APPENDIX 2: Quality Assurance Summary for Year 2 of the Coast Survey

The data generated for this section summarize the quality of chemical analyses for the second year of the Coast Survey. Thorough objectives that meet or exceed those in the Surface Water Ambient Monitoring Program (SWAMP) Quality Assurance Program Plan (QAPrP) are outlined in the Screening Study of Bioaccumulation on the California Coast Quality Assurance Project Plan (Coastal QAPP). In general, data quality is demonstrated through analysis of the following quality control (QC) samples:

- Laboratory method blanks;
- Surrogate spikes;
- Matrix spikes (MSs) and matrix spike duplicates (MSDs);
- Certified reference materials (CRMs)/laboratory control spikes (LCSs);
- Laboratory duplicates (DUP); and
- Composite blind duplicates.

The results of the QC samples are used to assess the level of precision and accuracy that can be associated with the data. This information helps guide the data validation process that is used to determine whether or not the data helps to address the questions put forth by the project. In addition, the QC information collected by the project helps pinpoint the specific areas of the overall process where problems may arise so that corrective actions can be implemented. Quality control samples prepared and analyzed by the laboratory provide information specific to the preparation and analysis of the samples.

Were the samples prepared and analyzed in a manner free from significant contamination?

The results of laboratory method blanks provide information on this.

How accurate and precise are the results of the samples?

This question is answered by assessment of a combination of QC sample results. Reference materials and laboratory control spikes provide information regarding the accuracy of the analytical protocols. The results of laboratory duplicates provide information regarding the homogeneity of the samples and consistency of laboratory analytical procedures. The results of matrix spikes provide information on the analytical bias associated with the sample matrix. Only by considering all of the pieces of QC information available as a whole can a determination of the precision and accuracy of the data (or in other words to answer the question "how good are the data?") be made.

Following submittal from the laboratory, data are validated against the data quality requirements in the Coastal QAPP to determine whether or not the data are suitable for their intended use. Quality control samples are analyzed with a discrete batch of samples, with the results of the associated QC samples applied to each sample in the batch. Sample batches where the associated QC samples met criteria and laboratory performance indicators were within control limits are considered suitable for their intended use without further assessment.

Data associated with QC results outside of acceptance limits are not automatically considered unsuitable for use. However, the type and scope of the QC problems must be assessed during data validation. In most instances the data are found to be suitable for its intended use even when accounting for the QC failures. Data associated with significant QC failures, or which meet the rejection criteria specified in the Coastal QAPP are unusable for the purposes of this project.

Data validation results are summarized for each QC sample type.

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Data for the Coast Survey Year 2 have been validated and compared against project-specific data quality objectives (DQOs). The counts in the following sections represent metal, Mercury, Organochlorine pesticide, and Polychlorinated Biphenyl as Congener (PCB) results from Coastal Year 2. The validation included verification of data according to SWAMP Standard Operating Procedures (SOPs) for chemistry data verification. Data were determined to be compliant with the individual measurement quality objectives (MQOs) specified in Tables 12a and 12b in the Coastal QAPP. Data were classified into one of the following classification levels:

Compliant

Data classified as "compliant" meet or exceed all of the MQOs and other data quality requirements specified in the Coastal QAPP. These data are considered usable for their intended purpose without additional scrutiny.

Qualified

Data classified as "qualified" do not meet one or more of the MQOs and other data quality requirements specified in the Coastal QAPP. These data are considered usable for its intended purpose following an additional assessment to determine the scope and impact of the quality control failure.

Estimated

Data classified as "estimated" are assigned to data batches and sample results that are not considered to be quantifiable. Included in this classification are results qualified with one of the following flags:

J–Estimated value (EPA Flag)

Rejected

Data classified as "rejected" do not meet the minimum data quality requirements specified in the Coastal QAPP. These data are not considered usable for its intended purpose.

Not applicable

Data classified as "not applicable" refers to data that were not validated since there were no project MQOs or QC requirements for the specific parameter, (i.e., Age) or a failure result was reported and could not be validated.

Quality Assurance Parameter Performance Assessment

Coastal Study criteria for percent recovery (%R) of surrogates, matrix spikes, Certified Reference Materials, laboratory control samples and relative percent difference (RPD) for field and laboratory duplicates for tissues are presented in Appendix 2, Table 1.

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Laboratory Method Blanks

Laboratory method blanks are used to evaluate laboratory contamination during sample preparation and analysis. Blank samples undergo the same analytical procedure as samples with at least one blank analyzed per 20 samples. The required frequency was met for all 69 batches.

Data that met the MQO for method blanks are those with values less than the method limit (ML) for that particular analyte within each analytical batch. All 155 laboratory method blanks met the MQO, with the exception of one method blank in batch WPCL_L-040-11_BS626_T_OCH. Dieldrin was detected above the ML in the method blank and was classified as "qualified".

Target analyte concentrations detected above the method detection limit (MDL) in the field samples were compared to the associated method blank concentrations. Results for target analyte concentrations in batches with blank contamination that were less than 3X the blank contamination were classified as "rejected". There were 113 rejections in the dataset. Twelve results were classified as "qualified" based on the blank contamination validation QC criteria.

Surrogate Spikes

Surrogate spikes are used to assess analyte losses during sample extraction and clean-up procedures, and must be added to every composite and quality control sample prior to extraction. Whenever possible, isotopically-labeled analogs of the analytes should be used.

All surrogate percent recoveries were within the acceptance criteria listed in Appendix 2, Table 1, with the exception of one out of 605 (0.2%) surrogate percent recoveries spiked in 406 field and laboratory QA/QC samples analyzed for Polychlorinated Biphenyls and Organochlorine Pesticides (Appendix 2, Table 2). The associated analytes in matrix spike CRM L-734-10_BS 621_SRM 1946 were classified as "qualified" with regard to the MQO for surrogates. No data were rejected.

Matrix Spikes and Matrix Spike Duplicates

A laboratory-fortified sample matrix (matrix spike, or MS) and a laboratory fortified sample matrix duplicate (MSD) are both used to evaluate the effect of the sample matrix on the recovery of the target analyte(s). Individually, these samples are used to assess the bias from an environmental sample matrix plus normal method performance. In addition, these duplicate samples can be used collectively to assess analytical precision.

Aliquots of randomly selected field samples were spiked with known amounts of target analytes. The percent recovery (%R) of each spike was calculated as follows:

$$\%R = (\text{MS Result} - \text{Sample Result}) / (\text{Expected Value} - \text{Sample Result}) * 100$$

The %R acceptance criteria vary according to analyte groups (Appendix 2, Table1).

This process was repeated on the same native samples to create a laboratory fortified sample matrix spike duplicate (MSD). MSDs were used to assess laboratory precision and accuracy. MS/MSD RPDs were calculated as follows:

RPD = (|(Value1-Value2)|/(AVERAGE(Value1+Value2)))*100

where:
Value1=matrix spike value
Value2=matrix spike duplicate value.

According to the Coastal QAPP for metal and organic analyses, at least one MS/MSD pair should be performed per 20 samples or one per batch, whichever is more frequent. The required frequency was met for all 69 batches.

Laboratory batches with MS/MSD %R and RPD values outside of acceptance criteria were either classified as "compliant" or "qualified" based on the number of QC elements outside the acceptance criteria. No data were rejected. In several OCH and PCB batches, MS/MSD %Rs and RPDs were not reported since the native concentrations were greater than 2X the spiked concentration and the lab was unable to calculate these values. Since the non-reported results were not validated, they were classifed as "not applicable. Values outside the acceptance criteria are presented in Appendix 2, Table 3. All other MS/MSD %Rs and RPDs were within acceptance criteria.

Certified Reference Materials and Laboratory Control Samples

A CRM or LCS is analyzed to assess the accuracy of a given analytical method. As required by the Coastal QAPP, one CRM or LCS should be analyzed per 20 samples or per batch, whichever is more frequent. The required frequency was met for all 69 batches.

Laboratory batches with CRM or LCS %R values outside of acceptance criteria were classified as "compliant" based on the number of QC elements outside criteria. No data were rejected. These are presented in Appendix 2, Table 4. All other CRM and LCS %Rs were within acceptance criteria.

Laboratory Duplicates

A laboratory duplicate (DUP) is analyzed to assess laboratory precision. As required by the Coastal QAPP, a duplicate of at least one field sample per batch was processed and analyzed. The required frequency was met for all 69 batches.

The duplicate results reported above the method limit (ML) were compared and an RPD was calculated as described in the MS/MSD Section. Results reported below the ML or as "non-detect" in either the parent sample or duplicate were not evaluated as stated in the Coastal QAPP. Any RPDs <25% were considered acceptable and classified as compliant as specified in the QAPP. Those >25% but <50% were classified as qualified. Finally, RPDs >50% were classified as rejected. No data were rejected.

Composite Blind Duplicates

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Composite blind duplicates are analyzed to assess composite homogeneity and laboratory precision. Although the Coastal QAPP does not address these samples or provide evaluation criteria, they were performed. Composite blind duplicates were obtained from homogenized tissue samples.

Holding Times

Eight percent of the results (1,524 out of 18,857 total results) in 699 tissue composites were classified as "qualified" due to holding time exceedances. Of the 1,524 results, 366 results were from 3 composites and 5 individuals that were archived beyond the 1 year holding time. The analysis of these composites was approved by the project lead. Three tissue samples analyzed for organochlorine pesticides and PCBs did not meet either the 12 month holding time criteria between collection and extraction and 18 tissue samples did not meet the 40 day holding time criteria from extraction to analysis. Fourteen tissue samples analyzed for metals and mercury exceeded the 12 month holding time criteria between collection and analysis.

QA/QC Summary

Were the samples prepared and analyzed in a manner free from significant contamination?

Review of lab blanks show that 0.6 % (113 out of 18,857) of the results are unusable because levels are <3X the concentration detected in the method blank. The remaining 18,744 (99.4%) results are unaffected. Overall, the samples were prepared and analyzed in a manner free from significant contamination.

How accurate and precise are the results of the samples?

Review of spiked QC samples show that all results are usable although there were percent recovery exceedances. Review of duplicate QC samples show that none of the 18,857 results were unusable due to percent difference exceedances. Overall, 100% of the data generated by laboratories met the accuracy and precision objectives.

There were 18,857 sample results for individual constituents including tissue composites and laboratory QA/QC samples. Of these:

- 16,772 (89%) were classified as "compliant"
- 1971 (10%) were classified as "qualified"
- 113 (0.6%) were classified as "rejected"; and
- 1 (0.005%) was classified as "NA", since the results were not reported due insufficient sample volume.

Classification of this dataset is summarized as follows:

- 113 results were classified as "rejected" and 12 results were classified as "qualified" due to blank contamination values.
- 1 result was classified as "qualified" due to surrogate recovery exceedances presented in Table 2.
- 73 results were classified as "qualified" due to recovery exceedances presented in Tables 3 and 4.
- 73 results were classified as "qualified" due to the RPD exceedances presented in Tables 3.
- 1,524 results were classified as "qualified" due to holding time exceedances.

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Data that meet all MQOs as specified in the QAPP are classified as "compliant" and considered usable without further evaluation. Data that fail to meet all program MQOs specified in the Coastal QAPP were classified as qualified but considered usable for the intended purpose. Data that are >2X MQO requirements or the result of blank contamination were classified as "rejected" and considered unusable. Data batches where results were not reported and therefore not validated were classified as not applicable.

All data with the exception of the 113 rejected results were considered usable for the intended purpose. A 99% completeness level was attained which met the 90% project completeness goal specified in the Coastal QAPP.