

## SECTION 6 QUALITY ASSURANCE/QUALITY CONTROL

### 6.1 INTRODUCTION

This appendix describes the quality control evaluation conducted for the water column, resident fish, sediment, and benthic invertebrate data collected from the lower Grasse River in 2006 as part of the SRS Program, Focused Studies, Post-ROPS Monitoring, and the 2006 Phase 1 Sediment Sampling Program. Guidelines set forth in the *Addendum Letter, Routine Monitoring Activities – 2006* (Alcoa, April 2006a), *2006 Post-ROPS Monitoring Work Plan* (Alcoa, July 2006), and the *2006 Sediment Sampling Program for the Lower Grasse River Work Plan* (Alcoa, April 2006b), 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 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 2006 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 input 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 sediment, water, and biota samples were about 0.080 micrograms per gram ( $\mu\text{g/g}$ ), 0.065 micrograms per liter ( $\mu\text{g/L}$ ), and 0.05 milligrams per kilogram ( $\text{mg/kg}$ ), respectively. MDLs for total PCB congeners were not specified. The MDL for TSS in water was 1.0  $\text{mg/L}$ . A MDL for the analysis of total organic carbon (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  $\text{mg/kg}$ .
- For sediment samples, a minimum of one blind duplicate and one MS/MSD pair was collected for every twenty field samples. No rinse blank samples were collected as field crews used 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 spring high flow/ice breakup TSS samples, a minimum of one duplicate sample was collected for every 20 samples during a mobilization, or a minimum of one duplicate per mobilization.
- 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 of sediment and water 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).
- 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.
- For benthic samples, extracted portions of sediment were re-examined until less than 5% of the originally extracted organisms were found. If the Percentage Similarity Index was

less than 95% between original and QA/QC identification and count, then organisms were re-identified and counted until the index showed greater than 95% similarity.

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 data collected in 2006. A discussion of the water column, resident fish, sediment, and benthic invertebrate data is provided below.

### **6.3.1 Water Column**

This subsection reports the assessment of QA/QC data collected during the 2006 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 planned for all seven transects during the 15 rounds of routine monitoring in 2006. However, four bottles (one collected on September 11, 2006 at WC007 and three collected on October 23, 2006 at WC131 and WC013) intended for PCB analysis arrived broken at the lab. Instead, the bottles planned for TSS analysis from the corresponding locations were analyzed for total PCBs and therefore, these four samples were not available for TSS analysis.

TSS sampling during spring high flow/ice breakup was not performed at the frequency outlined in the *Addendum Letter, Routine Monitoring Activities – 2006* (Alcoa, April 2006a), due to safety and logistical challenges. However, sampling was conducted up to three times per day, as conditions permitted, with emphasis on the time period when ice was clearing and moving through the lower river.

*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 met the requirement of 1.43 mg/L.

*Number of QA/QC samples.* The number of field duplicates collected during routine monitoring met the requirement of one per round (15). The number of MS/MSD pairs met the requirement of one per round with the exception of Round 2 when an MS was performed on two different samples and no MSD was performed. The number of rinse blanks collected 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 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 0.0<sup>6</sup> to 15.5 ng/L. All laboratory blank concentrations were below detection.

*Matrix spike and matrix spike duplicates.* All MS/MSD samples were within the prescribed range for MS/MSD percent recovery and relative percent difference.

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<sup>6</sup> 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.

*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 0.0% to 200% and 0.0% to 120.0%, respectively. For the spring high flow/ice breakup TSS monitoring, the RPD between the one sample and its duplicate was 33.3%. Criteria for the relative percent differences between samples and their duplicates analyzed for total PCBs and for TSS were not defined in the QAPP.

### **6.3.2 Resident Fish**

This subsection reports the assessment of QA/QC data collected during the resident fish monitoring program.

*Completeness.* All samples were collected as stated in the *Addendum Letter, Routine Monitoring Activities – 2006* (Alcoa, April 2006a). 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.* Twelve 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. 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, 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.

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

### 6.3.3 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.

#### 6.3.3.1 PCBs (*Aroclor*)

*Completeness.* Sediment samples collected during the post-ROPS and 2006 Phase 1 field activities were analyzed for PCBs on an Aroclor basis. All post-ROPS monitoring samples were collected as stated in the *2006 Post-ROPS Monitoring Work Plan* (Alcoa, July 2006). Cores intended for PCB and TOC analysis were collected from all 28 targeted locations, and a total of 238 samples were submitted to the laboratory. No samples were lost during shipment or analysis. In addition, 36 cores were collected, as planned, for visual observation of the cap material.

The 2006 Phase 1 sediment sampling was conducted as stated in the *2006 Sediment Sampling Program for the Lower Grasse River Work Plan* (Alcoa, April 2006b). The field crew attempted to collect cores from 61 locations (45 main channel; 16 side slope), but were unable to retrieve sediment from 19 main channel locations (4 located in fine sediment; 15 located in coarse sediment). Cores were collected from all targeted side slope locations. Overall, only 69% of targeted cores were retrieved. A total of 206 samples were submitted to the laboratory for PCB and TOC analysis. No samples were lost during shipment or analysis.

*Method detection limit.* Sixty-four of the post-ROPS sediment samples had PCB levels that were reported below the detection limit. All of these samples were analyzed at a detection

limit at or below 0.080 µg/g. It should be noted that samples were reported as non-detect by the laboratory if their concentrations were less than the PQL.

Twenty-seven of the Phase 1 sediment samples had PCB levels that were reported below the detection limit. All but five of these samples were analyzed at a detection limit at or below 0.080 µg/g. Detection limits for the five samples that did not conform to the prescribed detection limit were close to the detection limit, ranging between 0.0807 and 0.0960 µg/g, and, therefore, do not warrant exclusion from the database.

*Number of QA/QC samples.* The number of QA/QC samples collected, analyzed, and reported by the laboratory during post-ROPS sampling activities exceeded the requirement of 12. A total of 13 field duplicates and MS/MSD pairs were analyzed for PCBs.

During Phase 1 sampling activities, 11 field duplicates and MS/MSD pairs were analyzed for PCBs, exceeding the requirement of 10.

*Blanks.* All of the 31 sediment method blanks (16 post-ROPS and 15 Phase 1) contained non-detectable levels of PCBs.

*Matrix spike and matrix spike duplicates.* Of the 13 MS/MSD pairs collected as part of post-ROPS activities, one pair fell outside the prescribed limits for relative percent difference (40.4%). A separate pair had a MSD percent recovery of 161.0%, falling outside the prescribed range of 70 to 130%. See **Table 6-1** for a listing of these samples. Associated field samples have been qualified as estimated (“J”) in the data table sed\_aro\_ROPS found on the CD-ROM in **Appendix A**.

All of the 11 Phase 1 MS/MSD pairs had percent recoveries and relative percent differences within prescribed limits.

*Field duplicates.* The relative percent difference between the 13 post-ROPS and 11 Phase 1 pairs of samples and their duplicates ranged from 4 to 136%. Criteria for the relative



percent differences between samples and their duplicates analyzed for total PCBs were not defined in the QAPP.

### **6.3.3.2 Total Organic Carbon**

*Completeness.* In addition to being analyzed for total PCBs, sediment samples collected during post-ROPS monitoring and Phase 1 sampling were analyzed for TOC. No samples were lost during shipment or analysis. A total of 238 post-ROPS and 206 Phase 1 field samples were analyzed for TOC.

*Method detection limit.* Three of the 238 post-ROPS TOC samples were reported below the detection limit. It should be noted that samples were reported as non-detect by the laboratory if their concentrations were less than the PQL. Detection limits for these samples were greater than the laboratory-specified MDL of 81 mg/kg for the analytical method, ranging between 640 and 1,000 mg/kg. Since a MDL requirement is not specified in the QAPP, no data are excluded from the database.

None of the 206 Phase 1 TOC samples were reported below the detection limit.

*Number of QA/QC samples.* The collection and analysis of field duplicates for TOC during post-ROPS sampling exceeded the requirement of 12, with 13 duplicates analyzed.

During Phase 1 sampling, 11 field duplicates were collected and analyzed for TOC, exceeding the requirement of 10 duplicates.

*Blanks.* This criterion is not applicable.

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

*Field duplicates.* Of the 13 pairs of TOC samples and their duplicates collected as part of post-ROPS activities, three pairs had relative percent differences greater than 35% (**Table 6-1**). The relative percent differences of these pairs ranged from 37% to 60%.

Five of the 11 pairs of Phase 1 sediment TOC samples and their duplicates fell outside the prescribed limits for relative percent difference (**Table 6-1**). The relative percent differences of these pairs ranged from 36% to 165%.

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.

### **6.3.3.3 Grain Size**

*Completeness.* In addition to analysis for total PCBs, sediment samples from post-ROPS and Phase 1 sampling were collected and analyzed for grain size. No samples were lost during shipment, but three Phase 1 samples were lost during lab processing. In addition, seven post-ROPS and five Phase 1 samples could not be analyzed due to organic material. A total of 232 post-ROPS and 198 Phase 1 field samples were analyzed for grain size.

*Method detection limit.* This criterion is not applicable.

*Number of QA/QC samples.* The collection and analysis of field duplicates for TOC during post-ROPS sampling exceeded the requirement of 12, with 13 duplicates analyzed.

During Phase 1 sampling, 11 field duplicates were collected and analyzed for TOC, exceeding the requirement of 10 duplicates.

*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.

#### **6.3.4 Invertebrate Community**

QA/QC analyses were performed by GEI Consultants Inc./Chadwick Ecological Division (Chadwick) on 10% of the benthic samples that were collected as part of this monitoring event. The QA/QC analysis included sample analysis for correctness in organism identification.

To check for thoroughness in extraction, the extracted portions of sediment in each QA/QC sample were re-examined by another biologist to determine if any organisms remained. If more than 5% of the total originally extracted organisms were found, extraction continued and the sample was rechecked until less than 5% of the originally extracted organisms were found.

To check for accuracy in taxa identification, another biologist re-identified and re-counted the organisms found in each QA/QC sample. If the Percentage Similarity Index (Whittaker, 1975) was less than 95% between the original and subsequent QA/QC re-count and identification, the organisms were re-identified and counted again until greater than 95% similarity occurred.

As part of the QA/QC process associated with determination of biomass (wet-weight in milligrams), the electronic balance used to weigh benthic organisms was calibrated prior to use. In addition, the organisms were blotted with a lint-free cloth prior to weighing to remove any excess liquids (i.e., preservatives). All QA/QC results were recorded on laboratory bench sheets.

All reported results of the benthic invertebrate analyses meet the QA/QC requirements.

## 6.4 SUMMARY

In general, the quality of the data for water column, resident fish, sediment, and benthic invertebrate samples collected during 2006 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.

**Table 6-1**  
**2006 Monitoring Data**  
**Individual Samples Not Meeting QA/QC Guidelines**

**2006 Data Summary Report**  
**Grasse River Study Area, Massena, New York**

Sampling Program	Media	Analyte	Sample Date	Location (depth)	Field Sample	Field Duplicate	% Recovery		Relative % Difference		Reason for Non-Compliance
							MS	MSD	Field Duplicate	MS/MSD	
Post-ROPS	Sediment	PCB (Aroclor)	8/1/06	339 (20-23in)	---	---	118.0	<b><i>161.0</i></b>	---	30.8	MSD falls outside %R limit MS/MSD falls outside RPD
			8/2/06	714 (11-14in)	---	---	77.7	117.0	---	<b><i>40.4</i></b>	
	Sediment	TOC	7/25/06	39 (0-2in)	5500	8000	---	---	<b><i>37.0</i></b>	---	Field duplicate falls outside %RPD limit
Phase 1	Sediment	TOC	8/2/06	639 (21.5-24.5in)	7500	12000	---	---	<b><i>46.2</i></b>	---	Field duplicate falls outside %RPD limit
			8/3/06	265 (16-19in)	8500	4600	---	---	<b><i>59.5</i></b>	---	Field duplicate falls outside %RPD limit
			5/9/06	T8-MCM (6-12in)	2500	3700	---	---	<b><i>38.7</i></b>	---	Field duplicate falls outside %RPD limit
			5/9/06	T8.5-MCN (6-12in)	4000	16000	---	---	<b><i>120.0</i></b>	---	Field duplicate falls outside %RPD limit
			5/10/06	T9-MCN (6-12in)	32000	3100	---	---	<b><i>164.7</i></b>	---	Field duplicate falls outside %RPD limit
			5/10/06	T10-SSS (6-12in)	6300	4400	---	---	<b><i>35.5</i></b>	---	Field duplicate falls outside %RPD limit
			5/11/06	T9-SSS (3-9in)	6600	3400	---	---	<b><i>64.0</i></b>	---	Field duplicate falls outside %RPD limit

Notes:

- Units: PCB = micrograms/gram, TOC = milligrams/kilogram, in = inches
- Criteria listed in QAPP (BBL, September 1993): MS/MSD %R should be between 70 and 130%, RPD should be less than 35%.
- Bold and italicized numbers indicate where samples did not meet criteria.
- RPD of MS/MSD sample based on percent recoveries.
- RPD of field duplicate sample based on sample concentrations.
- $RPD = \frac{|(A-B)|}{((A+B)/2)} * 100$
- Not applicable; N/A not available.

MS = matrix spike

MSD = matrix spike duplicate

%R = Percent Recovery

RPD = Relative Percent Difference

PCB = polychlorinated biphenyl

TOC = total organic carbon