# APPLICATION OF THE DQO PROCESS TO THE DELAWARE ESTUARY PCB TMDL PROGRAM

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# Overview

- Objective: To provide information to other TMDL participants on how data quality objectives impact the TMDL process
  - All information is presented as a result of the ongoing work of many stakeholders
  - The information presented is the authors' best assessment of the information at hand – it is in essence a series of snapshots of the current data issues
  - The data collected is intended to provide a data set for good decision making today and decades in the future
  - Point Source discharges were the initial focus of this work, however data collection from all source categories and ambient conditions will be addressed in the future

### What are PCBs (Polychlorinated Biphenyls)?

- A group of 209 manufactured chemicals with a biphenyl base structure and between 1 and 10 chlorine substitution patterns.
- Hydrophobic and tend to partition to organic matter, including carbon in sediments, suspended solids and tissues
- PCBs are Persistent, Bioaccumulative and Toxic Pollutants (PBTs)

What is a TMDL? • A TMDL or Total Maximum Daily Load is a calculation of the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards, and an allocation of the TMDL to point and non point sources.

## What is a Water Quality Standard?

- Water quality standards are set by States, Territories, and Tribes. They identify the uses for each waterbody, for example, drinking water supply, contact recreation (swimming), and aquatic life support (fishing), and the scientific criteria to support that use.
- The PCB Water Quality Standard for the Delaware Estuary currently ranges from 7.9 to 44 pg/l (parts per quadrillion) *Similar to finding 44 people anywhere on the planet*

#### How Data Quality Impacts a TMDL?

#### Data needs to be adequate to characterize the pollutant in all loadings, pathways, and ambient media so that:

- Determinations can be made as to significant sources of PCBs to the environment and identification of banks of PCBs in the environment.
- Data is collected that is suitable for use in models and other scientific tools that may be used to understand fate and transport of PCBs – The question is: Is a source impacting the environment or is it impacted by the environment?
- Techniques are identified to ensure that progress can be measured as the TMDL process reduces the ambient concentrations of PCBs in each media.

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# Some Key Issues that Drive the DQO Process for PCBs

- The Applicable Goal or Water Quality Standard
- Selection of Program Analytical Method
- Number of PCB Congeners to Quantify
- Methods to Aggregate Congener Data to Total
- Continuing assessment of the magnitude and variability of data to characterize each Loading, Bank or Pathway to further inform the data collection process
- Sampling Methodology
- Specific Analytical Techniques Required
- Performance Metrics for Analytical Labs

#### **Program Analytical Method**

- Potential Analytical Methods

  EPA Method 8082
  EPA Method 1668 (draft)
  EPA Method 1668A (draft)
  Custom Methods by Academic
  - **Researchers and Supporting Agencies**

#### DRBC TAC Data Quality Subcommittee

- Dennis Blair (Philadelphia Water Department)
- David Blye (Environmental Standards, Inc.)
- John Bourbon (EPA Region II)
- Greg Cavallo (DRBC)
- Richard Greene (Delaware Dept. of Natural Resources & Env. Control)
- Tom Healey (Philadelphia Water Department)
- Tom Harlukowicz (PSEG Services Corporation)
- Dave Piller (Exelon)
- Larry Sandeen (Rohm and Haas Company)
- Dave Velinsky (Academy of Natural Sciences)
- Tim Wilson (US Geological Survey)
- Mike Webb (Pennsylvania Dept. of Environmental Protection)

## Data Quality Subcommittee Approach

- Identify issues that could impact the quality and defensibility of data collected for the Stage 2 PCB TMDL
- Develop and Implement detailed guidance for Analytical Laboratories
- Develop and Deploy detailed guidance for Sampling Entities
- Monitor and Continuously improve Data Quality Activities during the data collection portion of the Stage 2 PCB TMDL

#### Data Quality Issues Identified in Stage 1 TMDL Process

- Data Collected by different analytical methods is hard to aggregate and compare.
- Sensitivity needs were not defined initially. Decision-makers driving the data collection effort did not have a good "feel" for the capabilities of EPA Method 1668A, so data was run per the EPA methodology and reworked (after the fact) to report at lower reporting limits.
- EPA Method 1668A was recognized as the best method for lowlevel analysis of PCBs, however the method has not been validated and approved. Further, the method allows for significant flexibility by the laboratory in running the method (PBMS).
- The difficulty in collecting truly representative samples was not fully understood.
- The importance of the handoff between the sampling program and the analytical program was not well understood.

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# What are Data Quality Objectives (DQOs)?

- DQOs are qualitative and quantitative statements that translate non-technical project goals into technical project-specific decision goals. They:
  - Clarify project objectives
  - Define appropriate types of data to be collected
  - Establish overall decision quality or tolerable levels of potential decision errors

## Steps in EPA's DQO Process

- 1. State the Problem to be Solved
- 2. Identify the Decision to be Made
- 3. Identify the Inputs to the Decision
- 4. Define the Study Boundaries
- 5. Develop a Decision Rule
- 6. Specify Tolerable Limits on Decision Errors
- 7. Optimize the Design for Obtaining Data

### Examples of initial Goal Elements of Data Quality Subcommittee for Development of Sampling and Analysis Plans

- Determine within a %CV of 5% the average PCB concentration from each point source discharger
- Determine with at least 95% confidence the loading categories that contributed the greatest mass of PCBs to the Estuary
- Determine with greater that 95% confidence that the concentration of total PCBs from a point source discharge does not violate the water quality standard

These goals would have required 100s of expensive samples from each source, thousands from each source category, and could not be justified by the program

### Project Specific Requirements for the Analytical Program Determined by the DQSC

- List of analytes Specified target list of analytes (approximately 180 of 209 due to coelution issues)
- SPB-octyl column Method 1668A allows the use of more than one chromatography column this will minimize variability in the reporting of coeluters.
- Coeluting Congener Reporting Rules Defined
- Sensitivity DRBC modelers identified the need for accurate quantitation in the 10-15 pg/l range, so a 0.5 ng/mL calibration standard was specified, a two-liter sample volume and a final extract volume of 20ul.
- Replicate Samples Replicates were required to be collected and submitted for potential reanalysis by the laboratory in event of poor initial QC

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Project Specific Requirements for the

Analytical Program Determined by the DQSC

- Method Blank Contamination Rules:
  - No Individual Congener shall be present in the blank at >20 pg/l unless:
    - The associated sample exceeds 10X the amount in the blank
    - The congener is not found in the associated sample
    - If the total PCB concentrations in the blank are < 300 pg/l
- Rinsate Blank Contamination Rules:
  - No Individual Congener shall be present in the blank at >40 pg/l unless:
    - The associated sample exceeds 3X the amount in the blank
    - The congener is not found in the associated sample

• If the total PCB concentrations in the blank are < 600 pg/l WEF TMDL Conference 2005

### Project Specific Requirements for the Analytical Program Determined by the DQSC

- The entire sample volume shall be extracted
- Results shall be reported to the sample specific Estimated Detection Limit (EDL)

Examples of Project Specific Requirements for the Sampling Program Determined by the DQSC

- Continuous Discharges not significantly impacted by stormwater shall be sampled using 24 hour composite samples
- Continuous Discharges significantly impacted by stormwater shall be sampled using 24 hour composite samples starting no more than 2 hours prior to the storm event

Examples of Project Specific Requirements for the Sampling Program Determined by the DQSC

- Stormwater Outfalls are to be characterized using a grab sample within 30 minutes of the start of the wet weather flow
- Non Contact Cooling Water Impacted by other discharges may be evaluated using composite samples of the contributory process related streams

### Project Specific Requirements for the Sampling Program Determined by the DQSC

- Sample volume shall be a nominal 2 liters collected directly into a 2.5 liter bottle.
- Number of samples will be determined by DRBC, starting with 1 to 3 samples for each discharge of interest, with additional samples requested based on data previously collected.
- All data will be submitted in a standard format, including:
  - Discharge Location Information
  - Chain of Custody Information
  - Validated Laboratory Data

#### Implementation

- DRBC Website
- Sampling Seminars
- Analytical Seminars
- Shared information for RFPs for analytical Labs
- Common Database for Stakeholder Use
- Standardized EDD with input screening
- Recommended Independent Data Validation

## Conclusions

- The process was unique due to the open collaboration of:
  - the regulating and the regulated communities
  - the abstract world of analytical chemistry and the down to the earth world of environmental sampling
- All Parties were committed to the processes attendance was excellent, nearly 100%
- All Parties agreed that the resulting recommendations were practical and would establish a good baseline for the program.

## This Historical Perspective

 Fifty years from now, as the PCB problem attenuates, the stakeholders who will be continuing this work will have a high-quality, historical data set to use as a basis for predicting the fate and transport of PCBs into the future. Further many of the learning's about this persistent pollutant may help the environmental community to understand other environmental fate processes For a copy of this presentation, please Email the authors at: lsandeen@rohmhaas.com