Total Maximum Daily Load for Dioxin in the Houston Ship Channel

University of Houston
Parsons Water&Infrastructure
PBS&J
Main tasks Phase III – (WO7)

- Develop a QAPP for additional data collection
- Conduct dioxin monitoring and additional data collection in the HSC
- Model fate and transport of dioxins in the HSC using sophisticated models
- Participate in stakeholder process
- Estimate TMDL allocations
- Evaluate PCB data gathered to date
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Task 1 – Develop a QAPP

- QAPP approved on 01/27/2004
- Amendment 1, approved on 07/01/2004, developed to add:
  - vertical profiles of dioxin at 2 locations
  - high-resolution sediment sampling
  - boundary concentrations for model
- Amendment 2, approved on 08/19/2004, developed to:
  - add one set of runoff samples
  - modify dry/wet and add bulk deposition sampling
  - add air sampling by particle size
- Annual update, submitted on 01/20/2005
  - add flow measurements
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Task 2 – Monitoring and data collection

- Assess current levels and trends in the project area:
  - 17 in-channel locations for water (dissolved and particulate matter), sediment, fish, and crab twice
  - 11 tributary locations for fish and crab 1 time
  - Sediment cores from 6-8 locations to gather data on the historical deposition of dioxins and furans as well as accumulation rates
  - 2 locations for deep&shallow water sampling once
  - 15 locations for high-resolution sediment sampling once
  - 2 locations in upper watershed for water sampling once
Task 2 – Monitoring and data collection – cont’d

- Assess major sources:
  - Ambient water at confluences with main tributaries (11 locations, 2 times)
  - Ambient air, wet/dry/bulk deposition, and particle size at 1 location
  - Runoff sampling at 10 locations once
Sampling locations

- Water, sediment, and tissue (main channel)
- Water and tissue (tribs)
- Vertical profile (water)
Dioxin in water profiles

Texas WQS: 0.093 pg/L

Open symbols: spring 2004
Closed symbols: average WO4
Dioxin in catfish profiles

- Concentrations (ng/kg-wet wt)
- Distance from Morgan’s Point (km)
- Open symbols: spring 2004
- Closed symbols: average WO4

Texas TEQ health-based std: 0.47 ng/kg
Dioxin in crab profiles

Open symbols: → spring 2004
Closed symbols → average WO4

Texas TEQ health-based std: 0.47 ng/kg
Seasonal trends in water samples

Error bars correspond to the 95% confidence intervals
Seasonal trends in sediment-oc samples

Error bars correspond to the 95% confidence intervals.
Seasonal trends in tissue samples

Error bars correspond to the 95% confidence intervals.
Approach 1:
Water concentration target, relying on hi-vol water sampling

Approach 2:
Tissue-based WQS, using bioaccumulation factors to link water/sediment concentrations to tissue concentrations
Calculating bioaccumulation factors

Approach 1:
Use measures of central tendency of the $C_b/C_w$ and $C_b/C_{oc}$ ratios

Approach 2:
Calculate BAF and BSAF from average concentrations (EPA, 2003)

$$BAF = \frac{C_b}{C_w}$$
$$BSAF = \frac{C_b}{C_{sedOC}}$$

$C_b =$ concentration in biota [pg/kg-wet wt]
$C_w =$ concentration in water [pg/L]
$C_{oc} =$ organic-carbon normalized concentration [pg/kg-oc]
2378-TCDD HSC site-specific BAF ($C_b/C_w$)

Resulting WQ targets for catfish:
- App 1: 0.042 pg/L
- App 2: 0.045 pg/L

Resulting WQ targets for crab:
- App 1: 0.059 pg/L
- App 2: 0.061 pg/L

Data from 4 events
2378-TCDD HSC site-specific BSAF ($C_b/C_{soc}$)

Resulting sediment targets from catfish:
- App 1: 72 ng/kg-oc
- App 2: 151 ng/kg-oc

Resulting sediment targets from crab:
- App 1: 126 ng/kg-oc
- App 2: 253 ng/kg-oc

Data from 4 events
Dissolved-suspended fugacity ratios

Equilibrium

Fugacity Ratio (fs/fw)

sediment → water column flux

water column → sediment flux

sh=shallow
de=deep

11193-sh
11193-de
15979-sh
15979-de
Dissolved-bottom sediment fugacity ratios

Fugacity Ratio (fs/fw)

Equilibrium

sediment $\rightarrow$ water column flux

water column $\rightarrow$ sediment flux

$de$=deep
High-resolution sediment sampling
High-resolution sediment sampling results

Main Channel (segments 1007-1006) San Jacinto River

TEQ in Sediment (ng/kg-oc)

237/240Th in Sediment (ng/kg-oc)
Sediment concentrations along transect

- **TEQ in Sediment (ng/kg-oc)**
  - A: 500
  - B: 1000
  - C: 1500
  - D: 2000
  - E: 500

- **2378-TCDD in Sediment (ng/kg-oc)**
  - A: 200
  - B: 800
  - C: 1000
  - D: 600
  - E: 200
Sediment core locations

Sediment aging and deposition rate estimates underway
Dioxin concentrations in 11261 core

![Graph showing dioxin concentrations over depth and concentration. The graph includes symbols for various dioxin congeners: 2378-TCDD, 2378-TCDF, 12378-PeCDD, 23478-PeCDF, OCDD/100, and TEQ. The x-axis represents concentration (ng/kg-dry wt), and the y-axis represents depth (cm).]
Dioxin concentrations in 15244 core

Concentration (ng/kg-dry wt) vs. Depth (cm)

- **2378-TCDD**
- **2378-TCDF**
- **12378-PeCDD**
- **23478-PeCDF**
- **OCDD/100**
- **TEQ**

Inset map showing geographical context.
Dioxin concentrations in 11193 core

Concentration (ng/kg-dry wt)

Depth (cm)
Air monitoring locations

- Clinton Dr
- Bayland Park
- Haden Rd
- Lang
- Mont Belvieu
Dioxin in ambient air

- **Clinton Dr.**
- **Haden Rd.**
- **Bayland Park**
- **Lang**
- **Mont Belvieu**

Total TEQ in Ambient Air (fg/m³)
Monthly average concentrations in air

- **1,2,3,4,6,7,8-HpCDD, OCDD (fg/m³)**
- **2,3,7,8-TCDD**
- **1,2,3,7,8-PeCDD**
- **2,3,4,7,8-PeCDF**
- **2,3,7,8-HxCDDs**
- **1,2,3,7,8-HpCDDs**
- **OCDF (fg/m³)**

**Graphs:**
- Monthly average concentrations for various compounds in air, showing trends from September to August.

**Legend:**
- TEMP (°C)
- 2,3,7,8-TCDD
- 2,3,7,8-HxCDDs
- 1,2,3,7,8-HpCDD
- OCDF (fg/m³)
- 2,3,7,8-TCDF
- 2,3,7,8-PeCDD
- 2,3,7,8-PeCDF
- 2,3,7,8-HpCDFs
- OCDF
Dioxins by particle size

PCDDs & PCDFs concentration (fg/m$^3$)

- 2378-PCDDs
- 2378-PCDFs
- Particle mass conc

Cascade Impactor Stages

- >7.2 um
- 7.2-3.0
- 3.0-1.5
- 1.5-0.95
- 0.95-0.49
- <0.49 um

Particle Mass Concentration (ug/m$^3$)

- 2378-PCDDs
- 2378-PCDFs
- Particle mass conc
Dioxin in ambient air (Sept-Oct, 2004)

Concentrations (fg/m³)

- 2,3,7,8-TCDD
- 1,2,3,7,8-PeCDD
- 1,2,3,6,7,8-HxCDD
- 1,2,3,7,8,9-HxCDD
- 1,2,3,4,6,7,8-HpCDD

- 0.9
- 2
- 4
- 8
- 125
- 519

- OCDD

- 2,3,7,8-TCDF
- 1,2,3,7,8-PeCDF
- 2,3,4,7,8-PeCDF
- 1,2,3,4,7,8-HxCDF
- 1,2,3,6,7,8-HxCDF
- 2,3,4,6,7,8-HxCDF

- 1,2,3,7,8,9-HxCDF
- 1,2,3,4,6,7,8-HpCDF
- 1,2,3,4,7,8,9-HpCDF

- OCDF

- 28
- 2
- 54
Dry-deposition sampling

<table>
<thead>
<tr>
<th>Average deposition velocity (cm/sec)</th>
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<tbody>
<tr>
<td>2378-TCDD</td>
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<tr>
<td>OCDD</td>
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<tr>
<td>2378-TCDF</td>
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<tr>
<td>OCDF</td>
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</table>

Average deposition flux (fg/m²-hr)

<p>| | |</p>
<table>
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<tr>
<td>2378-TCDD</td>
<td>43</td>
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<td>44</td>
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<tr>
<td>OCDF</td>
<td>410</td>
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</table>
Total TEQ in runoff
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Main channel segment (14 in total)

Boundary segment (13 in total)

Loading segment (11 in total)

1 benthic segment (not shown)
<table>
<thead>
<tr>
<th>Segment</th>
<th>Total flow (m³/s)</th>
<th>2378-TCDD load (kg/day)</th>
<th>TSS load (kg/day)</th>
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<tbody>
<tr>
<td>1</td>
<td>3.9E-04</td>
<td>5.7E-13</td>
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<td>2</td>
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## NPS for simplified model

<table>
<thead>
<tr>
<th>Segment</th>
<th>Area (km²)</th>
<th>Avg. daily rainfall (in)</th>
<th>2378-TCDD load (kg/day)</th>
<th>TSS load (kg/day)</th>
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<tbody>
<tr>
<td>1</td>
<td>1244</td>
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<td>50</td>
<td>0.14</td>
<td>1.2E-09</td>
<td>3980</td>
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</tbody>
</table>
Sensitivity analysis-dissolved

- **Base case**
- **Benthic exchange x100**
- **Benthic exchange /10**
- **Benthic exchange /100**
- **No benthic exchange**

2378 TCDD (pg/L) vs Distance from Morgan's Point (km)

- Y-axis: 2378 TCDD (pg/L)
- X-axis: Distance from Morgan's Point (km)
- Legend:
  - Base case
  - Benthic exchange x100
  - Benthic exchange /10
  - Benthic exchange /100
  - No benthic exchange
Sensitivity analysis-suspended

![Graph showing sensitivity analysis](image)

- **Base case**
- **settling vel\*10**
- **settling vel\*100**
- **settling vel\*1000**
- **settling vel/10**
- **settling vel/100**
- **settling vel/1000**
- **no settling**

**2378-TCDD (ng/kg)**

**Distance from Morgan's Point (km)**

- 0.01
- 0.10
- 1.00
- 10.00

- 40 35 30 25 20 15 10 5 0
Sensitivity analysis-suspended

Distance from Morgan's Point (km)

Base case
benthic exchange*100
benthic exchange/10
benthic exchange/100
no benthic exchange

2378-TCDD (ng/kg)

0.001 0.01 0.1 1

0 1 2 3 4 5 10 15 20 25 30 35 40

Distance from Morgan's Point (km)
Sensitivity analysis-suspended

![Graph showing sensitivity analysis](attachment:image.png)
Sensitivity analysis-suspended
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Stakeholder process participation

- Meeting at Port of Houston Authority on 05/17/2004
- Meeting at UH on 05/24/2004
- Responses to comments from stakeholders
- Technical presentations at
  - The Haden Road CAP on 03/22/2004
  - Board Meeting of the GBEP on 04/22/2004
  - The Baytown Area CAP on 05/17/2004
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PCB assessment

- 209 congeners (EPA 1668A) vs Aroclors (EPA 8082)

- Texas WQS for total PCBs (based on Aroclors)
  - 1.3 ng/L in freshwater
  - 0.885 ng/L in saltwater

- TDH screening value 47 ng/g (based on Aroclors)
PCB and dioxin in water profiles

Texas PCB WQS: 885 pg/L
Texas dioxin WQS: 0.0933 pg/L

Open symbols: dioxin TEQ
Closed symbols: total PCBs
Plotted data are averages by station
PCB and dioxin in sediment-oc profiles

Concentrations (ng/kg-oc)

Open symbols → dioxin TEQ
Closed symbols → total PCBs
Plotted data are averages by station
PCB and dioxin in catfish profiles

Concentrations (pg/L)

Main channel • San Jacinto River • Side Bays • Tributaries

Distance from Morgan's Point (km)

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

TDH PCB screening value: 47,000 ng/kg
TDH dioxin screening value: 0.47 ng/kg
PCB and dioxin in crab profiles

Concentrations (pg/L)

Distance from Morgan’s Point (km)

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

TDH PCB screening value: 47,000 ng/kg
TDH dioxin screening value: 0.47 ng/kg
PCB assessment

- Water concentrations showed a *Tier-1 primary concern* based on congener analysis in segments 1006 and 1007. Aroclor data showed no concern.

- Tissue data confirms a concern for PCBs in catfish in segments 1001, 1006, and 1007 (congener data). Aroclor data showed concern in 1001 only.

- Congener data in catfish showed potential concerns in Sims Bayou, Vince Bayou, Patrick Bayou, Buffalo Bayou, and Whiteoak Bayou.

- Need to evaluate Aroclor and congener data and determine listings and define methodology to compare congener data and to establish criteria to assess use support.
## Total number of dioxin samples

<table>
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<th>Phase II</th>
<th>Phase III</th>
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</thead>
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<td>Sediment</td>
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<td>115</td>
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<tr>
<td>Catfish</td>
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<tr>
<td>Crab</td>
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<td>Sludge</td>
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<td>Effluent</td>
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### Total number of dioxin samples-cont’d

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<td>Bulk deposition</td>
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<tr>
<td>Particulate</td>
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