

SECTION 4

QUALITY ASSURANCE/QUALITY CONTROL

4.1 INTRODUCTION

This section describes the quality control evaluation conducted for data collected as part of the 2002 SRS Program. Guidelines set forth in the 2002 SRS Monitoring Work Plan (Alcoa, April 2002a) were supplemented, where appropriate, with those discussed in the Quality Assurance Project Plan (QAPP) developed for the project (BBL, February 1993). Both sets of 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 data collected during the 2002 SRS program 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 were 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 NEA 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 to the existing database using tools available in Excel. The majority of the QA/QC data and field data were entered by hand.

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 that were used in this evaluation included:

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

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 analysis.
- Method detection limits for total PCBs (Aroclor) in water and biota were about 65 ng/L and 0.05 mg/kg, respectively.
- For the routine water column samples, a minimum of two equipment rinse blanks were collected; one before and one after river sampling was completed. In addition, at least one duplicate sample and one MS/MSD pair per month were collected.

- For SPMD samples, a minimum of one trip blank and one duplicate per round (i.e., once per month) were collected.
- For resident fish samples, a minimum of one MS/MSD pair per 20 samples was collected.
- PCB levels in trip, dialysis, laboratory or equipment (rinse), and method blanks were near or below the detection limit.
- Percent recoveries for MS and MSD samples were between 70 and 130% (to evaluate accuracy).
- The relative percent difference between MS and MSD samples was less than 35% (to evaluate precision).
- The relative percent difference between the field sample and its duplicate was less than 35%.

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 2002 SRS Program data. A discussion of the water column and resident fish data is provided below.

4.3.1 Water Column

The water column program included the routine monitoring and SPMD sampling.

Routine Monitoring Program

Completeness. All 122 non-QA/QC samples were collected and analyzed as planned.

Method detection limit. The lower bound estimate of the nominal method detection limit for routine monitoring water samples was about 27.8 ng/L for total PCBs (Alcoa, April 2002b), below the QAPP requirement of 65 ng/L.

Number of QA/QC samples. During the six-month sampling period, a total of 166 samples (including QA/QC samples) were collected for PCB analysis. The number of field duplicates and MS/MSD samples fulfilled the requirement of 6 each; the number of rinse blanks met the requirement of 26. Additional QA/QC samples included 13 laboratory blanks.

A total of 128 TSS samples (including 6 field duplicates) were collected and submitted to the laboratory. The requirement of one field duplicate per month was fulfilled.

Blanks. All blank concentrations were below the nominal detection limit. Except for those collected during Rounds 5, 6, and 13, reported PCB levels in rinse blanks ranged from 0.0 to 3.1 ng/L. For Round 5, there may have been laboratory contamination (rinse blank concentrations were 8.5 and 9.7 ng/L and the laboratory blank concentration was 10.3 ng/L). Higher PCB levels were found in rinse blanks than laboratory blanks for the other two rounds: Round 6 (rinse blanks were reported at 0.3 and 8.1 ng/L; the laboratory blank was 0.0 ng/L) and Round 13 (rinse blanks were reported at 5.2 and 0.4 ng/L; the laboratory blank was reported at 0.3 ng/L). Other laboratory blank concentrations ranged from 0.0 to 1.0 ng/L.

Matrix and matrix spike duplicate. All MS/MSD pairs were within acceptable percent recoveries and relative percent differences.

Field duplicates. Four of the six (67%) PCB sample and duplicate pairs had relative percent differences less than 35% (**Table 4-1**). The two samples outside acceptable limits were collected at WC011 and WC007 (both at 0.8 times the total water column depth); these samples had relative percent differences of 63.4% and 65.3%, respectively. None of the 6 TSS sample and duplicate pairs had relative percent differences greater than 35%.

Semi-Permeable Membrane Device

Completeness. All but one (98%) non-QA/QC SPMD samples were submitted for analysis. The sample not submitted (WC012 at 0.2 times the total water column depth) was found destroyed/damaged in the field on July 17 (Set 3).

Method detection limit. No method detection limit for total PCBs in SPMDs was set in the QAPP.

Number of QA/QC samples. The 2002 SRS Work Plan called for one trip blank and one duplicate per event. The number of field duplicates and trip blanks fulfilled the requirement of 6 each. In addition, 6 laboratory blanks and 6 dialysis blanks were analyzed.

Blanks. All blank concentrations measured during each of the sampling events were low, ranging from 0.000 to 0.013 $\mu\text{g}/\text{SPMD}$. Laboratory rinse blanks ranged from 0.000 to 0.002 $\mu\text{g}/\text{SPMD}$. Trip blanks ranged from 0.001 to 0.013 $\mu\text{g}/\text{SPMD}$. Dialysis blanks ranged from 0.002 to 0.012 $\mu\text{g}/\text{SPMD}$. All were below the lowest detectable field concentration of 0.085 $\mu\text{g}/\text{SPMD}$.

Matrix and matrix spike duplicate. MS/MSD collection was not performed as part of the SPMD sampling program.

Field duplicates. Relative percent differences were within acceptable limits for all PCB sample and duplicate pairs.

4.3.2 Resident Fish

Completeness. Due to the scarcity of target fish encountered during sample collection, fewer samples were collected than planned (151 of 191). The following provides a summary of incomplete samples sets by species (see **Table 3-1** for more details):

- smallmouth bass: 68 of 90 (76%);
- brown bullhead: 71 of 77 (92%); and
- adult spottail shiner: 0 of 12 (0%)

No samples were lost during shipment or analysis.

Method detection limit. The method detection limits for total PCBs in field samples were about 0.05 mg/kg wet weight, as specified in the QAPP.

Number of QA/QC samples. The number of MS/MSD samples met the requirement outlined in the QAPP. In addition, 11 method blanks were included for analysis.

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

Matrix and matrix spike duplicate. All MS/MSD sample pairs had percent recoveries and relative percent differences within acceptable limits.

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 the 2002 SRS Program met or exceeded the guidelines established for the project. On the infrequent occasions when guidelines were not met, none of the affected samples warranted exclusion from the database. 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
2002 Supplemental Remedial Studies Program - Summary Report
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	
Water	PCB	5/7/02	WC-011(0.8)	16.2	31.2	100.0	101.0	63.4	1.0	Field duplicate falls outside %RPD limit
Routine Monitoring		7/2/02 ¹⁰	WC-007(0.8)	20.1	10.2	89.4	93.8	65.3	4.8	Field duplicate falls outside %RPD limit

Notes:

1. PCBs quantified on a congener basis.
2. Units: water (ng/L), SPMD (ng/SPMD)
3. MS - matrix spike; MSD - matrix spike duplicate; %R - Percent Recovery.
4. Criteria listed in QAPP (BBL, February 1993): MS/MSD %R should be between 70 and 130%, %RPD should be less than 35%. Surrogate %R should be between 60 and 150%.
5. Bold and italicized numbers indicate where samples did not meet the criteria.
6. %RPD of MS/MSD sample based on percent recoveries.
7. %RPD of field duplicate sample based on sample concentrations.
8. $\%RPD = |(A-B)| / ((A+B)/2) * 100$
9. --- Not applicable.
10. Laboratory contamination may have occurred during Round 5, as a PCB concentration of 10.3 ng/L was reported for the laboratory blank (rinse blanks had concentrations of 8.5 and 9.7 ng/L).