

SECTION 4 QUALITY ASSURANCE/QUALITY CONTROL

4.1 INTRODUCTION

This appendix describes the quality control evaluation conducted for the water column and resident fish data collected from the lower Grasse River in 2005 as part of the SRS Program and Focused Study. Guidelines set forth in the *2005 Monitoring Work Plan* (Alcoa, March 2005) were supplemented, where appropriate, with those discussed 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 4.2, while the results of the data evaluation are discussed in Section 4.3.

4.2 QA/QC PROCEDURES

The QA/QC procedures used to evaluate the data collected during 2005 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. All data from the laboratory were received electronically and appended, when possible, to the existing database using tools available in Excel. During the rare occasions when tools could not be used (i.e. data arrived in portable document format [PDF]), data were manually inputted into the databases.

After the data were incorporated into the project database, several metrics (as outlined in the QAPP) were evaluated to determine the quality of the 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 water and biota samples were about 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.

- 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 month.
- For resident fish samples, a minimum of one MS/MSD pair was collected per twenty 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 MS and MSD samples analyzed for total PCBs were less than 35% (to evaluate precision).
- Criteria for relative percent differences between field samples and their duplicates analyzed for total PCBs or TSS were not prescribed in the QAPP.

Data that did not comply with the guidelines outlined above are documented in Section 4.3.

4.3 RESULTS OF QA/QC ANALYSES

This section presents the results of the QA/QC analyses performed on the 2005 data. A discussion of the water column and resident fish data is provided below.

4.3.1 Water Column

This subsection reports the assessment of QA/QC data collected during the routine water monitoring program and the monitoring of TSS during spring high flow/ice breakup.

Completeness. Samples (one bottle for PCB analysis and one bottle for TSS analysis at each sampling transect) were collected as planned⁶ for all seven transects during the 15 rounds of routine monitoring in 2005. However, one bottle (collected at 0.2 times the total water column depth at WCT11 on 7/27/05) intended for PCB analysis arrived broken at the lab. Instead, the bottle planned for TSS analysis from the same location was analyzed for total PCBs and therefore, no sample was available for TSS analysis.

As per the 2005 Monitoring Work Plan, TSS samples were collected as conditions allowed during the rising limb of the hydrograph during the spring high flow/ice breakup. TSS sampling during the falling limb of the hydrograph was not conducted as planned due to safety and logistical challenges.

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 measured as part of routine monitoring met the requirement of 1.0 mg/L. For the TSS measurements during spring high flow/ice breakup, the MDL of 1.43 mg/L exceeded the requirement; however, results for all field samples during this study were greater than 13 times the MDL.

Number of QA/QC samples. The number of field duplicates and MS/MSD samples met the requirement of 15 each. The number of rinse blanks collected met the requirement of 30, but only 29 were analyzed as one sample arrived broken at the lab. Additional QA/QC samples for PCBs included 15 laboratory blanks and 15 laboratory control spikes.

⁶ During Round 13 (9/21/05-9/22/05), the following PCB congener samples were found to be broken upon arrival at the laboratory: WC-MSB-13(0.5), WC131-13(0.8), and WC-05-13 (duplicate). The laboratory analyzed the TSS samples for PCB congeners, and the TSS samples from these locations were re-collected in the field on 9/22/05 and analyzed.

The requirement of one field duplicate per sampling round for TSS analysis was fulfilled for routine monitoring. For the TSS measurements during spring high flow/ice breakup, the requirement of one duplicate TSS sample per 20 field samples during a mobilization or a minimum of one per mobilization was met.

Blanks. All blank concentrations were near or below the nominal detection limit. Reported PCB levels in rinse blanks ranged from 0.0⁷ to 14.4 ng/L, with one exception of 23.7 ng/L. Laboratory blank concentrations ranged from 0.0 to 1.9 ng/L, with one exception of 13.1 ng/L.

Matrix spike and matrix spike duplicates. One of the 15 MS/MSD pairs was not within the prescribed range for MS percent recovery and relative percent difference; this sample had a MS percent recovery of 63.0% and RPD of 40.9% (see Table 4-1).

Field duplicates. For the routine monitoring, the relative percent difference between the fifteen pairs of samples and their duplicates analyzed for total PCBs and for TSS ranged from 2.3% to 200% and 3.8% to 81.5%, respectively. For the spring high flow/ice breakup TSS monitoring, the RPD between the four pairs of samples and their duplicates ranged from 8.0% to 13.3%. Criteria for the relative percent differences between samples and their duplicates analyzed for total PCBs and for TSS were not defined in the QAPP.

4.3.2 Resident Fish

This subsection reports the assessment of QA/QC data collected during the resident fish monitoring program. Since the ROPS was on-going during the time of fish collection, this assessment can also be found in the draft ROPS Documentation Report (Alcoa, May 2006).

⁷ The concentrations of all PCB congeners were reported as non-detect (less than the per congener MDL of 0.2 ng/L). The total PCB concentration reported by the laboratory is the sum of all congener concentrations above the MDL.

Completeness. All samples were collected as stated in the 2005 Work Plan (Alcoa, March 2005). A total of 144 samples were submitted to the laboratory for PCB and lipid analysis. No samples were lost during shipment or analysis.

Method detection limit. Five of the 144 samples submitted to the laboratory had PCB levels that were reported below the detection limit. All samples were analyzed at the 0.05 mg/kg wet weight MDL defined in the QAPP, with the exception of one sample that was analyzed at a detection limit of 0.18 mg/kg. 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. Eight MS/MSD pairs were extracted, analyzed, and reported by the laboratory, meeting the requirement of seven pairs. In addition, eleven method blanks and eleven 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. One MS sample had a percent recovery of 67%, falling outside the prescribed limits (see **Table 4-1**).

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

4.4 SUMMARY

In general, the quality of the data for water column and resident fish samples collected during 2005 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 4-1
Data from 2005 SRS Program
Individual Samples Not Meeting QA/QC Guidelines

Media	Analyte	Sample Date	Location (depth)	Result		% Recovery		Relative % Difference		Reason for Non-Compliance
				Field Sample	Field Duplicate	MS	MSD	Field Duplicate	MS/MSD	
Water	PCB (Congener)	6/16/05	WC-T11 (0.8)	1321.8	---	63.00	95.40	---	40.91	MS falls outside %R limit; MS/MSD falls outside %RPD
Resident Fish	PCB (Aroclor)	8/30/05	Upper/ Sm Mouth Bass	12.00	---	66.90	76.00	---	14.40	MS falls outside %R limits

Notes:

1. Units: PCB (water) = nanograms/liter; PCB (Fish) = micrograms/gram
2. QA/QC - Quality Assurance/Quality Control; MS - matrix spike; MSD - matrix spike duplicate; %R - Percent Recovery; PCB - polychlorinated biphenyl
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.