Total Maximum Daily Loads for Dioxins

in the Houston Ship Channel

Contract No. 582-6-70860

Work Order No. 582-6-70860-08

Quarterly Report No. 3

Prepared by
University of Houston
Parsons Water & Infrastructure

Principal Investigator
Hanadi Rifai

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

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

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INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDF) and polychlorinated biphenyls (PCBs) are halogenated aromatic compounds that have been widely found in the environment. The PCDDs include 75 congeners and PCDFs include 135 different congeners. Only 7 out of the 75 PCDD congeners and 10 of the 135 PCDF congeners have been identified as having dioxin-like toxicity. There are 209 PCB congeners, of which 12 are identified as having dioxin-like toxicity. These dioxin-like compounds are highly toxic and persistent environmental contaminants and, consequently, have received a great deal of attention by environmental regulators and researchers.

Dioxin (the term used to refer to dioxin-like compounds) presents a likely cancer hazard to humans[1] (U. S. Environmental Protection Agency, 2000) and can cause health problems even at extremely low doses. Reproductive problems, behavioral abnormalities, and alterations in immune functions are among the health effects caused by exposure to dioxin. Because dioxin-like compounds have been proven to bioaccumulate in biological tissues, particularly in animals, the major route of human exposure is through the food chain. Thus, several food advisories have been issued across the United States to prevent people from consuming unhealthful doses of these compounds.

The overall purpose of this project is to develop a Total Maximum Daily Load (TMDL) allocation for dioxin in the Houston Ship Channel System, including upper Galveston Bay, and a plan for managing dioxins to correct existing water quality impairments and to maintain good water quality in the future.

The dioxin TMDL study has been divided into various phases. Phase I of the TMDL was focused on assessing current conditions and knowledge about dioxins. Phase II was focused on gathering data in all media to quantify dioxin levels in the channel and their sources. Phase III is focused on model development and load allocation.

Work Order (582-6-70860-08) is part of Phase III and includes the following tasks:

1. Project administration
2. Continuing development and refinement of TMDL models
3. Participating in stakeholder involvement with the dioxin TMDL project
4. TMDL allocations

This document constitutes the 3rd quarterly report for Work Order No. 582-6-70860-08 (Contract No. 582-6-70860) of the Dioxin TMDL Project and summarizes the activities undertaken by the

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[1] U.S. Environmental Protection Agency (2000). "Dioxin: Scientific Highlights from Draft Reassessment." *Information Sheet 2*, National Center for Environmental Assessment, Office of Research and Development, Washington, DC.

University of Houston, in conjunction with Parsons during the period March 1, 2007 through May 31, 2007. The progress over the past quarter will be summarized by task:

TASK 1 PROJECT ADMINISTRATION

Task is in progress.

TASK 2 CONTINUING DEVELOPMENT AND REFINEMENT OF TMDL MODELS

Progress over the past quarter on this task was focused on three main aspects: (i) recalibrating the dioxin WASP model in response to comments from the April 7, 2007 stakeholder meeting (see Task 3), (ii) evaluating contributions from measured and estimated sources into the channel and from direct discharge and boundary conditions, and (iii) developing a methodology for determining load reductions for dioxin.

Recalibrating Dioxin WASP Model. The calibrated WASP model was presented to the stakeholders during the April 7, 2007 meeting, and it was noted that the modeled 2,3,7,8 TCDD profile in the main channel was too “broad” and over-predicted concentrations down stream from the peak in Segment 1006 to the mouth (see slide 14 of stakeholder slides in Appendix I). One possible remedy that was suggested included the use of a higher settling rate to account for the exchange of contaminants between the water column and the benthic segments in locations other than the “hot spots”. Another suggestion was to exclude wet weather concentrations when comparing modeled and measured concentrations because all measured concentrations were dry weather data. A third suggestion included looking at median values from the model as opposed to average concentrations for the modeling period.

Therefore, over the past quarter, the WASP model was re-calibrated using higher settling rates to account for the exchange of contaminants between the water column and the benthic segments. Average measured concentrations were compared to the average concentrations predicted by the model for dry weather only. To separate dry from wet data, rainfall data from HCOEM (used as input to RMA2) were used. If the total rainfall for a given day was greater or equal than 0.1 inches, the day was considered a wet day, otherwise it was considered a dry day. The datasets were also divided based on flow instead of rainfall but the results were similar.

Longitudinal plots of the measured and modeled concentrations for dry days for the re-calibrated model are shown in Figures 1 and 2. The data shown in Figure 1 are all averages, whereas the data shown in Figure 2 are median values. Also shown in Figures 1 and 2 are the maximum and minimum values predicted using the model. The maximum represents the single-time-step maximum concentration during dry days at each model element, while the minimum represents the minimum single-time-step concentration during dry days. It can be seen from Figures 1 and 2 that the range of values (minimum to maximum) simulated using the model is comparable to the range of values observed in the measured data with the exception of the measured peak concentration in the channel. The modeled maximum concentration at the peak is below its observed counterpart.

The modeled maximum and average values for dry days shown in Figures 1 and 2 were also compared to the maximum concentrations for the entire time period considering both wet and dry days. In general, the maximum concentrations predicted by the model for the 3-year period were reduced when eliminating data from wet days, while the average concentrations did not change significantly.

Contributions from measured and estimated sources into the channel and from direct discharge and boundary conditions. The stakeholders requested that the project team prepare a summary of the 2378-TCDD contributions to the channel from point sources measured in the project and compare the result to the total contribution from sources for which a dioxin concentration was estimated instead of measured. Results are shown in Figure 3 and it can be seen that approximately two thirds of the load was based on measured data.

Additionally, the stakeholders requested a similar comparison between dioxin loads coming in from the tributaries via boundary conditions to those that are associated with direct discharges into the channel. The results are also shown in Figure 3 and it can be seen that approximately 60% of the load is from direct discharges with the remaining balance coming in from tributaries via a boundary condition to the model domain.

Methodology for Determining Dioxin Load Reductions. Determining the reductions needed for dioxins is complicated by the fact that the TEQ represents 17 different congeners, and by the complex interaction amongst the media involved: sediment, water and tissue. An approach is proposed here that develops a congener specific water quality target for the most prevalent of the 17 congeners in the HSC and that relies on site-specific bioaccumulation factors.

Water Quality Target. One of the key decisions to be made in the TMDL is the identification of the endpoint. Work completed as part of this project (see Final Report WO7 and Appendix II of this report) yielded recommended water- and sediment-based targets to be used in the dioxin TMDL. Recognizing that the TCEQ will need an in-stream water quality target with which to develop loading limits for permitting purposes, the proposed methodology consists of determining water quality targets for the congeners that contribute more than 1% to the total TEQ in tissue using site-specific bioaccumulation factors (BAFs) and suspended-dissolved partitioning relationships.

To develop congener-specific targets, the project team will use the Texas Department of State Health Services (DSHS) health-based tissue residue criterion (TRC) for total TEQ (0.47 ng/kg, calculated using the same risk assumptions employed by TCEQ in developing the standard). This is justified by the fact that the inclusion of the HSC segments in the §303(d) List was motivated by seafood consumption advisories.

The water quality targets for dissolved PCDD/Fs can be calculated from the TRC and the BAF from the following relationship:

$$C_{w,d} = \frac{TRC}{BAF} \qquad (1)$$

As mentioned in the Final Report for Work Order 7, while the tissue residue criterion is based on the TEQ, each of the congeners contributing to the dioxin TEQ has different physical and chemical properties and different bioaccumulation potentials. Thus, water quality targets for each of the major congeners contributing to the total equivalent concentration are desirable. However, no formal guidelines exist on developing targets for mixtures of compounds that contribute to an exceedance of a water quality criterion. In the absence of guidance, the project team proposes the following approach.

The fraction of the total TEQ in a sample attributable to a given congener f_i^{TEQ} can be calculated as:

$$f_i^{TEQ} = \frac{C_i * TEF_i}{\sum_{i=1}^{17} C_i * TEF_i} \qquad (2)$$

where C_i and TEF_i are the concentration and Toxic Equivalent Factor for congener i.

The water quality target for a given congener can be calculated using its average contribution to TEQ (f_i^{TEQ}) from the tissue samples collected between 2002 and 2005:

$$C_{w,d} = \frac{TRC * f_i^{TEQ}}{BAF_i * TEF_i} \qquad (3)$$

Individual targets for the six congeners contributing more than 1% to total TEQ in catfish are summarized in Table 1. It is noted that because BAFs were calculated from dissolved concentrations, the target concentrations obtained from equation 3 correspond to only the dissolved fraction. To calculate targets that apply to total water concentrations (dissolved+suspended), partitioning ratios calculated using the data collected between 2002 and 2005 were used. Table 1 includes targets derived using catfish data only since target concentrations obtained using crab data were higher and, thus, less conservative.

The water quality target for TEQ from the six major congeners was calculated to be 0.053 pg/L. This target translates to a water quality target for total TEQ of 0.064 pg/L, which is about 70% of the existing standard for dioxin in marine waters. This lower target will be necessary to ensure that reductions in loading will result in TRC concentrations that will allow the DSHS to lift the seafood consumption advisory for the Houston Ship Channel.

Modeling Approach. The WASP model for 2378-TCDD that has been developed and calibrated to data collected between 2002 and 2005 thus far will be used to model each of the five additional congeners that contribute more than 1% of the TEQ in tissue (12378-PeCDD, 123678-HxCDD, 2378-TCDF, 23478-PeCDF, and 123678-HxCDF).

A spreadsheet that summarizes average model concentrations and their resulting loads on a water quality segment basis for the various congeners will be developed. The results of the individual congeners will be linked together and compared to the allowable load calculated using the 0.053 pg/L target to determine the required load reductions. It should be noted, however, that this method assumes that a given source reduction will result in equivalent reductions for all the congeners.

TASK 3 PARTICIPATING IN STAKEHOLDER INVOLVMENT WITH THE DIOXIN TMDL PROJECT

A stakeholder meeting was held on April 5, 2007. A presentation was made to the stakeholders (see Appendix I). Comments were received from the stakeholders on the progress that was presented and these comments were addressed in the past quarter and are included in this report.

TASK 4 TMDL ALLOCATIONS

The recalibrated model for 2378-TCDD was used to evaluate various loading scenarios, including scenarios with only one source at a time. A summary of results is shown in Figure 4. The results shown in Figure 4 indicate that the sediment is the main contributor to the observed concentrations in the Channel. Removing sediment loading in 1006 and/or 1001 results in significant reductions and eliminating sediment loads entirely (point sources, runoff, and direct deposition are the only sources of dioxin to the HSC) allows the water quality target calculated for 2378-TCDD (0.022 pg/L – see discussion on Task 2 for a description of this value) to be met at all locations.

Table 1. Water Quality Target for the Selected Six Congeners

Congener	**Texas TEF**	**Average log BAF**[a]	**Average contribution to TEQ**[b]	**Water Quality Target - Diss (pg/L)**[c]	**Average log Kp**[d]	**Average contribution to TEQ in water**	**Average contribution to TEQ in sediment**	**Water Quality Target - Total (pg/L)**[e]
2378-TCDD	1	5.10	80.3%	0.0030	5.38	46.6%	51.7%	0.022
12378-PeCDD	0.5	4.78	4.5%	0.0007	5.40	5.3%	6.4%	0.005
123678-HxCDD	0.1	4.57	1.4%	0.0018	5.49	5.3%	4.4%	0.016
2378-TCDF	0.1	3.49	2.1%	0.0319	5.31	15.4%	14.3%	0.201
23478-PeCDF	0.5	4.60	6.5%	0.0015	5.32	8.4%	9.5%	0.010
123678-HxCDF	0.1	4.45	1.4%	0.0023	5.47	2.3%	1.5%	0.020
$\Sigma\ \text{TEQ}_{\text{major congeners}}$[f]			96.2%	0.0077		83.2%	87.7%	0.053
Total TEQ[g]								0.064

[a] Average of the logaritms of the catfish/dissolved ratios for samples collected in this project. Note that these values were updated from those presented in Table 4.10 of Final Report WO7.

[b] Average contribution of each congener to TEQ in catfish, similar contributions were obtained when using crab data

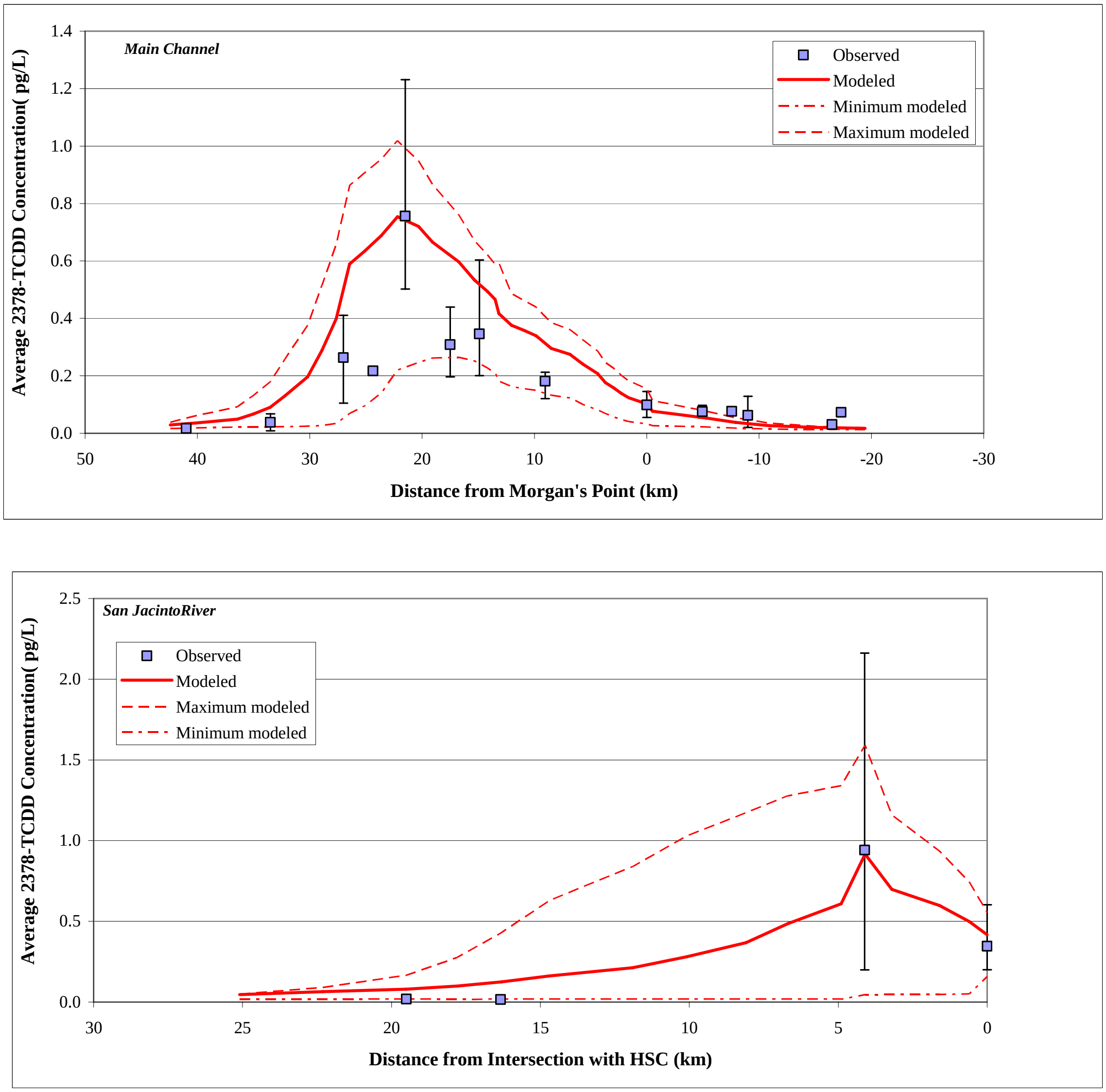
[c] Calculated using equation 3

[d] Average of the logaritms of the suspended/dissolved ratios for each of the water samples

[e] Dissolved + Suspended concentrations. Suspended concentrations are calculated as $C_{diss}*10^{\log Kp}*TSS_{average.}$ $TSS_{average}$ is 26 mg/L

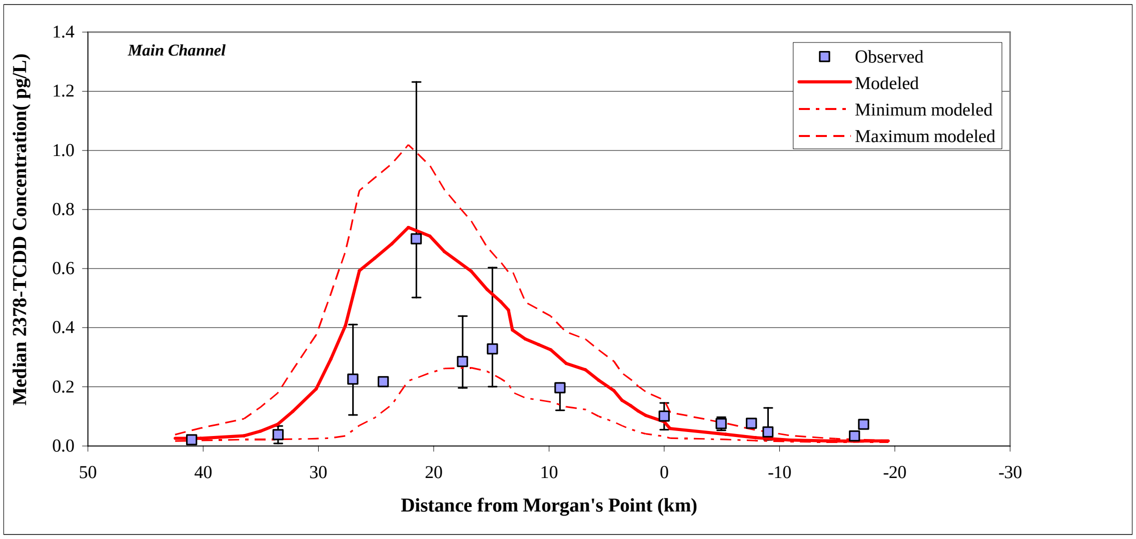
[f] $\Sigma\ \text{TEQ}_{\text{major congeners}} = (\Sigma\ \text{Target}_i*\text{TEF}_i)$ for the six major congeners

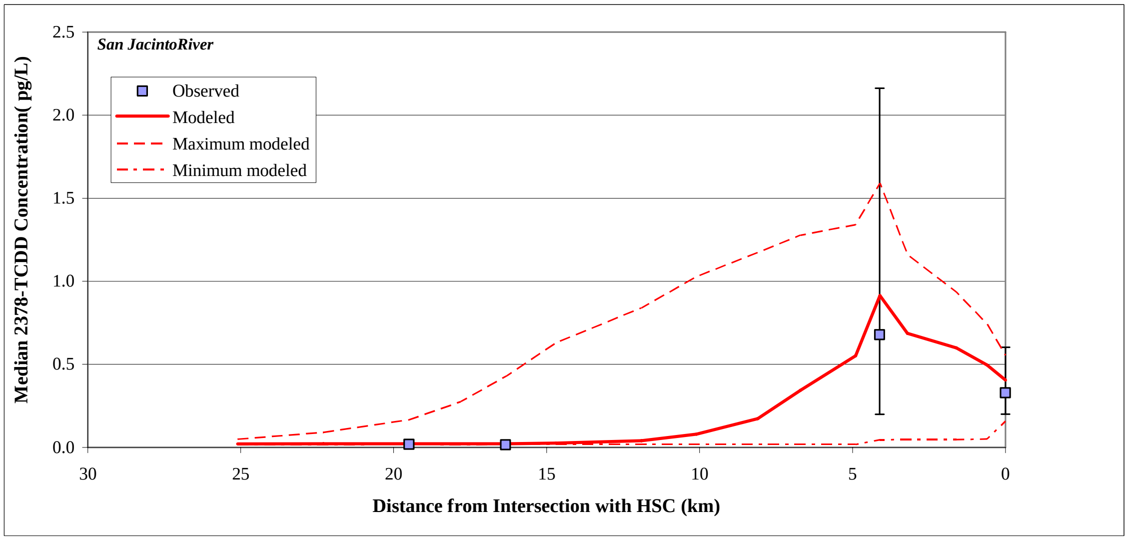
[g] Total TEQ target = Σ TEQmajor congeners/total contribution of the six congeners to TEQ in water = 0.053/0.832



Error bars denote the range of measured concentrations.
Maximum and minimum lines represent the *single-time-step* *max and min concentrations during dry days at each model segment.*

Figure 1. Modeled and Observed 2378-TCDD Concentrations (Averages)





Error bars denote the range of measured concentrations.
Maximum and minimum lines represent the *<u>single-time-step</u>* *max and min concentrations during dry days at each model segment.*

Figure 2. Modeled and Observed 2378-TCDD Concentrations (Medians)

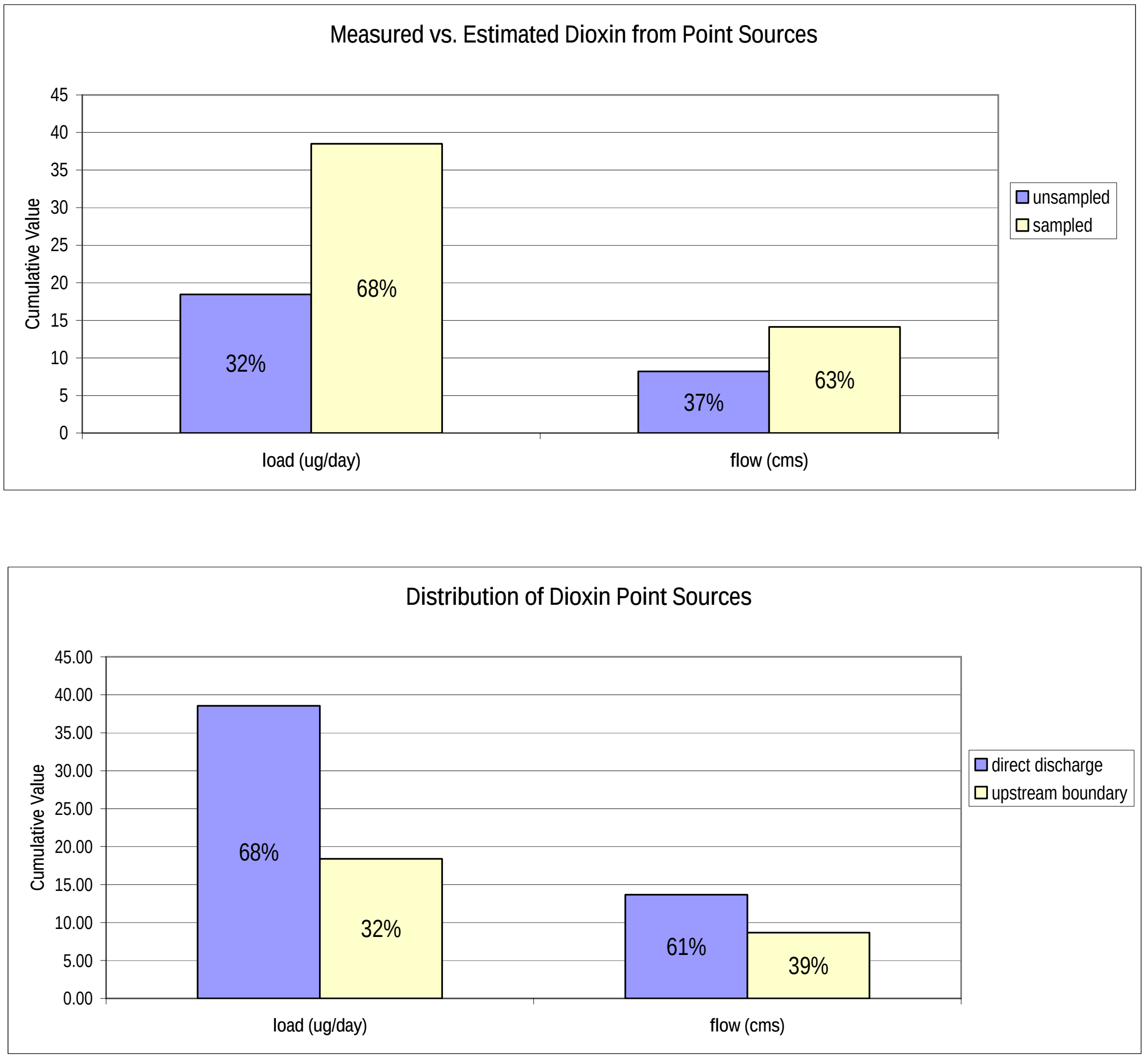
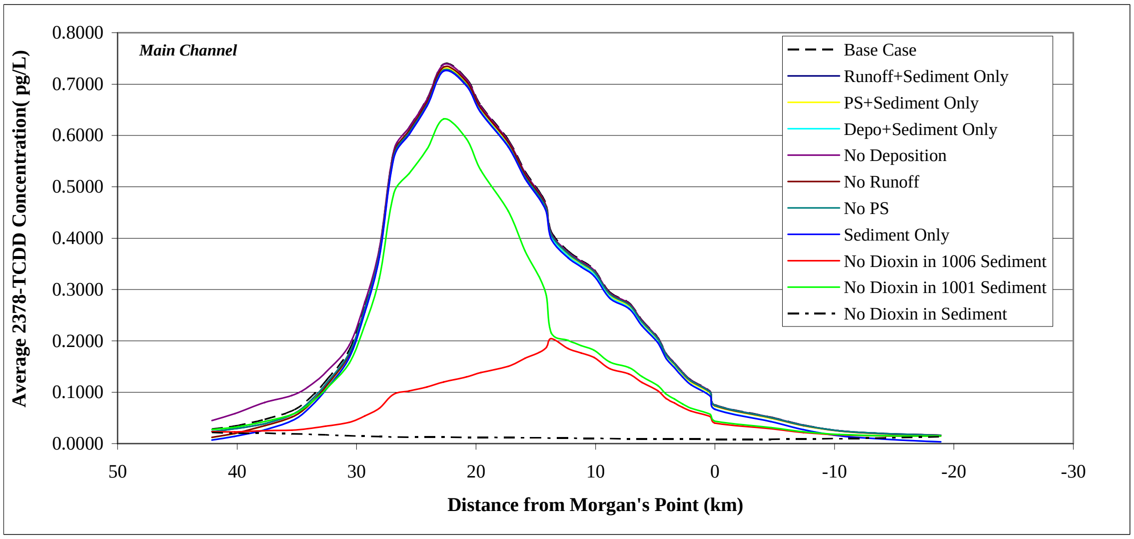


Figure 3. 2378-TCDD Loading from Point Sources



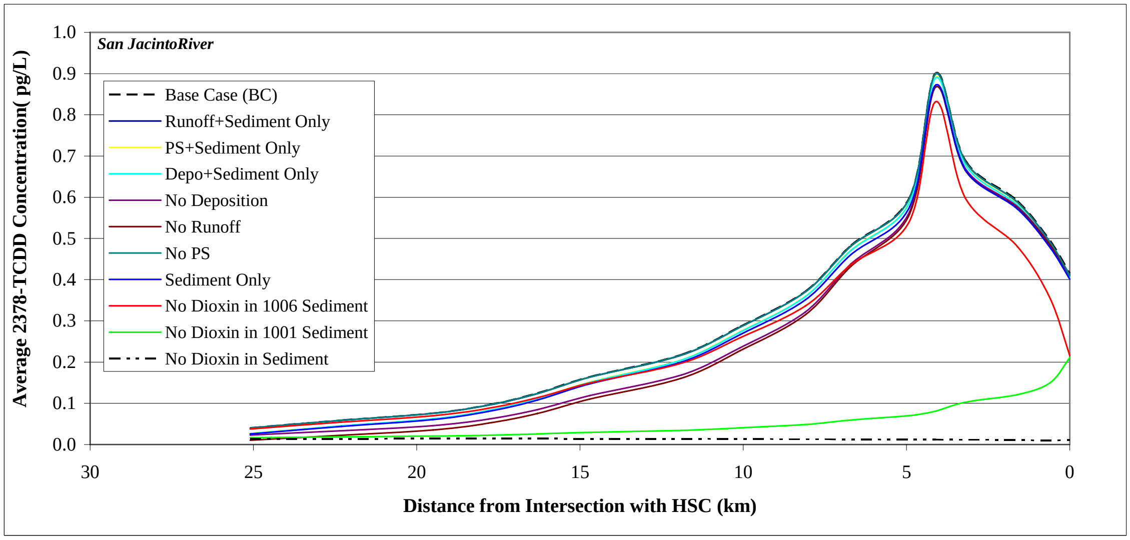
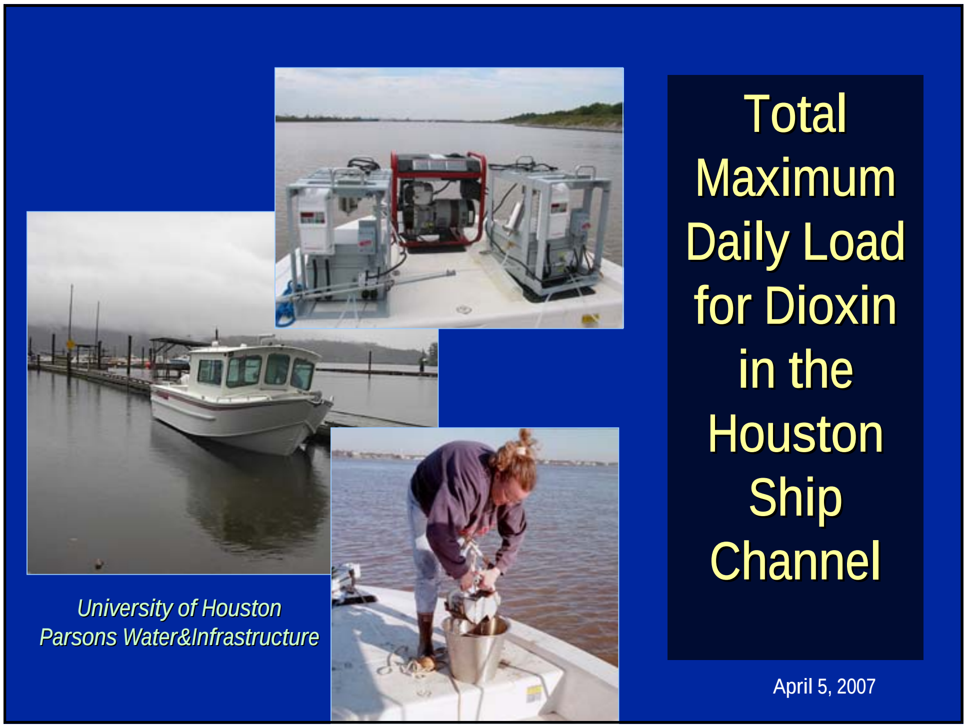


Figure 4. 2378-TCDD Load Scenarios

APPENDIX I

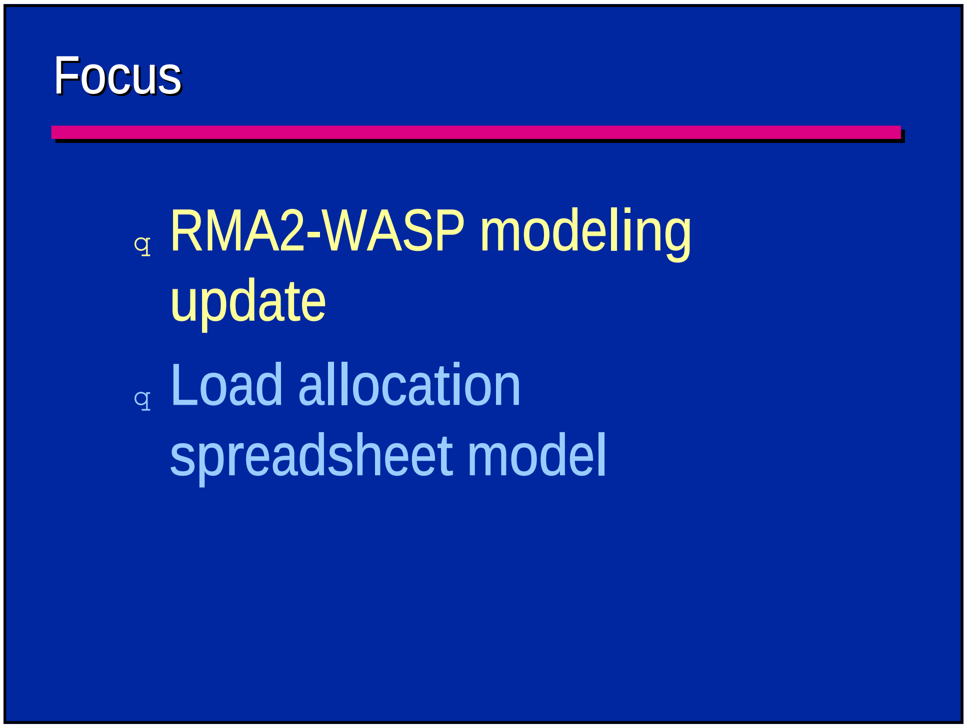
SLIDES FROM APRIL 5, 2007 STAKEHOLDER MEETING



Total Maximum Daily Load for Dioxin in the Houston Ship Channel

University of Houston
Parsons Water&Infrastructure

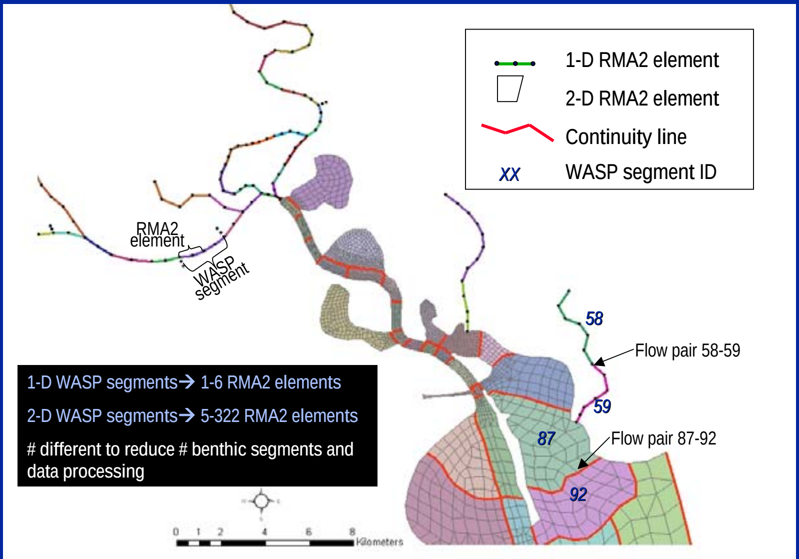
April 5, 2007



Focus

- RMA2-WASP modeling update
- Load allocation spreadsheet model

RMA2-WASP segmentation



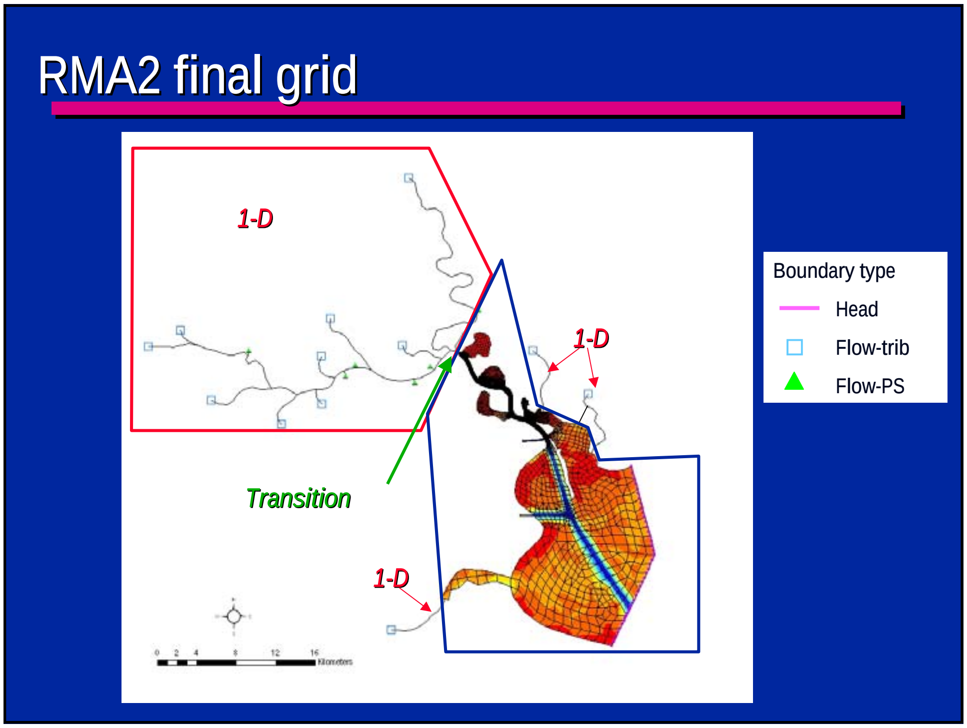
1-D WASP segments→ 1-6 RMA2 elements

2-D WASP segments→ 5-322 RMA2 elements

different to reduce # benthic segments and data processing

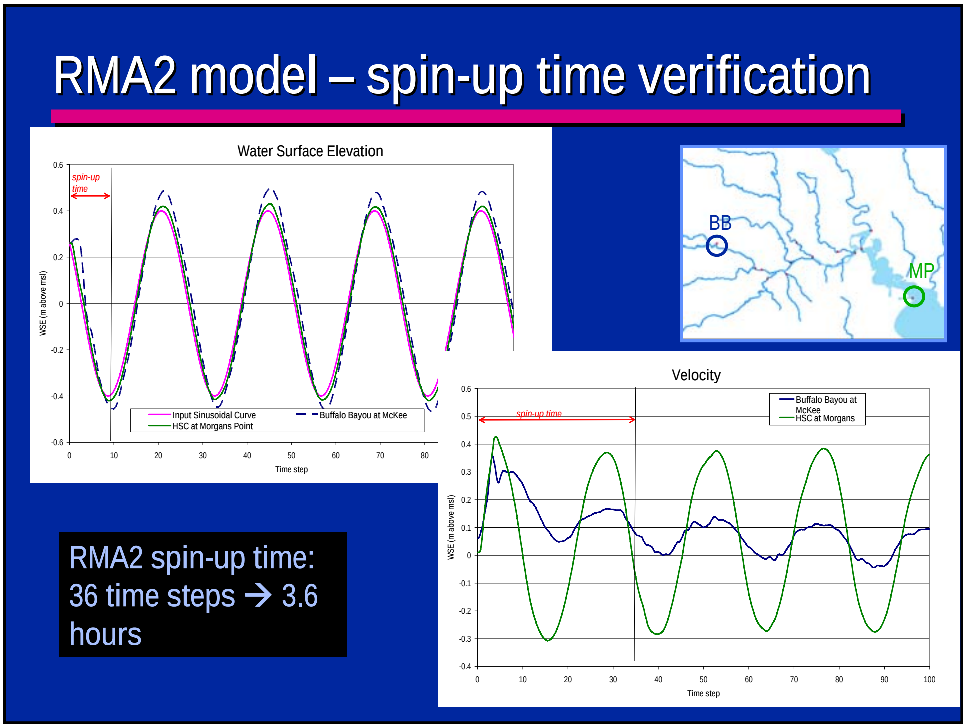
RMA2 Update

- Added segment to simulate flow out of the model domain at Cedar Bayou
- Verified spin-up time
- Completed 3-year runs with 30 minute time steps



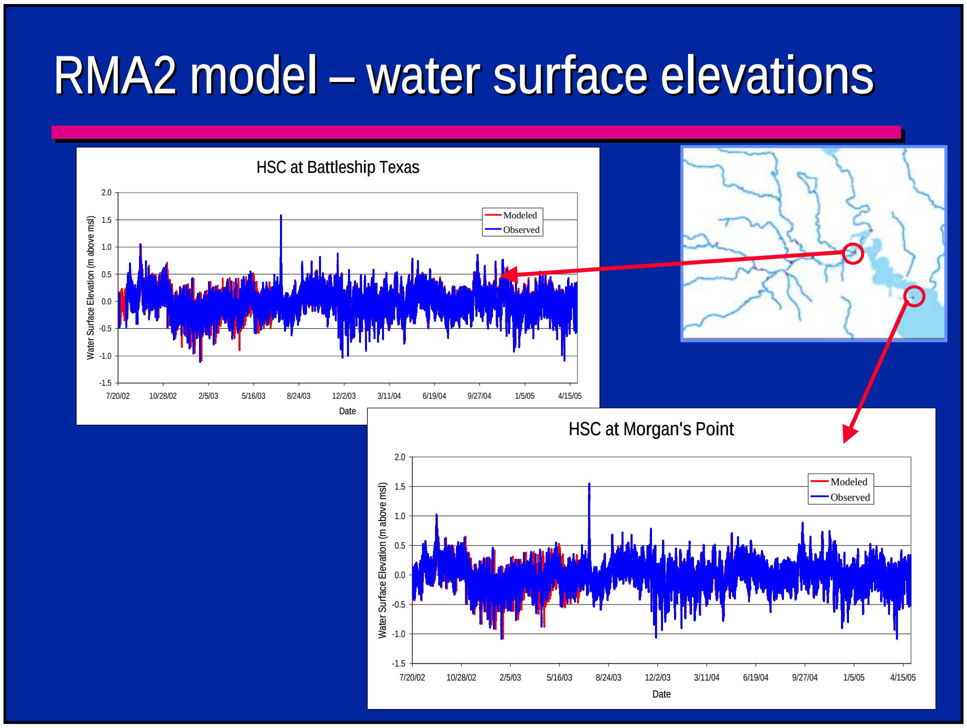
RMA2 final grid

Boundary type
- Head
- Flow-trib
- Flow-PS

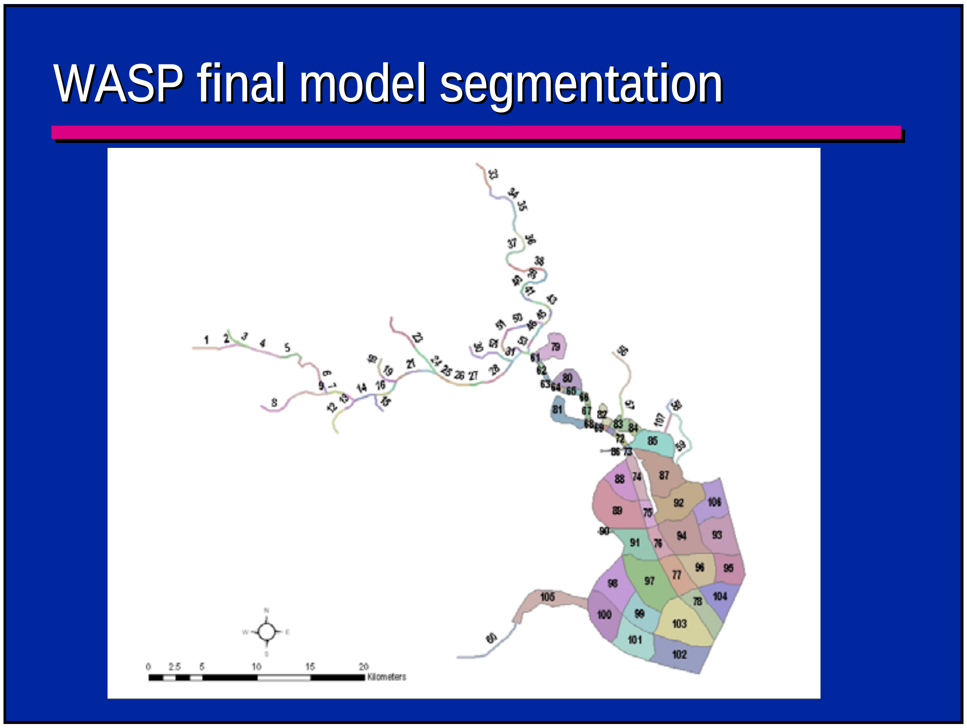


RMA2 model – spin-up time verification

RMA2 spin-up time:
36 time steps → 3.6 hours

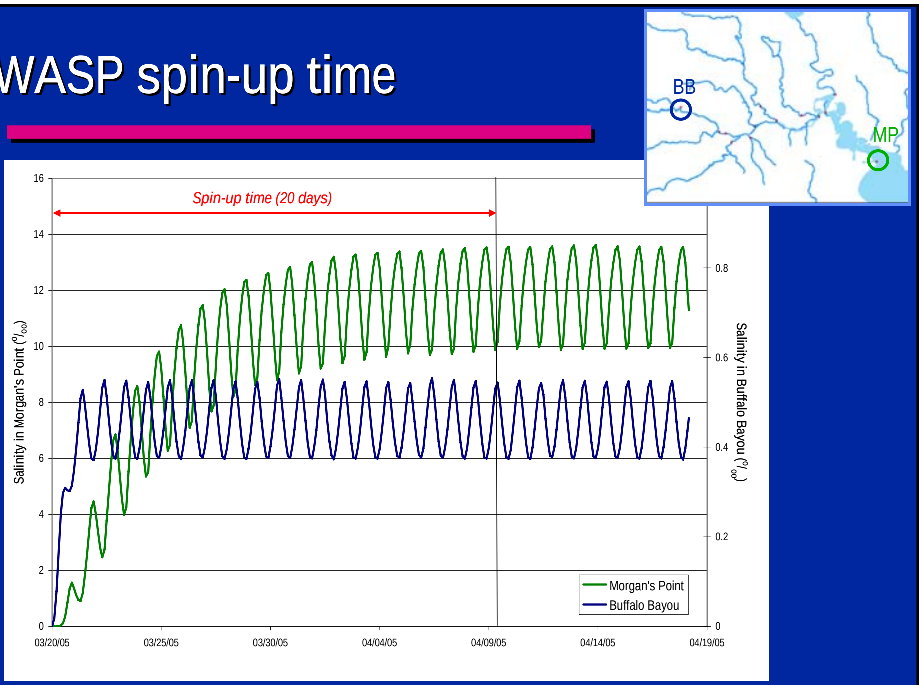


RMA2 model – water surface elevations

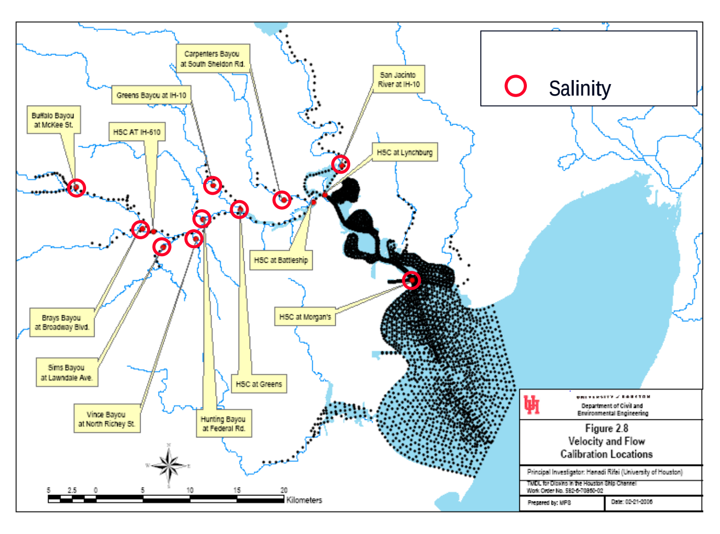


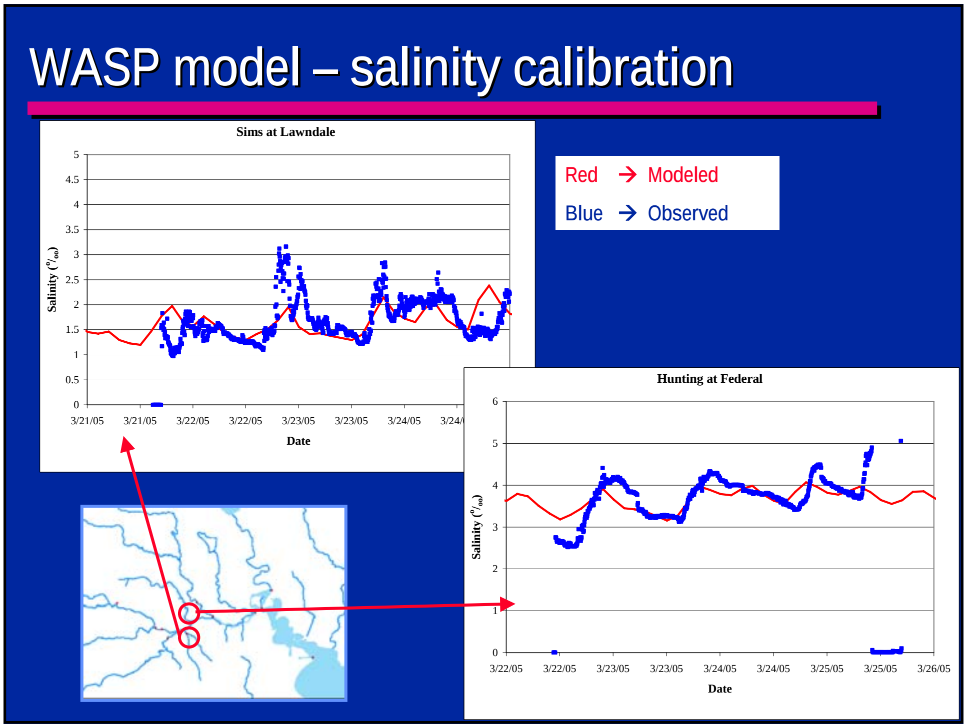
WASP final model segmentation

WASP spin-up time



Salinity model – calibration locations

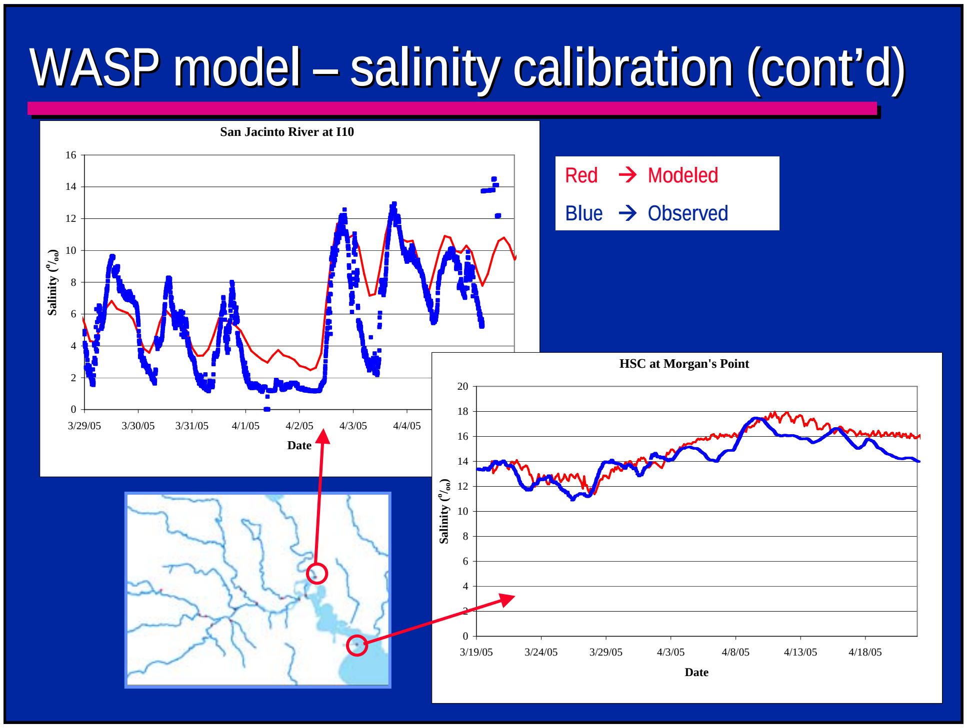




WASP model – salinity calibration

Red → Modeled

Blue → Observed



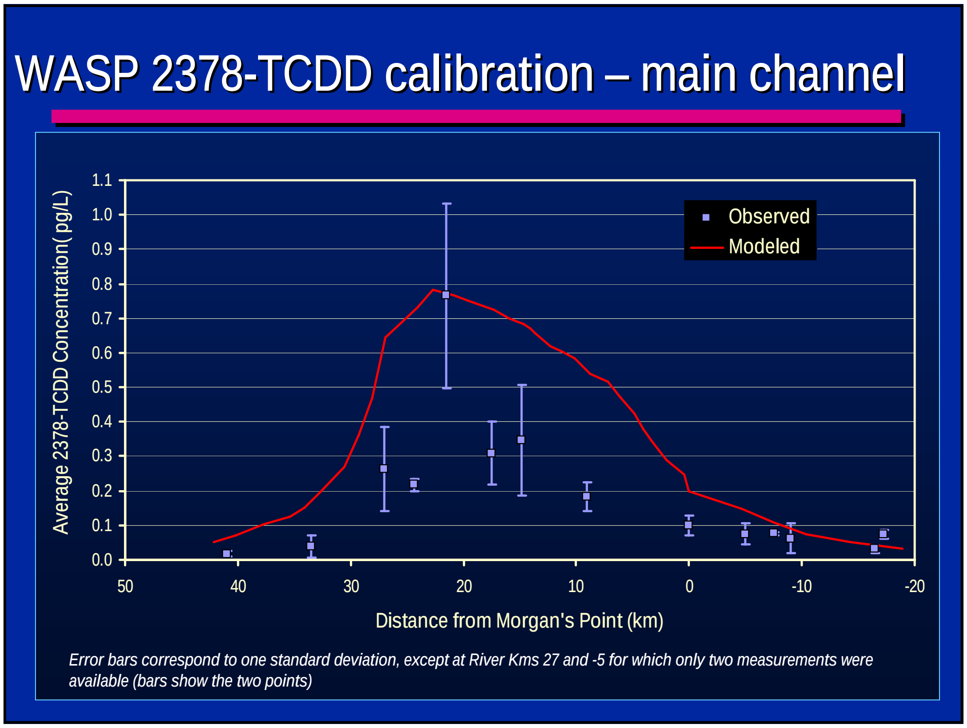
WASP model – salinity calibration (cont'd)

Red → Modeled

Blue → Observed

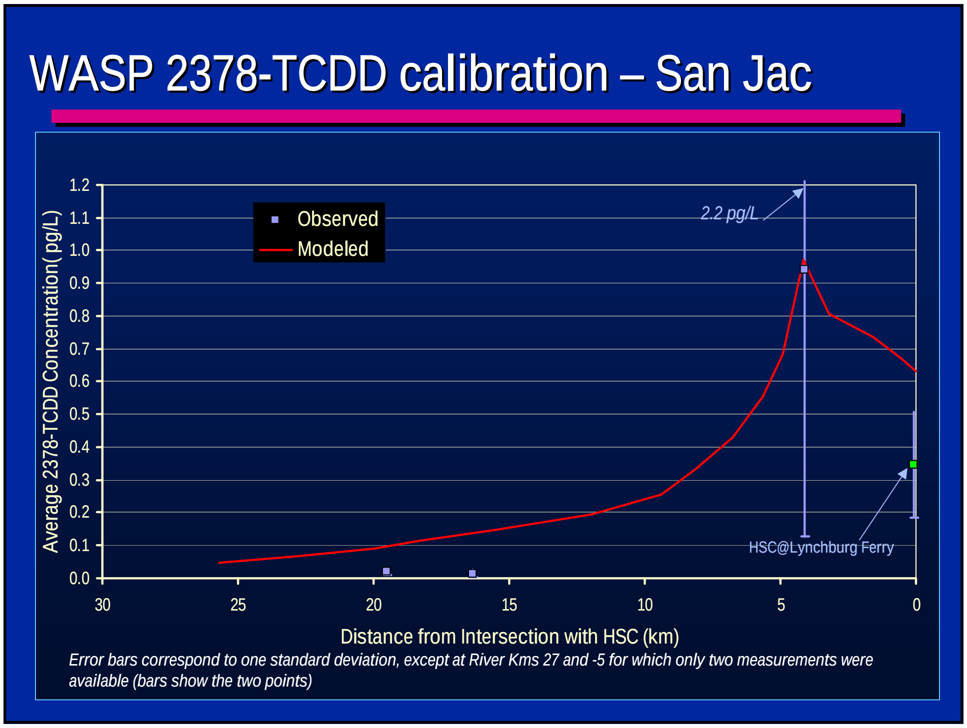
WASP 2378-TCDD model (2002-2005)

- Stormwater runoff and PS discharging u/s model segments: $Q_{\text{USGS gage}}$*Concentration. Concentration was determined as follows:
  - Dry days: (Load from PS)/Flow at USGS gage
  - Rainy days: (Runoff load + PS load)/Flow at USGS gage
- PS loads for direct discharges to WASP segments: $Q_{\text{self-reported}}$*Concentration
- Stormwater runoff discharging directly to WASP segments: Flow*Avg runoff concentration (0.017 pg/L). Flows determined using NCRS Method
- Direct deposition: deposition flux*area (rainy days → wet flux, dry days → dry flux)



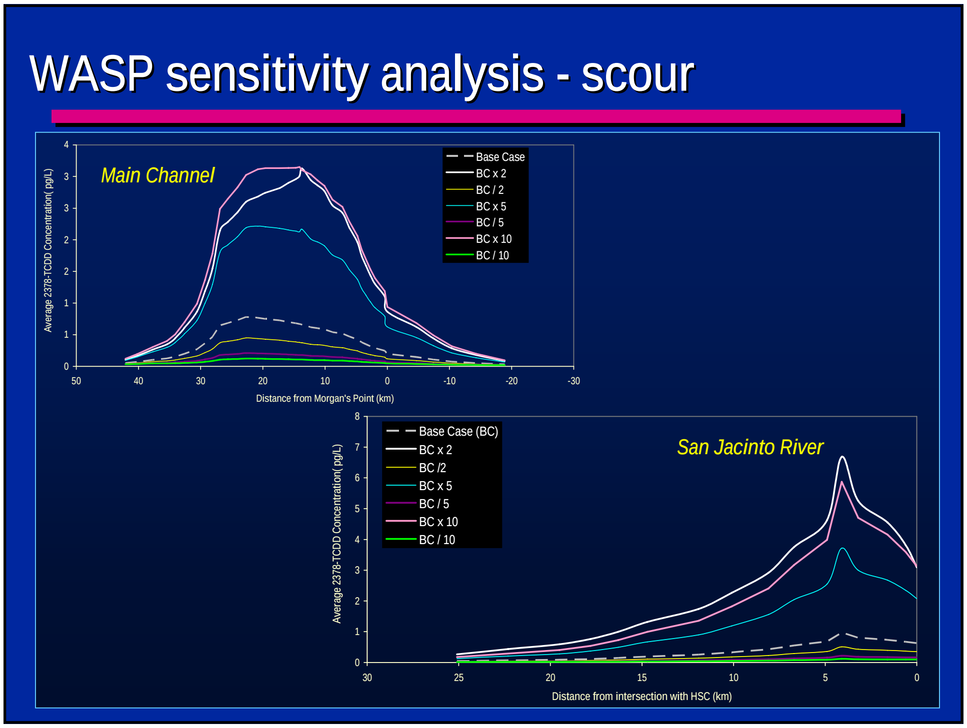
WASP 2378-TCDD calibration – main channel

Error bars correspond to one standard deviation, except at River Kms 27 and -5 for which only two measurements were available (bars show the two points)

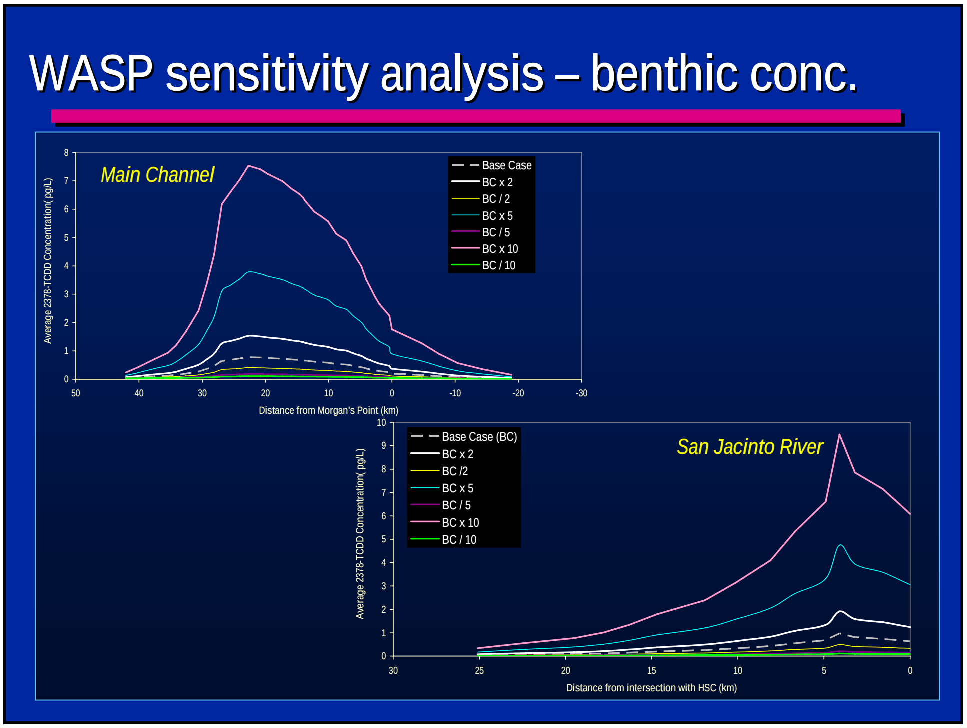


WASP 2378-TCDD calibration – San Jac

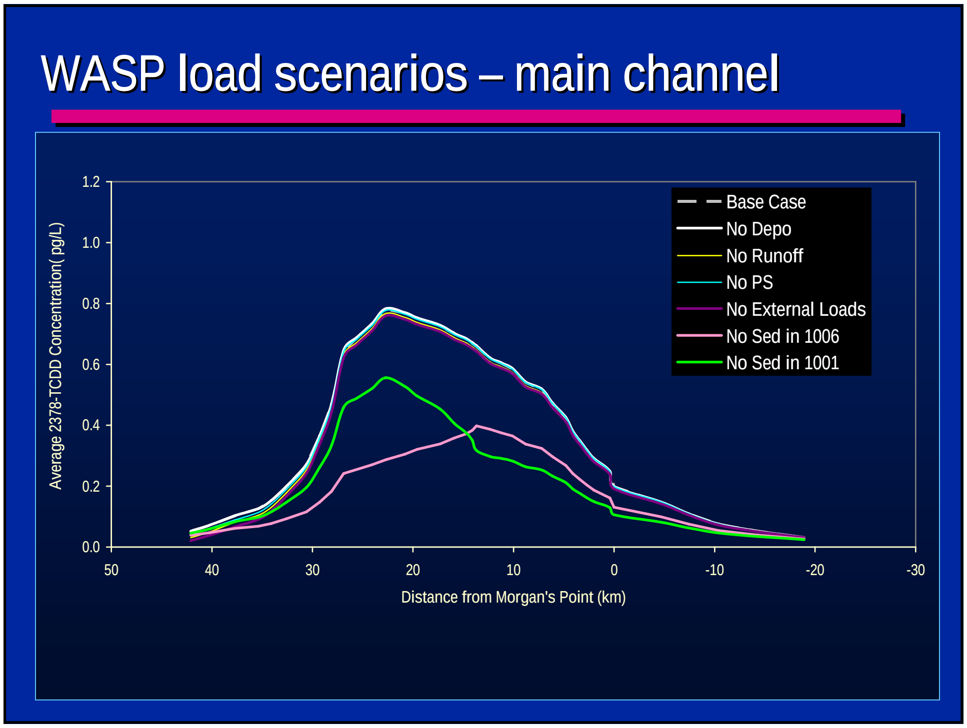
Error bars correspond to one standard deviation, except at River Kms 27 and -5 for which only two measurements were available (bars show the two points)



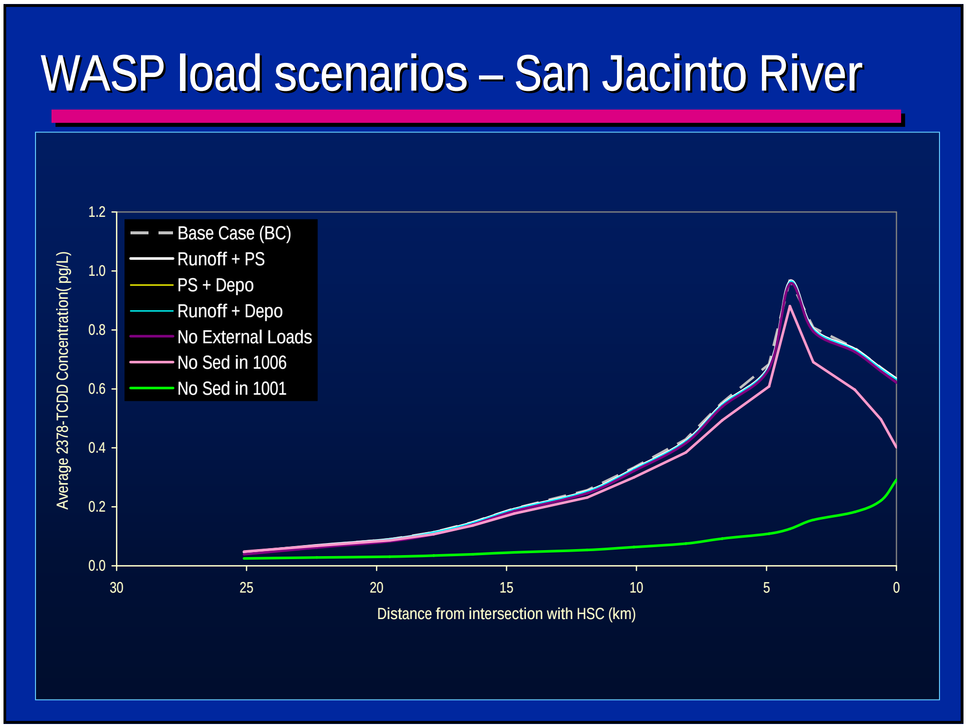
WASP sensitivity analysis - scour



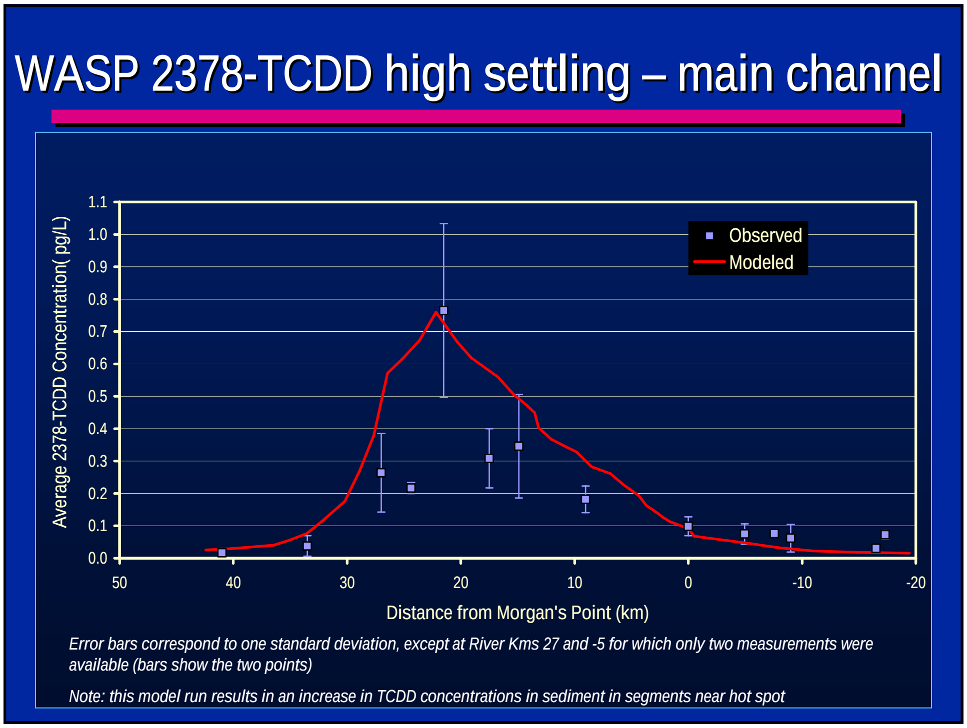
WASP sensitivity analysis – benthic conc.



WASP load scenarios – main channel



WASP load scenarios – San Jacinto River

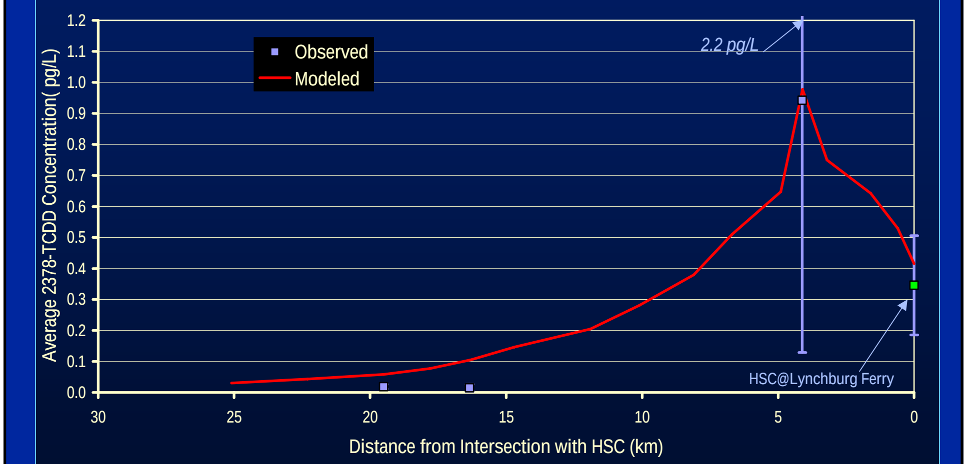


WASP 2378-TCDD high settling – main channel

Error bars correspond to one standard deviation, except at River Kms 27 and -5 for which only two measurements were available (bars show the two points)

Note: this model run results in an increase in TCDD concentrations in sediment in segments near hot spot

WASP 2378-TCDD high settling – San Jac



Error bars correspond to one standard deviation, except at River Kms 27 and -5 for which only two measurements were available (bars show the two points)

Note: this model run results in an increase in TCDD concentrations in sediment in segments near hot spot

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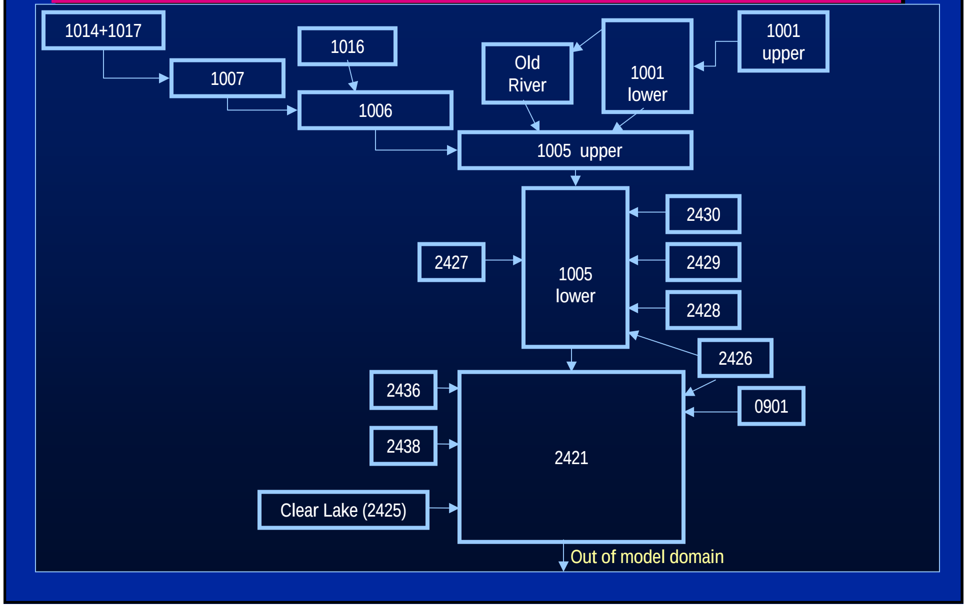
Load allocation spreadsheet model

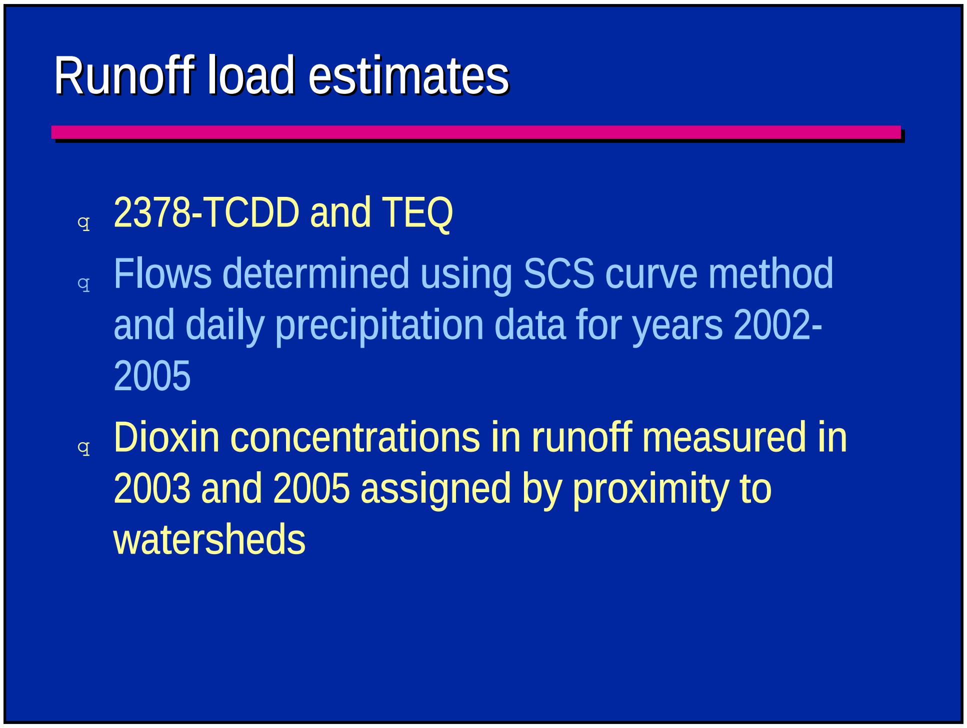
HSC spreadsheet segment structure



1014+1017
1007
1016
1006
Old River
1001 lower
1001 upper
1005 upper
2427
1005 lower
2430
2429
2428
2426
2436
2438
Clear Lake (2425)
2421
0901
Out of model domain

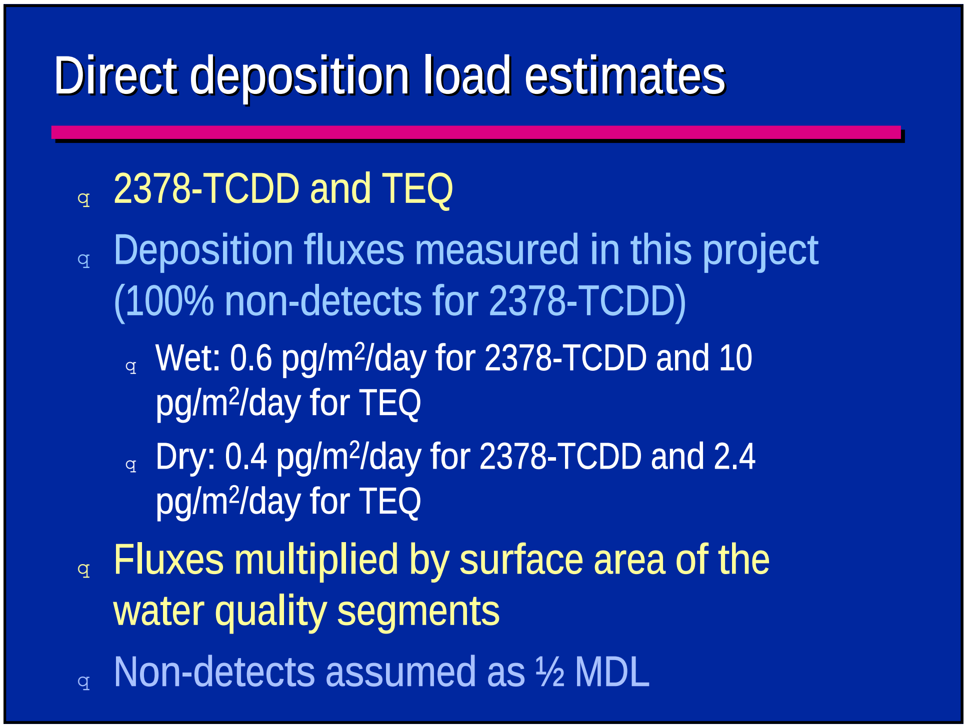
Point source load estimates

- 2378-TCDD and TEQ
- 5-year average of self-reported flows
- Dioxin concentrations
    - If effluent sampled in 2003, measured concentration
    - If only sludge measured in 2002, used sludge-effluent regression
    - If PS not sampled, average concentration for SIC code



Runoff load estimates

- 2378-TCDD and TEQ
- Flows determined using SCS curve method and daily precipitation data for years 2002-2005
- Dioxin concentrations in runoff measured in 2003 and 2005 assigned by proximity to watersheds



Direct deposition load estimates

- 2378-TCDD and TEQ
- Deposition fluxes measured in this project (100% non-detects for 2378-TCDD)
  - Wet: 0.6 pg/m^2/day for 2378-TCDD and 10 pg/m^2/day for TEQ
  - Dry: 0.4 pg/m^2/day for 2378-TCDD and 2.4 pg/m^2/day for TEQ
- Fluxes multiplied by surface area of the water quality segments
- Non-detects assumed as ½ MDL

In-stream load estimates

- 2378-TCDD and TEQ
- Net flow out of each segment (average of flows simulated for the period 07/2002 to 04/2005 at downstream end of segments)
- Average water concentrations at locations where flow was measured
- Load for a given segment is load out of the segment minus load from upstream segments

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Load spreadsheet – preliminary mass balance (TCDD)

Segment	In-stream load[a]	Source Loads (ng/day)			
		Point Sources	Stormwater Runoff	Direct deposition	Unaccounted[b]
1014+1017	17,937	3,294	60,117	165	-45,639
1007	913,848	30,407	44,010	1,611	837,819
1016	46,762	1,440	16,757	92	28,473
1006	2,331,415	13,564	4,255	1,367	2,312,230
1001 upper	222,001	1,890	249,779	719	-30,387
1001 lower	11,005,048	525	244	305	11,003,973
1005 upper	-7,707,187	134	62	385	
Old River	1,149[c]	0	463	312	374
2430	676	0	176	1,848	-1,347
2429	653	46	539	1,410	-1,343
2428	38	-	111	501	-575
2427	2,329	610	878	1,463	-622
2426	39,154	521	2,734	1,280	34,620
2436	38	39	72	90	-164
1005 lower	-4,019,124	2,112	452	2,499	
2438	0	1,074	32	69	-1,175
2421	207,974	631	1,545	87,948	117,850
901	13,903	643	3,437	102	9,722
Clear Lake	1,578[c]	-	5,679	3,393	-7,494

[a] Average concentration measured in 2002-2004 times modeled net flow out of segment

[b] Difference between in-stream load and the sum of loads from PS, runoff, and direct deposition

[c] No dioxin data are available, thus, values are rough estimates

Non-detects assumed equal to 1/2MDL for load calculations

Load spreadsheet – preliminary mass balance (TEQ)

Segment	In-stream load[a]	Source Loads (ng/day)			
		Point Sources	Stormwater Runoff	Direct deposition	Unaccounted[b]
1014+1017	154,909	10,983	518,096	939	-375,109
1007	1,282,711	154,986	375,338	9,195	743,193
1016	202,633	4,798	186,102	526	11,208
1006	3,226,564	115,829	53,378	7,901	3,049,457
1001 upper	935,748	14,236	2,127,661	4,149	-1,210,298
1001 lower	15,096,421	5,263	3,092	1,742	15,086,324
1005 upper	-9,623,786	3,888	778	2,207	
Old River	4,742[c]	0	5,860	1,794	-2,912
2430	1,167	0	2,220	10,546	-11,599
2429	1,068	546	6,820	8,108	-14,405
2428	112	-	1,408	2,883	-4,178
2427	3,442	1,975	11,107	9,111	-18,751
2426	73,570	2,310	38,094	7,355	25,810
2436	60	382	911	509	-1,742
1005 lower	-5,725,072	7,467	5,717	14,302	
2438	1	3,571	408	386	-4,364
2421	1,061,624	2,097	19,545	501,383	538,598
901	30,819	4,601	43,448	587	-17,817
Clear Lake	13,624[c]	-	71,824	19,563	-77,763

[a] Average concentration measured in 2002-2004 times modeled net flow out of segment

[b] Difference between in-stream load and the sum of loads from PS, runoff, and direct deposition

[c] No dioxin data are available, thus, values are rough estimates

Non-detects assumed equal to 1/2MDL for load calculations

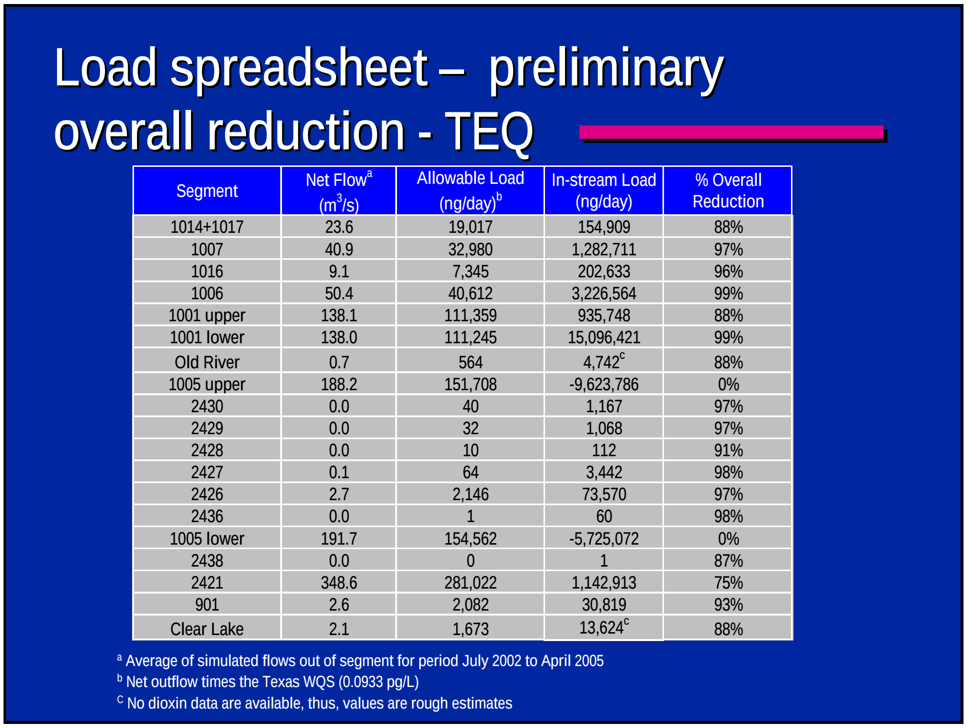
Load spreadsheet – preliminary overall reduction - TCDD

Segment	Net Flow[a] (m^3/s)	Allowable Load (ng/day)[b]	In-stream Load (ng/day)	% Overall Reduction
1014+1017	23.6	8,862	17,937	51%
1007	40.9	15,369	913,848	98%
1016	9.1	3,423	46,762	93%
1006	50.4	18,925	2,331,415	99%
1001 upper	138.1	51,893	222,001	77%
1001 lower	138.0	51,840	11,005,048	100%
Old River	0.7	263	1,149[c]	77%
1005 upper	188.2	70,696	-7,707,187	0%
2430	0.0	19	676	97%
2429	0.0	15	653	98%
2428	0.0	5	38	88%
2427	0.1	30	2,329	99%
2426	2.7	1,000	39,154	97%
2436	0.0	0	38	99%
1005 lower	191.7	72,026	-4,019,124	0%
2438	0.0	0	0	75%
2421	348.6	130,956	207,974	37%
901	2.6	970	13,903	93%
Clear Lake	2.1	779	1,578[c]	51%

[a] Average of simulated flows out of segment for period July 2002 to April 2005

[b] Net outflow times the Texas WQS (0.0933 pg/L) times the average contribution of TCDD to TEQ in water (46.6%)

[C] No dioxin data are available, thus, values are rough estimates



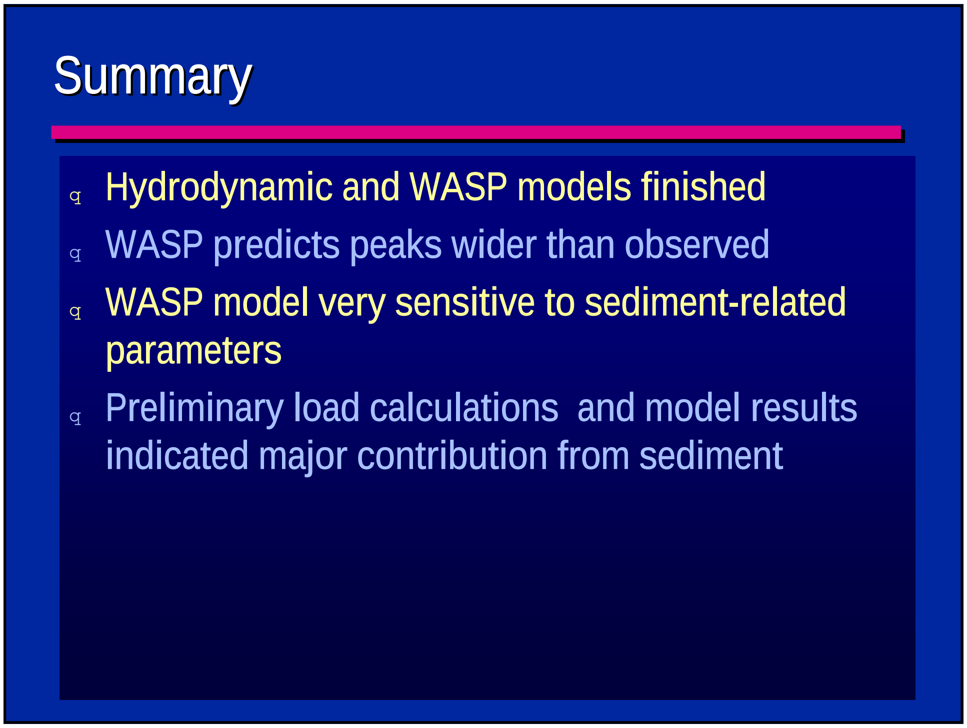
Load spreadsheet – preliminary overall reduction - TEQ

Segment	Net Flow[a] (m^3/s)	Allowable Load (ng/day)[b]	In-stream Load (ng/day)	% Overall Reduction
1014+1017	23.6	19,017	154,909	88%
1007	40.9	32,980	1,282,711	97%
1016	9.1	7,345	202,633	96%
1006	50.4	40,612	3,226,564	99%
1001 upper	138.1	111,359	935,748	88%
1001 lower	138.0	111,245	15,096,421	99%
Old River	0.7	564	4,742[c]	88%
1005 upper	188.2	151,708	-9,623,786	0%
2430	0.0	40	1,167	97%
2429	0.0	32	1,068	97%
2428	0.0	10	112	91%
2427	0.1	64	3,442	98%
2426	2.7	2,146	73,570	97%
2436	0.0	1	60	98%
1005 lower	191.7	154,562	-5,725,072	0%
2438	0.0	0	1	87%
2421	348.6	281,022	1,142,913	75%
901	2.6	2,082	30,819	93%
Clear Lake	2.1	1,673	13,624[c]	88%

[a] Average of simulated flows out of segment for period July 2002 to April 2005

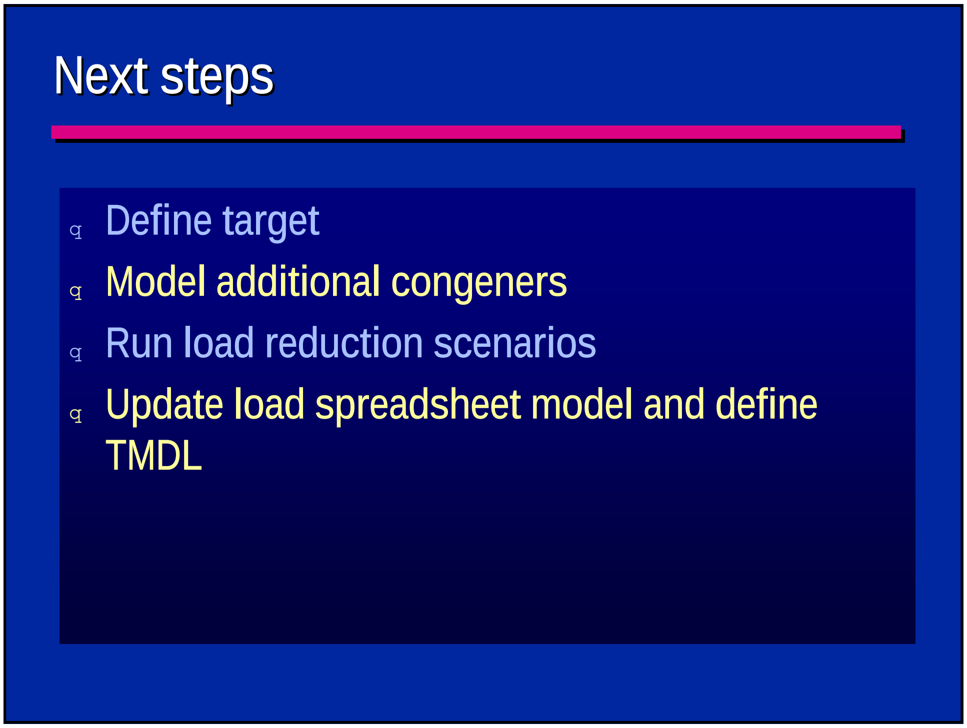
[b] Net outflow times the Texas WQS (0.0933 pg/L)

[C] No dioxin data are available, thus, values are rough estimates



Summary

- Hydrodynamic and WASP models finished
- WASP predicts peaks wider than observed
- WASP model very sensitive to sediment-related parameters
- Preliminary load calculations and model results indicated major contribution from sediment



Next steps

- Define target
- Model additional congeners
- Run load reduction scenarios
- Update load spreadsheet model and define TMDL

APPENDIX II

Bioaccumulation Factor Analysis from WO7 Final Report

CHAPTER 4

DATA ANALYSIS

4.1 SITE-SPECIFIC BIOACCUMULATION FACTORS AND WATER QUALITY TARGETS

4.1.1 Development of Site-specific Bioaccumulation Factors

The BAF is defined by the USEPA (2003) as the ratio (in liters per kilogram of tissue) of the concentration of a chemical in the tissue of an aquatic organism to its concentration in water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time. As is typical, in this project only the dissolved concentration in water, rather than the total water concentration (including the chemical associated with suspended particulate and colloidal material), was used in calculating the BAF.

$$BAF = \frac{C_{tissue}}{C_{water,diss}} \tag{4.1}$$

Because BAFs have been shown to vary in direct proportion to the lipid content of the tissue (USEPA 2003), the lipid-normalized tissue concentration is often used in lieu of the total tissue concentration in calculating a BAF. These BAFs are called lipid-normalized BAFs or BAF$_l$

$$BAF_l = \frac{C_{tissue} / F_{lipid}}{C_{water,diss}} \tag{4.2}$$

where F_{lipid} is the lipid fraction of the tissue by weight.

BAFs for catfish and crabs were calculated for each of the paired water and tissue samples collected in the spring, summer, and fall seasons from 2002 through 2004. Each fish or crab sample was a composite tissue sample from 3 to 5 animals. Because lipid normalization increased the variability in the BAF relationships, and the lipid measurement method used was imprecise, all BAFs were based on whole tissue concentrations and were not lipid-normalized. An effort was made to collect the fish, crab, and water samples from a given station on the same day. However, in practice this proved difficult and the samples from various media for a station were often collected several days apart.

BAFs[4] for PCDD/F congeners measured in 111 catfish and water samples from the HSC system are shown in Figure 4.1, and those measured in 106 blue crab and water samples are shown in Figure 4.2. BAFs varied widely both among and between congeners. The individual log BAF patterns are similar between catfish and crabs, indicating the importance of chemical properties in controlling BAFs. However, on average the BAFs for crabs were lower than those in fish for most congeners. For the dioxin congeners, a systematic decline in BAF with increasing hydrophobicity (as indicated by size and chlorination) was evident, which is consistent with independent observations that for very hydrophobic chemicals such as the larger PCDD/Fs, dietary uptake efficiencies decline with increasing hydrophobicity (Opperhuizen and Sijm 1990; Gobas et al. 1988). This pattern was not evident to the same extent in the furan congeners.

More importantly, and for a given congener, the log BAFs vary over a wide range. Possible factors accounting for the variability include seasonality, spatial factors, tissue properties

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[4] BAFs were calculated as the ratio of the tissue concentration to the dissolved concentration for each individual data point.

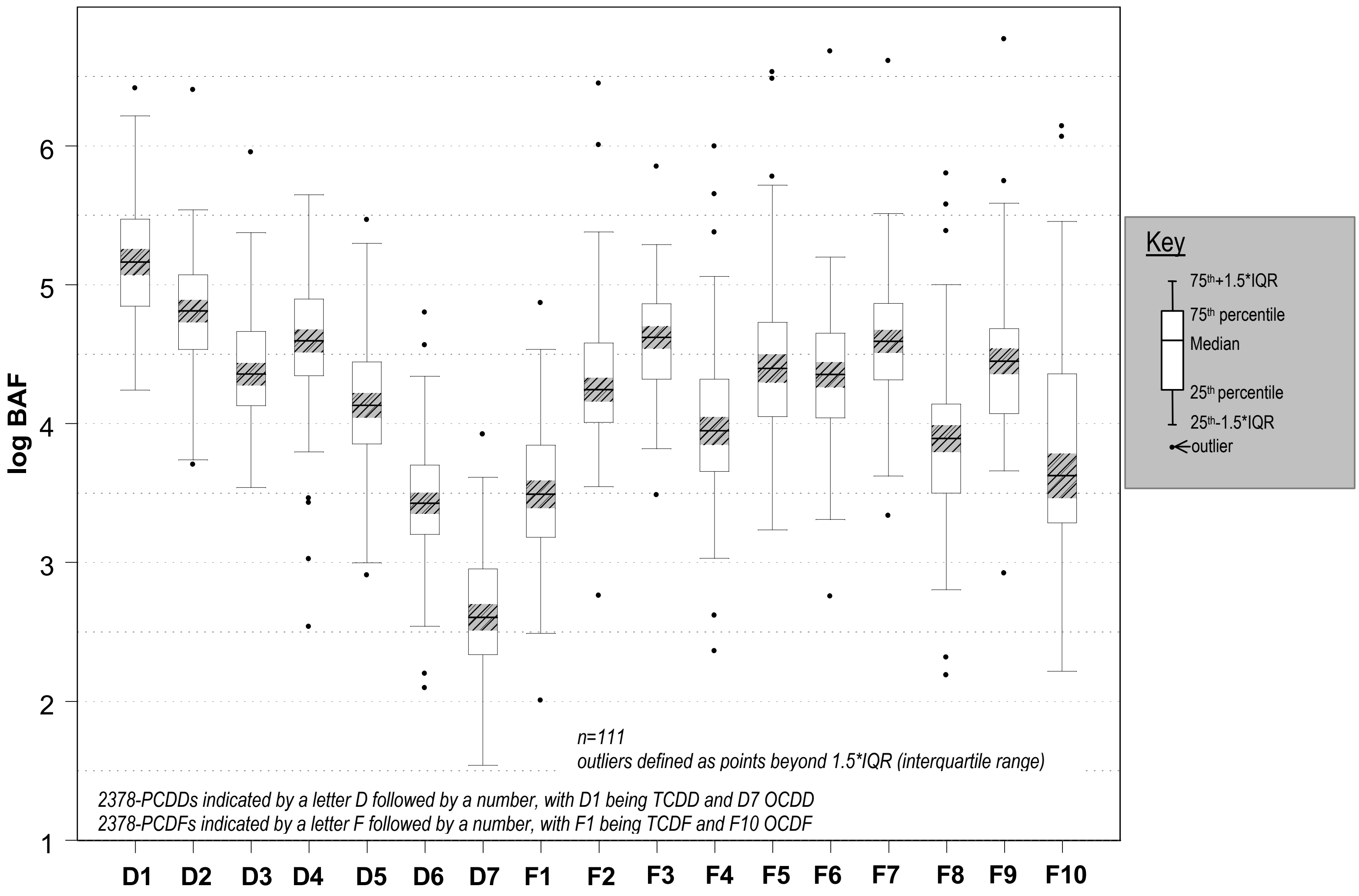

Figure 4.1 Distribution of Individual log BAFs for Catfish from the HSC

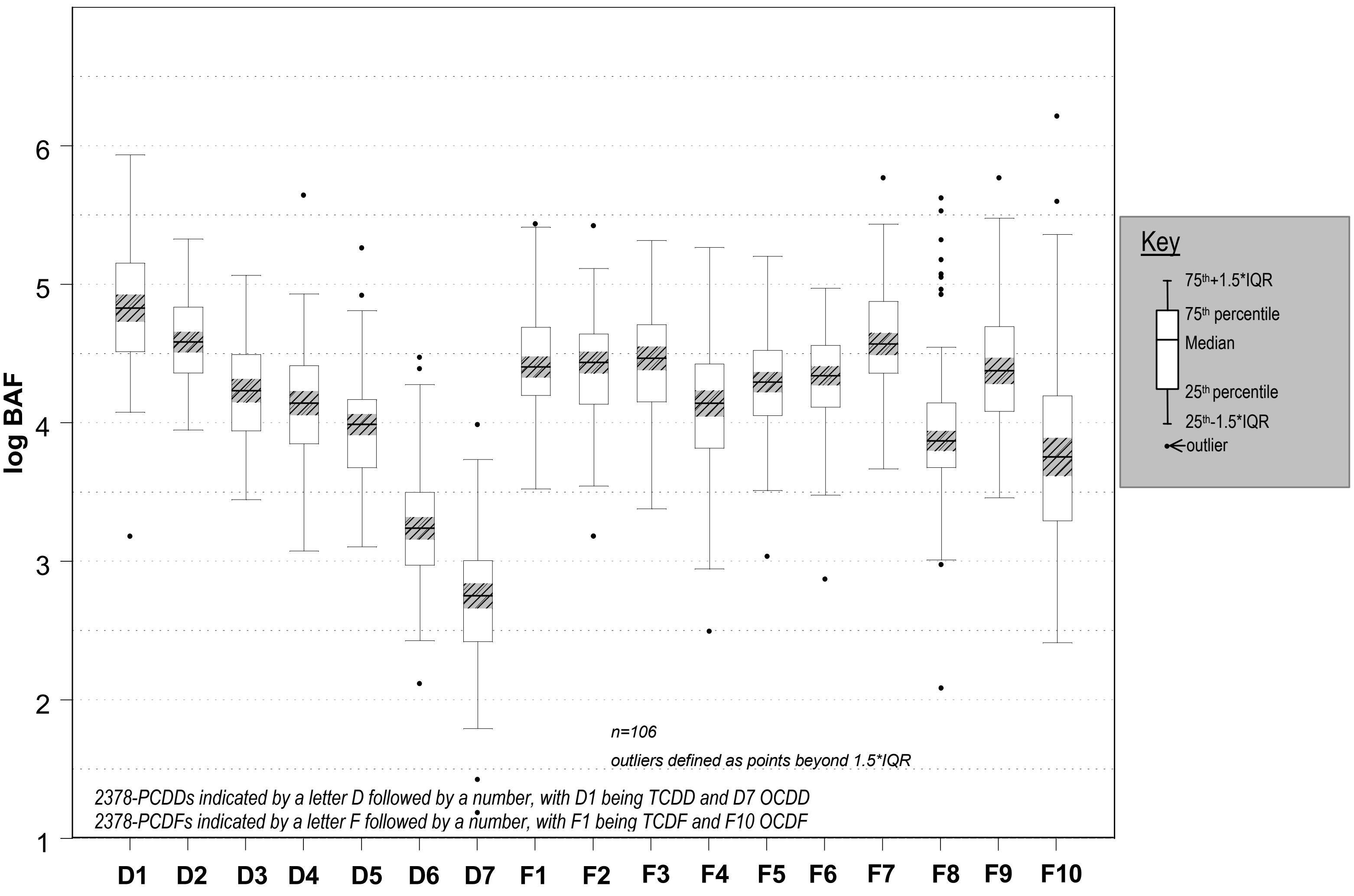

Figure 4.2 Distribution of Individual log BAFs for Crabs from the HSC

(species, size, lipid content, etc), water properties (salinity, temperature, TOC, etc), and random error due to the fact that many of the reported values were non-detects or between the detection limit and the reporting limit (Non-detects were assumed equal to half of the detection limit). Preliminary non-parametric correlations between tissue concentrations of 2378-TCDD and a number of explanatory variables are summarized in Table 4.1. Overall, there are few significant correlations between 2378-TCDD concentrations and other factors. For example, concentrations in catfish and crabs are correlated to the lipid content but the correlation coefficients are not very large. Table 4.2 summarizes correlation coefficients between log BAF for 2378-TCDD and some explanatory variables. It can be seen in Table 4.2 that while tissue lipid content did not explain a significant amount of variation in the tissue concentrations, BAFs did exhibit a small but statistically significant relationship with a measure of the "fatness" of the fish: the average weight to length ratio. Seasonal variations in BAF were not statistically significant. While the catfish species sampled included some gafftopsail catfish, blue catfish, channel catfish and black bullheads among the hardhead catfish, there was no significant variation in BAF among species.

In general, BAFs measured at less contaminated sites with low PCDD/F concentrations tended to be higher than those from sites with high water concentrations (Figure 4.3). This may be explained by the fact that fish are exposed to PCDD/F concentrations that vary over several orders of magnitude. Spatial variation in PCDD/F concentrations spans several orders of magnitude in the HSC system. Fish and crabs are of course mobile, and most leave the system for deeper waters between late November and March (USFWS 1983). Also, fish and crabs accumulate PCDD/Fs from direct exposure to PCDD/Fs in sediments and water, and from their diet of multiple prey species residing in those media. Tissue concentrations are expected to be substantially less dynamic than the concentrations in other media, resulting in a relative

Table 4.1 Spearman Correlation Coefficients for Concentrations of 2378-TCDD in Tissue and some Explanatory Variables

		% lipid	**Median weight**	**Median length**	**Weight/ length ratio**	**Temperature**	**Conductivity**	**DO**	**pH**	**Salinity**	**TSS**	**TOC**	**DOC**	**TDS**	**POC**
2378-TCDD in catfish	Spearman's rho[1]	**0.525**	-0.028	-0.141	-0.002	-0.113	-0.032	0.011	*-0.267*	0.133	*-0.265*	-0.132	-0.034	-0.181	-0.105
	Sig. (2-tailed)	0.000	0.766	0.139	0.983	0.356	0.793	0.932	0.026	0.277	0.017	0.241	0.764	0.106	0.352
	N	112	112	112	112	69	69	69	69	69	81	81	81	81	81
2378-TCDD in catfish-lipid	Spearman's rho[1]	-0.149	0.068	-0.074	0.100	0.148	0.011	-0.065	-0.067	0.105	*-0.259*	-0.054	0.028	-0.122	0.076
	Sig. (2-tailed)	0.118	0.475	0.439	0.296	0.226	0.931	0.598	0.583	0.389	0.020	0.633	0.801	0.277	0.501
	N	112	112	112	112	69	69	69	69	69	81	81	81	81	81
2378-TCDD in crab	Spearman's rho[1]	**0.326**	**0.414**	**0.407**	**0.406**	-0.026	**-0.348**	0.002	-0.224	0.005	*-0.244*	-0.059	0.038	*-0.236*	0.031
	Sig. (2-tailed)	0.001	0.000	0.000	0.000	0.836	0.004	0.984	0.067	0.965	0.027	0.599	0.732	0.032	0.779
	N	108	108	108	108	68	68	68	68	68	82	82	82	82	82
2378-TCDD in crab-lipid	Spearman's rho[1]	-0.141	**0.462**	**0.398**	**0.466**	-0.060	*-0.268*	-0.033	-0.170	0.067	**-0.289**	0.103	0.140	*-0.240*	0.077
	Sig. (2-tailed)	0.147	0.000	0.000	0.000	0.630	0.027	0.786	0.166	0.585	0.008	0.355	0.209	0.030	0.492
	N	108	108	108	108	68	68	68	68	68	82	82	82	82	82

[1] A nonparametric version of the Pearson correlation coefficient, based on the ranks of the data rather than the actual values. It is appropriate for ordinal data, or for interval data that do not satisfy the normality assumption. Values of the coefficient range from -1 to +1. The sign of the coefficient indicates the direction of the relationship, and its absolute value indicates the strength, with larger absolute values indicating stronger relationships.

Spearman coefficients in bold indicate that the correlation is significant at the 0.01 level (2-tailed).

Spearman coefficients in italics indicate that the correlation is significant at the 0.05 level (2-tailed).

Table 4.2 Pearson Correlation Coefficients for log BAF of 2378-TCDD and some Explanatory Variables

		% lipid	**Median weight**	**Median length**	**Weight/ length ratio**
2378-TCDD log BAF in catfish	Pearson correlation	**0.276**	0.059	**0.310**	**0.319**
	Sig. (2-tailed)	0.003	0.544	0.001	0.001
	N	111	109	109	109
2378-TCDD log BAF in crab	Pearson correlation	0.117	**0.269**	*0.195*	0.136
	Sig. (2-tailed)	0.229	0.006	0.048	0.168
	N	106	104	104	104

Pearson coefficients in bold indicate that the correlation is significant at the 0.01 level (2-tailed).

Pearson coefficients in italics indicate that the correlation is significant at the 0.05 level (2-tailed).

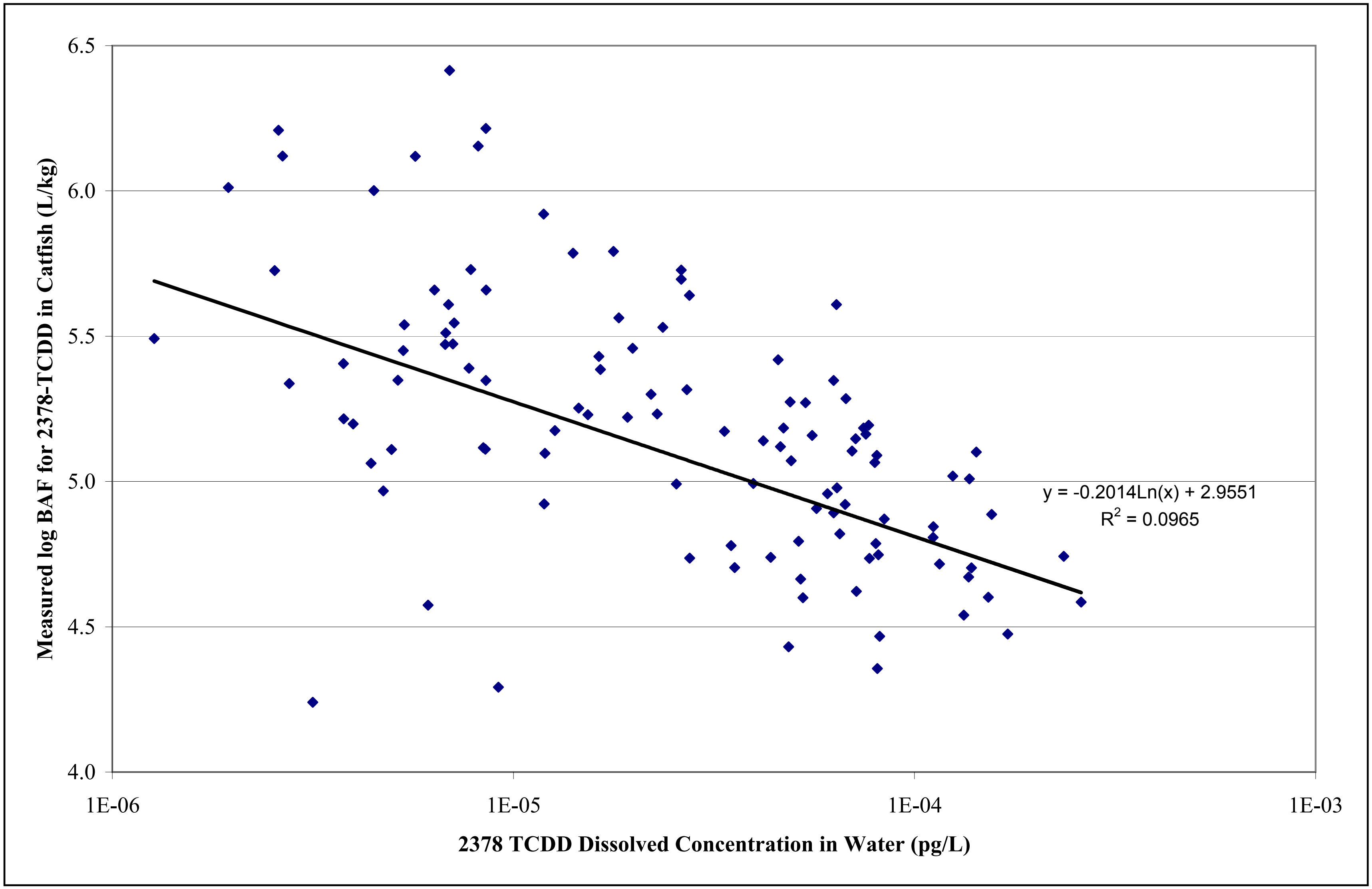

Figure 4.3 Variation in Catfish BAF with Dissolved Concentration in Water

"flattening" of the tissue:water concentration ratio and the observed decline in BAF with increasing dissolved concentration.

The next section describes the detailed methodology for estimating BAFs for the 17 congeners.

4.1.1.1 Estimation of BAF for 2378-TCDD

As a first step, regressions of 2378-TCDD concentrations in tissue and water were completed in order to establish the most appropriate regression model for estimating BAFs for the remaining congeners. Since dioxins and furans are members of a class of chemical compounds known as nonpolar hydrophobic organic compounds (HOCs), they partition preferentially into lipid matter. It is often found that the variability of BAFs or BCFs between species and individuals for HOCs is reduced if they are first normalized by the tissue lipid content (USEPA, 1995). The lipid-normalized bioaccumulation factor (BAF_l) is defined by Equation (4.2).

Combining Equations (4.1) and (4.2), the concentration of an HOC in tissue of biota can be predicted using:

$$C_b = BAF_i * F_i * C_w \tag{4.3}$$

The USEPA (1995) advises that BAFs and BCFs (bioconcentration factors) for organic compounds should be calculated from lipid-normalized tissue concentrations and dissolved concentrations in water.

BAFs are also typically adjusted to correct for chemical bioavailability. The water concentration of a chemical includes portions associated with suspended and colloidal particles and dissolved organic matter, as well as portions truly dissolved in water. However, only the freely dissolved concentration is bioavailable for uptake across gill membranes or external body surfaces (USEPA, 1995). It is likely that the dissolved data collected using the high-volume sampling technique correspond to the freely dissolved concentrations, as the colloidal fraction most probably passes through the XAD-2 resin.

In order to determine the strongest partitioning relationship for the HSC data (the USEPA (1995) suggest using either freely dissolved or total water concentrations), an analysis of correlation between the different measurements in water and tissue was performed and is included in Table 4.3. As indicated in Table 4.3, the strongest partitioning relationship was observed between measured 2378-TCDD in not lipid-normalized tissue and the dissolved concentrations. Thus, BAFs were calculated using regressions between tissue and dissolved concentrations.

Dissolved water concentrations and catfish data for 2378-TCDD were analyzed using different regression methods to determine the best-fit BAF. In general, linear regression is preferred because it would yield a BAF directly from the slope. However, since the HSC data do not meet the assumptions of constant variance and normality of the residuals for the Ordinary

Table 4.3 Pearson Correlation Coefficients between Water and Catfish Concentrations of 2378-TCDD

		2378-TCDD dissolved	**2378-TCDD in water-total**
2378-TCDD in catfish	Pearson coefficient	**0.434**	0.188
	Sig. (2-tailed)	0.000	0.087
	N	84	84
2378-TCDD in catfish-lipid	Pearson coefficient	*0.244*	**0.349**
	Sig. (2-tailed)	0.026	0.001
	N	84	84

Pearson coefficients in bold indicate that the correlation is significant at the 0.01 level (2-tailed).
Pearson coefficients in italics indicate that the correlation is significant at the 0.05 level (2-tailed).
Shading indicates the strongest correlation.

Least Square Method (OLS), and because there are outliers due to the various reasons cited earlier, alternative robust linear regression models were investigated. These alternative methods for regression include Robust Least Trimmed Squares (LTS)[5], Robust MM Regression, and Iterative Weighted Least Squares (WLS)[6]. Robust methods help to control the disproportionate influence of outliers that could well be legitimate data points (Helsel and Hirsch, 2002). In addition, a curve representing the average log BAF from individual measurements was also included in the analysis.

Figures 4.4 and 4.5 present the HSC 2378-TCDD data as well as the best-fit lines derived using the previously mentioned methods. A summary of the test statistics for each of the regression models for both catfish and crabs is included in Table 4.4. Two non-linear regressions (power and polynomial as indicated in Figures 4.4 and 4.5 and Table 4.4) were also evaluated for comparison purposes. As can be seen in Figures 4.4 and 4.5, there was a lot of variance in the relationships. It is noted that a simple linear BAF regression between tissue concentrations and dissolved concentrations does not work well to explain the data collected in the Houston Ship Channel. The linear BAFs have low r^2 and F values and high standard errors. The polynomial and power (log-transformed data) models seem to better represent the data but they have the disadvantage that a BAF cannot be directly derived from the equations. This might suggest the need for developing a multivariate regression model or it might indicate that the congener-specific BAF approach cannot be used for the HSC.

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[5] See Appendix F for a brief description of the used robust regression methods.

[6] Other methods such as Reduced Major Axis (also known as Geometric Mean Regression) and Least Median of Squares were also considered. However, results are not included due to the difficulty in obtaining test statistics to compare with the other methods employed in this analysis.

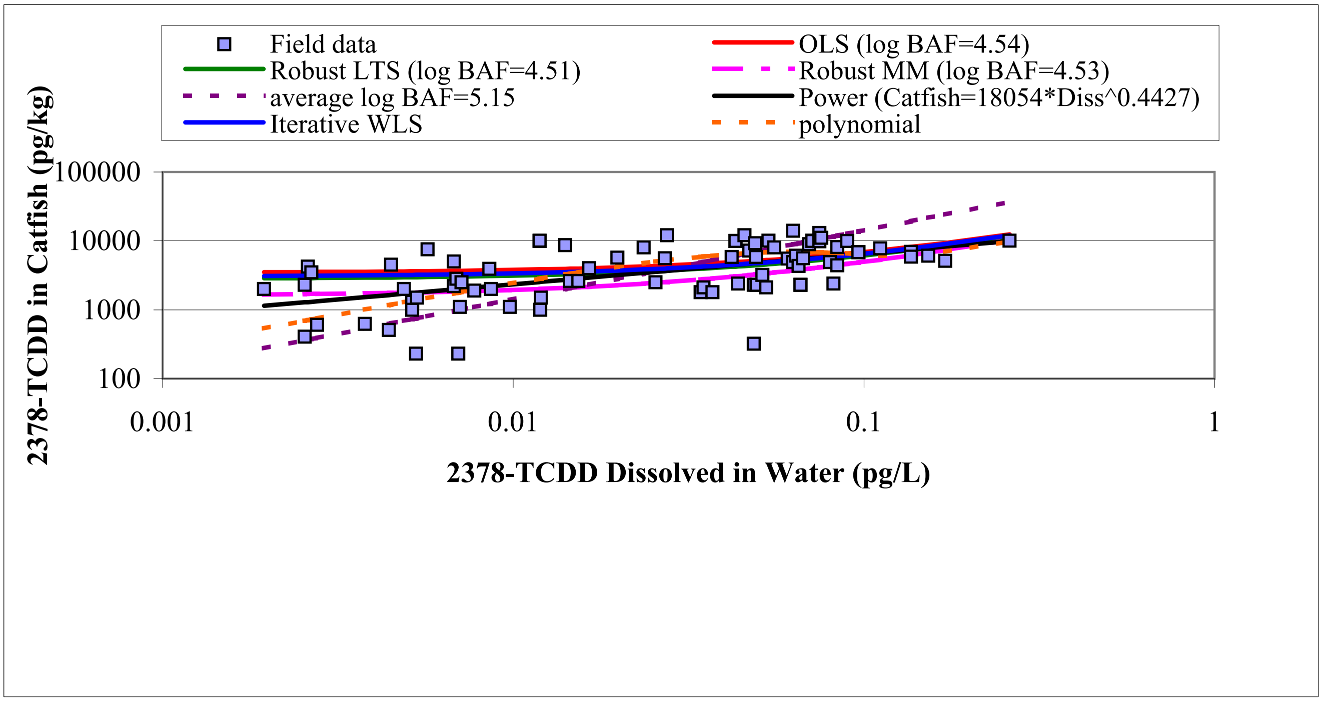


Figure 4.4 Partitioning of 2378-TCDD between Catfish and Dissolved Phase in the HSC

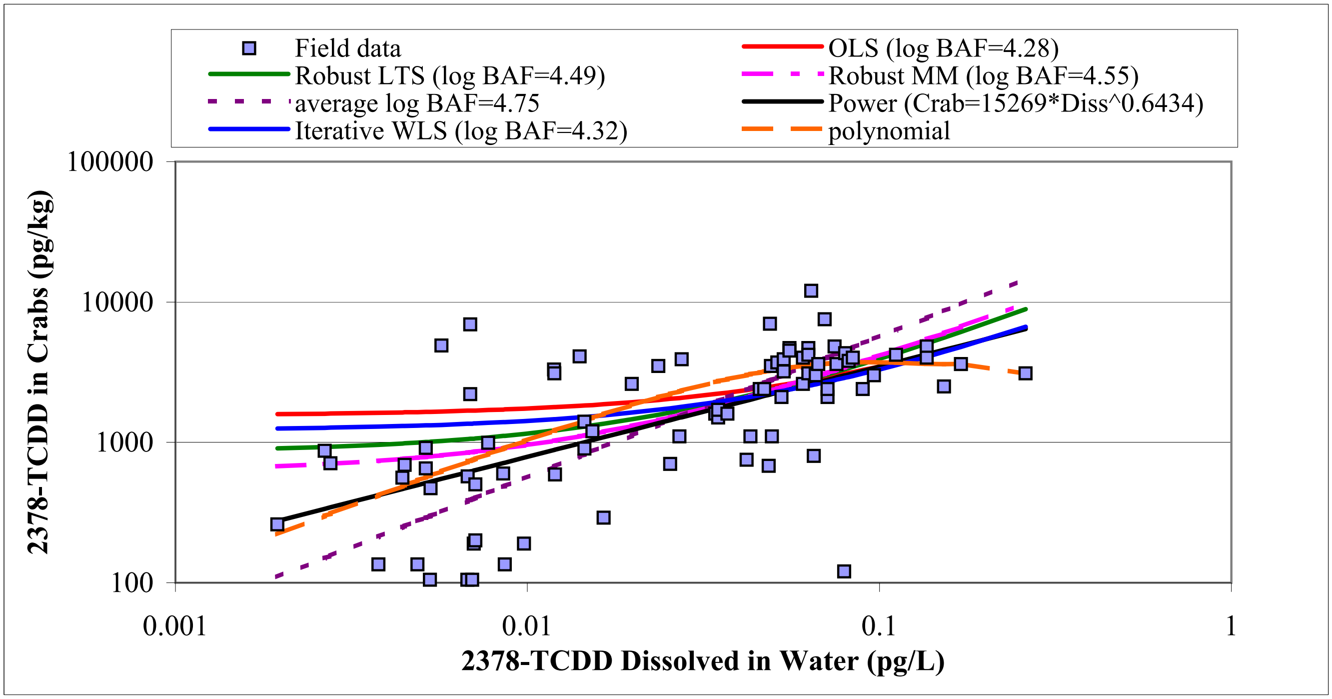


Figure 4.5 Partitioning of 2378-TCDD between Crabs and Dissolved Phase in the HSC

Table 4.4 Summary of Regression Statistics and Parameters for Tissue-Water Relationships

Catfish

Model	F-statistic	p-value	Residual SE	b0			b1 (BAF in linear regressions)			b2			b3		
				Value	SE	t-value[a]	Value	SE	t-value[a]	Value	SE	t-value(a)	Value	SE	t-value[a]
OLS	18.982	0.000038	3233.280	3442.86652	502.21325	6.855388	34617.64	7945.602	4.35683						
Robust LTS	22.678	8.68E-06	2820.080	3133.919	442.533	7.08	33154.95	6962.162	4.762						
Robust MM	9.51	0.00861	2527.180	1604.75	468.8	3.423	33642.7	6913.294	4.867						
Iterative WLS	26.0646	2.10E-06	2670.800	3032.742	434.41	6.981	34840.53	6824.318	5.105						
Polynomial			3184.840	-3.49E+07	2.37E+07	-1.472	2.03E+07	1.06E+07	1.915	-3.86E+06	1.37E+06	-2.81943	2.82E+05	5.07E+04	5.553
Power	38.553	2.08E-08	2.228	18054	1.3197996	35.321	0.4427	0.0712	6.209						

Crabs

Model	F-statistic	p-value	Residual SE	b0			b1 (BSAF in linear regressions)			b2			b3		
				Value	SE	t-value[a]	Value	SE	t-value[a]	Value	SE	t-value(a)	Value	SE	t-value[a]
OLS	15.9251	0.00015	1923.760	1551.086	303.779	5.106	19228.16	4818.324	3.991						
Robust LTS	57.24	9.89E-11	1154.000	964.31	199.339	4.837	26680.2	3526.449	7.566						
Robust MM	4.46	0.107	1036.950	606.473	320.854	1.89	35391.22	6062.389	5.838						
Iterative WLS	33.85	1.25E-07	1318.000	1214.18	219.757	5.525	20943.91	3599.663	5.818						
Polynomial			1821.890	-9.76E+06	1.38E+07	-0.707	5.93E+06	6.20E+06	0.957	-1.28E+06	8.02E+05	-1.601	1.16E+05	2.95E+04	3.931
Power	53.29	1.98E-10	8.515	15269.00	2.183	28.401	0.6434	0.0881	7.300						

[a] If |t-value|>2, the linear relationship is statistically significant atα=0.05.

It is noted that non-detects were assumed to be equal to half of the detection limit. Because the detection limits were variable, this should not have introduced a large bias towards a single value. It is noted, however, that those values have high uncertainty associated with them. The BAF regressions for 2378-TCDD presented earlier were compared to those completed assuming non-detects as zeros but no significant differences were evident and the relationships were not stronger.

To aid in selecting the linear regression method that would be used to estimate BAFs for all the 2378-substituted congeners, residuals versus fit plots for the different models were prepared and visually inspected (Figures 4.6 and 4.7 for catfish and crabs, respectively). The residuals present some clustering but, in general, they were distributed randomly in both directions. At the higher end of the predicted values, there were a few outliers that produced curvature. This confirmed the need for using a robust regression method. Figures 4.8 and 4.9 present histograms plotted along the probability mass function for a normal distribution for each set of residuals. As expected, the residuals of log-transformed data (power regression) are normally distributed. However, due to difficulties in calculating BAFs from non-linear regressions, the robust LTS regression was selected as the model to use for bioaccumulation factor estimation. As suggested by the data in Figures 4.8 and 4.9, residuals from the robust LTS had the distribution that differs the least from a normal distribution among all the linear methods.

The last step followed prior to completing regressions for all the congeners was to examine the plots of catfish residuals versus other explanatory variables. This helped in determining if other variables could have been included in a multiple regression model to explain the noise in the data. Figure 4.10 shows scatterplots of residuals versus sampling date, catfish

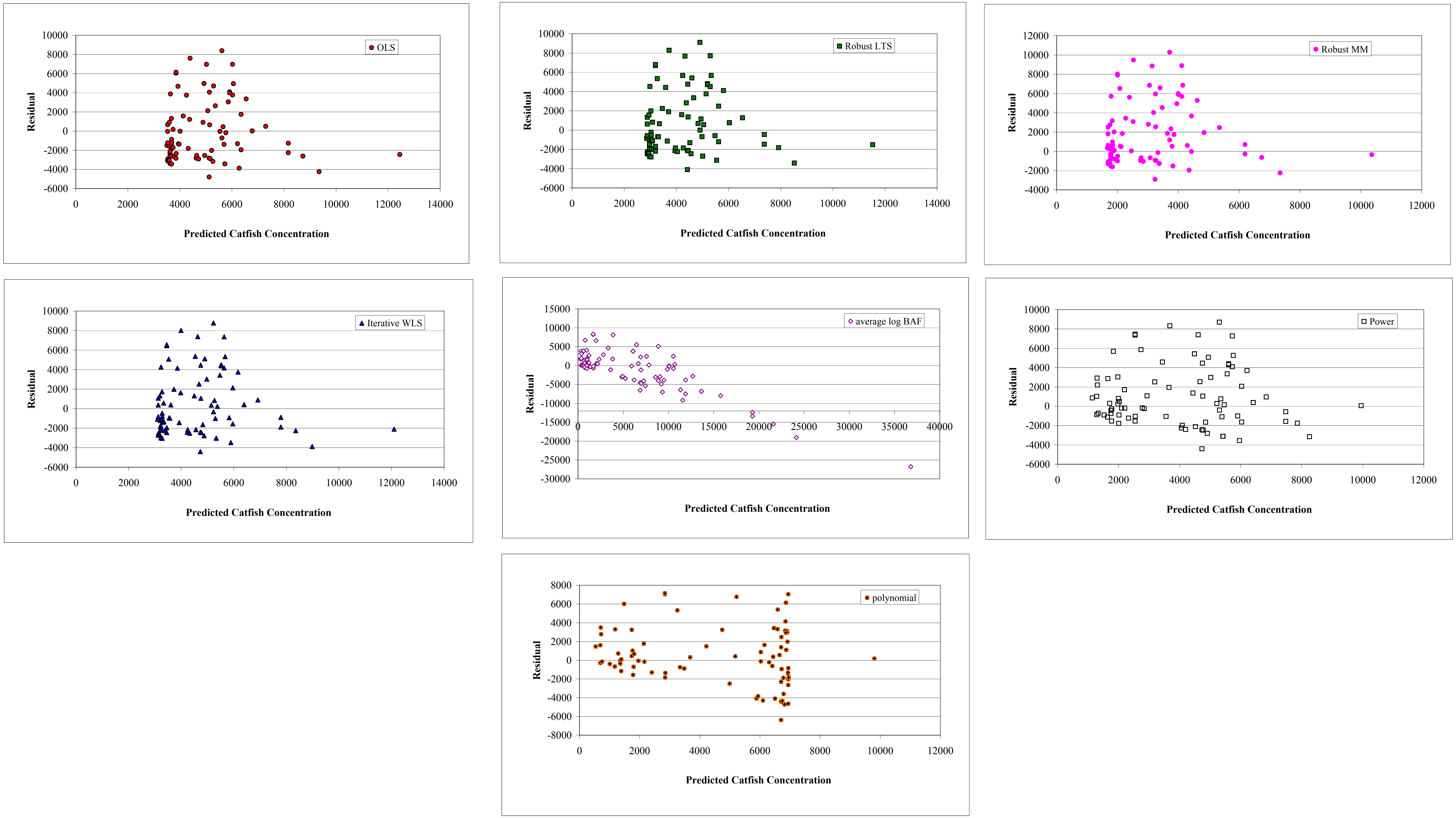


Figure 4.6 Residuals vs Fit Plots for Regressions between Catfish and Dissolved 2378-TCDD Concentrations

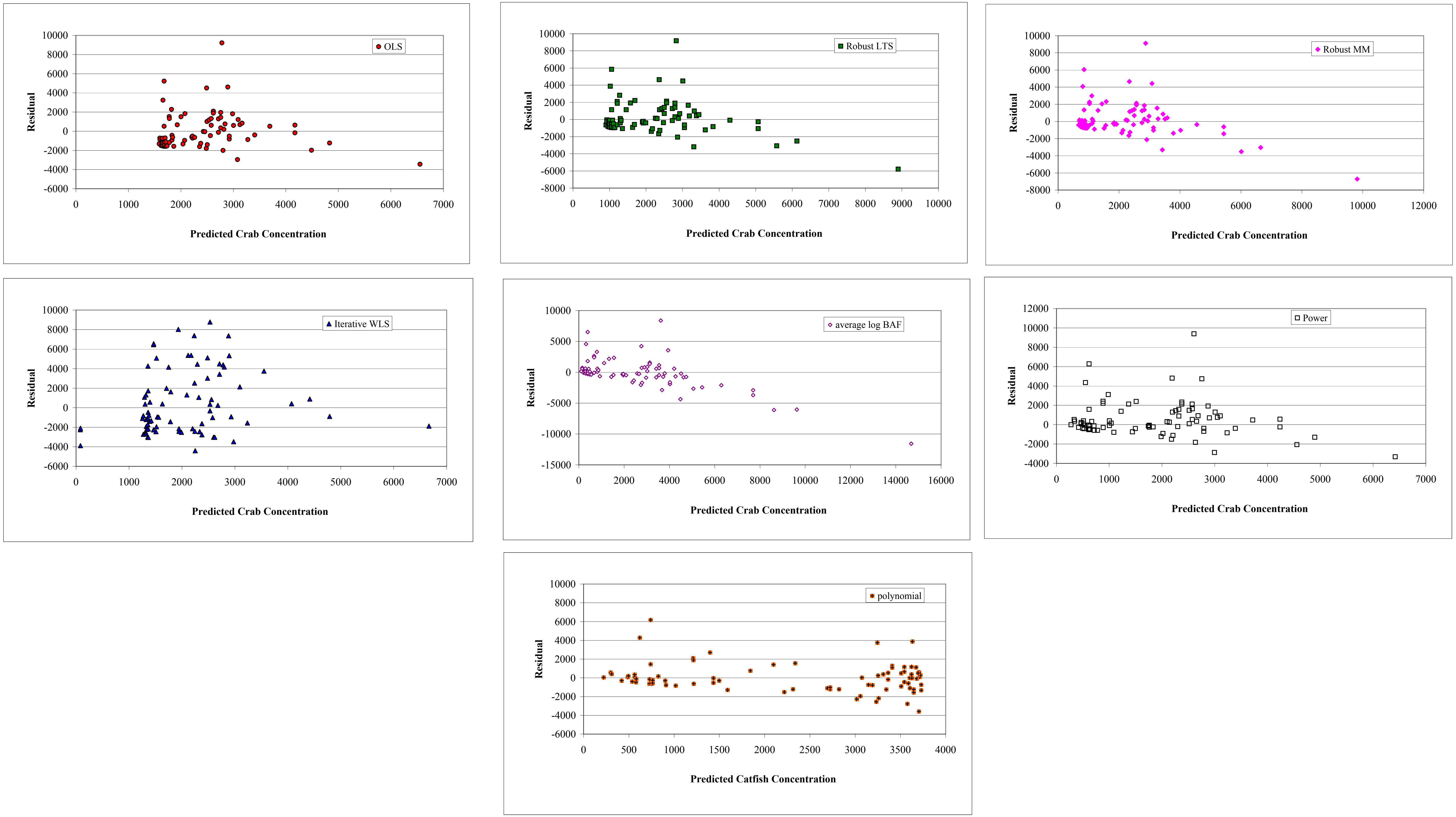


Figure 4.7 Residuals vs Fit Plots for Regressions between Crab and Dissolved 2378-TCDD Concentrations

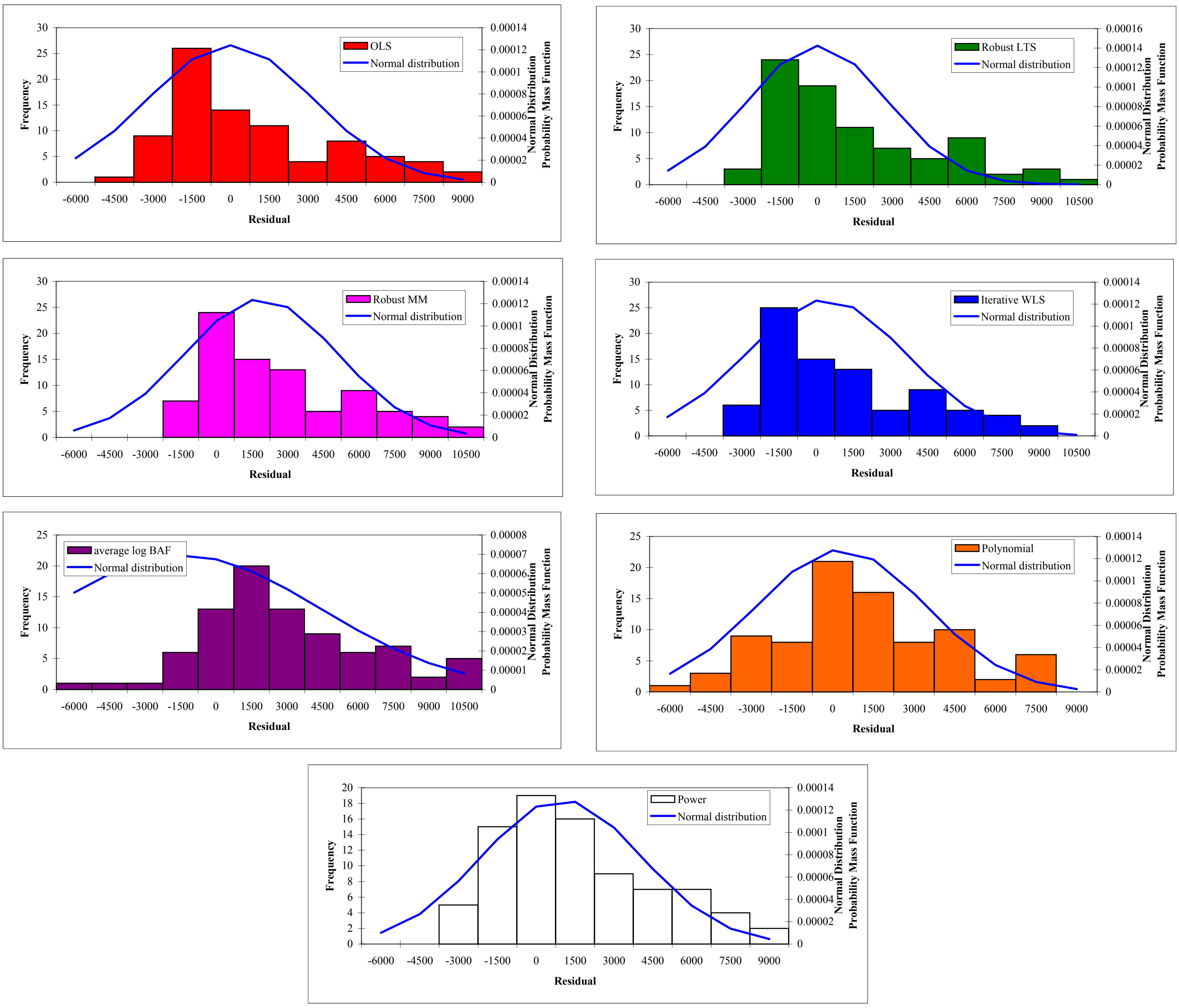


Figure 4.8 Histograms of Residuals for Regressions of Catfish and Dissolved Concentrations of 2378-TCDD

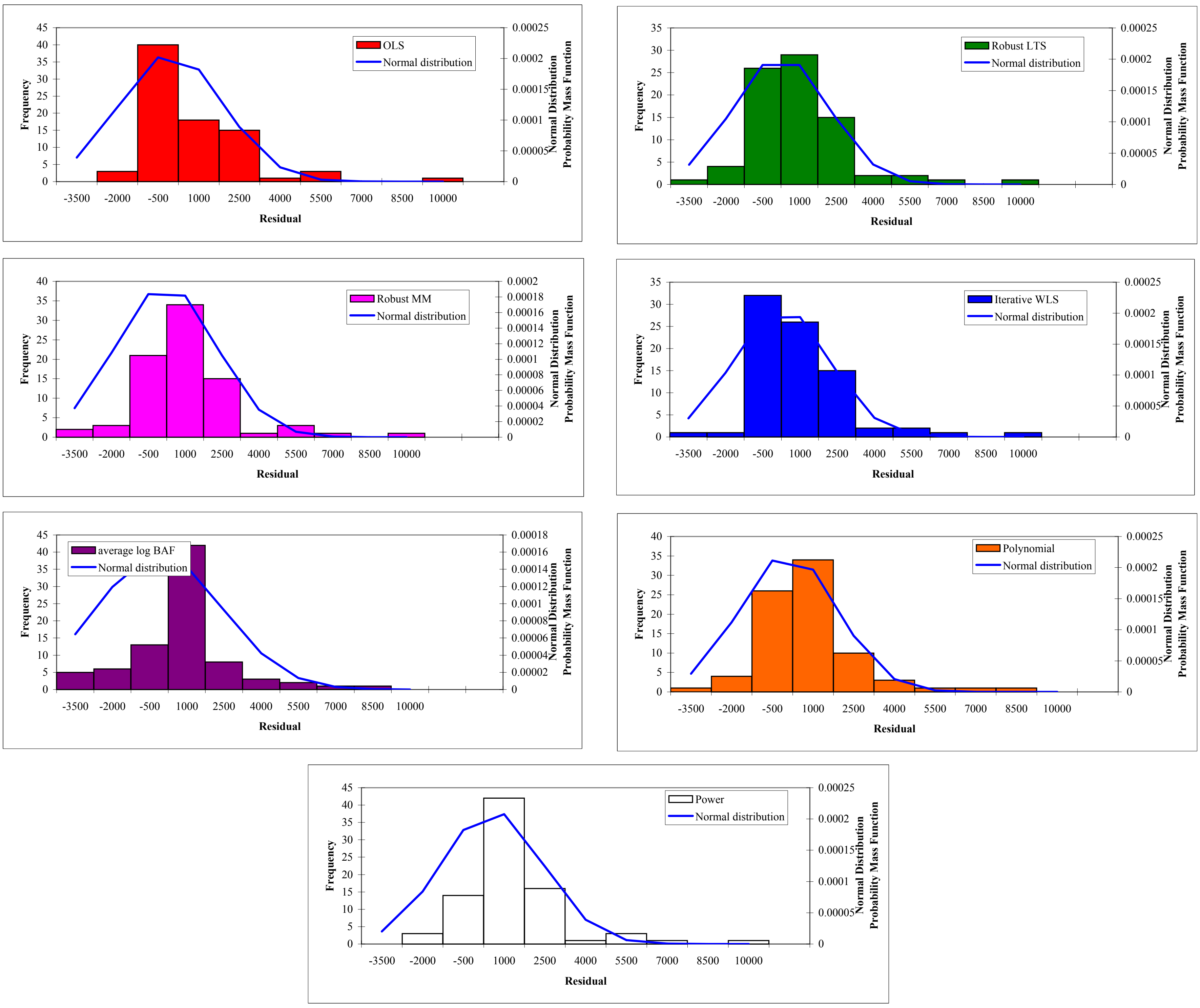
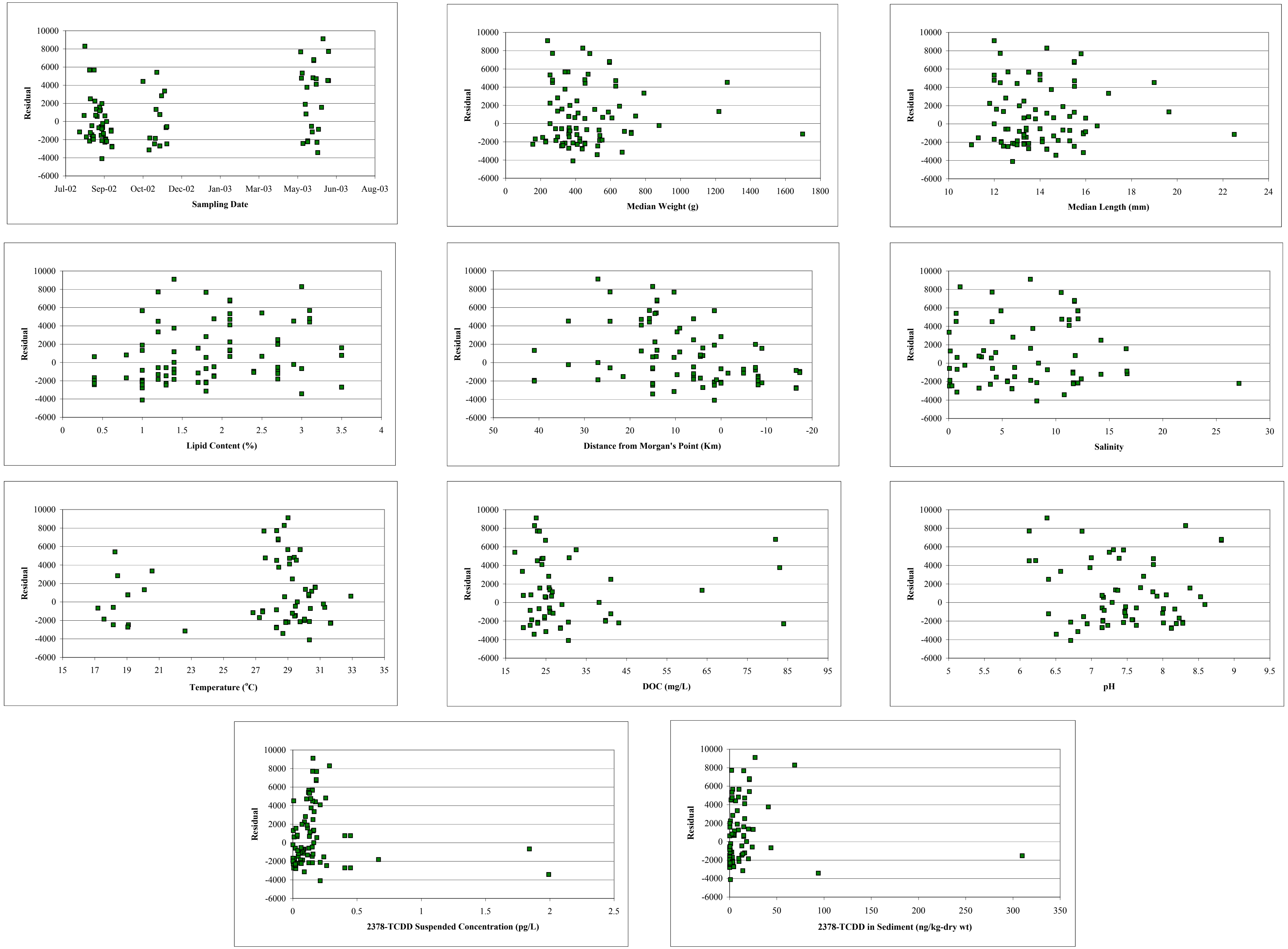


Figure 4.9 Histograms of Residuals for Regressions of Crab and Dissolved Concentrations of 2378-TCDD



NOTE: Only residuals from Robust LTS regression are plotted

Figure 4.10 Residuals from Catfish BAF Regressions Plotted by Additional Explanatory Variables

characteristics (weight, length, and lipid content), sampling location (distance from Morgan's Point), water properties (salinity, temperature, DOC, and pH), and suspended and bottom sediment 2378-TCDD concentrations. In addition, Figure 4.11 presents boxplots of the residuals by two categorical explanatory variables: fish species and water quality segment. In both cases, the goal was to identify a pattern that would pinpoint a variable affecting the relationship between catfish and dissolved concentrations. No obvious trend was inferred from the scatterplots in Figure 4.10. The residuals seem to be randomly distributed without being affected by seasonality or any other explanatory variable. The boxplots in Figure 4.11 indicate that the magnitude of the residuals is similar for the different segments, although segment 2421 seems to present slightly lower residuals. Regarding fish species, residuals from hardhead catfish appear to be considerably higher than those from blue catfish. However, sample sizes are very different which complicates comparison between the two datasets.

4.1.1.2 Estimation of BAF for All Congeners from Regressions

As mentioned earlier, because the dioxin congeners have a wide range of bioaccumulation potentials, it was considered necessary to estimate BAFs for each compound. As mentioned in the previous section, the robust LTS regression method was selected to fit the dioxin data in the HSC. While a non-linear model could represent the data more accurately, it would fail to provide a direct estimate of the bioaccumulation potential.

The following guidelines were used for BAF estimation:

1. The BAF was derived from linear regression between tissue concentrations and dissolved concentrations measured at the same location and approximately at the same time.
2. An effort was made to analyze all the data using the same regression method. However, if

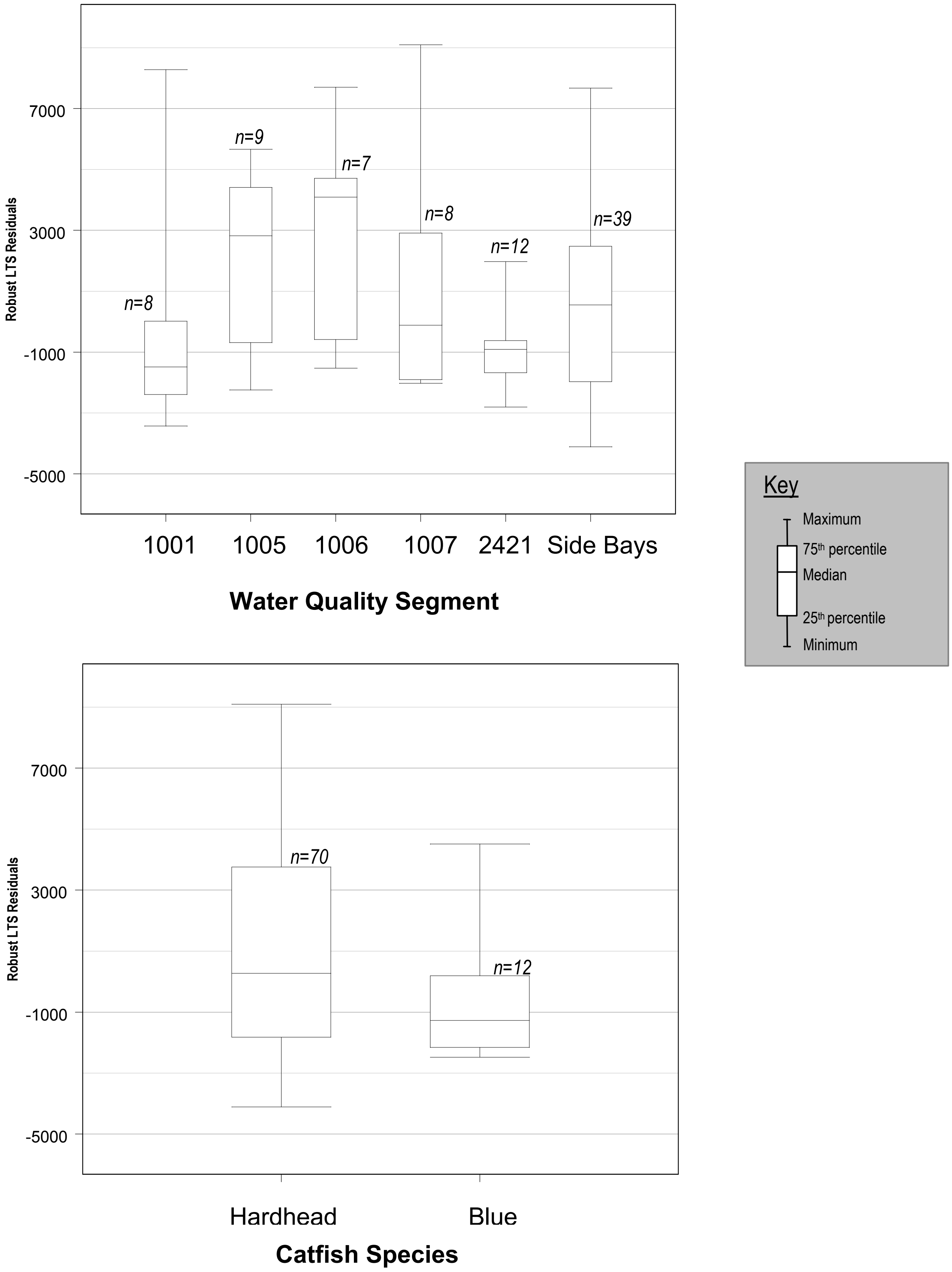


Figure 4.11 Distribution of Residuals from Catfish BAF Regressions by Categorical Variables

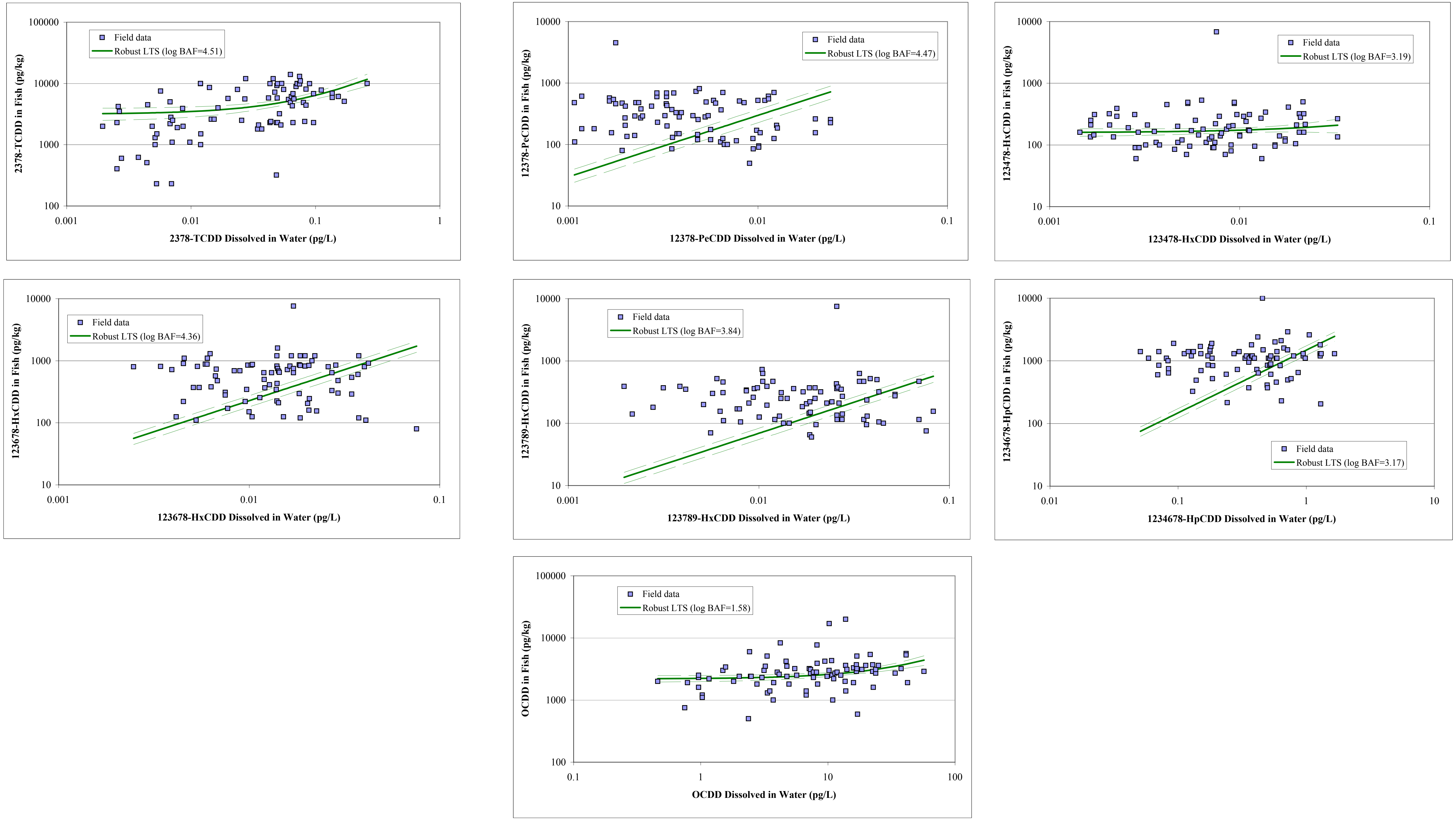
the BAF for a particular congener could not be derived using the LTS regression (i.e., the slope was not statistically significant or it was negative), the regression was performed using the WLS method.

3. All the test statistics and confidence intervals were calculated for a 95% confidence level (α=0.05).

Figures 4.12 and 4.13 present the best-fit lines along with the confidence intervals for dioxins in catfish and crabs, respectively. The relevant test statistics are summarized in Table 4.5. Estimated BAFs vary from 38±20 to 32617±13925 for catfish and from 15±41 to 26680±7030 for crabs. Bioaccumulation factors varied within 2 orders of magnitude among the different congeners and were generally higher for catfish than for crabs. This may be the result of higher lipid content in fish than in crabs. It is noted that for some congeners the relationships were not statistically significant at the 95% confidence level (e.g., 123478-HxCDD in catfish, *p*-value =0.23) and, thus, the uncertainty in the estimated bioaccumulation factors for these compounds is high. An attempt was made to fit the field data for those congeners using all the above-mentioned methods, but in all cases the regressions were weak.

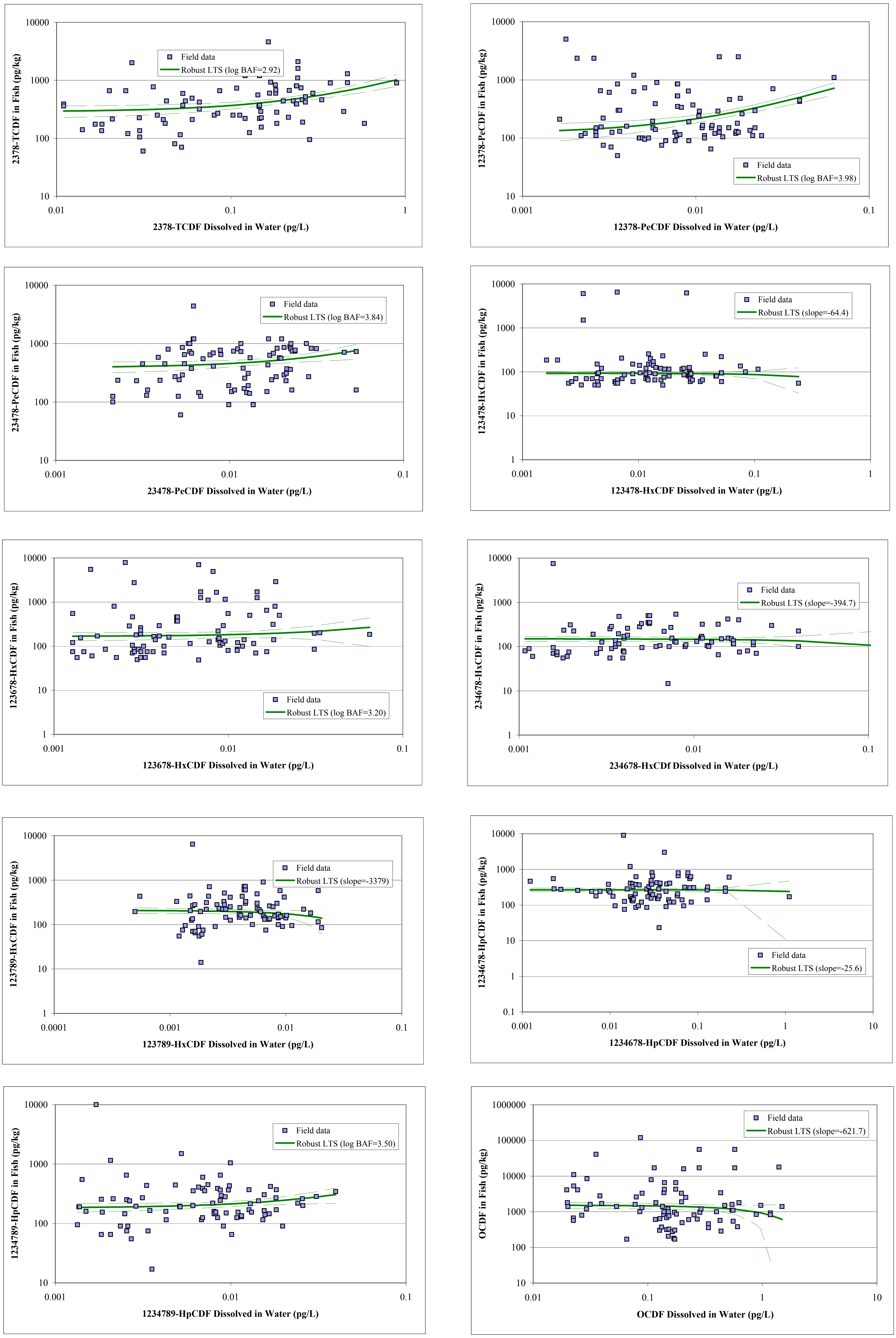
It is important to point out that the best-fit regression yielded negative slopes for congeners 123478-HxCDF, 234678-HxCDF, 123789-HxCDF, 1234678-HpCDF, and OCDF for catfish data and 123678-HxCDD, 123789-HxCDD, 23478-PeCDF, 123478-HxCDF, 123478-HpCDF, and OCDF for crab data. These negative slopes could be interpreted as a lack of bioaccumulation of the particular congeners in the sampled species or as the need for a more appropriate non-linear model.

It is noted that BAFs are equilibrium concepts. Aquatic animals are not infinite sinks for chemicals. As they take up chemicals, they also eliminate them via urine, feces, biochemical



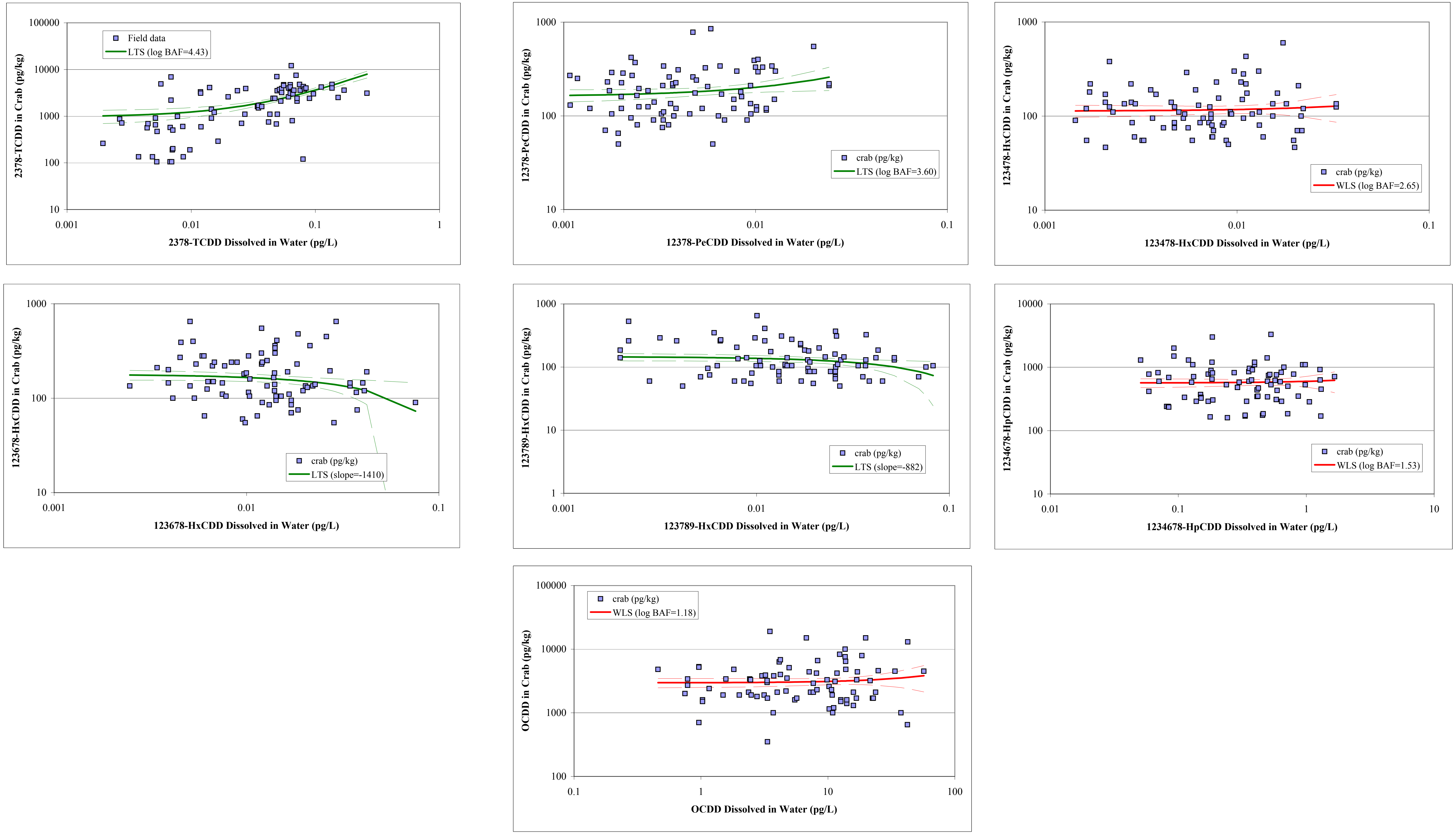
Dashed lines correspond to the 95% confidence intervals

Figure 4.12a Bioaccumulation Factors for Dioxins in Catfish from the HSC



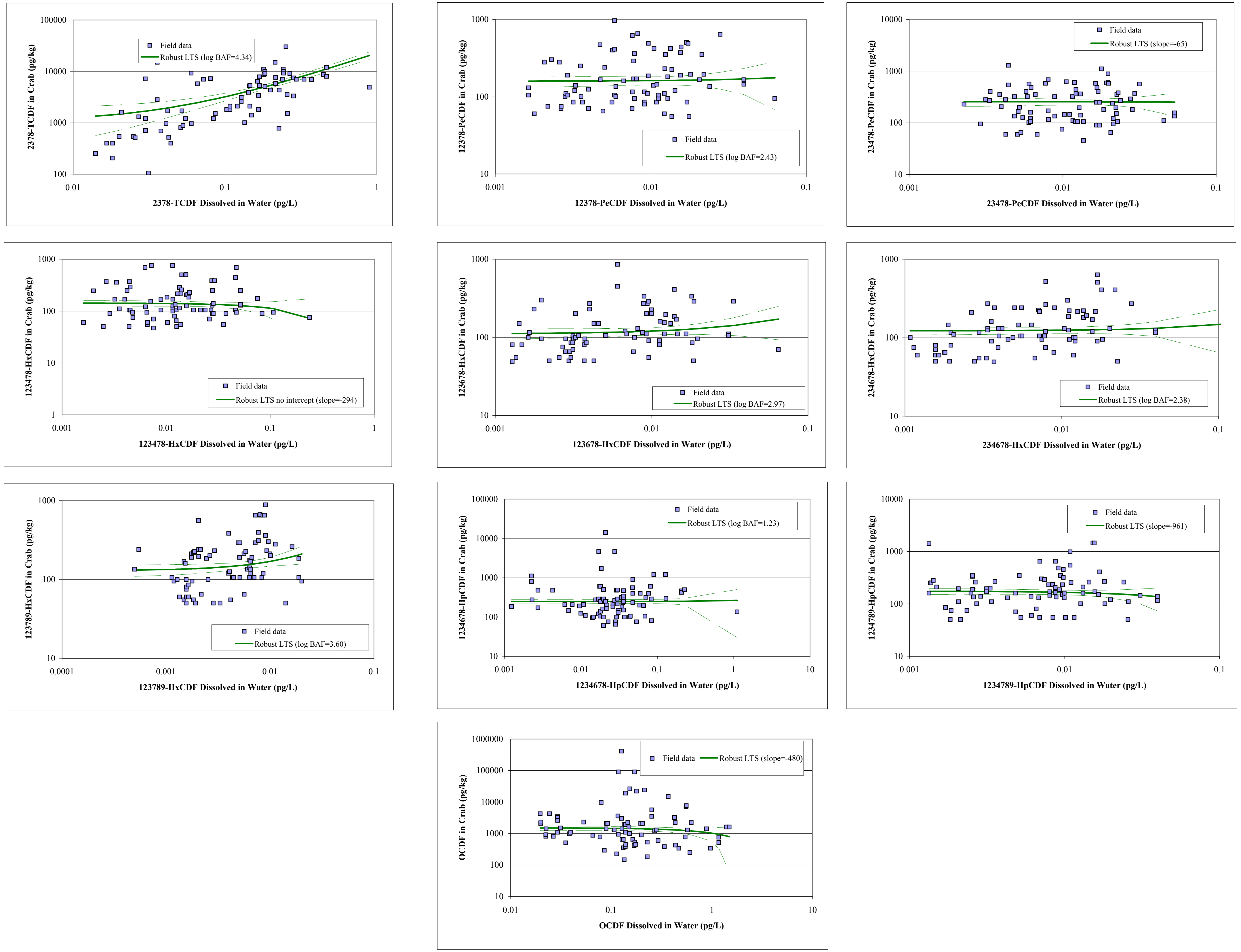
Dashed lines correspond to the 95% confidence intervals

Figure 4.12b Bioaccumulation Factors for Furans in Catish from the HSC



Dashed lines correspond to the 95% confidence intervals

Figure 4.13a Bioaccumulation Factors for Dioxins in Crabs from the HSC



Dashed lines correspond to the 95% confidence intervals

Figure 4.13b Bioaccumulation Factors for Furans in Crabs from the HSC

Table 4.5a Estimated Bioaccumulation Factors for HSC Catfish

Congener	Method	Regression		Slope	
		SE	Significance F	Estimated BAF	*p*-value
2378-TCDD	Robust LTS	2833.2	21.744	32617±13925	1.267E-05
12378-PeCDD	Robust LTS	299.2	-47.208	29777±8567	9.824E-10
123478-HxCDD	Robust LTS	77.5	1.455	1538±2542	0.2317
123678-HxCDD	Robust LTS	512.0	-44.925	22712±5556	4.106E-12
123789-HxCDD	Robust LTS	208.3	-47.771	6900±1689	4.864E-12
1234678-HpCDD	Robust LTS	787.5	-54.057	1481±302	3.136E-15
OCDD	Robust LTS	985.7	15.079	38±20	0.0002
2378-TCDF	Robust LTS	245.8	18.760	825±380	4.716E-05
12378-PeCDF	Robust LTS	163.6	24.547	9601±3865	4.848E-06
23478-PeCDF	Robust LTS	302.2	4.639	6942±6415	0.0343
123478-HxCDF	Robust LTS	33.8	0.274	N/A[1]	0.6023
123678-HxCDF	Robust LTS	145.2	0.770	1571±3574	0.3834
234678-HxCDF	Robust LTS	85.1	0.343	N/A[1]	0.5601
123789-HxCDF	Robust LTS	105.0	1.292	N/A[1]	0.2594
1234678-HpCDF	Robust LTS	147.2	0.038	N/A[1]	0.8452
1234789-HpCDF	Robust LTS	109.3	3.378	3145±3411	0.0701
OCDF	Robust LTS	1167.0	1.712	N/A[1]	0.1951

[1] The slope of the best-fit regression is negativ

The relationship is not statistically significant

Table 4.5b Estimated Bioaccumulation Factors for HSC Crabs

Congener	Method	Regression		Slope	
		SE	Significance F	Estimated BAF	*p*-value
2378-TCDD	Robust LTS	1154.3	57.240	26680±7030	9.889E-11
12378-PeCDD	Robust LTS	89.9	3.090	4018±4554	0.0829
123478-HxCDD	Iterative WLS	86.4	-49.599	451±1861	3.799E-13
123678-HxCDD	Robust LTS	71.9	3.958	N/A[1]	0.0500
123789-HxCDD	Robust LTS	64.9	3.673	N/A[1]	0.0590
1234678-HpCDD	Iterative WLS	477.9	-44.104	34±203	3.18E-12
OCDD	Iterative WLS	2655.4	-47.999	15±41	4.768E-08
2378-TCDF	Robust LTS	2588.4	63.411	21655±5420	1.652E-11
12378-PeCDF	Robust LTS	99.9	0.049	268±2420	0.8261
23478-PeCDF	Robust LTS	169.8	0.001	N/A[1]	0.9719
123478-HxCDF	Robust LTS	74.9	1.169	N/A[1]	0.2833
123678-HxCDF	Robust LTS	67.7	1.267	927±1641	0.2639
234678-HxCDF	Robust LTS	63.3	0.223	239±1010	0.6384
123789-HxCDF	Robust LTS	76.6	3.766	3977±4087	0.0563
1234678-HpCDF	Robust LTS	150.0	0.016	17±267	0.9001
1234789-HpCDF	Robust LTS	83.8	0.642	N/A[1]	0.4256
OCDF	Robust LTS	1019.0	1.638	N/A[1]	0.2051

[1] The slope of the best-fit regression is negativ

The relationship is not statistically significant reactions (in some cases), and other mechanisms. Elimination processes are grouped in the term "depuration". When an animal is exposed to a new chemical, its BAF will increase until the chemical uptake rate is balanced by the chemical depuration rate. As a general rule, when the term BAF is used, it can be assumed to refer to the steady-state, equilibrium BAF. However, because the uptake and elimination rates for large animals, such as fish and crabs, are slow relative to the dynamically changing concentrations in water, it is expected that individual measured BAFs always incorporate some disequilibrium. This may help explain the high scatter observed in the data.

4.1.1.3 Determination of BAF using Measures of Central Tendency

Since the linear regressions to estimate BAFs did not fit the observed data very well, an alternative approach was used. This approach uses measures of central tendency (i.e. mean or median) of the ratios of tissue concentrations to dissolved concentrations (Figures 4.1 and 4.2) rather than BAFs estimated from linear regressions. For tissue to water ratios, it was considered that the log BAF datasets followed a fairly normal distribution. Thus, the average log BAF is an appropriate measure of central tendency. Line fit plots for BAFs comparing fish and crabs for several important congeners are shown in Figure 4.14.

4.1.2 Development of Site-specific Biota-Sediment Accumulation Factors

The BSAF is defined by the USEPA (2003) as the ratio (in kilograms of sediment organic carbon per kilogram of lipid) of the lipid-normalized concentration of a chemical in the tissue of an aquatic organism to its organic carbon-normalized concentration in surface sediment, in situations where the ratio does not change substantially over time, both the organism and its food

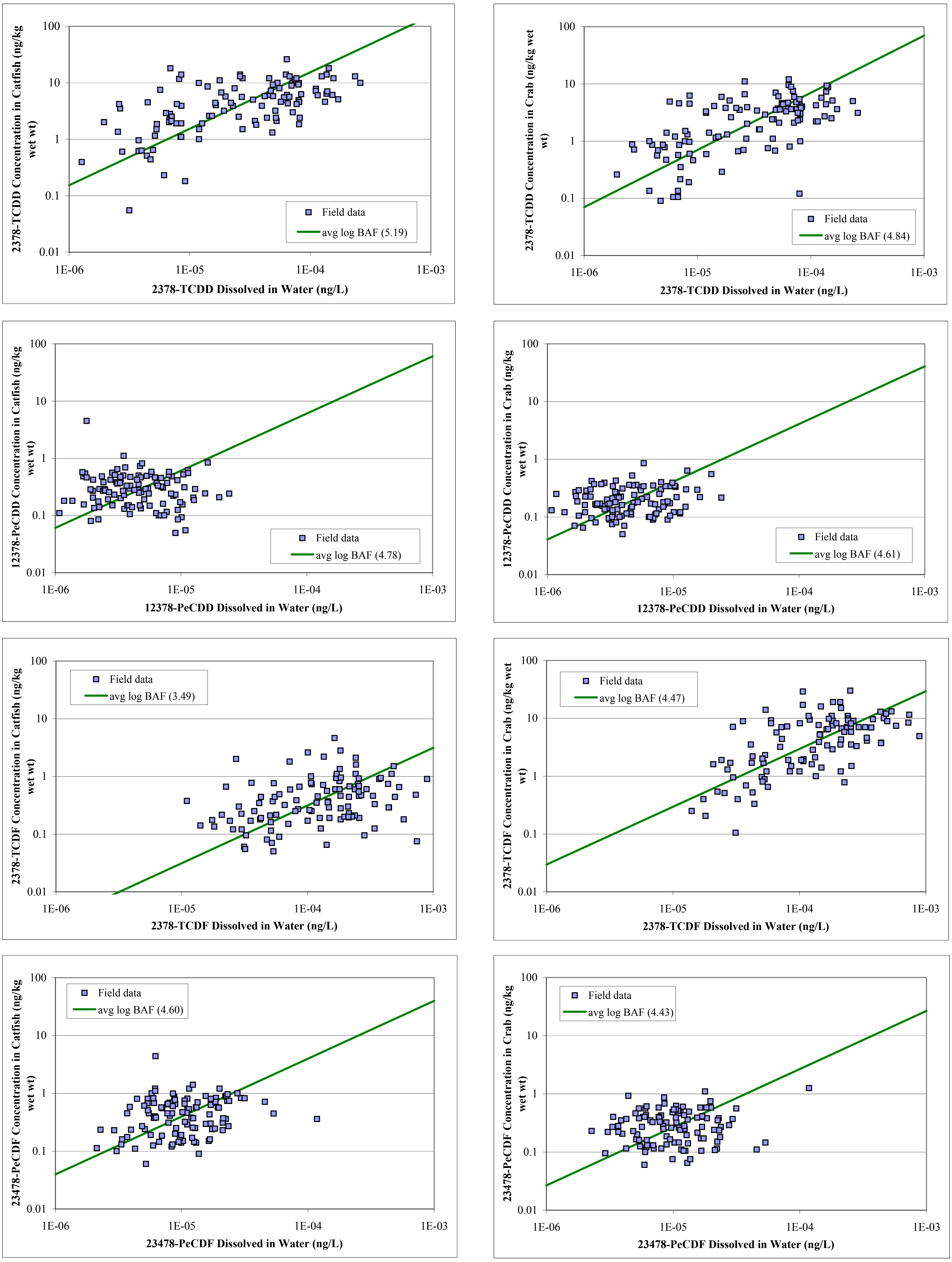


Figure 4.14 Line Fit Plots of BAF for Selected Congeners in Tissue from the HSC

are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism.

$$BSAF = \frac{C_{tissue} / F_{lipid}}{C_{sed} / F_{oc}} \quad (4.4)$$

where F_{oc} is the organic carbon fraction of the sediment by weight.

BSAFs for catfish and crabs were calculated for each of the paired water, tissue, and sediment samples collected in the spring, summer, and fall seasons from 2002 through 2004. Because lipid normalization increased the variability in the BAF/BSAF relationships, and the lipid measurement method used was imprecise, all BSAFs were based on raw tissue concentrations and were not lipid-normalized.

BSAFs for PCDD/F congeners measured in 130 catfish and sediment samples from the HSC system are shown in Figure 4.15. BSAFs for PCDD/F congeners measured in 131 blue crab and sediment samples from the HSC system are shown in Figure 4.16. As with the calculated BAFs, these BSAFs are calculated from the bulk tissue concentration, and not normalized to the tissue lipid concentrations. BSAFs exhibited many of the same patterns as BAFs, which is expected as they are based on the same tissue concentrations.

4.1.2.1 Estimation of BSAF for 2378-TCDD

Based on measurements from the Houston Ship Channel system, it was observed that the tissue lipid normalizations decrease the strength of the relationship between tissue dioxin concentrations and organic carbon-normalized sediment dioxin concentrations. Thus, BSAF relationships were developed using whole tissue dioxin concentrations.

Regressions for catfish and sediment-organic carbon concentrations of 2378-TCDD were

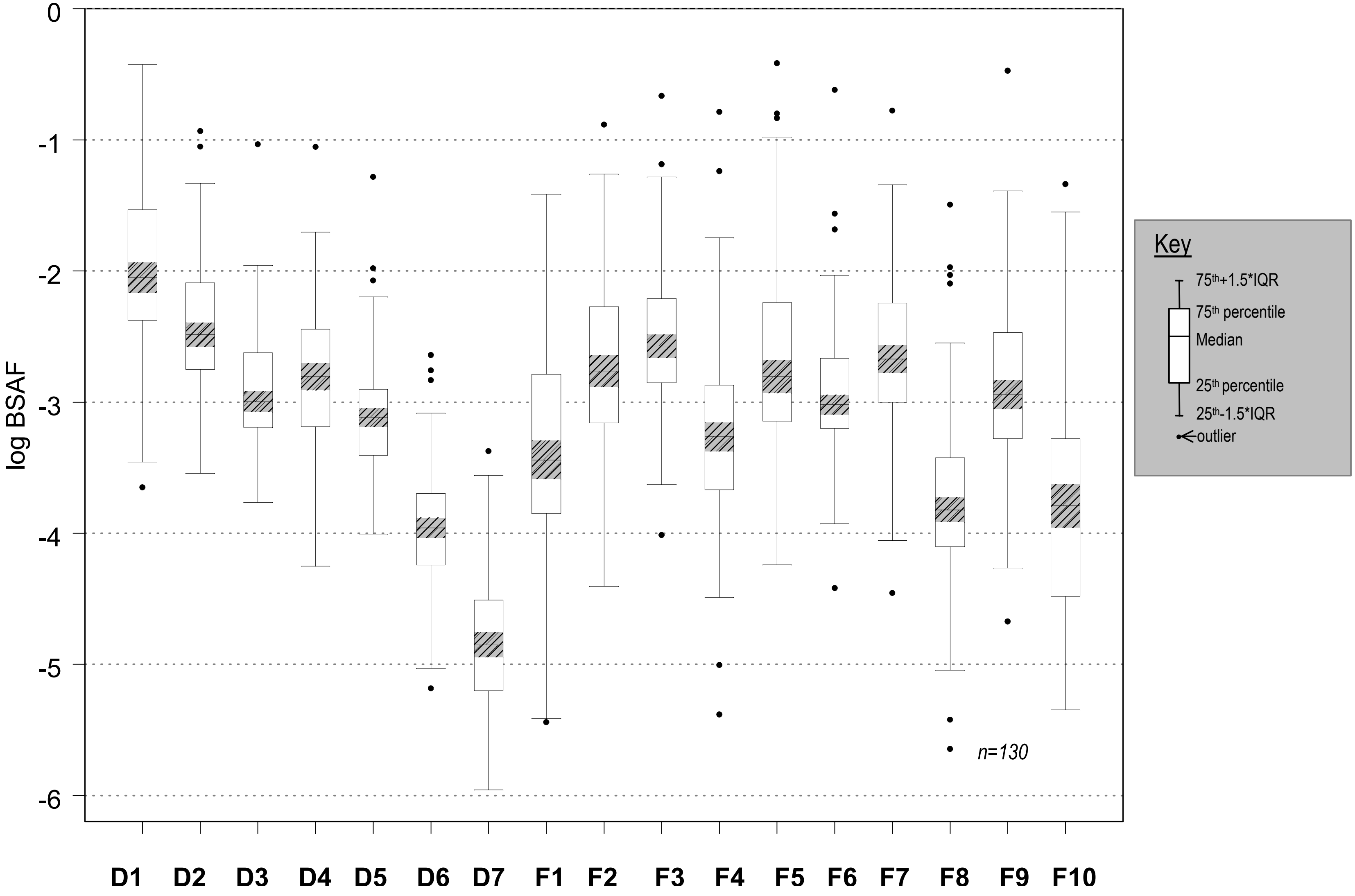


Figure 4.15 Distribution of Individual BSAFs for Catfish from the HSC

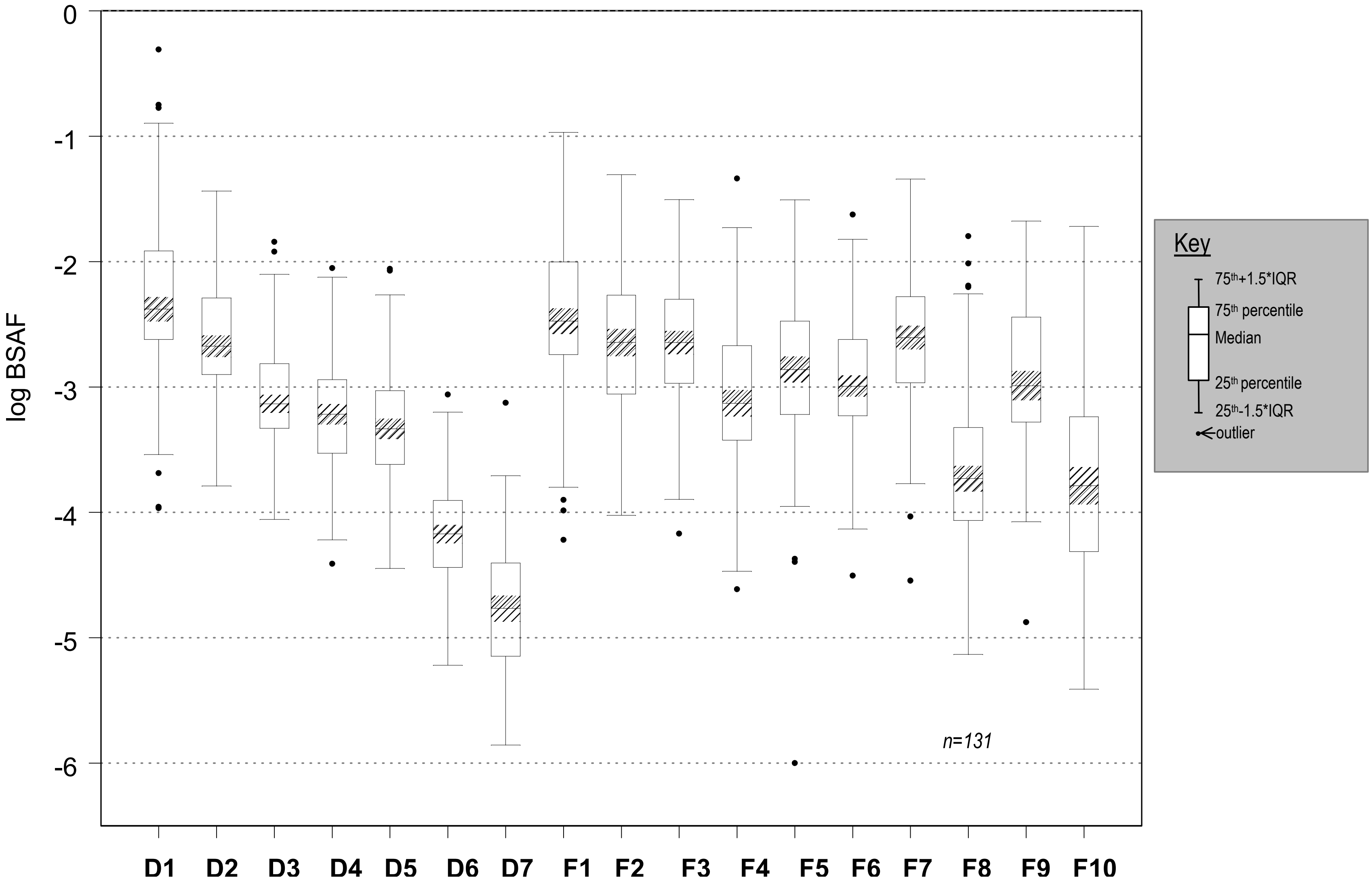


Figure 4.16 Distribution of Individual BSAFs for Crabs from the HSC

performed using the linear models employed to estimate BAFs. Again, two non-linear models (power and polynomial) were included for comparison purposes. Figure 4.17 shows the best-fit lines for the various regression methods and Table 4.6 summarizes the test statistics. Similar to what was observed with tissue-water relationships, linear models did not provide the best fit for the field data. However, they were preferred over the non-linear ones because a biota to sediment accumulation factor could be directly derived. Figure 4.18 presents residuals versus fit plots for the various models. Clustering of the residuals is more evident for the sediment data. However, for low to medium predicted concentrations, the residuals seem to be varying randomly around zero for most of the models. It is noted that all the models in this case (including the non-linear ones) exhibit tailing of the residuals. This is due to very high concentrations of 2378-TCDD in some of the sediment samples. The histograms for the residual datasets are presented in Figure 4.19. Data in Table 4.6 and Figures 4.18 and 4.19 suggest that the LTS model best describes the field data among the linear regressions and fairly meets the assumptions of normality of residuals and constant variance. Thus, this method was selected to estimate the BSAFs for the remaining congeners.

Prior to calculating BSAFs for the different dioxin and furan congeners, scatterplots of residuals versus several explanatory and categorical variables were examined to look for possible correlations (Figures 4.20 and 4.21). No evident patterns were observed in the data.

4.1.2.2 Estimation of BSAF for All Congeners

Biota to sediment accumulation factors were estimated using the robust LTS regression method and following the guidelines outlined in the BAF section. Plots of tissue concentrations of each congener versus the measured concentration in organic carbon-normalized sediment along

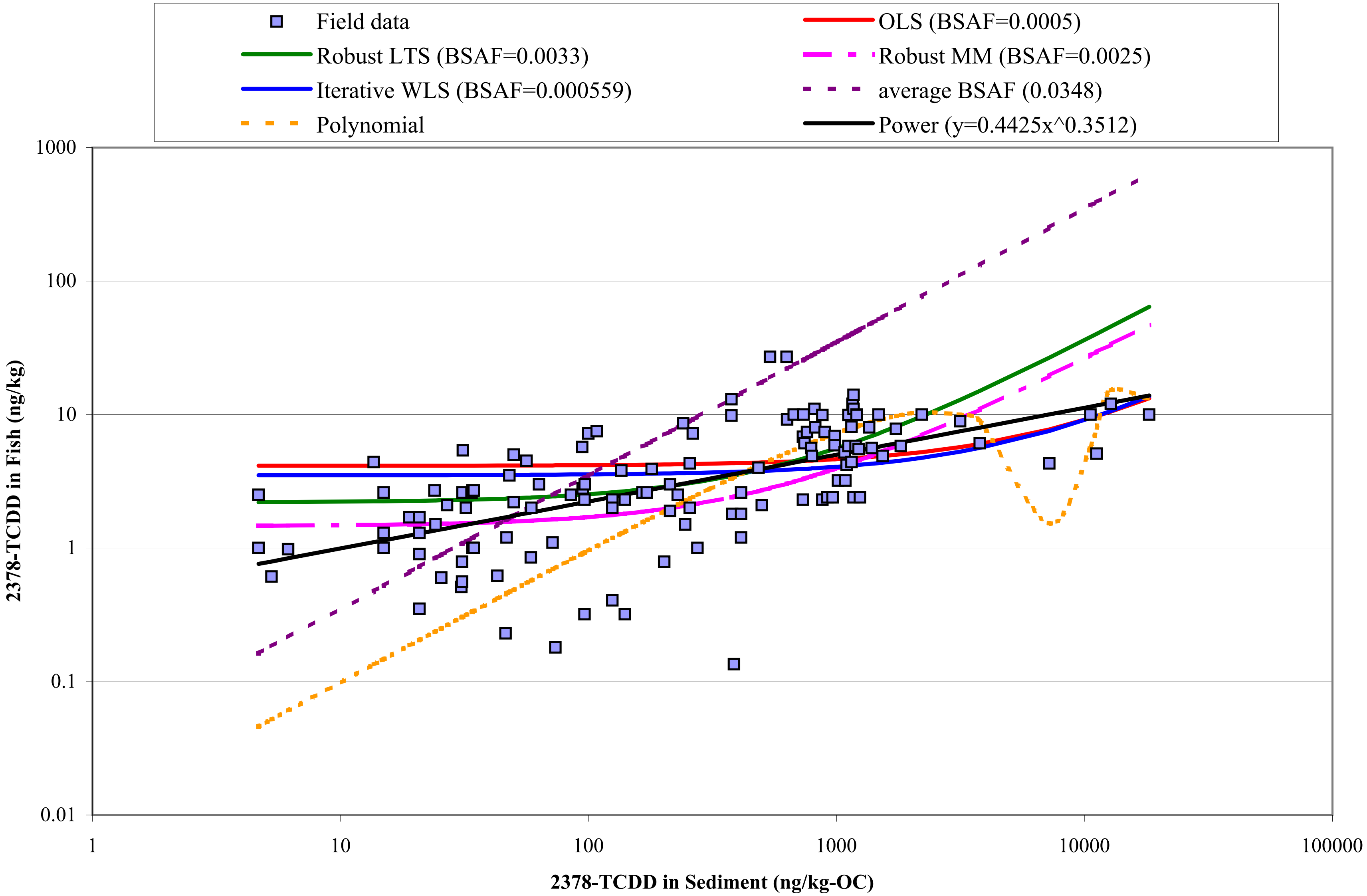


Figure 4.17 Partitioning of 2378-TCDD between Catfish and Carbon-normalized Sediment in the HSC

Table 4.6 Summary of Regression Statistics and Parameters for Catfish-Carbon Normalized Sediment Relationships

Model	**F-statistic**	**p-value**	**Residual SE**	**b0**			**b1 (BSAF in linear regressions)**			**b2**			**b3**		
				Value	**SE**	**t-value[a]**	**Value**	**SE**	**t-value[a]**	**Value**	**SE**	**t-value[a]**	**Value**	**SE**	**t-value[a]**
OLS	11.28	0.001037	4.242	4.1289	0.4037	10.2275	0.0005	0.0002	3.3585						
Robust LTS	90.56	1.11E-16	2.208	2.191	0.2674	8.1946	0.0034	0.0004	9.5165						
Robust MM	*11.1*	*0.0036*	2.061	1.4574	0.2371	6.147	0.0025	0.0004	7.2084						
Iterative WLS	27.67	6.10E-07	2.804	3.5067	0.2775	12.6376	0.0006	0.0001	5.2606						
Polynomial	7.13		4.024	-7.83E-15	1.61E-15	-4.86813	2.74E-10	5.01E-11	5.48E+00	-2.91E-06	4.23E-07	-6.90E+00	9.88E-03	8.41E-04	1.17E+01
Power			2.296	0.4425	0.1012	-3.49869	0.3512	0.0408	8.598						

[a] If |t-value|>2, the linear relationship is statistically significant at α=0.05.

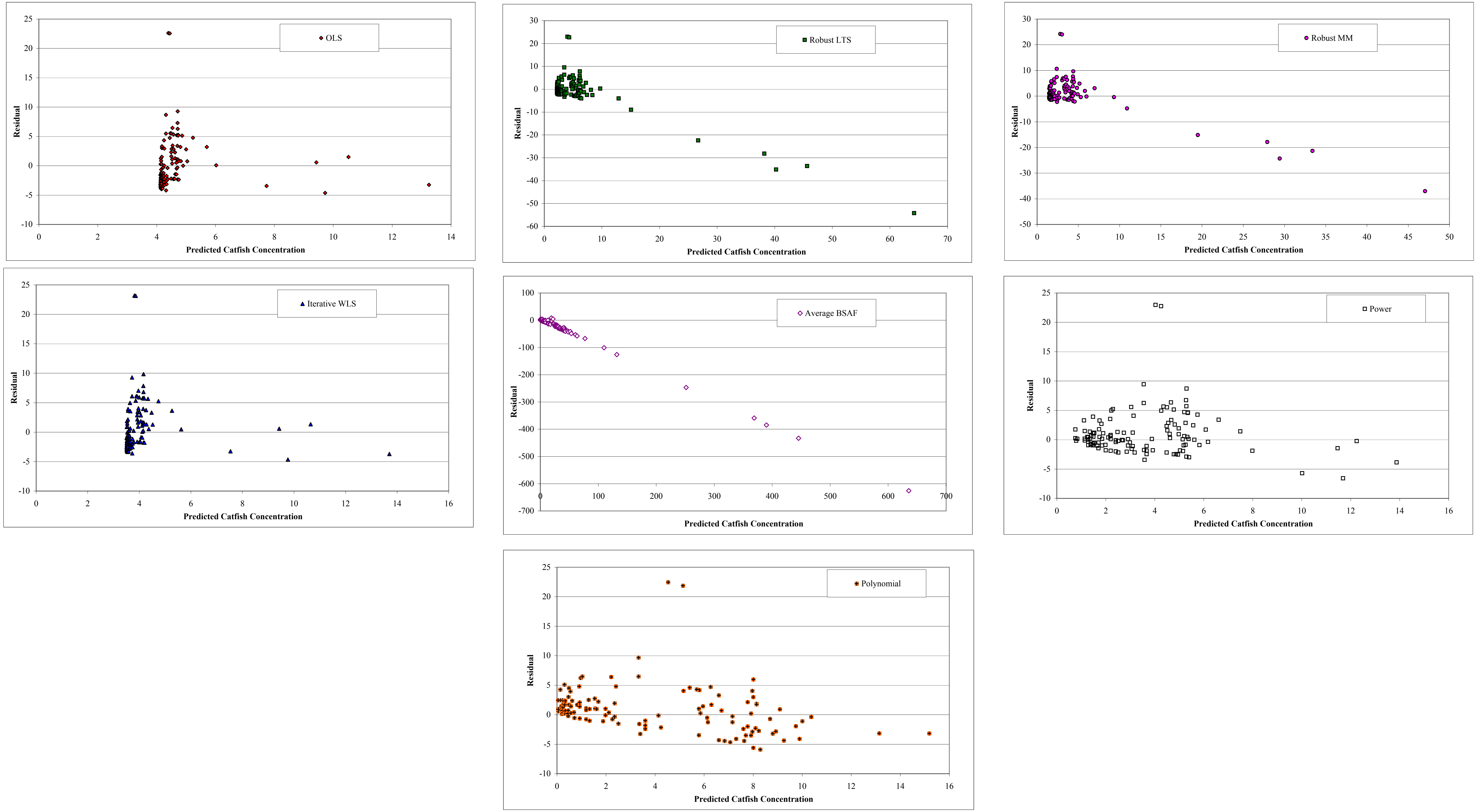


Figure 4.18 Residuals vs Fit Plots for Regressions between Catfish and Sediment-Organic Carbon 2378-TCDD Concentrations

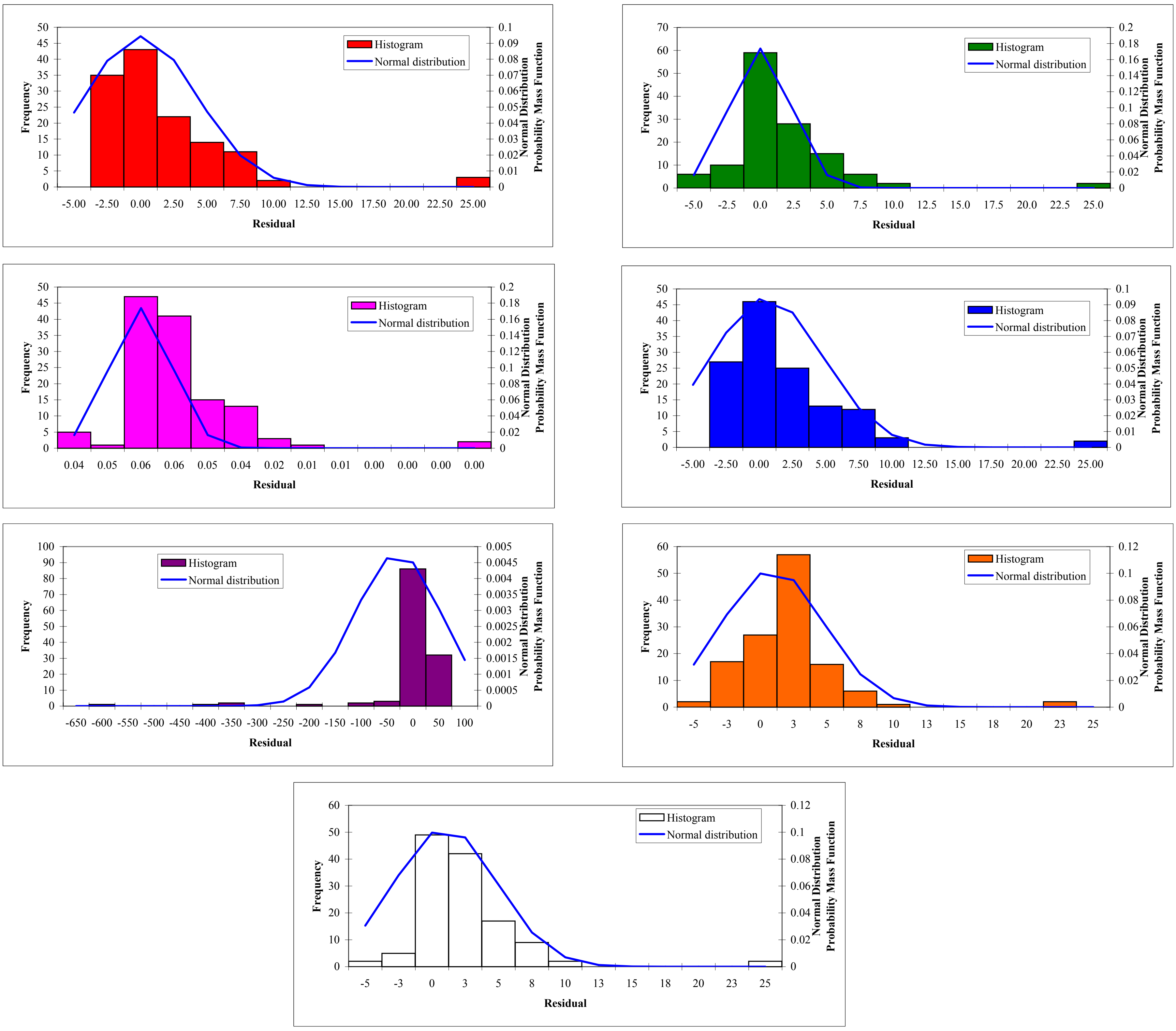


Figure 4.19 Histogram of Residuals for Regressions of Catfish and Sediment Concentrations of 2378-TCDD

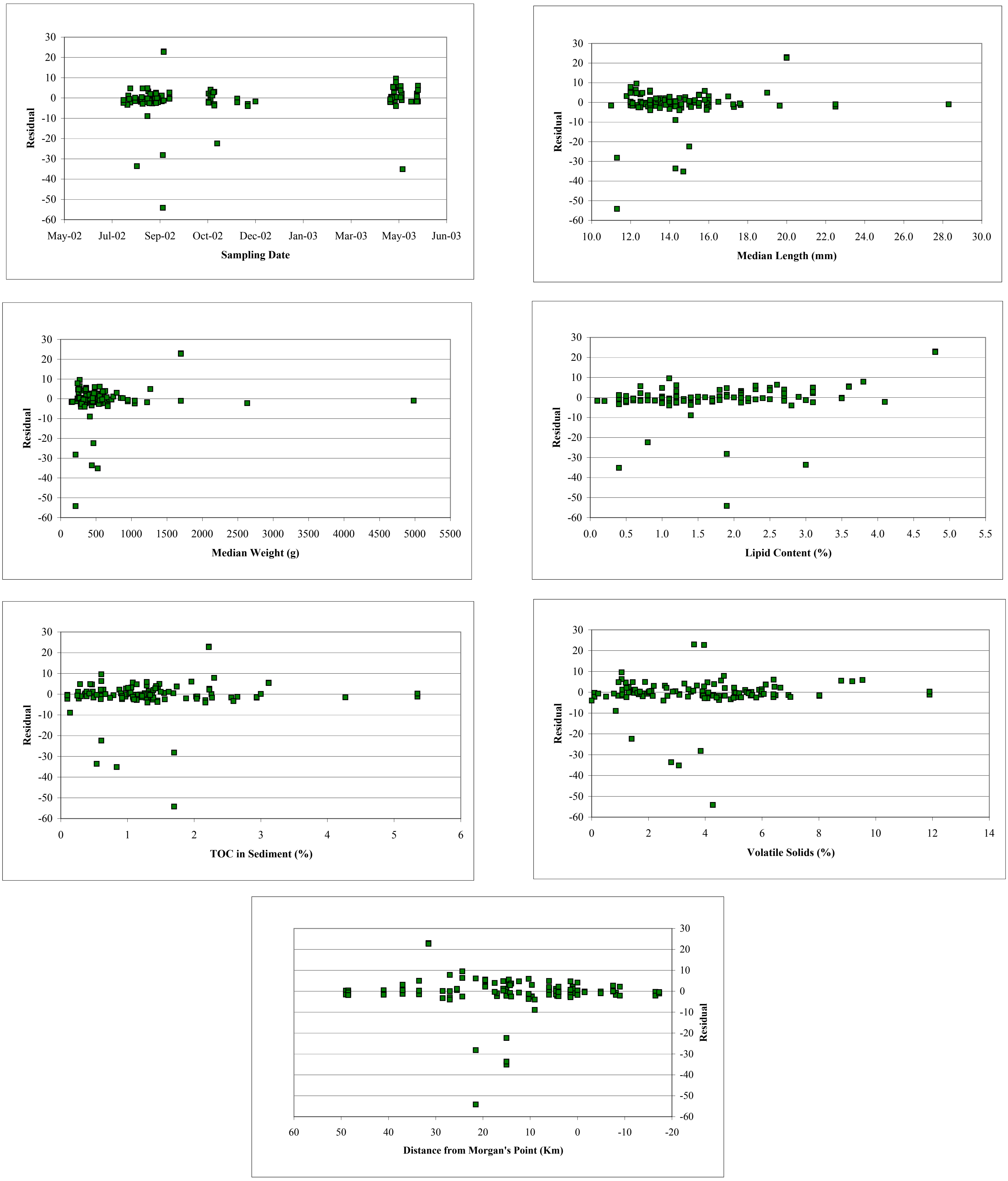


Figure 4.20 Residuals from Catfish BSAF Regressions Plotted by Additional Explanatory Variables

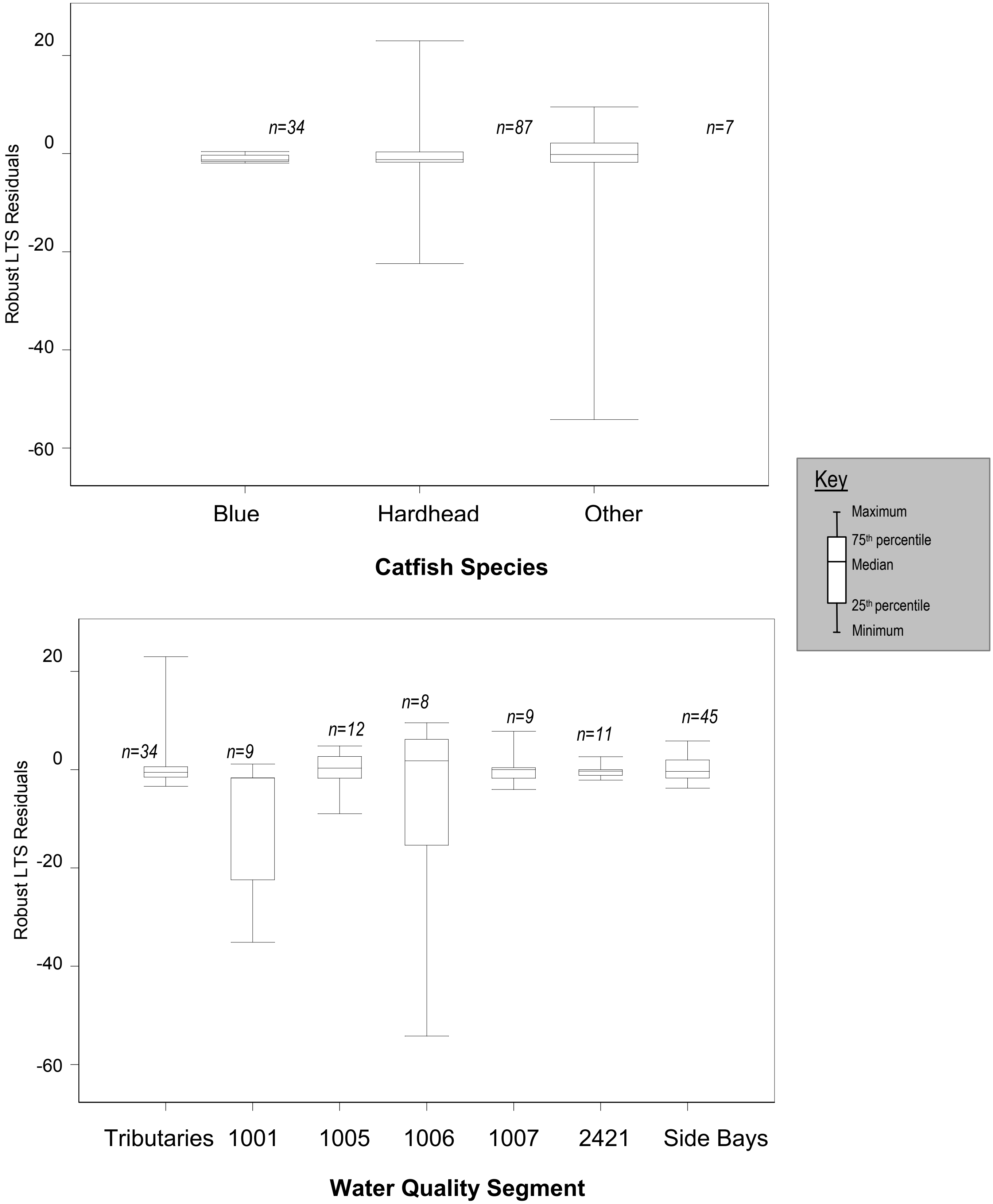


Figure 4.21 Distribution of Residuals from Catfish BSAF Regressions by Categorical Variables

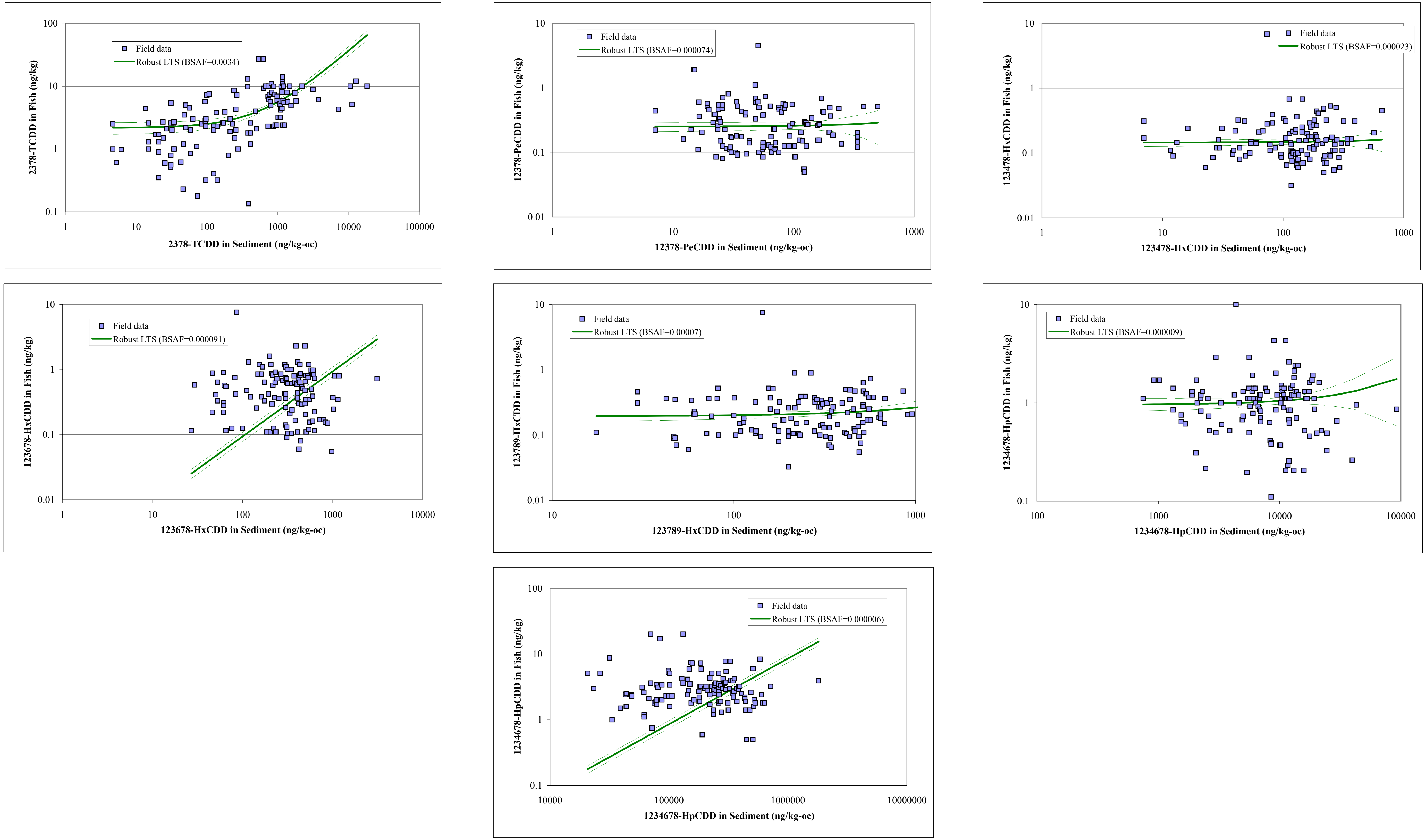
with the best-fit line and the confidence intervals are presented in Figures 4.22 and 4.23 for catfish and crabs, respectively. Table 4.7 summarizes the test statistics for each regression. Biota to sediment accumulation factors varied within 2 orders of magnitude among the different congeners and were generally higher for catfish than for crabs. This may be the result of higher lipid content in fish than in crabs. It is noted that for some congeners the relationships were not statistically significant at the 95% confidence level and, thus, the uncertainty in the estimated BSAFs for those compounds is high.

4.1.2.3 Determination of BSAF using Measures of Central Tendency

Similarly to the observations for BAFs, linear models did not fit BSAF relationships well. Thus, a measure of central tendency (i.e. mean or median) of the ratios of tissue concentrations to sediment concentrations (Figures 4.15 and 4.16) was used instead of BSAFs estimated from linear regressions. The tissue to organic carbon-sediment do not follow a normal distribution as indicated by large skeweness and kurtosis (up to 8 and 40, respectively). Thus, the median was selected as the most appropriate measure of central tendency. Figure 4.24 shows organic carbon-normalized sediment and tissue data and the BSAF fitting lines calculated for selected congeners in both catfish and crabs.

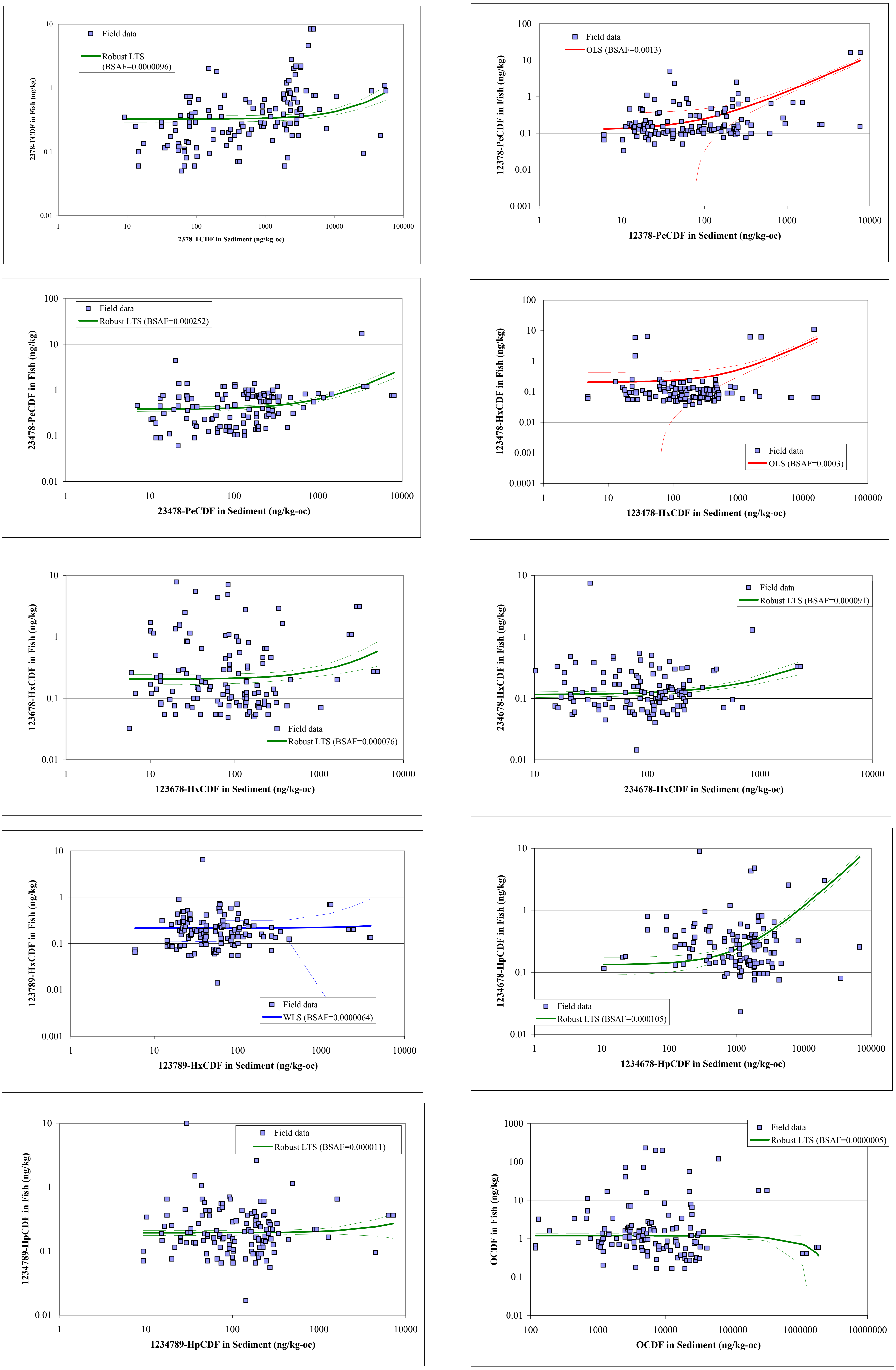
4.1.3 Combined Bioaccumulation and Biota to Sediment Accumulation Factors

In theory, the estimated BAFs include the effects of all routes of chemical exposure in the aquatic ecosystem. Thus, they do not assume simple water-biota partitioning but are an overall expression of the bioaccumulation using the concentration of the chemical in the water column as a reference point (USEPA, 1995). However, this holds true only if the dissolved and bed sediment



Dashed lines correspond to the 95% confidence intervals

Figure 4.22a Biota to Sediment Accumulation Factors for Dioxins in Catfish from the HSC



Dashed lines correspond to the 95% confidence intervals

Figure 4.22b Biota to Sediment Accumulation Factors for Furans in Catfish from the HSC

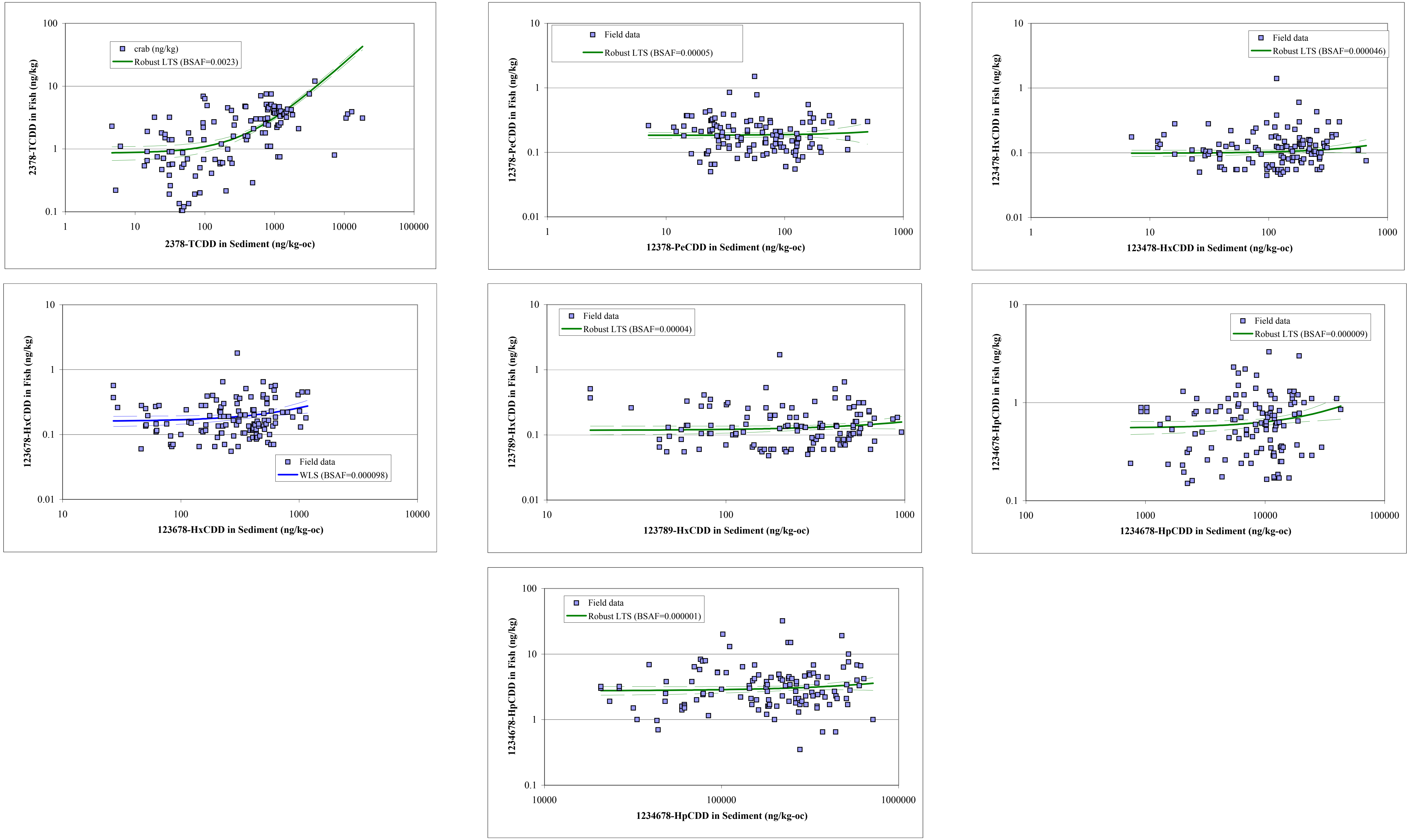


Figure 4.23a Biota to Sediment Accumulation Factors for Dioxins in Crabs from the HSC

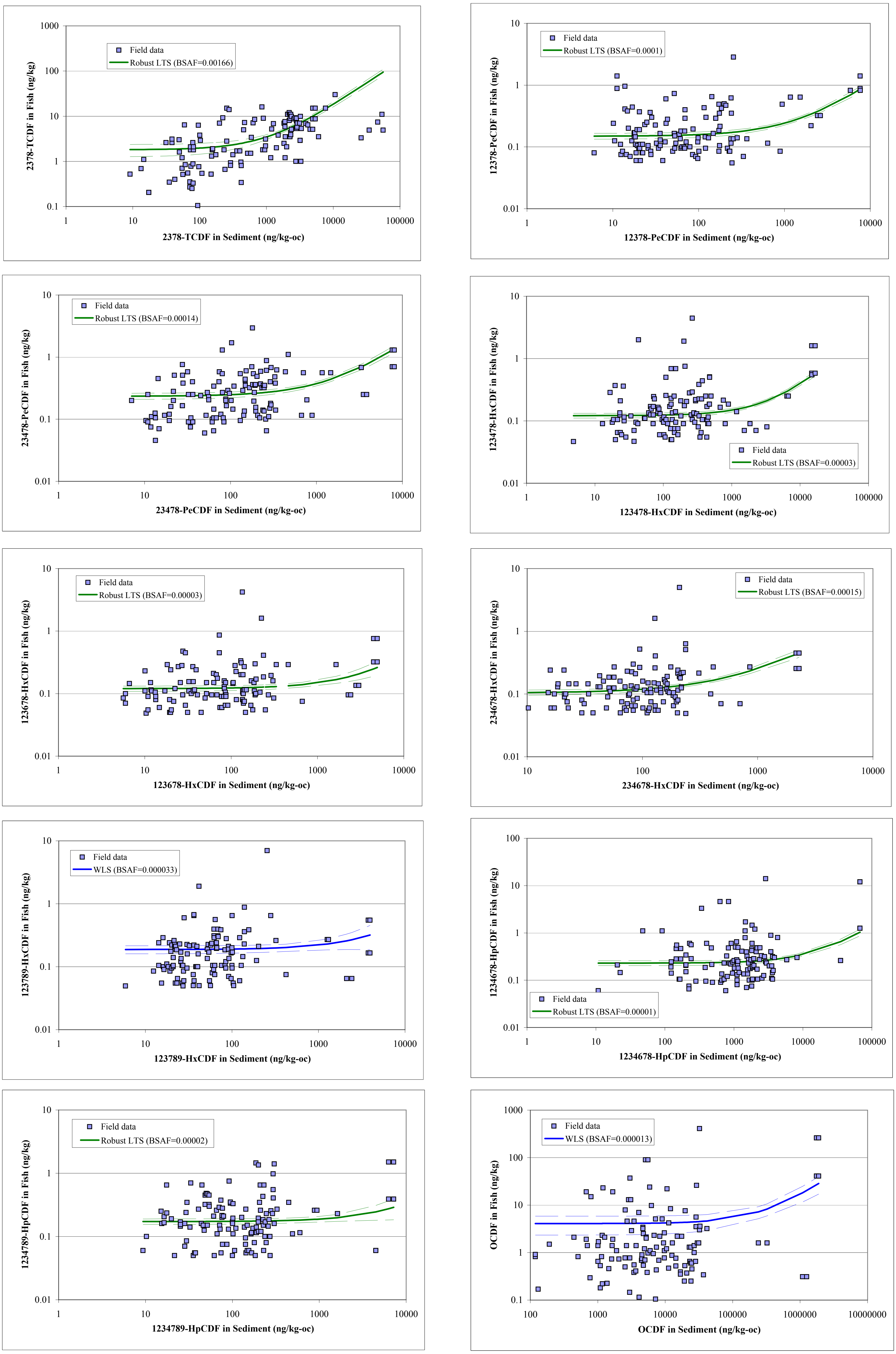


Figure 4.23b Biota to Sediment Accumulation Factors for Furans in Crabs from the HSC

Table 4.7a Estimated Biota to Sediment Accumulation Factors for HSC Catfish

Congener	Method	Regression		Slope	
		SE	Significance F	Estimated BAF	*p* -value
2378-TCDD	Robust LTS	2.3	84.254	0.00345±0.00074	2.266E-15
12378-PeCDD	Robust LTS	0.2	0.008	0.00007±0.00036	🟩 0.9297
123478-HxCDD	Robust LTS	0.1	0.129	0.00002±0.00013	🟩 0.7203
123678-HxCDD	Robust LTS	0.4	-54.482	0.00094±0.00018	3.063E-18
123789-HxCDD	Robust LTS	0.1	1.791	0.00007±0.0001	🟩 0.1834
1234678-HpCDD	Robust LTS	0.5	1.024	0.00001±0.00002	🟩 0.3136
OCDD	Robust LTS	2.1	-81.882	0.00001±0	7.009E-18
2378-TCDF	Robust LTS	0.2	15.760	0.00001±0	0.0001
12378-PeCDF	OLS	1.5	120.906	0.00127±0.00023	3.947E-20
23478-PeCDF	Robust LTS	0.3	28.694	0.00025±0.00009	4.519E-07
123478-HxCDF	OLS	1.5	44.888	0.00032±0.00009	6.232E-10
123678-HxCDF	Robust LTS	0.2	5.864	0.00008±0.00006	0.0172
234678-HxCDF	Robust LTS	0.1	17.009	0.00009±0.00004	7.169E-05
123789-HxCDF	Iterative WLS	0.6	0.027	0.00001±0.00018	🟩 0.8688
1234678-HpCDF	Robust LTS	0.2	114.428	0.0001±0.00002	7.962E-19
1234789-HpCDF	Robust LTS	0.1	1.194	0.00001±0.00002	🟩 0.2769
OCDF	Robust LTS	1.5	-68.643	0.0000004±0.0000009	🟩 0.3497

🟩 *The relationship is not statistically significant*

Table 4.7b Estimated Biota to Sediment Accumulation Factors for HSC Crabs

Congener	Method	Regression		Slope	
		SE	Significance F	Estimated BAF	*p* -value
2378-TCDD	Robust LTS	1.0	212.750	0.0023±0.00031	4.29E-27
12378-PeCDD	Robust LTS	0.1	0.220	0.00005±0.00021	🟩 0.6399
123478-HxCDD	Robust LTS	0.0	1.618	0.00005±0.00007	🟩 0.2061
123678-HxCDD	Iterative WLS	0.1	5.281	0.0001±0.00007	0.0233
123789-HxCDD	Robust LTS	0.1	1.875	0.00004±0.00006	🟩 0.1737
1234678-HpCDD	Robust LTS	0.3	4.003	0.00001±0.00001	0.0478
OCDD	Robust LTS	1.6	1.516	1.16E-06±1.87E-06	🟩 0.2208
2378-TCDF	Robust LTS	2.6	106.818	0.00166±0.00032	6.629E-18
12378-PeCDF	Robust LTS	0.1	144.845	0.00009±0.00002	1.504E-21
23478-PeCDF	Robust LTS	0.2	102.920	0.00014±0.00003	1.815E-17
123478-HxCDF	Robust LTS	0.1	179.169	0.00003±0	1.613E-24
123678-HxCDF	Robust LTS	0.1	11.470	0.00003±0.00002	0.0010
234678-HxCDF	Robust LTS	0.1	72.306	0.00015±0.00004	9.631E-14
123789-HxCDF	Iterative WLS	0.2	2.449	0.00003±0.00004	🟩 0.1202
1234678-HpCDF	Robust LTS	0.2	58.975	0.00001±0	8.369E-12
1234789-HpCDF	Robust LTS	0.1	3.148	0.00002±0.00002	0.0789
OCDF	Iterative WLS	11.2	11.970	0.00001±0.00001	0.0008

🟩 *The relationship is not statistically significant*

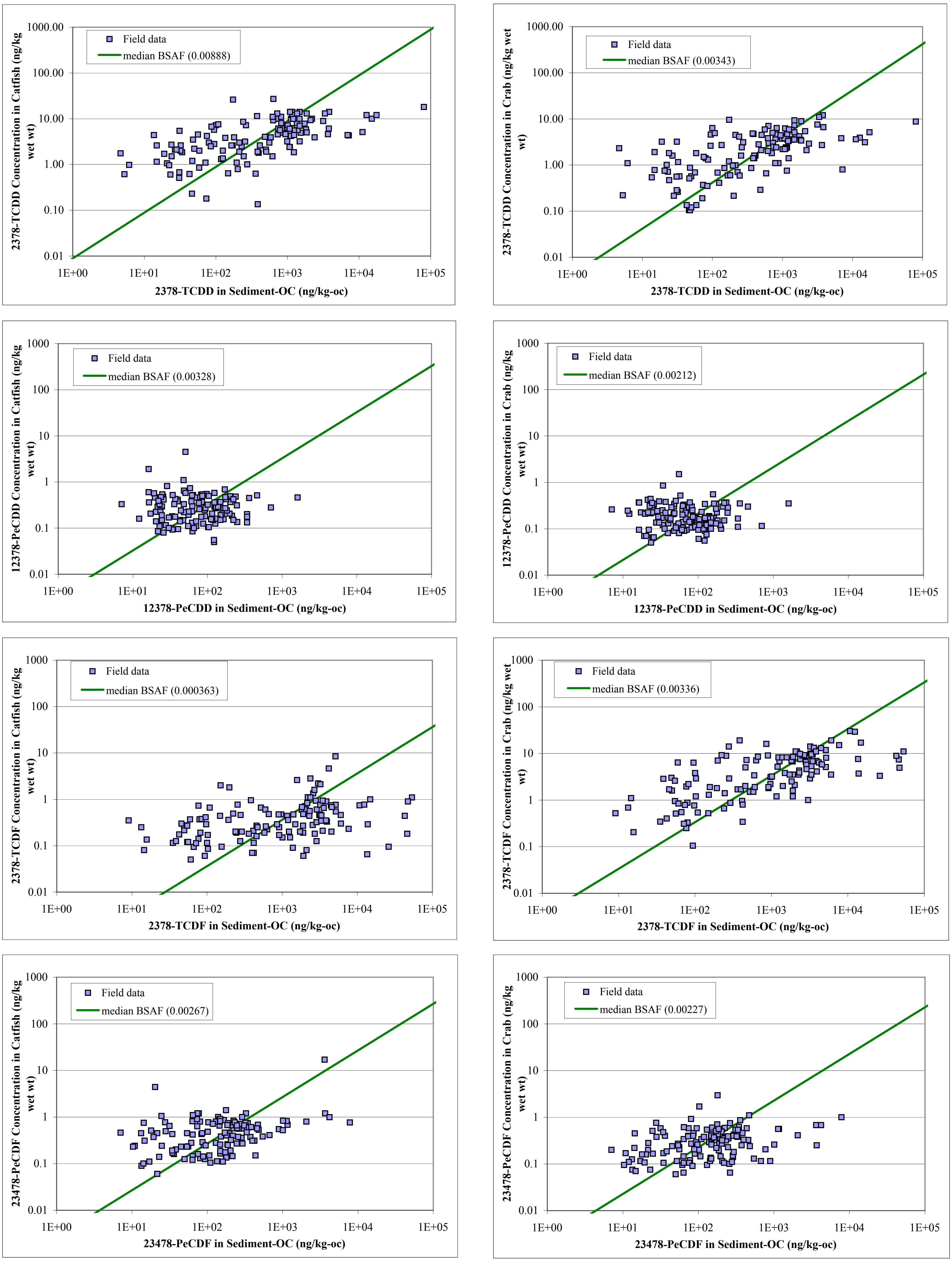


Figure 4.24 Line Fit Plots of BSAF for Selected Congeners in Tissue from the HSC

concentrations are at equilibrium, in which case sediment concentrations are related to the dissolved concentrations by an isotherm (linear or non-linear). For the HSC, it is unclear if the equilibrium assumption is valid, since the correlation between dissolved and bed sediment concentrations is rather poor.

Estimating BAFs and BSAFs independently using water-tissue and sediment-tissue data, respectively may overestimate their values. Thus, an alternative method that uses a combination of the two factors was used to account for all routes of exposure and eliminate overlapping effects. This method consists of multiple linear regressions among dissolved, organic carbon-normalized sediment, and tissue concentrations. It is noted, however, that a multiple regression assumes that the independent variables (dissolved and organic carbon-normalized sediment) are not correlated and that assumption is not completely valid for the HSC. The best-fit line equations will be of the form:

$$C_b = b0+BAF'*C_{w,diss}+BSAF'*C_{soc} \tag{4.5}$$

where *b0* is a coefficient and BAF' and BSAF' are the factors calculated using both water and sediment-oc data. A prime notation is used to differentiate between the independently calculated-factors and the combined factors. The robust LTS regression method was used to minimize the effect of outliers. Figures 4.25 and 4.26 show the results of the multiple regressions for the congeners that contribute more than 1.5% to the TEQ in catfish and crabs[7]. Table 4.8 summarizes the test statistics for each regression. The resulting BAF's were lower than their respective BAFs calculated in Section 4.1.1.2, with the exception of 123678-HxCDF in catfish. The estimated

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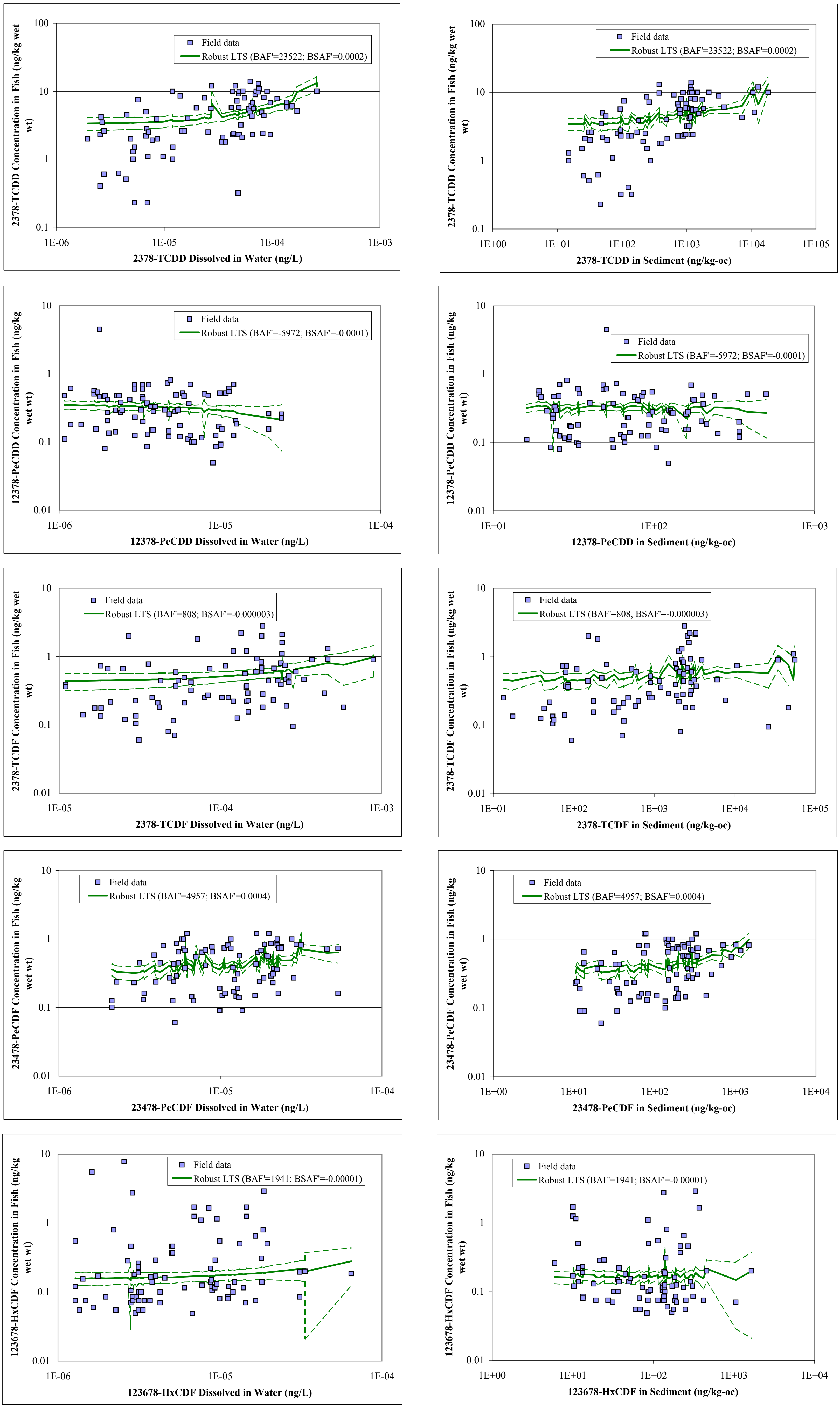
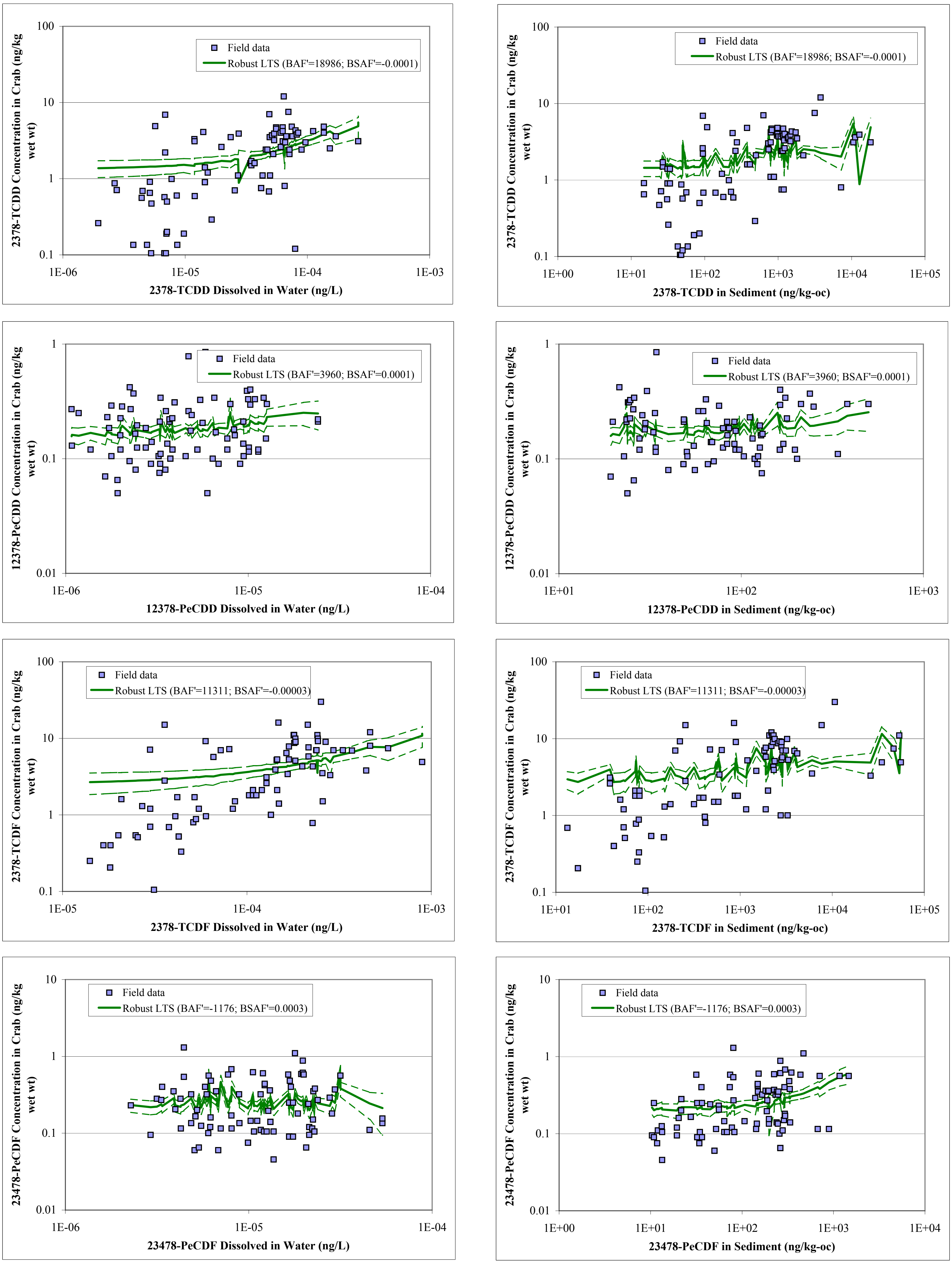
[7] 2378-TCDD, 12378-PeCDD, 2378-TCDF, 23478-PeCDF, and 123678-HxCDF for catfish and 2378-TCDD, 12378-PecDD, 2378-TCDF, and 23478-PeCDF for crabs.



Dashed lines correspond to the 95% confidence intervals

Figure 4.25 Line Fit Plots of Multiple Regressions for Selected Congeners in Catfish from the HSC



Dashed lines correspond to the 95% confidence intervals

Figure 4.26 Line Fit Plots of Multiple Regressions for Selected Congeners in Crabs from the HSC

Table 4.8a Estimated Combined Bioaccumulation and Biota to Sediment Accumulation Factors for HSC Catfish

Congener	Method	Regression		b0		b1		b2	
		SE	Significance F	Intercept	*p*-value	Estimated BAF'	*p*-value	Estimated BSAF'	*p*-value
2378-TCDD	Robust LTS	3.1	12.460	3.316	5.3E-11	23522±17355	0.0084	0.00021±0.0003	0.1705
12378-PeCDD	Robust LTS	0.2	1.018	0.359	5.3E-15	N/A[1]	0.1707	N/A[1]	0.7261
2378-TCDF	Robust LTS	0.5	2.194	0.430	2.6E-07	808±891	0.0748	N/A[1]	0.6597
23478-PeCDF	Robust LTS	0.3	7.740	0.302	4.1E-08	4957±5640	0.0842	0.00036±0.00023	0.0033
123678-HxCDF	Robust LTS	0.1	0.680	0.157	3.1E-10	1941±3336	0.2501	N/A[1]	0.8478

[1] The slope of the best-fit regression is negative

The relationship is not statistically significant

Table 4.8b Estimated Combined Bioaccumulation and Biota to Sediment Accumulation Factors for HSC Crabs

Congener	Method	Regression		b0		b1		b2	
		SE	Significance F	Intercept	*p*-value	Estimated BAF'	*p*-value	Estimated BSAF'	*p*-value
2378-TCDD	Robust LTS	1.4	14.030	1.342	9.9E-09	18986±8276	9.9912E-09	N/A[1]	0.2855
12378-PeCDD	Robust LTS	0.1	2.281	0.149	3.9E-11	3960±4417	0.0782	0.00015±0.00023	0.2055
2378-TCDF	Robust LTS	3.3	9.993	2.523	9.3E-06	11311±6621	0.0004	N/A[1]	0.5070
23478-PeCDF	Robust LTS	0.2	7.270	0.219	3.3E-10	N/A[1]	0.4982	0.00028±0.00015	0.0003

[1] The slope of the best-fit regression is negative

The relationship is not statistically significant

BSAF's for catfish were lower than the BSAF calculated in Section 4.1.2.2, while BSAF's for 12378-PeCDD and 23478-PeCDF in crabs were higher than their respective BSAFs. Note that in some cases, the best-fit line coefficients were negative (e.g., 12378-PeCDD in catfish). This was interpreted as a lack of bioaccumulation of the congener in biota from the HSC.

4.1.4 Texas Statewide Water Quality Criterion

Texas Surface Water Quality Standards (30 TAC §307.1-307.7) include a human health water quality criterion for dioxins/furans of 9.33×10^{-8} µg/L water (0.0933 pg/L), based on saltwater fish consumption. This criterion is based on 2378-tetrachloro-dibenzo-*p*-dioxin (TCDD) equivalent concentrations (TEQs) for the following congeners that are the toxic forms regulated by the Texas Commission on Environmental Quality (TCEQ):

Table 4.9 Toxicity Equivalent Factors (TEFs)

Congener/Isomer	TEF
2,3,7,8 TCDD	1
1,2,3,7,8 PeCDD	0.5
2,3,7,8 HxCDDs	0.1
2,3,7,8 TCDF	0.1
1,2,3,7,8 PeCDF	0.05
2,3,4,7,8 PeCDF	0.5
2,3,7,8 HxCDFs	0.1

The dioxins/furans human health water quality criterion was calculated by the TCEQ from the following equation and risk-based assumptions:

$$(RL \times BW) / (CSF \times CR \times BAF) \qquad (4.6)$$

where: RL = risk level = 10^{-5} or 1 in 100,000

BW = adult body weight = 70 kg

CSF = cancer slope factor = 10^5 kg-day/mg

CR = consumption rate of fish/shellfish = 0.015 kg/day

BAF = bioaccumulation factor for dioxins = 5000 L/kg

The human health criterion for dioxins in water is then:

$$(10^{-5} \times 70\ \text{kg})/(10^{5}\ \text{kg-day/mg} \times 0.015\ \text{kg/day} \times 5000\ \text{L/kg}) = \mathbf{9.33 \times 10^{-11}\ mg/L}, \text{ or } \mathbf{0.0933\ pg/L}$$

This criterion applies to the total dioxin concentration in water, including the suspended particulate plus dissolved fractions.

As stated previously, TMDLs are required for water bodies not meeting water quality standards. It is worth noting that the water bodies addressed by this project were not found to exceed this water quality standard, but instead were not expected to meet the water quality standard because high levels of dioxins were found in fish and crab tissue by the Texas Department of Health. Results of water sampling undertaken in this project, however, confirm that the water quality standard is indeed not met in many of the water bodies.

There are several inherent problems with using this human health water quality criterion as a water quality target for a TMDL. First, it is difficult to measure 0.0933 picograms per liter in ambient water, and it requires complex and expensive sampling equipment. Thus, it is difficult and expensive to evaluate compliance with this criterion. Also, some assumptions used to derive this water-based criterion, such as the BAF, are questionable. The applicability of the BAF of 5,000 L/kg used by the TCEQ in calculating this criterion was not known, and the USEPA recommends determination of site-specific field-measured bioaccumulation relationships

(Sections 4.1.1 and 4.1.2). Thus, a waterbody meeting the TCEQ human health water quality criterion for dioxins/furans in water does not necessarily guarantee that fish and shellfish tissue concentration levels will be safe for human consumption.

The primary advantage of using a water concentration as the water quality target for the TMDL is that it is facilitates calculations of loadings and permit limits. Water quality targets based on tissue or sediment concentrations offer other advantages. For example, it is easier and less expensive to sample and analyze concentrations in tissue and sediment to evaluate compliance.

The following sections are focused on using the data from this project for developing a WQ target that is based on a site-specific bioaccumulation factor as well as a sediment-based WQ target.

4.1.5 Tissue Residue Criterion

The fish or shellfish tissue residue criterion (TRC) is the target concentration in tissue considered acceptable for saltwater fish consumption and is calculated using the following equation and the TCEQ risk management assumptions:

$$TRC = RL \text{ x } BW / CSF \text{ x } CR \tag{4.7}$$

Note that Equation (4.7) is identical to Equation (4.6) except that it leaves out the BAF, which translates the tissue concentration to a water concentration. Thus, the target concentration for dioxins (TEQ) in fish or crab tissue based on TCEQ assumptions is:

$$(10^{-5} \text{x } 70 \text{ kg})/(10^{5} \text{ kg-day/mg x } 0.015 \text{ kg/day}) = 4.7\text{x}10^{-7} \text{ mg/kg} = 0.47 \text{ ng/kg}$$

4.1.6 Water Quality Target Calculations for Dissolved PCDD/Fs in Water

The water quality targets for dissolved PCDD/Fs can be calculated from the TRC and the BAF from the following relationship:

$$C_{w,d} = \frac{TRC}{BAF} \tag{4.8}$$

While the tissue residue criterion is based on TEQ, a composite measure of toxic contributions from twelve dioxin and furan congeners, each of the congeners contributing to the dioxin TEQ has different physical and chemical properties and different bioaccumulation potentials. Given that the BAFs of the various congeners vary so widely, use of a composite BAF for dioxin TEQ seemed inappropriate. Thus, water quality targets for each of the major congeners contributing to the total equivalent concentration are desirable. However, no formal guidelines exist on developing targets for mixtures of compounds that contribute to an exceedance of a WQ criterion.

The fraction of the total TEQ attributable to a given congener f_i^{TEQ} can be calculated as:

$$f_i^{TEQ} = \frac{C_i * BAF_i * TEF_i}{\sum_{i=1}^{17} C_i * BAF_i * TEF_i} \tag{4.9}$$

Then the water quality target for a given congener can be calculated as:

$$C_{w,d} = \frac{TRC * f_i^{TEQ}}{BAF_i * TEF_i} \tag{4.10}$$

In this way, each congener was assigned a water quality target concentration that corresponded to their average fraction of the total TEQ in catfish and crab tissue in the system[8].

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[8] For instance, if 2378-TCDD had contributed, on average, 80% of the TEQ in catfish, and 23478-PeCDD had

These congener-specific targets calculated for <u>all</u> congeners were summed to calculate the water quality target for dioxin TEQ. Note that only the targets for congeners contributing, on average, more than 2% of the TEQ (2378-TCDD, 12378-PeCDD, 2378-TCDF, 23478-PeCDF) were used to calculate exceedance rates in Section 4.1.9 below.

Site-specific water quality targets for dissolved PCDD/Fs in the HSC system calculated from the measured BAFs using Equation (4.10) and the average log BAF (Section 4.1.1.3) for all the data collected for this TMDL project are shown in Table 4.10. Because log BAFs exhibited a normal distribution, the average log BAF for each congener measured in the HSC system was used. The calculated water quality targets were lower for catfish than crabs for most congeners, and the lower target for the two species was selected as the overall water quality target. Typically, 2378-TCDD comprised half or more of the TEQ in all media. The water quality target for dissolved 2378-TCDD was calculated to be 0.0024 pg/L. The water quality target for dioxin TEQ dissolved in water was calculated to be 0.0081 pg/L. The 95% confidence limits for the average BAF also were calculated and used to identify the 95% confidence limits around the water quality target.

4.1.7 Water Quality Target Calculations for PCDD/Fs in Water

Since BAFs were calculated from dissolved concentrations, it is necessary to estimate partitioning relationships to calculate targets that would apply to total water concentrations (dissolved + suspended). Aquatic sediments take up PCDD/Fs just as aquatic animals do, and PCDD/Fs associated with suspended sediments typically exceed those dissolved in a given water sample. Partitioning between the suspended and dissolved phases can be quantitatively

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contributed 20%, the WQ target for 2378-TCDD would be calculated from a catfish TEQ of 0.47 * 80% = 0.376 ng/kg TEQ_{tcdd}, or 0.376 ng/kg TCDD, and the WQ target for 23478-PeCDD would be 0.47 * 20% = 0.094 ng/kg TEQ_{tcdd}, or 0.188 ng/kg PeCDD (TEF=0.5).

Table 4.10a Summary of BAFs and the Resulting Water Quality Targets for Catfish in the HSC

Congener	Texas TEF	log BAF (L/kg)			Average contribution to TEQ[a]	Water Quality Target - Diss (pg/L)			Dissolved-Suspended Isotherm		Water Quality Target - Total (pg/L)		
		BAF	LCL95	UCL95		Value using avg log BAF	LCL95	UCL95	log k	1/n	Value using avg log BAF	LCL95	UCL95
2378-TCDD	1	5.19	5.10	5.27	80.3%	0.0024	0.0020	0.0030	5.16	1.001	0.011	0.010	0.014
12378-PeCDD	0.5	4.78	4.70	4.86	4.5%	0.0007	0.0006	0.0008	2.96	0.057	0.016	0.016	0.017
123478-HxCDD	0.1	4.40	4.32	4.48	0.6%	0.0011	0.0009	0.0013	3.34	0.076	0.035	0.035	0.036
123678-HxCDD	0.1	4.57	4.49	4.66	1.4%	0.0018	0.0014	0.0021	3.54	-0.004	0.094	0.094	0.094
123789-HxCDD	0.1	4.15	4.06	4.24	0.8%	0.0026	0.0021	0.0032	3.58	0.000	0.101	0.101	0.102
1234678-HpCDD		3.46	3.38	3.55	0.0%				5.12	-0.071			
OCDD		2.63	2.55	2.72	0.0%				6.50	0.109			
2378-TCDF	0.1	3.49	3.41	3.58	2.1%	0.0319	0.0260	0.0384	5.08	1.065	0.112	0.090	0.136
12378-PeCDF	0.05	4.34	4.24	4.43	0.4%	0.0017	0.0014	0.0022	4.74	0.786	0.011	0.010	0.014
23478-PeCDF	0.5	4.60	4.53	4.67	6.5%	0.0015	0.0013	0.0018	4.38	0.662	0.010	0.009	0.011
123478-HxCDF	0.1	4.01	3.90	4.11	0.6%	0.0029	0.0023	0.0037	4.21	0.372	0.051	0.047	0.057
123678-HxCDF	0.1	4.45	4.34	4.55	1.4%	0.0023	0.0019	0.0030	4.00	0.377	0.029	0.026	0.032
234678-HxCDF	0.1	4.35	4.26	4.44	0.6%	0.0013	0.0010	0.0016	3.73	0.308	0.019	0.018	0.021
123789-HxCDF	0.1	4.62	4.54	4.70	0.7%	0.0008	0.0007	0.0010	4.81	0.932	0.003	0.003	0.004
1234678-HpCDF		3.89	3.78	3.99	0.0%				4.57	0.270			
1234789-HpCDF		4.44	4.35	4.53	0.0%				4.19	0.480			
OCDF		3.77	3.62	3.91	0.0%				5.52	0.646			
Σ TEQ$_{\text{major congeners in catfish}}$					93.4%	0.0067	0.0056	0.0082			0.036	0.031	0.042
Total TEQ[b]						0.0081	0.0067	0.0099			0.070	0.064	0.077

[a] Average contribution of each congener to TEQ in catfish

[b] Σ TEQ$_{\text{all congeners}}$ (Σ Target$_i$*TEF$_i$)

Water quality targets in blue indicate values for congeners contributing less than 2% to the total TEQ

LCL95 = lower confidence level (α=0.05)

UCL95 = upper confidence level (α=0.05)

Bioaccumulation factors were calculated using data for all the events conducted during this TMDL study

Table 4.10b Summary of BAFs and the Resulting Water Quality Targets for Crabs in the HSC

Congener	Texas TEF	log BAF (L/kg)			Average contribution to TEQ[a]	Water Quality Target - Diss (pg/L)			Dissolved-Suspended Isotherm		Water Quality Target - Total (pg/L)		
		BAF	LCL95	UCL95		Value using avg log BAF	LCL95	UCL95	log k	1/n	Value using avg log BAF	LCL95	UCL95
2378-TCDD	1	4.84	4.76	4.93	68.0%	0.0046	0.0038	0.0056	4.91	0.867	0.025	0.020	0.029
12378-PeCDD	0.5	4.61	4.55	4.67	5.3%	0.0012	0.0011	0.0014	2.69	-0.038	0.018	0.017	0.018
123478-HxCDD	0.1	4.24	4.17	4.31	0.7%	0.0019	0.0016	0.0022	3.26	0.073	0.032	0.031	0.033
123678-HxCDD	0.1	4.17	4.09	4.25	1.1%	0.0035	0.0029	0.0042	3.37	-0.043	0.081	0.081	0.081
123789-HxCDD	0.1	3.97	3.89	4.05	0.9%	0.0045	0.0038	0.0054	3.75	0.049	0.116	0.114	0.118
1234678-HpCDD		3.27	3.19	3.36	0.0%				5.10	0.013			
OCDD		2.72	2.62	2.81	0.0%				6.37	0.183			
2378-TCDF	0.1	4.47	4.39	4.55	13.0%	0.0207	0.0172	0.0249	4.85	0.860	0.087	0.087	0.087
12378-PeCDF	0.05	4.39	4.32	4.46	0.5%	0.0019	0.0016	0.0022	3.92	0.435	0.016	0.015	0.018
23478-PeCDF	0.5	4.43	4.35	4.50	6.8%	0.0024	0.0020	0.0029	3.94	0.481	0.015	0.015	0.015
123478-HxCDF	0.1	4.13	4.03	4.22	1.0%	0.0035	0.0028	0.0044	3.93	0.266	0.053	0.050	0.057
123678-HxCDF	0.1	4.29	4.22	4.37	0.8%	0.0019	0.0016	0.0023	3.64	0.273	0.023	0.021	0.024
234678-HxCDF	0.1	4.32	4.25	4.38	0.8%	0.0018	0.0016	0.0021	3.54	0.254	0.020	0.019	0.021
123789-HxCDF	0.1	4.59	4.52	4.66	1.1%	0.0013	0.0011	0.0016	4.32	0.764	0.005	0.004	0.005
1234678-HpCDF		3.95	3.85	4.05	0.0%				4.41	0.175			
1234789-HpCDF		4.39	4.31	4.48	0.0%				3.62	0.266			
OCDF		3.82	3.68	3.96	0.0%				5.35	0.546			
Σ TEQ$_{\text{major congeners in crabs}}$					93.1%	0.0085	0.0070	0.0102			0.049	0.045	0.054
Total TEQ[b]						0.0104	0.0086	0.0125			0.083	0.078	0.089

[a] Average contribution of each congener to TEQ in crab

[b] Σ TEQ$_{\text{all congeners}}$ (Σ Target$_i$*TEF$_i$)

Water quality targets in blue indicate values for congeners contributing less than 2% to the total TEQ

LCL95 = lower confidence level (α=0.05)

UCL95 = upper confidence level (α=0.05)

Bioaccumulation factors were calculated using data for all the events conducted during this TMDL study characterized by the linear partitioning coefficient (K_p) or by the partitioning constants derived either from the Freundlich or Langmuir sorption equations (Mansour 1993).

The partition coefficient, K_p, describes the ratio of a chemical's concentration in sediment and water at steady-state equilibrium conditions.

$$C_s = K_p * C_{w,d} \tag{4.11}$$

where C_s is the concentration of the chemical in the solid phase, in pg/kg, and $C_{w,d}$ is the dissolved concentration in water, in pg/L. It was noted, however, that the linear partitioning coefficient did not fit the observed HSC data for many congeners (Figure 4.27). Thus, log-transformed data were used to estimate suspended-dissolved partitioning. This is equivalent to using the Freundlich isotherm:

$$C_s = K * C_{w,d}^{1/n} \tag{4.12}$$

where K is the adsorption constant and $1/n$ is another constant providing a rough estimate of the intensity of adsorption (Mansour 1993). The linear partitioning approach is equivalent to the Freundlich isotherm with an exponent ($1/n$) of 1. Congener-specific partitioning constants for the HSC are summarized in Table 4.11.

Water quality targets for total water concentrations (dissolved + suspended) were calculated assuming the average measured suspended particulate matter concentration in the HSC system of 26 mg/L and Equation (4.13):

$$C_{w,total} = C_{w,d} + K * C_{w,d}^{1/n} * [SPM] \tag{4.13}$$

where $C_{w,total}$ is the water quality target concentration for whole water samples, $C_{w,d}$ is the water quality target for dissolved concentrations in water, and [SPM] is the concentration of suspended particulate matter. Site-specific water quality targets for PCDD/Fs in water samples from the

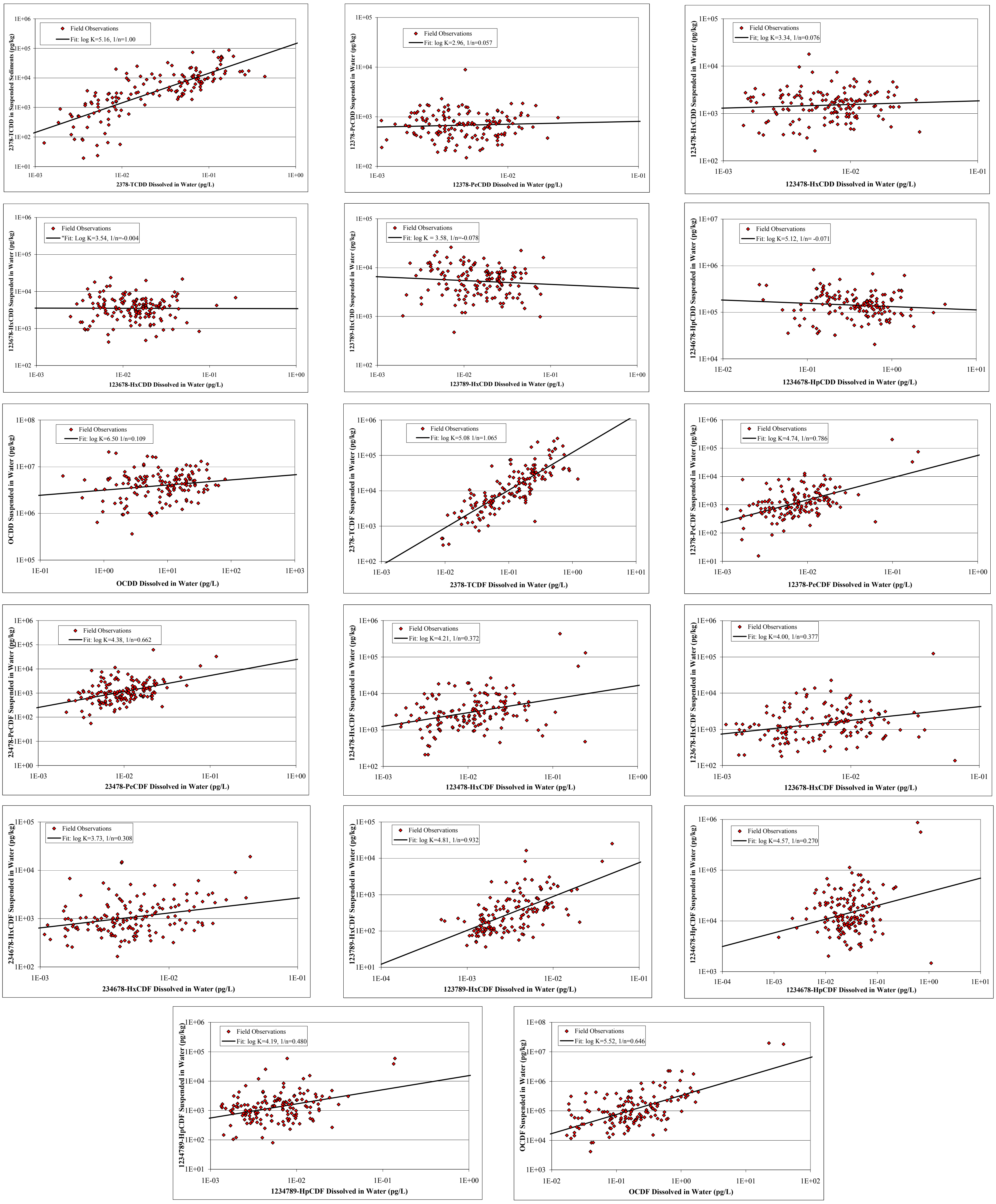

Figure 4.27 Partitioning of Dioxins between Suspended and Dissolved Phases

Table 4.11 Summary of Suspended-Dissolved Partitioning

Congener	r^2	F-statistic	p-value	log K			1/n		
				Value	SE	t-value[a]	Value	SE	t-value[a]
2378-TCDD	0.614	231.99	5.82E-32	5.16	0.11	45.32	1.001	0.07	15.23
12378-PeCDD	0.003	0.50	4.82E-01	2.96	0.19	15.53	0.057	0.08	0.70
123478-HxCDD	0.006	0.84	3.61E-01	3.34	0.18	18.26	0.076	0.08	0.92
123678-HxCDD	0.000	0.00	9.57E-01	3.54	0.16	22.81	-0.004	0.08	-0.05
123789-HxCDD	0.008	1.23	2.69E-01	3.58	0.13	27.22	-0.078	0.07	-1.11
1234678-HpCDD	0.010	1.53	2.18E-01	5.12	0.03	151.38	-0.071	0.06	-1.24
OCDD	0.031	4.63	3.30E-02	6.50	0.05	127.45	0.109	0.05	2.15
2378-TCDF	0.674	301.64	2.42E-37	5.08	0.07	77.55	1.065	0.06	17.37
12378-PeCDF	0.288	58.99	2.11E-12	4.74	0.22	21.61	0.786	0.10	7.68
23478-PeCDF	0.190	34.34	2.95E-08	4.38	0.23	19.09	0.662	0.11	5.86
123478-HxCDF	0.119	19.73	1.75E-05	4.21	0.17	25.08	0.372	0.08	4.44
123678-HxCDF	0.095	15.26	1.43E-04	4.00	0.22	18.53	0.377	0.10	3.91
234678-HxCDF	0.085	13.58	3.22E-04	3.73	0.19	19.41	0.308	0.08	3.68
123789-HxCDF	0.376	87.87	1.23E-16	4.81	0.25	19.29	0.932	0.10	9.37
1234678-HpCDF	0.071	11.14	1.07E-03	4.57	0.13	35.19	0.270	0.08	3.34
1234789-HpCDF	0.133	22.47	5.01E-06	4.19	0.23	18.25	0.480	0.10	4.74
OCDF	0.387	92.00	3.37E-17	5.52	0.06	87.61	0.646	0.07	9.59

[a] If |t-value|>2, the linear relationship is statistically significant at a=0.05.

The relationship is not statistically significant

SE = standard error

Partitioning coefficients were calculated using all the data collected under this TMDL project

HSC system are shown in Table 4.10. The water quality target for 2378-TCDD in water was calculated to be 0.011 pg/L, and the water quality target for dioxin TEQ in water was calculated to be 0.070 pg/L. These targets are several times higher than for dissolved concentrations, indicating that a large portion of the total dioxin is associated with the suspended particulate phase in water. This calculated target for dioxin TEQ in water is approximately 75% of the state water quality criterion of 0.093 pg/L.

4.1.8 Water Quality Target Calculations for PCDD/Fs in Sediments

The water quality target concentration in sediment can be calculated using the following equation:

$$C_{sed,oc} = \frac{TRC}{BSAF} \tag{4.14}$$

The water quality targets for individual congeners contributing to the composite TEQ concentration can be calculated as:

$$C_{sed,oc} = \frac{TRC * f_i^{TEQ}}{BSAF_i * TEF_i} \tag{4.15}$$

Site-specific sediment quality targets for PCDD/Fs in the HSC system calculated from the measured BSAFs using Equation (4.15) and the entire database collected for this TMDL project are shown in Table 4.12. For BSAFs, which exhibited non-normality, the median BSAF was selected as the most appropriate measure of the typical BSAF for each congener. Also note that this target is based on the organic carbon-normalized sediment concentration, calculated as the bulk sediment concentration divided by its organic carbon content. The calculated targets were lower for fish than crabs for most congeners, and the lower target for the two species was selected as the overall water quality target. Typically, 2378-TCDD comprised half or more of the TEQ

Table 4.12a Summary of BSAFs and the Resulting Water Quality Targets for Catfish in the HSC

Congener	Texas TEF	BSAF			Average contribution to TEQ[b]	Sediment-based Quality Target (ng/kg-oc)		
		Median BSAF	LCL95[a]	UCL95[a]		Value using median BSAF	LCL95	UCL95
2378-TCDD	1	8.88E-03	6.29E-03	1.23E-02	80.3%	43	31	60
12378-PeCDD	0.5	3.28E-03	2.71E-03	4.68E-03	4.5%	13	9	16
123478-HxCDD	0.1	1.01E-03	8.30E-04	1.41E-03	0.6%	28	20	34
123678-HxCDD	0.1	1.57E-03	1.25E-03	1.81E-03	1.4%	42	36	53
123789-HxCDD	0.1	7.70E-04	5.60E-04	9.50E-04	0.8%	48	39	66
1234678-HpCDD		1.10E-04	1.00E-04	1.30E-04	0.0%			
OCDD		1.40E-05	1.10E-05	1.80E-05	0.0%			
2378-TCDF	0.1	3.63E-04	2.74E-04	5.21E-04	2.1%	272	189	360
12378-PeCDF	0.05	1.72E-03	1.35E-03	2.40E-03	0.4%	22	16	28
23478-PeCDF	0.5	2.67E-03	2.22E-03	3.90E-03	6.5%	23	16	28
123478-HxCDF	0.1	5.44E-04	3.73E-04	6.23E-04	0.6%	54	47	79
123678-HxCDF	0.1	1.57E-03	1.00E-03	2.34E-03	1.4%	42	28	66
234678-HxCDF	0.1	9.60E-04	8.20E-04	1.23E-03	0.6%	30	23	35
123789-HxCDF	0.1	2.14E-03	1.80E-03	3.59E-03	0.7%	16	10	19
1234678-HpCDF		1.51E-04	1.27E-04	1.90E-04	0.0%			
1234789-HpCDF		1.14E-03	8.68E-04	1.54E-03	0.0%			
OCDF		1.62E-04	8.38E-05	2.33E-04	0.0%			
Σ TEQ$_{\text{major congeners in catfish}}$					93.4%	88	62	118
Total TEQ$_{\text{soc}}$[c]						115	83	154

[a] LCL95 = lower confidence level (α=0.05)
UCL95 = upper confidence level (α=0.05)

[b] Average contribution of each congener to TEQ in catfish

[c] Σ TEQ$_{\text{all congeners}}$ (Σ Target$_i$*TEF$_i$)

Sediment-based quality targets in blue indicate values for congeners contributing less than 2% to the total TEQ

Biota-to-sediment accumulation factors were calculated using data for all the events conducted during this TMDL study

Table 4.12b Summary of BSAFs and the Resulting Water Quality Targets for Crabs in the HSC

Congener	Texas TEF	BSAF			Average contribution to TEQ[b]	Sediment-based Quality Target (ng/kg-oc)		
		Median BSAF	LCL95[a]	UCL95[a]		Value using median BSAF	LCL95	UCL95
2378-TCDD	1	4.18E-03	3.43E-03	5.60E-03	68.0%	76	57	93
12378-PeCDD	0.5	2.12E-03	1.82E-03	3.22E-03	5.3%	24	15	27
123478-HxCDD	0.1	7.36E-04	5.90E-04	8.88E-04	0.7%	45	37	56
123678-HxCDD	0.1	6.07E-04	4.55E-04	7.80E-04	1.1%	85	66	114
123789-HxCDD	0.1	4.65E-04	3.64E-04	5.96E-04	0.9%	91	71	116
1234678-HpCDD		6.75E-05	5.90E-05	7.98E-05	0.0%			
OCDD		1.72E-05	1.29E-05	2.27E-05	0.0%			
2378-TCDF	0.1	3.36E-03	2.84E-03	4.35E-03	13.0%	182	140	215
12378-PeCDF	0.05	2.27E-03	1.87E-03	2.94E-03	0.5%	21	16	25
23478-PeCDF	0.5	2.27E-03	1.61E-03	2.84E-03	6.8%	28	23	40
123478-HxCDF	0.1	7.44E-04	6.18E-04	1.06E-03	1.0%	63	44	76
123678-HxCDF	0.1	1.38E-03	8.74E-04	1.73E-03	0.8%	27	22	43
234678-HxCDF	0.1	1.02E-03	8.37E-04	1.34E-03	0.8%	37	28	45
123789-HxCDF	0.1	2.49E-03	1.75E-03	3.28E-03	1.1%	21	16	30
1234678-HpCDF		1.86E-04	1.25E-04	2.31E-04	0.0%			
1234789-HpCDF		1.03E-03	7.71E-04	1.70E-03	0.0%			
OCDF		1.64E-04	1.10E-04	1.97E-04	0.0%			
Σ TEQ$_{\text{major congeners in crabs}}$					93.1%	120	90	148
Total TEQ$_{\text{soc}}$[c]						158	119	197

[a] LCL95 = lower confidence level (α=0.05)
UCL95 = upper confidence level (α=0.05)

[b] Average contribution of each congener to TEQ in crabs

[c] Σ TEQ$_{\text{all congeners}}$ (Σ Target$_i$*TEF$_i$)

Sediment-based quality targets in blue indicate values for congeners contributing less than 2% to the total TEQ

Biota-to-sediment accumulation factors were calculated using data for all the events conducted during this TMDL study in all media. The sediment quality target for 2378-TCDD was calculated to be 43 ng/kg oc. The water quality target for dioxin TEQ in sediments was calculated to be 115 ng/kg oc. The 95% confidence limits for the average BSAF also were calculated and used to identify the 95% confidence limits around the water quality target.

4.1.9 Observed Target Exceedance Rates

The water quality targets are summarized in Table 4.13 below.

Table 4.13 Summary of Site-Specific Water Quality Targets in Various Media

Congener	Water – Dissolved pg/L	Water - Total pg/L	Sediment ng/kg-OC
2378-TCDD	0.0024	0.011	43
12378-PeCDD	0.0007	0.016	13
2378-TCDF	0.0207	0.087	182
23478-PeCDF	0.0015	0.010	23
Total TEQ	0.0081	0.070	115

For each congener, the lower target for the two species (catfish or crab) was selected.

Water and sediment data collected in Phases II and III of the project were compared to the estimated media-specific water quality targets to evaluate the current state of impairment of the HSC system, and the concentration reductions required to meet the water quality targets. Table 4.14 summarizes the percent target exceedances by congener for both water and sediment samples. Water quality targets are exceeded in most samples for most congeners, and overall exceedance rates are currently greater than 90%. Note that for many congeners, these exceedance rates may be high, as the exceedance status for nonquantifiable measurements could not be compared to the targets unless the quantitation limit was less than the target. The percent reductions in ambient dioxin levels required to meet the water quality targets in various media are shown in Table 4.15. Overall, it appears that an 85-90% reduction in concentrations, or one order of magnitude, will be required for the water quality targets to be met.

Table 4.14 Summary of Exceedances of the Estimated Water Quality Targets

Congener	Dissolved Water Samples[a]	Total Water Samples[a]	Sediment Samples[a]
Number of samples	*148*	*148*	*173*
2378-TCDD	96% (84)	83% (93)	84% (167)
12378-PeCDD	100% (64)	39% (127)	95% (86)
2378-TCDF	93% (147)	89% (148)	76% (174)
23478-PeCDF	100% (93)	91% (95)	88% (154)
Total TEQ	100% (148)	91% (148)	93% (174)

[a] Value in parentheses represents the number of samples that could be used for determination of target exceedance because either the concentrations were quantifiable or, if the concentrations were not quantifiable, the quantitation limits were below the water quality target

Table 4.15 Median Measured Congener Concentrations and Percent Reductions Required To Meet Water Quality Targets by Media

Congener	Dissolved Water Samples		Total Water Samples		Sediment Samples	
Number of samples	*148*		*148*		*173*	
	Median Concentration	% Reduction	Median Concentration	% Reduction	Median Concentration	% Reduction
2378-TCDD	0.027	91%	0.106	90%	621	93%
12378-PeCDD	0.0043	84%	0.016	0%	75	83%
2378-TCDF	0.13	84%	0.40	78%	1,582	88%
23478-PeCDF	0.0095	84%	0.030	67%	147	84%
Total TEQ	0.066	88%	0.23	69%	1,065	89%