WEF/A&WMA 10th Annual Industrial Waste Technical and Regulatory Conference

Addressing Data Quality Issues in the Development of a PCB TMDL

Lawrence R. Sandeen, P.E. Rohm and Haas Company 200 Route 413 Bristol, PA 19007

Rao Sankarmanchi, P.E. CDM 205 Granite Run Drive, Suite 350 Lancaster, PA 17601

ABSTRACT

Polychlorinated biphenyls (PCBs) are persistent, bioaccumulative, toxic pollutants that have caused water quality impairments in a number of water bodies in the United States. More than 1.5 billion pounds of PCBs were manufactured in the United States before their manufacture and general use was almost completely banned by the EPA in the late 1970s. PCBs were used in a wide variety of applications, and are found, at low levels, in the soil, water, sediments and air throughout the continent, and are present at levels above some water quality standards in the open ocean.

Water quality standards for the total of 209 PCB congeners can be as low as 7.9 picograms per liter (pg/l), while EPA's best analytical method for quantifying PCBs, EPA Method 1668A, has stated detection limits that range from 4 to 455 pg/l and reporting limits that range from 10 to 1,000 pg/l for individual congeners. EPA Method 1668A is currently the best available technology for quantifying low levels of PCBs in the environment, however, it has not been validated and approved the EPA. The method effectively separates roughly 160 of the 209 PCB congeners, and was developed with the specific intent of quantifying PCB congeners that EPA felt had the most significant environmental. The analytical method is believed by many experts to be capable of accurately quantifying PCBs at concentrations at least an order of magnitude below the EPA stated reporting limits; however, the cost of analysis, the uncertainty of the measurements, and the impacts of the ubiquitous presence of PCBs in the field and lab environment increases as the reporting level is pushed downward.

The TMDL (Total Maximum Daily Load) process determines the maximum loading of a pollutant that can be assimilated by a water body, and outlines a strategy for reducing the quantity of the pollutant that is entering the water body. Developing a TMDL for PCBs is problematic, in that the applicable water quality standards may be several orders of magnitude lower than can be accurately sampled and measured using the best available techniques. Because the goal of the TMDL process is to reduce impacts to the water body, the environment and the food chain, it is important to develop strategies and tools that will allow less than ideal data to be used to make good decisions.

This paper discusses the impact of data quality on the development of the Stage 1 PCB TMDL for the Delaware River Estuary, and work that is ongoing to improve the quality of the data that will be collected and used for decision making in Stage 2 of the TMDL. Collected data is intended to accurately characterize the loadings, pathways, and ambient concentrations of a given pollutant 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.
- Techniques are identified to ensure that progress can be measured as the TMDL process reduces the ambient concentrations of PCBs in each media.

KEYWORDS

Total Maximum Daily Load (TMDL), Polychlorinated biphenyls (PCBs), Data Quality, Congener, Delaware River Basin Commission (DRBC)

INTRODUCTION

The collection of representative data for scientific use and practical decision-making for any purpose is a difficult task. Obtaining the data quality required for creating compliance metrics and measuring performance against those metrics is significantly more difficult. This discussion outlines many of the considerations that should be addressed to collect and evaluate data that is suitable for the TMDL process. Obtaining data of high quality will facilitate good decisions that will lead to meaningful improvements in water quality. It is important to recall that while a TMDL has regulatory underpinnings, it is ultimately a scientific process intended to identify actions that can be taken to resolve a problem. Ultimately, poor data quality will delay and possibly prevent real progress from being made to address issues in the water body.

It is impossible to address all of the data quality issues that impact the PCB TMDL in the Delaware Estuary in a paper of this length. However, this discussion does address many of the issues that are presented by a large number of closely related persistent pollutants, such as the 209 PCB congeners. The discussion in this paper is broken into four major areas:

- Questions that Drive the Establishment of Data Quality Objectives
- Data Quality Objectives
- Data Storage and Availability
- Data Quality Assessment

Finally, it is important to note that the Delaware Estuary PCB TMDL Stakeholders are currently working to determine the best methods for collecting and evaluating low concentration PCB data. This paper represents a snapshot of issues that impact data collection and use, and includes some strategies to identify and address those issues as we strive to collect representative data for the PCB TMDL process. Many of the concepts are applicable to other data collection efforts.

QUESTIONS THAT DRIVE THE ESTABLISHMENT OF DATA QUALITY OBJECTIVES

Can the parameter(s) be reliably quantified in the appropriate media at the water quality standard concentration? - In the case of most TMDLs, the data collection techniques are adequate to characterize the parameter of concern well below the applicable standards. However, as we work to address materials that are persistent and have impact at very low concentrations data collection issues are extremely significant. Some issues that impact this evaluation are:

What is the number of parameters that aggregate to the Water Quality Standard? - Since the goal of the TMDL process is to determine the assimilative capacity of a water body, it is important to collect data that is significantly more sensitive than the water quality standard. If the parameter is a single parameter, such as a nutrient, then a quantitation limit on the order of 10% of the water quality standard is acceptable, however, if a significant number of parameters must be aggregated to compare against the water quality standard, then the quantitation limit must be significantly better for each individual parameter. The ability to reliably measure concentrations significantly below the water quality standard significantly reduces the uncertainty in the TMDL process.

Normally, the individual measurement of each component of the water quality standard would be ideal. However, there are 209 PCB congeners of which we can readily resolve approximately 160. Some of the PCBs were probably never manufactured, and are not degradation products of other PCBs. These PCBs could be considered for exclusion from the analysis, which could simplify the aggregation process. Chart 1 was created from the DRBC's data set for water column PCBs in the Delaware Estuary, and graphically displays the fact that by measuring a relatively few number of PCBs, we can quantify a majority of the PCB mass in a sample. In this chart, the sum of the first 7 PCB congeners represents 50% of the mass, the first 33 PCB congeners represents 90% of the mass, and the first 70 PCB congeners represents 99% of the mass.

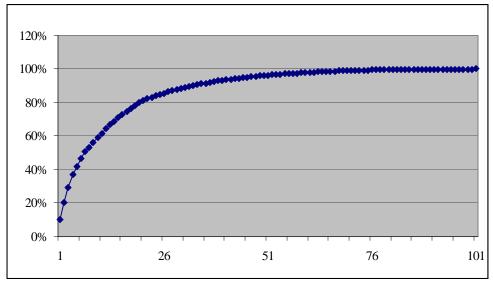


Chart 1 – Cumulative Percent of Total for 101 Measured PCB Congeners

What is the expected fate and transport of the parameter(s)? – Parameters that are persistent in the environment tend to be present in a variety of media, requiring the collection of multimedia data to fully characterize the impacts of the parameter. The range of expected concentrations that are likely to be present in each media (air, water, sediments, tissue, etc) must be defined so that appropriate data quality objectives can be established for the relevant media.

What are the existing ambient concentrations? - The water quality standard for a given parameter may be well beyond the capability of existing sampling and analytical methods to measure. EPA Method 1668A is currently the most sensitive and accurate method for quantifying PCBs in various media, however, it is not capable of meaningful measurement at the range of current and proposed water quality standards. In part, our inability to measure PCBs at these low levels is due to the ubiquitous presence of these compounds in the environment. We are fortunate to have collected enough data over the last four years to be able to make some assessment as to what the likely range of ambient concentrations are in the Delaware Estuary.

PCBs, by their very nature, are found in higher concentrations in media that contains significant solids and organic carbon. Consequently, it is easier to quantify PCBs in sediments, soils and tissues than in the water column and air. The PCB TMDL process is primarily concerned with water column concentrations due to the regulatory framework it serves. To assess the current ambient conditions in the Delaware, the existing ambient water column data set was evaluated. Since the DRBC TMDL data set is not housed in a formal data store, significant effort was made to create a meaningful subset of data for use in studying existing ambient conditions. Several steps were manually executed to prepare the data for this evaluation, including:

- (1) Removed data that was not representative of general ambient conditions, including some DRBC collected discharger data and data from municipal track down efforts.
- (2) Removed data from quality assurance activities, such as field blanks, calibration verification standards, and method blanks.
- (3) Identified samples that were reanalyzed by the laboratory, and selected the final analysis for inclusion in the data set.
- (4) Aggregated separate analysis results for dissolved and particulate PCBs for a single sample to achieve a total water column concentration.
- (5) Removed data from the lower estuary (below the Delaware Memorial Bridge) from the data set, as it appeared to be from a different population. Thus this analysis of ambient conditions is limited to the fresh water portions of the estuary.
- (6) For the purpose of this analysis, all data, including results reported below the methods minimum level was used, and zero was used if the congener was not detected.

Chart 2 details the distribution of the Tidal River and Tributary data set, which ultimately contained 142 distinct measurements. It is clear from a cursory view of this data that it is not a normally distributed population. Chart 3 details the distribution of the log of this data, and the data appears to be from a population that can be represented by a log normal distribution.

Chart 2 – Histogram Detailing Distribution of River and Tributary Data

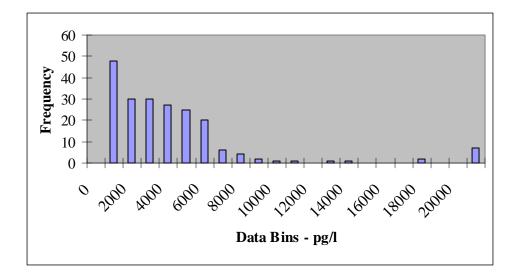


Chart 3 – Histogram Detailing Distribution of the Log of River and Tributary Data

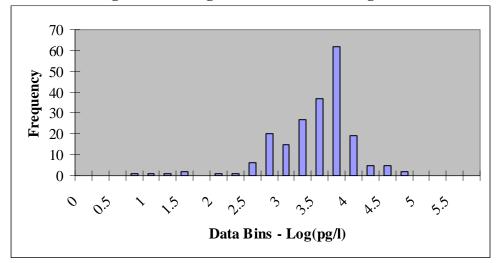


Chart 4 displays probability plots of both the normal and log data from the tidal river and tributary data set. The data appears to be relatively linear, however, there is some degradation in this relationship at the lower portion of the plot. The loss of linearity in the lower portion of the plot may be in part due to the fact that much the congener data for those samples was less statistically powerful as it was below the methods minimum level. In addition, the river and tributary data set includes data that is highly variable, both temporally and spatially, in addition the data includes both wet and dry weather flows. A similar analysis of the data from below the Delaware Estuary (58 data points) was accomplished, though the data set did not appear to be as well represented by the log normal distribution.

Chart 4 – Probability Distribution of Normal and Log of River and Tributary Data

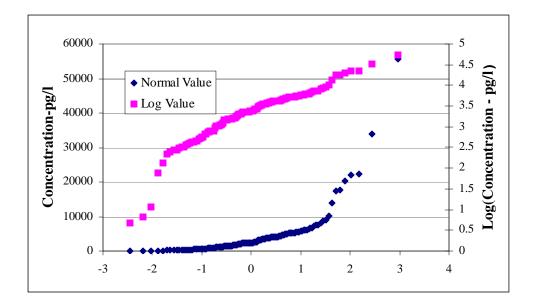


Table 1 summarizes the information provided by this analysis, and includes both the River and Tributary and the Bay and Saline analysis. The two sets of data have similar median (50th percentile) values, of 2,400 and 3,000 pg/l. However, the average concentration for the rivers and tributaries data set is almost twice the median concentration, whereas the average concentration for the bay and saline data set is virtually identical to the median.

Percentile	Rivers and Tributaries (pg/l)	Bay and Saline (pg/l)
5%	251	455
10%	392	487
25%	1,031	988
50%	2,403	2,990
75%	4,720	4,034
90%	7,144	5,352
95%	13,779	5,627
Average	4,171	2,775

 Table 1 – PCB Concentrations at Select Percentiles of the Data

Thus the typical measured concentrations of PCBs in the Delaware Estuary are in the 1,000 to 4,000 pg/l range. This data also indicates that areas represented by the rivers and tributaries data set are primarily impacted by sources with high concentrations of PCBs, while it is likely that the areas represented by the Bay and Saline data sets are likely impacted by more dispersed sources, possibly sediments or air.

The ubiquitous nature of PCBs and the resultant fact that all laboratories suffer from contamination of blank water, glassware and equipment complicates the identification of real sources of PCBs to the environment. Identification of general ambient concentrations will allow

more efficient use of limited sampling and analytical resources, since it provides a strategy to differentiate those sources and pathways that are impacting ambient conditions from those that are impacted by ambient conditions. In this manner, progress can be made, even when the analytical methods cannot precisely measure concentrations within an order of magnitude of the water quality standard.

What are the intended mathematical uses of the data? – Data that is destined for use for modeling or mathematical manipulation may require more precision than data that is directly measured and compared to the water quality standard. This is due to the fact that error may be compounded as it is aggregated and related to other parameters. Expert modelers and statisticians can provide insight as to the precision required in the modeling data set.

How do we ensure the collection of a data set that is representative of different sources and pathways? - The upfront decision to standardize sampling and analytical techniques for the TMDL program is a key issue to ensure comparability of data and is discussed later in this paper. Some estimate of the temporal and spatial variability of each source category must be accomplished to determine the number of data points that should be collected to characterize the impact of that source category on the estuary. There is always a tradeoff between limited human and financial resources and the desire for more data to reduce variability. A good strategy is to collect a limited data set for the purpose of better understanding the variability inherent in the different source categories. The Stage 1 TMDL for the Delaware Estuary provided a good initial data set that can be used to determine the focus of future data collection efforts. Table 2 uses the loadings from the Stage 1 TMDL and DRBC estimates of uncertainty to predict where the greatest data collection effort should be focused. Based on a simple multiplication of the loadings and the uncertainty, it is relatively clear that the Contaminated Sites, Delaware at Trenton and Non-Point Sources are the least understood significant sources of PCBs to the estuary, and that Point Sources and CSOs are better understood and less significant. Use of decision matrices such as this to guide future data collection will improve the quality of decisionmaking in the TMDL process.

Source Category	PCBs from PCB TMDL (mg/Day)	% of Total from TMDL	DRBC Assigned Uncertainty	Product of % of Load and % Uncertainty	Rank
Contaminated Sites	13.046	13.9%	105%	15%	2
Non-Point Sources	7.211	7.7%	157%	12%	3
Delaware at Trenton	54.841	58.4%	74%	43%	1
Schuylkill	9.129	9.7%	73%	7%	4
Point Source Discharge	5.758	6.1%	30%	2%	6
CSOs	1.327	1.4%	77%	1%	7
Tributaries			32%		
Atmospheric Loads			32%		
MS-4s	2.63	2.8%	157%	4%	5
Total Penta PCB Load	93.942	100%			

Table 2 – Decision Tool for Ensuring the Comparability of Future Data Collection

DATA QUALITY OBJECTIVES

Based on an evaluation of current conditions and likely targets, the stakeholders need to collaborate to establish a set of data quality objectives that will support the TMDL process. The data quality objectives will consider the needs of the TMDL process, and define specific sampling and analytical procedures and performance metrics to ensure adequate data quality. Some key issues are discussed in the following paragraphs.

Program Data Glossary – The specific terminology used in any data collection process is relatively unique, and the specific uses of terms can vary even among analytical chemists. It is critical that a common set of terms be used when discussing sampling and analytical issues, and this should become the basis for a formal data glossary. Terms that are used generically in the environmental field may have very precise meanings. Clarity in this area is required both to get comparable data deliverables from different analytical laboratories and for clear communication concerning analytical issues. For example, three specific terms that are critical to these discussions, yet somewhat unique to EPA Method 1668A are defined below. The high level of specificity provided in these definitions may appear to be excessive, but it is important to ensure that all stakeholders and laboratories are working to the same standards:

Detection Limit (DL) – The Detection Limit or Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs are analyte and matrix specific and may be laboratory dependent.

Estimated Detection Limit (EDL) –The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. This concentration is determined by measuring the noise height of the two quantitation ions for a given congener at the region of the SICP where the congener is expected to elute, converting this height into area based on the associated internal standard area, and taking the internal standard concentration, internal standard area, initial calibration average RRF, minimum signal-to-noise factor, and sample weight/volume into account. This definition of EDL is common to high resolution mass spectrometry isotope dilution methods like Method 1668A. Method 1668A only provides a definition for Estimated Method Detection Limit (EMDL) which states, "The lowest concentration at which a CB [PCB congener] can be <u>detected</u> with common laboratory interferences present."

Minimum Level of Quantitation (ML) – The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. According to Method 1668A, laboratories may establish MLs lower that EMLs [EMLs are Estimated Minimum Levels specified in EPA Method 1668A]: MLs may be established as low as the lowest calibration point provided that the concentration of the congener in a minimum of 10 blanks for a sample medium (e.g., water, solid, sludge, tissue) is significantly below the EML. Significant means

that the ML for the congener is no less than the average (mean) plus 2 standard deviations above the level in the minimum of 10 blanks. The blanks must be analyzed during the same period that the sample is analyzed, ideally over an approximately 1 month period.

Program Analytical Method – Determine the analytical method(s) to be used to gather data to characterize each source, pathway, or bank. It is important that data gathered for regulatory purposes be collected in accordance with approved EPA methodologies. However, some non-regulatory data may be best collected using more economical methods that stakeholders concur are adequate to meet the needs of the program. For example, track down studies that are quantifying large concentrations may not need to use the most sensitive methods, as well as researchers who have customized methods for the needs of their studies. It is important that all methods be governed by consistent data quality objectives and quantitative performance metrics in order to ensure that the collected data is useful. The stakeholders must establish guidelines for combining data collected using different methods.

The data collected for the Stage 1 PCB TMDL in the Delaware Estuary was collected using several EPA methods. These include EPA Method 8082, EPA Method 1668 (draft) and EPA Method 1668A (draft). It is generally recognized that the data produced by EPA Method 1668A (draft) is of higher quality than any other PCB analytical method.

Sampling Methods – Determine sampling methods that are suitable for use to characterize each given source or pathway. The sampling strategies will be very different for continuous point sources, tributaries, dry weather, and wet weather. As a practical example, the decision to use composite sampling versus grab sampling may appear to have no adverse implications. Composite samples have the advantage of being better able to characterize the temporal and flow variability of a discharge as compared to grab samples. It is important to assess and minimize the impact of limitations incurred by the selected sample method. Some issues to consider include:

- (1) Composite samples are more expensive to collect than grab samples.
- (2) Duplicate composite samples require duplicate sampling equipment, or the splitting of the primary sample, whereas two relatively equivalent grabs samples can be collected at the same time.
- (3) Splitting samples from one composite container to multiple containers is difficult, especially if the samples contain parameters that adhere to containers, volatilize to the air, or can be transferred by air to the containers. PCBs and the solids and organic carbon associated with their samples suffer from many of these considerations. Grab samples can be quickly collected and closed, minimizing these issues.
- (4) Rinsate and equipment blanks for composite sampling may not be representative of the actual sampling conditions, due to the fact that the rinsate blank is usually collected in a few minutes, while a composite sample may be collected over a longer, 24 hour period.

Treatment of Censored Data – Implement a standard treatment for all data sets, so that numerical values (loadings) from all sources and blanks shall be comparable. This includes parallel treatment of non-detects, 'J' values, coeluters, and values flagged for blank contamination. Chart 5 details how significantly the treatment of results which are not detected in analyses, and are flagged with a "U" or "ND" can impact the calculation of total PCBs. For

the purposes of this analysis, all reported results above the detection limit, including "J" flagged data are summed. This use of "J" flagged data is considered inappropriate to many, as these results are valid indications that the target compound is present, but a value less than the analytical methods minimum level of quantitation (ML). Data for point source characterization for the Stage 1 TMDL was aggregated to total PCBs using ½ the ML for all ND results. Examination of the two highest peaks in the middle of the plot details how dramatically this treatment of the data can impact the aggregation of the congener data. The two points are among the smallest peaks when NDs are treated as zero, but setting the NDs to ½ the ML raises the total PCB value by an order of magnitude. It is informative to note that these two sample analysis results are from a field blank, and a discharge sample. The performance of the laboratory, and the detection limits and minimum levels that are achieved are significant factors impacting this issue. The greater the sensitivity of the method, the smaller the impacts of non-detect treatment on aggregated total PCB number. The DRBCs Data Quality Subcommittee is working to address this issue prior to the development of the Stage 2 TMDL.

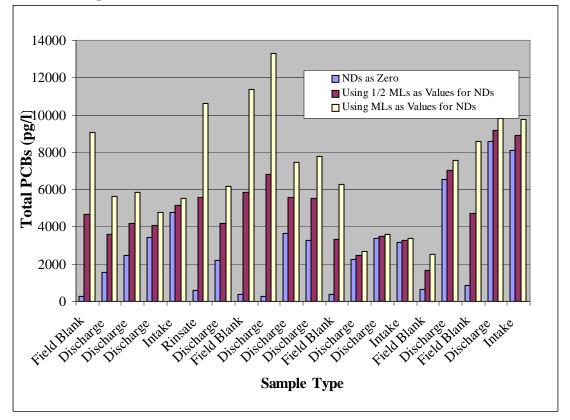


Chart 5 – Impact of Treatment of Non Detects on Calculation of Total PCBs

Aggregation of components (e.g.: PCB congeners) to total "parameter" concentration – The program must define the mathematical techniques used to take "building block" data and aggregate to totals for the TMDL regulated parameter. This protocol should be detailed prior to the start of data collection.

Statistical Significance Test - For persistent pollutants that are ubiquitous in the environment, a statistical test may be appropriate to determine whether a given source, pathway or bank is

significantly above the existing concentration in that media in the environment. This allows rapid prioritization of action planning, so that significant sources and pathways are addressed as a priority. Expert advise should be obtained to ensure that the appropriate statistical method is selected and properly applied.

DATA STORAGE AND AVAILABILITY

Data handling for a multiple parameter TMDL requires a significant resource commitment. The PCB data collection requires collection the following set of data or a subset of the following data for each sample, equipment blank, rinsate blank and trip blank.

- PCB Congener Results Results for 82 to 209 congeners, which include a specific result, detection limit, minimum (reporting) level and a host of supporting QA/QC information for each of up to 209 congeners.
- Isotope Labeled Calibration Congeners 32 Discrete Results
- Total/Dissolved/Particulate Organic Carbon
- Total/Dissolved/Suspended Solids
- Flow or Mass for Calculations

In addition, there is a great deal of additional supporting data that must be collected/stored, such as GPS information, latitude, longitude, sample date/time, sample types, matrix, weather and hydrologic conditions.

The data files that were used to accomplish the analysis in this paper contained over 160,000 records, and consumed approximately 200 MBs in a very rudimentary MS Access database. The accuracy and speed of data analysis is a direct function of the thought and discipline that starts before the first analytical result is added to the electronic record. Weeks of time were invested understanding the data, removing duplicate records, removing initial results that were replaced by resubmitted data. Much of this invested time is basically wasted, as there is no master database for the validated and accepted data, so each interested party must assess and tailor the data to create a dataset that is unique to their specific use. These user-specific data sets are fraught with errors, and basically frozen in time. The real danger in this practice is that different stakeholders, coming from different perspectives, may create data sets that are incomplete or contain errant data. These divergent data sets could result in needless contention, as well as faulty recommendations, strategies and decisions.

MS Access or a similar relational database application can be used to create a simple data store, an outline of which you will find below in Example 1. The creation of a data store is a relatively simple task, and should be accomplished even if there is no money for sophisticated front ends and reporting systems.

Example 1 – O	outline of Simple	Relational Data Store
---------------	-------------------	------------------------------

Sample Information	
Sample ID	
Media	
Total/Dissolved/Particulate	
Location ID	

Results	
IUPAC #	
Result	

Parameter Information
IUPAC #
PCB Name
PCB Number
Molecular Weight

Sample Type (Method Blank Field Blank, Field Sample) Date Collected By Grab/Composite Composite Time	Qualifiers (Q, U, J, B, E, C,?) Detection Limit Reporting Limit Unit of Measure (pg/l) Sample ID	Water Sediment Partitioning Coefficient Vapor Pressure @5C Vapor Pressure @20C Vapor Pressure @35C
Flow Temp	Analysis ID	
Location Information		Analysis Information Analysis ID
Location Name		Laboratory Name
Responsible Entity		Lot Number
Lat/Long		Date of Analysis
Zone		Date of QA/QC
River Mile		Method Blank ID
Depth		Calibration Standard ID
		Method
		Dilution
		Validation Type (Standard, Considers Blanks,

The data structure should be independent of the sample name, though there may be advantages to using a smart sample naming system. The DRBC has used a partial "smart" sample naming system to some success. For example, the sample name "EST 05 031502 FILTER", is a sample from the main channel of the Estuary, at location 5, on March 15, 2002. Further, this is a filtered sample designed to determine particulate PCBs. The use of "smart" sample names may help those involved in sample collection and receiving analytical results and supplemental information about the samples, however it is critical that all attributes for describing the sample should be contained in appropriate fields in the database, so that the data can be filtered and sorted easily. Some of these parameters are outlined in Table 3:

Considers Intakes)

Attribute Classification	Examples	
Weather/Flow Conditions	Dry Weather / Wet Weather	
Sample Type	Particulate / Dissolved / Total / Pisces / Method	
	Blank / Rinsate Blank / Equipment Blank	
Media	Water / Sediments / Tissue / Air	
Location Type	Tributary, River, Bay, WWTP Discharge	
Water Type	Fresh, Brackish, Salt	
Program Acceptance Code	Not Reviewed / Provisional / Accepted /	
	Rejected	
Re-analysis Code	Original Data Set / Replaced with Corrected	
	Data Set / Corrected Data Set	

Table 3 – Sample Attributes

The data structure will need to be able to link samples/analysis that are components of a single sampling event, and will need to be aggregated to a total PCB value. Finally the data must be able to be readily entered into the data store upon receipt, and be reclassified as it is validated and approved for use in the TMDL program. This will provide an audit trail so that all stakeholders can see all collected data, and understand why it is included or excluded from the program.

DATA QUALITY ASSESSMENT

There are a number of relatively simple ways to gain some feel as to the reliability and precision of the total analytical program. The strategies outlined below are not a replacement for the very important data validation processes that are integral to the laboratory and that can be accomplished by independent data validators. With the power now at the hands of the typical PC user, it is possible to automatically prepare plots of the results and the related QA/QC data using a data from a simple, well-organized data store. Table 4 includes a description of several of these tools. Most rely on readily available data, however, the Carryover Plot would require that the analytical laboratory share the results of its entire batch, including all results, detection limits and minimum levels with the TMDL stakeholders.

	Y Axis	X Axis	Use
Laboratory	Method Blanks	Batch or Lot ID or	Display the labs
Consistency Plot	Minimum Level	Analysis Date	ability to deliver
	Detection Limit		consistent results over
	Results (Include qualified		time
	data)		
Carryover Plot	Result (Include qualified	Batch and Sample	Displays the impact of
	data)	Number	individual samples on
	Minimum Level		the subsequent
	Detection Limit		samples and
			respective reporting
			limits
Sampling	Trip Blanks		Displays the impact of
Background Plot	Rinsate/Equipment Blanks		filed/sampling
	Results (Include qualified		contamination on
	data)		results

Table 4 – Data Quality Assessment Tools

Graphical analysis of results and QA/QC data over time is an ideal way to gain some understanding of trends in the performance of the sampling processes, the analytical processes and the reporting processes.

Chart 6 and Chart 7 are Laboratory Consistency Plots as described in Table 4, and display the results and data quality information for PCB congener 129 results from a single analytical laboratory during a two-year period. Chart 6 has the vertical scales expanded so that all data is visible. Chart 6 reveals the fact that two extremely highly contaminated samples (approximately 8,000,000 pg/l) were reported, and that these samples coincide with some elevation of the

Detection Limit (DL) and Minimum Level (ML). Chart 7 looks at the results using a scale of 80 pg/l for all data. Examination of this chart reveals a number of significant analytical concerns. The ML (Green Triangles) varies from 4 to 40 during the first half of the chart; this variability is significant and should be investigated with the analytical laboratory. During that latter half of the chart, the variability of the DL and ML further increases. It is likely that some form of blank or equipment contamination is contributing to this noise in late 2003 and early 2004.

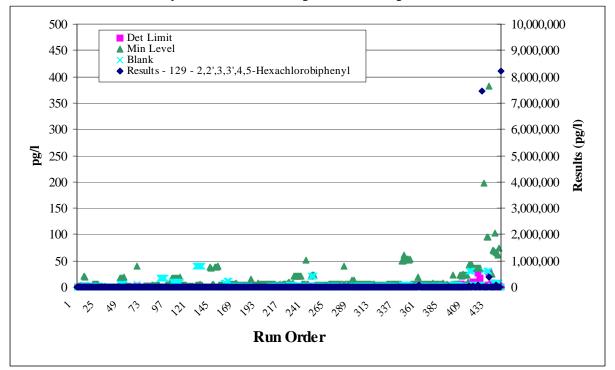
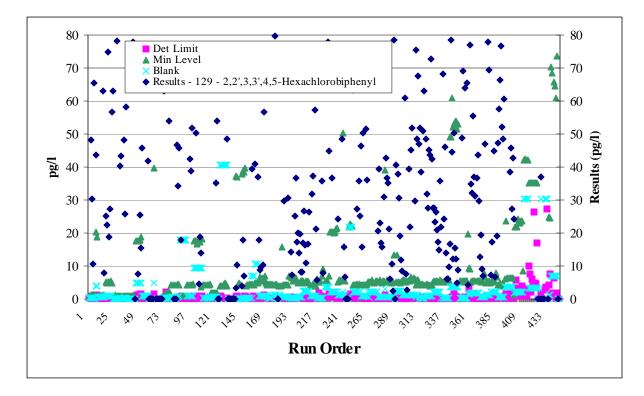


Chart 6 – PCB 129 Analysis Results from April 2002 to April 2004 for PCB-129

Chart 7 – PCB 129 Analysis Results from April 2002 to April 2004 for PCB-129



While the data problems indicated above are significant, they can be addressed by establishing performance metrics for the program, which detail to the laboratory specifically what detection limits and minimum levels are acceptable for samples and standards. Further establishing performance standards for method, rinsate, equipment, and trip blanks will inform the sample provider and the laboratory as to the need to resample and reanalyze the samples which do not meet requirements.

The increased use of automation in our data collection efforts has allowed the generation of much more data, which can be significantly more statistically powerful. However, the shear volume of the data that is generated can overwhelm the limited stakeholder resources available to evaluate and ensure the quality of that data. At the present time, the plotting of data, and the review of those plots by expert stakeholders is a key method to monitor the quality of our data collection processes.

Summary

The stakeholders in the Delaware Estuary have made significant progress toward understanding the issues that impact data quality and are implementing changes that will ensure that we continually improve the quality of the data collected. It is clear that sorting out disparate data sets is far more difficult and potentially contentious than setting and adhering to sound data quality objectives up front. In addition, it has become very clear to the authors that the data collected to support a multi parameter TMDL, such as the Delaware Estuary PCB TMDL cannot be managed or evaluated on paper or even in spreadsheets. At a minimum, a basic relational data structure is required to allow ready analysis and evaluation of the data. Finally, some investment in automating the production of certain graphical tools for evaluating data on a real

time basis is an invaluable asset to the TMDL process. In summary, the following processes are key to efficiently collecting high quality data for use in a TMDL

- Determine the intended uses for the data, the data quality requirements for a simple mass balance, multimedia modeling, track down or other purposes may be dramatically different.
- Establish data quality objectives for the sampling, analysis and reporting of data, in addition, establish clear performance criteria to ensure that analytical results are representative and useful.
- If using data collected from a variety of methods, establish the methodology for ensuring comparability, combining the data and collectively analyzing it.
- Establish a data store to immediately accept all new data, with a coding structure to allow data to be flagged with regard to acceptance status.
- Develop simple "common sense" tools to allow stakeholders to review the quality of the data that is being generated.

Acknowledgements

This paper would not have been possible without the collaboration of many stakeholders in the Delaware Estuary. In particular the members of the DRBC Toxics Advisory Committee's Data Quality Subcommittee have provided much of the information and insight required to write this paper. They have also provided a forum for discussing how to improve the process of ensuring the quality of the date collected for the PCB TMDL.

This paper is not being written after the TMDL process is completed, rather in the midst of a period of intense effort by the Data Quality Subcommittee to address both the issues identified in this paper and other issues of equal import. This paper should be viewed only as a snapshot of issues, and strategies to improve the TMDL process.

References

Calibration of the PCB Water Quality Model for the Delaware Estuary for Penta-PCBs and Carbon by DRBC dated December 2003

US EPA Regions II and III TMDL for PCBs for Zones 2 - 5 of the Tidal Delaware River prepared by the Delaware River Basin Commission – December 15, 2003

U. S. Environmental Protection Agency (1999) *Method 1668A, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS*, EPA-821-R-00-002: Washington, DC