DATA MANAGEMENT IN SUPPORT OF TMDL EFFORTS

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ABSTRACT

Data management is the foundation for water resource assessment. The ability to successfully manage large amounts of data (>100MB to 1 GB) collected and submitted during an extended period is essential to evaluate long-term trends, conduct modeling and determine the effectiveness of remedial efforts. The Delaware River Basin Commission, on behalf of the U.S. Environmental Protection Agency, has concluded the Stage 1 Total Maximum Daily Loads (TMDLs) for polychlorinated biphenyls (PCBs) for the Delaware Estuary in December 2003, DRBC (2003). Monitoring efforts in support of the Stage 1 TMDLs and subsequent data submission posed significant difficulties in assimilating the analytical results into a comprehensive database. The use of different analytical methodologies, and reporting conventions by the various laboratories involved in this effort required extensive data manipulation and limited the usefulness of the reported results. The Delaware River Basin Commission is currently developing the Stage 2 Total Maximum Daily Loads (TMDLs) for PCBs for the Delaware Estuary. The objective of the Stage 2 TMDL is to develop more accurate TMDLs, which require a more precise quantification of the concentrations and/or loads from the various PCB source categories. This task is made more complex by the requirements to evaluate different source categories i.e. point source discharges, ambient river water, sediment, tributary and contaminated site runoff, analysis of 209 compounds, and the collection of multiple samples. To streamline the Stage 2 process, data quality objectives (DQOs) were specified to provide a consistent approach to sample collection, analysis and data reporting.

1. INTRODUCTION

The DQOs were developed by the Data Quality Subcommittee (DQS) of the DRBC Toxic Advisory Committee to provide uniformity between samples collected from the various source categories, in order to more accurately quantify the various PCB categories being investigated as part of the Stage 2 PCB TMDL. Membership includes representatives from the regulated community including municipal and industrial dischargers, U.S. EPA Regions II and III, State Permitting Agencies, and

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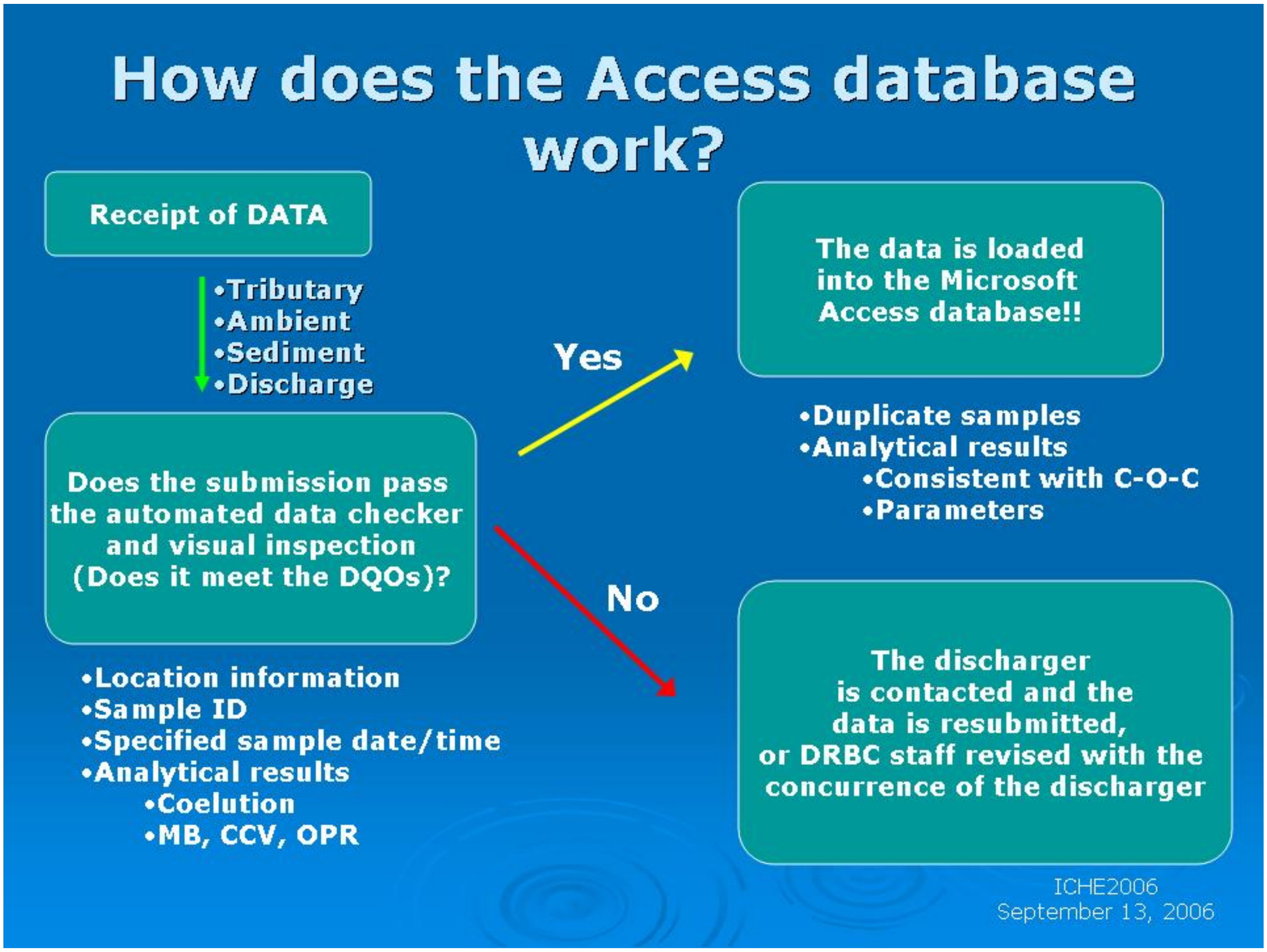
Environmental groups. Additionally, the DQS invited a select group of laboratories to participate in discussion regarding analytical approaches. Data quality objectives were specified primarily for:

1. Analytical methods, and data qualifier conventions
2. Sample size and collection techniques
3. Sample identification protocols
4. Electronic data deliverable formats

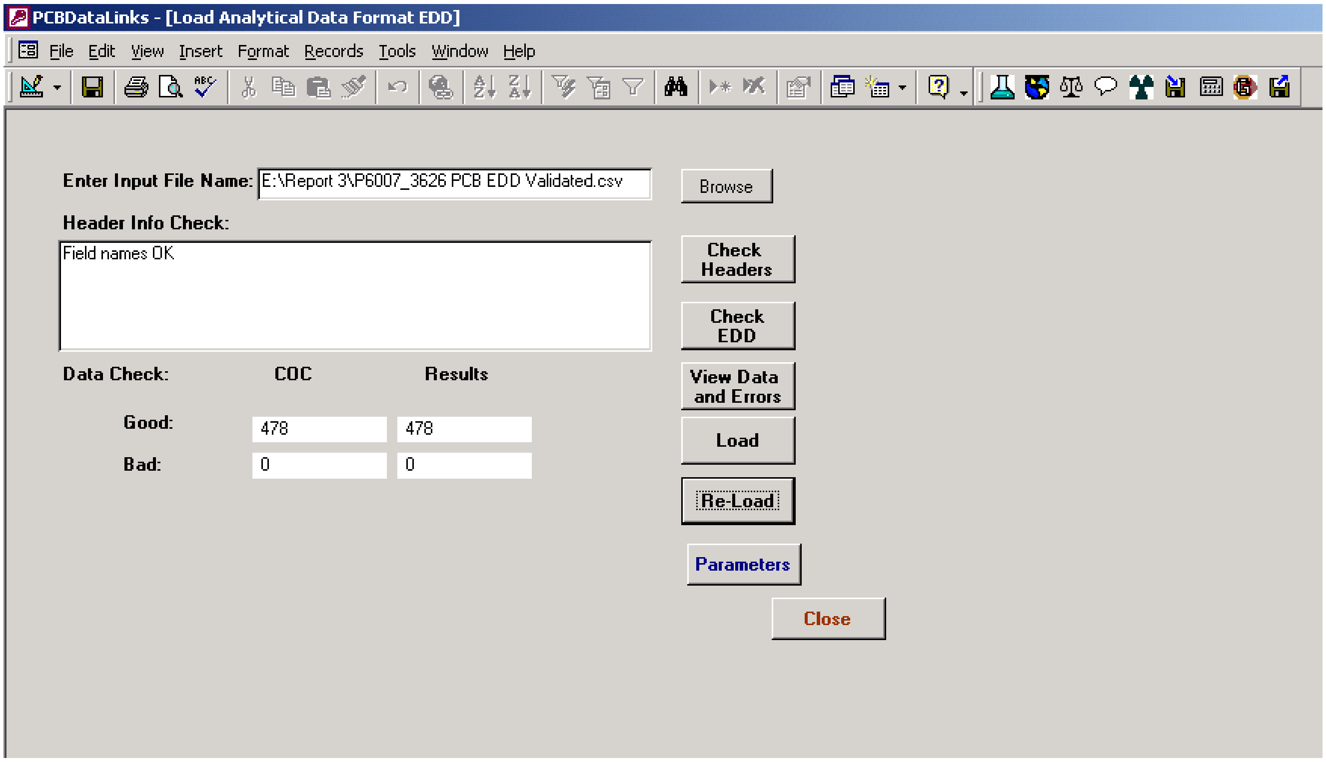
These data quality objectives and others were made available to all interested parties via the internet and can be found at http://www.state.nj.us/drbc/PCB_info.htm. Subsequent training classes were held to discuss sample collection techniques and address any questions.

A Microsoft Access database with a point and click user interface was developed for data review, storage and retrieval. Three separate electronic data deliverables were required; analytical, chain of custody and location deliverables.



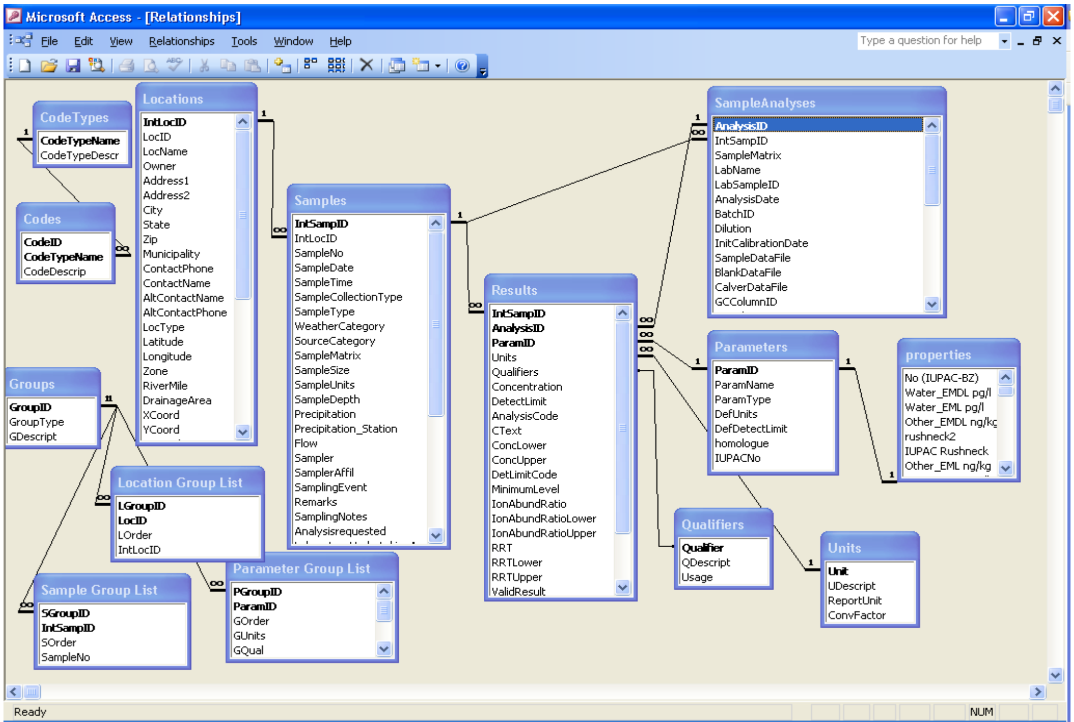
1. Overview of the complete data loading process

Through the use of visual basic programming available in the Access database, submitted data sets are screened for adequacy of formats and other requirements prior to incorporation into the database.

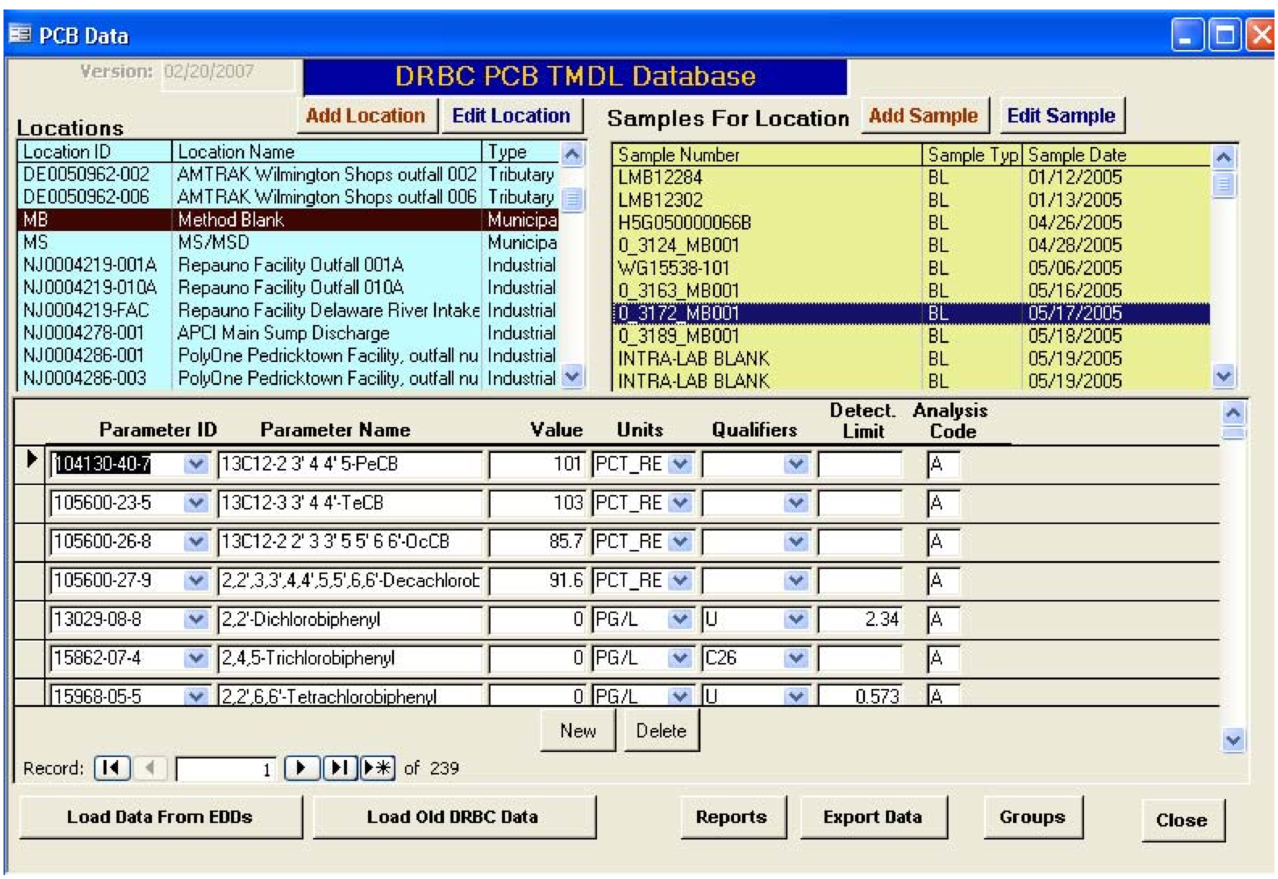


2. User interface of the database loader.

The relational database design provides for a robust, efficient analysis tool that can be queried and evaluated quickly and efficiently. The relationships between the various database elements, - chain of custody, location and analytical results provide the ability to evaluate the data both temporally and spatially.



3. Overview of the database structure.



4. Illustration of the search engine provided in the database.

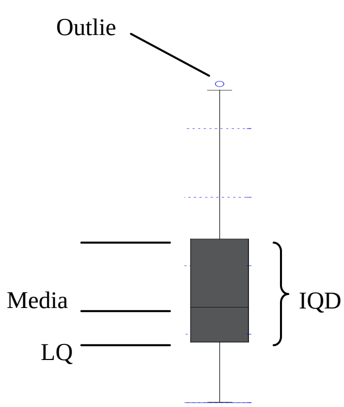
. The data loading is achieved using visual basic for applications built into the loading forms. The user interface is a fairly simple point and click application that has been developed in Microsoft Access using the standard queries, forms and reports available within the program. The intent of the database is to provide quick and efficient tools for data compilation and evaluation.

2. RESULTS

Analytical results have been evaluated for the point source discharger data and compared to the data quality objectives specified for laboratory analysis. Laboratory analytical requirements included the use of a six-point calibration curve utilizing a low calibration standard of 0.5 ng/ml, from which the Estimated Detection Limits (EDLs) were calculated using the protocols provided at http://www.state.nj.us/drbc/PCB-EDL.pdf. Two-liter samples were collected for analysis employing the protocols provided at http://www.state.nj.us/drbc/PCB-Techniques.pdf. and provided to the laboratories for analysis. Through the approach referenced above for the calculation of the EDL with a low calibration standard of 0.5 ng/ml, a minimum level of 5 pg/L was calculated using the following equation:

$$ML = \frac{0.5ng/ml \times 20ul \times 1ml/1000ul}{2.0L} = 0.005ng/L = 5pg/L \quad (1)$$

Estimated Detection Limits were expected to be approximately one-third the minimum level. A review of the discharger data (n=386) indicates that EDLs between 1 and 3 pg/L per congener were achieved. Figure 6 illustrates the range of concentrations summarized by homolog of the EDLs (see Figure 5 for the definition of a Box Plot).



Where:
Median: midpoint value of the highest and lowest data points
UQ: Upper Quartile - midpoint value of the median and highest data point;
LQ: Lower Quartile - midpoint value of the median and lowest data point;
IQD: Interquartile Distance or (UQ – LQ);
Outliers: x > UQ + 1.5*IQD or x < LQ – 1.5*IQD

Figure 5. Box Plot Definition.

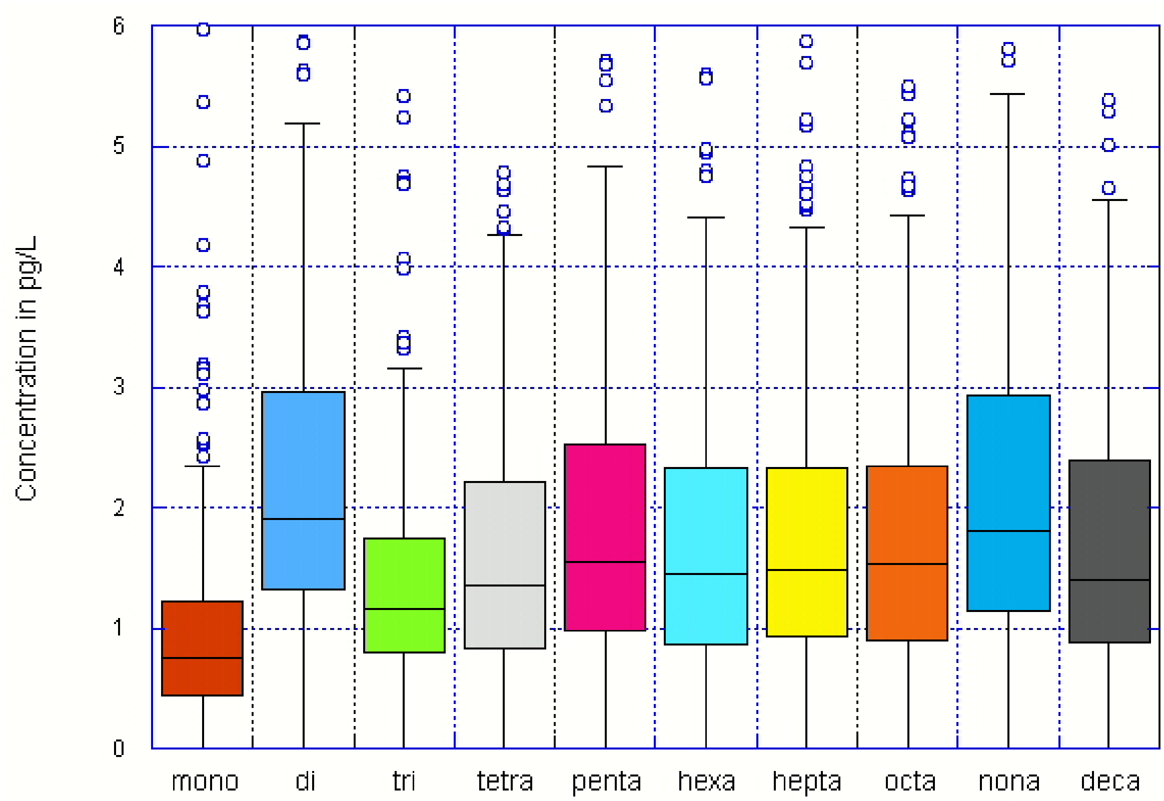


Figure 6. Estimated Detection Limits (EDLs) categorized by homolog for analyzed effluent samples (n=386).

Method Blank (MB) acceptance criteria were also specified with congener specific and total sample concentration requirements. The flow diagram for MB acceptance criteria is provided in Figure 7 and is also referenced at http://www.state.nj.us/drbc/PCB-MethodBlankRules.pdf.

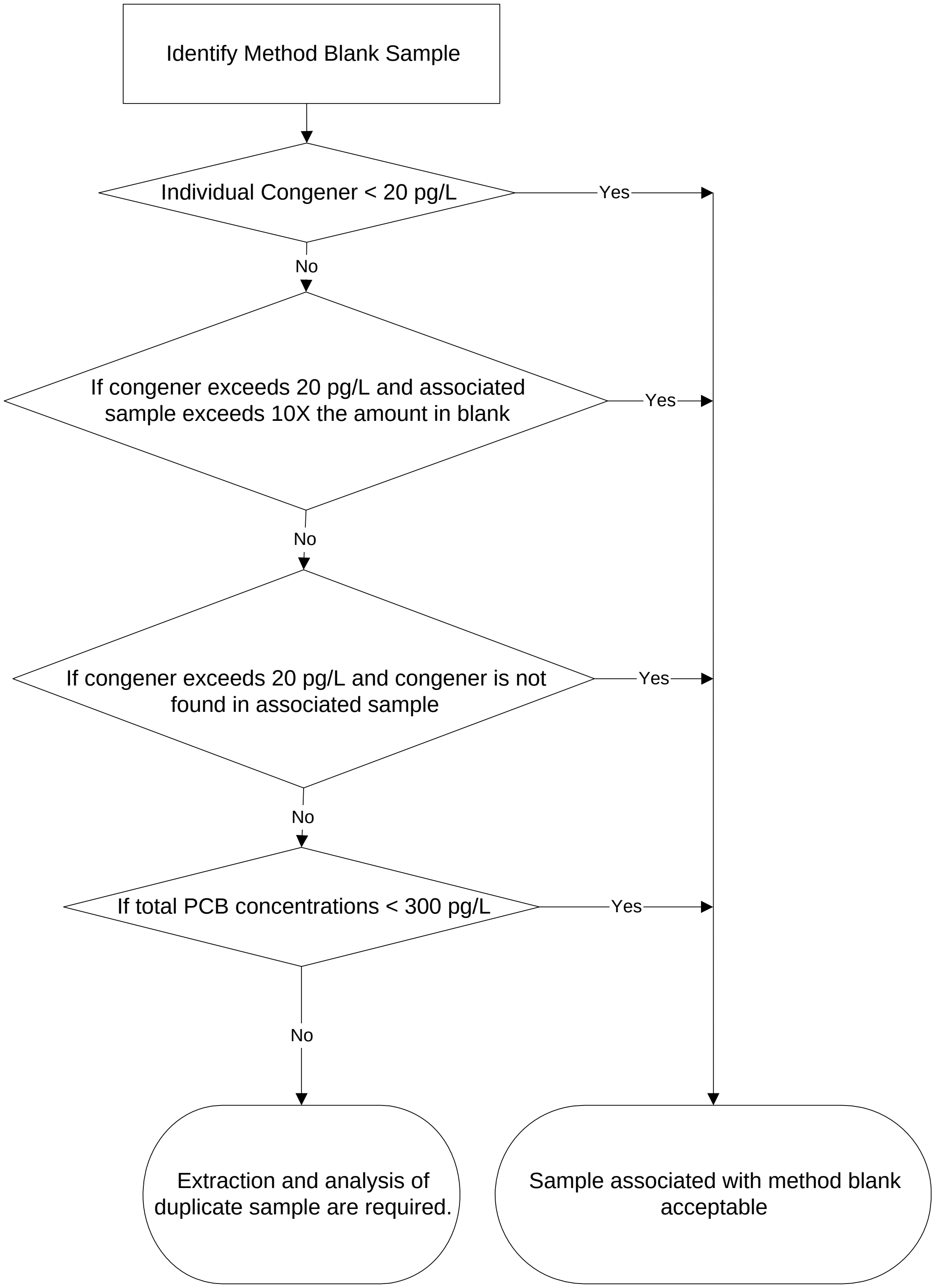


Figure 7. Flow diagram illustrating the method blank acceptance criteria.

Analytical results for 119 Method Blank samples have been reported. Method Blank concentrations have been summarized by homolog and are presented in figure 8. Seventeen of the MB samples exceeded the acceptability criteria for total PCB concentrations (14%). Further investigation of contamination associated with the Method Blank indicates that individual congener exceedances occurred less than 1% of the time (n=24,832). These individual congener exceedances represent a median contribution of 27% to the total concentration for the 17 samples that exceeded acceptability criteria for total PCB concentrations. Figure 9 illustrates the distribution of the individual congener mass contribution for these seventeen samples.

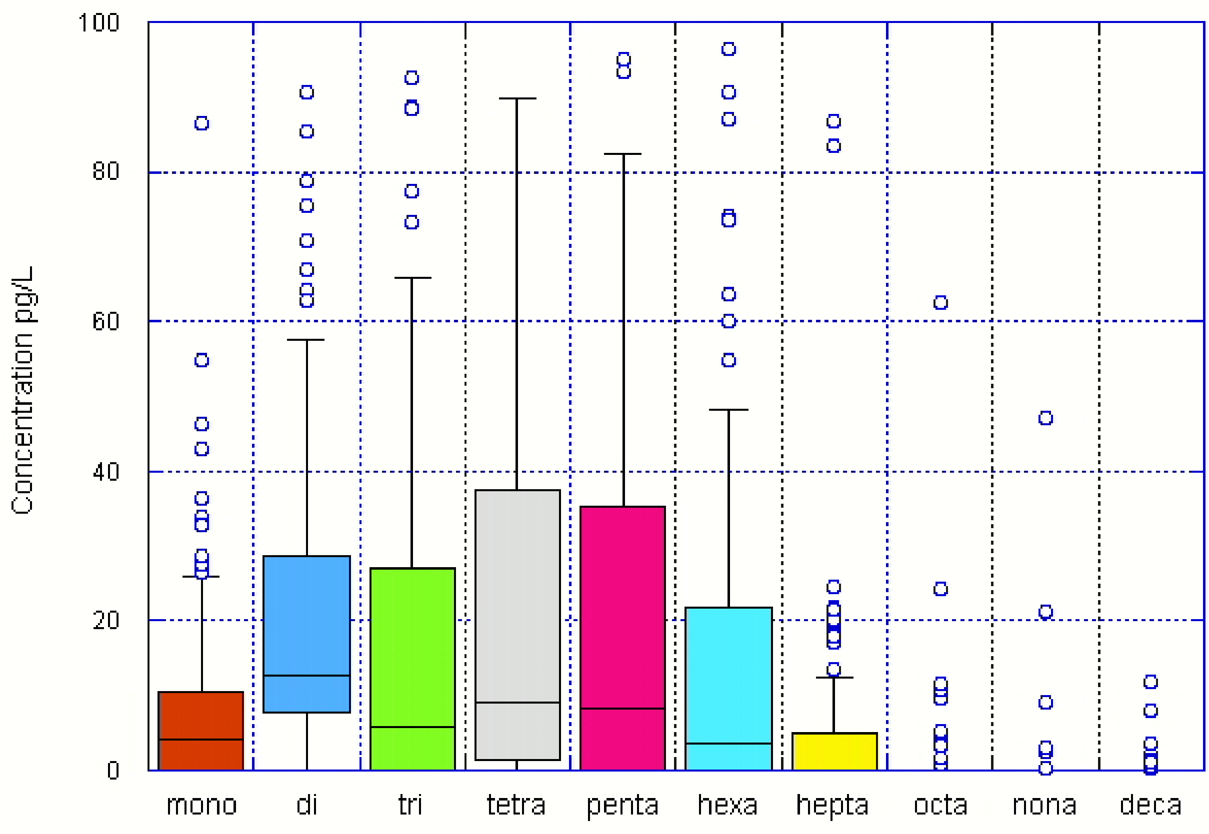


Figure 8. Median value of Method Blank concentrations summed by homolog (n=119).

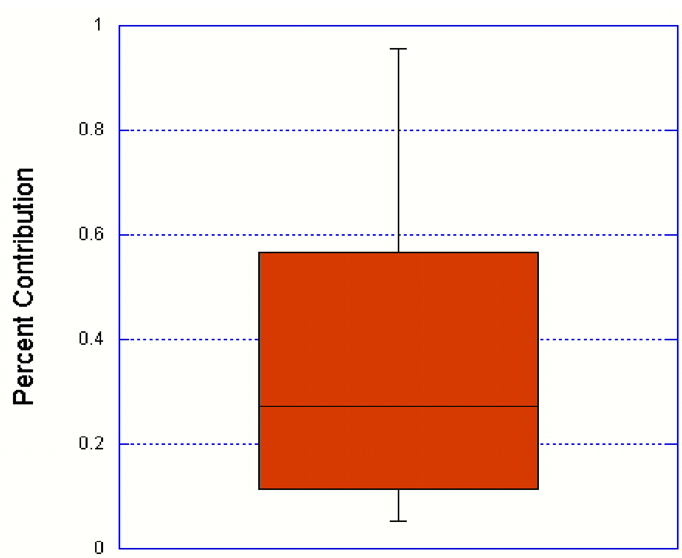


Figure 9. The percent contribution of individual PCB congeners to the total concentration of 17 MBs exceeding the acceptability criteria for total PCB concentrations.

3. DISCUSSION AND SUMMARY

The data quality objective for this study, to obtain a more precise quantification of concentrations from various PCB source categories, has been met for the effluent data set analyzed. Estimated Detection Limits are between 1 and 3 pg/L on a congener basis and have met the objective of achieving an EDL of one-third the minimum level. The effluent data set does exhibit outliers, which exceed 1.5x the Interquartile distance. However, these outliers appear to be artifacts of sample dilution, thereby resulting in elevated EDLs for those samples. Analysis of the Method Blank dataset exhibits median values by homolog of less than 20 pg/L with > 85% of all method blank samples achieving the Method Blank Contamination decision rules for total PCB concentrations. Median values were not calculated for the octa, nona and deca homologs due to the large percentage of non-detected values, 87%, 95% and 85% respectively.

The advantages of a consistent approach to sample collection, analysis and data reporting are comparability of analytical results between samples, reduced analytical uncertainty, and therefore greater accuracy in estimating loadings, as well as, the ability to more accurately monitor long-term trends. Additional information can be added as is necessary and existing analysis will be updated to contain the new information. However, the greatest benefit is in the transparency of approach, the readily understandable objectives and the ease of data transferability. This ability provides a critical link for an open dialogue between regulated community and regulatory agencies for evaluating effectiveness of remedial efforts in support of the TMDL process.

REFERENCES

Delaware River Basin Commission. (2003) U.S. Environmental Protection Agency Regions II and III. Total Maximum Daily Loads for Polychlorinated Biphenyls (PCBs) for Zones 2-5 of the Tidal Delaware River. Delaware River Basin Commission, West Trenton, New Jersey.