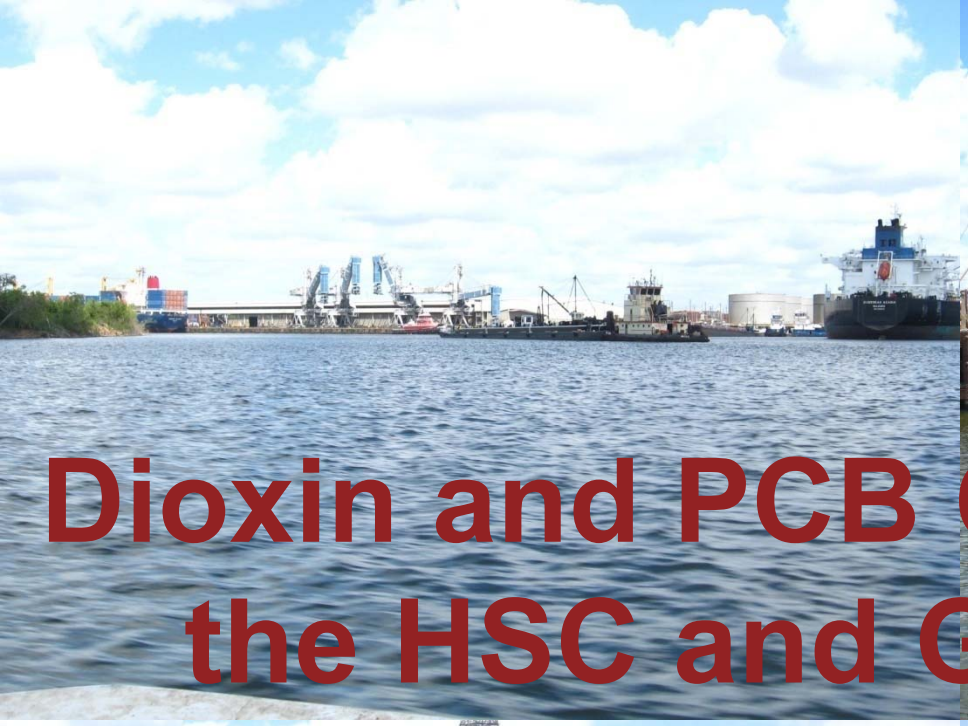
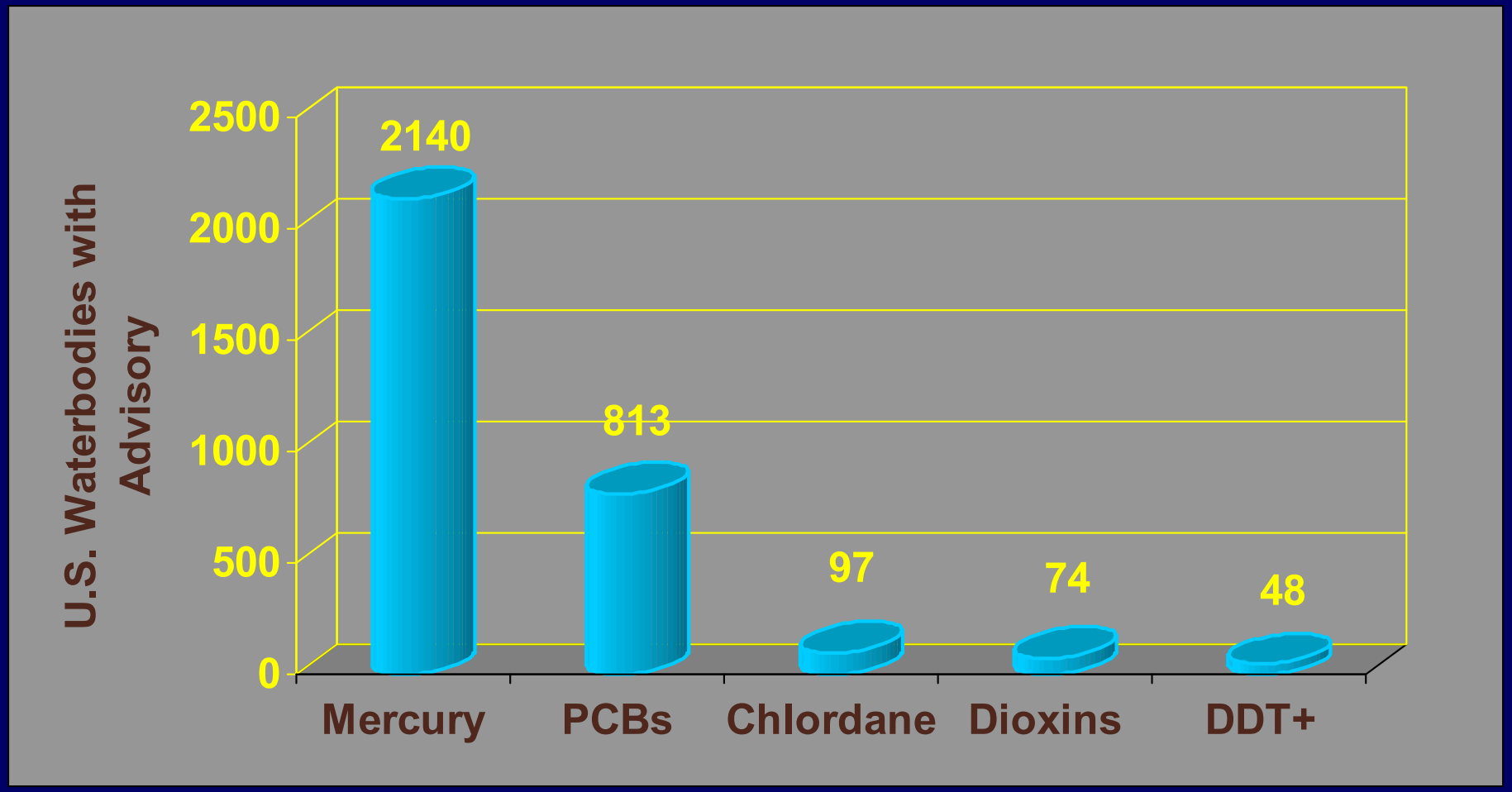



Dioxin and PCB Contamination in the HSC and Galveston Bay: Past, Present, and Future

Hanadi Rifai, PhD, PE
Civil and Environmental Engineering
University of Houston

November 18, 2010

Pollutants Causing Fish Consumption Advisories



What are PCBs and dioxins?

- Dioxins are chlorinated aromatic compounds unintentionally produced
- PCBs are also chlorinated hydrocarbons but manufactured between 1926 and 1977
- Both persistent and bio-accumulative
- Can affect human health at low levels
- TDH established a dioxin fish and crab consumption advisory in HSC and Upper Galveston Bay in 1990
- PCB advisory in 1999 and 2001 and more recently for speckled trout in 2005

Likely sources of dioxin

- Medical waste incineration
- Bleaching paper with chlorine (historic)
- Polyvinylchloride (PVC) production
- Chlorinated solvent/pesticide/herbicide production
- Refining metals
- Refining oil
- Incinerators
- Municipal wastewater treatment plants that chlorinate effluent

Dioxin Health effects

Exposure to dioxin levels above MCL can have the following effects:

Acute exposure	***Chronic exposure***
Liver damage	Variety of reproductive effects, from reduced fertility to birth defects
Weight loss	Potential carcinogen
Atrophy of thymus gland	
Immune suppression	

Uses and Sources of PCBs

- Coolants & lubricants in electrical transformers and capacitors
- Hydraulic fluids
- Paint additives
- Fire retardants
- Pesticide & Petroleum additives
- Carbonless copy paper
- Plasticizers & Adhesives

Complexities with Dioxins

- TEQ is calculated as:

$$TEQ = \sum C_i \cdot TEF_i$$

- where C_i and TEF_i are concentration and toxicity equivalent factor for congener *i*

- Texas TEFs:

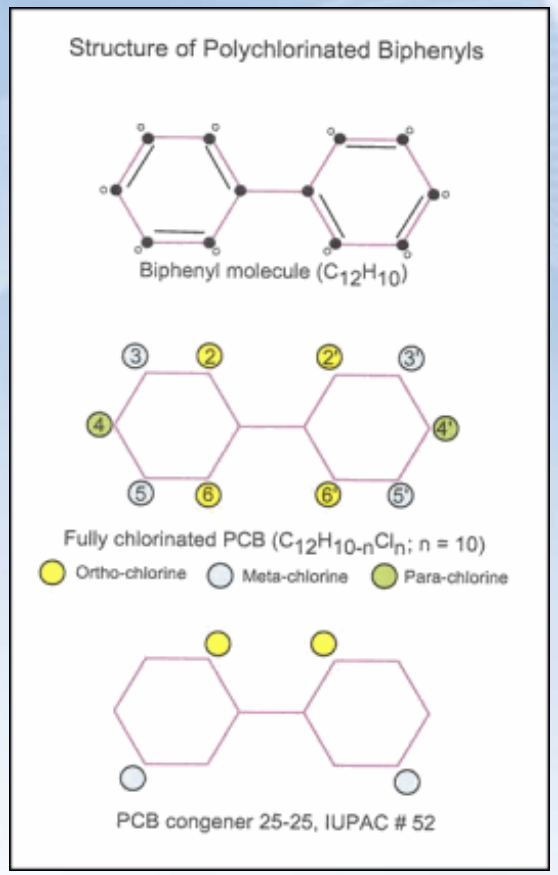
Congener	Texas TEF
2378-TCDD	1
12378-PeCDD	0.5
123478-HxCDD	0.1
123678-HxCDD	0.1
123789-HxCDD	0.1
2378-TCDF	0.1
12378-PeCDF	0.05
23478-PeCDF	0.5
123478-HxCDF	0.1
123678-HxCDF	0.1
123789-HxCDF	0.1

Congeners in orange contribute more than 96% of the TEQ in tissues from the HSC. Those six congeners were modeled in WASP.

Complexities with PCBs

Time Line

- 1881: PCBs first synthesized
- 1929: First commercial production of Aroclors
- 1937: Health effects noted by Surgeon General
- 1966: PCBs reported in Swedish environmental media
- 1968: Rice oil contamination in Yushio, Japan
- 1976: First PCB regulation Toxic Substances Control Act
- 1977: Manufacture, processing, or use of PCBs in other than totally enclosed applications banned in U.S.
- 1989: EPA's Safe Drinking Water Act, PCB Maximum Contaminant Level (MCL) set at 0.5 ppb
- 2001: Persistent Organic Pollutants (POPs) treaty signed by 100 nations



Congener/Homolog

- Individual PCBs or congeners vary by the number and position of chlorine molecules
- Individual congeners or isomers can have 1 to 10 chlorines resulting in 209 different, but related, structures.
- Three different chlorine attachment sites on the biphenyl molecule occur – ortho-, meta-, and para-sites
- Coplanar PCBs are the most dioxin-like and have the greatest toxicity
- PCB homolog's are groupings of congeners with the same number of chlorines
  - Range from monochlorobiphenyls (1) to decachlorobiphenyl s(10)
- Homolog groupings share similar physical properties by their chlorination level

Name of Homolog Group	Formula	Approximate Mol. Wt.	Chlorine Percentage	No. of Congeners
Biphenyl	$C_{12}H_{10}$	154	0	1
Monochlorobiphenyl	$C_{12}H_9Cl$	189	19	3
Dichlorobiphenyl	$C_{12}H_8Cl_2$	223	32	12
Trichlorobiphenyl	$C_{12}H_7Cl_3$	258	41	24
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	292	49	42
Pentachlorobiphenyl	$C_{12}H_5Cl_5$	326	54	46
Hexachlorobiphenyl	$C_{12}H_4Cl_6$	361	59	42
Heptachlorobiphenyl	$C_{12}H_3Cl_7$	395	63	24
Octachlorobiphenyl	$C_{12}H_2Cl_8$	430	66	12
Nonachlorobiphenyl	$C_{12}H_1Cl_9$	464	69	3
Decachloroboiphenyl	$C_{12}Cl_{10}$	499	71	1

Table of PCB Homolog Groups and fundamental properties.

More complexities with PCBs

Commercial PCB mixtures

- Aroclors
  - Aroclor is the trade name for technical mixture of PCBs manufactured by Monsanto
  - Technical mixtures made are called Aroclors and vary by weight % chlorine
  - Common Aroclors include 1242,1248, 1254, and 1260
- Asbestol, Askarel. Bakola131, Hydol, Inerteen, Noflamol, Pyranol/Pyrenol , Saf-T-Kuhl,Therminol

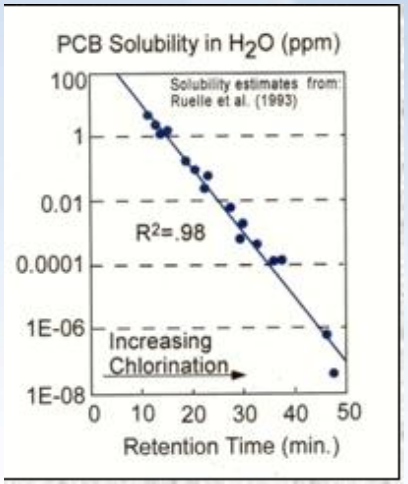
Properties

- Anthropogenic
- Clear yellow oils or sticky white solids
- Chlorinated (1-10 chlorines)
- Hydrophobic
- Limited solubility
- Limited volatility (semi-volatile compound)
- Environmentally persistent
- Bioaccumulative
- Lipophilic (fat, oil soluble)
- Carcinogenic

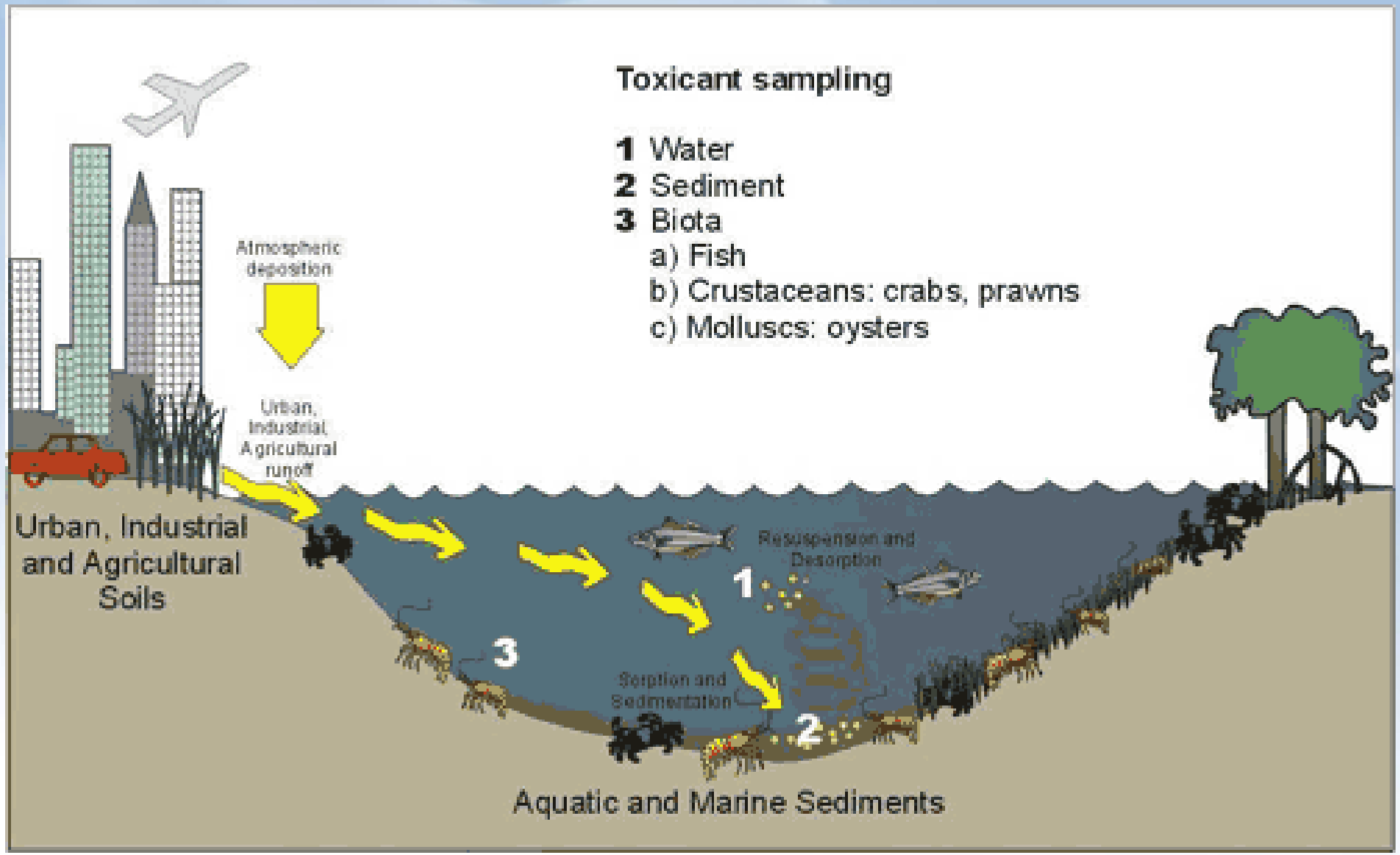
Non- Aroclor PCBs are produced as inadvertent byproducts of other chemical manufacturing processes and when burned in uncontrolled fires can result in the production of polychlorinated dibenzofurans (PCDFs)

Uses

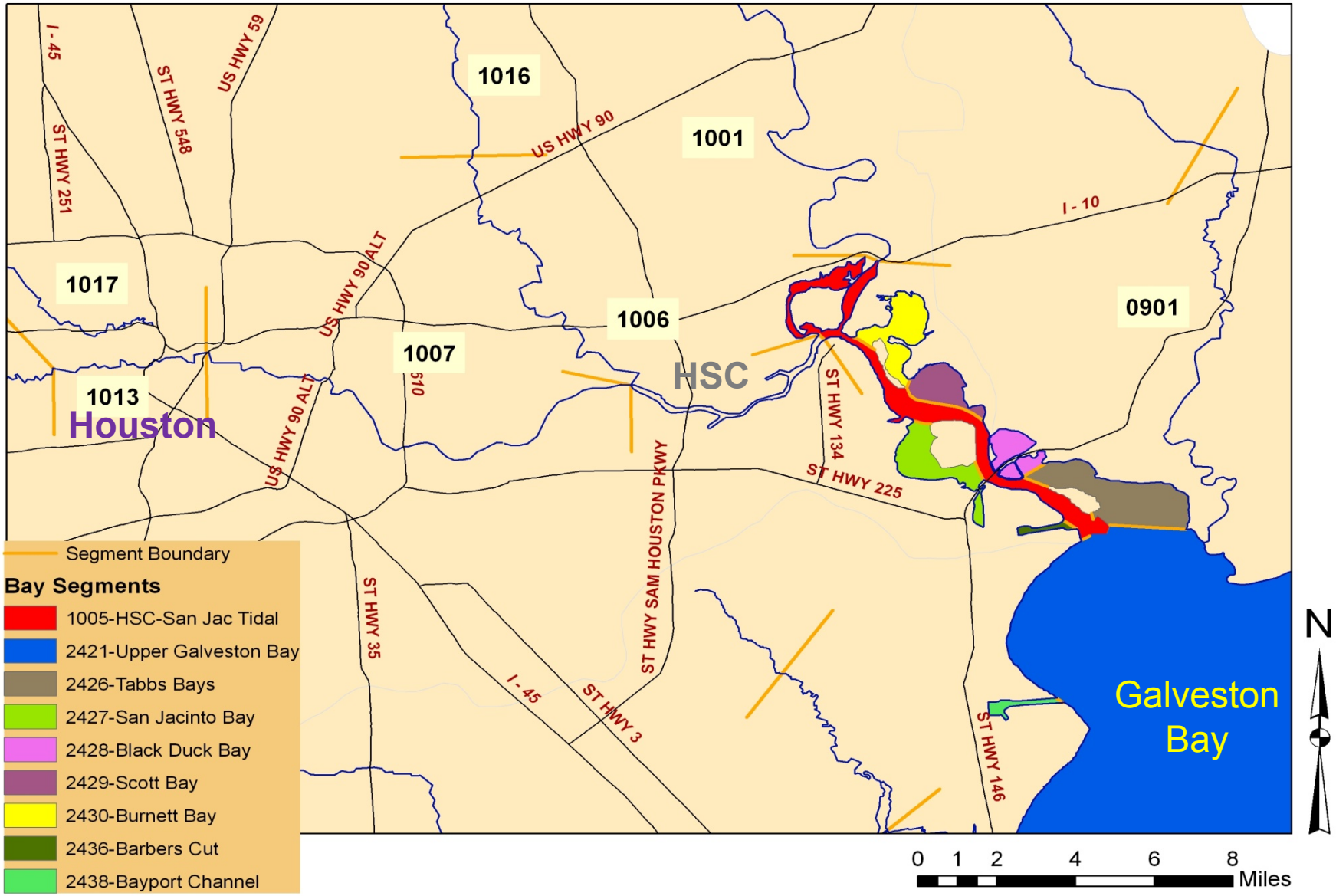
- Coolants and insulating fluids for transformers and capacitors
- Plasticizers in paints and cements
- Stabilizing additives in flexible PVC coatings
- Carbonless copy ("NCR") paper
- Hydraulic lubricants and cutting oils
- Sealants (for caulking in schools and commercial buildings),
- Miscellaneous -- Adhesives, wood floor finishes, pesticide extenders, reactive flame retardants, paints, de-dusting agents, water-proofing compounds, casting agents, vacuum pump fluids, fixatives in microscopy, surgical implants.



Conceptual Source Schematic

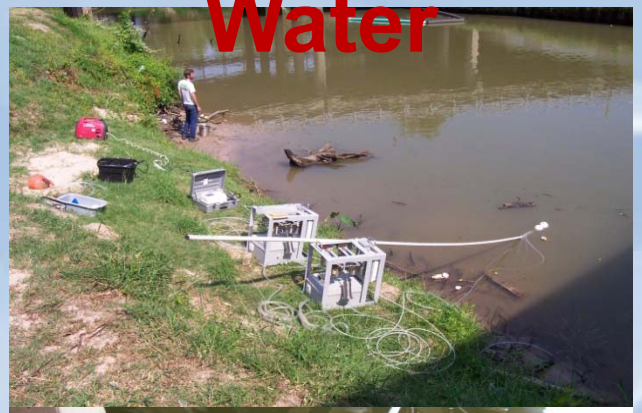


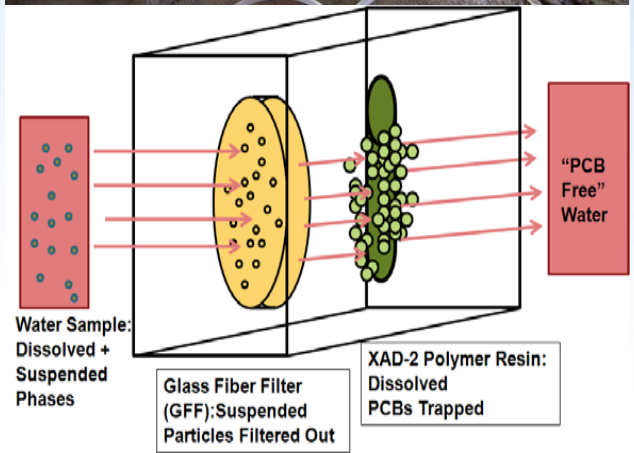
Houston Ship Channel Segments



Media Sampling Methods

Water





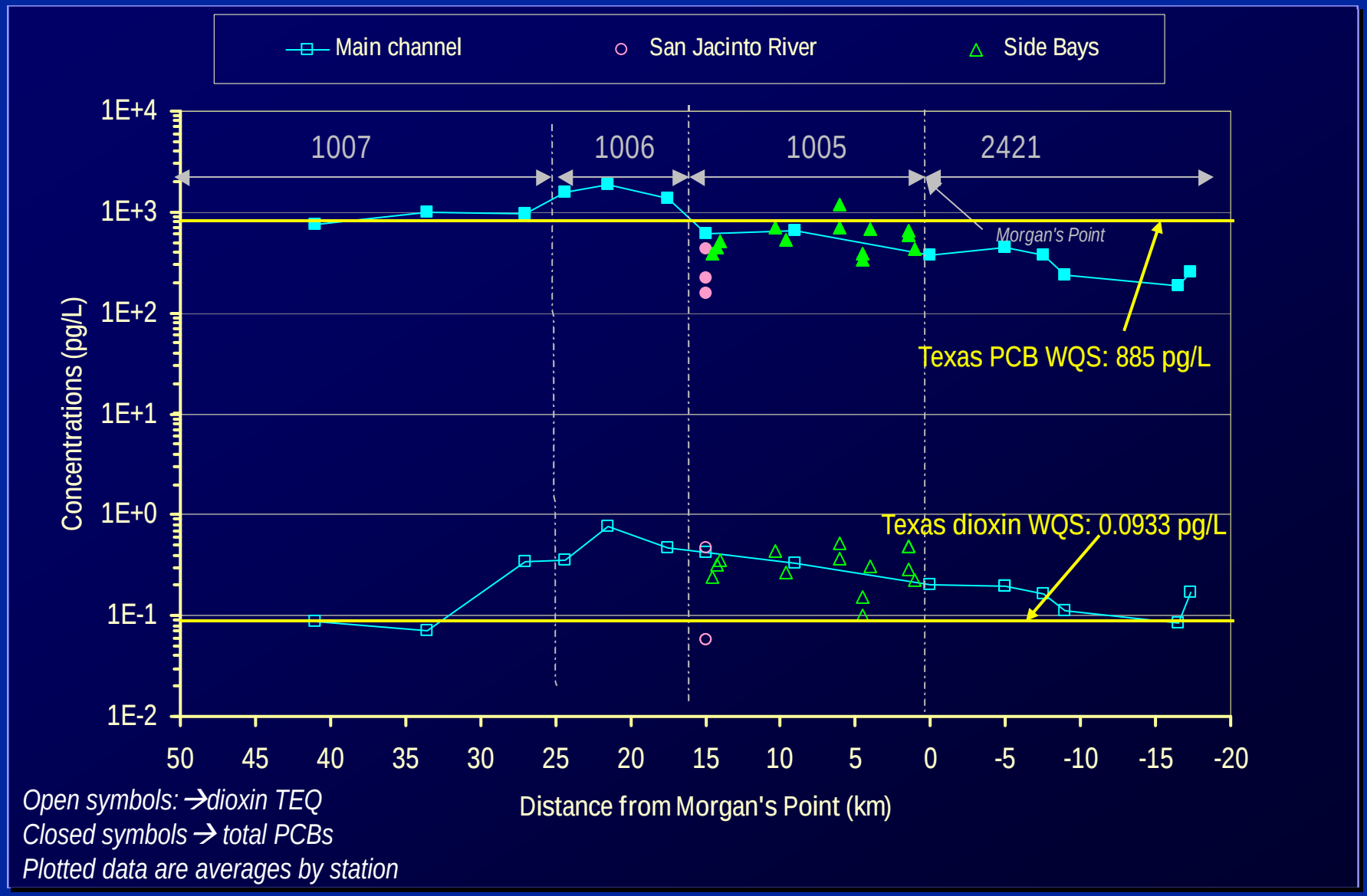
Sediment

Tissue

Past

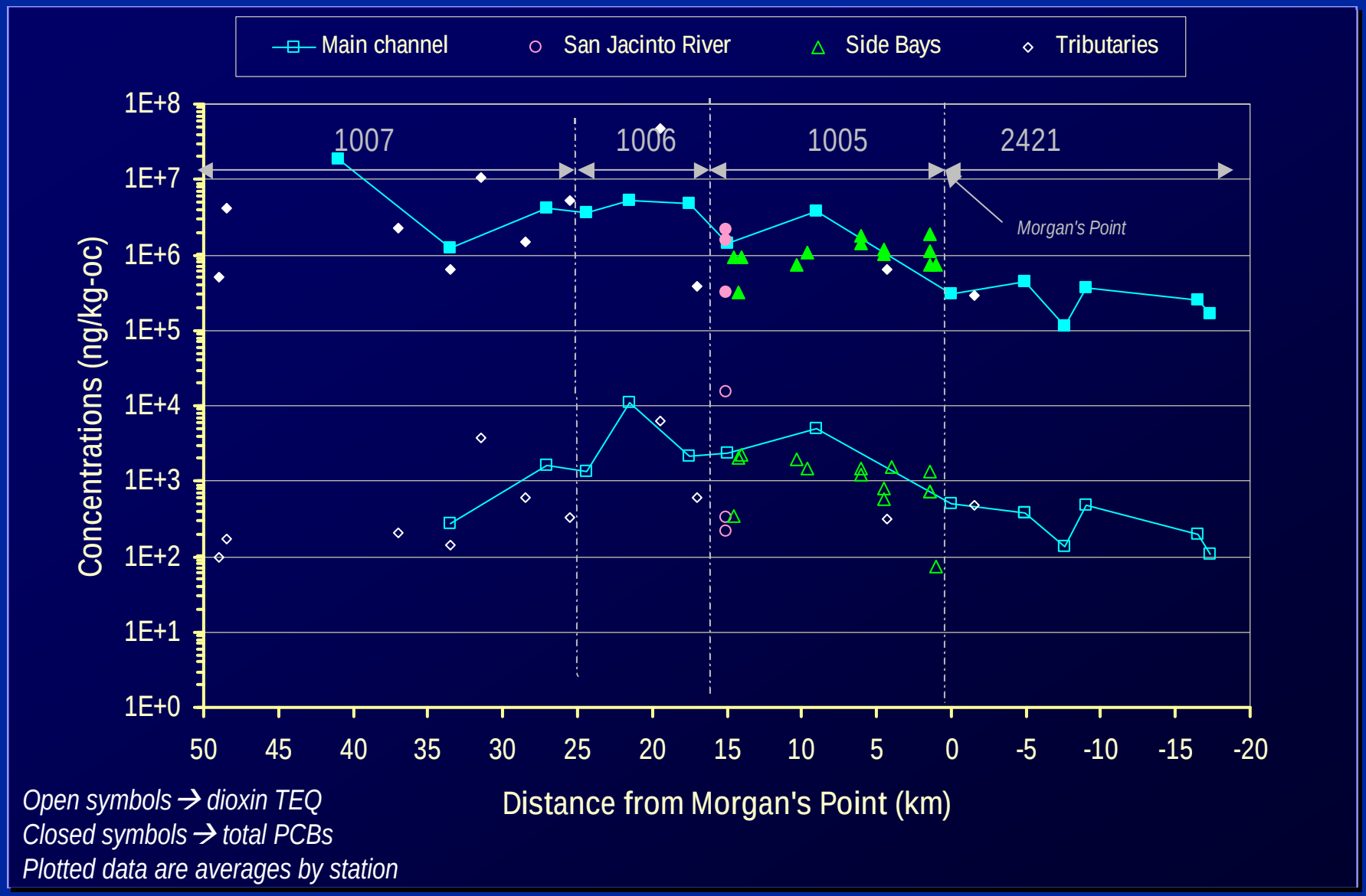
Dioxin and PCB Results
2002-2005

PCB and dioxin in water profiles

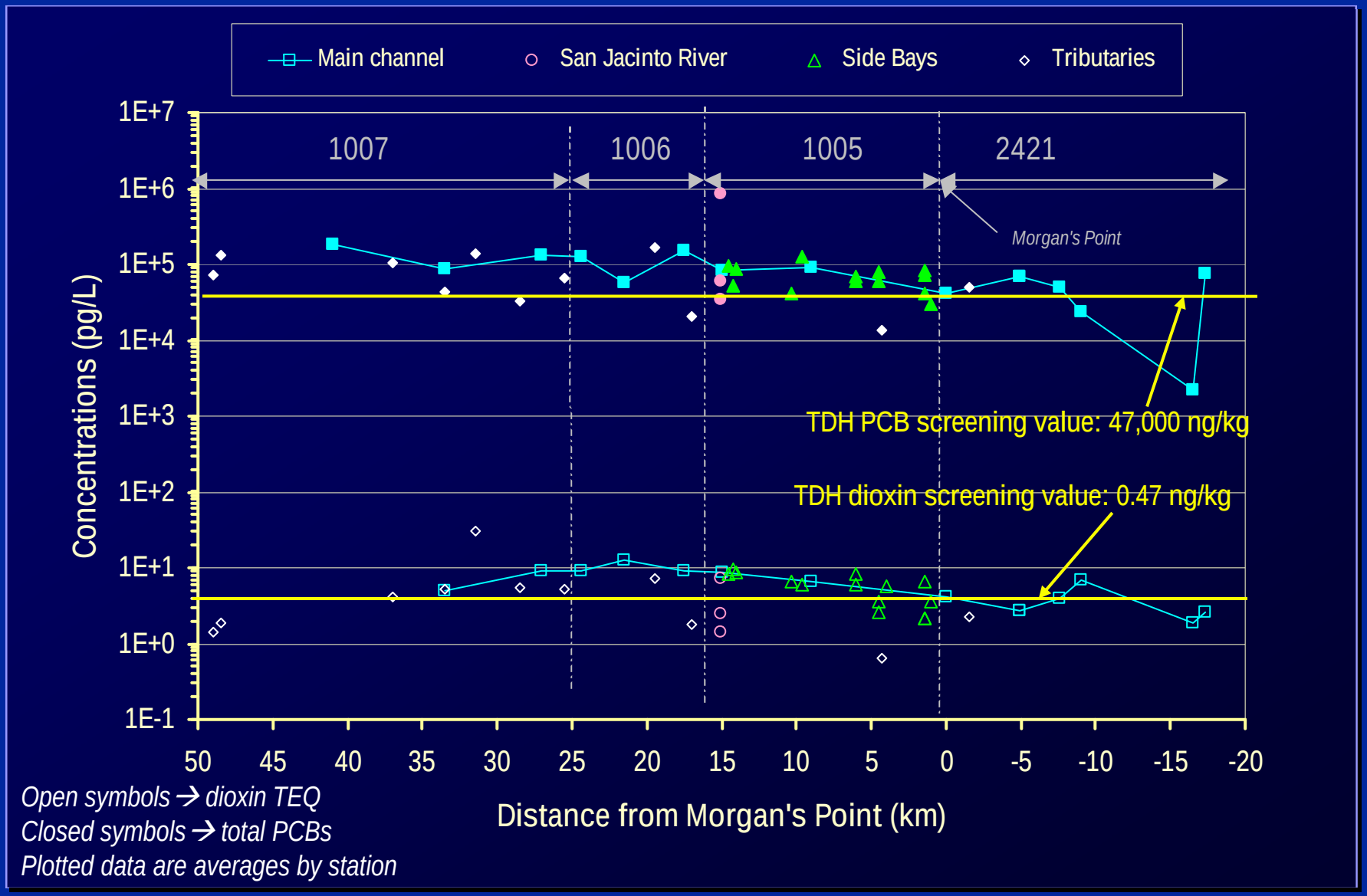


Open symbols: →dioxin TEQ
Closed symbols → total PCBs
Plotted data are averages by station

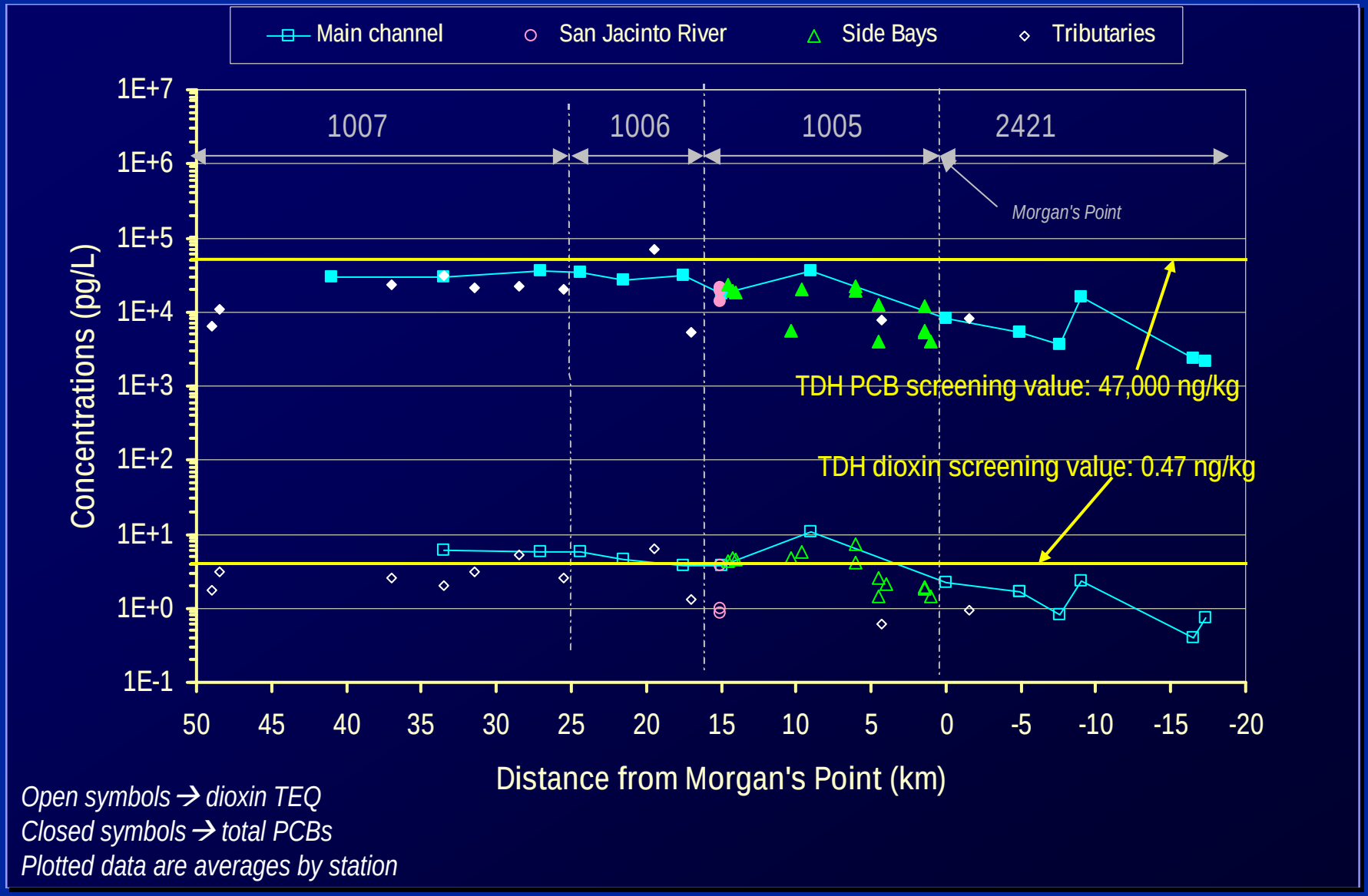
PCB and dioxin in sediment-oc profiles



PCB and dioxin in catfish profiles

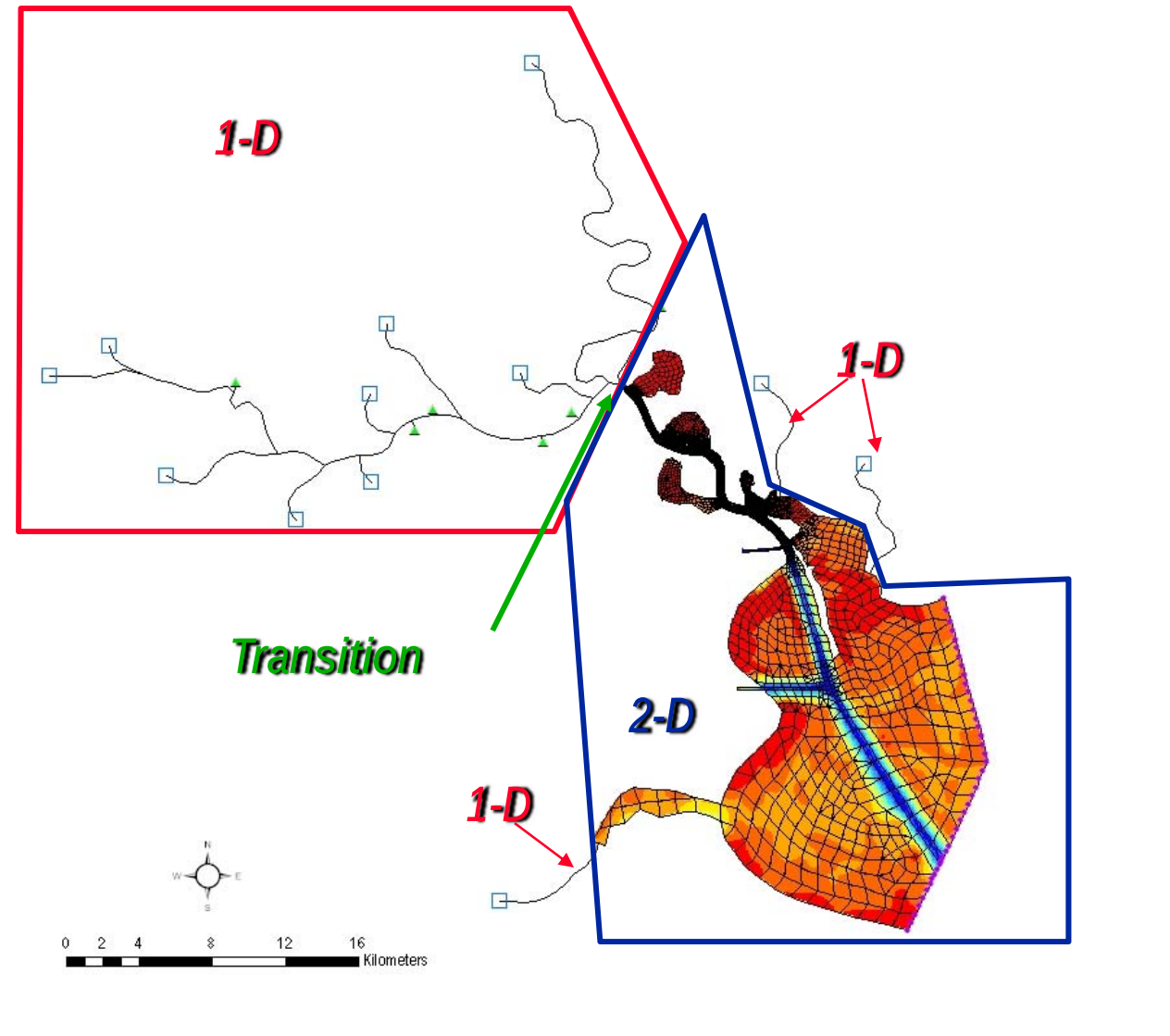


PCB and dioxin in crab profiles

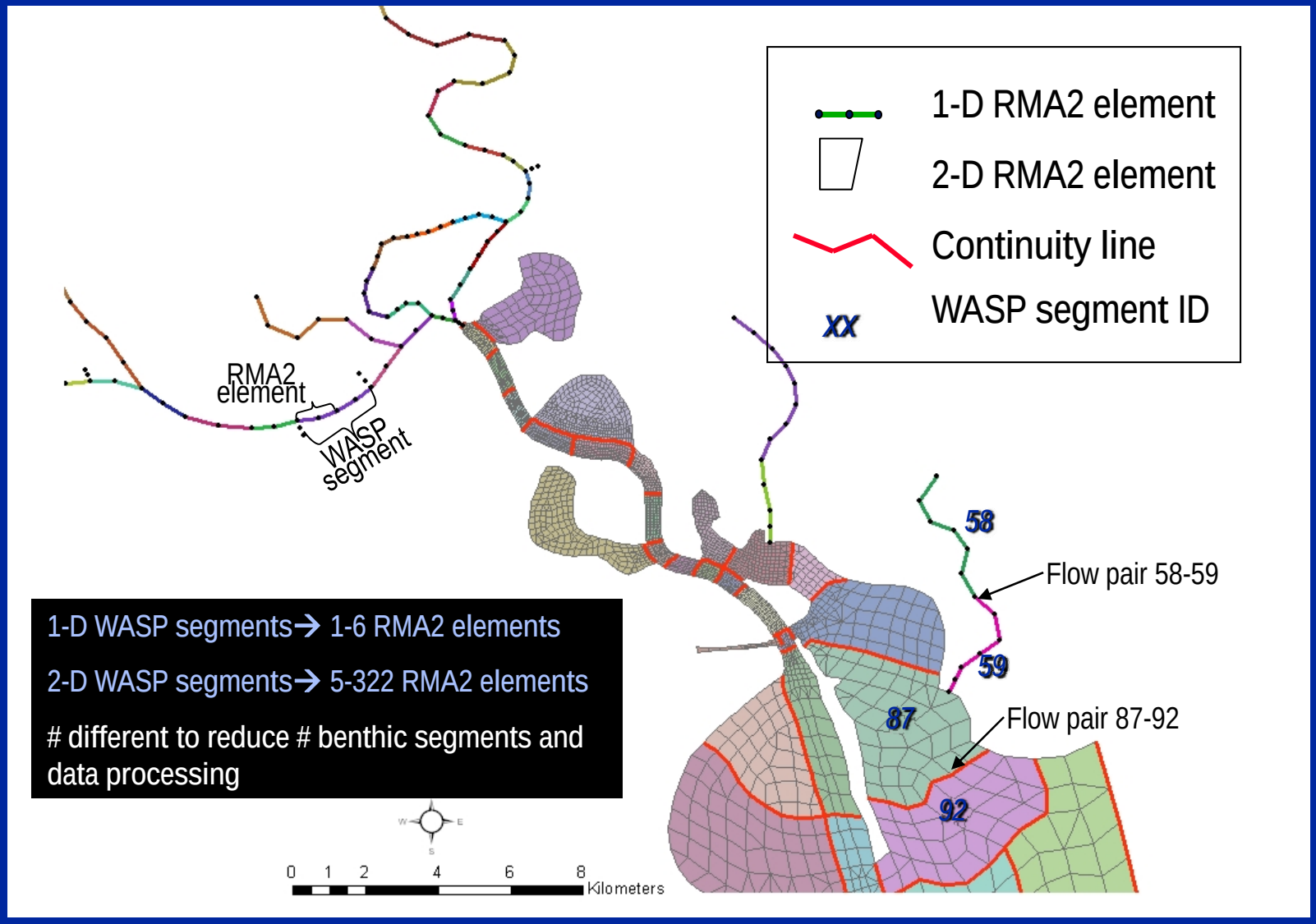


Open symbols → dioxin TEQ
Closed symbols → total PCBs
Plotted data are averages by station

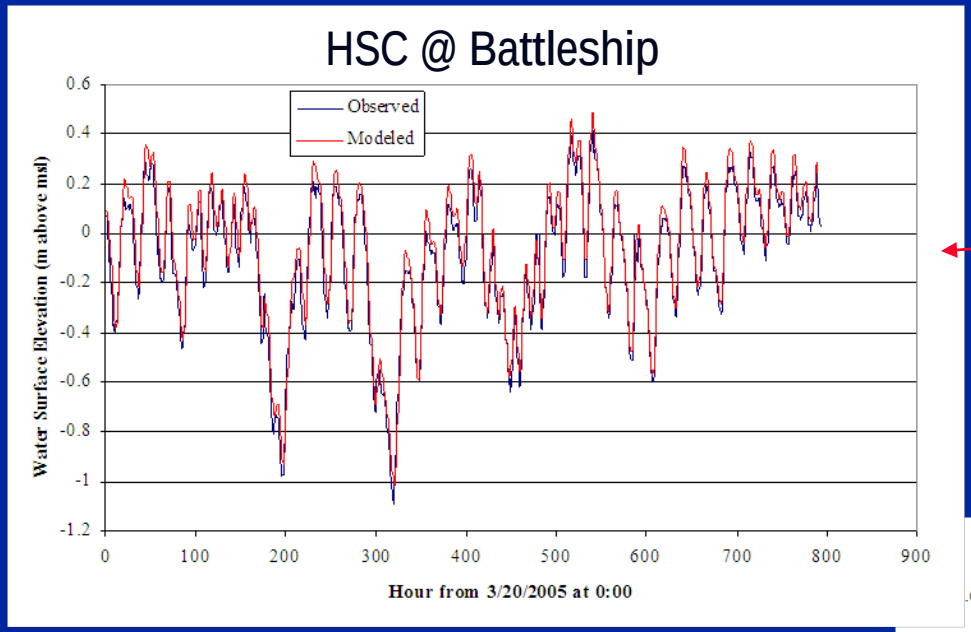
RMA2 model segmentation

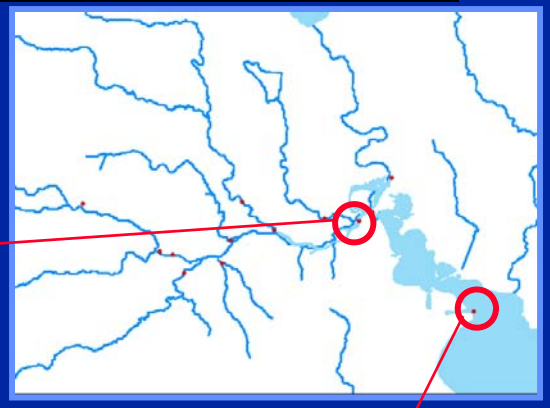


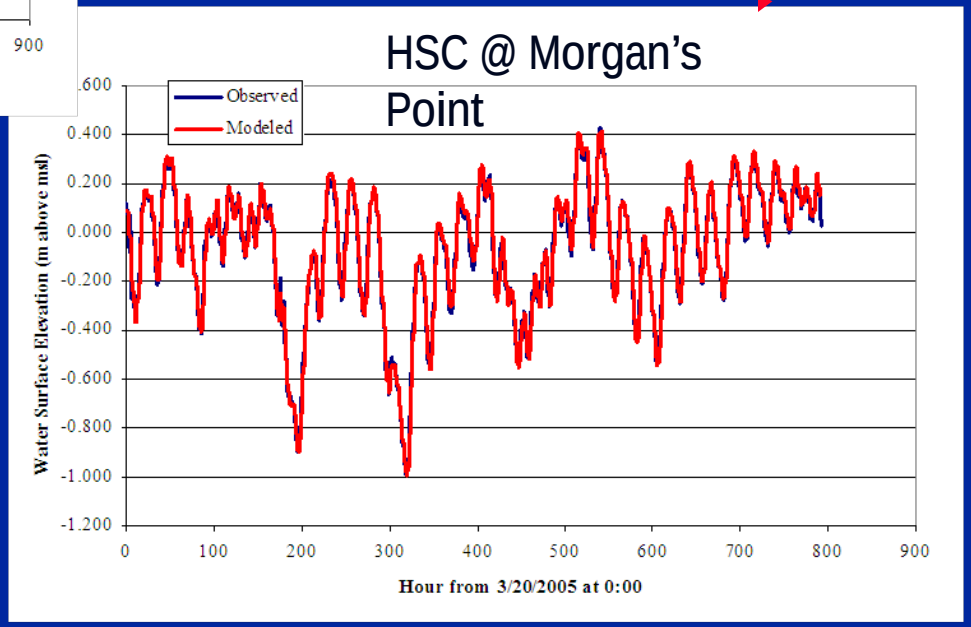
RMA2-WASP segmentation



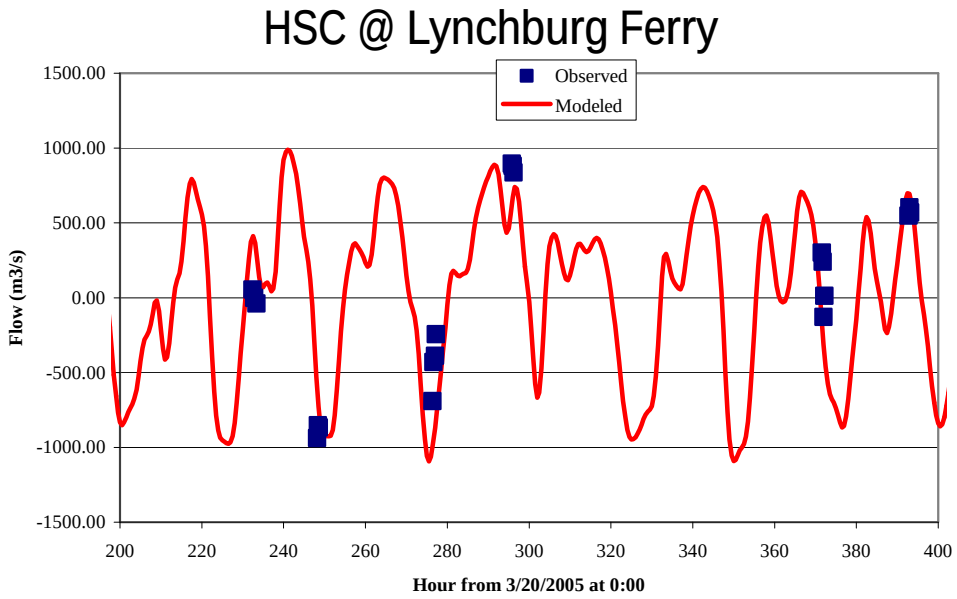
RMA2 model – WSE calibration

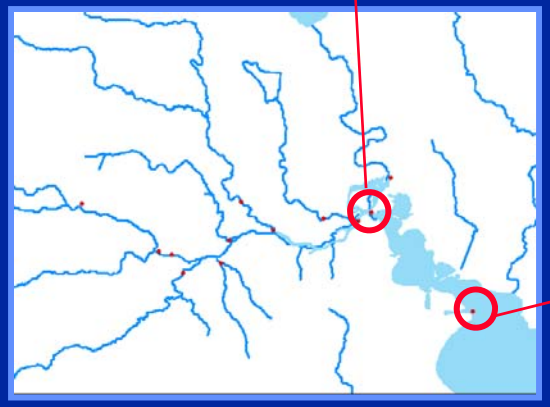


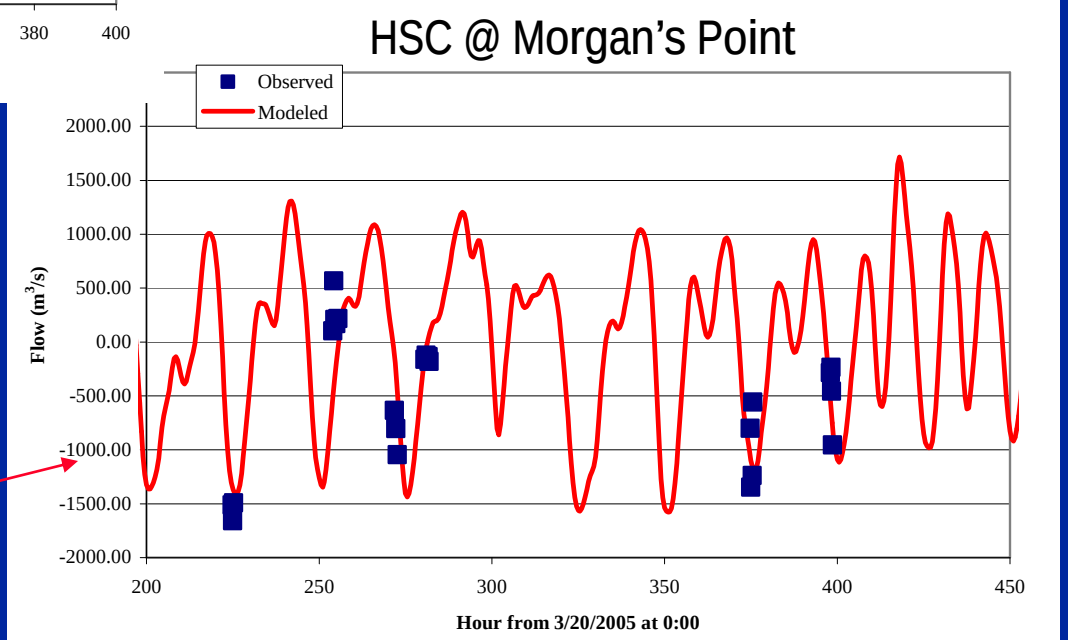




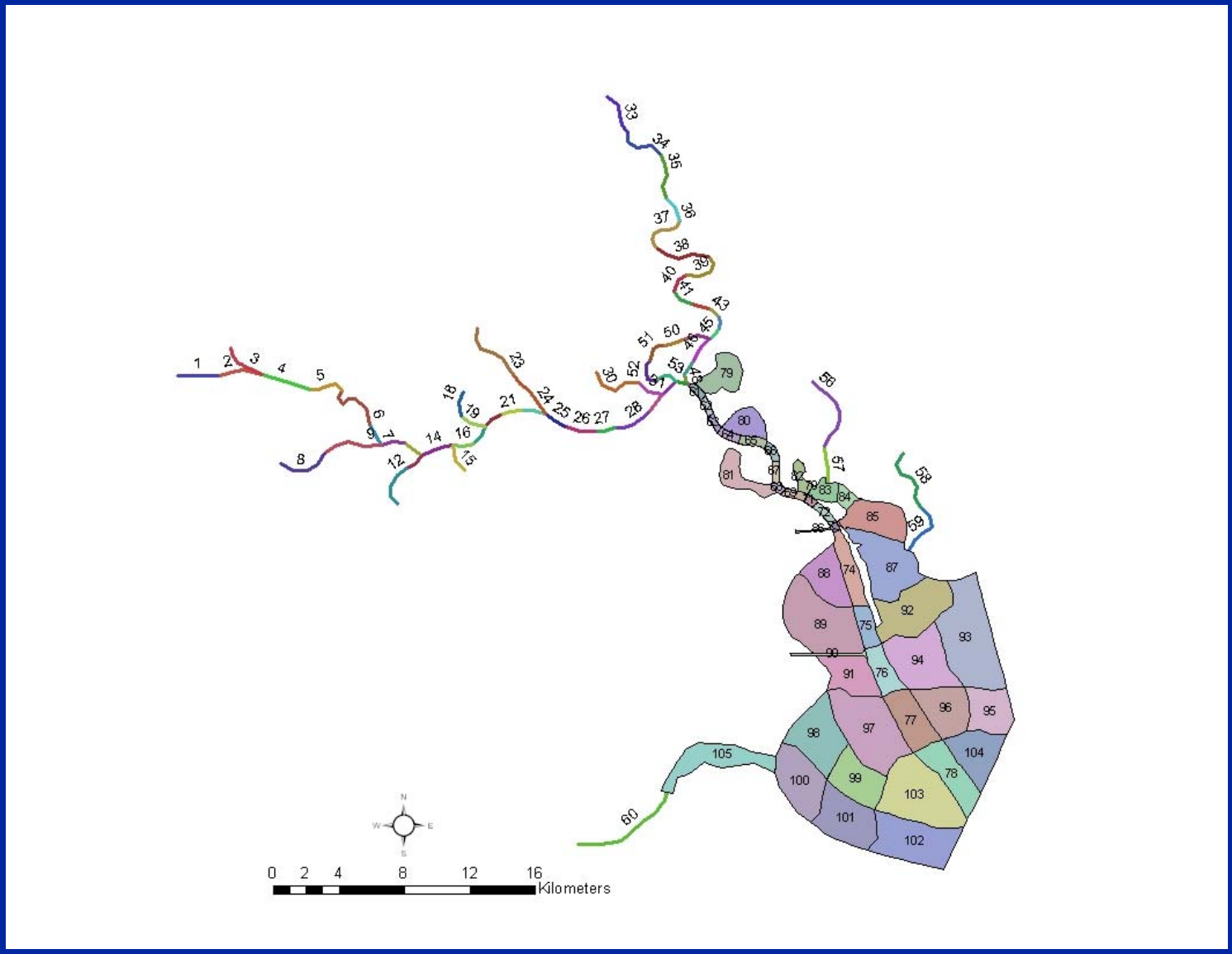
RMA2 model – Flow calibration



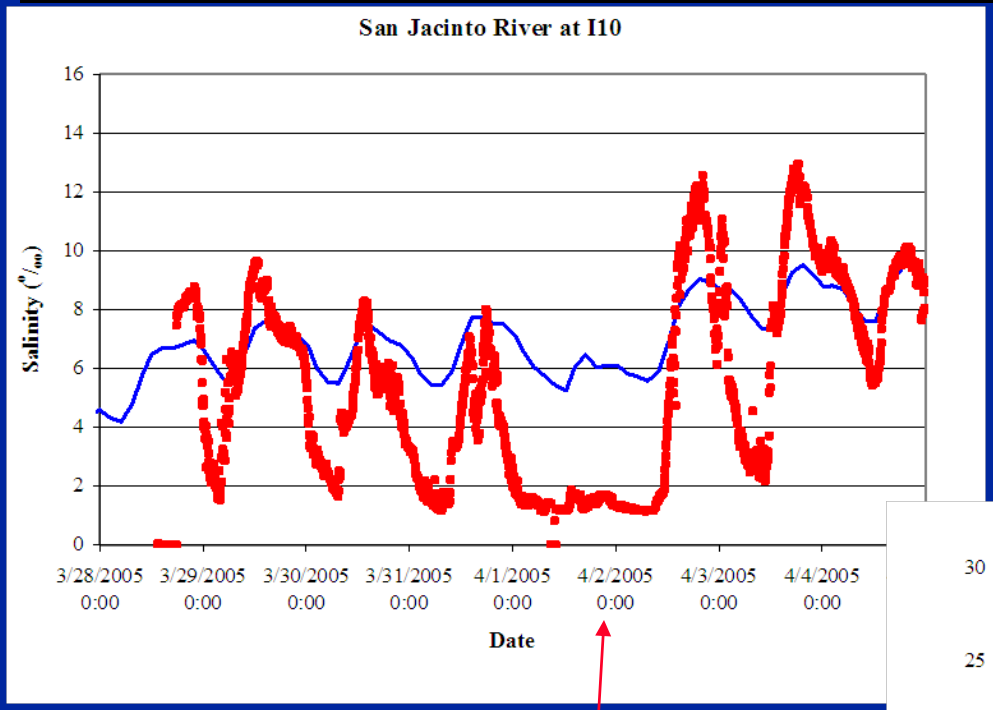




WASP model segmentation

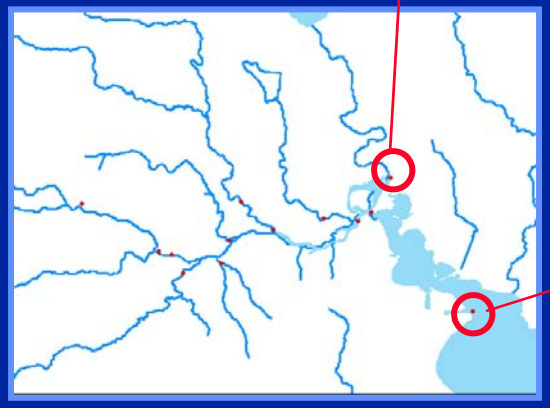


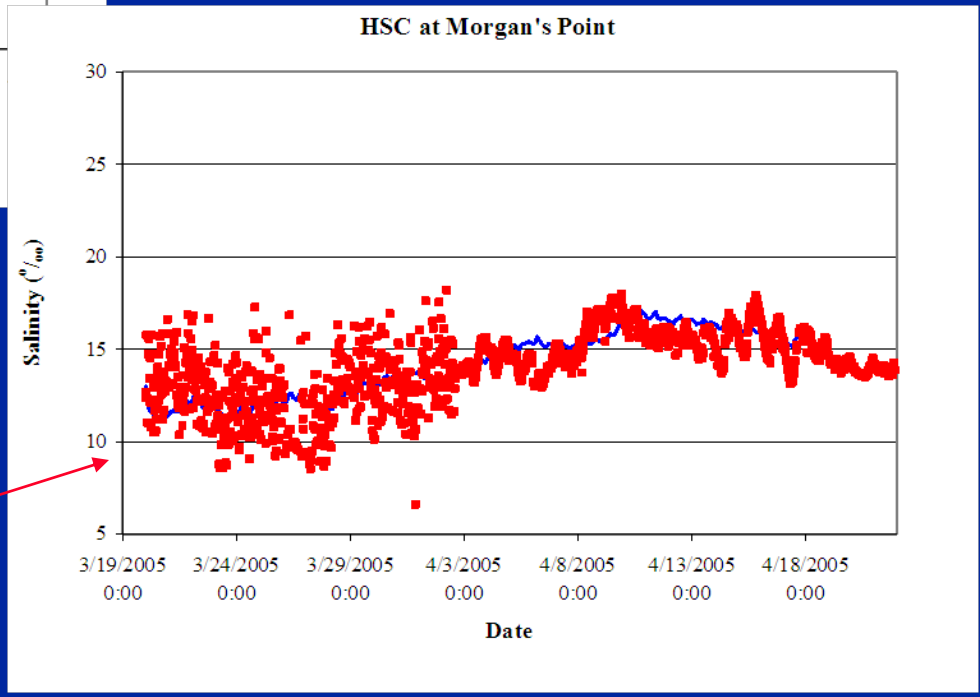
WASP model – salinity calibration (cont'd)



Red → Modeled

Blue → Observed

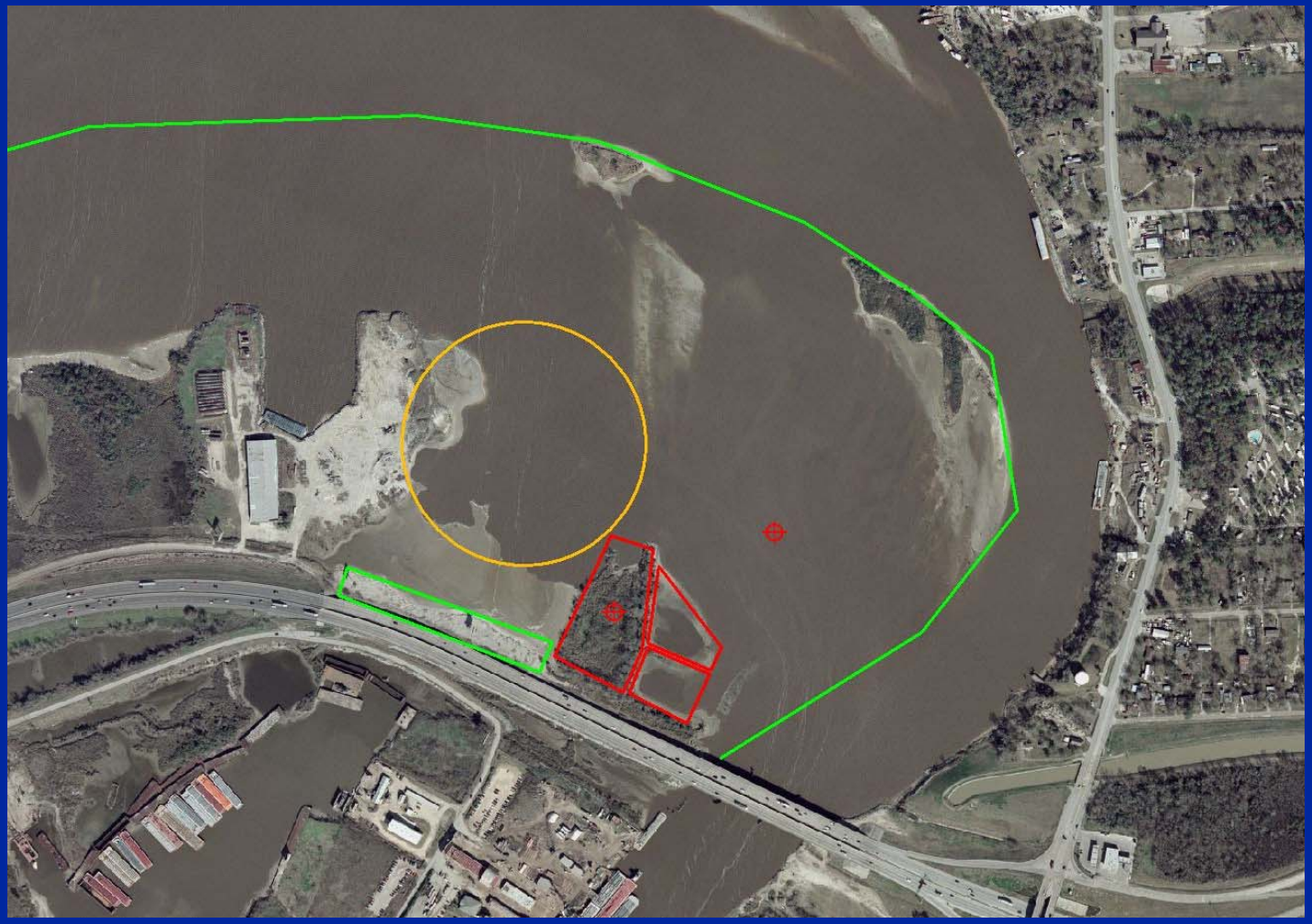




Sources of Dioxins in GB Watershed

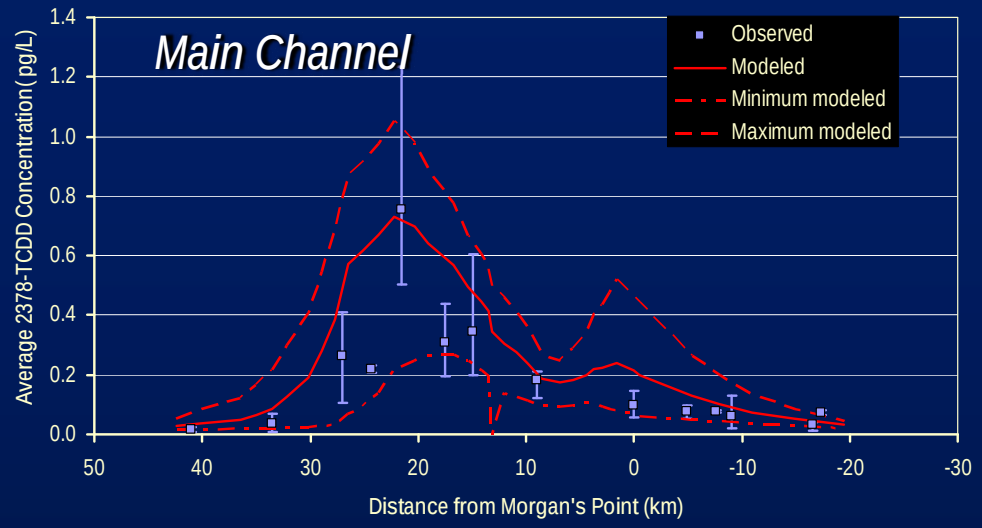
- Dischargers (municipal and industrial)
- Runoff
- Air Deposition
- Sediment
- Other

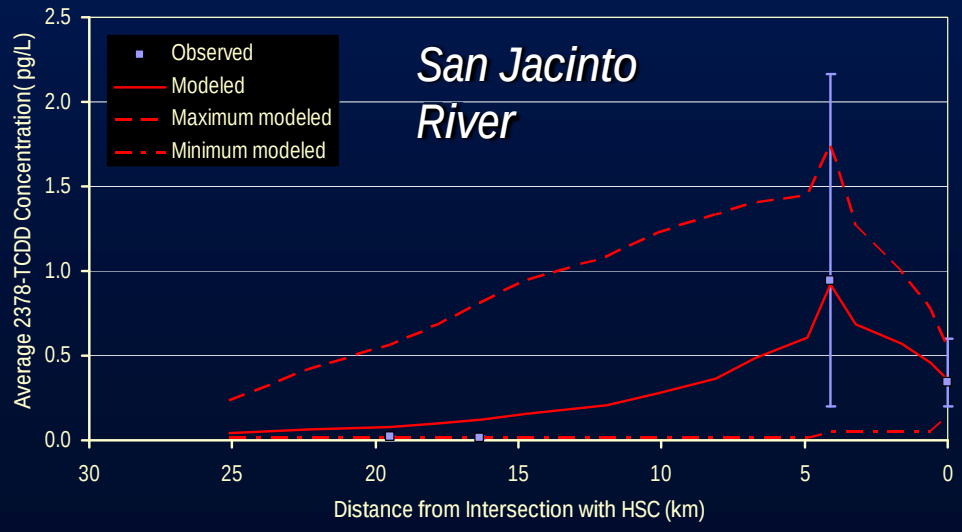
Significant Dioxin Source in 1001



The McGinnis Sunken Pits are now a Superfund site

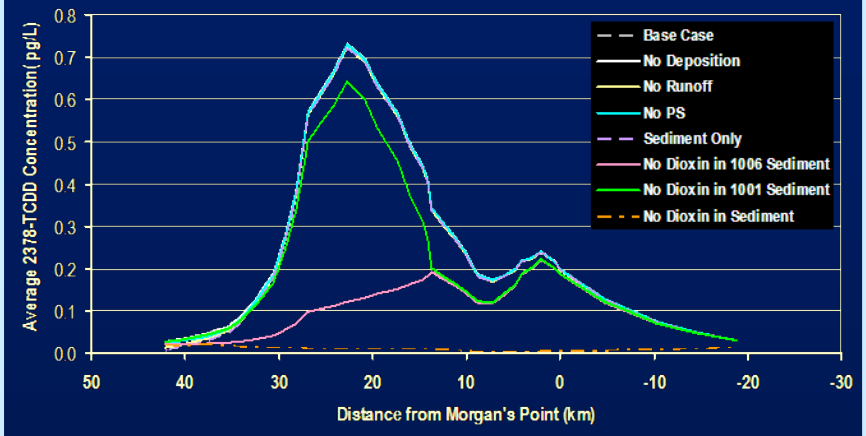
WASP 2378-TCDD calibration

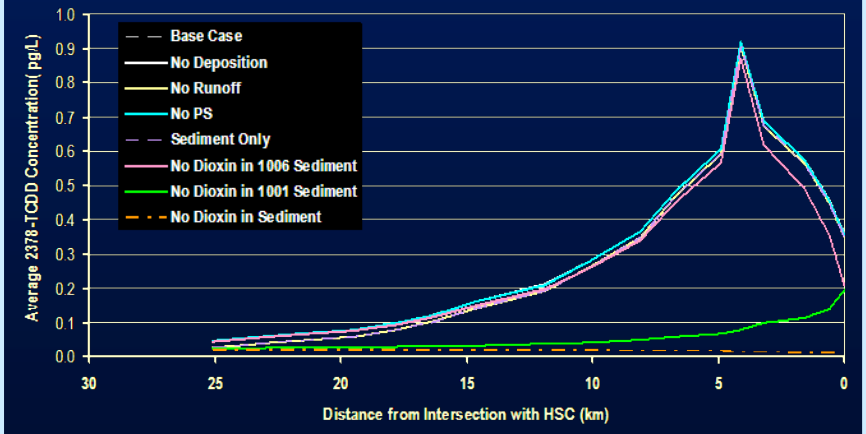




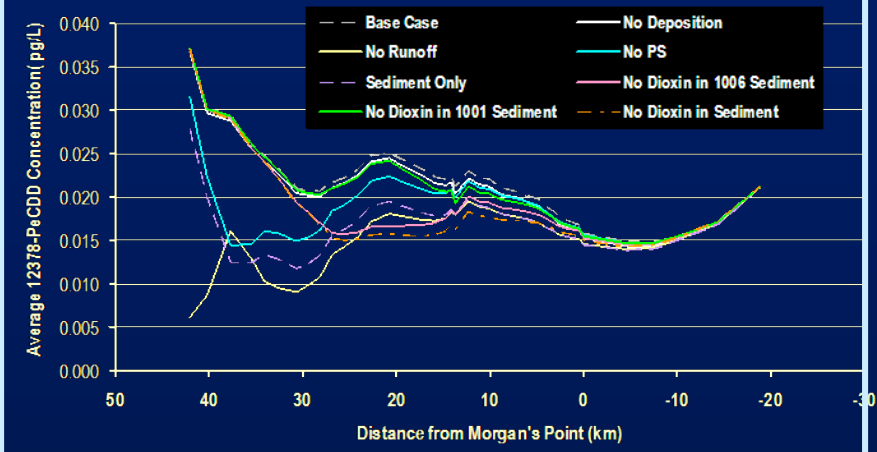
Plotted values are averages over modeling period (7/20/02-4/30/05)
Error bars denote the range of measured values.
Maximum and minimum lines represent the single-time-step max and min concentrations during dry days at each model segment.

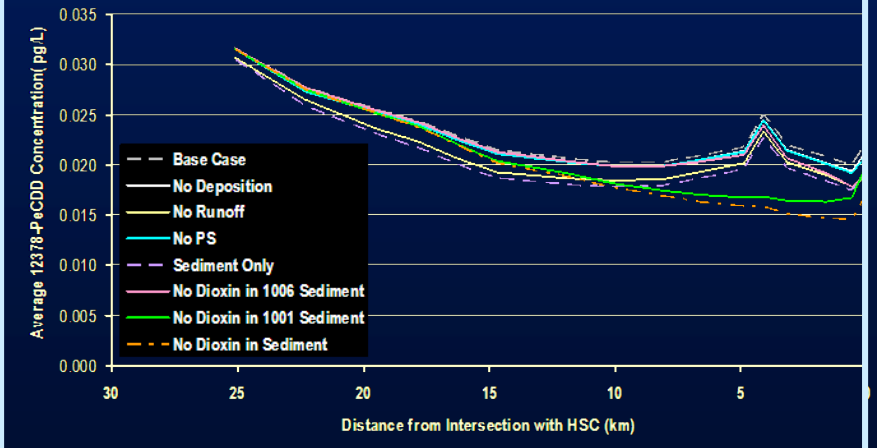
WASP load scenarios





2378-TCDD and 2378-TCDF are similar: sediment contributes more than 90% of load



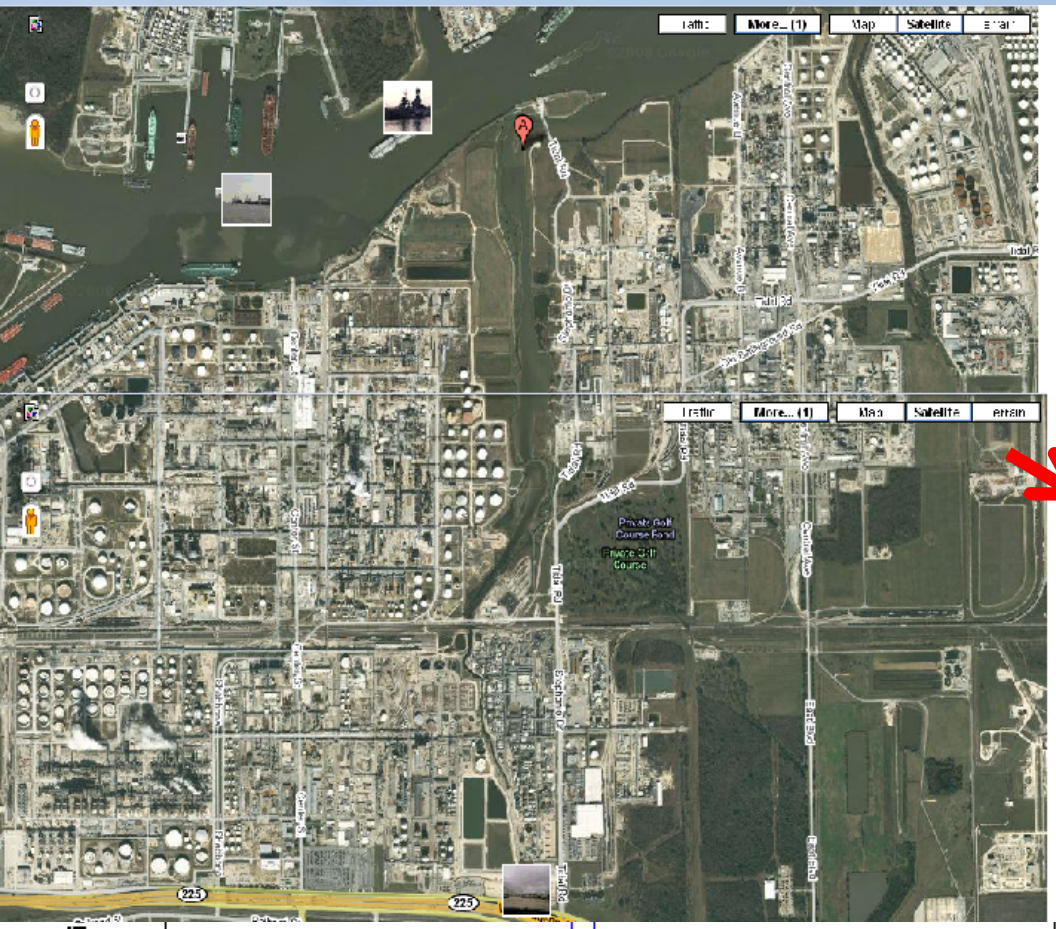


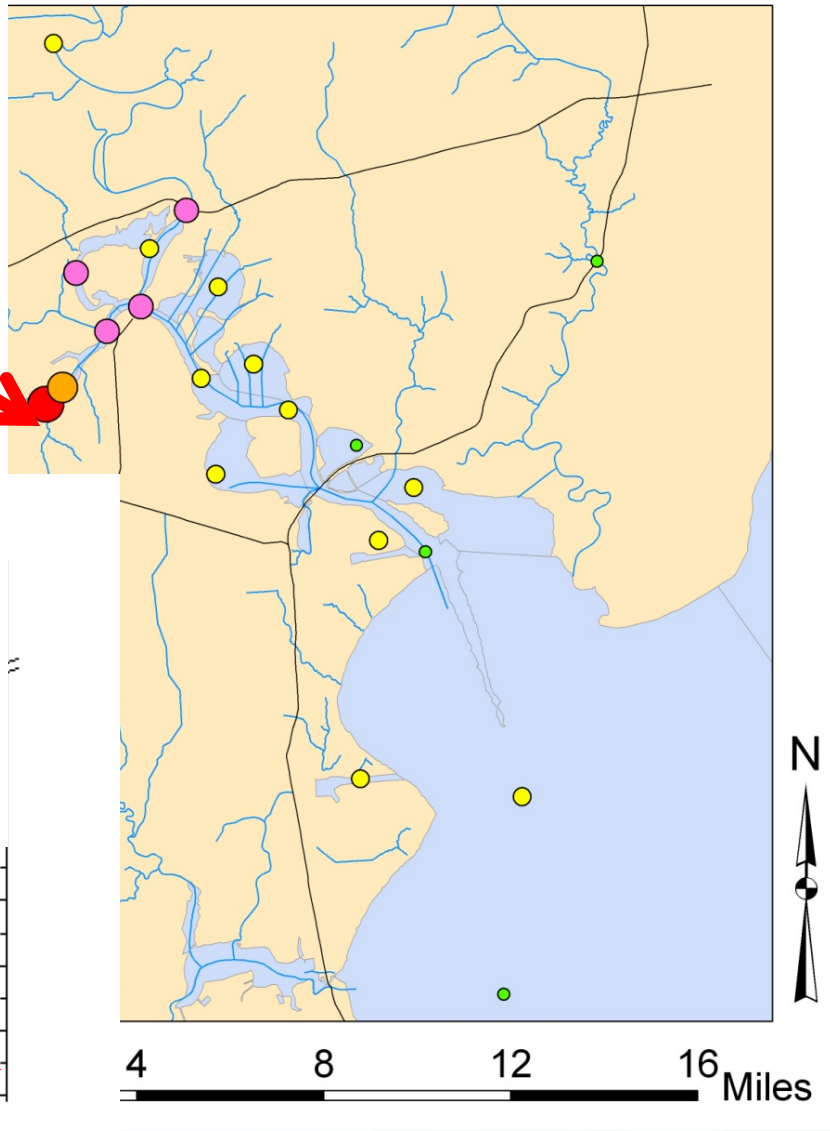
Remaining congeners: sediment still major source, boundary RO and PS also significant

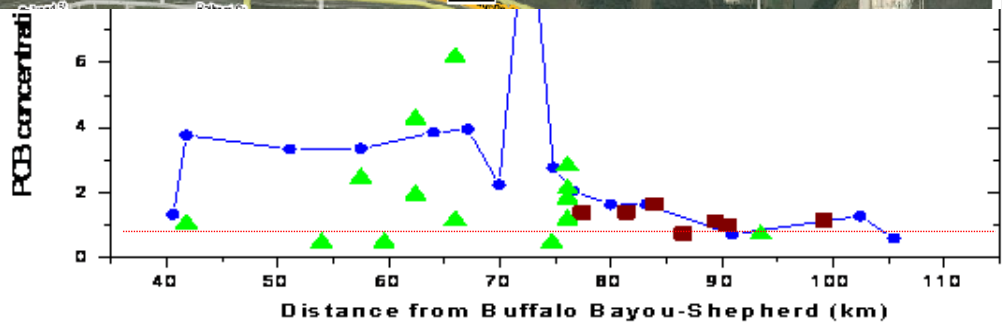
Present

2008-2009 PCB Datasets

PCB Concentrations in Water (2008)

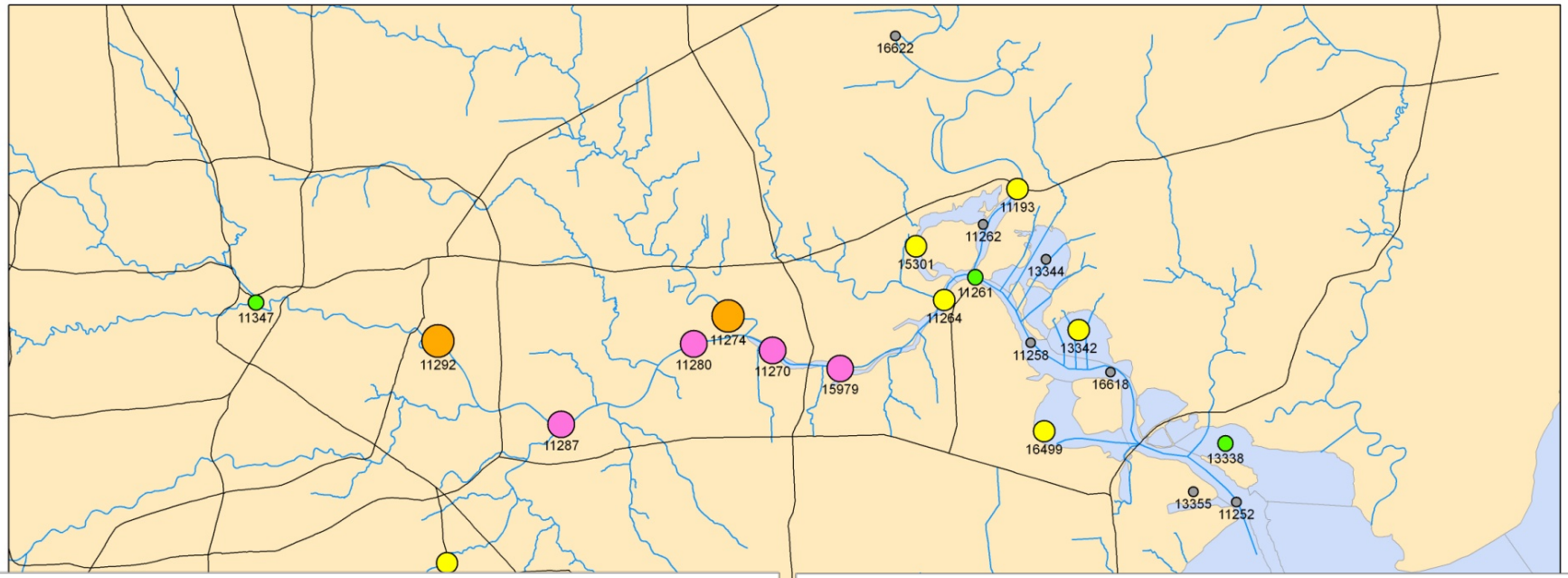


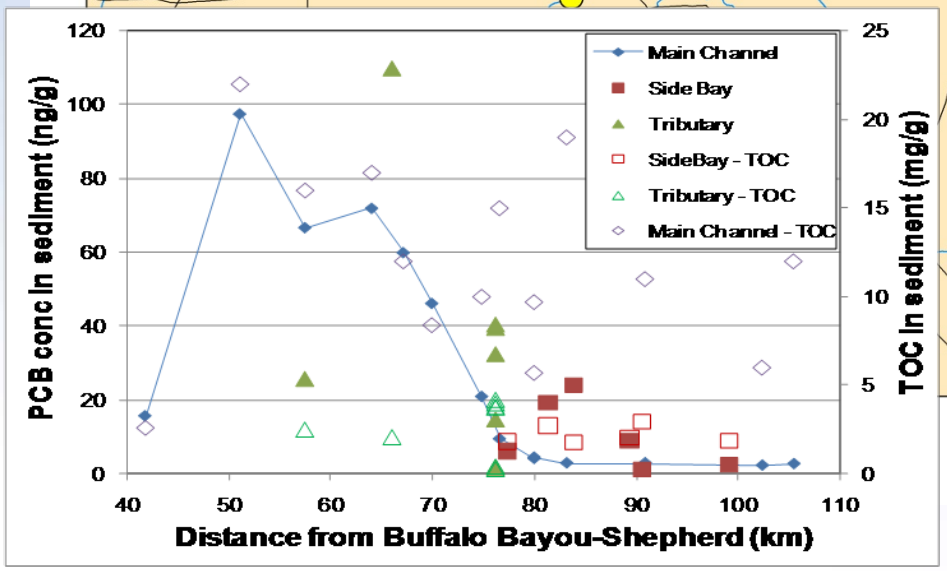


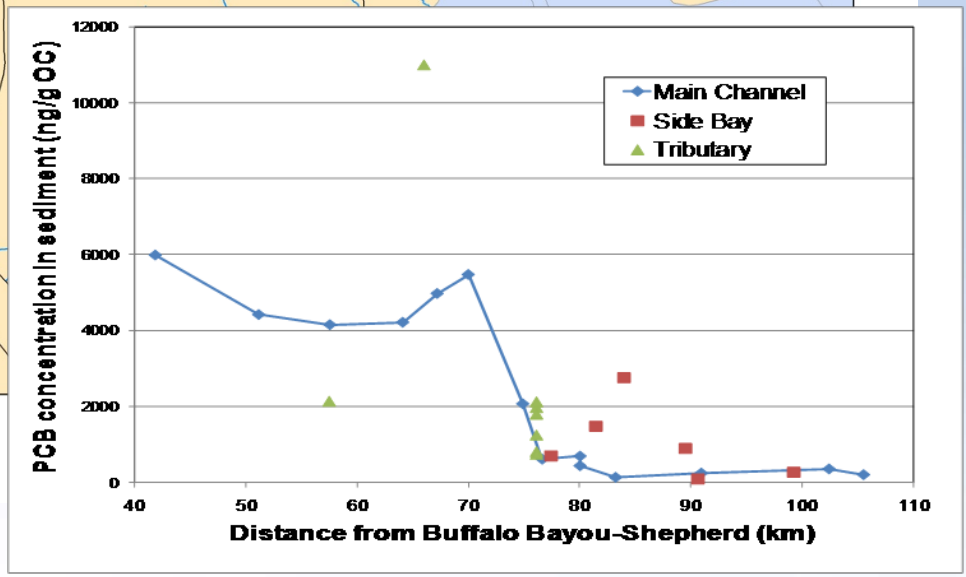


* PCB concentrations calculated as sum of 209 congeners; non-detects assumed as ½ MDL

PCB Concentrations in Sediment (2008)

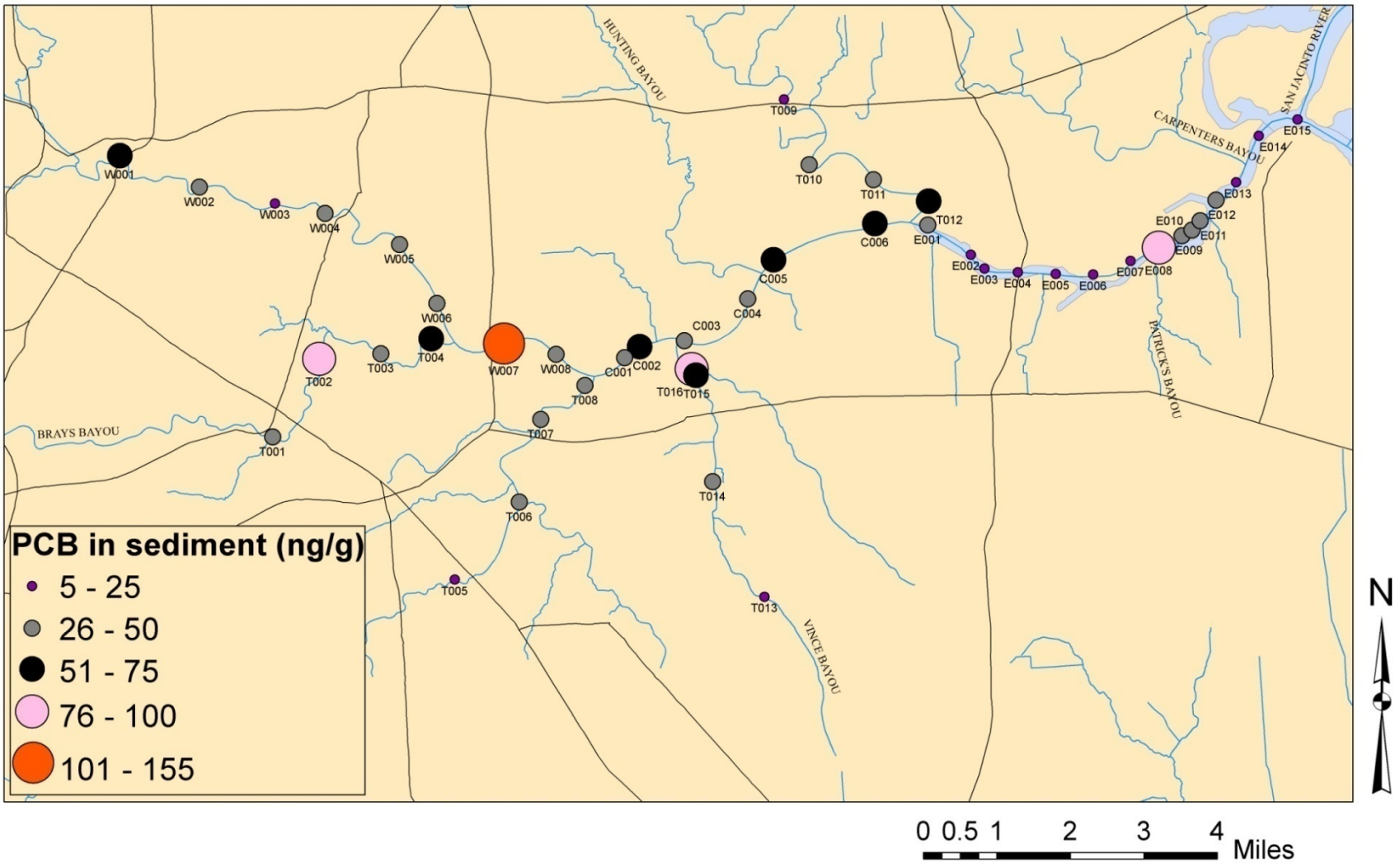






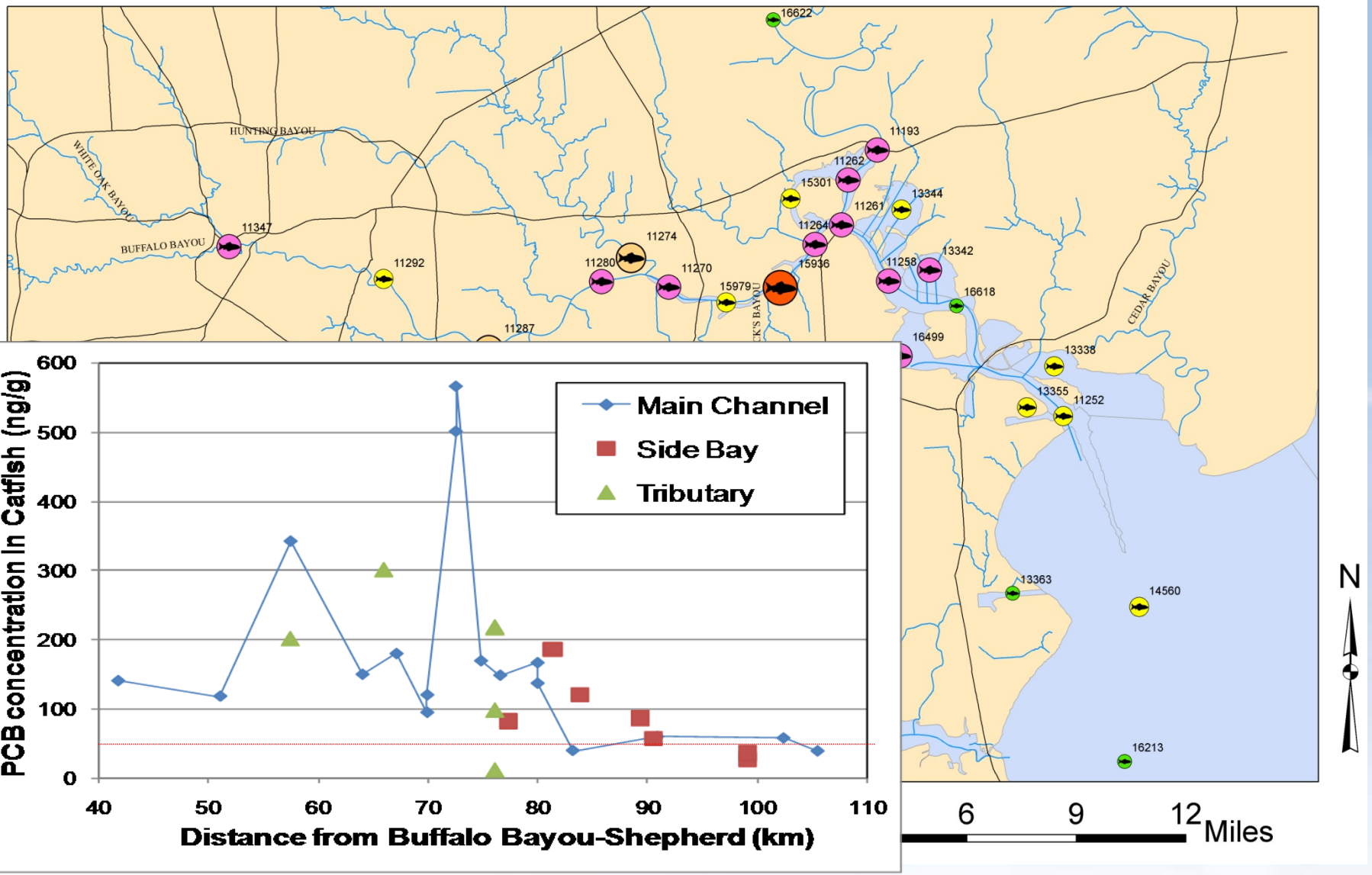
* PCB concentrations calculated as sum of 209 congeners; non-detects assumed as ½ MDL

PCB Concentrations in Sediment (Intensive Sediment Sampling 2008)



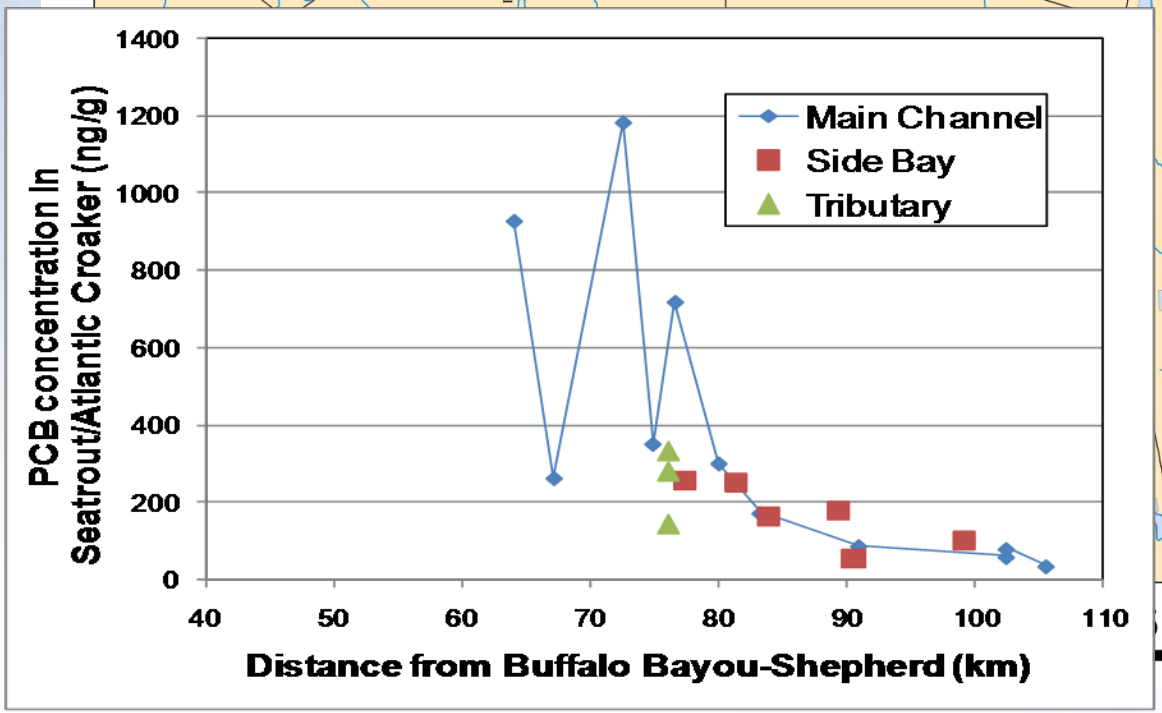
* PCB concentrations calculated as sum of 43 congeners (McFarland and Clarke, 1989); non-detects assumed as ½ MDL

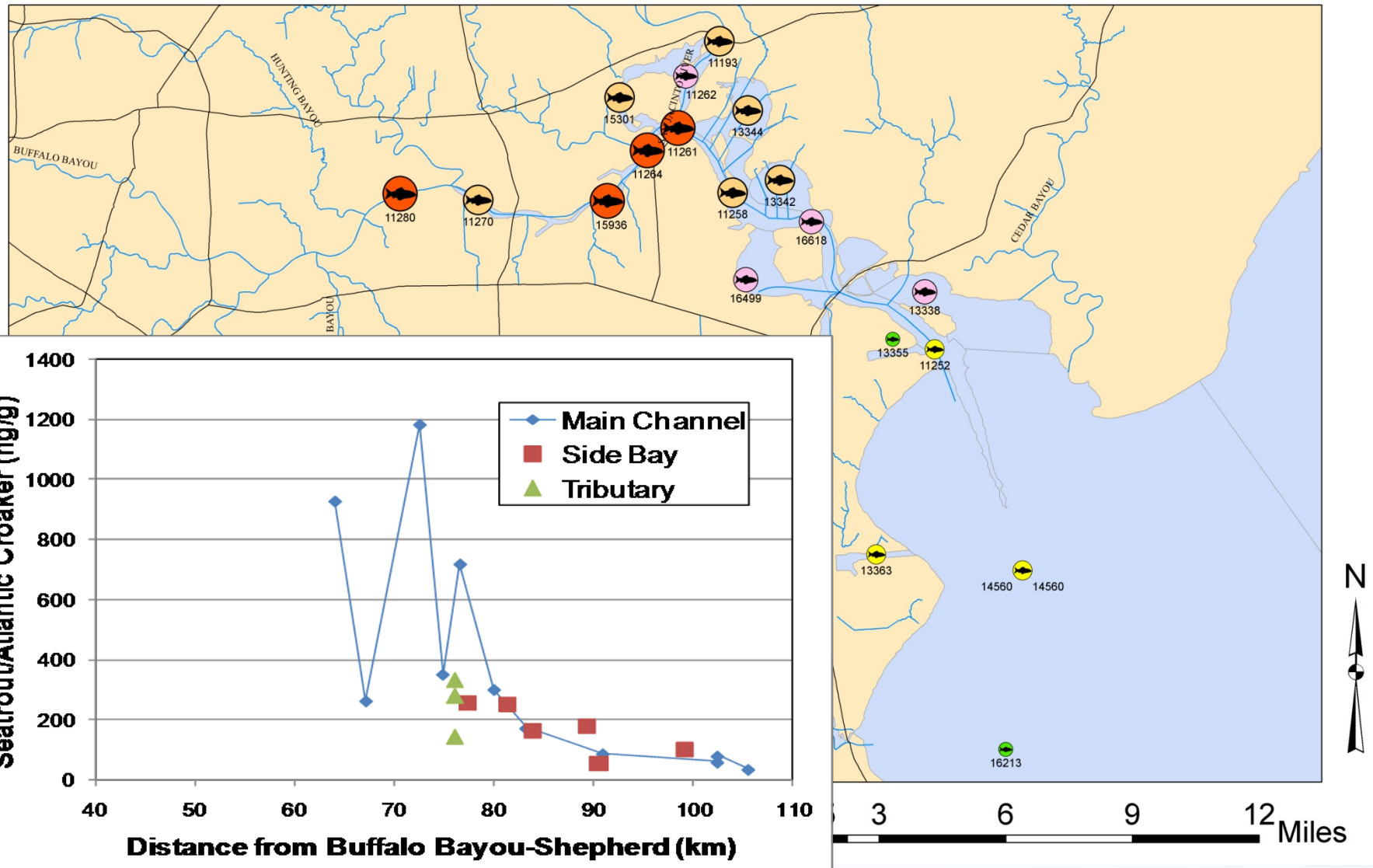
PCB Concentrations in Catfish (2008)



* PCB concentrations calculated as sum of 209 congeners; non-detects assumed as ½ MDL

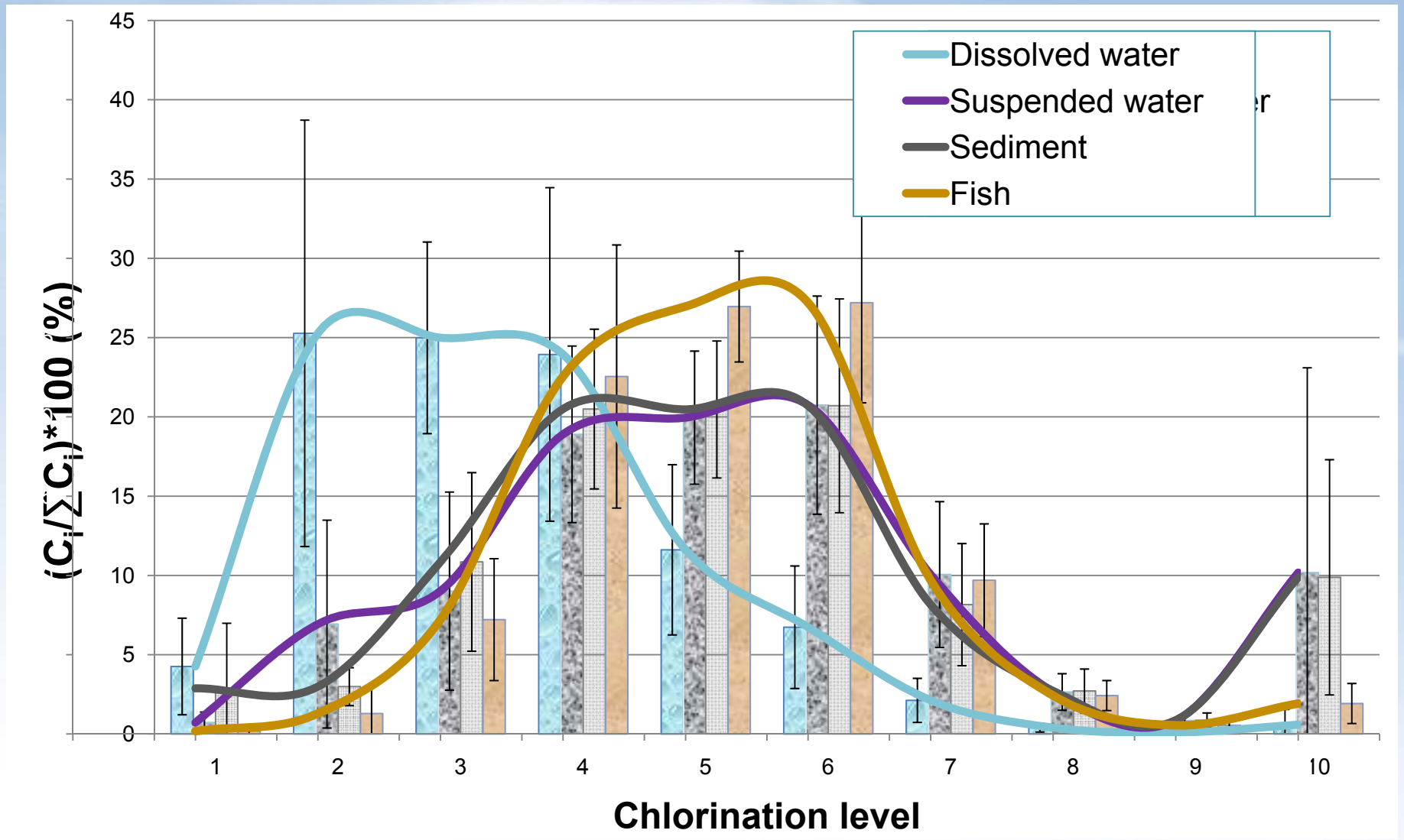
PCB Concentrations in Seatrout/Atlantic Croaker (2008)





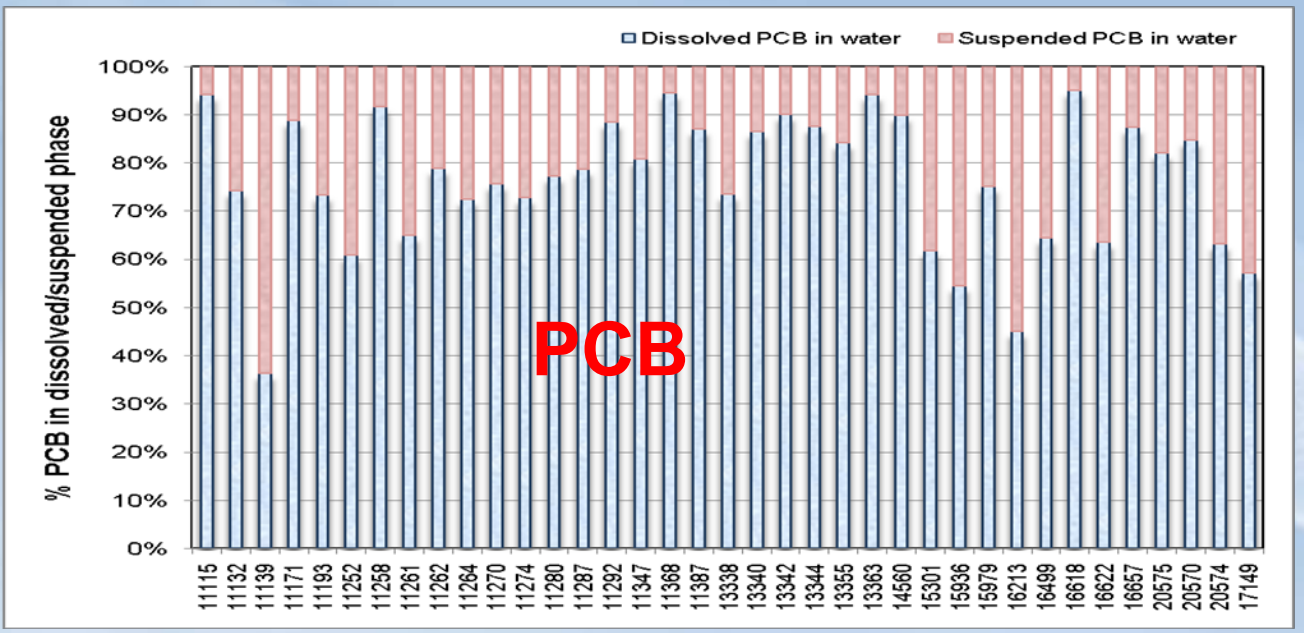
* PCB concentrations calculated as sum of 209 congeners; non-detects assumed as ½ MDL

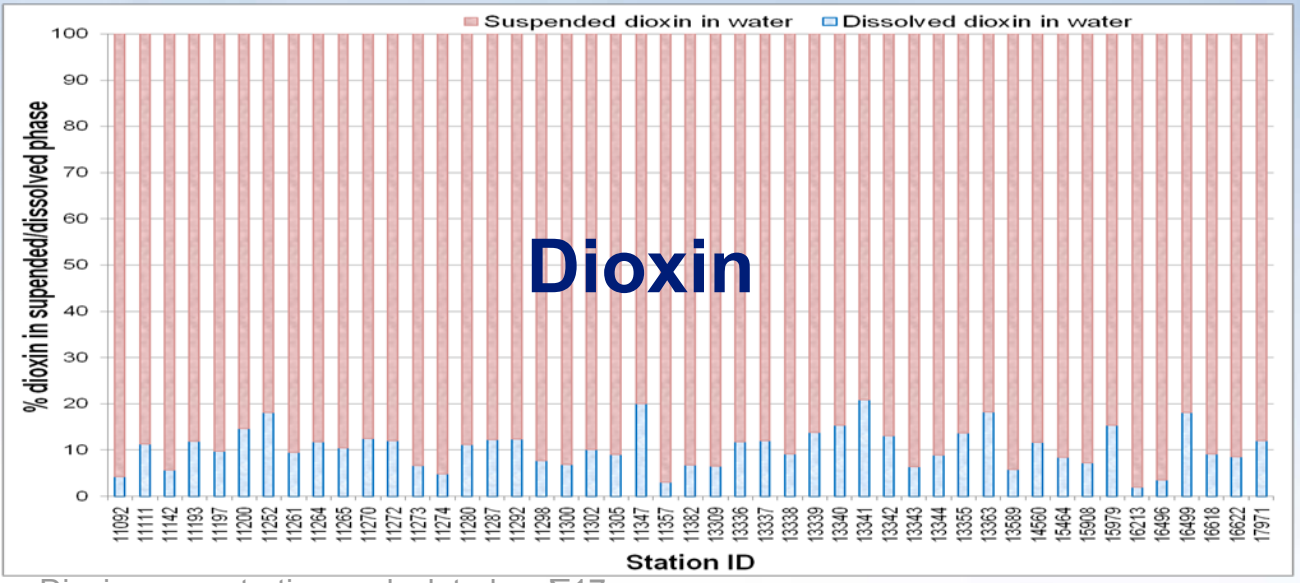
PCB Homologue Distribution in Water, Sediment, and Fish



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

Suspended vs Dissolved Dioxin/PCB in Water



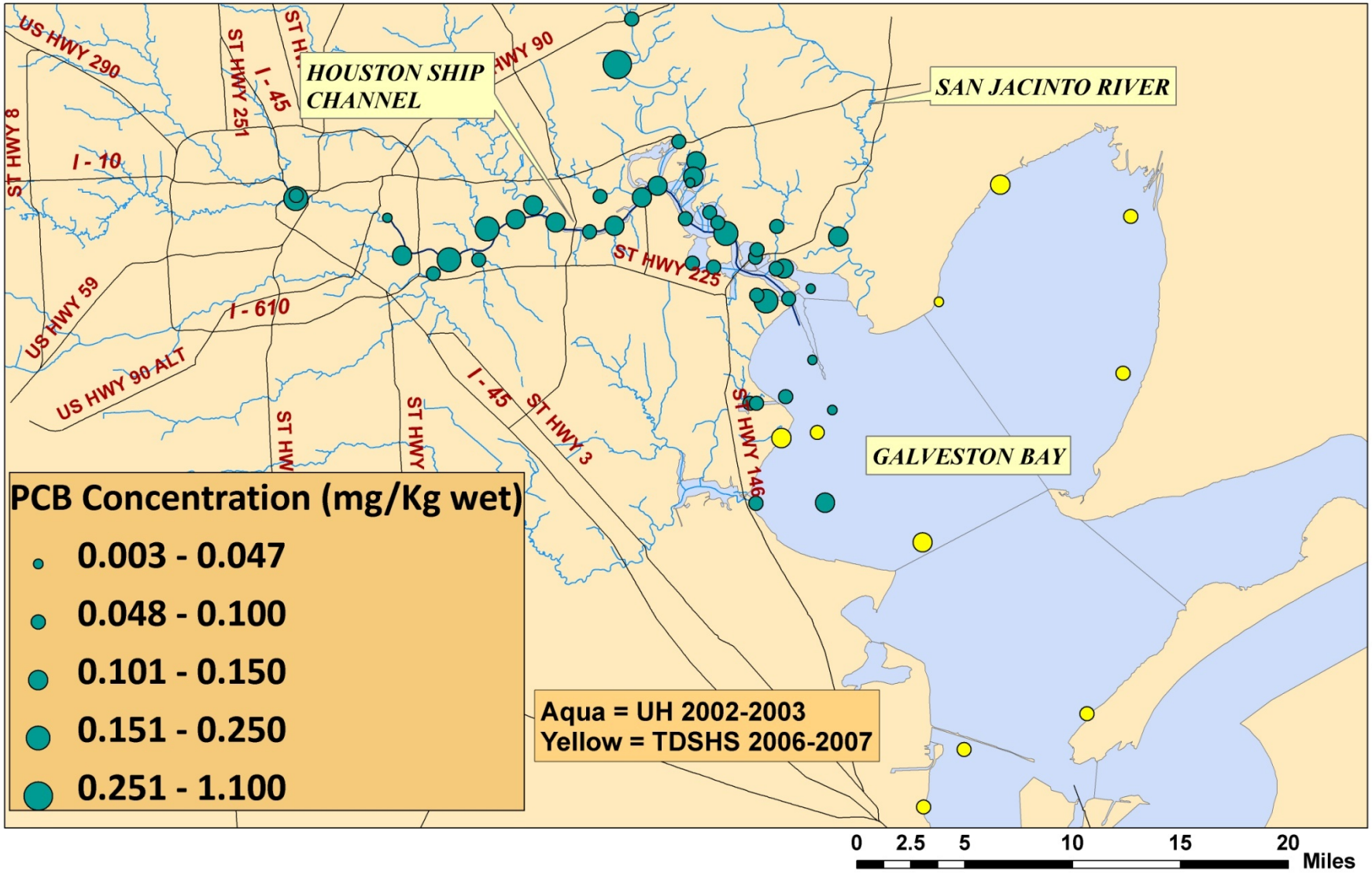


- Dioxin concentrations calculated as ∑17 congeners;
- PCB concentrations calculated as ∑ 209 congeners

Water bodies reported to have PCB higher in dissolved phase

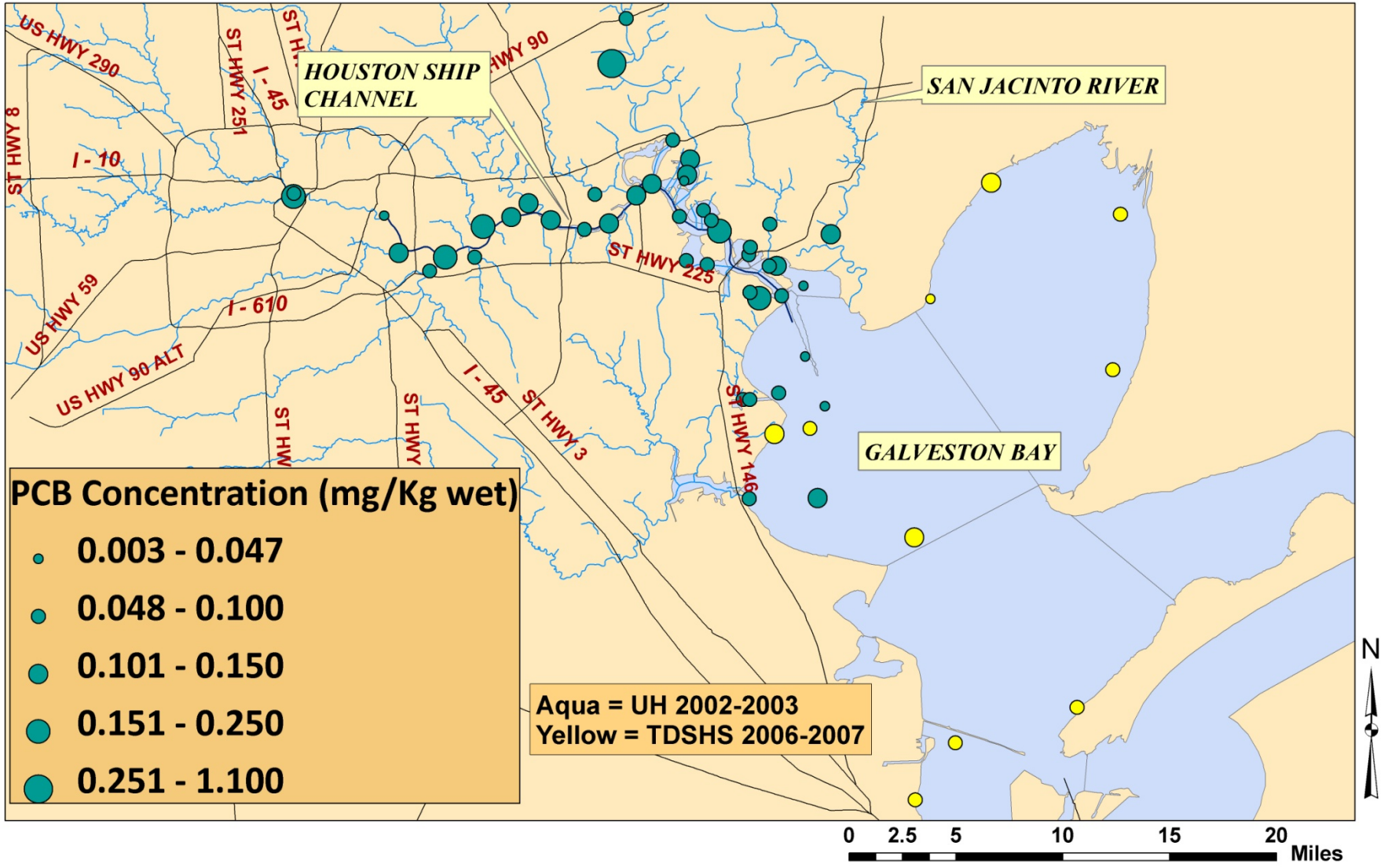
Location	Reference
Coastal locations in Hong Kong, China	Wurl et al., 2006
Yangtse river, China	Jiang et al., 2000
Singapore	Wurl et al., 2006a
Delaware River	Rowe et al., 2007
Barcelona, Spain	Garcıa-Flor et al., 2005
Banyuls-sur-Mer, France	Garcıa-Flor et al., 2005
Lake Michigan	Swackhamer et al.,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

UH 2002-2003 Catfish PCB Comparison



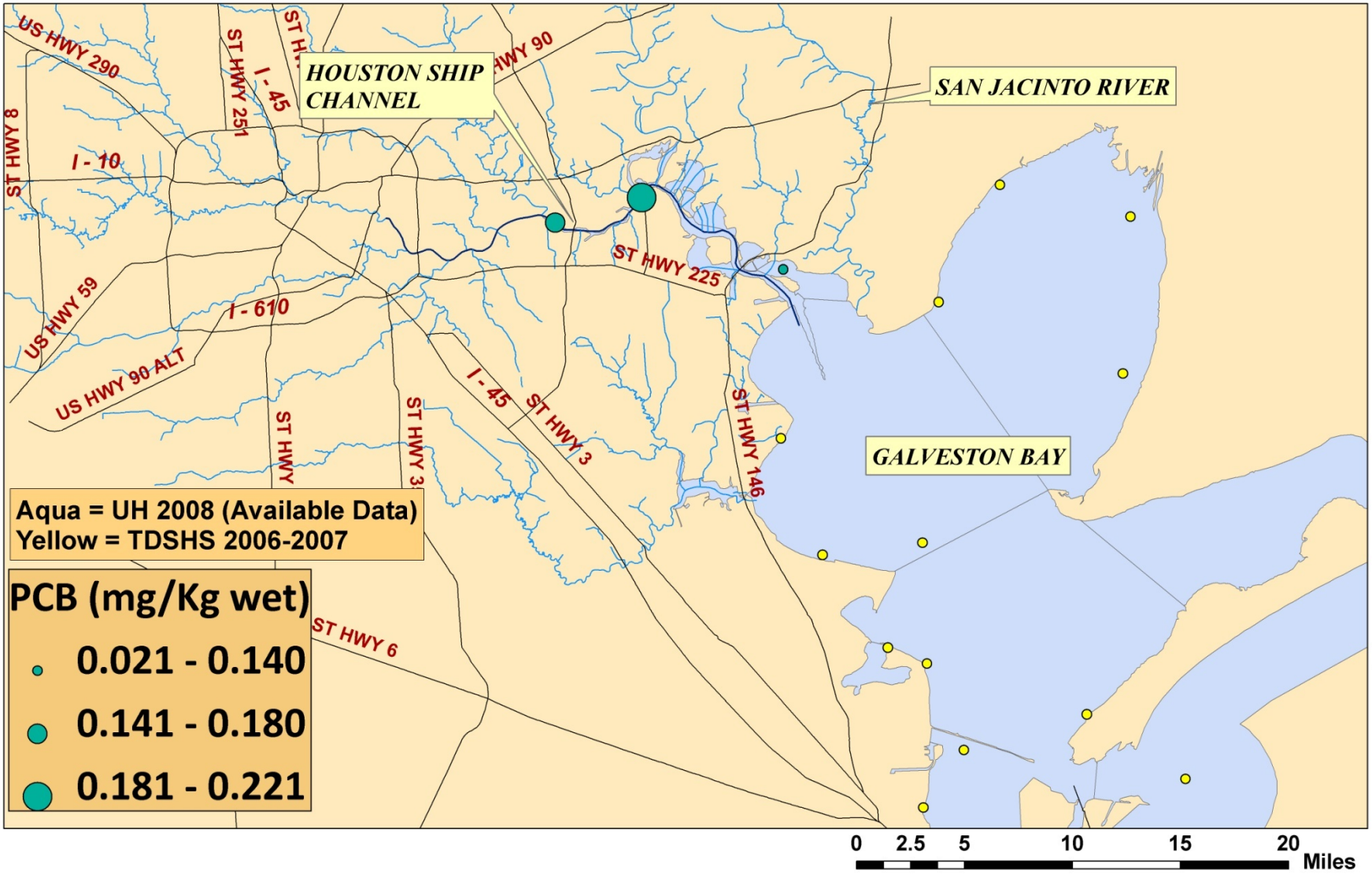
- UH catfish species collected in the order of Hardhead> Blue> Gafftopsail>Channel
- PCB concentration = sum of 43 congeners in McFarland and Clarke (1989)

UH 2008 Catfish PCB Comparison

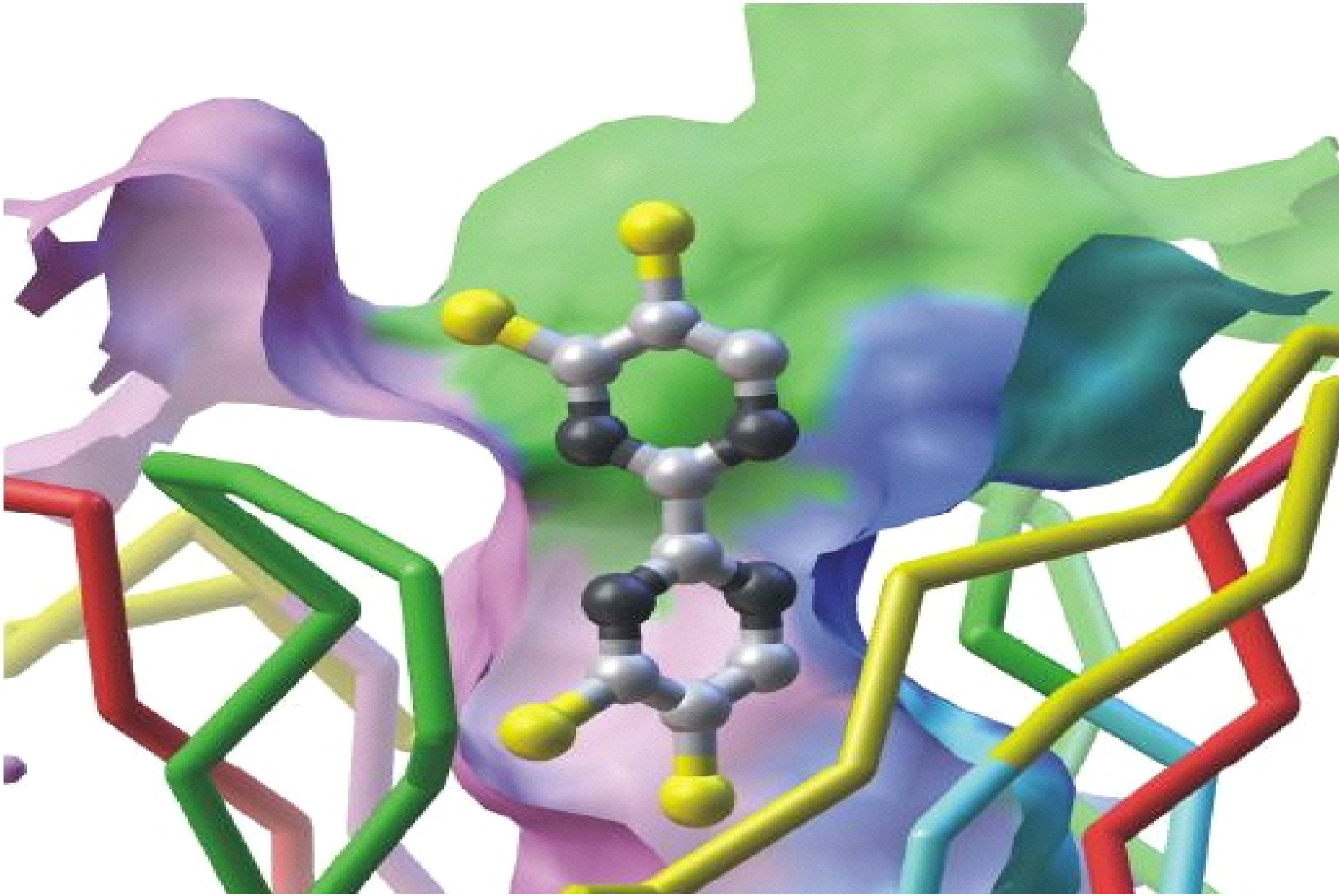


- UH catfish species collected in order of Hardhead> Blue> Gafftopsail> Channel
- PCB concentration = sum of 43 congeners in McFarland and Clarke (1989)
- Sample results only available for a few samples and data have not be QA/QC'd

UH 2008 Speckled Trout PCB Comparison

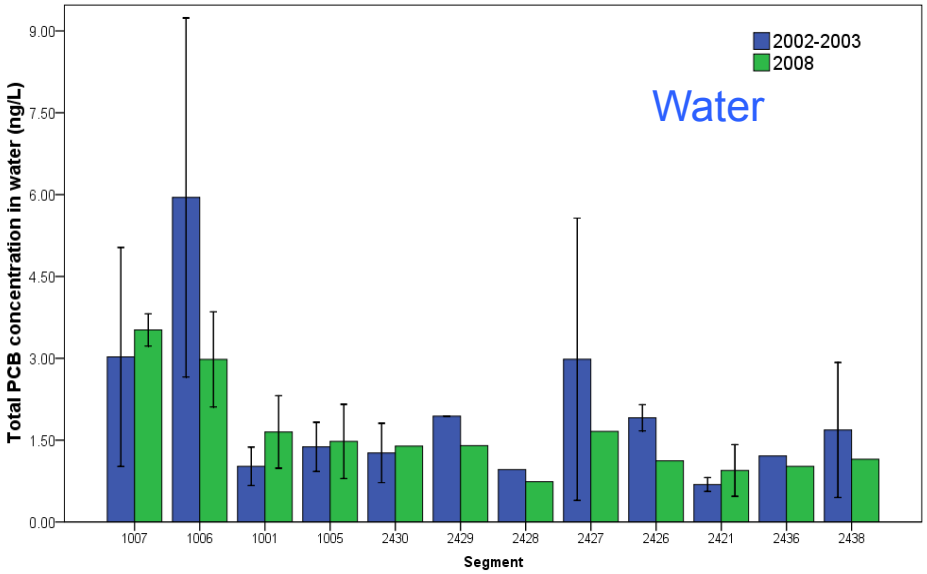


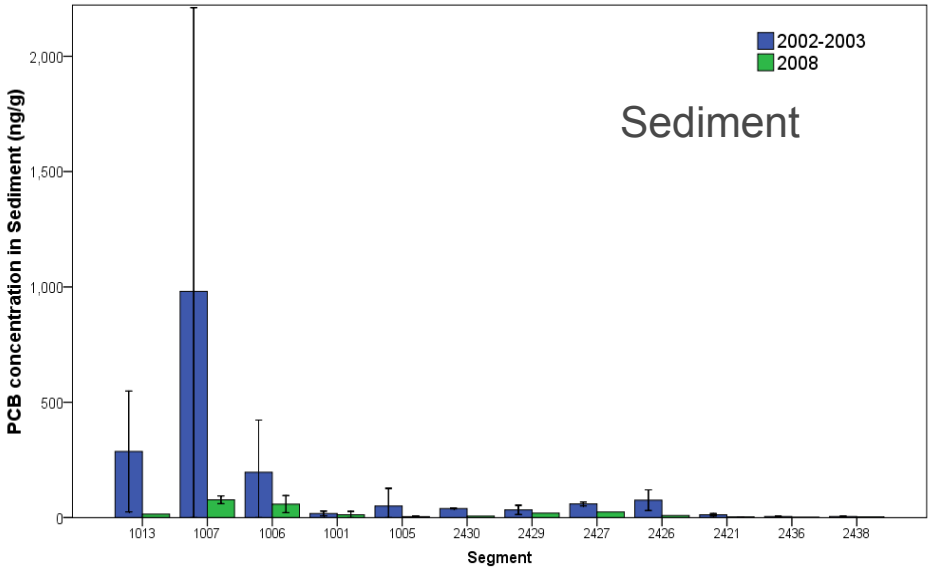
- PCB concentration = sum of 43 congeners in McFarland and Clarke (1989)
- Sample results only available for a few samples and data have not be QA/QC'd

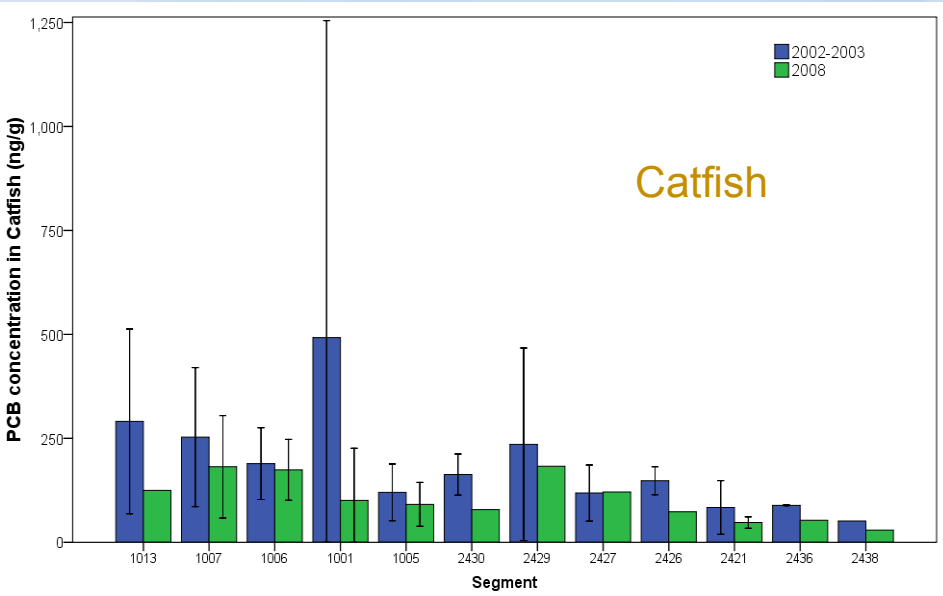


PCB Concentration Over Time

PCB Concentration by Segment (2002-2003 vs 2008)

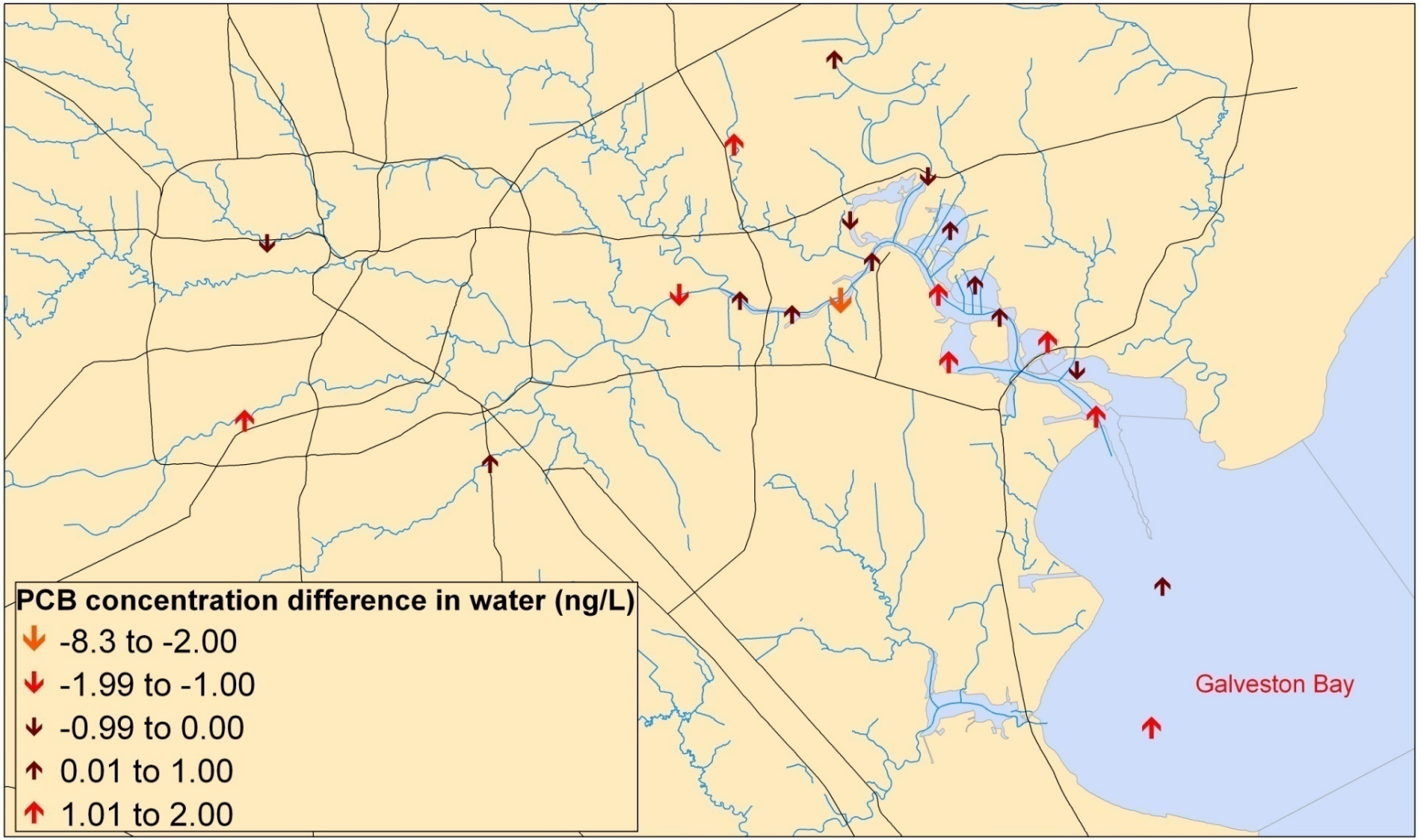






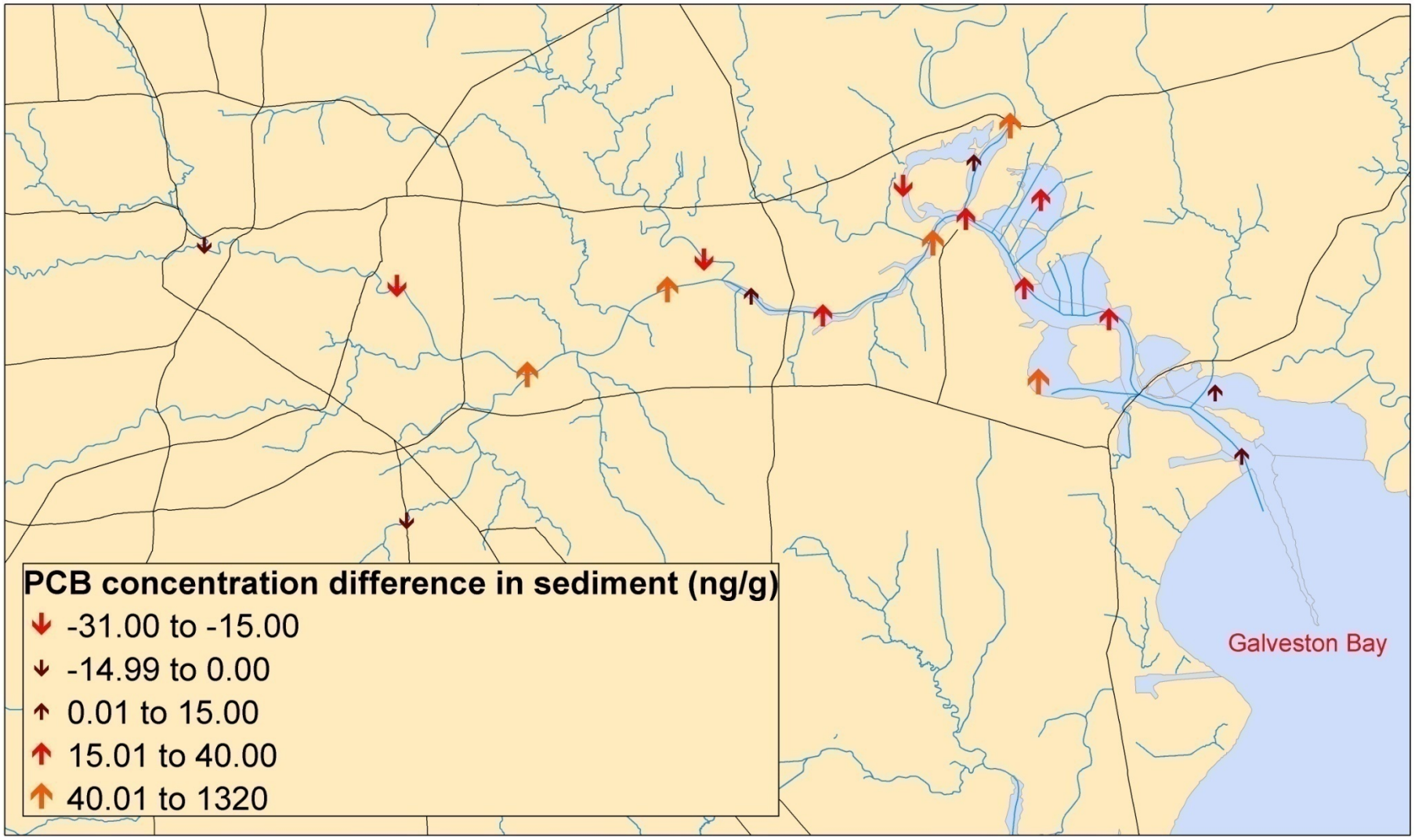

HURRICANE
IKE

PCB Water Concentration (2008 vs 2009)



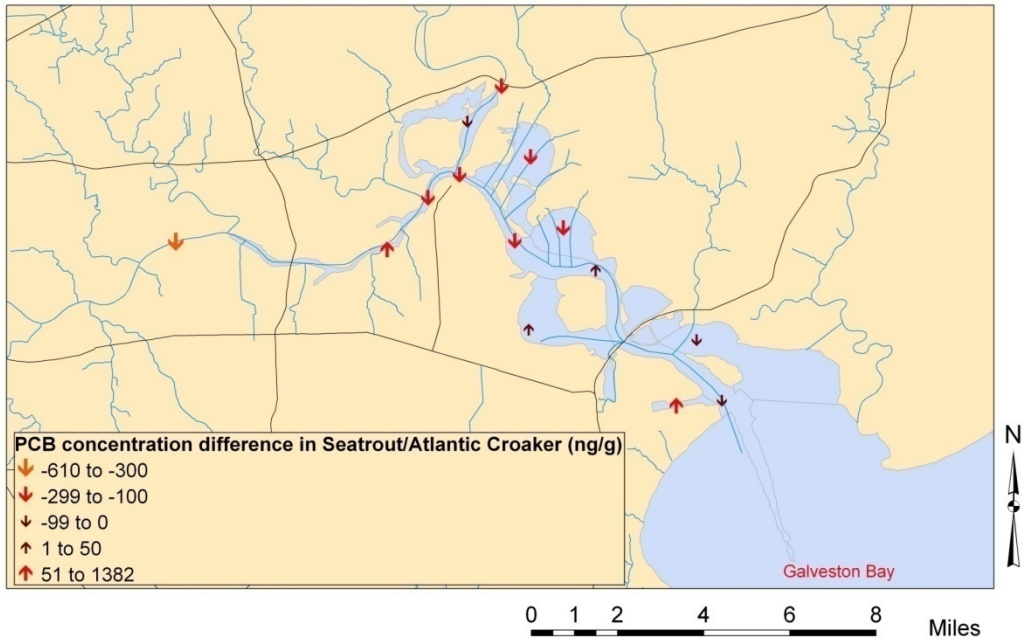
* All concentrations based on 1/2 detection limit for non-detects and ∑209 congeners.

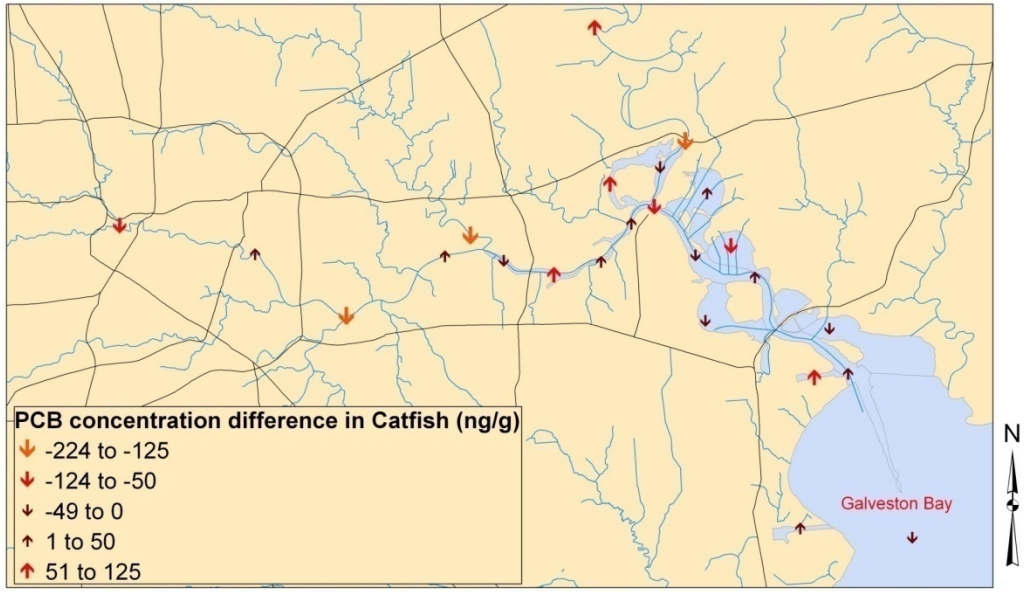
Sediment PCB Concentration (2008 vs 2009)



* All concentrations based on 1/2 detection limit for non-detects and ∑209 congeners.

Tissue PCB Concentration (2008 vs 2009)

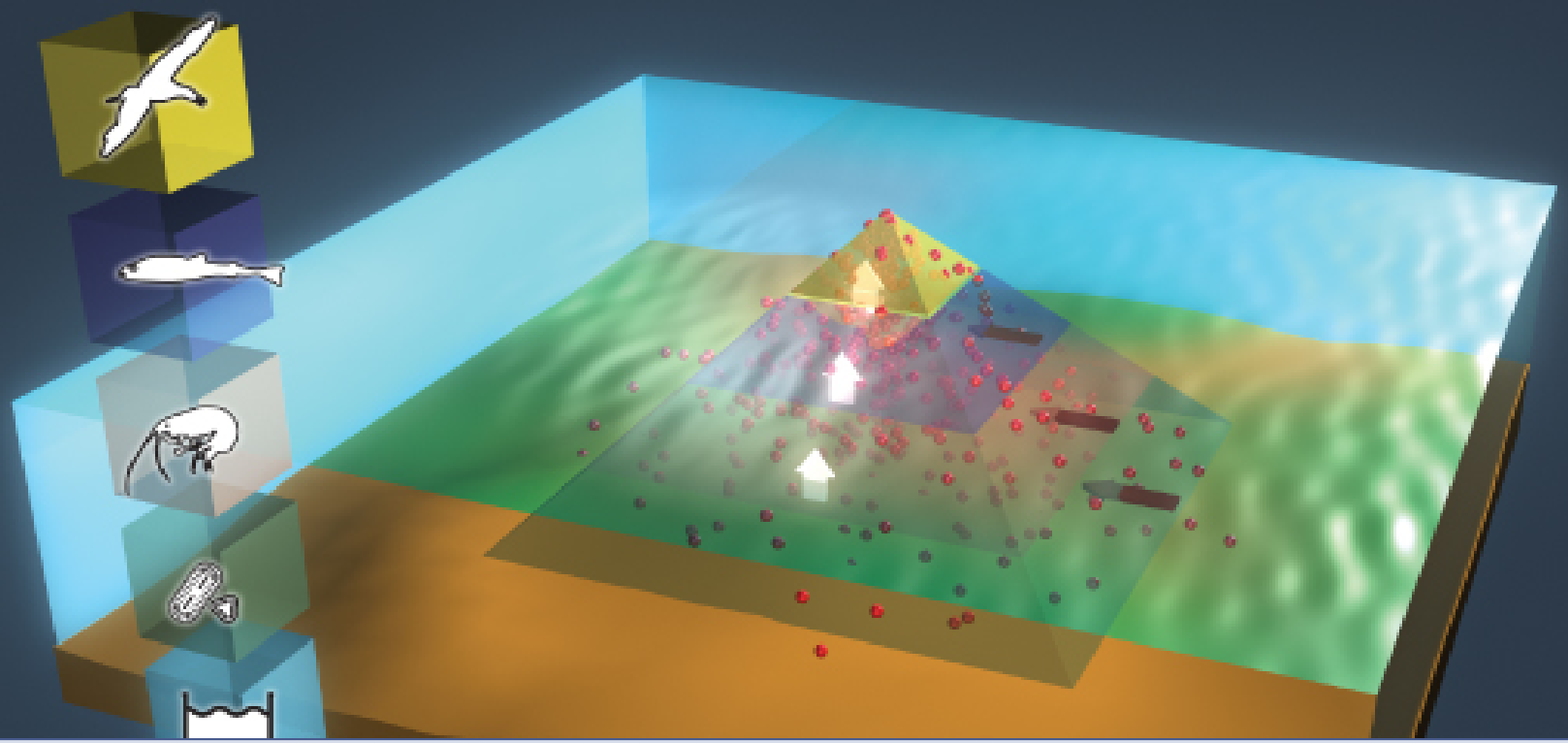




* All concentrations based on 1/2 detection limit for non-detects and ∑209 congeners.

Future

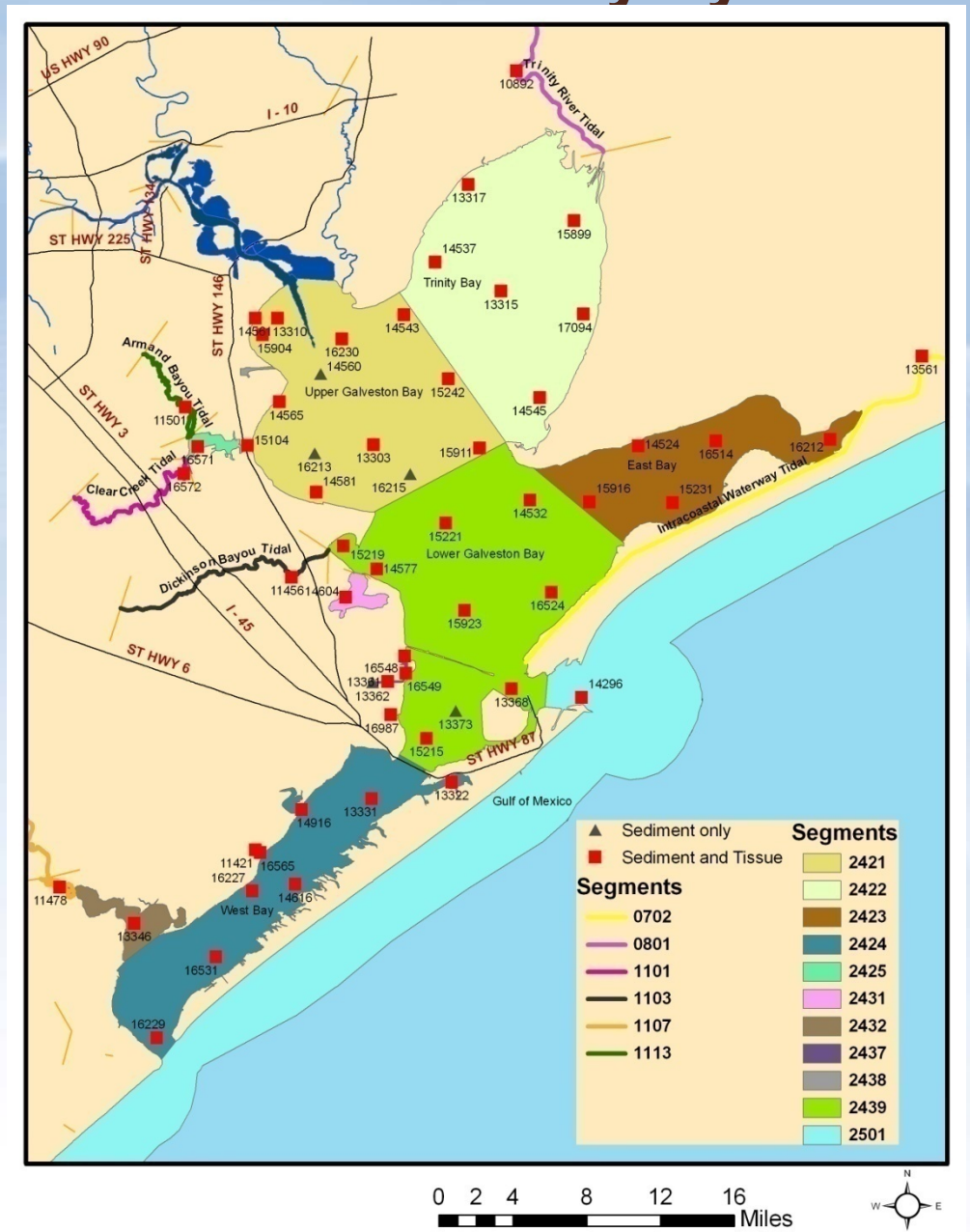
Dioxin and PCB
System wide study of Galveston Bay



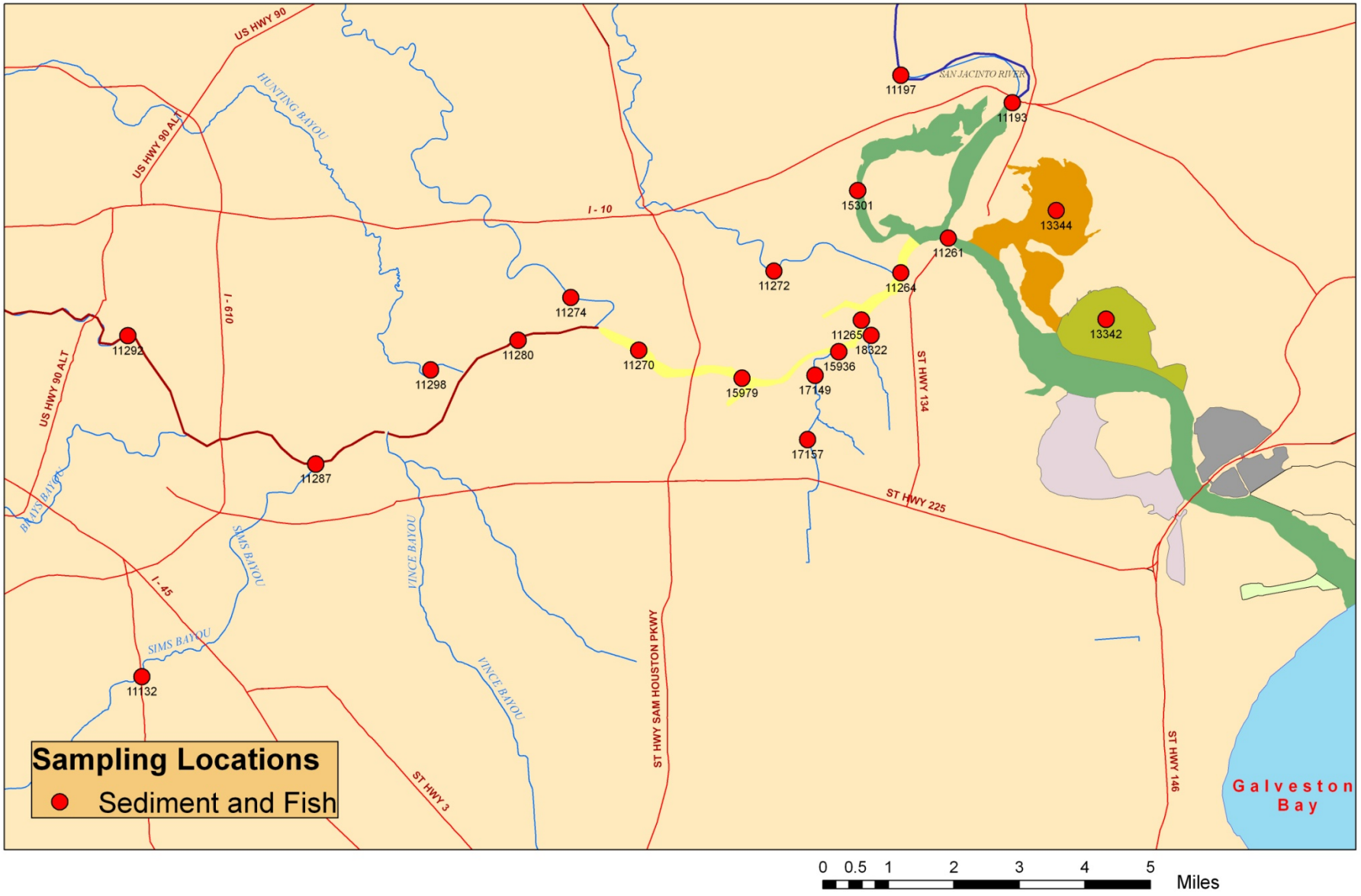
Proposed Sampling

- Snapshot of PCBs and Dioxin in the Houston Ship Channel and Galveston Bay
- Survey of PCBs and Dioxin in the Galveston Bay System

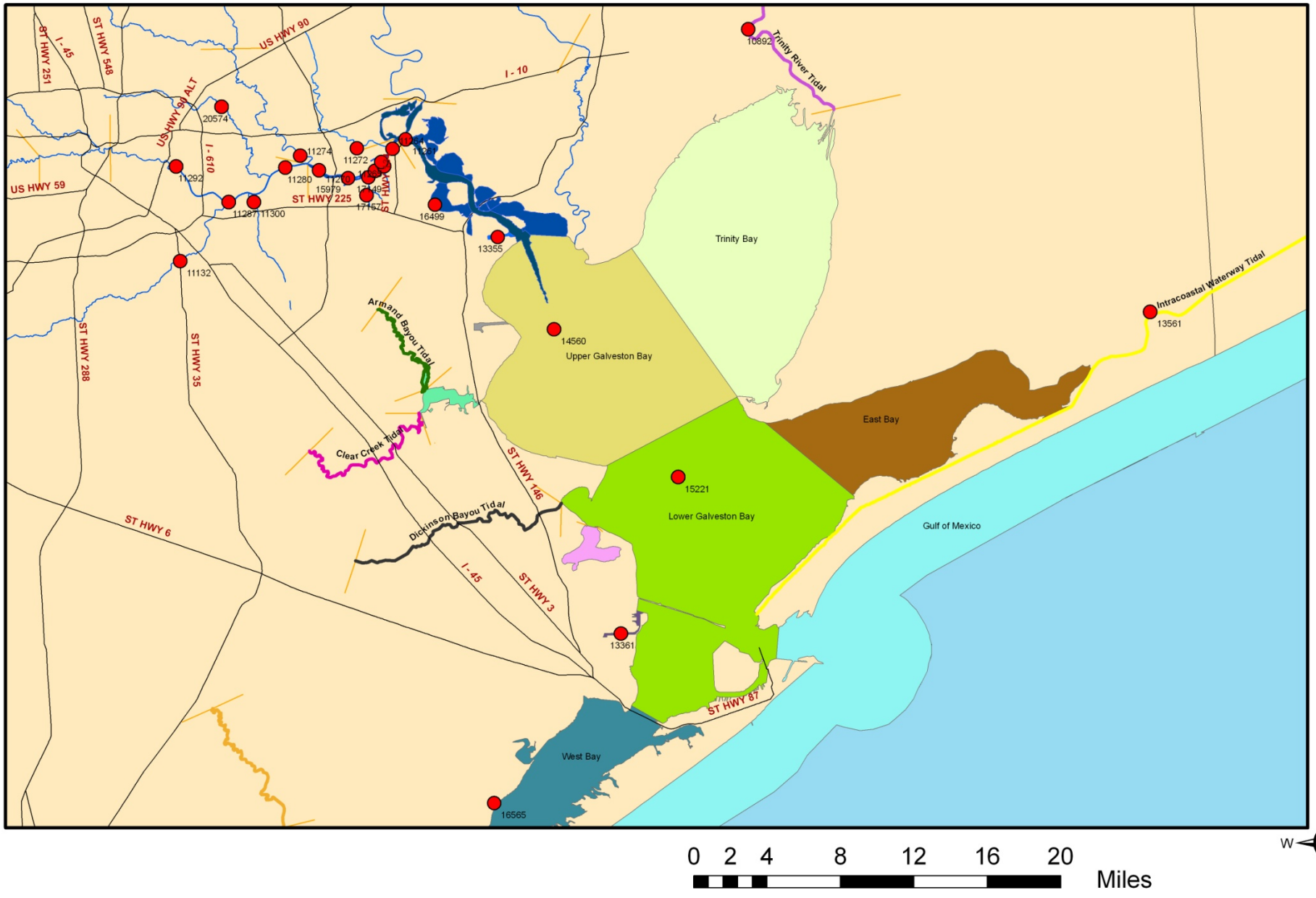
Proposed Sediment and Fish Sampling Locations in the Galveston Bay System



Proposed Sediment and Fish Sampling Locations in Houston Ship Channel



Proposed Water Sampling Locations in Houston Ship Channel and Galveston Bay



CONCLUSIONS

Conclusions

- Water Dioxin and PCB standards exceeded in some segments, while fish standards exceeded in most segments.
- Sediment main source for dioxin.
- Dissolved PCB concentration higher than suspended PCB concentration, contrary to dioxin observations.
- An unusually high fraction of the deca-chlorinated congener (PCB-209) was found in all media pointing to possible current PCB sources.
- Even though PCB concentrations (2008) appear to be attenuating from 2002-2003 levels, the decrease is not statistically significant.
- PCB sediment concentrations have increased after Hurricane Ike.
- Evidence of dioxin + PCB within Gal Bay system

Acknowledgements

- TCEQ, EPA, Houston Endowment
- My team: Divagar Lakshmanan, Maria Modelska, Nathan Howell, Anu Desai, Norma Moreno, Emil Helfer, Stephen Ray, Yinfei Sun, Megan Hochstedler, Taft Tucker, Dan Burleson, Bora Turan, Jaejin Kim, Nhu Vo
- TAEP for inviting us to share our research


I'M CONVINCED...WE HAVE PCB'S, DDT'S AND MERCURY IN OUR STREAMS!
search ID: dro0197
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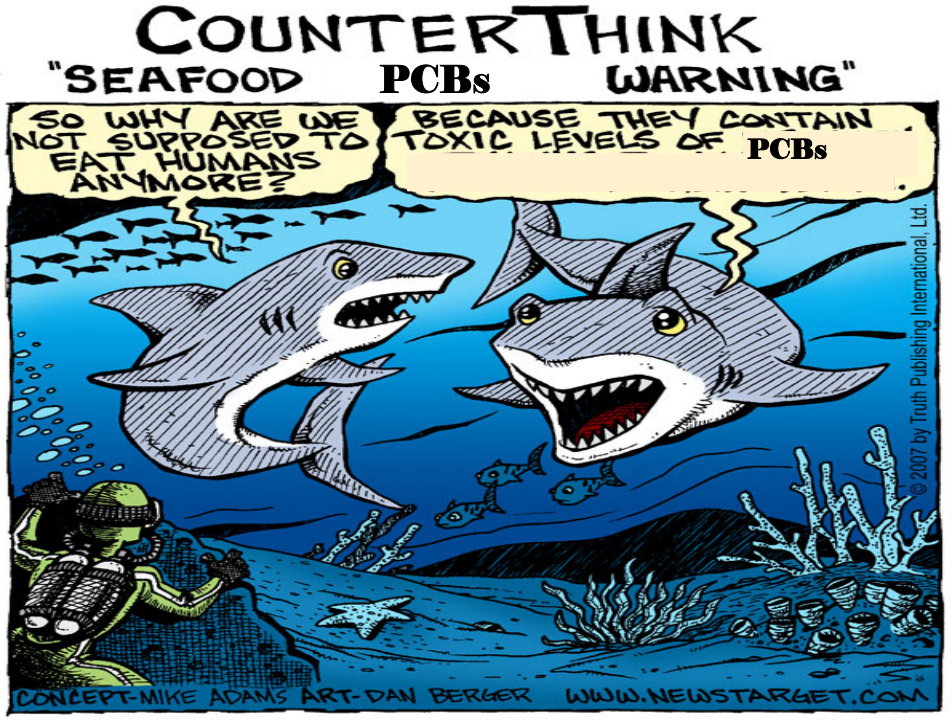
COUNTERTHINK
"SEAFOOD PCBs WARNING"
SO WHY ARE WE NOT SUPPOSED TO EAT HUMANS ANYMORE?
BECAUSE THEY CONTAIN TOXIC LEVELS OF PCBs
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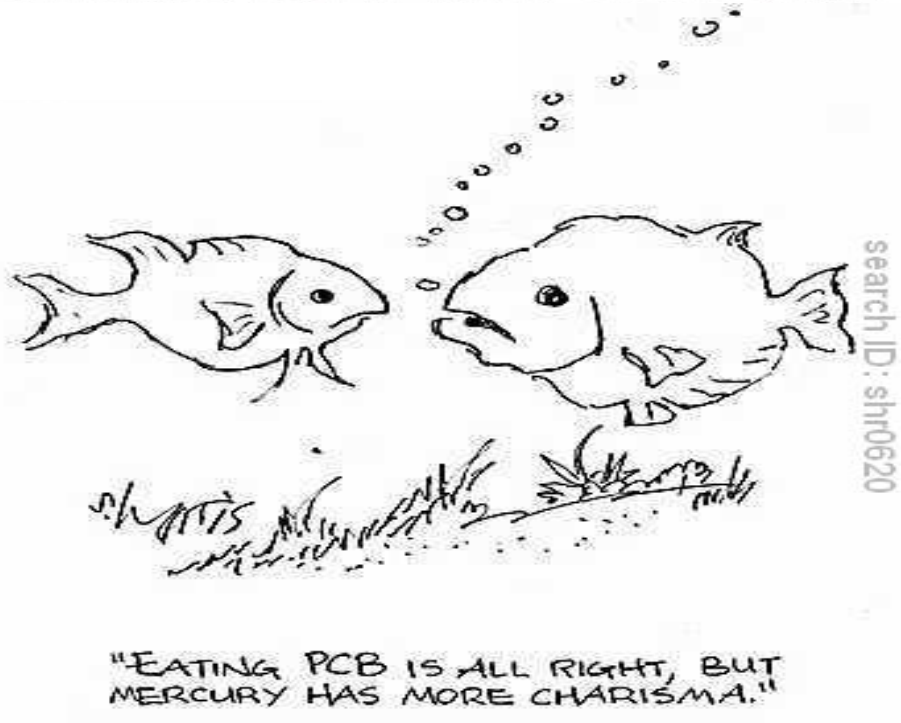
Questions
STOP TOXIC Pollution from PCBs!


search ID: shr0620
"EATING PCB IS ALL RIGHT, BUT MERCURY HAS MORE CHARISMA."

The 43 PCB Congeners

8	77	126	169
18	81	128	170
28	82	138	177
37	87	151	179
44	99	153	180
49	101	156	183
52	105	157	187
60	114	158	189
66	118	166	194
70	119	167	201
74	123	168	