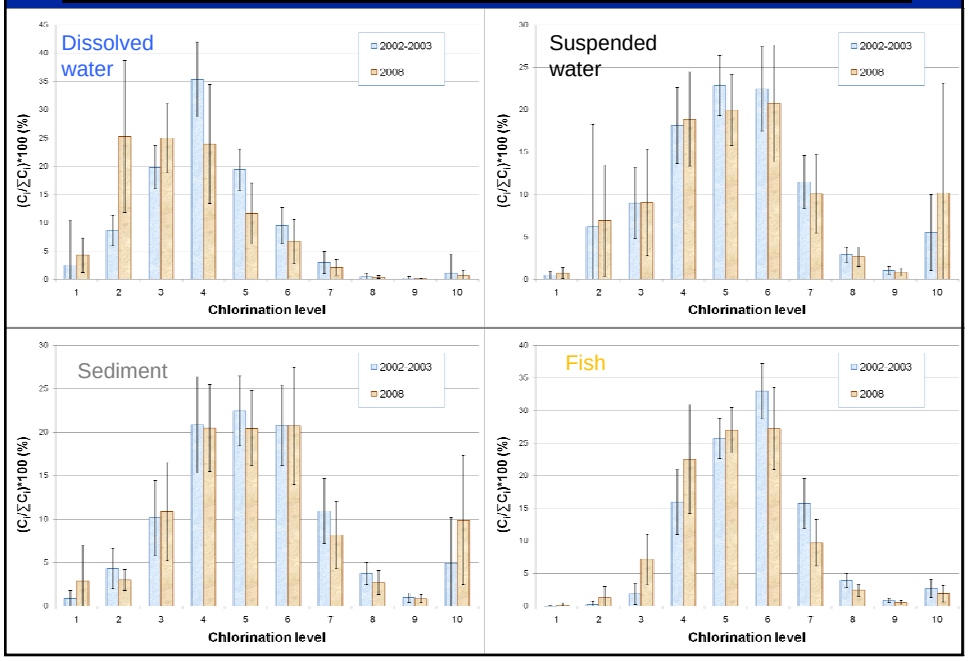
- Second round of ambient sampling almost complete for water, sediment and tissue
- Runoff sampling on-going
- Effluent sampling planned for near future

PCB Conc. Comparison: 2002-2003 & 2008 by Segment





PCB Homologue Distribution Comparison



Comparison of Water/tissue Quality Standard Exceedance

Media	2008 Sampling			2002-2003 Sampling		
	Stations sampled	Stations that exceed standard	Station exceedance (%)	Stations sampled	Stations that exceed standard	Station exceedance (%)
Water[a]	37	15	41%	32	12	38%
Catfish[b]	26	19	73%	45	36	80%
Seatrout/Atlantic Croaker[b]	19	16	84%	Not sampled		

* Concentrations based on 1/2 detection limit and ∑43 congeners

[a] WQS (0.885 ng/L)

[b] DSHS Health Assessment Comparison Value (47 ng/g)