Independent Data Validation

All laboratory data generated during the course of this project was subject to review by a third party consultant, Marcia Kuehl. The scope of this review included assessing the completeness of the data package received from the lab, the compliance of the lab procedures to established protocols, the presence of any unusual lab quality control sample results, and the overall data usability.

The established protocols for the analysis are established in the laboratory's standard operating procedure document (SOP), and include holding times and preservation of samples, calibration procedures and frequency, and quality control sample criteria. No Aroclor 1242 data considered unusable was reported for any of the air samples.

However, a significant portion of the samples (178) did not comply with the holding time criteria and have been flagged as "estimated" values by the data validator. The criteria violated refers to the amount of time a sample can be held before extraction in the laboratory, a period limited to two weeks at $4^{o}C$ by the SOP.

Maintaining this rate of extraction and analysis was not possible given the rate of sample collection, so that as the project progressed, sample extraction got farther and farther behind. This could lead to sample loss, where some of the captured PCBs migrate from the sampling materials and thus are not reflected in the analytical results.

Whether or not this effect actually occurs, however, is subject to question. Holding time criteria are frequently established as "ideal world" situations, without any substantive tests indicating that there is any sample loss over time. This type of test involves preparing sample materials with known quantities of the analyte of interest, and then extracting them for analysis after variable amounts of time.

Contact with the authors of the EPA method (TO-4) on this topic revealed that the holding time criteria was not based on storage stability data, but rather referenced directly from American Standard Test Methods (ASTM). One of these methods (ASTM D4861) does contain some storage data in an appendix. This data indicates that Aroclor 1242 has a mean recovery of 99.3% after 30 days at room temperature ($24^{o}C$). In spite of this data, the method quotes a holding time of 2 weeks at $4^{o}C$ between sampling and extraction.

In light of the reported recovery after a month at higher temperatures, the temperature dependence of PCB mobilization, and the near freezing storage of the samples in the lab, sample loss associated with this criteria is considered unlikely. Although these samples were flagged "estimated" during data validation, they are treated no differently than unflagged results in this report.

Sampler Calibrations and Audits

High volume air samplers are calibrated to determine actual air flow rate, from which valid sample volumes can be calculated. The calibration procedure involves attaching a calibrated orifice to the sampler, and measuring the flow rate at different sampler settings. Volume calculations are then based on the settings recorded with each sample. A total of 74 calibrations were performed on 27 samplers during the course of this project.

Each calibration, whether actively used for sample calculations or not, was assigned a unique calibration code, and both hard copy and Excel spreadsheet files maintained. Slopes and intercepts of each calibration were incorporated into the Access database for volume calculations. All sample volume calculations are based on standard temperature and pressure flow rates, adjusted to established seasonal averages employed by the WDNR Air Monitoring Network.

The goal for volume determinations is to be within ± 10% of the actual value. A total of 47 sequential calibrations on the same samplers were compared to determine whether this goal was met. The RPD between calibrations ranged from – 5.3% to 5.9%, with an overall average of –0.05% (average of the absolute values is ± 1.1%). Thus the precision of the calibrations is within the data quality limit.

Basim Dihue of Region 5 EPA in Chicago conducted sampler audits to verify the accuracy of the calibration procedures. The auditing procedure involves attaching a different calibrated orifice to the sampler, determining the flow rate at a single point, and then comparing this to the flow rate calculated from the sampler setting and initial calibration. Calculated flows must differ by less than 10% to pass the audit.

A total of 16 audits were conducted on 14 samplers at 13 different sites on 2 separate days. Percent differences are shown in the table below, and ranged from –7.0% to 6.3%, with an average of 1.1% (average of the absolute values is ± 2.5%). All audits passed the quality control criteria, so that sample volumes can be considered correct within ± 10%.

Table Q-1: Sampler Flow Audit Results

Site	09/29/1999	11/23/1999	Site	09/29/1999	11/23/1999
LF01	-7.00%	-2.21%	**FR09**	0.81%	
LF02	0.80%	5.00%	**FR10**	-1.63%	
LF03	3.50%		**FR16**		6.30%
FR03		3.60%	**FR17**	-0.40%	
FR03d		0.87%	**FR18**	0.41%	
FR06		0.77%	**FR19**	3.06%	
FR07	1.66%		**FR21**	2.64%	

Completeness and Representativeness

The completeness parameter evaluates the ratio of valid samples collected to scheduled sampling days. As a general rule of thumb, a completeness of 75% is considered acceptable for applying the data to a description of the overall ambient conditions during the sampling period.

An evaluation of completeness in a variety of ways is included in Appendix D, including overall project, individual sampling runs and sites, and quality control samples. Sufficient samples were obtained from most sites and all sample runs. Results obtained from sites which have not achieved the required completeness goal are ***italicized*** in the result tables.

Representativeness is a quality which attempts to evaluate the applicability of the data set to actual ambient conditions. It is based on a combination of location, sampling frequency, and intent of project. For example, a single sample obtained next to the settling basins during the course of the dredging would not yield a result representative of the general area throughout the operation.

The large number and geographical spread of sites involved in these determinations, as well as the relatively large number of samples collected overall increase the likelihood that the results obtained are generally applicable to ambient conditions prevailing during the dredging project.

Quality Control Samples

Blank Results

A total of 25 blanks were collected during the course of this project, representing 10.1% of the ambient samples submitted. Several types of blanks were collected, with the most prevalent being field blanks (a total of 10). Field blanks represent samples which were treated as an ambient sample without drawing air through it. Most of these samples (8) were obtained from samplers which failed to run properly, and sampled less than 5 cubic meters of air.

Blanks obtained in this manner are the most representative of conditions the ambient samples are sampled under, and therefore provide a good indication of whether extraneous contamination in the field is a problem. Of the 8 in field blanks, 4 were obtained from samplers within the remediation property line, and therefore represent the highest likelihood of in-field contamination.

Although not specified in the original design, the submission of lot blanks to verify cleanliness of sampling materials as obtained from the supplier is a standard operating procedure. The standard frequency for this type of blank is one per lot, as labeled by the supplier. A total of 4 different PUF plug lots were used in this project. Three lot blanks were submitted specifically for this project. The fourth lot in use was also used for the

Wisconsin Urban Air Toxics Monitoring program, and had a lot blank submitted previously.

Trip and preparation blanks are categories which were included after the original design to ensure that the sometimes high concentrations observed were not leading to cross-contamination of samples. Trip blanks traveled with samples between Madison and Green Bay multiple times, without being set up at any stations, before being packaged and submitted to the laboratory. The purpose of these samples was to determine whether migration of PCBs was occurring during the sample shipping procedures. A total of 3 trip blanks was submitted.

Preparation blanks were including to determine whether or not the cleaning procedures employed between samples were sufficient to minimize carryover on the sampling equipment, and to examine whether preparation room contamination was a source of concern. A total of nine preparation blanks was submitted, most of which examined the sampling heads from the most contaminated locations.

There were no detectable quantities of Aroclor 1242 in any of the blank samples submitted. The implication of this is that neither the sample material nor the handling procedures introduced contamination that would interfere with analysis. As such, no results are modified for background values in further discussion of results.

Duplicate Samples

A total of 15 pairs of valid duplicate samples was submitted to the laboratory for analysis. Two of these pair are spiked duplicates discussed in the Spiked Samples section following. Of the remaining 13 pairs, 12 (93.3%) are within the quality control guideline of ±25% Relative Percent Difference (RPD), with an overall average of ±17.2%. No apparent cause for the single failed sample (6.7%) could be discerned. Excluding this sample yields an average RPD of ± 13.3%.

The table below presents all non-spiked duplicate data collected during the course of sampling. Results are in nanograms total Aroclor 1242 per cubic meter. The sample which failed the criteria is in ***italics***. As a second duplicate sample collected during the same period passed the criteria (±16.7%), results from that run are treated as all other runs.

Table Q-2: Duplicate Sample Results (ng/m^3)

Date	Primary	Duplicate	Average	RPD (%)	Date	Primary	Duplicate	Average	RPD (%)
28-Aug-99	0.7	0.8	0.7	24.1%	**06-Nov-99**	21.6	20.3	20.9	5.8%
01-Oct-99	14.7	14.9	14.8	1.1%	**06-Nov-99**	2.0	2.3	2.1	14.8%
07-Oct-99	28.5	27.5	28.0	3.3%	***12-Nov-99***	*15.8*	*8.2*	*12.0*	*63.3%*
25-Oct-99	10.0	9.4	9.7	6.7%	**12-Nov-99**	1.8	1.5	1.7	16.7%
31-Oct-99	9.7	11.7	10.7	18.8%	**18-Nov-99**	15.4	12.7	14.1	19.5%
31-Oct-99	0.9	1.0	0.9	16.7%	**18-Nov-99**	2.3	1.8	2.1	23.6%
24-Nov-99	1.6	1.7	1.6	9.1%					

Back Half Samples

Sampling with 2 separate PUF cartridges in a single sample was incorporated for the 72 hour samples as a way to measure potential sample breakthrough and loss during the longer sampling time. This addition was necessary because the method had not previously been verified for this extended sampling time.

This technique uses the quantity recovered from the second cartridge (or back half) relative to the total amount recovered from both cartridges to evaluate the potential for sample loss. The general criteria for a valid sample without loss is for the back half to contain less than 10% of the total material recovered.

Not all 72 hour samples included back half cartridges, largely because of a shortage of sampling material which persisted through the 11th sampling period. A total of 94 successful 72 hour samples were set up, of which 73 (77.7%) included back half portions. Of these, a total of 13 (13.8% of total 72 hour samples) were submitted for separate analysis. The remainder of these exposed cartridges have been stored at 0^{o}C in case further clarification of the potential sample loss from these samples is desired.

Most of the back halves analyzed showed traces of PCB congeners, but only 5 showed quantities above the detection limit. The lowest concentration sample with a detectable back half portion contained a total of 4.9 ug Total PCB as Aroclor 1242. With the exception of a spiked blank, all samples with non-detect back half portions had less than 1.2 ug recovered from the front halves.

It should be noted that the congener pattern observed in these samples does not match that of Aroclor 1242. Each of the congeners observed does occur in the 1242 mixture. However, the relative concentrations of the congeners is skewed in favor of the lighter, more volatile components. The front portions of these samples did show typical Aroclor 1242 patterns, qualitatively indicating that the sample breakthrough, while occurring to some extent, was not significantly depleting any particular congeners.

This skewing of congeners complicates quantification of material recovered from the back half samples, because instrument calibrations are based on a series of 13 separate peaks associated with Aroclor 1242, and only 4 or 5 of them were present in the typical back half extract. Rather than attempting to re-calibrate the instrument on the basis of the individual congeners to provide the most accurate possible quantification of these samples, the back half sample values were based on the same 13 peak calibration as the rest of the samples. This could potentially result in underestimating PCB concentration.

The table below presents the results from the back half analysis. All units are ug Aroclor 1242 recovered from the sampling materials, not ambient concentrations. All detects are evaluated as reported from the laboratory. The percentage of recovered analyte on the back halves ranged from 3.4% - 6.2%, with an average of 4.7%.

Evaluation of the worst case scenario for sample loss involves evaluating non-detect back half samples as if they contained Aroclor 1242 at the detection limit (0.1 ug), at which

point any sample with an overall PCB content less than 1.0 ug automatically has greater than 10% of the recovered material on the back half. The overall average theoretical back half percent including non-detects in this way is 9.0%, which is still within the sample loss criteria of less than 10%.

Results from the back half analysis indicate that sample loss from breakthrough during the 72 hour sampling period is not likely to have been a problem during this sampling program. To maintain comparability between the 72 hour samples, all back half results obtained are ignored in further analysis.

Table Q-3: Detected Back Half Sample Analysis

Sample ID	Front	Back	Total	% Back Half
FR99-269	22.	0.8	22.8	**3.4%**
FR99-177	11.	0.6	11.6	**5.5%**
FR99-180	7.7	0.4	8.1	**4.3%**
FR99-179	6.8	0.5	7.3	**6.2%**
FR99-178	4.7	0.2	4.9	**3.9%**
	Average Detects			**4.7%**

Spiked Samples

Method accuracy is measured by adding a known quantity of Aroclor 1242 to several samples before deployment in the field. Two sets of samples spiked in this manner were prepared; one during 24 hour sampling, and the second during 72 hour sampling. Each set of spiked samples includes an ambient sample, a spiked duplicate ambient sample, and a spiked blank.

The blank serves as a blind check on the laboratory's ability to quantitatively recover a known amount of PCB. Evaluation is simply the direct ratio of the lab results to the quantity added. The quality control criteria for all spiked samples is a recovery of 100 ± 25%. The ambient/duplicate pair are evaluated both for recovery and duplicate precision. All spiked samples are within the ± 25% limits, with an average recovery of 103.7%, and an average precision of ± 2.9%.

There are two sources of Aroclor to the duplicate sample: the quantity initially added, and the ambient air during sampling. Evaluation of the spiked duplicate results involves several assumptions to account for this. First, the primary ambient sample results are assumed to accurately reflect ambient concentrations, and the duplicate sample volume is used to determine the theoretical ambient loading to the PUF cartridge. This loading is then subtracted from the actual results to obtain a recovery value. The table on the following page presents results of this calculation.

Table Q-4: Analytical Recovery (ug)

Date	Type	Aroclor Added	Recovered	% Recovery
19-Oct-99	Blank	0.98	1.0	101.9%
19-Oct-99	Duplicate	0.98	1.0	106.2%
24-Nov-99	Blank	5.44	5.2	95.6%
24-Nov-99	Duplicate	5.44	6.0	111.0%

Duplicate precision is evaluated using two different assumptions. The first is to assume 100% recovery, wherein the original spike level is retained and recovered from the sample. In this case, the Aroclor added is subtracted from the lab result to calculate the ambient concentration. The second assumes that the amount recovered is the same as the corresponding blank, and that quantity subtracted from the duplicate result for calculating the ambient concentration. The table below presents these results.

Table Q-5: Spike Duplicate Precision (ng/m^3)

Date	Primary	At Actual	Average	RDP (%)	At Blank	Average	RPD (%)
19-Oct-99	8.9	9.1	9.0	1.8%	9.0	9.0	1.2%
24-Nov-99	16.1	16.7	16.4	3.7%	17.0	16.5	5.1%

Meteorological Data

A meteorological station was established within the remediation area by the site contractors. This station included wind speed, wind direction, ambient temperature, relative humidity and rainfall. Although the original intention was to use the data obtained from this station to provide data for emission calculations and modeling attempts, there are several compelling reasons to disregard this data.

The sensors were located on top of a ten foot tower, instead of a ten meter tower which is the usual requirement for air monitoring meteorological data. The site was never subjected to an independent audit verifying the validity of readings. In addition, when the site was removed, there was apparently no final check of the orientation of the wind vane, which would clarify whether or not the sensor had moved during the course of the project.

None of these details would necessarily invalidate the data. However, comparison with the National Weather Service (NWS) data collected at Austin Straubel airport reveals systematic differences which appear to go beyond the differences that might be expected to exist between two different sites. While at first, the wind direction data are generally close, they suddenly become very consistently about 100^0 off. This indicates the possibility that the sensors were knocked out of place through some happenstance. As a result, meteorological data incorporated into this report are based on NWS data.