Development and Applications of CARP Numerical Models

Kevin J. Farley
Robin Landeck Miller

Cleaning up the Harbor
Results of the Contamination Assessment & Reduction Project
The National Museum of the American Indian, New York, New York
November 29, 2007

HydroQual

Environmental Engineers & Scientists

Contamination Assessment Reduction Project

201•529•5151
www.hydroqual.com
# Acknowledgements

<table>
<thead>
<tr>
<th>HydroQual, Inc.</th>
<th>Port Authority NY/NJ</th>
<th>CARP Data Collection</th>
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<td>• James Wands</td>
<td>• NJ DOT OMR</td>
<td>• NYSDEC</td>
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<td>• Subir Saha</td>
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<td>• NY USGS</td>
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<td>• Bob Santore</td>
<td>• CARP MEG</td>
<td>• NJDEP</td>
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<td>• Aaron Redman</td>
<td>• Joel Baker</td>
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<td>• Nick Kim</td>
<td>• Frank Bohlen</td>
<td>• NJHDG</td>
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<tr>
<td>• John St. John</td>
<td>• Richard Bopp</td>
<td>• NJADN</td>
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<tr>
<td>Scientific Advisors:</td>
<td>• Joe DeLorenzo</td>
<td>Rutgers University</td>
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<tr>
<td>• Dominic Di Toro</td>
<td>• Joe DePinto</td>
<td>Stevens Institute</td>
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<td>HRF</td>
<td>• Rocky Geyer</td>
<td>• Mark Reiss</td>
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<td>• Jim Lodge</td>
<td>• Larry Sanford</td>
<td>• Jim Meador</td>
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<td>• Dennis Suszkowski</td>
<td>• Jay Taft</td>
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CARP Model Goals

Model Development

... to develop a mechanistically-based mass balance model for toxic contaminants in NY/NJ Harbor

Model Application

... to determine the impacts of external loads and in-place contaminants on current contaminant levels in water, sediment and biota

... to project future conditions in the harbor based on source reduction programs and other remedial actions
Overall Framework

Source Characterization

Exposure Assessment (Mass Balance Model)

Effects/Endpoint Assessment

Regulatory Issues/Initiatives
- Dredged Material Guidelines for Beneficial Use (e.g., HARS Placement)
- Water Quality Standards and Toxics TMDL
- Superfund / NRDA
- HRE Restoration Efforts
- Harbor Roundtable Objectives
Presentation Outline

- CARP Modeling Goals/Framework
- Study Area / Loading Estimates
- Modeling Approach / Calibration Results
- Model “Hindcast” / “Clean Bed” Analyses

Coffee Break (15 minutes)

- Bioaccumulation / Endpoints
- Contaminant Component Analysis
- 2040 Projections
Model Grid

16,000 water column and 16,000 sediment cells
## CARP Contaminants of Concern

<table>
<thead>
<tr>
<th>Category</th>
<th>Details</th>
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<tr>
<td>PCBs</td>
<td>209 PCB Congeners (modeled as 10 homologs)</td>
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<td>Dioxin/Furans</td>
<td>17 congeners (including 2,3,7,8-TCDD)</td>
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<tr>
<td>Metals</td>
<td>Cadmium and Mercury (including MeHg)</td>
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<td>PAHs</td>
<td>22 PAH compounds</td>
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<tr>
<td>Pesticides</td>
<td>6 DDT related compounds</td>
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<tr>
<td></td>
<td>5 forms of chlordane</td>
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Source Characterization (Total of 63 Contaminants)

- 34 Tributaries
- 99 STPs
- > 700 CSOs
- > 1,000 SWOs
- Atmosphere
- 6 Landfills
- In-Place Contaminants (Sediment Initial Conditions)
- Plus Sediment, Organic Carbon and Nutrient Loads
Sediment Loads
Normalized Sediment Load (HydroQual, 1996)

Mohawk River, NY: NSL Analysis (log scale)

- Linear (Flood): $y = 2.982x - 0.4191$, $R^2 = 0.7834$
- Linear (Non-Flood): $y = 1.2602x + 0.0843$, $R^2 = 0.6986$
Summary: Annual Sediment Loads (1992-2001)
Organic Carbon and Nutrient Loads (2001-02)

Flows
- STPs: (monthly) DMRs
- CSOs / Storm Water: (hourly) landside models
- Tributaries: (daily) USGS flow data

Concentrations
- 1994-95 SWEM data
- Separate evaluations for “above Poughkeepsie” loads
Chemical Loads
(STPs, CSO/SWOs, Landfills, Atmosphere)

Chemical Load = Q \cdot C

Concentrations
- 99 STPs (~120 samples)
- > 700 CSOs (~20 samples)
- > 1,000 SWOs (~20 samples)
- 6 Landfills (~20 samples)
- Load estimates based on medians of measured total concentrations

Atmospheric Loads
- Annual estimates largely from NJADN

Flows
- STPs: (monthly) DMRs
- CSOs / Storm Water: (hourly) landside models
- Landfills: (annual) from Litten (2003)
New York and New Jersey STPs (Combined)

Figure 3-11. Probability distribution of STP effluent cadmium concentrations.
Chemical Loads
(Tributaries)

- 34 Tributaries (~50 samples)
- Large variations in measured total concentrations

Wallkill (New Paltz) – Tetra-CB

Concentrations

- 34 Tributaries (~50 samples)
- Large variations in measured total concentrations
Chemical Loads (Tributaries)

Chemical Load = $Q \cdot C_{dis} + L_{POC} \cdot r_{oc}$

- Flow: (daily) USGS
- $L_{POC}$: (daily) from Normalized POC Load (NPL) evaluations
CARP Loads
(2,3,7,8 TCDD)

2,3,7,8-TeCDD Loads (Kg/d)

- Storm Water: 57.7%
- Hudson River: 8.9%
- Other Heads of Tide: 17.5%
- Sewage Treatment Plants: 6.0%
- Combined Sewer Overflows: 2.6%
- Atmosphere: 7.3%

Legend:
- Hudson River
- Other Heads of Tide
- Atmosphere
- Storm Water
- Sewage Treatment Plants
- Combined Sewer Overflows
CARP Loads
(Hexa-CB)

Hexa-CB Loads (Kg/d)

- Hudson River: 28.4%
- Storm Water: 15.0%
- Atmosphere: 3.6%
- Other Heads of Tide: 5.3%
- Sewage Treatment Plants: 12.0%
- Combined Sewer Overflows: 35.7%
Exposure Assessment
(Mass Balance Modeling)

Purpose of Modeling

- To evaluate mechanistic descriptions of contaminant fate processes through model calibration
- To confirm / extend interpretation of field data
- To determine contaminant contributions from various sources
- To provide forecasts of future conditions under various remedial options
ECOM (Hydrodynamic Sub-Model)

ECOM

- Developed as part of SWEM
- Reviewed as part of previous studies
- **Model Input**: freshwater flows, meteorology, ocean boundary condition
- **Model Output**: detailed 3-D flows, temperature, salinity, bottom shear stress

**Hydrodynamic Results**

- Moderately strong tidal action in main stem
- Density-driven estuarine circulation
- Large seasonal movement of salt wedge
ST-SWEM

(Sediment Transport / Organic Carbon Sub-model)

- Extension of SWEM to include sediment transport
- Settling velocities = f(TSS, salinity) to simulate coagulation effects
- Resuspension = f(excess shear stress) for “fluff” and consolidated sediment
- Model Input: hydrodynamics; sediment, carbon and nutrient loads, meteorology
- Model Output: detailed sediment, POC and DOC transport (plus sediment sulfide and SRR for Cd and Hg model)
Seasonal Transport (Continued)

Sediment Deposition: Fall

ST-SWEM Results
- Estuarine trapping of sediment
- Seasonal mixing of sediment in main stem
- Spatial / seasonal carbon dynamics
RCA-TOX
(Chemical Fate and Transport Sub-model)

HOCs

- 3-phase partitioning = f(Temp., Salinity)
- Volatilization = f(Two-film Theory, Temp-dependent Henry’s Constant)
- Chemical degradation considered negligible
- **Model Input**: contaminant loads, sediment initial conditions
- **Model Parameters**: Chemical-specific K_{ow}, field-derived K_{POC}, Henry’s Constant
- **Model Output**: water and sediment exposure concentrations
Field-derived Partition Coefficients (Chlorine Substitution Pattern)

Planar PCB Congeners

Temp. and Salinity Correction
\( a_{DOCS} = 0.08 \); No Temp or Salinity DOC adj.
(0 and 1 Ortho Chlorines)

Non-Planar PCB Congeners

Temp. and Salinity Correction
\( a_{DOCS} = 0.08 \); No Temp DOC adj.
(2, 3 and 4 Ortho Chlorines)

Effect of black carbon (soot) on partitioning of co-planar PCBs
Ghosh et al. (2003), Accardi-Dey and Gschwend (2003), Lohmann et al. (2005)
RCA-TOX Calibration / Verification
(~110 Water and ~70 Sediment Samples)
RCA-TOX Calibration Results (Tetra-CB)
RCA-TOX Calibration Results (Tetra-CB)

Field Data Model Results

- WC Dissolved (ng/L)
  - n = 144.
  - n < 10 x = 141.
  - n < 5 x = 137.
  - n < 3 x = 131.
  - n < 2 x = 107.

- Sed Particulate (ug/gm-OC)
  - n = 67.
  - n < 10 x = 66.
  - n < 5 x = 66.
  - n < 3 x = 61.
  - n < 2 x = 54.
Calculated/Observed PCB Concentrations

WC Total

WC Dissolved

WC Particulate (OC Normalized)

Sed Particulate (OC Normalized)

LogKow

RUN=060.C2
Calculated/Observed Dioxin-Furan Concentrations

LogKow

RUN=048.C2
HOC Validation for PAHs and Pesticides
- 22 PAHs
- 6 DDT Related Compounds
- 5 Forms of Chlordane

Metals Model Development
- Cadmium
- Mercury (including MeHg)
The hindcast and clean bed analyses are important diagnostics of the temporal dynamics of the CARP models. More importantly, these results provided preliminary information for management decisions.
Hindcast Verification Analysis

Why?
- Model Hindcasts provide a more rigorous test than the current conditions calibrations of the basic contaminant model and of time-sensitive model coefficients (i.e., particle mixing depths and rates in sediments, burial, diffusive exchange)
- Current conditions calibrations were run from 1998 through 2002
- Hindcast simulations were run from 1966 through 2002

How?
- Hindcast hydrodynamics/sediment transport/carbon for 37 years in series selected from six available water years based on similarities in Hudson River flows
- Hindcasts were performed for $^{137}$Cs, 2,3,7,8-TCDD, & 4 PCB homologs (di-, tetra-, hexa- and octa-)
Hindcast Analysis Requirements

- Measurements or “reasonable knowledge” of historical loadings
- Ability to calculate fate and transport
- Reliable historical ambient measurements

The selection of $^{137}\text{Cs}$, 2,3,7,8-TCDD and PCBs was not arbitrary
Example $^{137}$Cs model and data comparison result at one location.

Top 1cm
Top 1-10 cm
96 years of current loadings were simulated starting with a “clean bed”

Based on interim version of calibration

Performed for 10 PCB homologs and 17 dioxin/furan congeners

Not a contract deliverable, but a modeler’s test

Shows time to achieve a “steady state” between the water column and sediments
Clean Bed Analysis

- Demonstrates potential for a recontamination after cleanup
- Demonstrates whether or not many years of the current external loadings could have produced the sediments concentrations measured in 1998 (i.e., present day vs. historical)
2,3,7,8-TCDD in Harbor surficial sediments if current loads occurred for 100 years on a clean bed
2,3,7,8-TCDD in Harbor surficial sediments based on 1998 interpolated data
2,3,7,8-TCDD in Harbor surficial sediments not explained by 100 years of current loads

2,3,7,8-TCDD DIOXIN (ng/gm-OC) Clean Bed Versus Interpolated Field Data
Summary of 2,3,7,8-TCDD interim “clean bed” analysis

2,3,7,8-TCDD DIOXIN (ng/gm-OC) Clean Bed Versus Interpolated Field Data
Clean Bed Analysis Findings

- Time to achieve a “steady state” between the water column and sediments is under 30 years in most portions of the Harbor.
- Observed levels of contamination in NY/NJ Harbor surficial sediments are due to both current day and historical sources.
- Historical sources were much larger than on-going sources.
- Historical sources continue to play a role due to “estuarine trapping” of sediment bound contaminants (varies by contaminant) and the persistence of the contaminants.
- If NY/NJ Harbor sediments were to undergo remediation, on-going sources would likely produce some surficial recontamination but not to the extent of current levels.
Break (15 minutes)
Effects/Endpoint Assessment
(Regulatory Issues / Initiatives)

Source Characterization

Exposure Assessment (Mass Balance Model)

Effects/Endpoint Assessment

Effects / Endpoints
- Water Quality Standards
- Tissue-based Concentrations (for human and ecological risk)
- Bioaccumulation in Dredged Material Test Organisms (for determination of HARS-suitability and other beneficial uses)
FOODCHAIN (Bioaccumulation)

…. to link water / sediment exposure concentrations to accumulation in biota

1. **Field-derived BAFs and BSAFs**: for HOCs

\[
BAF_{\text{lipid}} = \frac{V_{\text{lipid}}}{C_{\text{dis}}} \quad ; \quad BSAF_{\text{lipid}} = \frac{V_{\text{lipid}}}{r_{\text{oc}}}
\]

where exposure concentrations are taken from coincident field measurements or 5-day, average model results for bottom water and top 10-cm sediment

2. **Bioaccumulation modeling**: to examine causal behavior of observed BAFs and BSAFs
Bioaccumulation: PCBs

\[ BAF_{\text{lipid}} = \frac{V_{\text{lipid}}}{C_{\text{freely}}} \]

Graphs showing the relationship between log \( BAF_{\text{lipid}} \) and log \( K_{ow} \) for Zooplankton and White Perch.
Bioaccumulation: PAHs
(Effects of Metabolism)
Bioaccumulation: Dioxin/Furans
(Ineffective Trophic Transfer or Metabolism in Fish)
BSAF\textsubscript{lipid} = \frac{V\text{\textsubscript{lipid}}}{\Gamma\text{\textsubscript{oc}}}

"Urban myth" or serious implications in setting targets for sediment cleanup
Bioaccumulation Modeling (PCB Homologs)

**Initial Fit (Inner Harbor Sites)**
- More contaminated sites

**For Outer Harbor Sites**
- Increased Respiration (decreased toxic stress)
- Increased Chemical Assimilatory Efficiency (higher quality food)

**Laboratory Studies**
- Similar behavior observed in laboratory exposures (Meador et al. 1997)
Bioaccumulation Effects/Endpoints

For Ecological and Human Risk Assessment

- Field-derived BAFs / BSAFs for fish, blue crabs, clams and worms

For Determination of HARS-suitability

- *Nereis* BSAFs from NY-NJ Harbor dredged material testing data

### NY-NJ Harbor: Worm BSAFs – g(dry wt)/g(wet wt)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Field-Derived</th>
<th>Dredged Material Testing</th>
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<tbody>
<tr>
<td>2,3,7,8-TCDD</td>
<td>0.17</td>
<td>0.05(2)</td>
</tr>
<tr>
<td>2,3,4,7,8-PCDF</td>
<td>0.20</td>
<td>NA</td>
</tr>
<tr>
<td>di-CB</td>
<td>0.20</td>
<td>0.24(3)</td>
</tr>
<tr>
<td>tetra-CB</td>
<td>0.97</td>
<td>0.30(3)</td>
</tr>
<tr>
<td>hexa-CB</td>
<td>1.81</td>
<td>0.50(3)</td>
</tr>
<tr>
<td>octa-CB</td>
<td>1.41</td>
<td>0.22(3)</td>
</tr>
</tbody>
</table>

Notes:

1. From average of field-derived BSAFs for inner and outer harbor sites.
2. Based on information in Schrock et al. (1997) assuming 7 g (wet wt)/g(dry wt) for worms
3. Derived from dredged material testing data provided by USEPA Region 2
CARP Model Goals

Model Development

... to develop a mechanistically-based mass balance model for toxic contaminants in NY/NJ Harbor

Model Application

... to determine the impacts of external loads and in-place contaminants on current contaminant levels in water, sediment and biota

... to project future conditions in the harbor based on source reduction programs and other remedial actions
Contaminant Source Component Analysis

The model was used to diagnose future contaminant concentrations in water, sediment, and biota throughout the system resulting from a specific source modeled over a more than three decade simulation period.
Objective:
Define relative effects of various contaminant loading sources on ambient concentrations in water, sediment, and biota.
CARP Loading Component Method

- Run the CARP Model for 32 years with a loading component as the only contaminant source
- Repeat for each component
- Store results in a spreadsheet for “what if” calculations (see poster session)
- Results show how load reductions may affect contaminant levels in water, sediment, and biota throughout the estuary.
CARP Loading Components

- Components for 4 PCB homologs, 2,3,7,8-TCDD, 2,3,4,7,8-PCDF, Hg, & Cd: atmospheric deposition, ocean boundary, STPs, CSOs, SW, head-of-tide, & in-place sediment

- 3 additional components target known problems: Passaic River sediment, Newark Bay sediment, and the Upper Hudson for 4 PCB homologs, 2,3,7,8-TCDD, & 2,3,4,7,8-PCDF
These Scale Factors Are Adjusted By Adjusting the Individual Homologue Scale Factors

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Location</th>
<th>Unadjusted Load (Kg/d)</th>
<th>Scale Factor</th>
<th>Adjusted Load (Kg/d)</th>
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<tr>
<td>1</td>
<td>Hudson River</td>
<td>150.8 to 143.9</td>
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<tr>
<td>2</td>
<td>Hudson River</td>
<td>143.9 to 131.8</td>
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<td>3</td>
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<td>133.8 to 123.6</td>
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<td>Jamaica Bay</td>
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<td>39</td>
<td>Open Ocean</td>
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</table>

PCB example of component results in the spreadsheet tool.
● Legacy sediments are a major component of observed 2,3,7,8-TCDD contamination.

● Over time, 2,3,7,8-TCDD contaminant levels in surficial sediments will drop as on-going sources are smaller than legacy sources.

● Of the current 2,3,7,8-TCDD sources, runoff and head-of-tide appear to be important.

● CARP model results will help focus future TMDL, Superfund, and Restoration data collection and modeling efforts.
Component Run Sediment Time Series for 2,3,7,8-TeCDD (ng/gm-OC)
Scenarios involving implementation of the Hudson River PCBs Superfund Site dredging and remediation of the highly contaminated sediments in the lower Passaic River were modeled over a more than three decade simulation period.

- Extreme events were not specifically considered.
- A risk assessment was not performed.
- There is not a dynamic linking of hydrodynamics and sediment transport. Any projected net accumulation over long time horizons is not fed into the bathymetry for hydrodynamic transport calculations.
“Future with current loads” and “with action” cases considered

“With Action” defined as implementation of Upper Hudson River ROD and a full-cleanup (i.e., 17 miles) of the Passaic River

Focus on HARS suitability for 2,3,7,8-TCDD & PCBs.

HARS = Historic Area Remediation Site
PCB Current Conditions

Results Doubled for DMT BSAF to HARS Human Health Comparison

Ratio of Sediment Total PCB Concentration to the Value Required for HARS Disposal
Based on Mono-Deca BSAFs = 0.00, 0.24, 0.24, 0.30, 0.34, 0.50, 0.33, 0.22, 0.28, and 0.18 (gm-DW/gm-WW) from Reiss Data and a Worm Target Concentration of 113 ppb (Interim HARS Non-Cancer)
Future PCB Results with No Action

**Results for Year 37**

**Future with Current Loads**

Total PCB Estimated as
2 * (Di+Tetra+Hexa+Octa)
Results Doubled for DMT BSAF
To HARS Human Health Comparison

Log (Total PCB Ratio)

- > 8 * HARS
- > 4 * HARS
- > 2 * HARS
- > HARS
- < HARS
- < HARS / 2
- < HARS / 4
- < HARS / 8

Ratio of Sediment Total PCB Concentration to the Value Required for HARS Disposal
Based on Di, Tetra, Hexa, and Octa BSAF values = 0.24, 0.30, 0.50, and 0.22 (gm-DW/gm-WW) from Reiss Data
and a Worm Target Concentration of 113 ppb (Interim HARS Non-Cancer)
Results for Year 37
Dredging in the Full 17 Miles of the Passaic, End of Year 6

Total PCB Estimated as
2 * (Di+Tetra+Hexa+Octa)
Results Doubled for DMT BSAsF
to HARS Human Health Comparison

PCB Results after Both Projects

Ratio of Sediment Total PCB Concentration to the Value Required for HARS Disposal
Based on Di, Tetra, Hexa, and Octa BSAsF = 0.24, 0.30, 0.50, and 0.22 (gm-DW/gm WW) from Reiss Data
and a Worm Target Concentration of 113 ppb (Interim HARS Non-Cancer)
Projection Run, Sediment, Time Series for Total PCB = 2*(Di+Tetra+Hexa+Octa) (ug/gm-OC)
Dioxin Current Conditions

Ratio of Sediment 2,3,7,8-TeCDD Concentration to the Value Required for HARS Disposal
Based on a BSAF of 0.363 (gm-DW/gm-DW) From Schrock Data / 7 (gm-WW/gm-DW) = 0.052 (gm-DW/gm-WW)
and a Worm Target Concentration of 1 ppt
Future Dioxin Results with No Action

Results for Year 37
Future with Current Loads

Ratio of Sediment 2,3,7,8-TeCDD Concentration to the Value Required for HARS Disposal
Based on a BSAF of 0.363 (gm-DW/gm-DW) From Schrock Data / 7 (gm-WW/gm-DW) = 0.052 (gm-DW/gm-WW)
and a Worm Target Concentration of 1 ppt
Results for Year 37
Dredging in the Full 17 Miles of the Passaic, End of Year 6

Dioxin Results
after Both
Projects

Ratio of Sediment 2,3,7,8-TeCDD Concentration to the Value Required for HARS Disposal
Based on a BSAF of 0.363 (gm-DW/gm-DW) From Schrock Data / 7 (gm-WW/gm-DW) = 0.052 (gm-DW/gm-WW)
and a Worm Target Concentration of 1 ppt
Projection Run, Sediment, Time Series for 2,3,7,8-TeCDD (ng/gm-OC)
2040 Projection Findings

- 2040 results have further application (e.g., TMDL, Superfund, restoration) than HARS suitability determinations presented here
- Progress will be made toward achieving HARS suitability between now and 2040
- PCBs more of a problem than 2,3,7,8-TCDD
- More worm BSAF data should be collected under field and lab test conditions
- Need clam BSAF data
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Questions?