Total Maximum Daily Loads for PCBs in the Houston Ship Channel

Contract No. 582-6-70860
Work Order No. 582-6-70860-22

Quarterly Report 2

Prepared by
University of Houston
Parsons Water & Infrastructure

Principal Investigators
Hanadi Rifai
Randy Palachek

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

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

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

March 2009

TABLE OF CONTENTS

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 the Texas Department of State Health Services (TDSHS) to issue seafood consumption advisories, and some of these advisories have been issued for the Houston Ship Channel (HSC). Three specific advisories have been issued recently for all finfish species based on concentrations of PCBs, organochlorine pesticides, and dioxins. ADV-20 was issued in October 2001 and includes the HSC upstream of the Lynchburg Ferry crossing and all contiguous waters, including the San Jacinto River Tidal below the U.S. Highway 90 bridge. ADV-28 was issued in January 2005 for Upper Galveston Bay (UGB) and the HSC and all contiguous waters north of a line drawn from Red Bluff Point to Five Mile Cut Marker to Morgan's Point. In addition to these two finfish advisories, the TDSHS issued ADV-35 (for PCBs and dioxins) that advises against consumption of gafftopsail Catfish and speckled trout in upper Galveston Bay, lower Galveston Bay, and Trinity Bay. These advisories represent a large surface water system for which a PCB TMDL needs to be developed and implemented. The overall purpose of this project is to develop a total maximum daily load (TMDL) allocation for PCBs in the Houston Ship Channel System, including upper Galveston Bay. Though ADV-35 covers surface water beyond upper Galveston Bay, the TMDL boundary is currently set for upper Galveston Bay. Tasks performed under this work order include monitoring and data collection, as well as data evaluation and analysis in the Houston Ship Channel. Chapter 2 presents the status of the QAPP for the project, while Chapter 3 presents the quality assurance activities. Chapter 4 presents information about potential sources

of PCB while Chapter 5 presents the data analysis from the sampling activities undertaken in FY08.

2. QUALITY ASSURANCE PROJECT PLAN

Appendix A of this report includes the annual update of the Quality Assurance Project Plan (QAPP) for this fiscal year. An amendment to the approved QAPP (April 2007) was developed and submitted to TCEQ in the last fiscal year. Several minor changes to the approved QAPP were made in the amendment. These changes have been incorporated in the revised annual QAPP in their corresponding sections. The changes included:

1. Correction of the lab limit of quantification (LOQ) for all PCB in sediment parameters.
2. Replacing parameters 19913 and 19957 with a new parameter for PCB 83/99.
3. Replacing parameter 19980 with a new parameter for PCB 108/124.
4. Replacing parameter 20320 with a new parameter for PCB 109/119/86/97/125/87.
5. Changing recovery limits to 65-135% for PCBs in water, 60-140% for PCBs in sediment and tissue, and DOC/POC to 70-130%.
6. Correcting eleven parameter codes for PCBs in suspended sediments.
7. Updating the method to be used to determine the dissolved organic content (DOC) of water samples to Standard Method 5310C.
8. Updating the method to be used to determine Solids Content in sediment to be Standard Method 2540B.
9. Adding EPA 440 as the method to be used for determining the particulate organic content (POC) of water samples.
10. Specifying that the units for PCB in sediments and tissue are ng/kg dry wt. and ng/g wet wt., respectively.

12. Outline of POC collection and analysis. An SOP for particulate filtration was added.
13. A detailed location of sediment intensive sampling locations was added to the work plan. The sediment intensive plan called for width-composited sediment samples, transect samples, and core samples.
14. The total sample volume of the water TPH samples was changed from 40 mL to 80 mL.
15. The sample volume of water for DOC samples was changed from 40 mL to 80 mL.
16. The container for POC water samples was changed from a precombusted borosilicate glass bottle to a clear DI rinsed Pyrex bottle.

3. QUALITY ASSURANCE/QUALITY CONTROL

3.1 QA/QC of sampling results

The quality assurance/quality control (QA/QC) tasks that were conducted included monitoring/coordinating sample deliveries to the laboratories, verifying laboratory compliance with the QAPP, and verification of data packages. There were no major noncompliant issues encountered in the shipping and receiving of the samples collected except for one sample (water for station 13363). All samples were received from the sample site to the UH laboratory and from the UH laboratory to analytical laboratories without incident and were within the temperature range specified in the QAPP. The water samples (filter and trap) collected for site 13363 for PCB analysis on 5/27/2008 was found to be contaminated with ice water and so had to be resampled.

Once the sample results were obtained from the labs, the results were reviewed by UH/Parsons personnel using QA/QC criteria specified in the QAPP. The QA/QC requirements outlined in the QAPP included: holding times, method blanks, initial calibration curves, ambient water reporting limits (AWRL) verification, laboratory control sample (LCS), field duplicates, matrix spikes/matrix spike duplicates, laboratory duplicates, continuing calibration samples, surrogates, and internal standards. Table 3.1 lists the samples collected, data received and data reviewed from the Spring-Summer 2008 sampling. The POC measurements were not completed for 3 stations (11171, 11270 and 11287) due to insufficient volume of water sample for filtration. Table 3.2 shows the data flags that were used to designate the data as needed based on the QA/QC review. Appendix B of this report contains the data verification reports for all the data gathered in FY08.

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

Laboratory	Media	Analysis	Number of samples collected	Number of sample results obtained from laboratory	Number of sample results reviewed for QA/QC	% Results reviewed for QA/QC
Xenco	Water	TPH, TSS, DOC	44	44	44	100%
Xenco/PTS	Sediment	TPH, Grain size and Solids content	100	100	100	100%
Maxxam	Water	POC	40	40	40	100%
Maxxam	Water	PCB (209 Congeners)	91	91	91	100%
Maxxam	Sediment	PCB (209 Congeners), TOC	100	100	100	100%
Maxxam	Fish	PCB (209 Congeners), Lipid and Moisture content	53	53	53	100%

Table 3.2 Standardized flags assigned to sample results

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

Table 3.3 below lists the percent of samples that have been flagged as a result of QA/QC activities. As can be seen from Table 3.3, the majority of the flags were associated with the PCB results in water.

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

Analysis	Samples QA/QC reviewed/Samples collected*	Percentage results flagged for			
		U	B	J	H,I,F,L,S,Q,D,R
TPH-Water	41/41	2.40%	0%	0%	0%
DOC-Water	41/41	0%	0%	0%	0%
TSS-Water	41/41	2.40%	0%	0%	19.50%
TPH-Sediment	95/95	96%	0%	1.10%	0%
TOC-Sediment	95/95	0%	0%	0%	2.10%
POC-Water	38/38	0%	0%	0%	97.4%
PCB (209 Congeners)[¶] -Water	82/82	34%	1.90%	28.70%	51.50%
PCB (209 Congeners)[¶]-Fish	50/50	25.34	3.05%	9.82%	4.90%
PCB (209 Congeners) [¶] -Sediment	95/95	19.50%	0.04%	14.30%	7.40%

*Samples do not include trip blanks and equipment rinse blanks

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

3.2 Internal Audit

An on-site internal audit of the University of Houston in Houston, Texas was performed on February 5, 2009 for TMDL of PCBs in the Houston Ship Channel. The purpose of this internal audit was to verify the accuracy and completeness of the laboratory's performance in accordance with project Quality Assurance Project Plan (QAPP), accuracy of the Standard Operating Procedures (SOP) involved in these projects, accuracy of subcontractor's reports, processing of the data, and all quality assurance related matters. Appendix C of this report contains the internal

audit report. A response to the audit and corrective actions are currently underway and will be documented in the next quarterly report..

4. POTENTIAL SOURCES

4.1 Major Sources of PCBs

PCBs are a group of synthetic organic chemicals containing 209 possible individual congeners, which vary in chemical and physical properties, toxicity, environmental persistence, and degree of bioaccumulation (USEPA 1999; Erickson 2001). PCBs were manufactured beginning in 1929 as mixtures of different congeners, and generally sold under the trade name Aroclor. PCBs were used in a wide variety of applications, including coolants and lubricants in transformers, capacitors, and other electrical equipment, heat transfer fluids, hydraulic fluids, lubricating and cutting oils, and as additives in pesticides, paints, copying paper, carbonless copy paper, adhesives, sealants, and plastics (Erickson 2001). The dominant use was in capacitors and transformers. In 1976, the Toxic Substances Control Act (TSCA) banned, with limited exceptions, the manufacture, processing, distribution in commerce, and use of PCBs (Erickson 2001). TSCA also required the USEPA to promulgate regulations for proper use, cleanup, and disposal of PCBs. TSCA and subsequent USEPA rules did not require PCB-containing materials to be removed from service, and many are still in use (USEPA 1999). An estimate of the amount of PCBs produced globally between 1929 and 1979 is 1.5 million metric tons (De Voogt and Brinkman, 1989). Large–scale disposal continued for some time after the cessation of production, but at present there are few primary sources of PCBs to the environment. Most PCBs that enter a particular water body or biosphere are transported from another contaminated environment and are thus secondary sources. A substantial portion of the PCBs manufactured prior to 1977 remain in use,

although these are being phased out as equipment is replaced or decontaminated. Because of their past heavy and widespread use, strong affinities for sorption to sediment organic matter and tissue, and slow rates of decomposition, PCBs frequently remain at elevated levels in the environment for many years after widespread use has ended (Moore and Ramamoorthy 1984; Smith et al. 1988; Jones and de Voogt 1999). PCBs can enter the environment via direct and indirect sources such as industrial and municipal waste discharges, spills and leaks, transformer fires, improper disposal methods, and leaching from landfills (Tanabe 1988; Eisler and Belisle 1996). The current major source of PCBs is probably environmental reservoirs caused by past releases (USEPA 1999). Past releases from production and storage facilities have resulted in many of the more heavily contaminated sites (Smith et al. 1988; Renner 1998; Bergen et al. 1998; Bremle and Larsson 1998; O'Meara et al. 2000; Steuer 2000; USEPA 2002).

4.1.1 Primary PCB Sources

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

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

- Large Amount PCB Disposal (>2 pounds): Dielectric fluids from transformers and large capacitors, which are disposed according to regulations,
- Small Amount PCB Disposal (<2 pounds): Disposal of small capacitors, light fixtures, and waste papers in municipal landfills,
- Leaks and spills from devices that still contain PCBs, and
- Illegal PCB disposal

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

Some researchers have noted that what might be seen as a secondary source of PCB emissions is in fact a re-emission from water, soil, and sediment concentrations. Temperature increases can also volatize more old sources of PCBs and make them appear as new sources (Breivik et al. 2004). It should also be noted that PCB coproduction was at least considered a possibility for a new primary source after the production ban of PCBs. It was estimated in 1982 that USA alone produced 50 tons of PCBs annually as byproducts in the production of other organic chemicals. The EPA in 1982 rated at least 80 chemicals with the potential of having PCB byproducts in them (De Voogt and Brinkman, 1989). Byproduct PCBs were a large enough consideration that the EPA produced a report on the GC/MS analysis of PCBs in commercial products (Erickson, 1982). Erickson et al. (1988) gives a list of potential chemical products that might contain PCB byproducts: chlorophenylsilane adhesives, technical tetrachlorobenzene, tear gas, phthalocyanine pigments, chlorinated paraffins, chlorinated phenols, and phenolic resins. Product waste examples that are given include chlorinated aromatic still bottoms, TCE production waste, asphaltenes, and used solvents.

Further understanding of coproductive PCB sourcing relates less to products that are made alongside PCB and more to the disposal of waste by way of incineration. Ikonmou et al. (2002) presented the first study on municipal waste incinerators that examined all PCB congeners. They found that some incinerator conditions produce no PCBs, others actually generate new PCBs that are mostly lower level chlorinated PCBs, while still others generate high levels of non-ortho and mono-ortho highly toxic PCBs. Even more recent work was conducted in this area by Ishikawa et al. (2007). That group examined thermal waste treatment technology PCB-producing effects on Refuse-Derived

Fuel (RFD) and Automobile Shredder Residue (ASR). ASR was especially interesting because it contains high amounts of catalytic iron and copper, the same types of catalysts used to intentionally produce chlorinated hydrocarbons. Their results showed that RDF produces more light congeners while ASR produces heavier congeners. At the outlet of these systems, an activated carbon adsorption tower removes most of the PCBs from the system, and so it is unclear how much of the products formed in incineration would actually be available in the environment.

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

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

4.1.2 Secondary Sources

Swackhamer (1996) developed a total mass balance on the Great Lakes PCB system in 1996 which shows a reasonable concept for secondary PCB sources in any large body of water. The balance showed that the Great Lakes were mostly in a steady state of total influx to out flux of PCBs, but the internal transport processes are the

mechanisms by which that steady state is maintained. The major sources Swackhamer lists and discusses are atmospheric deposition (mainly to water in this case although it also occurs to land) and its reverse process, volatilization from water to air. The other "sources" which should be considered include the partitioning from water to sediment and sediment back to water. These would only be considered sources insofar as the reference sink is just the sediment or just the bulk water phase outside of the sediment pore spaces.

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

4.2 Environmental fate and transport

Transport of PCBs within the environment occurs via volatilization, atmospheric transport and precipitation, runoff, and sediment disturbance (Eisler and Belisle 1996; Wania and Mackay 1996; Erickson 2001). Atmospheric deposition can be a major source

of PCB input to water bodies (Stapleton et al. 2001b; Dinkins et al. 2002; Wethington and Hornbuckle 2005). In other cases, volatilization to the atmosphere can be a major mechanism for the removal of PCBs from water bodies (Swackhamer and Armstrong 1986; Jeremiason et al. 1994; Gevao et al. 2000; Bamford et al. 2002). A primary method of transport of PCBs and other legacy pollutants into aquatic systems is by erosion of soil and attached contaminants (Munn and Gruber 1997; Van Metre et al. 2003b). Sediment deposition is a dominant process in reservoirs (Thornton 1990), and thus can be a major cause of legacy pollutant loss from the water column to the sediments.

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

The main transport and fate mechanisms within the water column itself are:

- Volatilization
- Solids partioning
- Degradation of the dissolved phase
- Turbulent diffusion
- Vertical advection

Aquatic sediments can act as a reservoir for PCBs and other hydrophobic contaminants (Moore and Ramamoorthy 1984; Chen et al. 2000). PCBs may be present in sediment at concentrations that are orders of magnitude higher than in the water column, where they are typically very low or undetectable (Smith et al. 1988). Sediments act as long-term sources of contamination through desorption of contaminants, and as a result of the resuspension of sediment particles by disturbances (Oliver et al. 1989; Baker et al. 1991; Gevao et al. 1997; Maher et al. 1999; Davis 2004; Apitz et al. 2005). Contaminated sediment can be a major PCB source, with biota and water column concentrations controlled by the underlying sediment levels (Eisler and Belisle 1996; Morrison et al. 2002). Larsson et al. (1990) determined that sediment from a contaminated lake acted as a source of PCBs entering the associated river system. Steuer et al. (1999a, 1999b) found that episodic increases in suspended particle-associated PCB concentrations were associated with bed sediment resuspension during storms.

Widespread low-level contamination found during Ohio River TMDL studies suggested that resuspension of sediment during periods of high flow may contribute significant PCB loads to the water column (Dinkins et al. 2002). Water pumped through a transfer canal in south Texas is thought to have kept PCB-contaminated canal sediment in

suspension, making the exposure pathway to fish tissue more direct (Mahler and Van Metre 2003). Significant resuspension of sediment and associated contaminants may occur at fall turnover in stratified lakes (Evans 1994; Larsson et al. 1998).

Secondary sedimentation caused by wind-induced resuspension is an important process in large, shallow lakes (Douglas and Rippey 2000). Sediment disturbance by organisms that live or feed in contact with the sediment can also provide a route for the reintroduction of contaminants into the food web (Larsson 1986; Reynoldson 1987; Klump et al. 1991; Lester and McIntosh 1994; Zhou and Wong 2000; Khan 2003; Thibodeaux and Bierman 2003).

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

The Hudson River system showed high concentrations of PCBs, which was mostly attributable to sediment. Model predictions show that increasing amounts of cohesive sediment deposition combined with PCB flux to the water column from noncohesive sediments from pore water will lower the overall PCB sediment concentrations (Connolly et al., 2000). Thus, distinctions in sediment type between that which is cohesive and that which is non-cohesive increases the accuracy of PCB transport predictions. In the Baltic Sea, the highest concentrations of PCB sediment were found in the areas of highest sedimentation, not in areas close to probable pollutant sources (Konat and Kowalewska 2001). So as in the case of the Hudson River, the sediment load was a significant source of PCBs to the system and should be focused on as much or more than historical waste PCB sources.

It has been stated for a few decades that generally the sorption of PCBs and other hydrocarbons to sediments is directly related to the amount of organic matter in the sediment (Karickhoff, 1981; Feng et al., 1998). While this relationship seems intuitively accurate based on simple concepts of the hydrophobicity of PCBs, some recent studies did not reproduce the correlation, and this effect brings further explanation to the TOC-PCB relationship. Ouyang et al. (2006) found that in a Florida river basin that PCB and TOC were not correlated. They postulated that the reason for this was different source locations. TOC was sourced from a different watershed than PCBs because the two watersheds contributed a runoff that was land-use specific. The PCB-sourcing watershed was in an industrial area, and the TOC-sourcing was in a forested area. Vane et al. (2007) also found no correlation between TOC and PCB in a Mersey Estuary near Liverpool. They state that “sorption of PCBs to organic matter is masked by other geochemical

processes and local PCB inputs." It is not clear exactly what geochemical processes are in view, but the "local PCB input" suggests that the authors are saying that the rate of PCB introduction into the sediment precludes any equilibrium concepts such as TOC-PCB correlation.

4.3 Sources of PCB to Houston Ship Channel

The sources of PCBs to the HSC, contemporary and historical, are just as important to understanding how to define and implement a TMDL as the assessment of current conditions . Historical sources are sometimes difficult to find information on, and they cannot be altered to influence water quality. Contemporary PCB sources are useful to study because through them, concentration levels in the channel can be better explained, and those sources can be adjusted today to improve water quality. In order to gain this understanding, contemporary PCB sources, both proven sources and possible sources, are examined spatially to determine after

- Likely pathways of PCB introduction into the HSC,
- Areas of the HSC which may be more strongly influenced by contemporary sources, and
- The validity of current sample location selection in relation to confirmed and probable source locations, and
- Locations that need to be sampled in future for better understanding of the sources.

The method by which the sourcing was examined thus far was to gather various publicly available data sources, query those sources based on proximity to the HSC and

the type of industrial activity at the facility, and finally map the queried locations in reference to channel geography and sample locations to facilitate analysis. The data sources that were used are shown in Table 4.1.

Table 4.1 PCB source public data retrievals

Data	Data Source	Nature of PCB source	Release
Toxic Release Inventory	USEPA Envirofacts	Regulated facilities that intentionally or accidently release/dispose PCBs	Waste treatment, air, land, recycling, disposed non-metals, water, or offsite disposal
PCB Activity Database system	USEPA PADS	Generators, disposers, and transporters	Land, air, or water
PCB transformers	USEPA PCB transformer database	Users/disposers of PCB transformers as permitted exceptions to the PCB	Land, air, or water
Spill Incident	National Response Center	Incident spill queried by PCB	Land, air, or water
Air emissions inventory	TCEQ Air emissions inventory	Emissions from facilities that could likely coproduce PCB	Air
Wastewater outfalls	TCEQ NPDES permit record	Wastewater outfalls queried by SIC codes known to be potential PCB sources	Wastewater

It is especially important to note the distinctions between the various data sources in the areas of the actual presence of PCBs and the actual release of those PCBs. TRI releases are the most confirmed facilities for PCB sourcing because PCBs were definitely present at those facilities, and they were definitely released. Those releases may not have made it to the HSC based on the media to which they were released and proximity to the

HSC, but the TRI releases can be considered to be more important than the Wastewater Outfalls. These outfalls may not have ever had PCBs at the facility, and it is not clear if those possible PCBs would ever even have been released since PCBs are not regularly monitored in those waste streams. The other sources fall somewhere in between these two extremes.

4.3.1 Toxic Release Inventory (TRI) Data

TRI may be easily queried in various forms from the USEPA envirofacts website. It represents a record of facilities regulated within the United States for various contaminants, and in this case PCBs. Any on-site or off-site disposal of PCBs that is known by the facility managers will be reported to the system. In the case of PCBs, major releases in the HSC included releases by way of air fug (Fugitive or non-point air emissions), air stack (Stack or Point air emissions), water (discharges to receiving streams or water bodies), disposed non-metals, RCRA C (disposal to on-site RCRA Subtitle C landfills), disposal to other on-site landfills, waste treatment, and recycling. Figure 4.1 presents the results of the TRI facility mapping of these releases except offsite disposals. The PCB offsite transfer to areas in and around the HSC area was also queried and the results are shown as Figure 4.2.

Six facilities exist in the HSC that have known PCB releases for the last 25 years, one facility exits near Galveston (Figure 4.1). The total quantities of those PCB releases from those facilities are quite small. Especially noteworthy is that direct water is the smallest category of release to the HSC at 14.4 lb by Oxyvinyl plant. GBB and Oxyvinyls LP LaPorte VCM plant may be the only known confirmed PCB producer since Agrifos

Fertilizer has not had any PCBs reported in any form since 1989. The presence of one land release of a significant PCB quantity by Clean Harbors Deer Park LP (819 lb) would seem to point to the likelihood of groundwater sourcing, at least in the Tuckers Bayou area. The other important source is the waste treatment and disposed non-metals. Known air releases constitute a sizeable amount of PCBs, but it is not clear how much enters the HSC system. Recent years show less reported releases, which may mean that air has a lower contemporary impact. Air may have a lower impact in more recent years, but it should be remembered that it is likely that most of the air impact from PCBs is likely in the form of unreported and unknown releases in byproduct waste streams, streams which are not usually analyzed for all constituents and therefore not reported to TCEQ.

Offsite disposal would not normally be a major concern for PCB sourcing since the material is being safely transported to another location. If that location is within the HSC region, however, then this could be significant. There were five facilities that were listed as final disposal locations for PCBs, and they are shown in Figure 4.2. The offsite transfer disposal sites shown in the Figure are extremely close to the Channel area or to the bayous and are possible sources of PCB into the HSC.

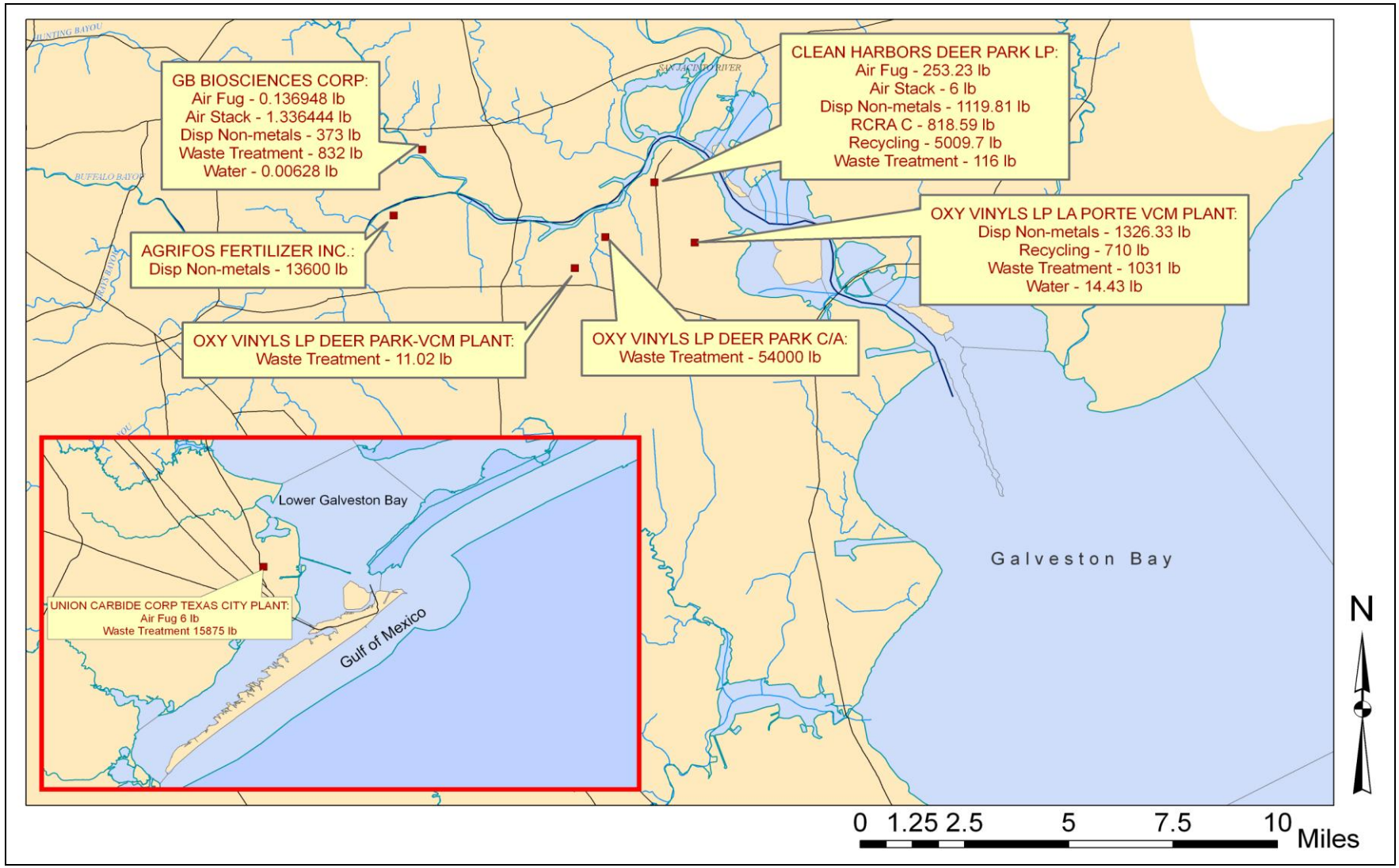


Figure 4.1 Toxic Release Inventory (TRI) PCB Releases in and around HSC

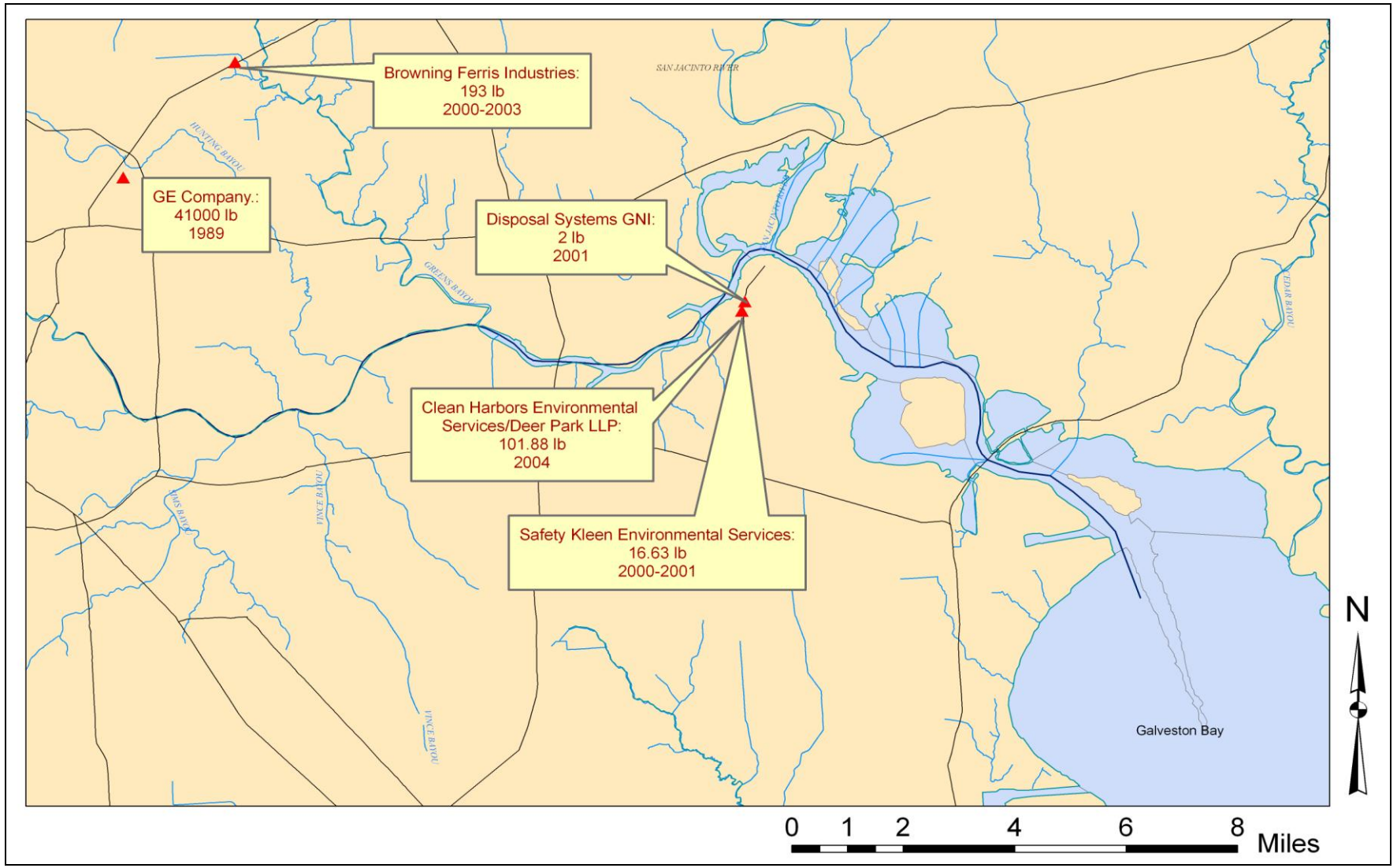


Figure 4.2 PCB Off site transfers in and around HSC

4.3.2 PCB Activity Database System (PADS)

The PADS system is a database maintained by the USEPA that monitors the activities of all PCB handlers in the United States. Though PCBs are banned for nearly all uses, activities involving waste and disposal of older PCBs as well as research still require some facilities to use PCBs. These facilities are highly regulated, monitored, and documented. Mapping results of PADS facilities in the Greater Houston area are shown in Figure 4.3[*]. Although the database does provide the activity of PCB handlers, no quantity is provided in PADS neither is any information given as to how active each facility is at present (some of the PADS entries have not been updated for five years or more). In general a heavier geographic concentration of PADS facilities exists in the near Channel region. In fact, 37 of the total 62 facilities, 60% are near the HSC in terms of either total distance or by hydrologic connection, many of them in the Upper HSC (upstream of SJR confluence).

The facility names are listed in Table 4.2. With so many noted users of PCBs, it is difficult to make many definite conclusions concerning sourcing. What can be seen are proximities to surface waters and clustering. Most of the major bayous that enter the HSC have at least one PCB activity nearby including Sims, Vince, Hunting, Greens, Carpenters, Patricks, and Tuckers. The one notable exception is Brays Bayou, which only has noted PCB activity in the farthest upstream reaches (Keegans Bayou). Four major PCB facility clusters exist at the following locations: in upper Hunting Bayou, between Sims-Vince Bayous on Highway 225, along Greens Bayou, and around Patricks-Tuckers

[*] Note that the PADS database query used for the analysis in this report conducted in the summer of 2006. More current additions or deletions from the database were not added because the database has since been converted into a format that is more difficult to use.

Bayous. The Hunting Bayou cluster is unique from the other clusters in that all of the facilities are far upstream from the confluence with HSC. All of the facilities here are waste handling transporters of PCB except for the General Electric Service Shop, which engages in all four PCB activities listed. The Sims-Vince Bayou area facilities all appear to be environmental waste handling in some way, and the facilities along Greens Bayou are all generators. The cluster at Patricks-Tuckers Bayou is by far the largest with seven PCB generators, some of them related to chemical production. Note that not all of the facilities shown will have wastewater outfalls, which may make them far less suspect of PCB sourcing to the HSC.

The clusters do bear some relation to concentrations that were obtained from the 2008 PCB samplings (Section 5). The water concentrations in Hunting Bayou are generally higher in upstream Hunting Bayou versus downstream, which matches well with the locations of the five PADS facilities in Hunting. Also, two of the three sediment PCB clusters found in the sediment intensive exist on Greens Bayou and along Patrick-Tuckers Bayous, which correspond exactly to the locations of two PADS facility clusters in those areas.

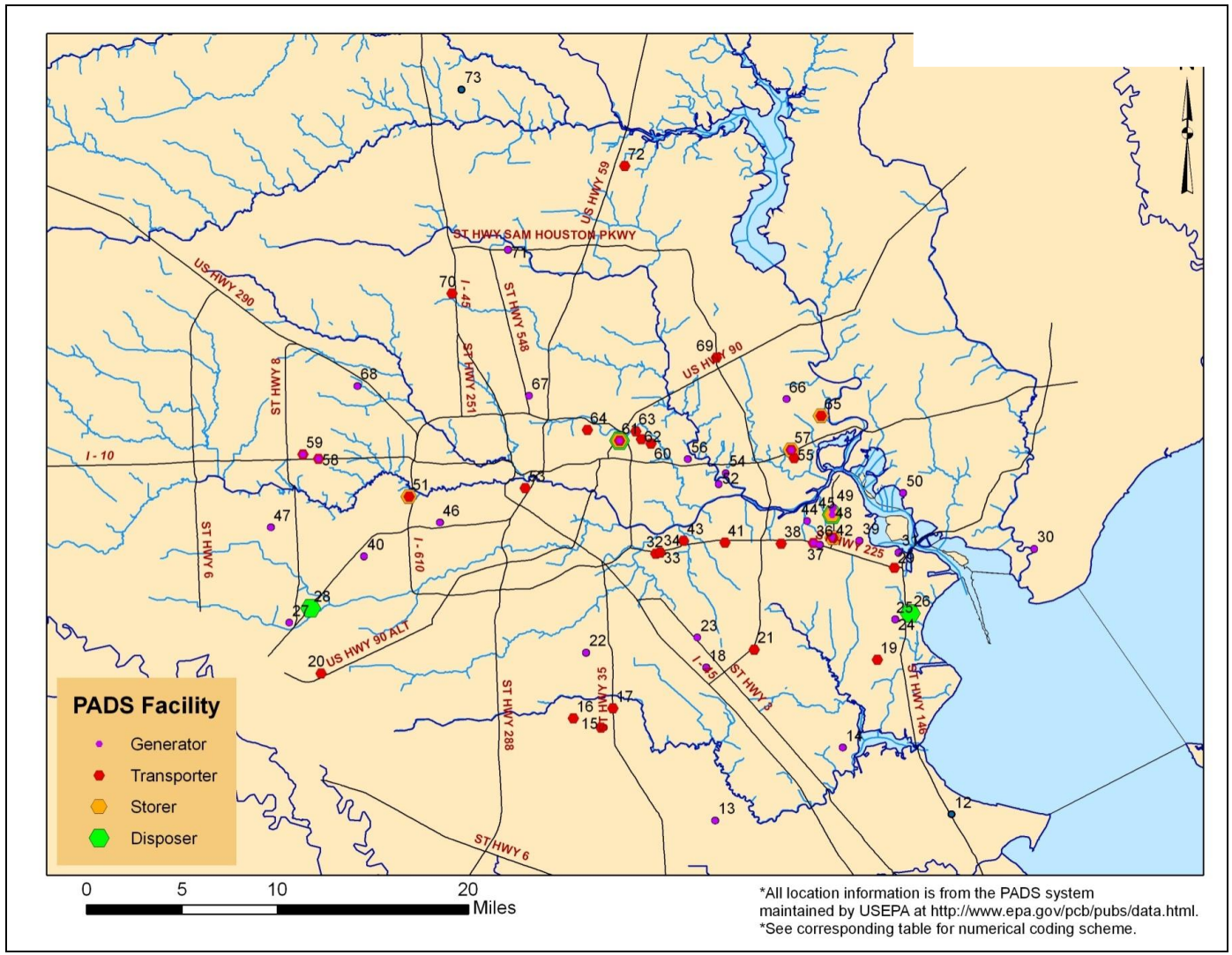


Figure 4.3a PCB Activity Database System (PADS) Facilities in Greater Houston Area

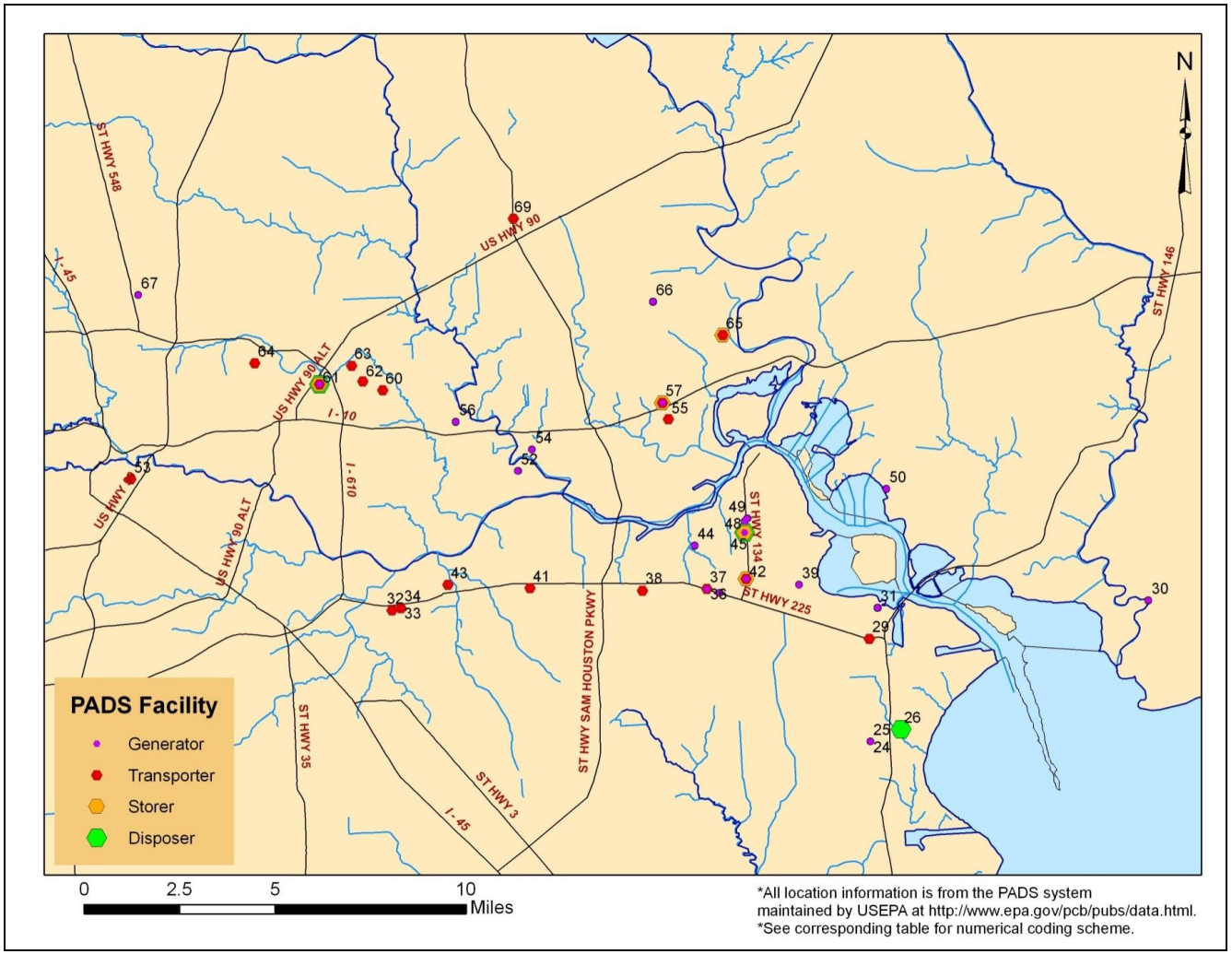


Figure 4.3b PCB Activity Database System (PADS) Facilities in the vicinity of Houston Ship Channel. Some stations from larger extent have been removed if they either were not within ~10 miles of the HSC or not hydrologically connected with the HSC.

Table 4.2 PADS facilities in the Greater Houston Area

Facility Count	Map ID	Facility	Owner	City	Generator	Storer	Transporter	Disposer	Near HSC?	Likely Receiving Waters
1	24	WESTINGHOUSE ELEC CORP	Tim O'Brien	La Porte	X				Yes	Clear Creek
2	25	Central Div. Headquarters	Exxon Pipeline Company	La Porte	X				Yes	Clear Creek
3	26	La Porte Fractionation Plant	Tenneco Natural Gas Liquids	La Porte				X	Yes	Upper Galveston Bay
4	29	JBC Transportation, Inc.	Charles C. Stout	La Porte			X		Yes	San Jacinto Bay
5	30	Jindal United Steel	US Denro Steels, Inc	Baytown	X				Yes	Cedar Bayou
6	31	DuPont La Porte Plant	E.I. Dupont de Nemours	La Porte	X				Yes	San Jacinto Bay
7	32	Garner Environmental Services	L.D. (Lynn) Garner	Houston			X		Yes	Sims Bayou
8	33	Bayou City Waste Solutions	Bayou City Waste Solutions	Houston			X		Yes	Sims Bayou
9	34	Bayou City Environmental Services, LP	Bayou City Environmental Services, LP	Houston			X		Yes	Sims Bayou
10	35	Rohm & Hass Texas Inc	Joseph Foster	Deer Park	X				Yes	Patricks Bayou
11	36	Technical Transporters, Inc.	Technical Transporters, Inc.	Deer Park			X		Yes	Patricks Bayou
12	37	Unite Texas Transport Deer Park Wholesale	United Texas Transport Co	Deer Park	X				Yes	Patricks Bayou

Facility Count	Map ID	Facility	Owner	City	Generator	Storer	Transporter	Disposer	Near HSC?	Likely Receiving Waters
13	38	Allwaste Env. Services of Texas, Inc.	-	Deer Park			X		Yes	Boggy Bayou
14	39	Quantum Chemical Corp USI Div	Quantum Chemical Corp	La Porte	X				Yes	San Jacinto Bay
15	40	USEPA Houston BR Laboratory	USEPA	Houston	X				Yes	Brays Bayou
16	41	Technical Transporters, Inc.	Technical Transporters , Inc.	Pasadena			X		Yes	Cotton Patch Bayou
17	42	Clean Harbors La Porte, LP	Clean Harbors La Porte, LP	La Porte	X	X	X		Yes	Tuckers Bayou
18	43	WPI Transportation, Inc.	American Ecology Corp.	Pasadena			X		Yes	Vince Bayou
19	44	Occidental Chemical Deer Park Plant	Occidental Chemical Corp.	Deer Park	X				Yes	Patricks Bayou
20	45	Clean Harbors Deer Park, LP	Clean Harbors Deer Park, LP	Deer Park	X	X		X	Yes	Tuckers Bayou
21	48	Dow Chemical Co La Porte	Dow Chemical Co.	La Porte	X				Yes	Tuckers Bayou
22	49	Battleground Site, HSTN CH CMP	Occidental Chemical Corp.	La Porte	X				Yes	Tuckers Bayou
23	50	Exxon Research & Eng Co	Exxon Research & Eng Co	Baytown	X				Yes	Scott Bay

Facility Count	Map ID	Facility	Owner	City	Generator	Storer	Transporter	Disposer	Near HSC?	Likely Receiving Waters
24	52	ARMCO, Inc. Greens Port Industrial Park	ARMCO, Inc.	Houston	X				Yes	Greens Bayou
25	53	Port Terminal Railroad Association	Port Terminal Railroad Association	Houston			X		Yes	Buffalo Bayou
26	54	Fermenta ASC Corp	Fermenta ASC Corp	Houston	X				Yes	Greens Bayou
27	55	WPI Trucking, Inc.	WPI Trucking, Inc.	Channelview			X		Yes	Carpenters Bayou
28	56	Greens Bayou Landfill ARMCO	ARMCO, Inc.	Houston	X				Yes	Greens Bayou
29	57	AAR Warehouse	AAR Incorporated	Channelview	X	X	X		Yes	Carpenters Bayou
30	61	General Electric Service Shop	General Electric	Houston	X	X	X	X	Yes	Hunting Bayou
31	62	Postserv Transportation	Postserv Transportation	Houston			X		Yes	Hunting Bayou
32	63	Envirogistics	Dave LaMar	Houston			X		Yes	Hunting Bayou
33	64	Meklo Inc. DBA Eltex Chemical	Brian J. Recatto	Houston			X		Yes	Hunting Bayou
34	65	Poll Cont Man Corp Warehouse	Pollution Control Man. Corp	Channelview		X	X		Yes	San Jacinto River
35	66	ARCO Chemical Co. Channelview	ARCO Chemical Co.	Channelview	X				Yes	San Jacinto River
36	67	Magnetek Ohio Transformer	Magnetek, Inc.	Houston	X				Yes	Hunting Bayou
37	69	U.S. Liquids of Houston LLC	U.S. Liquids of Houston LLC	Houston			X		Yes	Greens Bayou

Facility Count	Map ID	Facility	Owner	City	Generator	Storer	Transporter	Disposer	Near HSC?	Likely Receiving Waters
38	12	Corsan Trucking Inc	Corsan Trucking Inc	Baclif					No	Dickinson Bayou
39	13	Friendswood Construction Center	Texas New Mexico Power Co	Friendswood	X				No	Clear Creek
40	14	NASA Johnson Space Center	NASA	Houston	X				No	Clear Creek
41	15	Gulf Coast Vacuum Service, Inc.	Carolyn Smith	Pearland			X		No	Clear Creek
42	16	Coastal Contractors, Inc.	Coastal Contractors, Inc.	Pearland			X		No	Clear Creek
43	17	Hub City Environmental, Inc.	Pat Hubbard	Pearland			X		No	Clear Creek
44	18	Energy Development Complex	Texas Genco, L.P.	Houston	X				No	Clear Creek
45	19	Bealine Service Co Inc	Jack D. Beal, Jr	Pasadena			X		No	Clear Creek
46	20	Safety-Kleen Systems, Inc.	Safety-Kleen Systems, Inc.	Missouri City			X		No	Brays Bayou
47	21	Laidlaw Env Services (FS) Inc	Laidlaw Environmental Services	Houston			X		No	Armand Bayou
48	22	Alamo Transfer Supply co	Thomas W. Zimmerman	Houston	X				No	Sims Bayou
49	23	South Houston Facility	Houston Lighting & Power Co.	Houston	X				No	Sims Bayou
50	27	USEPA Region 6 Houston Lab	Dienna Simpkins Company	Houston	X				No	Bray Bayou

Facility Count	Map ID	Facility	Owner	City	Generator	Storer	Transporter	Disposer	Near HSC?	Likely Receiving Waters
51	28	Detox Industries, Inc.	Detox Industries, Inc.	Houston				X	No	Brays Bayou
52	46	Greenway Plaza/Senterra Dev	Greenway Plaza LTD	Houston	X				No	Brays Bayou
53	47	XENCO Laboratories	B&A Labs, Eduardo Builes PhD	Houston	X				No	Brays Bayou
54	51	Integrated Energy Resources	Mr. Chudi Izegbu	Houston		X	X		No	Buffalo Bayou
55	58	Energy Enterprises Corp	Ormonde Smith, III	Houston	X		X		No	Buffalo Bayou
56	59	Energy Enterprises Corp	Ormonde Smith, III	Houston	X		X		No	Buffalo Bayou
57	60	Environmental Logistics, Inc.	Rudy M. Johnson	Houston			X		No	Hunting Bayou
58	68	Konsberg Maritime	Konsberg Maritime	Houston	X				No	White Oak Bayou
59	70	Waste Solutions, Inc.	James B. Hobby	Houston			X		No	Halls Bayou
60	71	Commodore Applied Technologies	Commodore	Houston	X				No	Greens Bayou
61	72	Environmental Logistics, Inc.	Dollye R. Scruggs	Humble			X		No	San Jacinto River
62	73	US Pollution Control, Inc.	US Pollution Control, Inc.	Spring					No	Spring Creek

*Grayed cells are those deemed to be outside of the immediate HSC area.

4.3.3 PCB Transformers Facilities

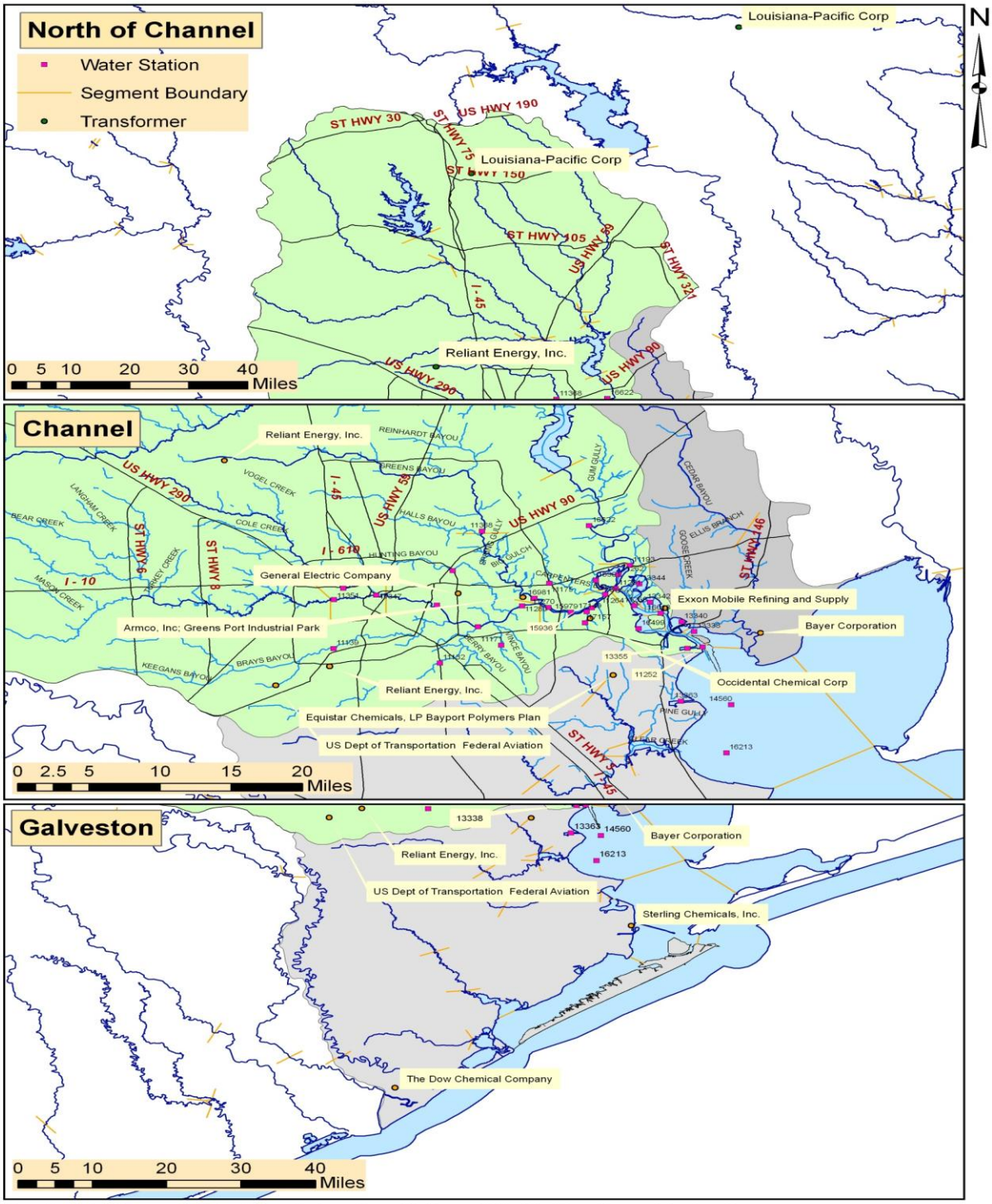
The PCB transformer facilities are those facilities that have transformers with assumed or measured concentrations greater than 500 ppm of PCB dielectric contained within[2]. These transformers have been registered and approved for continued use by USEPA. The information may be found at the EPA website. Locations of the geographically relevant facilities are shown in Figure 4.4. Most of the transformer facilities are distant from the study area and are thus not likely sources to the HSC. Table 4.3 presents a list of facilities that might influence the HSC and an explanation for their inclusion in that list. Segment 1006 is already known to have high PCB concentrations. The Greens Port Industrial Park at Greens Bayou and the Occidental Chemical site at Patrick Bayou may be a contemporary contributor to PCB concentration in this zone. The Exxon Mobil site at Scott Bay is an interesting locale for a PCB transformer point since concentrations at that point were not exceedingly high. The amount of water here that could cause dilution might mask any effect of PCB sourcing. The transformer facility at Bayer Corporation should be considered in the choice of the Cedar Bayou sample station. Previous sediment sampling conducted at a station upstream of this location showed a low concentration. Since water sampling has never been conducted in this Bayou, and the previous station was upstream of this facility containing 44 transformers, it is unknown whether this facility is a continuing source of PCBs. In order for this to occur, however, it would need to be determined if the intake area for the cooling water pumps would prevent outfall wastewater from being sampled in the bayou. More information is needed

[2] For further information on EPA classification of PCB dielectric as either Transformer or "PCB-Contaminated Electric Equipment", see 40 CFR 761.2 at http://www.access.gpo.gov/nara/cfr/waisidx_07/40cfr761_07.html.

to determine if this is currently an issue at Bayer. The other two sites shown in Table 4.3 are upstream tributary stations that are outside of the modeling perspective, but the presence of these facilities may help explain tributary inflow to channel concentrations.

Table 4.3 Likely PCB Transformers to the HSC

Count	Facility Name	Location Description	No. of Transformers	Reason for Likely Source Consideration
1	US Dept of Transportation Federal Aviation	Willow Water Hole, an upper tributary of Brays Bayou	2	HSC tributary location
2	T.H. Wharton Generating Station - Reliant Energy	Upper Greens Bayou	3	HSC tributary location
3	Armco Inc., Greens Port Industrial Park	Greens Bayou-HSC Confluence	2	HSC location
4	Occidental Chemical Corp	Patrick Bayou	4	HSC tributary location and high number of transformers
5	Exxon Mobil Refining and Supply	Lower Scott Bay	1	HSC location
6	Bayer Corporation	Lower Cedar Bayou	33	Cedar Bayou location, extremely high number of transformers



*All transformer locations represent transformers that are still permitted to use PCBs. The information was taken from the EPA PCB Transformer Registration System located at http://www.epa.gov/pcb/pubs/data.html.

Figure 4.4 PCB transformers near the HSC

4.3.4 Air Emissions Inventory

The TCEQ conducts a yearly emissions inventory from air permitted waste stacks in an effort to monitor particular constituents. PCB is not one of those constituents, but, as was the case with Wastewater Outfalls, SIC Code querying can be used to select particular facilities. The facilities are mapped in Figure 4.5. Potential PCB air emitters are dispersed throughout all of the HSC study area. Since there is no PCB stack testing, it is difficult to truly state that a particular facility or region is contributing much to the HSC. The highest emission density of facilities is along the HSC, and the Bayport Channel. However, the Bayport Channel water samples did not show particularly high PCB concentrations in the 2002-2003 sampling (0.57 ng/L and 2.08 ng/L for two stations, 13589 and 13363, averaged over the three events) and 2008 sampling (1.15 ng/L in station 13363). Thus, it does not seem like a localized air impact made a noticeable difference in concentrations in this case. Particular SIC code frequencies for the facilities shown in Figure 4.5 are given in Table 4.4. The highest frequency categories were industrial organic chemicals, plastics, synthetic resins, and nonvulcanizable elastomers, and metal coating and allied services. There is no data to help determine the loading contribution from these facilities to the air.

Table 4.4 SIC code frequencies among emission stacks

SIC Description	No of Stacks
Adhesives and Sealants	1
Alkalies and Chlorine	2
Blast Furnaces and Steel Mills	1
Chemical Preparations, Nec	2
Cyclic Crudes and Intermediates	2
Fabricated Metal Products, Nec	1
Fabricated Plate Work (Boiler Shops)	3
Industrial Gases	7
Industrial Inorganic Chemicals, NEC	9
Industrial Organic Chemicals, NEC	*61*
Iron and Steel Forgings	2
Metal Coating and Allied Services	*11*
Motors and Generators	1
Paints and Allied Products	3
Paper Mills	1
Pesticides and Agricultural Chemicals, NEC	1
Petroleum Refining	9
Phosphatic Fertilizers	1
Plastics,SyntheticResins,nonvulcanizable elastomer	*17*
Plating and Polishing	2
Pulp Mills	1
Refrigeration and Heating Equipment	2
Refuse Systems	9
Repair Services, Nec	2
Ship Building and Repairing	6
Steel Pipe and Tubes	3

*Most numerous types presented in *italics.*

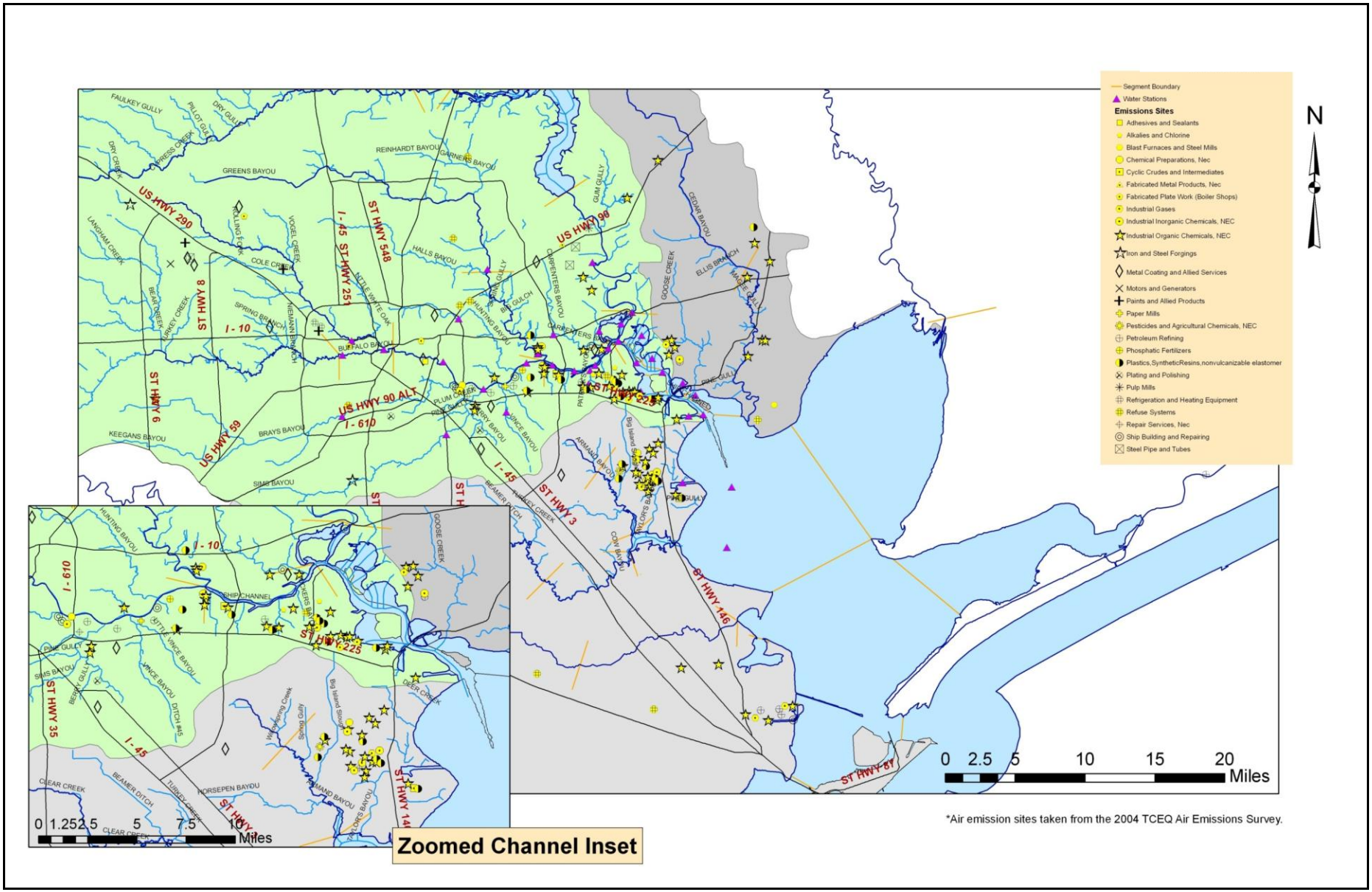


Figure 4.5 Air emission sites queried by SIC code

4.3.5 TCEQ Wastewater Outfalls

TCEQ wastewater outfalls were selected from large statewide outfall database according to SIC codes deemed to be likely involved[‡] in PCB coproduction. One note of caution with the data for wastewater outfalls is that of the approximately 1000 wastewater outfalls in the HSC region (Galveston, Chambers, Harris counties), only about a third of them could actually be queried by SIC code, which means that only about 330 of the 1000 could actually be considered in this analysis. A smaller subset that met the criteria of potential PCB coproduction facility was evaluated and the subset contained 175 facilities (out of 373, 47%) that actually were potential PCB coproducers shown in Figure 4.6. Three main sections appear to exist along the HSC. Moving from upstream to downstream, there is a section at the Sims Bayou-HSC confluence, a section at the Greens Bayou confluence, and a section at Patrick Bayou on the HSC. Statistics for the chosen SIC codes are given in Table 4.5. It is seen that the three most numerous types of potential PCB coproducers are industrial organic chemicals, petroleum refining, and plastics, synthetics, resins, nonvulcanizable elastomer. These highest frequency categories are not surprising when considering that the major industry along the HSC is petrochemical.

The major conclusion from the analysis of wastewater is mainly what was already intuitive-that the most industrialized parts of the Channel, which are also the most PCB-laden parts of the Channel, have the greatest number of potential PCB coproduction wastewater outfalls. Furthermore, most of the outfalls that drop directly into the HSC are

[‡] These SIC codes were retrieved from industries with known TRI releases in the area or from Appendix H1 in the Great Lakes Binational Toxics Strategy report (USEPA, 1998).

near a sampling point. Two other important areas in regard to the WW outfalls are the upper San Jacinto River, which has a paper mill facility and some industrial organics facilities, and upper Cedar Bayou, which has several plastics, synthetic resins, and nonvulcanizable elastomer outfalls.

Table 4.5 SIC code frequencies among WW outfalls

SIC Description	No of Outfalls
Alkalies and Chlorine	7
Blast Furnaces and Steel Mills	1
Chemical Preparations, Nec	1
Commercial Physical and Biological Research	4
Cyclic Crudes and Intermediates	7
Fabricated Plate Work (Boiler Shops)	1
Industrial Gases	6
Industrial Inorganic Chemicals, NEC	4
Industrial Organic Chemicals, NEC	*50*
Paper Mills	4
Paperboard Mills	1
Pesticides and Agricultural Chemicals, NEC	1
Petroleum Refining	*46*
Phosphatic Fertilizers	2
Plastics,SyntheticResins,nonvulcanizable elastomer	*31*
Refuse Systems	4
Ship Building and Repairing	5
*Most numerous types presented in *italics.*	

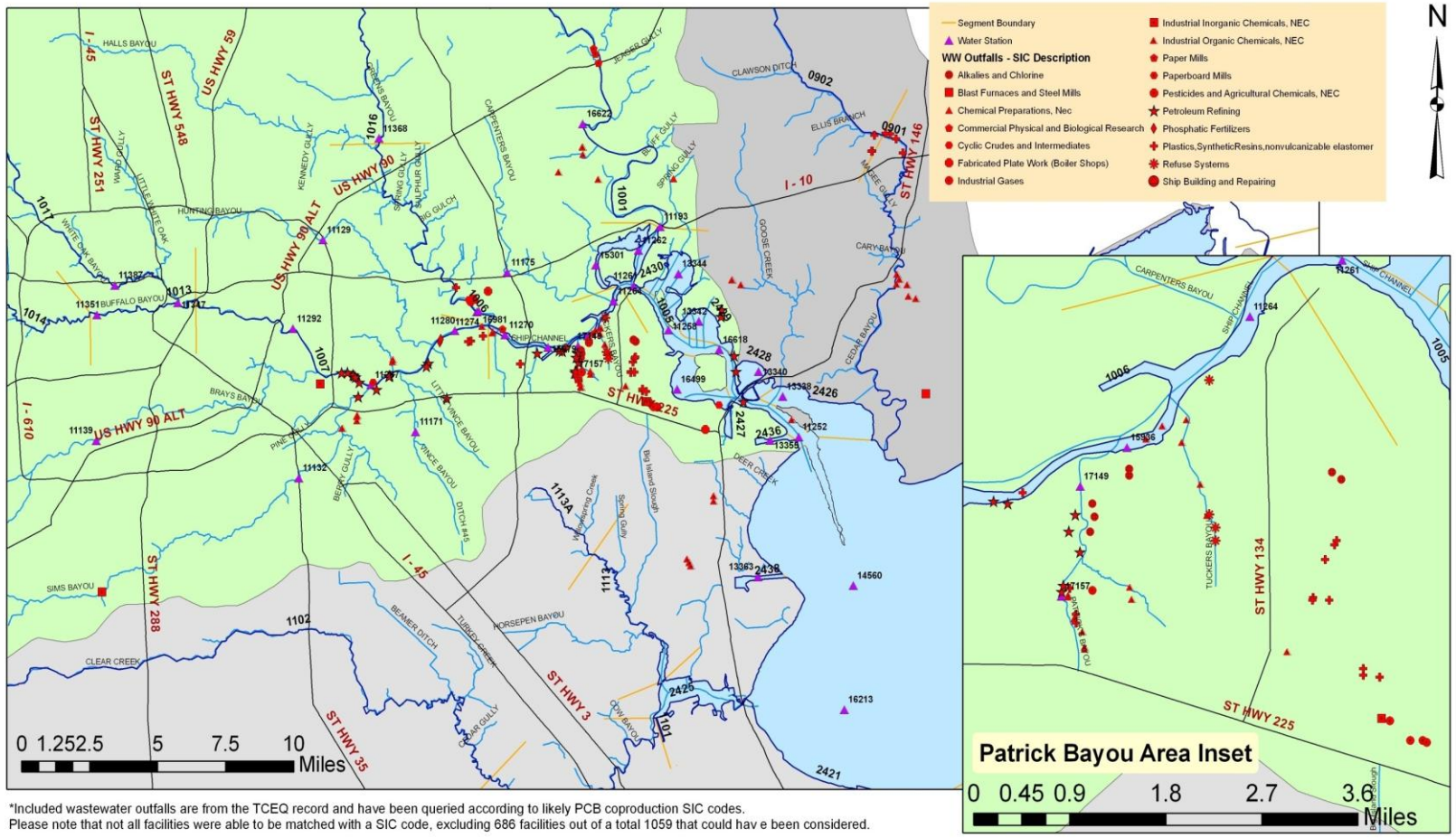


Figure 4.6 Wastewater outfalls as selected by potential PCB coproduction SIC code

4.3.6 Spill Incidents

The Freedom of Information Act (FOIA) requires that all federal agencies make available in electronic form, data that will serve the public interest. The National Response Center (NRC) supports an on-line query system that provides all oil and chemical spill data reported to the Center. This system provides full query capability on all non-Privacy Act data collected by the NRC since 1990. Searches can be done based on spiller, location, material involved, state, county, etc., and can be customized for each request. Figure 4.7 presents the result of this analysis queried by PCB spills in the HSC area. As can be seen from the figure, there have been several spills from 1990 to 2009. However, the NRC does not provide the amount of PCB that was spilled. On-land spill sites and unenclosed sources are locations of initial release of PCBs into the environment. Once released, PCBs are conveyed to and accumulate in the watershed including locations in stormwater facilities and bay tributaries. Thus, while it is useful to know the initial release site, it is much more complicated to determine the fate and transport of the PCBs from the spilled location to the HSC.

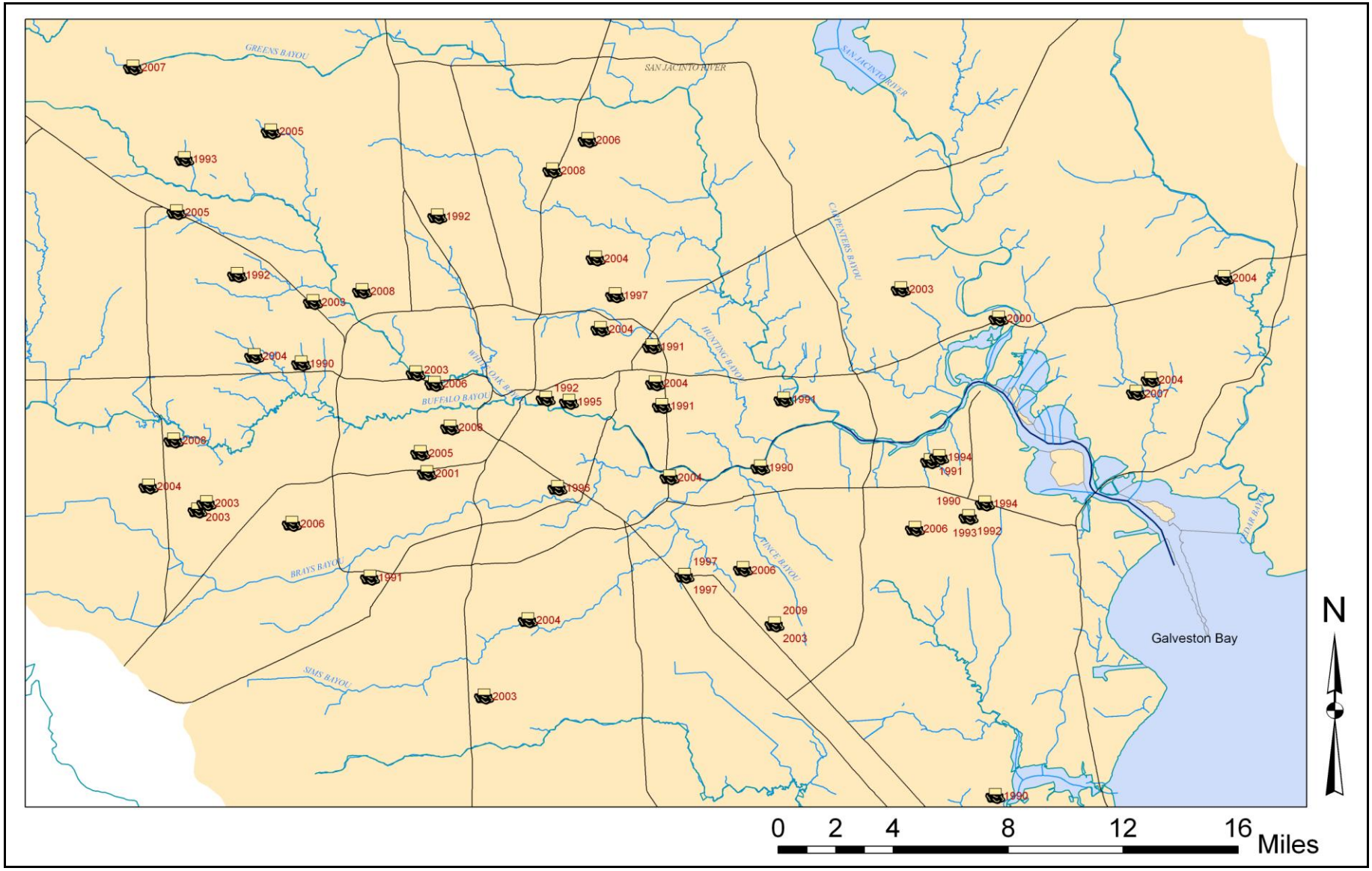


Figure 4.7 Reported land spills as selected by potential PCB release in the HSC area

Overall trends show a concentration of facilities along the main body of the Channel all the way upstream to the Sims Bayou-HSC confluence. The San Jacinto River in the 2002-2003 and 2008 sampling showed lower concentrations of PCB in water and sediment, though given the history of dioxin contamination in that area, it is still suspect for PCB introduction to the Channel. If it is a pathway of downstream PCB load, then there are not very many facilities along that segment that could, at least in this analysis, be explanatory sources. Then either most of the PCB sourcing is historical or one or two facilities can explain a contemporary load. The most valuable part of this analysis is the use of geo-matching to see where one particular facility shows up in multiple datasets. The figure shows three facilities that match in this way—General Electric, Agrifos Fertilizer, and Oxy Vinyls Deer Park. General Electric has shown activity in many different PADS categories and harbors PCB transformers, but this facility is not on a direct tributary to the Channel as far as can be seen from figure. Agrifos Fertilizer has disposed of large quantities of PCBs in the past and is in an industry that potentially coproduces PCBs. This industry, phosphatic fertilizers, may be more than potential in light of the definite presence of PCBs here in 1989. And Oxy Vinyls with a location on Patrick Bayou (highest concentration in water in 2008 sampling), yearly TRI PCB releases to both water and offsite, four PCB transformers, and coproductive potential in both water and air would seem to be a contemporary source though the status of the plant's chlorination-based processes is not currently known. These three facilities together represent the most likely PCB sources contemporarily and in recent history under this analysis and should be considered first in sampling and in later data analysis. Confirmed water release in the last 20 years of HSC record keeping amounts to only approximately 15 lbs. Other pathways have confirmed amounts that may or may not have ever made their way to the Channel. Any other information in regards to contemporary sourcing from

specific facilities is speculative though worth considering. The only confirmed TRI PCB water releases on record were at GB Bioscience along Greens Bayou and Oxy Vinyls La Porte VCM Plant. Air emission into the Channel air space has been confirmed in recent years and especially in large quantities as recently as 2002. The locational proximity of potential PCB coproduction facilities and the amount that those facilities may have released should be considered in conceptualizing PCB loadings from air. Other than the two facilities in recent years that have confirmed PCB air releases, localizing air PCBs without facility specific sampling will be difficult especially when considering how little is still currently known about potential PCB coproduction.

All datasets show a high concentration of actual PCB housing, releasing, and potentially releasing facilities along the main section of the HSC. Historical sourcing from sediments seems to be a likely explanation for much of the high PCB concentrations, but at the same time the high concentration of potential PCB facilities should not be ignored or considered a geographical coincidence.

5. WATER, SEDIMENT AND TISSUE RESULTS

Data analysis from the 2008 sampling results was performed and summarized in the last quarter. Further analysis was done in this quarter and the results are summarized below.

5.1 In-stream Water PCB Concentrations

The total PCB concentrations in water (dissolved plus suspended PCB) were calculated using sum of all 209 congeners. For stations for which duplicate samples were collected, the PCB results for that station were calculated as the average of duplicate and parent sample. The summation of 209 congeners yielded total PCB concentrations in the range of 0.469 and 69.1 ng/L with an average concentration of 4.02 ng/L for the 37 locations sampled. A total of 30 out of the 37 locations (81%) sampled in Summer 2008 exceeded the Texas Surface Water Quality Standard (WQS) for human health protection of 0.885 ng/L.

Figures 5.1a, 5.1b, and 5.1c show the dissolved, suspended and total PCBs in water respectively along the Houston Ship Channel. Figure 5.1d shows the spatial distribution of total PCBs in water in the Houston Ship Channel System. The concentrations observed in the Side Bays and tributaries are also plotted in order to provide the possible sourcing of PCB contamination from the Side Bays and tributaries into the HSC. The following observations were inferred from the figures:

1. The suspended and dissolved concentrations in the HSC followed a similar pattern along the HSC and the dissolved concentration was higher than the suspended concentrations. All the stations except 11139 and 16213 had PCB concentrations higher in the dissolved phase (>50%) than in the suspended phase.

2. The top five concentration sites observed during 2008 sampling were in the following order: Patrick Bayou > HSC at OxyChem Ditch > Greens Bayou > Hunting Bayou > HSC upstream of Beltway 8. Of the top five, three stations were tributaries.
    - Patrick Bayou had the highest concentration (both suspended and dissolved) of all stations sampled (30 times higher than the average concentrations observed during 2008 sampling). The second highest concentration was observed in the station in the HSC which is downstream of the confluence of Patrick Bayou and HSC. So it seems that Patrick Bayou is one of the highly contaminated areas in the HSC area. However sampling was not conducted for other media (sediment and fish) during 2008 sampling. So it will be useful to sample for another location upstream of Patrick Bayou and also sample for sediment in the 2009 sampling study to better understand the impact of PCB contamination from Patrick Bayou onto the HSC.
    - The third highest PCB concentration in water was observed at a station in the downstream part of Greens Bayou (11274). That same station had the highest PCB concentrations in sediment during the 2008 sampling and so a higher concentration in water is understandable. However another station sampled in the upstream part of Greens Bayou (11368) had a lower concentration compared to station in the downstream part of Greens Bayou (11274). So it seems that the PCB contamination is more downstream of Greens Bayou. It seems sensible to sample for another station in Greens Bayou between the two stations mentioned above to understand more on the exact location of sourcing in Greens Bayou.

- The fourth highest PCB concentration in water was observed at the station in the upstream part of Hunting Bayou (20574). However, another station sampled in the downstream part of Hunting Bayou (16657) had a lower concentration compared to station 20574. So it was not clear whether the concentration upstream of Hunting Bayou is more localized. The concentrations in the HSC after the confluence with Hunting Bayou are high and so it seems Hunting Bayou could be a major source into the HSC. However sampling was not conducted for other media (sediment and fish) during the 2008 sampling. So it will be useful to sample for another location downstream before the confluence and also sample for sediment in the 2009 sampling study to better understand the impact of PCB contamination from Hunting Bayou and also the source of contamination.
- The sampling stations that had the highest PCB concentrations were in general along the Buffalo Bayou branch of the HSC above the SJR confluence.

3. Apart from the tributaries discussed above, all other tributaries and Side Bays had PCB concentrations lower than the concentrations observed along the channel.
4. The PCB concentration in water (dissolved as well as suspended) along the HSC decreased significantly after confluence with SJR probably due to dilution effect.
5. The figures show lower PCB concentrations in the San Jacinto river and downstream of San Jacinto in the HSC. Though given the history of dioxin contamination in that area, it is still suspect for PCB introduction to the Channel.

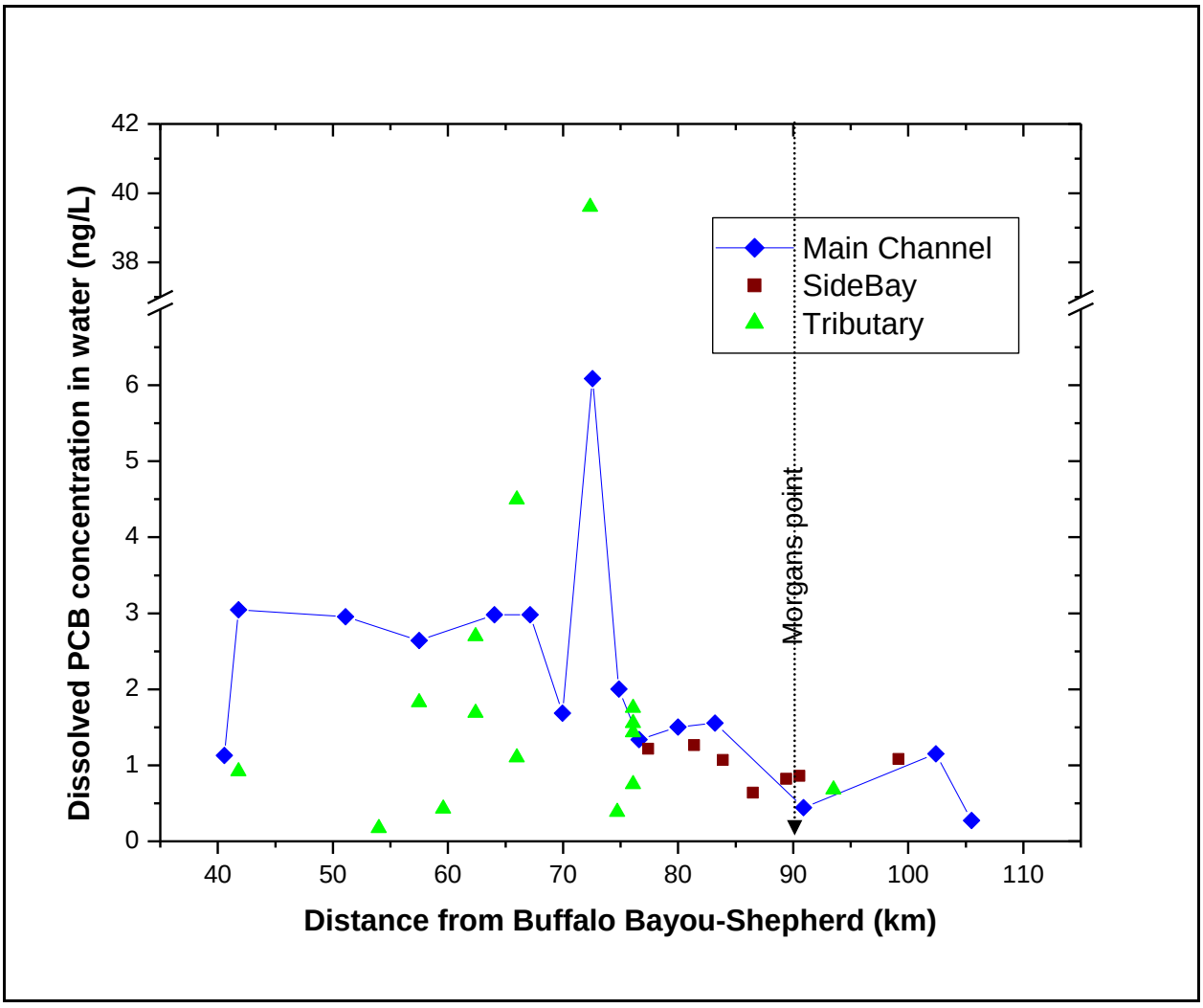


Figure 5.1a Dissolved PCB concentrations in water along the Main Channel and in the Side Bays and Tributaries

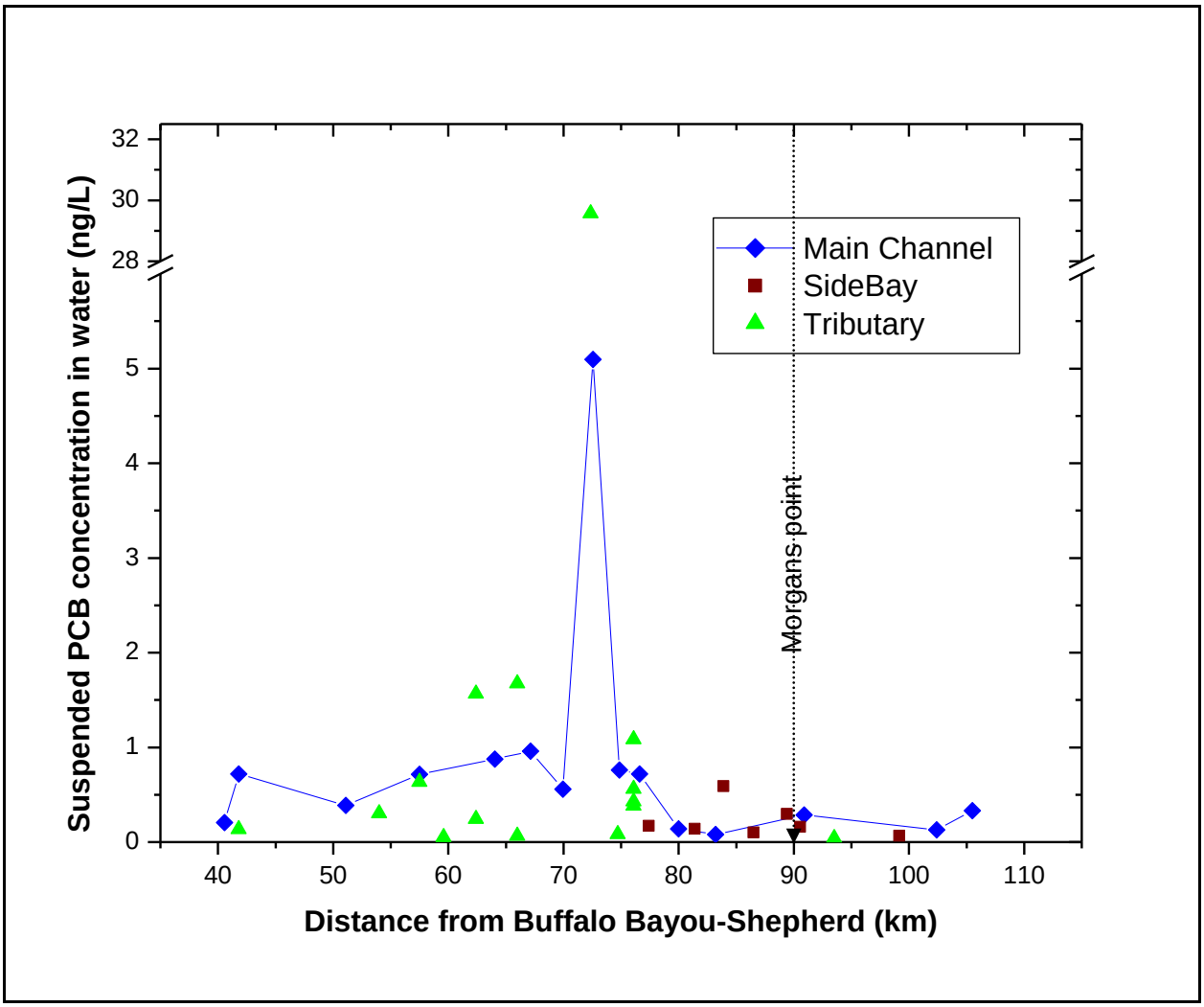


Figure 5.1b Suspended PCB concentrations in water along the Main Channel and in the Side Bays and Tributaries

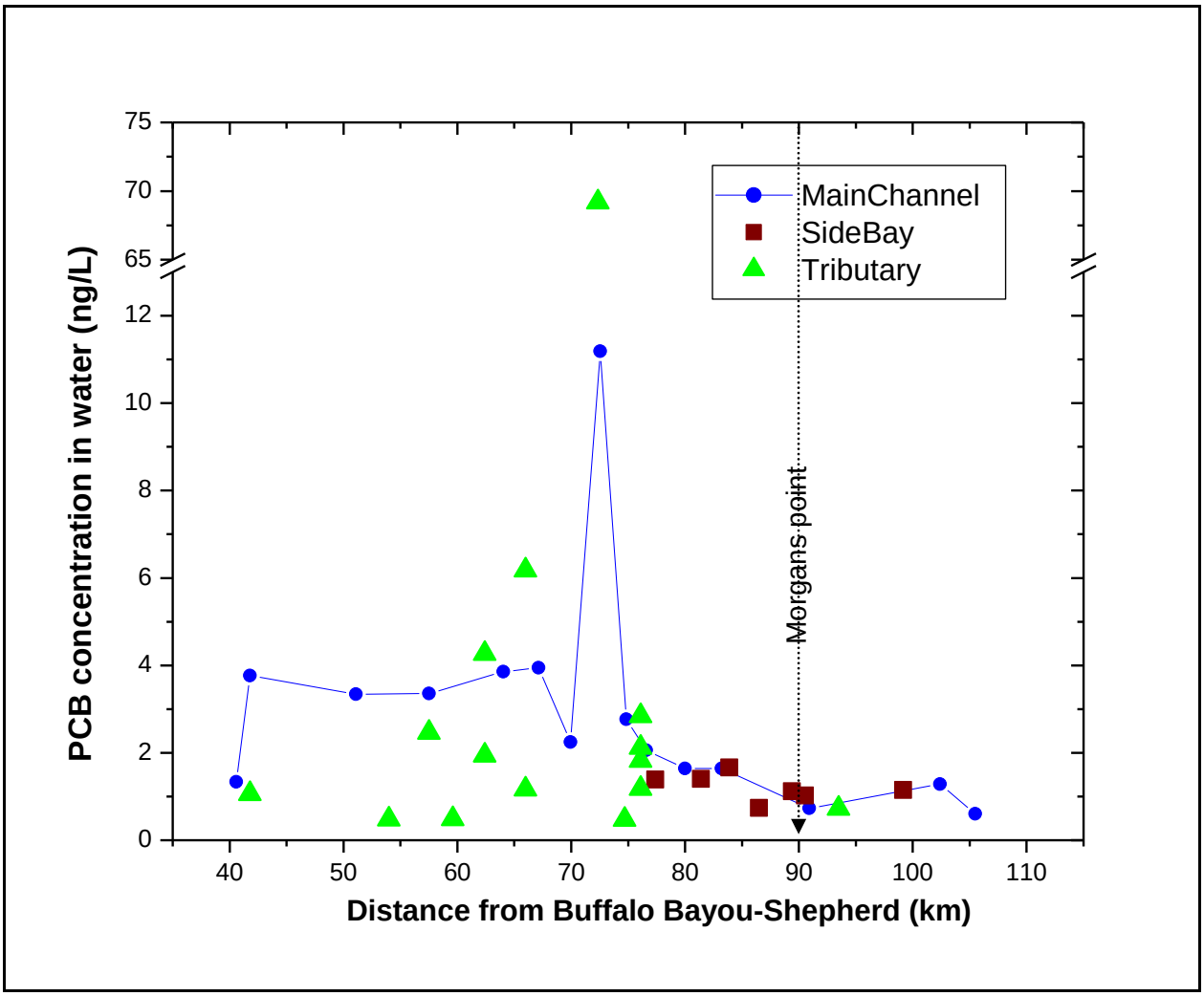


Figure 5.1c Total PCB concentrations in water along the Main Channel and in the Side Bays and Tributaries

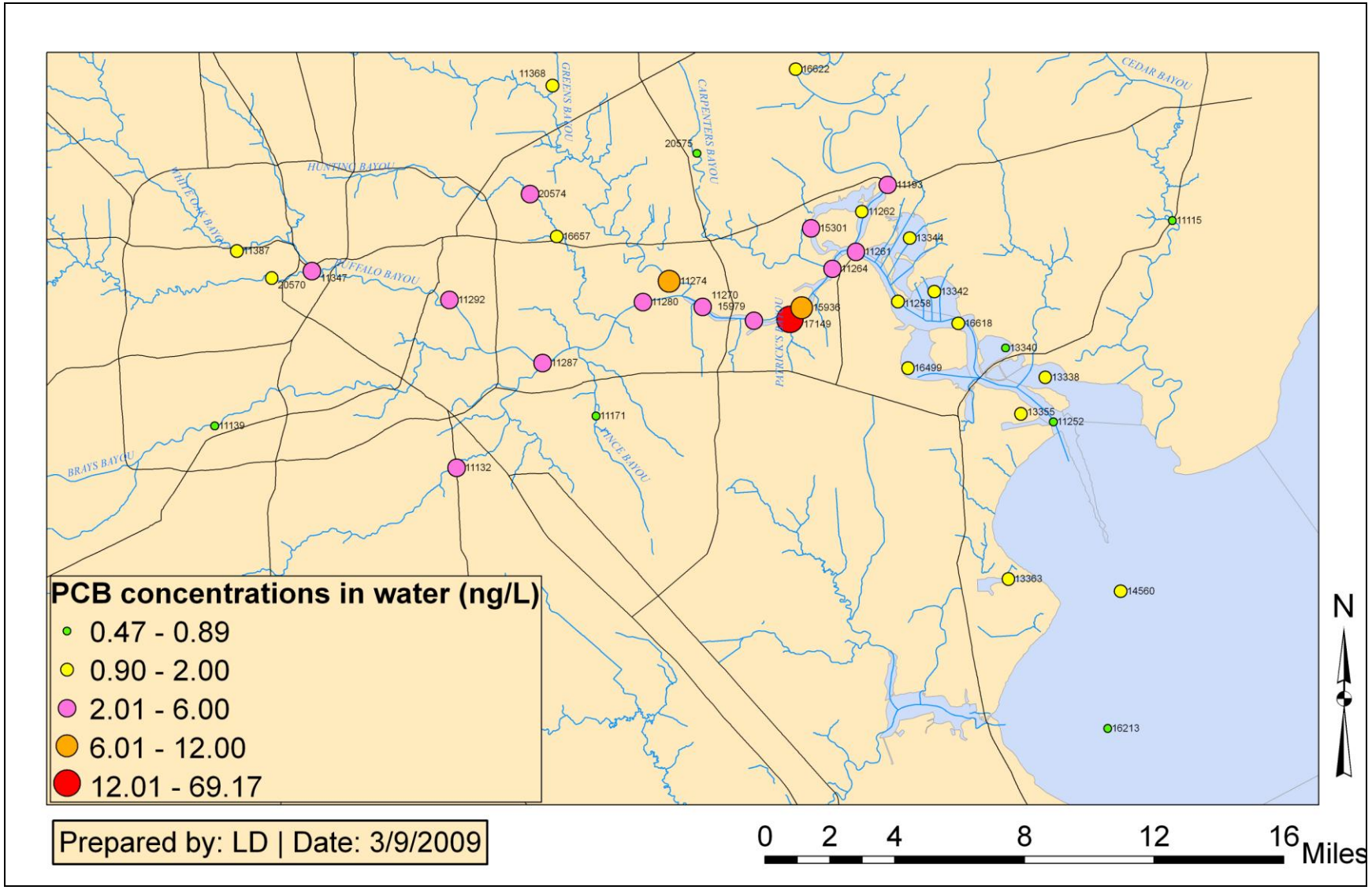


Figure 5.1d Total PCB concentrations in water calculated as sum of 209 congeners

5.2 Sediment PCB Concentrations

The summation of 209 congeners yielded total PCB concentrations in the range of 1.4 and 108 ng/g with an average concentration of 25 ng/g for the 25 locations sampled in May-June 2008[4]. Figure 5.2a shows the PCB concentration in sediment along the HSC, while Figure 5.2b shows the PCB concentration in sediment normalized to organic carbon. Figure 5.2c show the distribution of total PCBs in sediment. The concentrations observed in the Side Bays and tributaries are also plotted in order to provide the possible PCB contamination from the Side Bays and tributaries into the HSC. The highest PCB concentrations in sediment were in the HSC upstream of the confluence with the San Jacinto River (Figure 5.2a and 5.2b). The highest PCB concentration in sediment was observed at a station in the downstream part of Greens Bayou (11274). The same station had a higher concentration in water and so the partitioning of PCB between water and sediment is understandable. However another station upstream of Greens Bayou (11368) was not sampled for sediment and so and so might be possible station for future sampling. The PCB concentrations normalized to organic carbon showed a similar PCB concentration in the HSC up until the confluence of HSC with SJR. All tributaries except Greens showed lower or similar concentrations along the HSC. Patrick bayou was not sampled for sediment and so a possible peak, observed in water concentrations, was not observed in sediment results. The difference to be noted from Figures 5.2a and 5.2b is that PCB concentration trends along the HSC are different on a total PCB basis and on PCB normalized to organic carbon basis. When PCB concentrations were normalized to organic carbon, the concentration profile in the HSC up until SJR confluence remained nearly constant (5 ng/g OC). This is in contrast to the

[4] An analysis of all 70 sediment sampling locations, which includes the sediment intensive sampling of July 2008, is given in a subsequent section.

varying PCB concentration profile when analyzed on dry weighted basis. The figures also show that PCB concentrations in sediment are much lower downstream of Morgans Point and in the Galveston Bay.

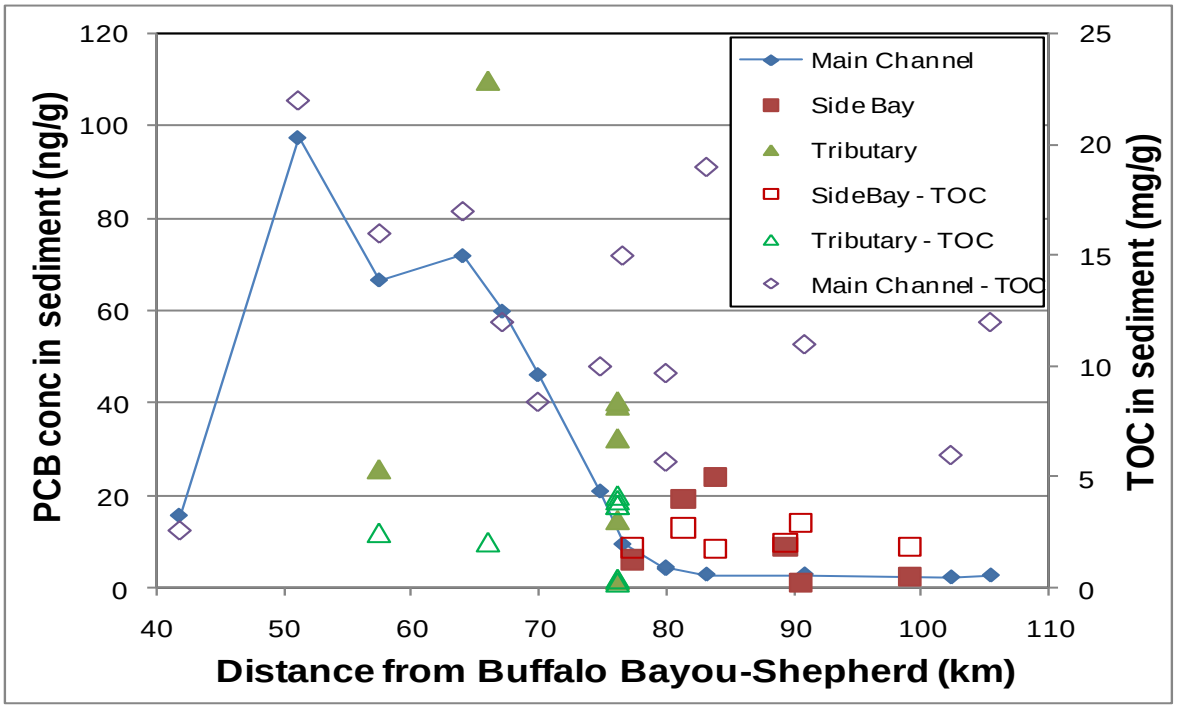


Figure 5.2a Total PCB concentrations in sediment along the Main Channel and in the Side Bays and Tributaries

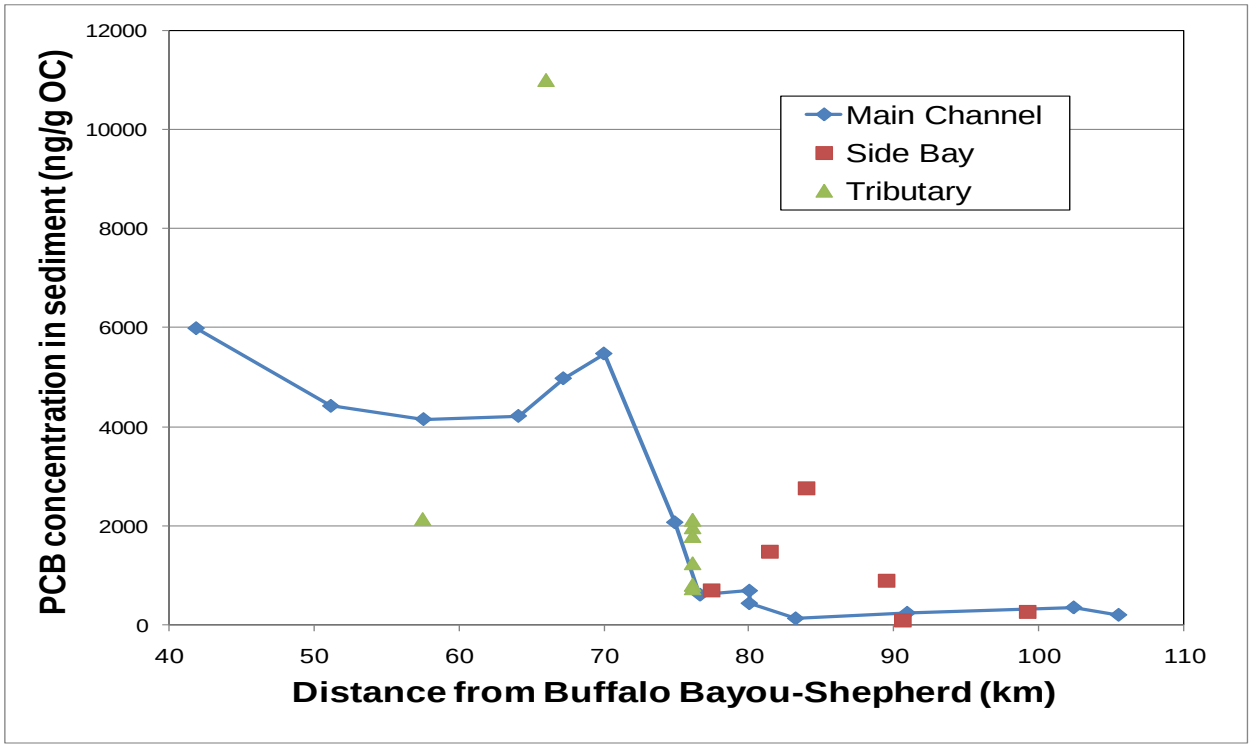


Figure 5.2b Total PCB concentrations in sediment normalized to organic carbon along the Main Channel and in the Side Bays and Tributaries

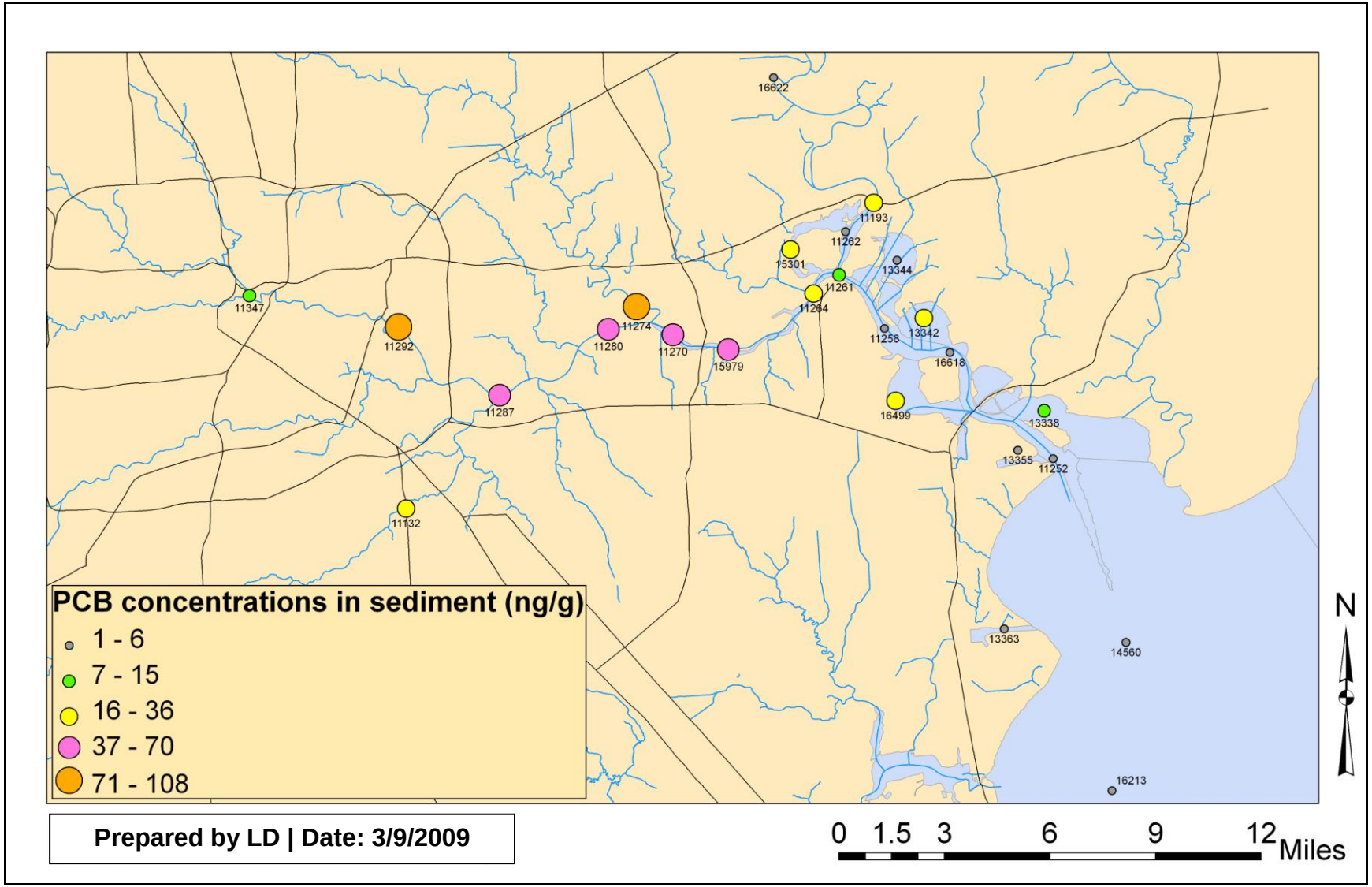


Figure 5.2c Total PCB concentrations in sediment calculated as sum of 209 congeners

5.3 Tissue PCB Concentrations

The summation of 209 congeners yielded tissue PCB concentrations in the range of 12-522 ng/g in the case of Catfish, and 33-1180 ng/g in the case of Speckled Seatrout/atlantic Croaker. A total of 22 out of the 26 locations (85%) sampled for Catfish and 17 out of 19 locations (90%) sampled for Seatrout/Atlantic Croaker exceeded the DSHS Health Assessment Comparison Value (47 ng/g). In addition, the average concentration of Catfish (137 ng/g) and Speckled Seatrout/Atlantic Croaker (285 ng/g) was also higher than the Health Assessment Comparison Value. Figures 5.3a, and 5.3b show the PCBs in Catfish and Seatrout/Atlantic Croaker, respectively along the Houston Ship Channel. The PCB concentrations in Catfish and Seatrout/Atlantic Croaker are mapped in Figures 5.3c and 5.3d, respectively. Even though the fish are capable of moving long distances along the channel, the PCB concentrations observed along the HSC indicate probably the fish are more localized in their living. This is observable from the figures that PCB concentrations in both Catfish and Speckled Seatrout/Atlantic Croaker caught along HSC upstream of confluence with SJR had significantly higher concentrations than fish caught downstream of SJR confluence. This correlates with higher PCB concentrations in water and sediment upstream of SJR compared to concentrations downstream.

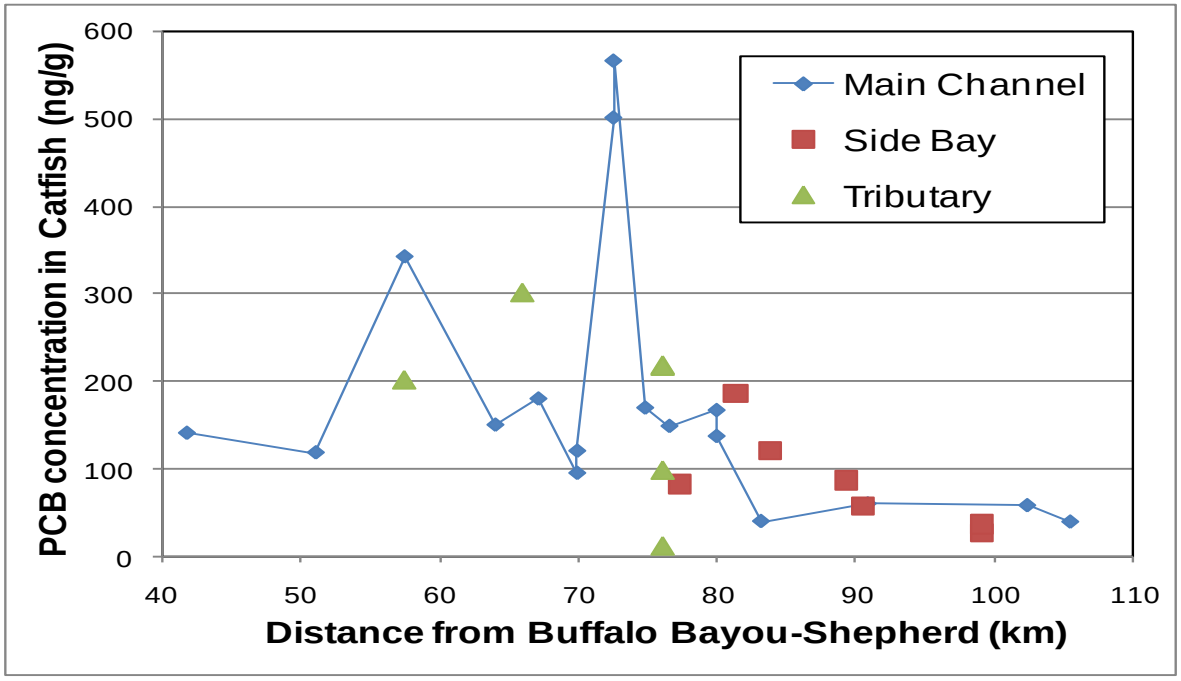


Figure 5.3a Total PCB concentrations in Catfish along the Main Channel and in the Side bays and Tributaries

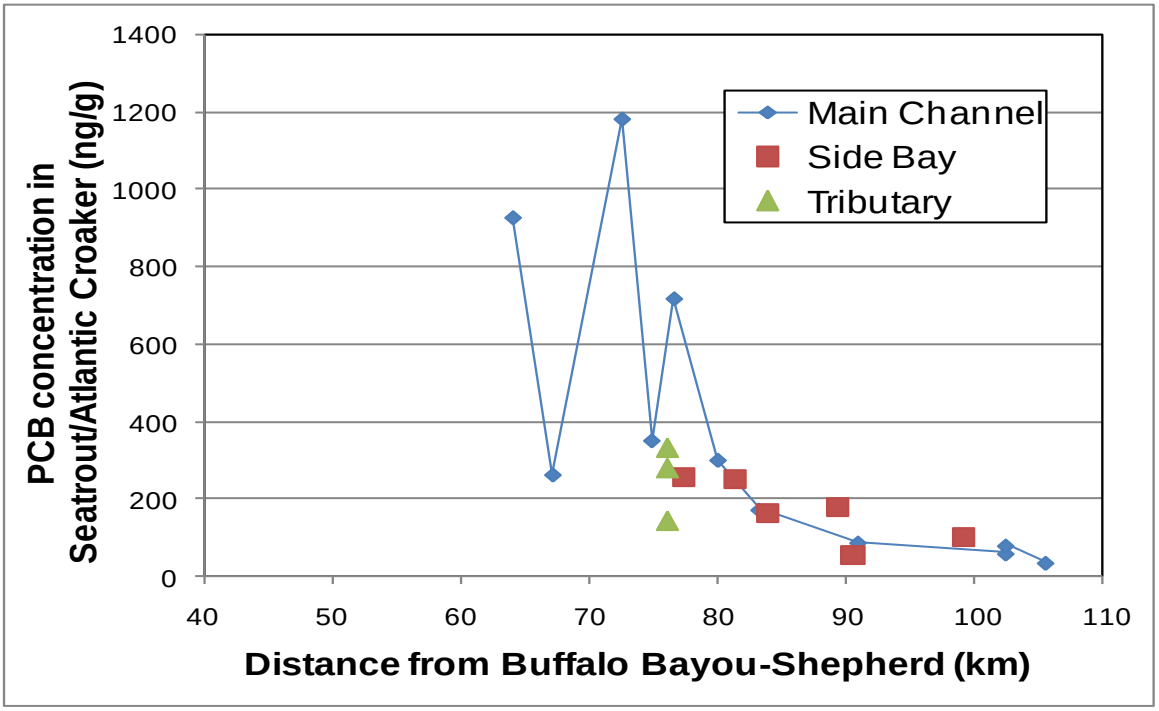


Figure 5.3b Total PCB concentrations in Seatrout/Atlantic Croaker along the Main Channel and in the Side Bays and Tributaries

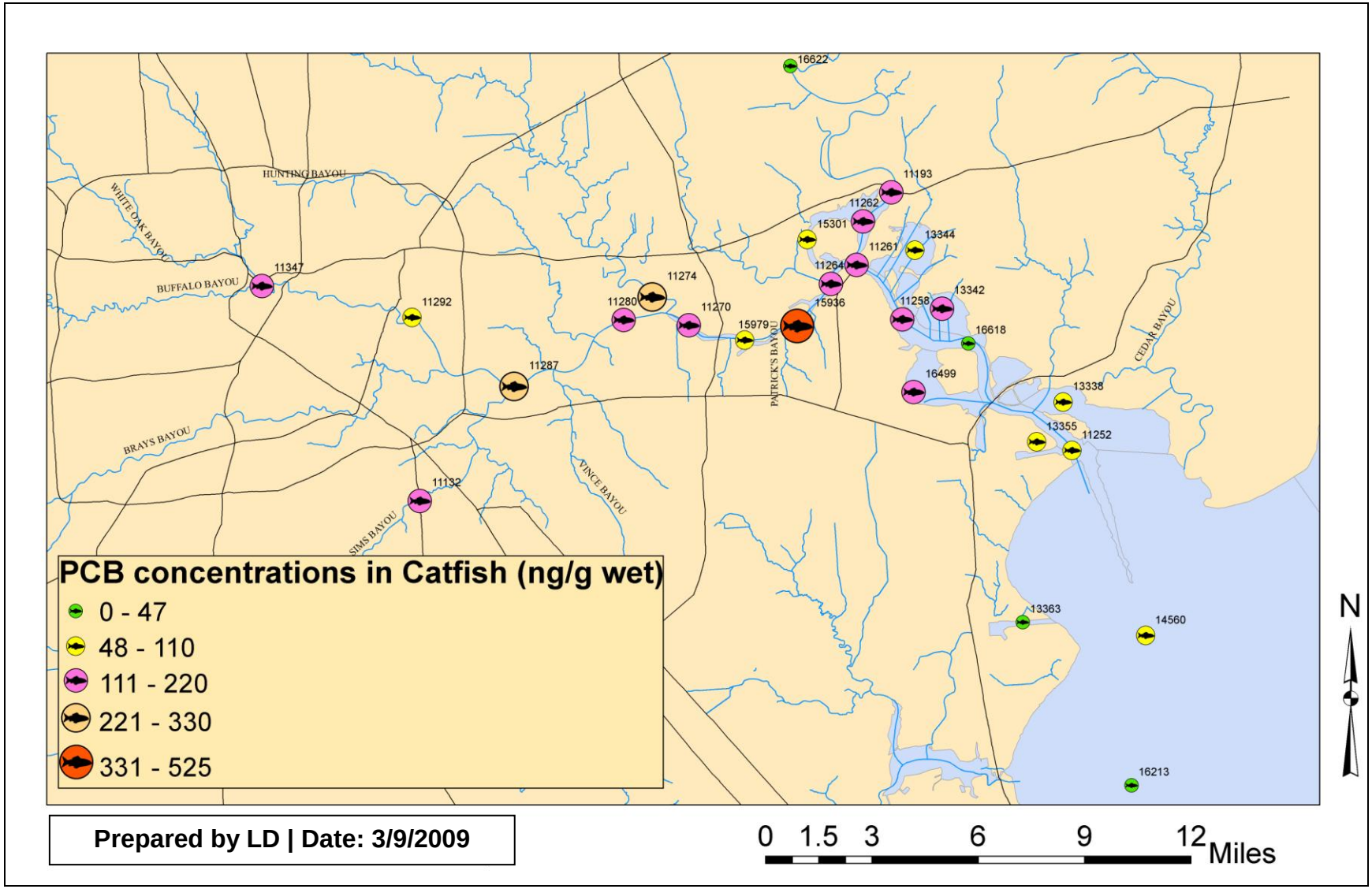


Figure 5.3c Total PCB concentrations in Catfish calculated as sum of 209 congeners

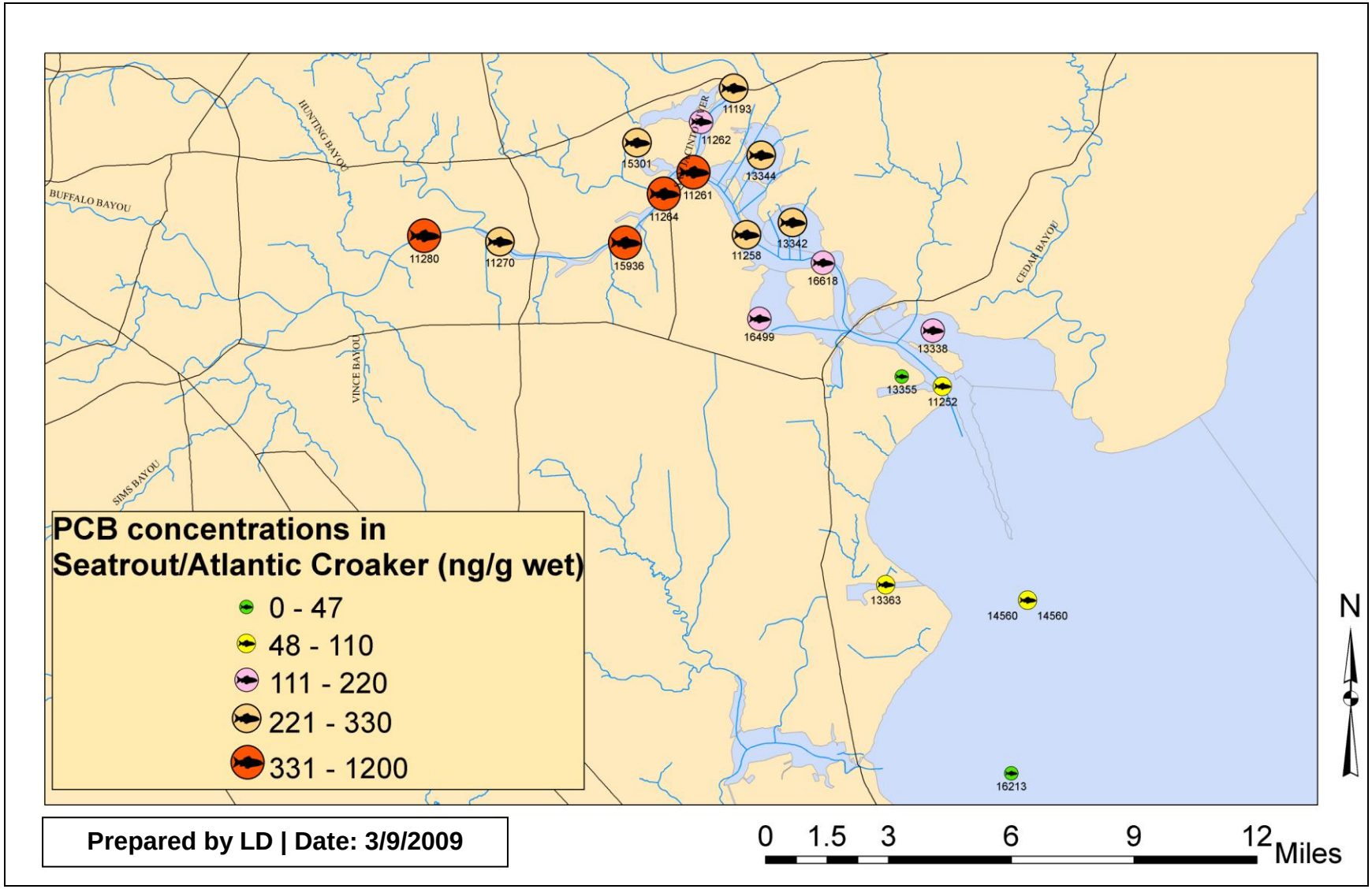


Figure 5.3d Total PCB concentrations in Seatrout/Atlantic Croaker calculated as sum of 209 congeners

5.4 Homologue pattern along the HSC in water, sediment and tissue

Homologue PCBs are groups of congeners that have the same level of chlorination; there are 10 homologues representing 1-10 chlorine atoms on the biphenyl rings. For classification purposes, homologues were combined together based on the low, medium and high amounts of chlorination: homologues 1-3 (Congeners 1-39), homologues 4-6 (Congeners 40-169), homologues 7-9 (Congeners 170-208), and homologue 10 (Congener 209). The homologue PCB distributions in HSC and in Side Bays and tributaries are shown in Figures 5.4-5.6.

The huge spikes in all homologue groups shown in Figure 5.4 are due to the high concentrations observed in Patrick Bayou and Patrick Bayou confluence with HSC. The total PCB concentrations in water along the HSC and in tributaries had significant concentration of homologues 4-6 followed by homologues 1-3 in almost all stations. In general homologue 10, and homologues 7-9, the highly chlorinated congeners were insignificant in HSC and in Side Bays. However homologue 10 in particular, and homologues 7-9 were high compared to other areas in Patrick Bayou and in the HSC at the confluence of Patrick Bayou. So it seems that there is significant source of highly chlorinated congeners from Patrick Bayou. In summary, the PCB is mostly made up of low chlorinated congeners in the water media.

The total PCB concentrations in sediment along the HSC and in tributaries were found to be mainly constituted of homologues 4-6 in almost all stations (Figure 5.5). In general, highly chlorinated congeners (homologue 10, and homologues 7-9) and homologues 1-3 were insignificant compared to homologues 4-6. The homologue profiles were different when the PCB was considered on a soil weight and on an organic carbon basis (Figure 5.5a and Figure 5.5b), however, the dominant homologues were 4-6 in both cases. The concentration of homologue 4-6 almost remained constant in the HSC up until the confluence with SJR.

The total PCB concentrations in fish along the HSC and in tributaries were found to be mainly constituted of homologues 4-6, similar to what was observed with sediment (Figure 5.6a, b). In general highly chlorinated congeners (homologue 10, and homologues 7-9) and homologues 1-3 were insignificant compared to homologues 4-6.

The comparison of homologue groups in water, sediment, and fish are shown in Figures 5.7- 5.10. For homologues 1-3, 4-6, and 7-9, a spike in water homologue at a station follows a spike in fish media which indicates possible transport of PCB from water to fish. However, no such correlation was possible with sediment and water with those homologue groups. In the case of homologue 10, there was a good correlation between all three media.

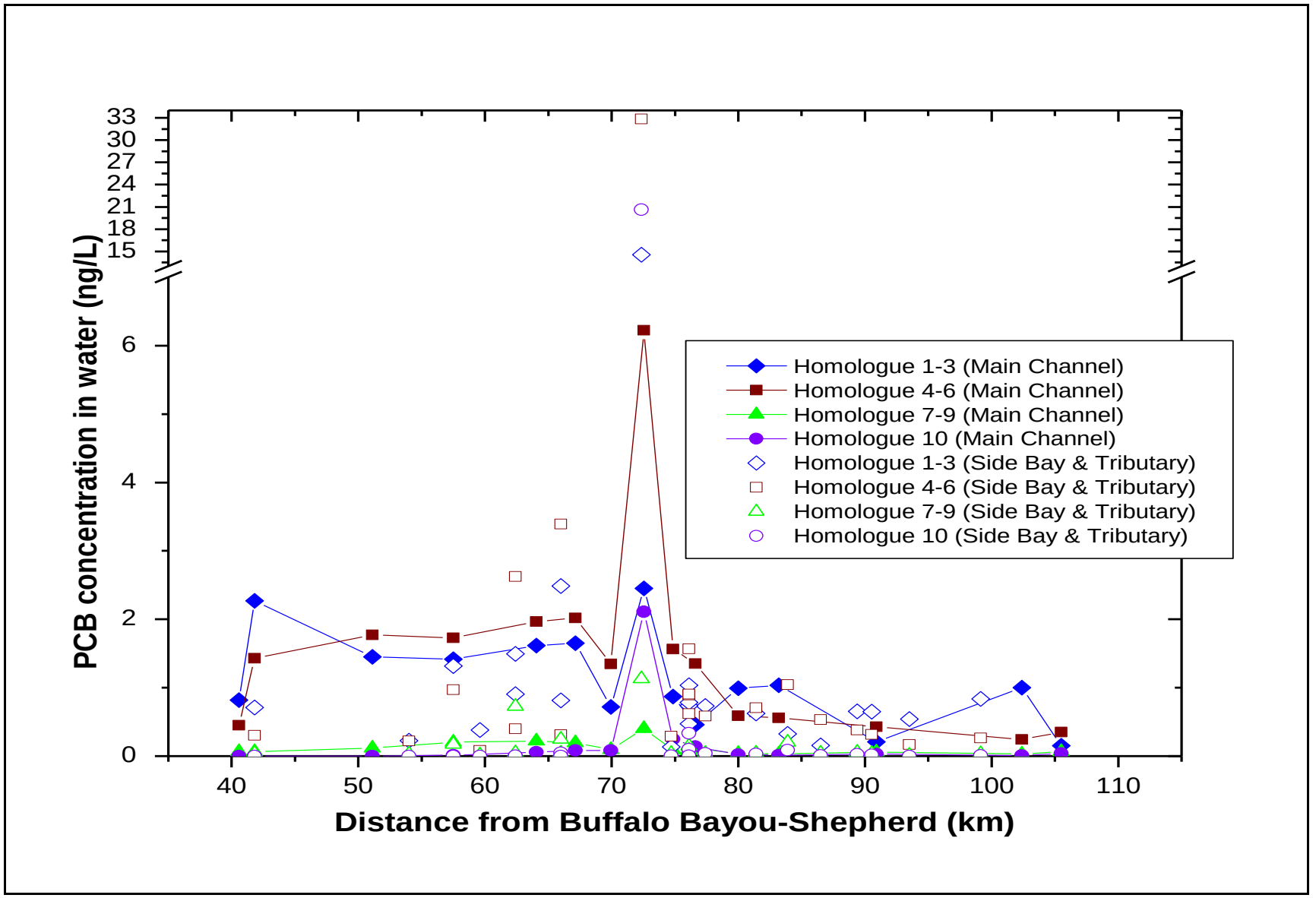


Figure 5.4 PCB homologue distribution in water

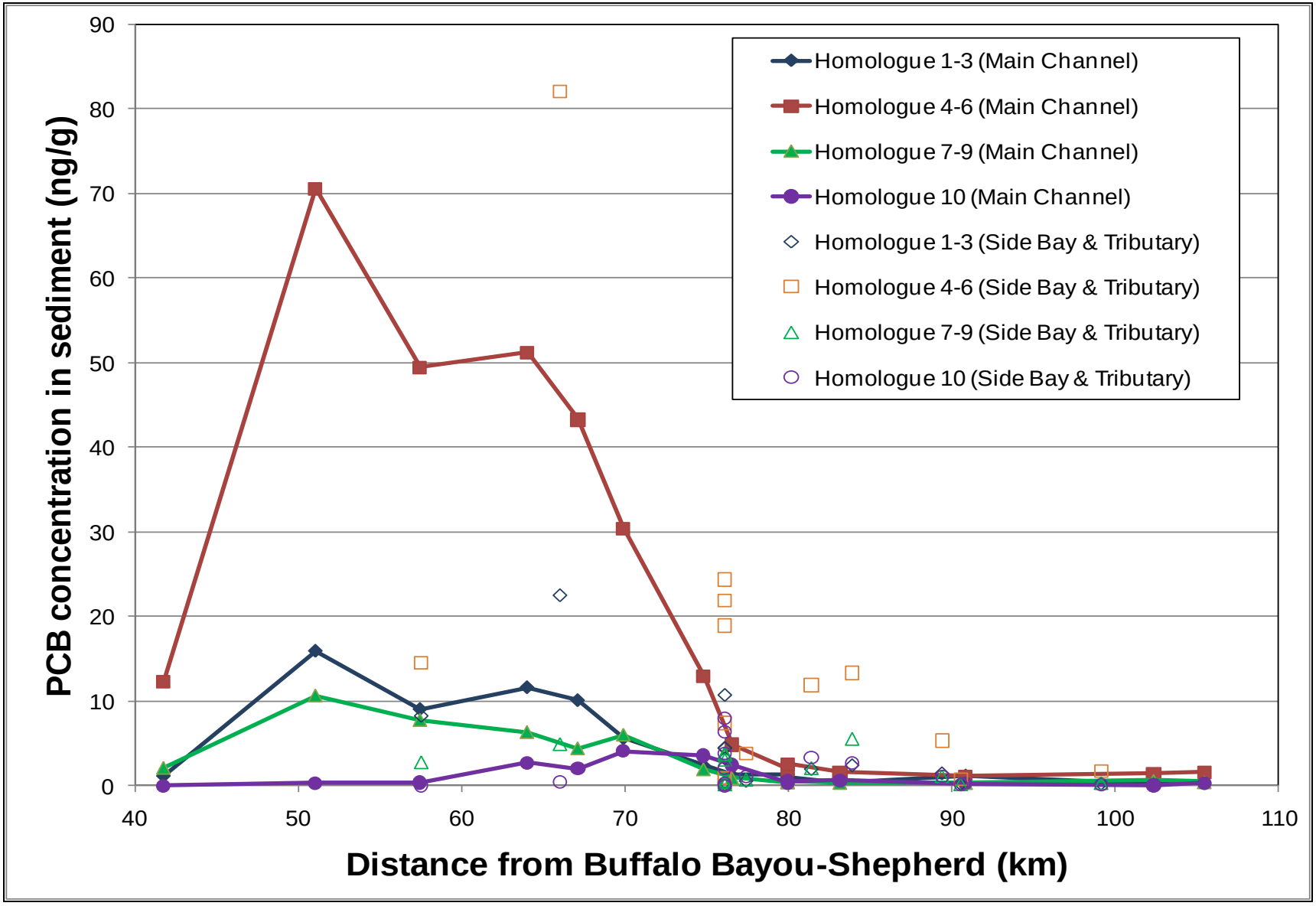


Figure 5.5a PCB homologue distribution in sediment

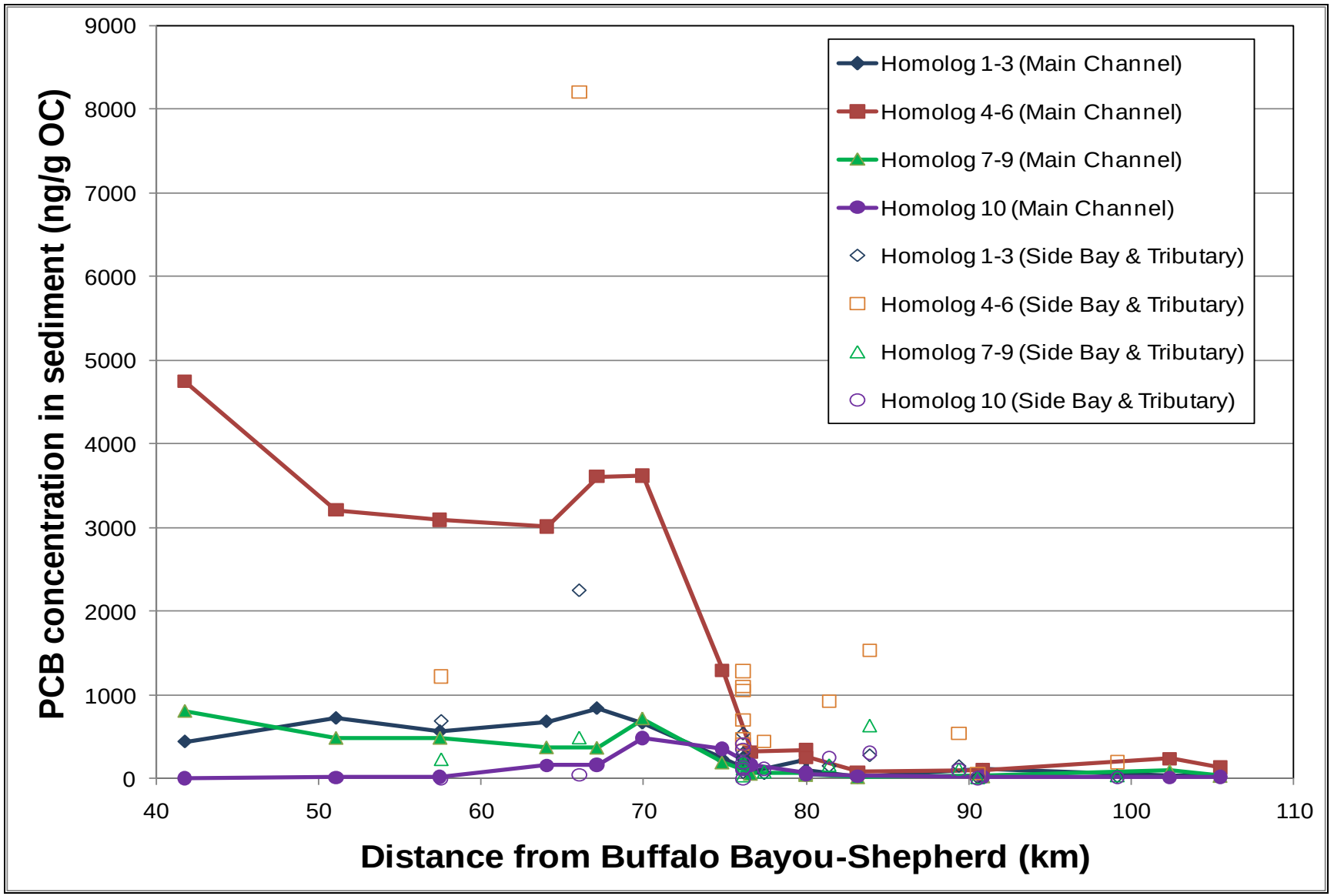


Figure 5.5b PCB homologue distribution in sediment (normalized to organic carbon)

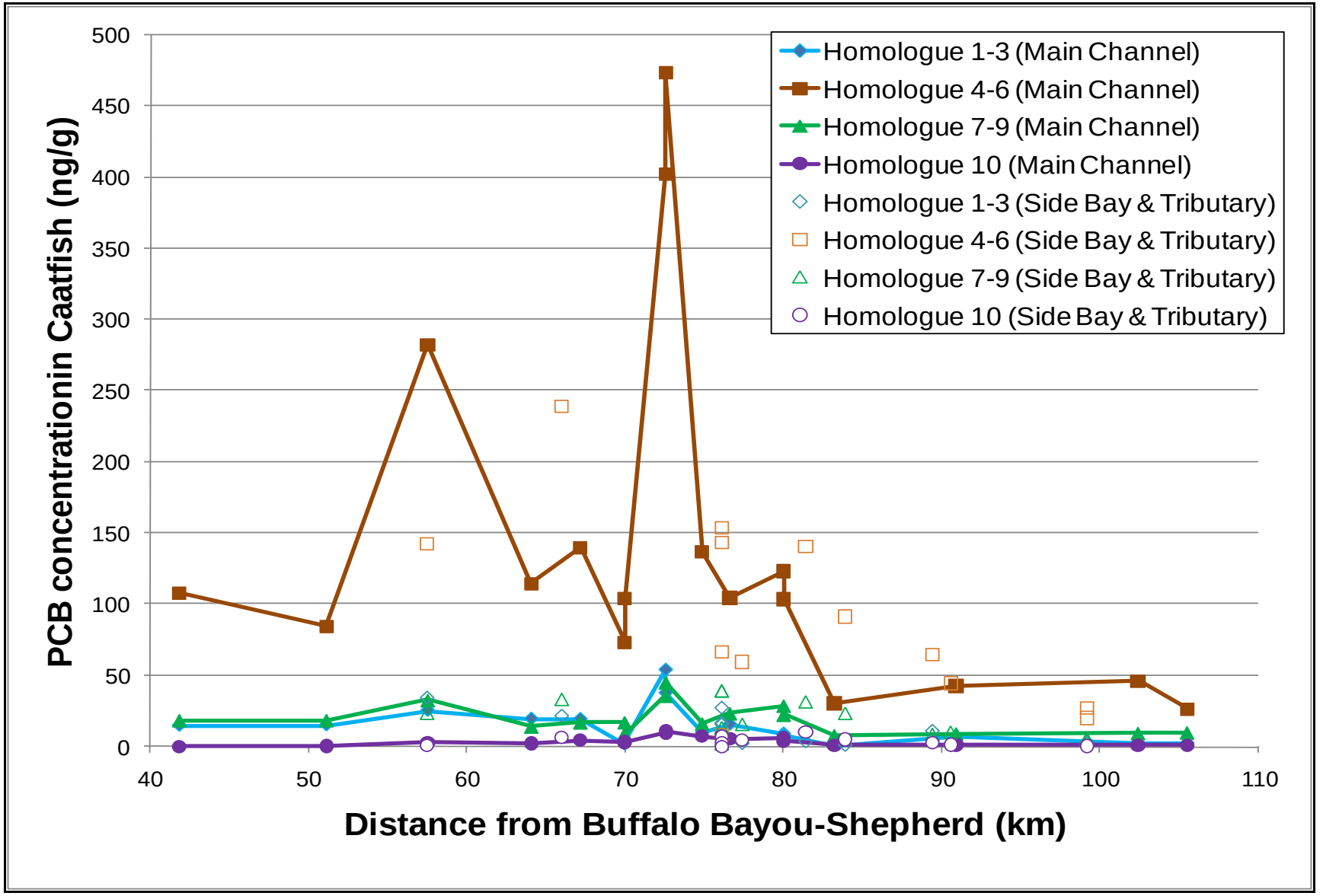


Figure 5.6a PCB homologue distribution in Catfish

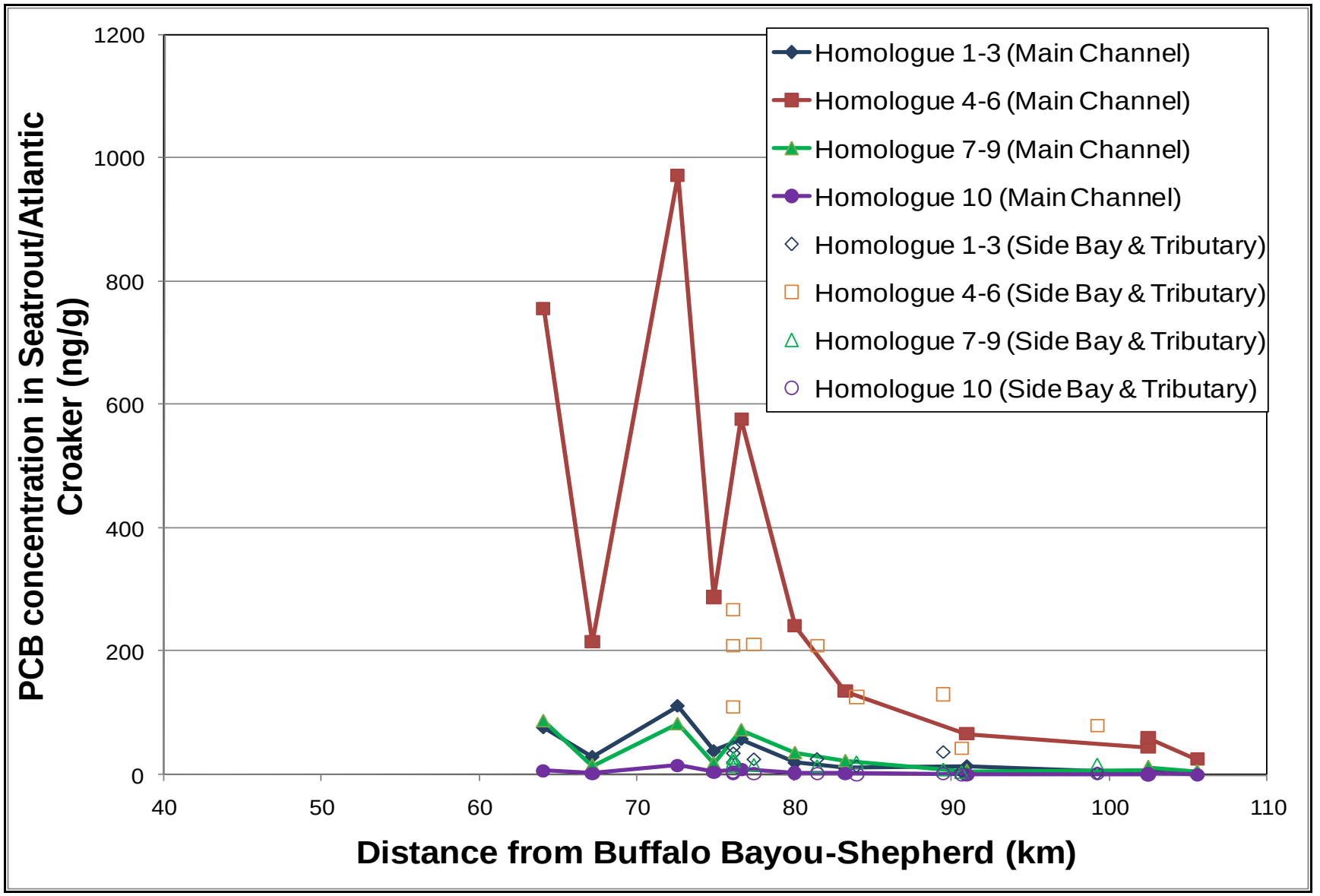


Figure 5.6b PCB homologue distribution in Seatrout/Atlantic Croaker

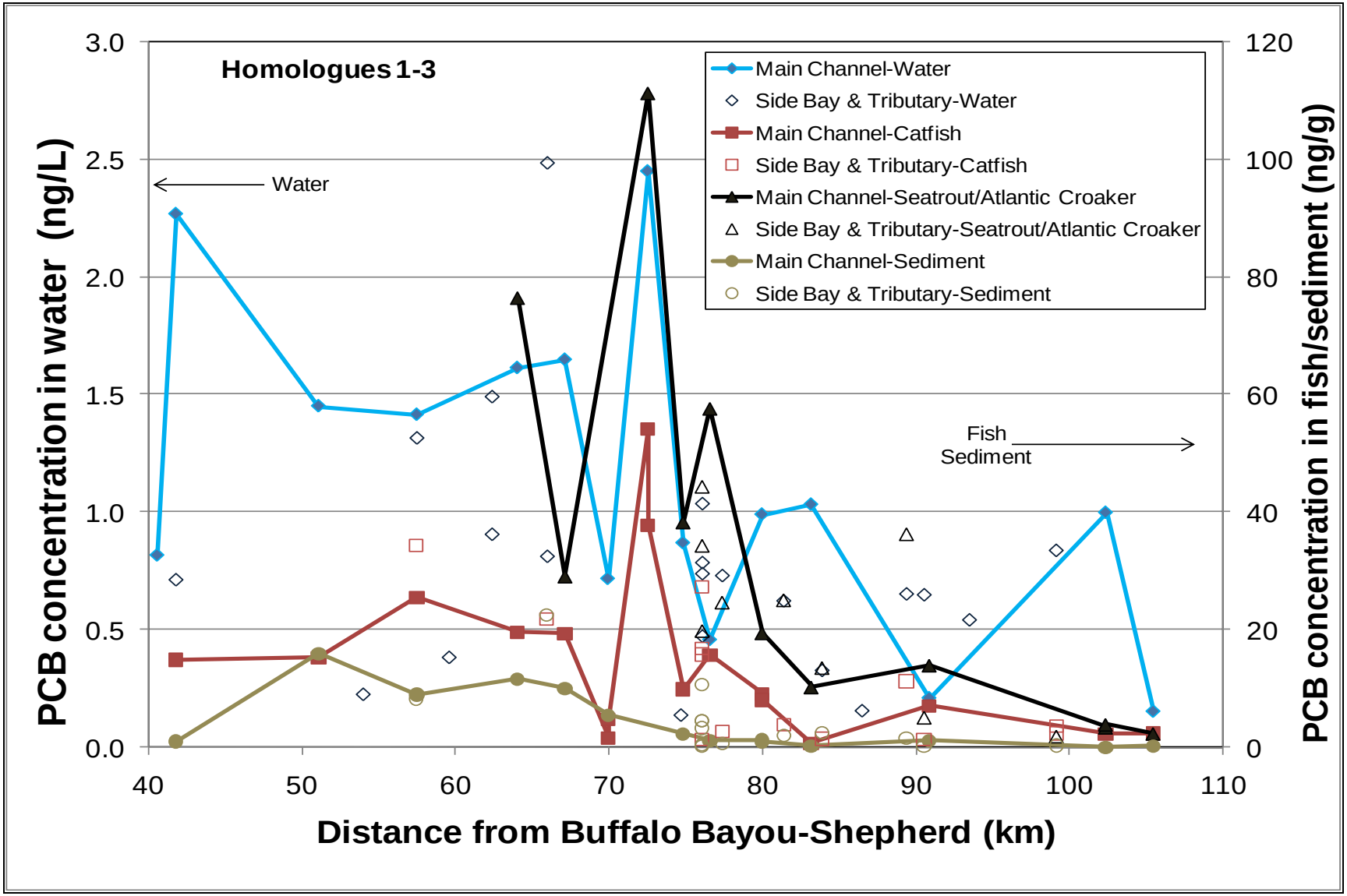


Figure 5.7 Comparison of homologues 1-3 in the water, sediment, and fish

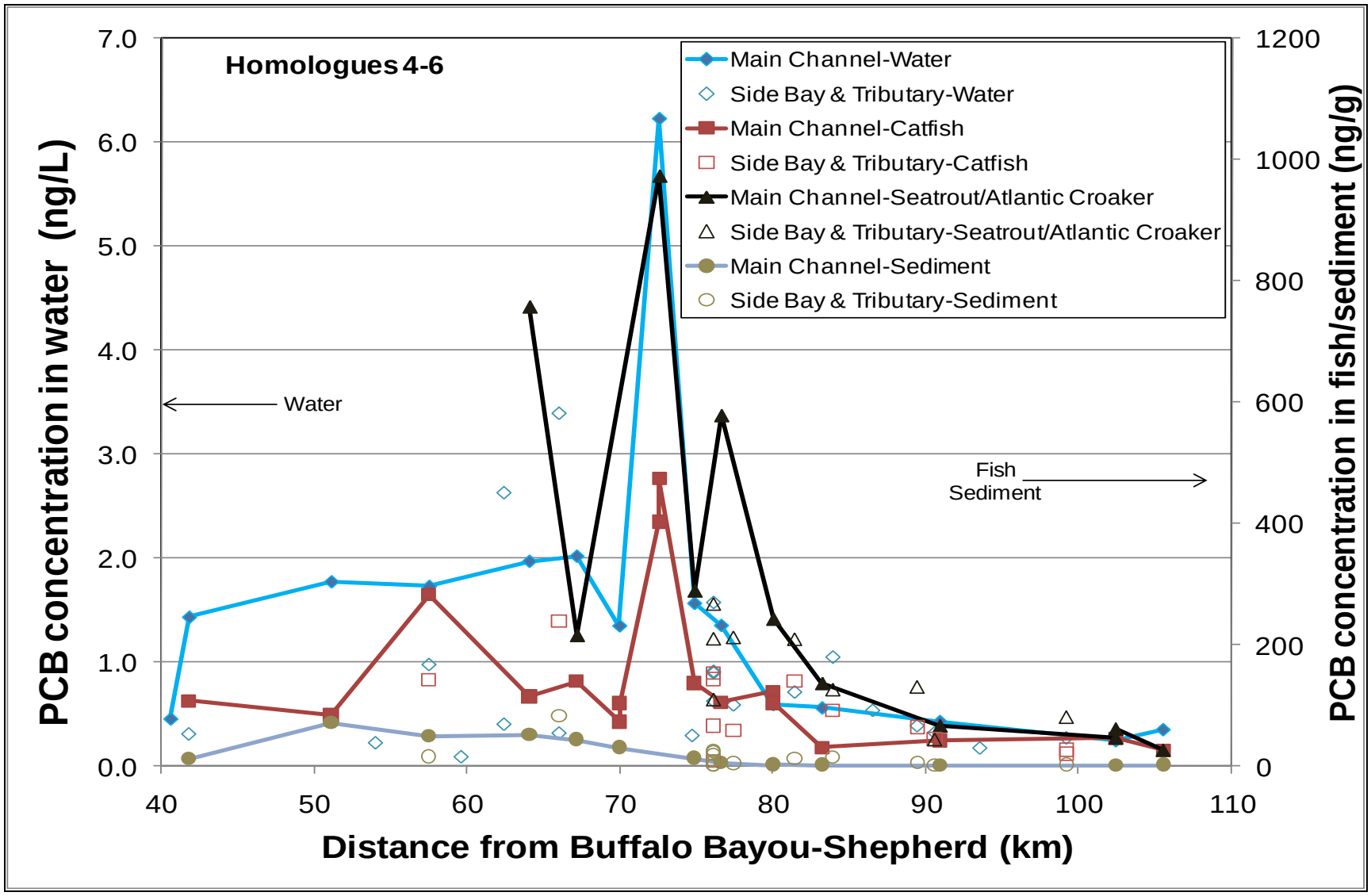


Figure 5.8 Comparison of homologues 4-6 in the water, sediment, and fish

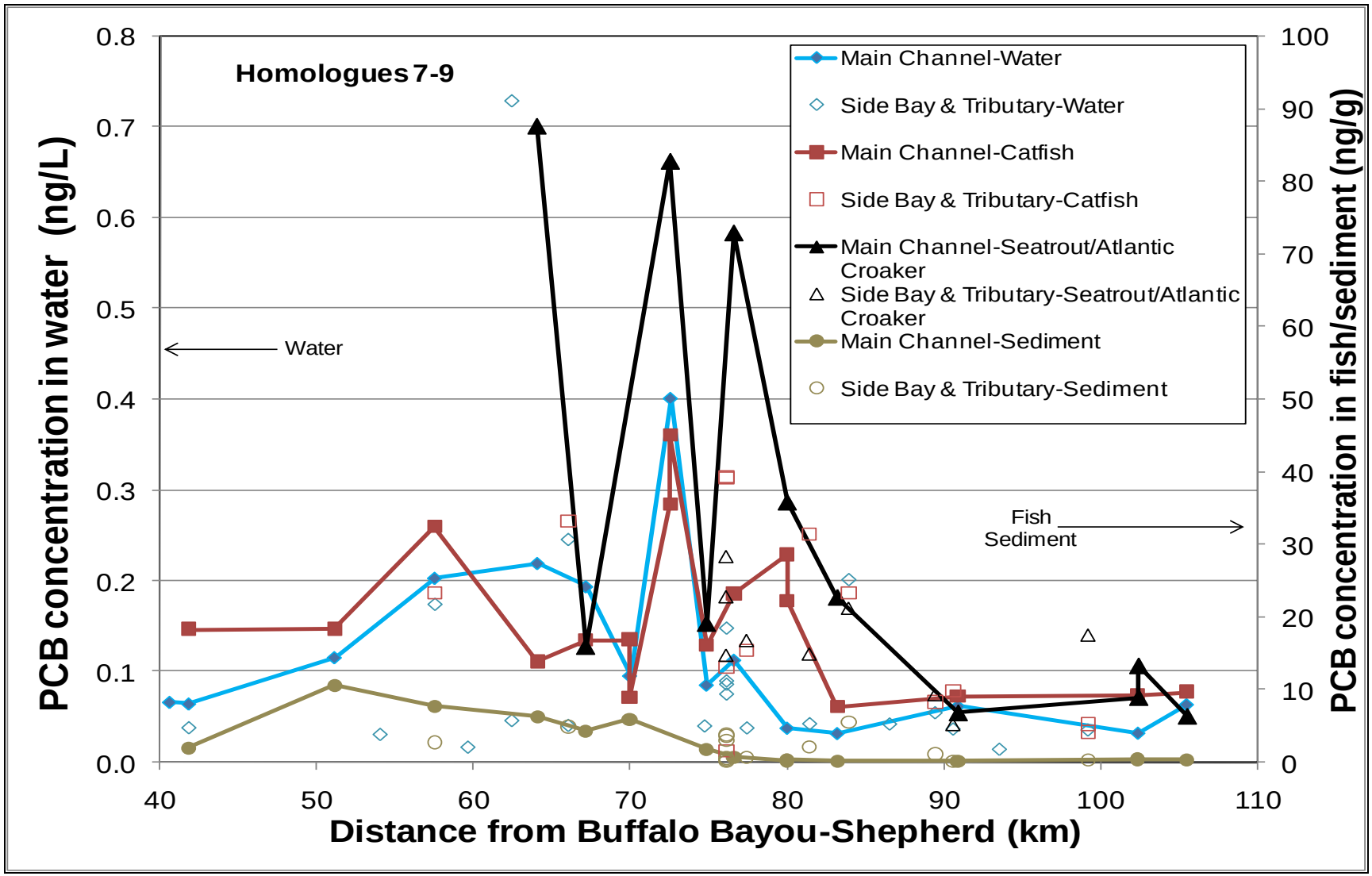


Figure 5.9 Comparison of homologues 7-9 in the water, sediment, and fish

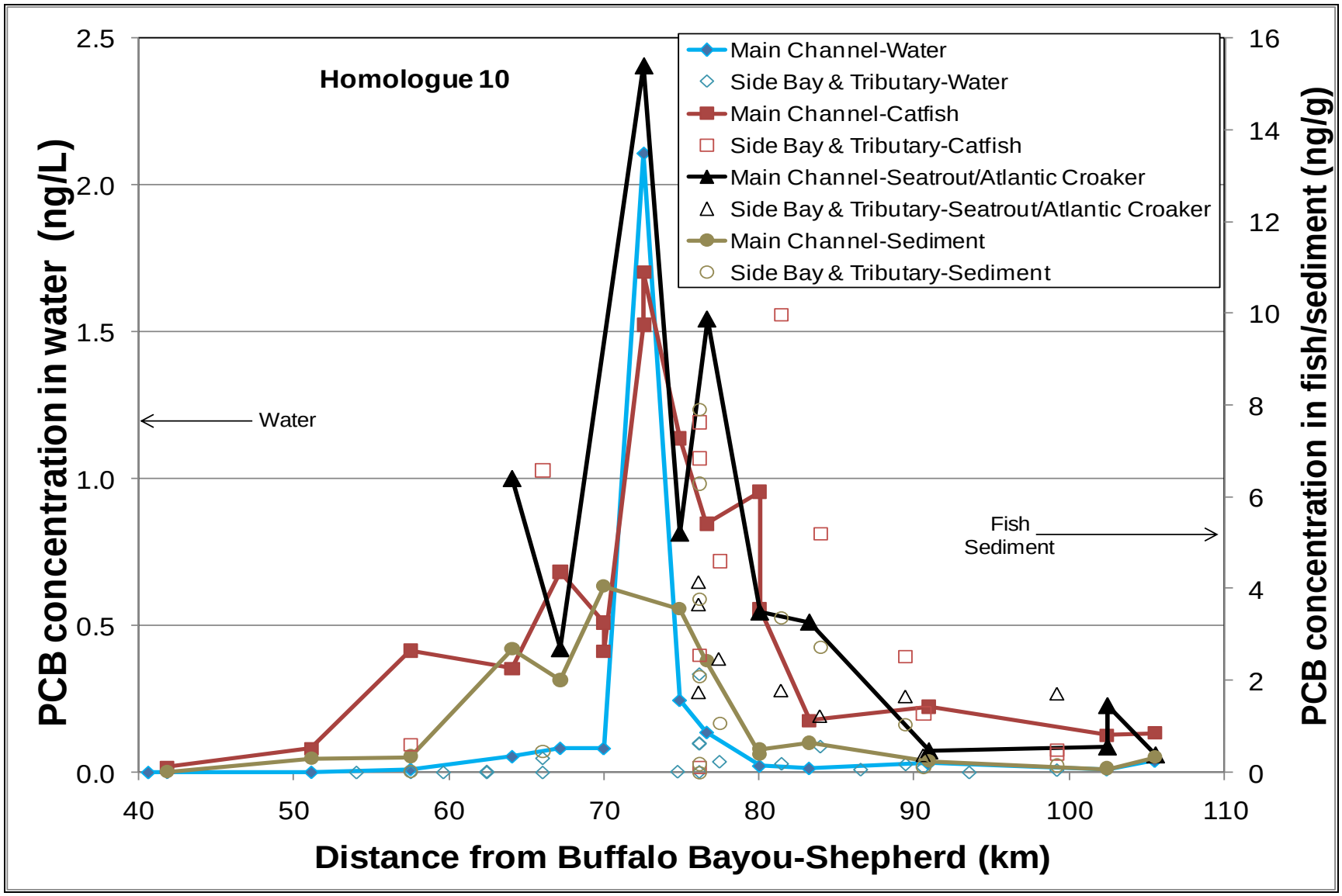


Figure 5.10 Comparison of homologue 10 in the water, sediment, and fish

5.5 Sediment Intensive Sampling Results

Initial sediment sampling was conducted using 25 sampling locations in May-June 2008 as was presented in the previous section. In addition to these, another 45 sampling locations were selected that were intended to provide more resolution for the PCB contamination in the upper HSC region (between US59-Buffalo Bayou and the SJR-HSC confluence). Figure 5.11 shows the sampling locations of all sediment samples gathered in 2008, the May-June samples and the July samples. When three five-sample transect locations are included, there were a total of 85 samples collected at 70 sites excluding another 15 field QA/QC samples consisting of duplicates, trip blanks, and equipment rinse blanks. For purposes of analysis and planning, the sediment intensive field study divided the upper part of the HSC into four parts—West, Central, East, and Tributary (Table 5.1). All 2008 samples fell into one of these four strata, or they were classified as outside of the sediment intensive sampling area.

Table 5.1 2008 sediment sampling design

Region	Composite Samples	Transect Location	Avg Distance Between Samples (km)[a]
East	18	1	0.62
Central	8	1	1.1
West	9	1	1.7
Tributary	17	0	1.9
Outside Intensive[b]	18	0	7.7
Total	***70***	***3***	***2.4***

[a]This distance is the mean distance between consecutive samples along the main reach flowline contained within each stratum, and the total row is the average of the consecutive distance for all 2008 sediment samples. The distance represents a form of linear "data density" along a flow segment.

[b]The Outside Intensive region includes side bay samples. These samples for purposes of "Avg Distance Between Samples" were considered as if they were on the main navigation channel of the HSC. They may be considered to be "projected" onto the flow path for that distance calculation only.

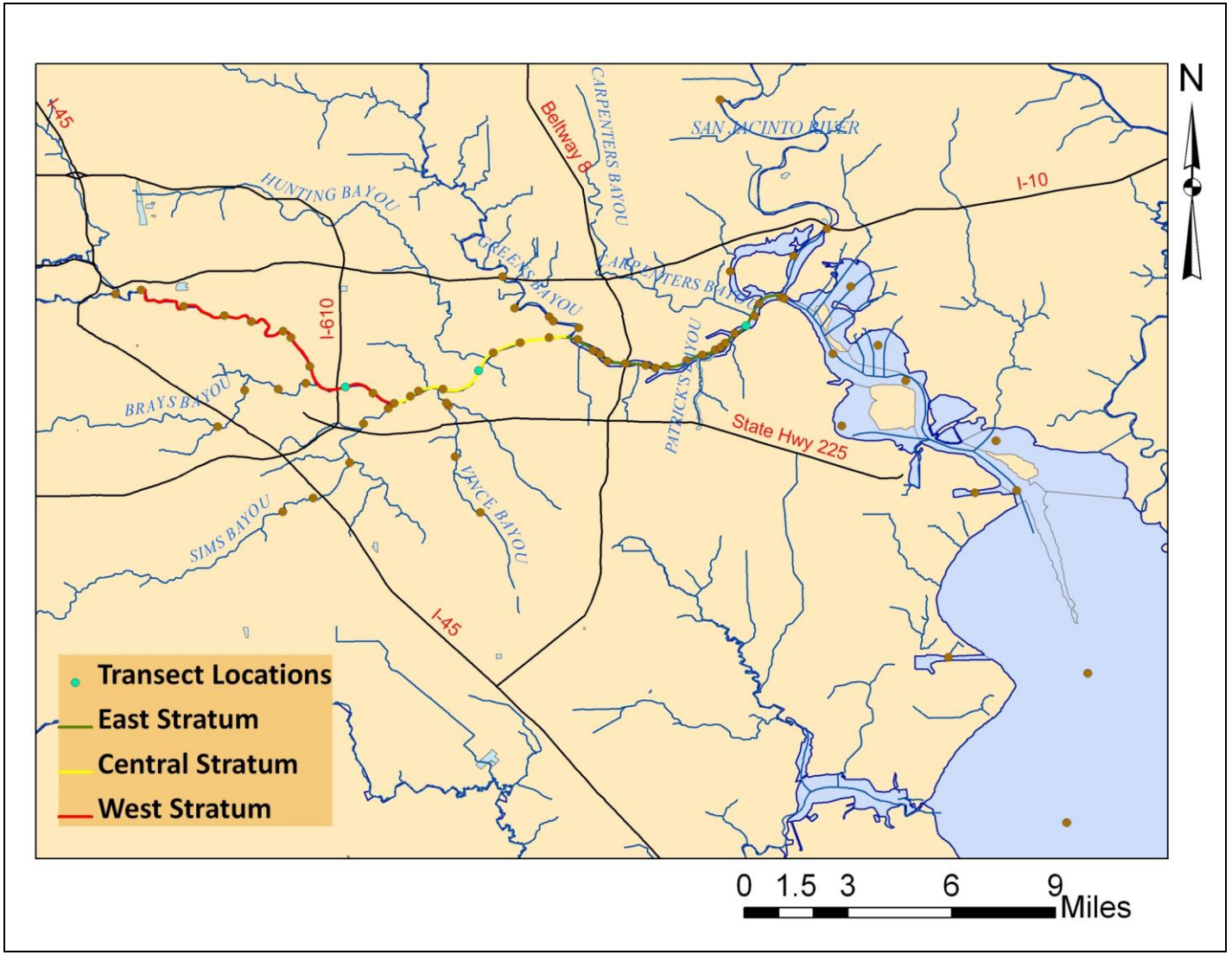


Figure 5.11 All 2008 sediment sampling locations. All transect locations were sampled as both one five-part composite sample and five individual samples equally spanning the transect

Results for the grain size analysis (Figure 5.12) are given in terms of median grain size diameter, and they show that most of the sediment in the study area is of silt and clay sizes. The grain size begins to get sandier in the upstream reaches of Buffalo Bayou past the Turning Basin, and there are a few other exceptions scattered in the SJR tidal area.

The PCB results are presented in distributional form in Figure 5.13. For the purposes of determining a relevant impact level, a "background" concentration of 545 ng PCB/g OC was developed based on the total PCB sediment concentrations of the five lowest samples from each of the 2002-2003 and 2008 datasets. Anything above this conservatively high background level is considered to be anthropogenically impacted, and this impact was present in all but six samples, all of which were in the lower HSC. The distribution also is somewhat right skewed indicating that there are likely sample hot spot concentrations. Also important in the skewness of the distribution is the role of non-detects in samples, which yield average total PCB concentrations of 0.37 ng/g dry or 11 – 244 ng/g OC[**]. Because a ½ estimated detection limit (EDL) estimate was used for non-detects, these concentration areas are where the practical "zero" concentration actually exists along the distribution. The large number of samples (11) in the left-most bar suggests that a fair amount of samples fall in the zero region, and all of these samples are in the lower HSC. Further evidence for a lower impact in the lower HSC is seen in the box plot comparison where only one sample from the lower HSC breaks even into the second quartile of the upper HSC dataset.

[**] Calculated by averaging the estimated detection limits (EDL) for all sediment samples and then summing them.

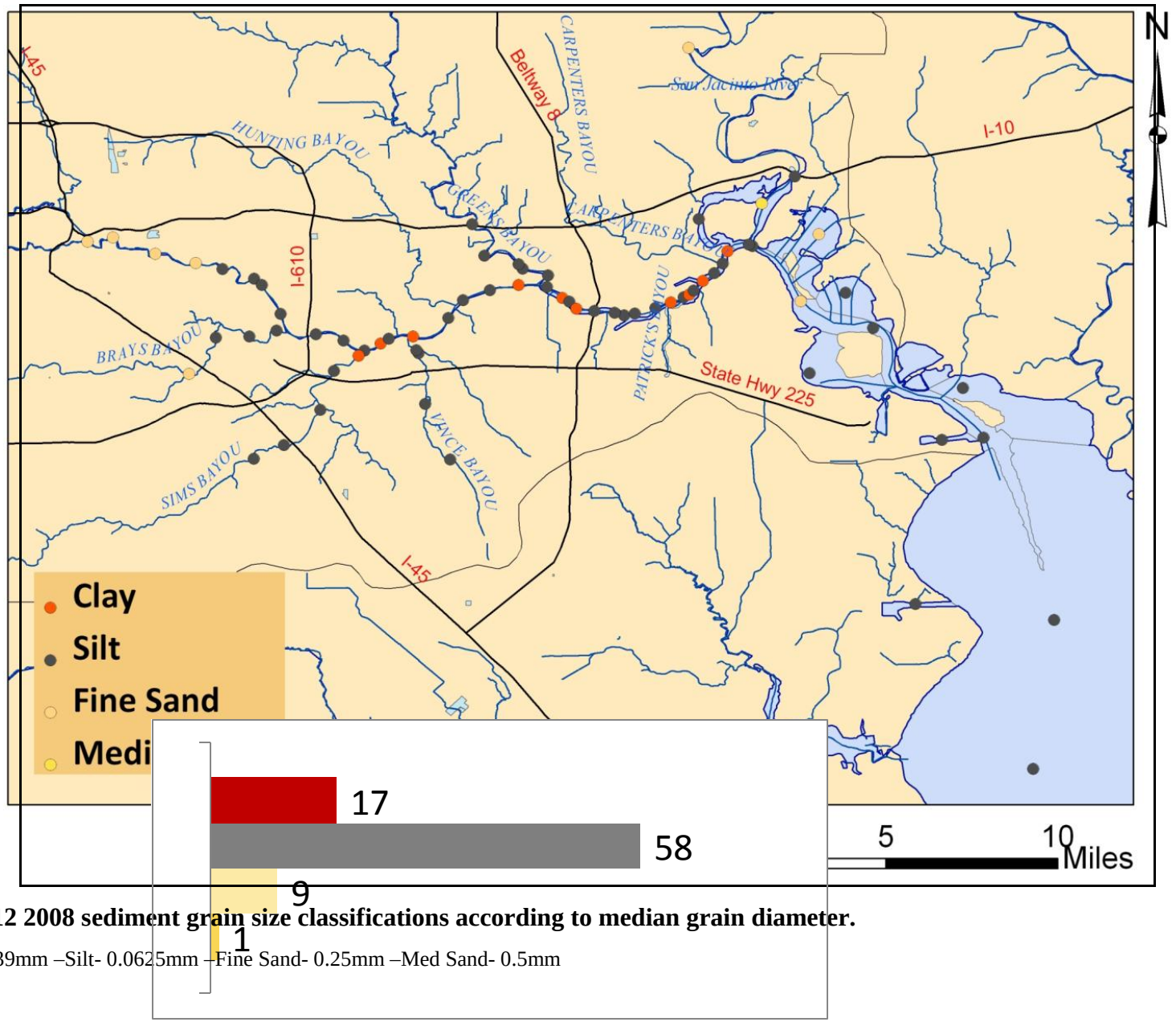


Figure 5.12 2008 sediment grain size classifications according to median grain diameter.

Clay < 0.0039mm –Silt- 0.0625mm –Fine Sand- 0.25mm –Med Sand- 0.5mm

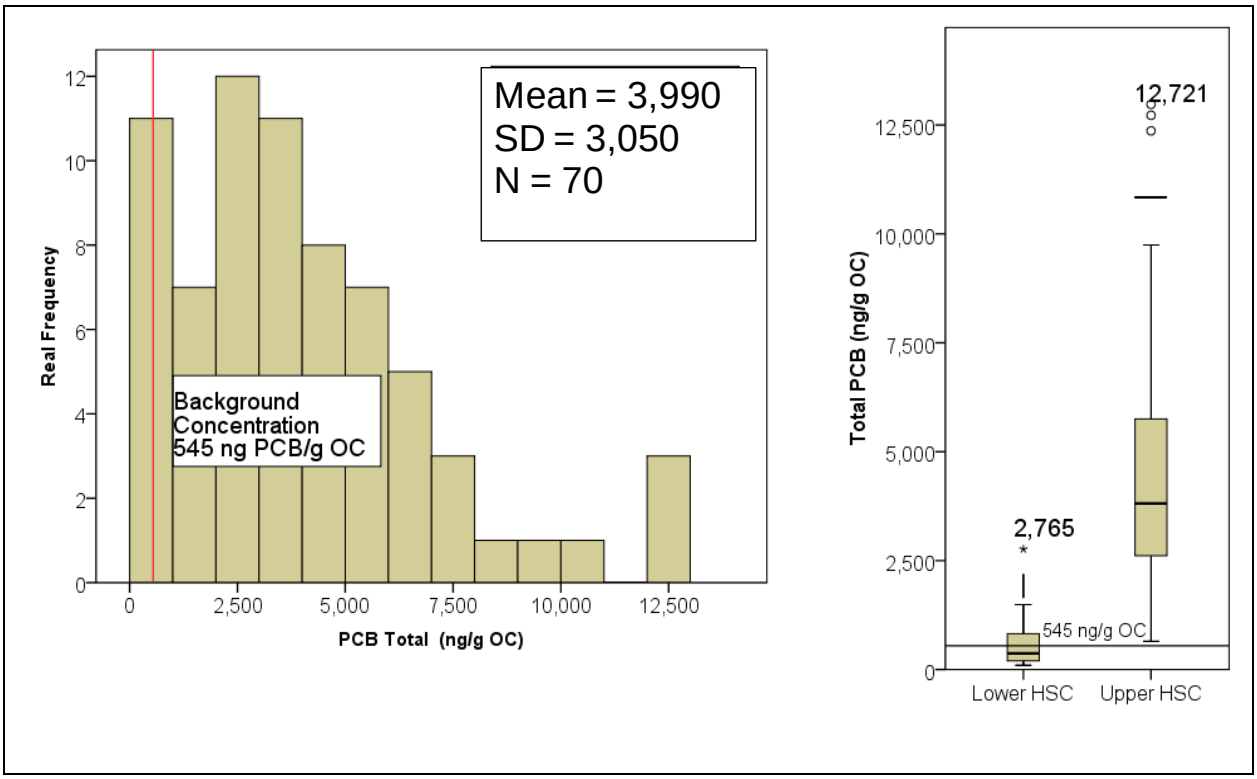


Figure 5.13 2008 PCB sediment sampling results by total histogram and by upper and lower HSC (tributary samples considered to be upper). Background concentration determined by the upper 95% confidence limit of the five lowest PCB concentration values (total of 10 values) from each of the 2008 and 2002-2003 datasets

The spatial distribution of the individual samples (field duplicates averaged) in Figure 5.14 and Figure 5.15 reveals that there are areas in the lower HSC that would be considered contaminated, but all of the moderately and very contaminated samples were in the upper HSC. These very contaminated samples (n = 6 and >8,850 ng/g OC) can be grouped into three general clusters according to proximity to one another—HSC at 610 (1 sample, cluster C1), Greens Bayou (3 samples, cluster C2), and Patrick/Tucker Bayou (2 samples, cluster C3[††]). The average

[††] It is noted that there are three sediment samples between these two locations (E009, E010, and E011) that do not score nearly as high for total PCBs as the two (E008 and E012) being placed in the C3 cluster. Since the homolog profiles between E008 and E012 are so similar, however, the clustering seems justified.

total PCB for each area is in decreasing concentration 12,971, 11,000, and 10,800 ng/g OC at HSC at 610, Patrick/Tucker Bayou, and Greens Bayou, respectively. A glance at the homolog profiles of these clusters (Figure 5.16) reveals that at least three fairly distinct signatures exist. C1 has a balanced middle signature with high 4-6 homologs that increase in percentage with increase in chlorination. C2 generally has high 3-6 homologs, and the 4-6 homologs decrease with increasing chlorination. The third cluster, C3, has a 3-6 homolog section that is fairly similar to C2, but these profiles are over 15% homolog 10. The presence of homolog 10 is in contrast to the other two clusters where homolog 10 is virtually non-existent. The one exception to these trends is in the T012 sample (Greens Bayou 0.3 miles upstream from the confluence with HSC), where the profile appears to be more of a mixture of the C2 and C3 profiles rather than a strict C2 profile. The number 10 homolog is present in this profile though not at the relative level of the East stratum samples found in the Patrick/Tucker area (C3).

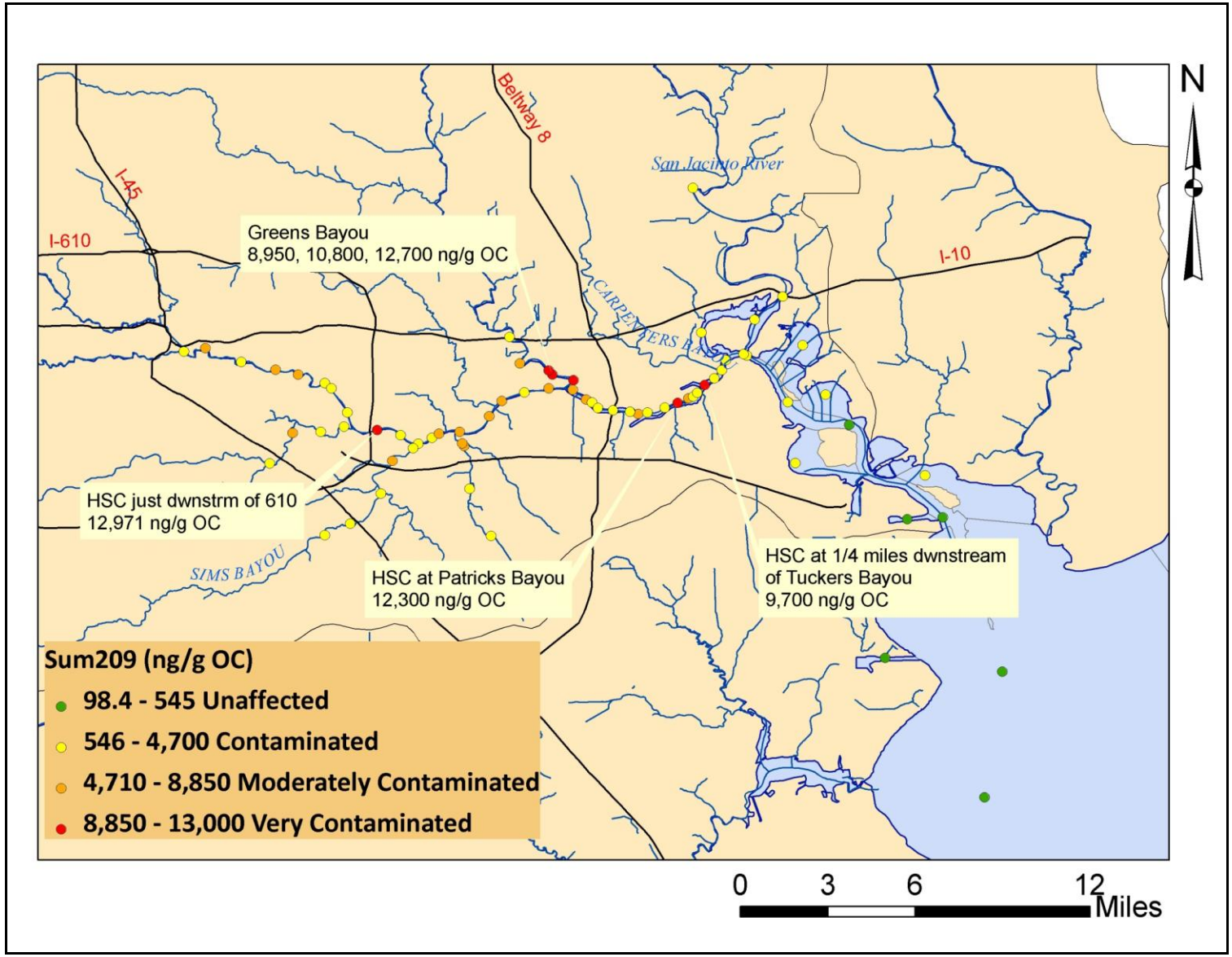


Figure 5.14 2008 sediment PCB concentration map

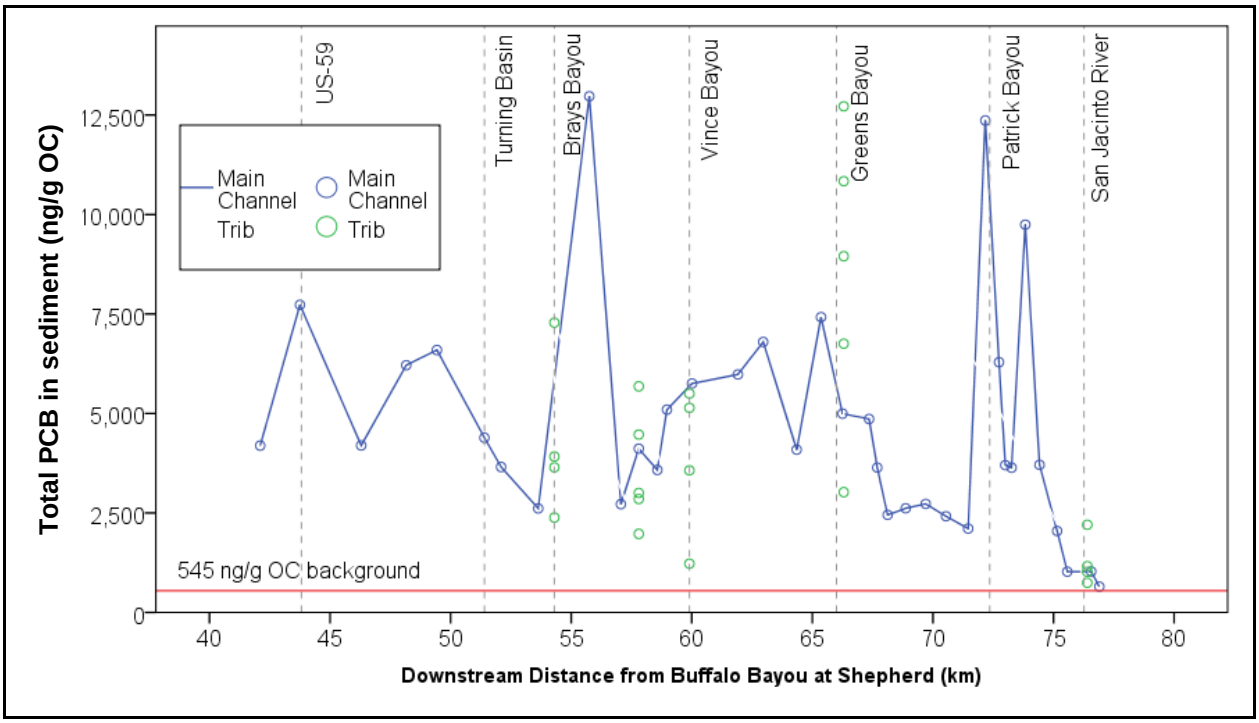


Figure 5.15 Main channel 2008 total PCB in sediment trend

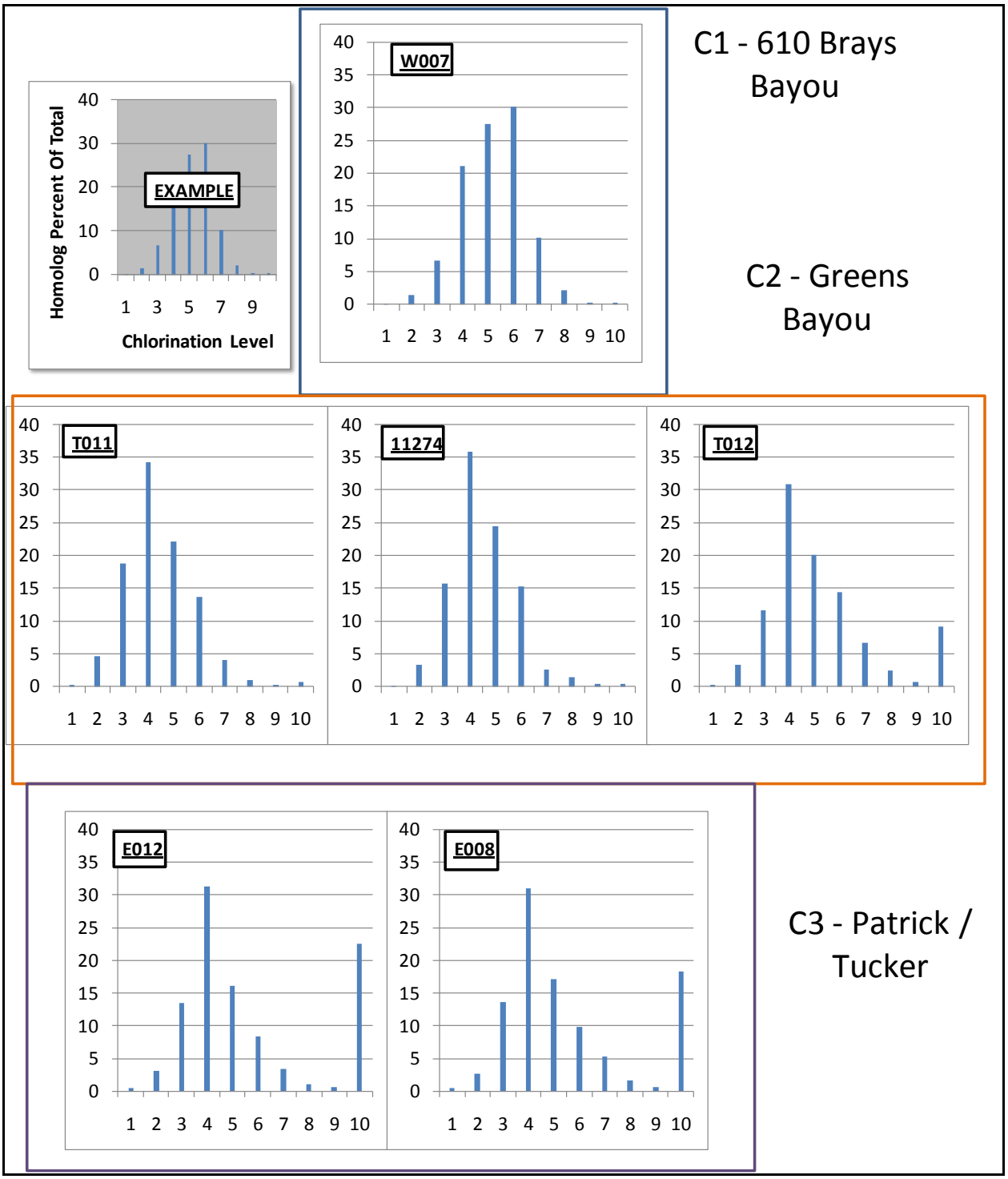


Figure 5.16 Sediment PCB homolog profiles at the highest six total concentrations of 2008

In addition to the analysis of spatial patterns in the 2008 sediment data, an attempt was also made to compare temporal changes from the 2002-2003 dataset. The distributions shown in Figure 5.17 show that the general shape of the two sampling seasons are not that different. The main distinction is simply that there are no extremely high samples above 20,000 ng/g OC in 2008 whereas in 2002-2003, there are three samples above that mark with the max at 147,000 ng/g OC (an average of two sampling events) in Patrick Bayou at Tidal Road. A sediment sample was not collected from that location in 2008 to compare with the 2002-2003 station average. Overall, however, statistical tests do show significant differences in sampling means. For all samples that were sampled in both 2002-2003 and 2008 sampling campaigns (comparison made in paired fashion between stations sampled at both times only), a Wilcoxon Signed Ranks tests indicated statistical dissimilarity at the $p < 0.05$ level. Mann-Whitney U tests were performed on the 2002-2003 and 2008 datasets in total as well as the 2002-2003 set compared only with Upper HSC. The entire 2008 dataset comparison did not show significant differences from all 2002-2003 samples in the mean though the Upper HSC portion of the data did at the 95% significance level.

An examination of change over time can be seen in the data along the channel profile (Figure 5.18), and the data can be used to elucidate where major attenuations have occurred. The overall statistical tests indicated that the total PCB sediment concentration was decreasing in the 5 years between samplings, but that decrease is not uniform at all locations. The profile reveals that concentrations have decreased dramatically all throughout the main channel with an attenuation factor of 2.2 (Upper and Lower HSC at 3.2 and 11.3 attenuation, respectively) when the averages of each profile are compared one against the other. The general shape of the profile is fairly similar over the channel length with the notable exceptions at the Turning Basin and

Lower HSC. The exact same location within the Turning Basin was used in both sampling seasons with one sample collected there in 2008 and three samples collected there in 2002-2003. Given that the PCB concentration difference between these two time frames is a factor of 11, it may be that spatial variability in the region and the specific location of grabs has created the appearance of large attenuation when in fact this may not be the case. More sampling will be required to tell for certain, but what is also interesting in this area is that immediately downstream of Brays Bayou is the C1 hot spot cluster. The spatial profile gives the appearance that the Turning Basin PCB concentration peak that existed in 2002-2003 has moved and attenuated to this new location approximately 4.7 km downstream.[‡‡]

The sediment intensive was designed to increase the precision of the PCB concentration mean for the different strata (Rifai and Palachek, 2008), and that is what has happened as shown in Figure 5.19. The plot shows large error bars for each of the four strata for 2002-2003 with average relative standard deviations (RSD = s/μ_{sample}) between them of 1.00 (standard deviation approximately the same size as the mean). The 2008 sediment sampling nearly doubled the precision to RSD = 0.54 (standard deviation approximately half of the mean). Put another way, the means for each stratum are now known 21-44% either side of the value (upper/lower 95% confidence interval divided by the mean) whereas the 2002-2003 datasets exhibited a range of 78-663% (West stratum excluded because sample size < 2). The design for the sediment intensive sampling was to choose sample sizes according to a desired precision of 70% either side of the mean, a goal which was met and exceeded.

A comparison of the actual mean concentrations for each stratum yields similar conclusions to what is seen in the previous spatial analysis, an overall decrease in concentration

[‡‡] A higher spatial resolution sampling in 2002-2003 would have made this determination much more certain, but spatial plot still seems to support this hypothesis.

at all locations. The Central stratum had the lowest total PCB average in 2002-2003, but due to the large confidence interval (± 49,000 ng/g OC or ± 663% of mean) surrounding that value, it wasn't completely certain if that was truly the least impacted segment of the study area. Now it is seen while the Central stratum is low, it may not definitively be the lowest average concentration stratum (though none of the three cited hot spots exist in this region). The other three strata exhibit more sizeable attenuation levels than the Central though all exhibited large decreases with 95% upper confidence limits lower than the strata means found in 2002-2003. The West and Tributary strata exhibited the greatest decreases though these two strata still contain hot spot regions. Statistical comparisons between the means of strata and tributary (Figure 5.20) were performed using independent sample t-tests between all combinations (24 excluding tributary stratum comparison to individual tributaries), and there were only five statistically significant differences at either the p=0.05 or p=0.1 level. Greens Bayou with the highest average altogether was statistically higher than Brays ($p<0.1$), Sims ($p<0.05$), Vince ($p<0.1$), and East ($p<0.05$) areas. Sims Bayou was considered to be statistically lower than the Central stratum even though the p value was slightly higher than the 0.05 cutoff ($p = 0.051$). The implication of these distinction are that Greens Bayou, in addition to being a hot spot cluster, is also more PCB-impacted than any of the other three major tributaries in the region. Furthermore, though the East stratum has one of the hot spot locations, it as a whole has a lower concentration than Greens Bayou, and of course Greens Bayou is as a whole at least numerically higher in average than all other regions in the study. It was also interesting that Sims Bayou was statistically lower than the Central stratum because the upper boundary of the Central stratum is the HSC confluence with Sims Bayou. The comparison seems to indicate that sediment sources apart from Sims Bayou are more noticeably affecting the Central sediment concentrations than these tributaries, sources

such as the HSC-610 hot spot. In fact, the nearest Sims tributary sample (T008) compared to the nearest Central sample (11287) reveals a 44% *increase* in total PCB concentration (ng/g OC) from tributary to main channel.

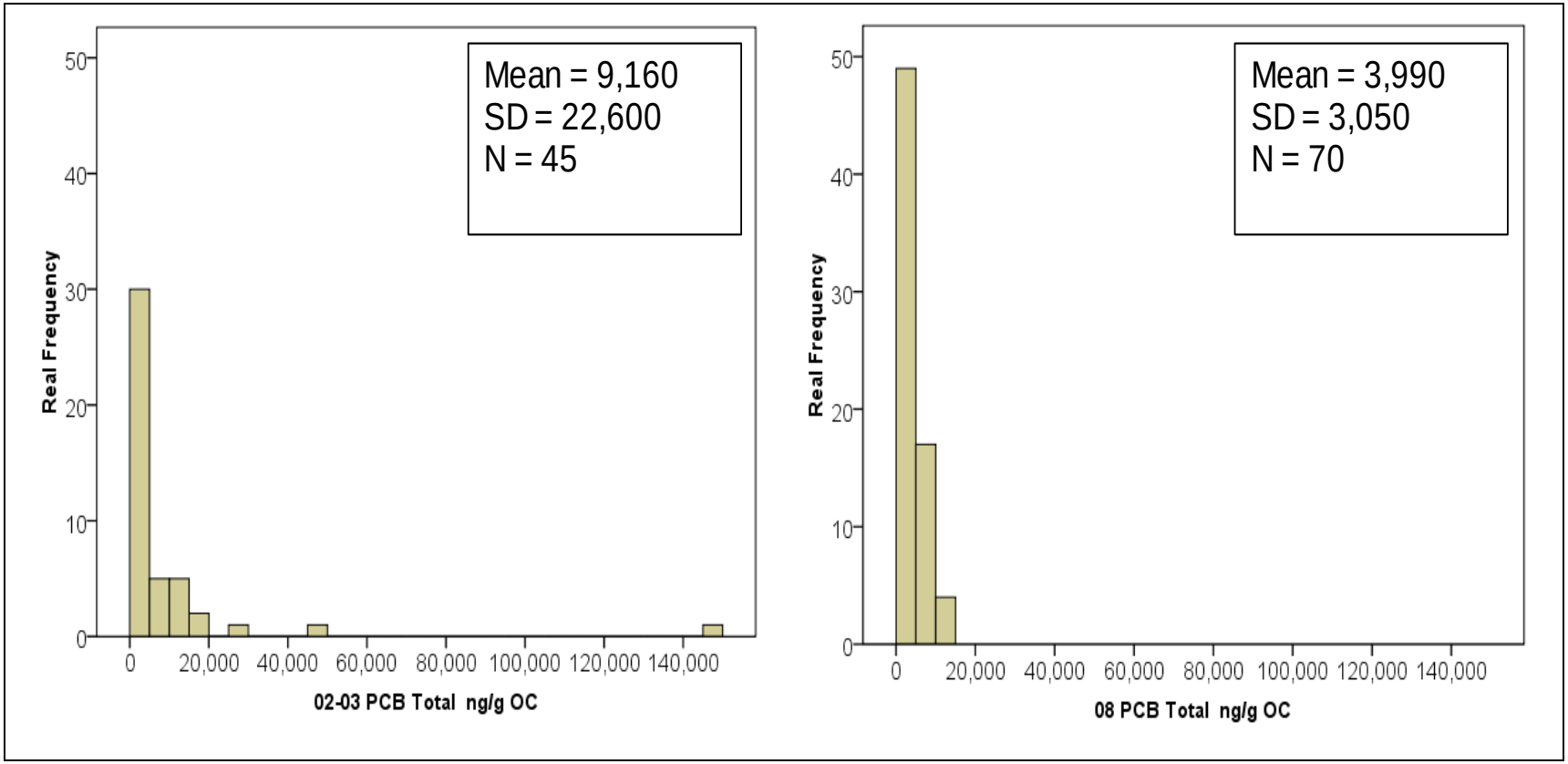


Figure 5.17 Comparison between 2002-2003 PCB and 2008 PCB sediment datasets

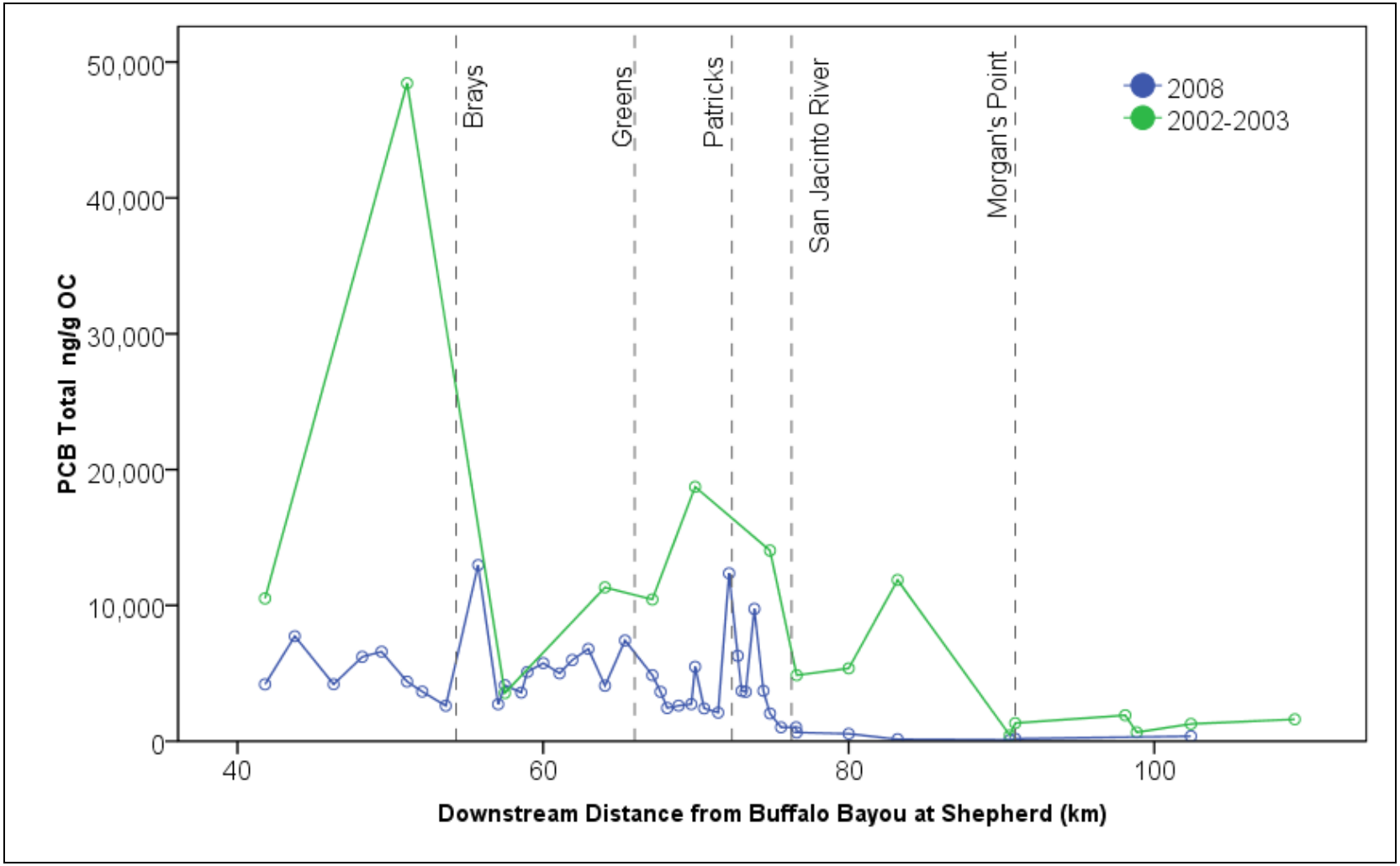


Figure 5.18 Main channel trends in PCB for 2002-2003 and 2008 sampling seasons

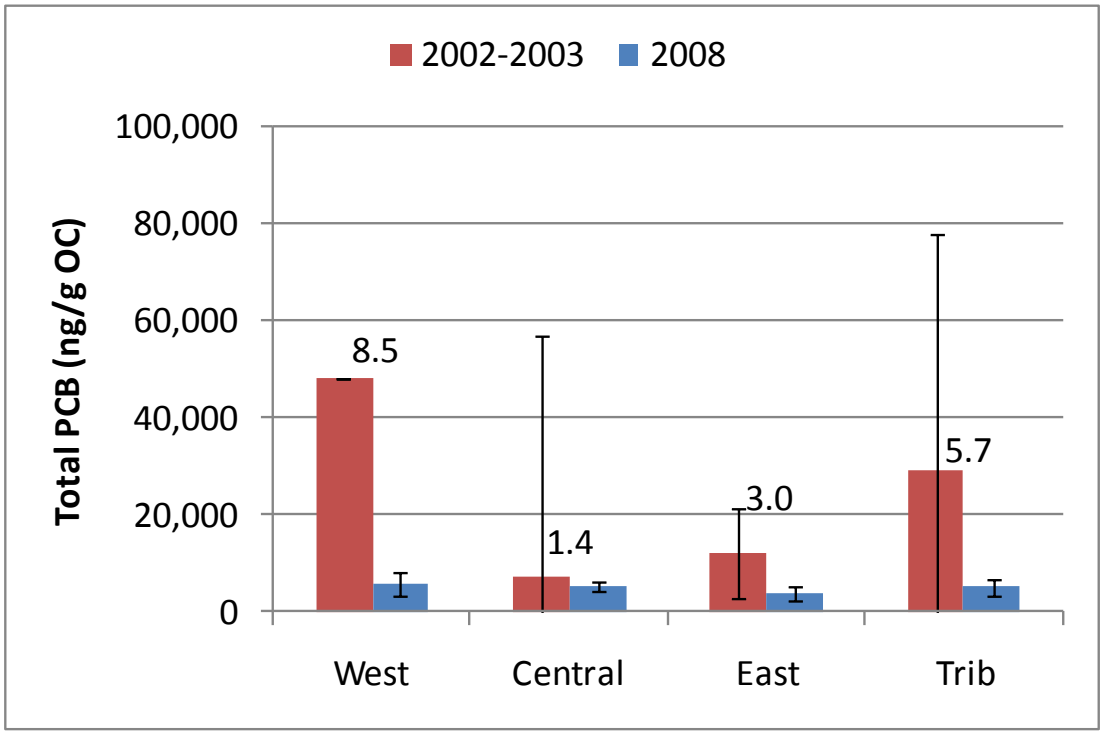


Figure 5.19 PCB sediment strata means for 2002-2003 and 2008

Error bars represent 95% confidence limits, and numbers above each pair of bars is the PCB attenuation in time. Note that the West stratum for 2002-2003 has not errors bars because there was only one station from that time frame. Data labels represent attenuation between the PCB concentration means of the two time frames.

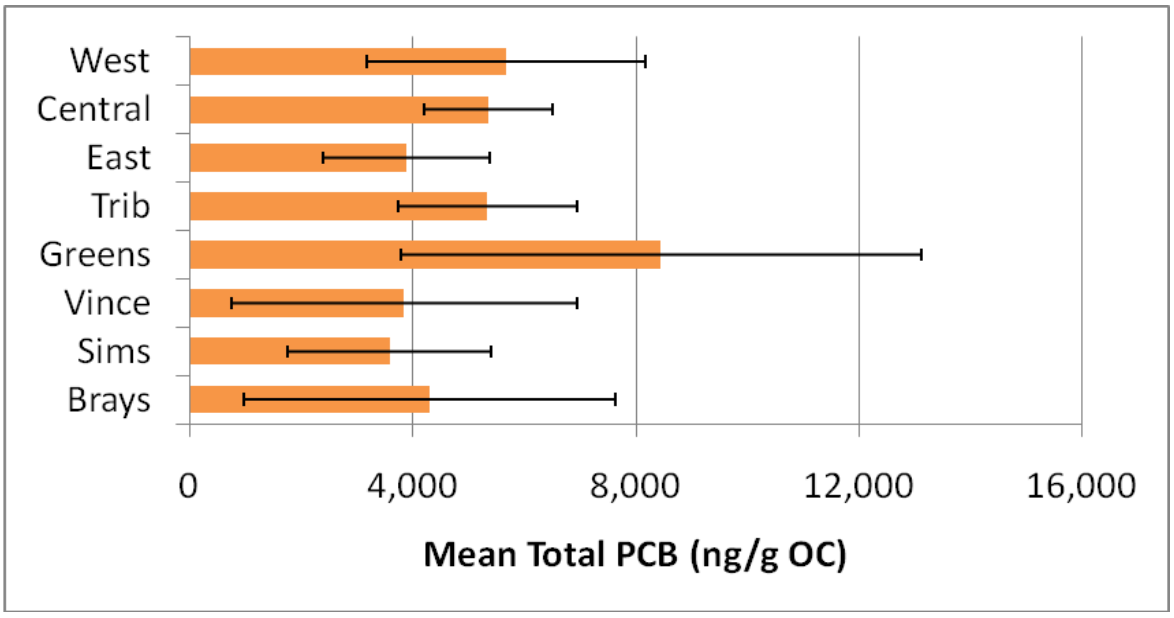


Figure 5.20 PCB concentration averages per strata and tributary

The sediment intensive sampling was different from the standard sampling protocols that where used in that it sought to explore other types of spatial variation beyond the characterizing the general state of PCB in the ship channel, and these other variations are along a channel transect width (Figure 5.21) and the longitudinal profile of tributaries (Figure 5.22). Intra-transect profiles were important because the standard sampling procedure composites samples along a transect, and yet it is not always certain if contamination is ever more localized to a particular part of the transect. Since the Upper HSC is often wide (as much 400+ meters in some places) and dredging (both local harbor and main channel navigational) occurs throughout the region, the possibility for large transverse variation exists. Variation exists along tributary lengths as well, but a different reason for understanding tributary variation is that tributaries appear to be sourcing the main channel at times. Thus, pinpointing source potential location is significant.

The transverse channel transect data[§§] do not show much variation in PCB concentration for the three sites chosen except in the case of the W007 site (western most green dot in Figure 5.11), which happens to be the same location as one of the three sediment hot spots (an unforeseen coincidence). Visually the W007 transect shows extreme variation on the far left side, which yields an RSD that is much higher (1.1) than the East (0.71) and Central (0.85) strata sites. Not only does W007 show high variation, but the source of the variation is extremely localized to that one side of the channel. The concentration at the far left is 105,000 ng/g OC whereas the average for the other four locations in the transect is 5,070 ng/g OC, a factor of 21 difference. Some explanation may be found in the fact that the level of TOC is diminished on the left side of the channel, which actually was a similar result for TOC in the Central stratum transect as well.

[§§] Please note that all uses of far left, left, etc. in describing the transect are referenced as if one were looking downstream also known as a "descending" reference.

Not surprisingly, this decrease in TOC coincides with an increase in grain size to fine sand (0.0625-0.25 mm), a grain type that normally does not have as high an organic content as silts and clays. These differences cannot completely explain the difference in concentration since the dry weight (ng/g dry) concentration total PCB concentration between far left sample and the average of the other four are still separated by factor of 5.6. Thus, it is likely that the high concentration at the 610-Brays Bayou hot spot (C1) is related to sourcing specific to the left side of the channel.

Since one of the valuable results in the transect samplings is to determine variability as a measure of accuracy for current transect-compositing samples, the values of a simulated composite sample from each transect were also determined. The transect sample-averaged values for W007, C004, and E013 were (mean±95% CL) were 25,100±25,000, 6,800±3,900, and 3,700±830 ng/g OC, respectively. The separate transect-composite samples agree within the 95% confidence limits, and the relative percent differences (RPD) between the two measurements are 64%, 44%, and 14% for W007, C004, and E013. Some of these RPDs are quite high, however, and thus illustrate how much a wide swing in concentration such as seen in W007 can give a somewhat quantitatively myopic view of the sediment sampling location. Specifically for the case of W007, the high left side concentration is actually 2.2 times higher than the highest main channel event-averaged concentration seen in the Turning Basin (11292) in 2002-2003 (Figure 5.18, 48,443 ng/g OC). This difference in PCB concentration may indicate that the attenuation from 2002-2003 to 2008 is not as significant as transect-composite sampling might lead one to believe.

The tributary PCB concentration profiles in Figure 5.22 are interesting because they do not all bear the same general shape. Vince and Sims Bayous are somewhat similar in that they

start out at a relatively low concentration, increase to a maximum, and then fall off just before the confluence with HSC. The two most downstream samples for Vince Bayou (T015 and T016) are closer together because they split the confluence that Vince Bayou makes with its tributary Little Vince Bayou. The difference in sediment concentration is fairly close, which suggests that Little Vince Bayou may not transport much sediment (either low PCB sediment which would dilute or high PCB sediment which would concentrate) to the larger Vince Bayou. Brays Bayou is different from the rest because its profile fluctuates up and down without any net trend, and this fluctuation is dissimilar from the other three profiles because it is the only profile that does not decrease in concentration immediately prior to the HSC confluence. Greens Bayou of course represents a hot spot region in the whole of upper HSC though it does exhibit the decrease in sediment PCB as it moves closer to HSC. What is not clear from its profiles is how the concentration moves from 6750 ng/g OC to 12,700 ng/g OC in a space of 2 km. One might wonder if it truly is a gradual linear increase or there is some particular place where the concentration suddenly spikes possibly to even a higher value than what was seen at T011.

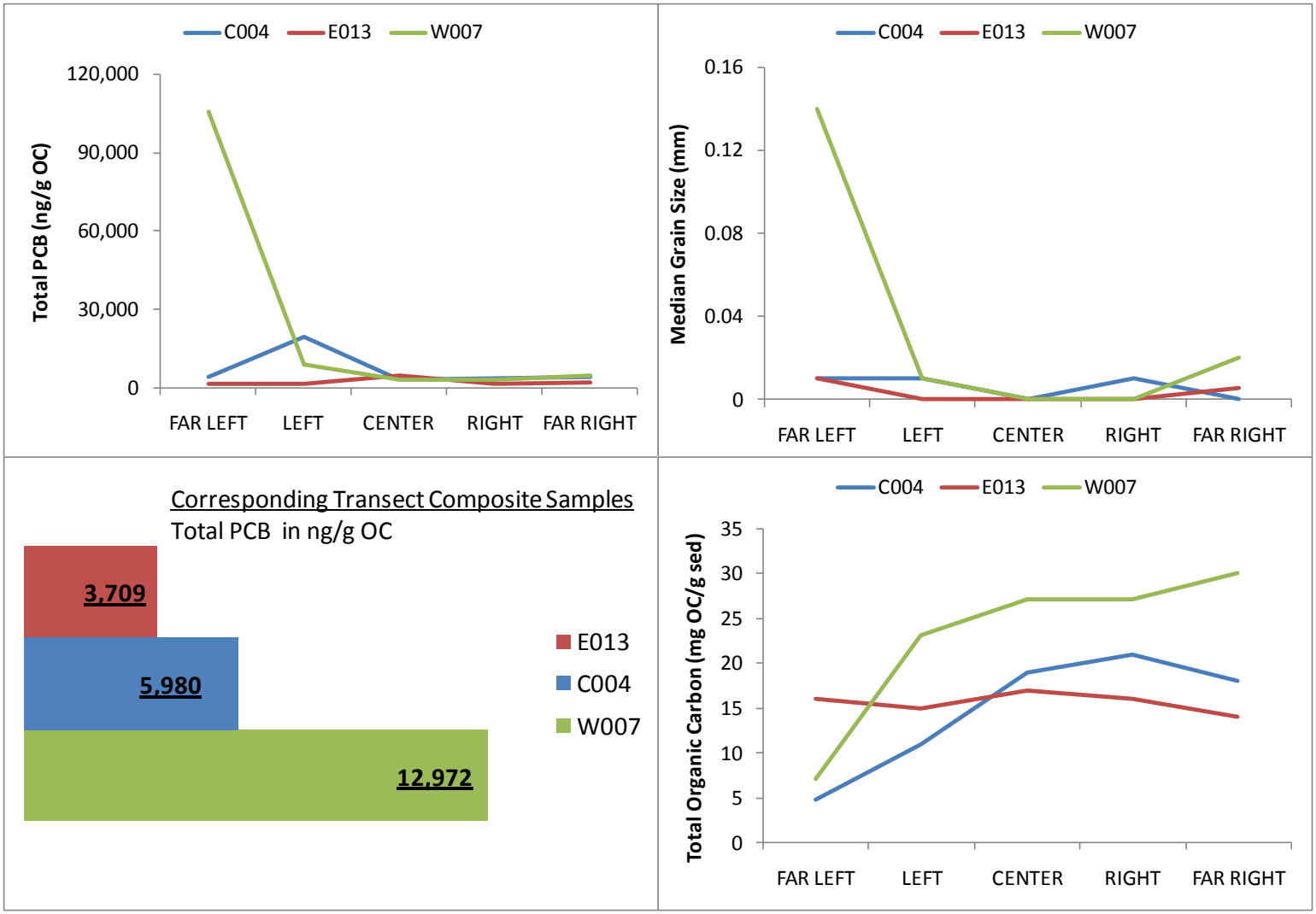


Figure 5.21 Sediment intensive transect sample results. Note that the transect composite samples are included for reference at each location. Positions along the transect are given in view of someone looking downstream in the flow also known as a "descending" view.

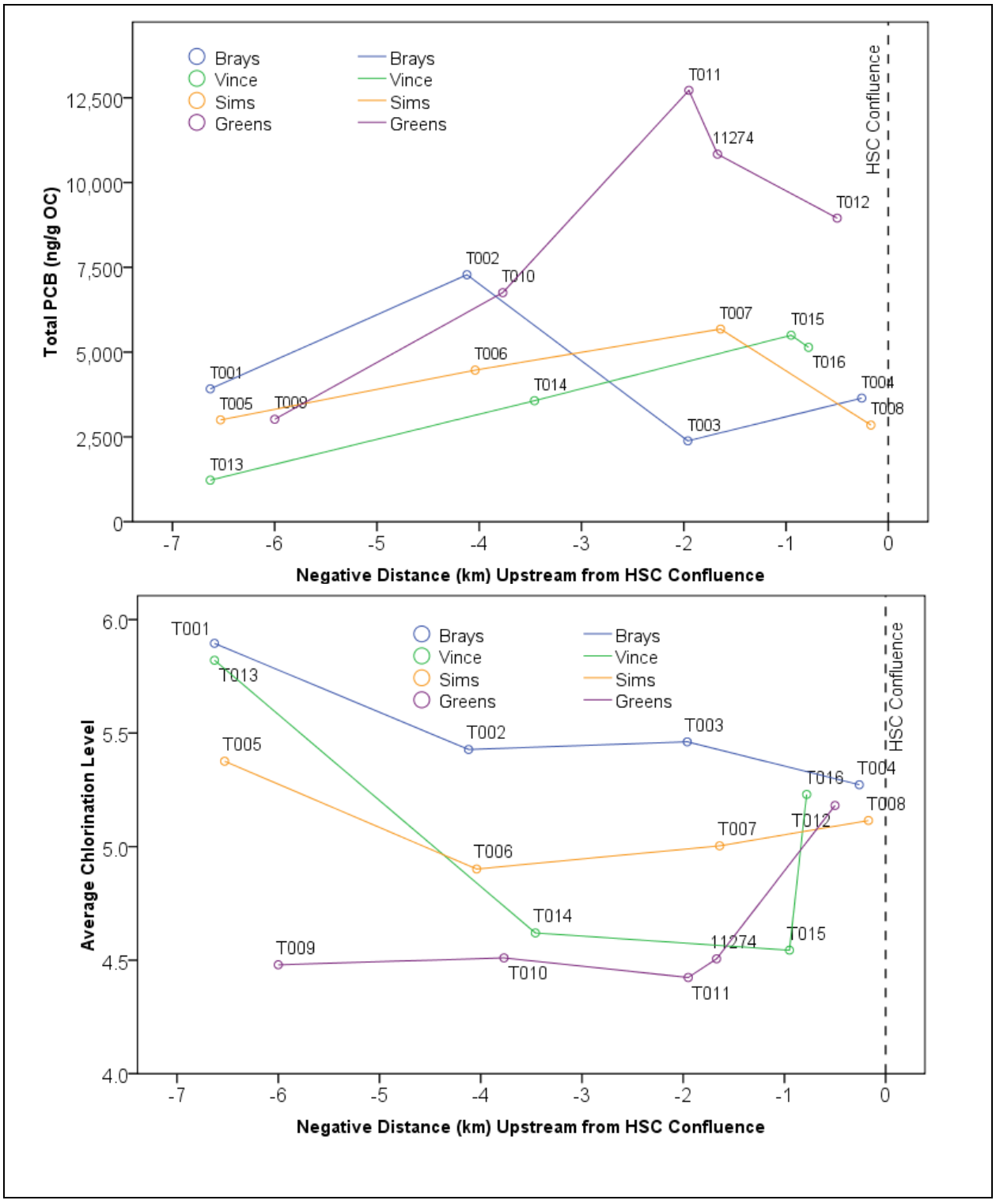


Figure 5.22 Total PCB and average chlorination sediment profiles along tributaries

6. REFERENCES

Baker, J.E., S.J. Eisenreich, and B.J. Eadie. 1991. Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior. *Environmental Science and Technology*. 25, 500-509.

Bamford, H.A., F.C. Ko, and J.E. Baker. 2002. Seasonal and annual air-water exchange of polychlorinated biphenyls across Baltimore Harbor and the northern Chesapeake Bay. *Environmental Science and Technology*. 36, 4245-4252.

Bergen, B.J., K.A. Rahn, and W.G. Nelson. 1998. Remediation at a marine Superfund site: surficial sediment PCB congener concentration, composition, and redistribution. *Environmental Science and Technology*. 32:3496-3501.

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

Bremle, G., and P. Larsson. 1998. PCB concentration in fish in a river system after remediation of contaminated sediment. *Environmental Science and Technology*. 32, 3491-3495.

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

Chen, W., A.T. Kan, G. Fu, and M.B. Tomson. 2000. Factors affecting the release of hydrophobic contaminants from natural sediments. *Environmental Toxicology and Chemistry*. 19, 2401-2408.

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

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

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

Dinkins, S., J. Heath, and E. Hobbins. 2002. Development of Ohio River Total Maximum Daily Load for PCBs. Proceedings - National TMDL Science and Policy 2002 Conference, Phoenix, Arizona, November 2002.

Douglas, R.W., and B. Rippey. 2000. The random redistribution of sediment by wind in a lake. *Limnology and Oceanography*. 45, 686-694.

Eisler, R, and A.A. Belisle. 1996. Planar PCB Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. National Biological Service Biological Report 31, U.S. Department of the Interior Contaminant Hazard Reviews, 75pp.

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

Erickson, M.D., Stanley, J.S., Turman, J.K., Going, J.E., Redford, D.P., Heggem, D.T. 1988. Determination of byproduct polychlorobiphenyls in commercial products

and wastes by high-resolution gas chromatography/electron impact mass spectrometry *Environ. Sci. Technol*. 22, 71-76.

Erickson, M.D. 2001. Introduction: PCB properties, uses, occurrence, and regulatory history. Pages xi-xxx in L.W. Robertson and L.G. Hansen (editors). PCBs: Recent Advances in Environmental Toxicology and Health Effects. University of Kentucky Press, Lexington, Kentucky.

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

Gevao, B., J. Hamilton-Taylor, and K.C. Jones. 2000. Towards a complete mass balance and model for PCBs and PAHs in a small rural lake, Cumbria, U.K. *Limnology and Oceanography*. 45, 881-894.

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

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

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

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

Jeremiason, J.D., K.C. Hornbuckle, and S.J. Eisenreich. 1994. PCBs in Lake Superior, 1978- 1992: decreases in water concentrations reflect loss by volatilization. *Environmental Science and Technology*. 28, 903-914.

Jones, K.C., and P. de Voogt. 1999. Persistent organic pollutants (POPs): state of the science. *Environmental Pollution*. 100, 209-221.

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

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

Larsson, P., L. Okla, S.-O. Ryding, and B. Westöö. 1990. Contaminated sediment as a source of PCBs in a river system. *Canadian Journal of Fisheries and Aquatic Sciences*. 47, 746-754.

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

Mahler, B.J., and P.C. Van Metre. 2003. A simplified approach for monitoring hydrophobic organic contaminants associated with suspended sediment: methodology and applications. *Archives of Environmental Contamination and Toxicology*. 44, 288-297.

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

Moore, J.W., and S. Ramamoorthy. 1984. Organic Chemicals in Natural Waters – Applied Monitoring and Impact Assessment. Springer-Verlag, New York, 289p.

Morrison, H.A., D.M. Whittle, and G.D. Haffner. 2002. A comparison of the transport and fate of polychlorinated biphenyl congeners in three Great Lakes food webs. *Environmental Toxicology and Chemistry*. 21, 683-692.

Munn, M.D., and S.J. Gruber. 1997. The relationship between land use and organochlorine compounds in streambed sediment and fish in the Central Columbia Plateau, Washington and Idaho, USA. *Environmental Toxicology and Chemistry*. 16, 1877- 1887.

Oliver, B.G., M.N. Charlton, and R.W. Durham. 1989. Distribution, redistribution, and geochronology of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in Lake Ontario sediments. *Environmental Science and Technology*. 23, 200-208.

O'Meara, J., J. Murray, and J. Ridgway. 2000. $11.8 million project removes PCBs, restores life to Newburgh Lake. *Water Environment Federation Watershed and Wet Weather Technical Bulletin*. 5(3),12-15.

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

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

Renner, R. 1998. Natural remediation of DDT, PCBs debated. *Environmental Science and Technology*. 32, 360A-363A.

Rifai, H.S., Palachek, R., University of Houston. 2008. 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. Houston, p. 78

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

Smith, J.A., P.J. Witkowski, and T.V. Fusillo. 1988. Manmade Organic Compounds in the Surface Waters of the United States - A Review of Current Understanding. U.S. Geological Survey Circular 1007.

Stapleton, H.M., C. Masterson, J. Skubinna, P. Ostrom, N.E. Ostrom, and J.E. Baker. 2001. Accumulation of atmospheric and sedimentary PCBs and toxaphene in a Lake Michigan food web. *Environmental Science and Technology*. 35, 3287-3293.

Steuer, J.S., S.A. Fitzgerald, and D.W. Hall. 1999a. Distribution and Transport of Polychlorinated Biphenyls and Associated Particulates in the Milwaukee River System, Wisconsin, 1993-95. U.S. Geological Survey Water-Resources Investigations Report 99-4100.

Steuer, J.S., D.W. Hall, and S.A. Fitzgerald. 1999b. Distribution and Transport of Polychlorinated Biphenyls and Associated Particulates in the Hayton Millpond, South Branch Manitowoc River, 1993-95. U.S. Geological Survey Water-Resources Investigations Report 99-4101.

Steuer, J.J. 2000. A Mass-Balance Approach for Assessing PCB Movement During Remediation of a PCB-Contaminated Deposit on the Fox River, Wisconsin. U.S. Geological Survey Water-Resources Investigations Report 00-4245.

Swackhamer, D.L., and D.E. Armstrong. 1986. Estimation of the atmospheric and nonatmospheric contributions and losses of polychlorinated biphenyls for Lake Michigan on the basis of sediment records of remote lakes. *Environmental Science and Technology.* 20, 879-883.

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

Tanabe, S. 1988. PCB problems in the future: foresight from current knowledge. Environmental Pollution 50, 5-28.

Thornton, K.W. 1990. Sedimentary processes. Pages 43-69 in K.W. Thornton, B.L. Kimmel, and F.E. Payne (editors). Reservoir Limnology: Ecological Perspectives. John Wiley and Sons, Inc., New York

Ueno, D., Darling, C., Alaee, M., Campbell, L., Pacepavicius, G., Teixeira, C., Muir, D. 2007. Detection of Hydroxylated Polychlorinated Biphenyls (OH-PCBs) in the Abiotic Environment: Surface Water and Precipitation from Ontario, Canada. *Environ. Sci. Technol*. 41, 1841-1848.

USEPA, 1998. Great Lakes Binational Toxics Strategy, Implementing The Binational Toxics Strategy, PCBs Workgroup.

USEPA (U.S. Environmental Protection Agency). 1999. "Polychlorinated Biphenyls (PCBs) Update: Impact on Fish Advisories." Fact Sheet, September 1999. EPA-823-F-99-019.

USEPA (U.S. Environmental Protection Agency). 2002. Record of Decision, Hudson River PCBs Site, New York. February 1, 2002. Obtained on 11 February 2002 at <http://www.epa.gov/hudson/>.

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

Van Metre, P.C., J.T. Wilson, G.R. Harwell, M.O. Gary, F.T. Heitmuller, and B.J. Mahler. 2003. Occurrence, Trends, and Sources in Particle-Associated Contaminants in Selected Streams and Lakes in Fort Worth, Texas. USGS Water-Resources Investigations Report 03-4169.

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

Wethington, D.M., III, and K.C. Hornbuckle. 2005. Milwaukee, WI, as a source of atmospheric PCBs to Lake Michigan. *Environmental Science and Technology*. 39, 57- 63.

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

APPENDICES

APPENDIX A

QUALITY ASSURANCE PROJECT PLAN