

SECTION 6 QUALITY ASSURANCE/QUALITY CONTROL

6.1 INTRODUCTION

This section describes the quality control evaluation conducted for the sediment, water, and resident fish data collected from the lower Grasse River in 2004 as part of routine monitoring and focused studies. Guidelines set forth in the Phase II Grasse River Sampling Work Plan (Alcoa, November 2003) and 2004 Monitoring Work Plan (Alcoa, April 2004a) were supplemented, where appropriate, with those contained in the Quality Assurance Project Plan (QAPP) developed for the Grasse River project (Blasland, Bouck & Lee, Inc. [BBL], September 1993). These guidelines were established to assess whether field, laboratory, and data management activities were performed in a manner that is appropriate for accomplishing the project objectives.

The procedures and metrics used in the QA/QC evaluation are presented in Section 6.2, while the results of the data evaluation are discussed in Section 6.3.

6.2 QA/QC PROCEDURES

The QA/QC procedures used to evaluate the data collected during 2004 consisted of several steps, including:

- review of the field chain-of-custody (COC) forms and data received from the laboratory for completeness;
- automation of data compilation, when possible, to minimize errors within the database; and
- review of the QA/QC data to assure that results of the quality control analyses are within the control limits developed for the project.

Upon receipt of the data, the field COC forms were reviewed and compared to the data received from the laboratory to ensure that sample identifications listed on the COC forms matched those reported in the data packages. This process was used to check that results were reported for all field and QA/QC samples (such as MS and MSD).

Following this review, the data were compiled and entered into an Excel database. Almost all data from the laboratory were received electronically and appended to the existing database using tools available in Excel. Some of the QA/QC data were entered by hand from electronic copies of laboratory data summary packages.

After the data were incorporated into the project database, several metrics (as outlined in the QAPP) were evaluated to determine the quality of the sediment, water column, and resident fish data. Data metrics used in this evaluation included:

- overall data completeness;
- method detection limits (MDL);
- number of QA/QC samples collected and analyzed;
- blank analysis;
- MS and MSD analyses; and
- field duplicate analysis.

Data were deemed acceptable if the following criteria were satisfied:

- Overall data completeness equaled or exceeded 90%. Overall data completeness was computed by dividing the number of valid data obtained by the total number of data planned for collection and analyses.
- MDLs from the QAPP for total PCBs quantified on an Aroclor basis in sediment, water, and biota samples were about 0.08 milligrams per kilogram (mg/kg), 65 ng/L, and 0.05 mg/kg, respectively. MDLs for total PCB congeners were not specified. The MDL for TSS in water was 1.0 mg/L. An MDL for the analysis of TOC in sediment via the

USEPA Lloyd Kahn method was not specified in the QAPP. The MDL reported by NEA for this method was approximately 81 mg/kg.

- For sediment samples, a minimum of one blind duplicate and one MS/MSD pair was collected for every 20 field samples. Rinse blanks were collected at least once per week when field crews were using non-disposable equipment.
- For the routine water column samples, a minimum of one equipment rinse blank was collected before and after sampling. In addition, at least one duplicate sample and one MS/MSD pair were collected each round.
- For resident fish samples, a minimum of one MS/MSD pair was to be prepared by the laboratory for every twenty submitted field samples.
- PCB levels in laboratory, equipment (rinse), and method blanks were near or below the detection limit.
- Percent recoveries for MS/MSD samples analyzed for total PCBs were between 70% and 130% (to evaluate accuracy).
- The relative percent difference between percent recoveries for MS and MSD samples analyzed for total PCBs were less than 35% (to evaluate precision).
- The relative percent difference between the field sample and its duplicate analyzed for TOC was less than 35%. Criteria for relative percent differences between field samples and their duplicates analyzed for total PCBs, grain size, or TSS were not prescribed in the QAPP.

Data that did not comply with the guidelines outlined above are documented in Section 6.3.

6.3 RESULTS OF QA/QC ANALYSES

This section presents the results of the QA/QC analyses performed on the 2004 data. Discussions of the sediment, water column, and resident fish data are provided below.

6.3.1 Sediment

The results of the QA/QC evaluation of the sediment data are provided below. Individual data that did not comply with the method guidelines and project requirements are listed in **Table 6-1**. Sediment results are separated by the following analysis types: PCBs, TOC, and grain size.

6.3.1.1 PCBs (Aroclor)

Completeness. Sediment samples collected during Focused Studies field activities were analyzed for PCBs on an Aroclor basis. Samples were collected at 100% of the 30 planned core locations.

Method detection limit. One hundred five sediment samples had PCB levels that were reported below the detection limit. Sixty-five of these samples were analyzed at a detection limit at or below 0.08 mg/kg. Detection limits⁵ for the 40 samples that did not conform to the prescribed detection limit were low, ranging between 0.0801 and 0.154 mg/kg, and, therefore, do not warrant exclusion from the database. It should be noted that samples were reported as non-detect by the laboratory if their concentrations were less than the practical quantitation limit (PQL).

Number of QA/QC samples. During the Focused Studies sampling activities, 21 field duplicates and 21 MS/MSD pairs were required for PCB analysis. The number of QA/QC samples collected, analyzed, and reported by the laboratory exceeded these requirements; 26 field duplicates, 26 MS, and 25 MSD were analyzed for PCBs. The MSD for location NST10-S was not reported due to insufficient material after re-extraction.

Blanks. All of the 35 sediment method blanks contained non-detectable levels of PCBs.

⁵ The reported sediment detection limits are adjusted from the base PQL (0.05 mg/kg) by the sample dry weight and final dilution factors. Several samples had high percent moisture values and were subsequently diluted to bring the PCB concentration within the calibration range of the instrument.

Matrix spike and matrix spike duplicates. Percent recoveries for four of the 25 MS and one of the 25 MSD samples were outside of the prescribed limits (see **Table 6-1**). Percent recoveries below the lower limit (i.e., 70%) ranged from 27% to 67%; the percent recovery above the upper limit (i.e., 130%) was 138%. Three pairs of MS/MSD samples had greater than 35% relative percent difference (see **Table 6-1**). The relative percent differences of these ranged from 63% to 118%.

MS and/or MSD samples whose percent recoveries were below 70% or above 130% and their parent sample are qualified as estimated (“J”) in the data table sediment_aro. Although the recoveries for the MS/MSD samples fall outside the requirement, results from their parent samples are still useable since other laboratory controls (such as surrogate spikes and laboratory control spikes) indicate that the inability to recover these matrix spikes accurately is likely associated with the sample matrix.

Field duplicates. The relative percent differences between the 26 field samples and corresponding duplicates ranged from 4% to 200%. A criterion for relative percent difference between samples and their duplicates analyzed for total PCBs was not prescribed for this project.

6.3.1.2 Total Organic Carbon

Completeness. In addition to analysis for total PCBs, sediment samples collected during the Focused Studies field activities were analyzed for TOC. No samples were lost during shipment or analysis. A total of 420 field samples were analyzed for TOC.

Method detection limit. All TOC samples were reported above the PQL. The MDL for TOC is 81 mg/kg for the USEPA Lloyd Kahn method.

Number of QA/QC samples. The collection and analysis of 26 field duplicates for TOC exceeded the requirement of 21 duplicates.

Blanks. This criterion is not applicable.

Matrix spike and matrix spike duplicates. This criterion is not applicable.

Field duplicates. Twenty of 26 field duplicates had relative percent differences within prescribed limits. The relative percent difference between the six field samples and corresponding duplicates not meeting this requirement ranged from 38% to 122% (see **Table 6-1**). Given the inherent variability (historic range of non-detect to over 300,000 mg/kg) in TOC levels in the Grasse River and the small amount (i.e., milligrams) of sediment used for TOC analysis, difficulty reproducing TOC results is expected and, thus, does not warrant exclusion of these data.

6.3.1.3 Grain Size

Completeness. During Focused Studies field activities, sediment samples were collected from 20 locations and analyzed for grain size. No samples were lost during shipment or analysis.

Method detection limit. This criterion is not applicable.

Number of QA/QC samples. Eight field duplicate samples were collected and analyzed for grain size, which met the requirement.

Blanks. This criterion is not applicable.

Matrix spike and matrix spike duplicates. This criterion is not applicable.

Field duplicates. A criterion for relative percent difference between grain size results for samples and their duplicates was not specified in the QAPP.

6.3.2 Water Column

QA/QC samples were inadvertently not collected during the monitoring of TSS during the spring high flow/ice breakup (one duplicate TSS sample per 20 field samples during a mobilization or a minimum of one per mobilization). This subsection reports the assessment of QA/QC data collected during the routine water monitoring program.

Completeness. Samples (one bottle for PCB analysis and one bottle for TSS analysis at each sampling transect) were collected as planned for all seven transects during the 15 rounds of routine monitoring in 2004.

Method detection limit. Since a MDL was not prescribed for PCB congeners, the MDL for Aroclors was used for comparison. The lower bound estimate of the nominal MDL for routine monitoring water samples was about 27.8 ng/L for total PCBs (Alcoa, April 2002), below the QAPP requirement of 65 ng/L.

The MDL for TSS met the requirement of 1.0 mg/L.

Number of QA/QC samples. The number of field duplicates met the requirement of one per round (15). The number of MS/MSD pairs met the requirement one per round with the exception of Round 1 when there was insufficient sample volume for MSD analysis. The number of rinse blanks met the requirement of 30. Additional QA/QC samples for PCBs included 15 laboratory blanks and 15 laboratory control spikes.

The requirement of one field duplicate per month for TSS analysis was fulfilled.

Blanks. All blank concentrations were near or below the nominal detection limit. Reported PCB levels in rinse blanks ranged from 0.0 to 11.1 ng/L, with one exception at 29.1 ng/L. Laboratory blank concentrations ranged from 0.0 to 3.1 ng/L, with one exception at 14.5 ng/L.

Matrix spike and matrix spike duplicates. One of the 14 MS/MSD pairs was not within the prescribed relative percent differences; it had a RPD of 44.1% (see **Table 6-1**). The percent recovery for the same MSD was not within the acceptable limits; it had 52% recovery (see Table 6-1).

Field duplicates. The relative percent difference between the fifteen pairs of samples and their duplicates analyzed for total PCBs and for TSS ranged from 3% to 182% and 0% to 71%, respectively (see **Table 6-1**). Criteria for the relative percent differences between samples and their duplicates analyzed for total PCBs and for TSS were not defined in the QAPP.

6.3.3 Resident Fish

Completeness. Due to the scarcity of target fish encountered during sample collection, fewer samples were collected than planned (141 of 156 or 90%). The following provides a summary of incomplete samples sets by species (see **Table 4-3** in Section 4 of the main report for more details):

- smallmouth bass: 73 of 73 (100%);
- brown bullhead: 59 of 59 (100%);
- adult spottail shiner: 0 of 12 (0%); and
- YOY spottail shiner: 9 of 12 (75%).

No samples were lost during shipment or analysis.

Method detection limit. The detection limits for total PCBs in field samples were about 0.05 mg/kg wet weight, as specified in the QAPP. It should be noted that samples were reported as non-detect by the laboratory if their concentrations were less than the PQL.

Number of QA/QC samples. Seven MS/MSD pairs were required; only five pairs were extracted, analyzed, and reported by the laboratory. In addition, nine method blanks and nine laboratory control spikes were included for analysis.

Blanks. All method blanks contained non-detectable PCB levels.

Matrix spike and matrix spike duplicates. All MS/MSD sample pairs had relative percent differences within prescribed limits. Two of the MS percent recoveries fell outside the prescribed limits at 136% and 138% (see **Table 6-1**).

Field duplicates. The collection of field duplicates was not performed as part of the resident fish sampling program.

6.4 SUMMARY

In general, the quality of the data for sediment, water column, and resident fish samples collected during 2004 met the guidelines established for the project. On the infrequent occasions when guidelines were not met, the affected samples are identified in the database as appropriate. As a result of the QA/QC evaluation, all data that were collected were deemed appropriate for use in performing qualitative and quantitative evaluations required to satisfy the project objectives.

GRASSE RIVER STUDY AREA
MASSENA, NEW YORK

Table 6-1
2004 Data from Routine Monitoring and Focused Studies
Individual Samples Not Meeting QA/QC Guidelines

Media	Analyte	Sample Date	Location	Field Sample	Field Duplicate	% Recovery		Relative % Difference		Reason for Non-Compliance
						MS	MSD	Field Duplicate	MS/MSD	
Sediment	PCB (Aroclor)	5/25/04	T71-NA (34-35cm)	29.10	14.70	---	---	65.75	---	Field duplicate falls outside %RPD limit
		5/26/04	T37-NA (9-10cm)	17.87	31.63	---	---	55.60	---	Field duplicate falls outside %RPD limit
		5/27/04	T37-NB (6-12in)	14.49	---	49.30	94.60	---	63.00	MS falls outside %R limit; MS/MSD fall outside %RPD limit
		5/27/04	T37-NB (60-67in)	79.00	123.50	---	---	43.95	---	Field duplicate falls outside %RPD limit
		9/13/04	NST10-N (0-1cm)	0.09	1.33	---	---	175.15	---	Field duplicate falls outside %RPD limit
		9/13/04	NST10-N (54-55cm)	-0.07 ⁹	385.00	66.80	78.80	200.07	16.50	Field duplicate falls outside %RPD limit; MS falls outside %R limit
		9/13/04	NST10-S (9-10cm)	0.09	---	117.00	N/A	---	N/A	No MSD reported by the lab due to insufficient material after re-extraction
		9/14/04	NST54-S (19-20cm)	-0.08 ⁹	---	35.60	138.00	---	118.00	MS and MSD fall outside %R limit; MS/MSD fall outside %RPD limit
		9/15/04	NST48-S (6-7cm)	0.70	0.49	---	---	35.37	---	Field duplicate falls outside %RPD limit
	9/15/04	NST26-S (14-15cm)	0.07	0.70	27.30	87.70	165.25	105.00	Field duplicate and MS/MSD fall outside %RPD limit;MS falls outside %R	
	TOC	9/13/04	NST10-N (0-1cm)	14000	3400	---	---	121.84	---	Field duplicate falls outside %RPD limit
		9/14/04	NST26-N (14-15cm)	6100	21000	---	---	109.96	---	Field duplicate falls outside %RPD limit
		9/14/04	NST54-N (6-7cm)	23000	14000	---	---	48.65	---	Field duplicate falls outside %RPD limit
		9/14/04	NST54-N (34-35cm)	3000	1600	---	---	60.87	---	Field duplicate falls outside %RPD limit
		9/15/04	NST48-N (9-10cm)	14000	8200	---	---	52.25	---	Field duplicate falls outside %RPD limit
9/15/04		NST26-S (14-15cm)	1700	2500	---	---	38.10	---	Field duplicate falls outside %RPD limit	
Water	PCB (Congener)	4/5/04	WC-007(0.2)	1.83	0.58	---	---	104.27	---	Field duplicate falls outside %RPD limit
		4/5/04	WC-T11(0.2)	---	---	94.4	N/A	---	N/A	No MSD reported by the lab
		4/21/04	WC-007(0.8)	2.57	5.68	---	---	75.56	---	Field duplicate falls outside %RPD limit
		5/5/04	WC-T11(0.2)	2.83	8.16	---	---	96.93	---	Field duplicate falls outside %RPD limit
		6/2/04	WC-T11(0.2)	6.05	8.76	---	---	36.56	---	Field duplicate falls outside %RPD limit
		6/17/04	WC-007(0.2)	21.54	5.27	---	---	121.41	---	Field duplicate falls outside %RPD limit
		6/28/04	WC-T11(0.2)	18.91	8.23	---	---	78.71	---	Field duplicate falls outside %RPD limit
		9/20/04	WC-007(0.2)	16.80	---	81.60	52.10	---	44.10	MSD falls outside %R limit, MS/MSD falls outside %RPD
		10/19/04	WC-T11(0.2)	3.16	66.33	---	---	181.79	---	Field duplicate falls outside %RPD limit
	TSS	4/5/04	WC-007(0.2)	3.20	1.80	---	---	56.00	---	Field duplicate falls outside %RPD limit
		9/20/04	WC-T11(0.2)	1.00	2.10	---	---	70.97	---	Field duplicate falls outside %RPD limit
Resident Fish	PCB (Aroclor)	9/1/04	Lower/ Sm Mouth Bass	0.79	---	136.00	127.00	---	5.40	MS falls outside %R limits
		9/2/04	Back/ Sm Mouth Bass	-0.05 ⁹	---	138.00	124.00	---	7.10	MS falls outside %R limits

Notes:

1. Units:

Sediment: PCB (mg/kg dry)

Water: PCB (ng/L)

Fish: PCB (mg/kg wet)

2. MS - matrix spike; MSD - matrix spike duplicate; %R - Percent Recovery; PCB - polychlorinated biphenyl, TOC - total organic carbon, cm - centimeters, in - inches, TSS - total suspended solids

3. Criteria listed in QAPP (BBL, September 1993): MS/MSD %R should be between 70 and 130%, %RPD should be less than 35%, Surrogate %R should be between 60 and 150%.

4. Bold and italicized numbers indicate where samples did not meet criteria.

5. %RPD of MS/MSD sample based on percent recoveries.

6. %RPD of field duplicate sample based on sample concentrations.

7. %RPD = |(A-B)| / ((A+B)/2) * 100

8. --- Not applicable; N/A not available.

9. Result is listed at negative of the detection limit; where applicable, the %RPD is computed using the detection limit.