Quality Assurance/Quality Control Report
For Trace Metals

Coastal Fish Contaminant Project Year 1, 1998-1999

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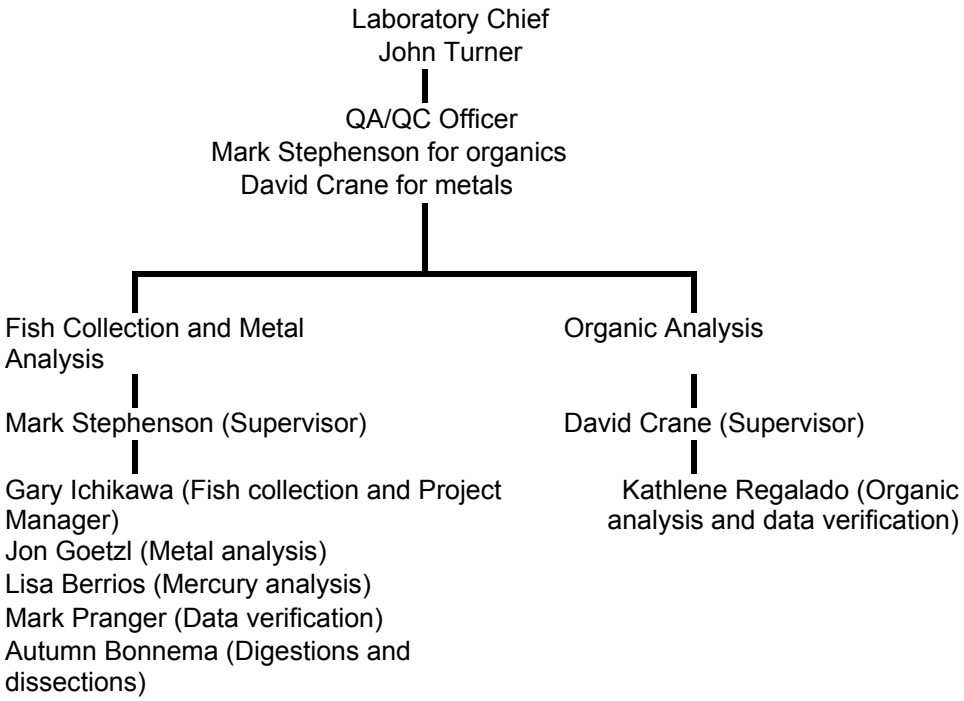
Introduction

In July 1998, the State Water Resources Control Board (SWRCB) initiated the Coastal Fish Contamination Project. By February 1999, the planning phase was completed and the Department of Fish and Game (DFG) initiated the field work. The purpose of the program was twofold: 1. Determine if sport-caught fish contained concentrations of pollutants that were too high for human consumption based on the Office of Environmental Health Hazard Assessment (OEHHA) criteria and, if so, OEHHA would issue health advisories, and 2. Determine if the concentration of pollutants in sport-caught fish was increasing or decreasing. This report contains the QA/QC evaluation of the trace metal data from the first year of the program. The station information and analysis results are listed in Appendix A by order of the region.

Laboratory Organization

The Department of Fish and Game was contracted to conduct the study for the State Water Resources Control Board and coastal Regional Water Quality Control Boards. This involved catching the fish and analyzing the samples for pollutants. The organizational chart is as follows:



Description of Methods:

The Field Sampling Methods Standard Operating Procedures (SOPs) and the Analytical Methods SOPs are contained in the Department of Fish and Game Quality Assurance Plan for the Marine Pollution Studies Laboratories (Moss Landing, CA) and the Water Pollution Control Laboratory (Nimbus, CA), which are available by request from David Crane or Mark Stephenson.

Standard collection and laboratory procedures were followed in preparing samples. Fish collected, to large to fit in our clean bags (>500 mm) were initially dissected in the field. A large cross section from behind the pectoral fins to the gut was saved. For bat rays, a section of the wing was cut and saved. These sections were wrapped in Teflon ®, double bagged and packed in dry ice before transfer to the freezer. During lab dissection, a subsection of the filet was removed, discarding any tissue exposed by field dissection.

Sampling SOPs call for the smallest fish in a sample to be no less then 75% of the largest fish. Eight samples analyzed were outside this range, indicated by a Y in the >25% column in Appendix A. Five of these samples were within 70% of the largest fish size. Weights and lengths for individual fish and crabs are given in Appendix A. For bivalves, fifteen were chosen at random from each sample for length measurements. Total weights are for all the bivalves in a sample were reported (n= 20-45), Appendix A. Samples were analyzed for arsenic, cadmium, mercury and selenium. Some samples from Region 2 were also analyzed for copper, chromium, lead, nickel, silver and zinc or for just arsenic and mercury by request of the San Francisco Bay Regional Board.

QAPP and Control Limits

A Quality Assurance Project Plan (QAPP) has not yet been written for this program. In lieu of this document, the QA/QC parameters for collection and analysis are contained in the Department of Fish and Game Quality Assurance Plan for each lab as described in the preceding paragraph. In addition, guidelines that are specific to fish contamination studies have been modified from the EPA document entitled "Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 1. Fish Sampling and Analysis. Second edition. 1995." The control limits adapted from this document are found in Table 1. These limits have been agreed to by DFG, OEHHA, and SWRCB, and are the interim parameters until a QAPP can be written.

Table 1—QA Control Limits for Coastal Fish Contaminant Year 1

Sample Type (definition)	Frequency of Analysis	Recommended Control Limits	Recommended Corrective Action
External Calibration Calibration Standards (3-5 standards over the expected range of sample target analyte conc., with the lowest conc. Std at or near the MDL)	Follow manufacturer's or procedures in specific analytical protocols. A min., 3 point calib. Each set up, major disruption, and when routine calib check exceeds specific control limits	Linear regression, r>0.995	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Continuing Calibration Verification (CCV) Calibration Check Standards (minimum of one mid-range standard prepared independently from initial calibration standards: an instrument internal standard must be added to each calib. check std. when internal std. calib. is being used)	After initial calibration (ICV) or recalibration. Every 10 samples (CCV) or every 2 hr., whichever is more frequent	Mercury %R = 80-120%, all other metals %R = 90-110%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Method Detection Limit Determination Spiked matrix samples (analyte-free tissue samples to which known amounts of target analytes have been added; one spike for each target analyte at 3-10 times the estimated MDL)	Seven replicate analyses prior to use of method. Reevaluation of MDL annually	MDLs (in ppm) are as follows; Arsenic 0.1, Cadmium 0.002, Mercury 0.06, Selenium 0.1	Redetermine MDL

Table 1 (continued)

Sample Type	Frequency of Analysis	Recommended Control Limits	Recommended Corrective Actions
Accuracy and Precision Assessment			
Reference materials (SRMs or CRMs, prepared from actual contaminated fish or shellfish tissue if possible, covering the range of expected target analyte conc.)	Method validation: As many as required to assess accuracy and precision of method before routine analysis of samples. Routine accuracy assessment: one per 20 samples or one batch.	Method validation and Routine accuracy assessment: %R = 75-125%	If matrix spikes are in control then proceed. If not, determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Matrix spikes (MS) (composite tissue homogenates of field samples to which known amounts of target analytes have been added: 0.5 to 10 times the concentration of the analyte of interest or 10 times the MQL).	One per 20 samples or one per batch, whichever is more frequent.	%R = 75-125%	If SRMs are in control then proceed. If not, determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data.
Matrix spike replicates (replicate aliquots of matrix spike samples; 0.5 to10 times the concentration of the analyte of interest or 10 times the MQL.). MS-MSD	One duplicate per 20 samples or one per batch, whichever is more frequent.	RPD <25% for duplicates.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Laboratory replicates (replicate aliquots of composite tissue homogenates of field samples).	One replicate (duplicate) sample per 20 samples or one per batch, whichever is more frequent.	RPD <25% for duplicates.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data

Table 1 (continued)

Sample Type	Frequency of Analysis	Recommended Control Limits	Recommended Corrective Actions
Analytical replicates (replicate aliquots of final sample extract or digestate)	One duplicate per 20 samples or one per batch, if laboratory replicates are out of control	RPD <25% for replicates.	Determine cause of problem, take appropriate corrective action, and reanalyze sample
Field replicates (replicate composite tissue samples)	No field replicates for the screening sites. The number of replicates used in the health risk assessment sites will be determined by consensus of program manager, OEHHA, State and Regional Board.		Determined by program manager
External QA Assessment			
Accuracy-based performance evaluation samples (NOAA intercalibration)	Once prior to routine analysis of field samples	%R=85-115%	Determine cause of problem and reanalyze sample
	One exercise per year	%R = 75-125%	Determine cause of problem and reanalyze sample. Do not continue analysis of field samples until laboratory capability is clearly demonstrated

General Provisions

For a Data Set to be considered acceptable the CCV Recoveries must be within control limits and either the SRM or Spiked Matrix recoveries must also be within control limits

Quality Assurance and Quality Control

The following summarizes the results of the main QA/QC parameters for trace metals and are also shown in Table 2. Appendix B lists the batch number for mercury and the other metals and the samples associated with each batch.

Accuracy

Mercury

The QA/QC parameters for accuracy include SRM and spiked matrix recoveries. They were within control limits (75-125%) 7 of 13 times for the SRMs and 26 of 26 times for spiked matrices. There were four samples for which these QA/QC parameters for accuracy were out of range. One of these SRM recoveries was 208% in Batch 1, and was most likely due to a sample aliquoting error (the other SRM in Batch 1 was 92%). This type of recovery is very rare in our laboratory and is not thought to affect the sample quality. The recovery of SRMs in Batch 2 (135%) and Batch 9 (69%) were slightly outside of the control limits (75-125%).

These batches are accompanied by acceptable spiked matrix recoveries and good continuing calibration verification data--all within the control limits. In addition, these batches were accompanied by SRM spikes (not required in this program), whose recoveries were all within the control limits (75-125%). This data is available for review upon request. There is an additional QA/QC check on Batch 2 (where recoveries of the SRM were 135%) from the preliminary analysis that was done on the Tomales Bay samples. The QA/QC on this preliminary analysis was identical to the QA/QC on the analysis contained in this report, except that no spiked matrix samples were analyzed. In this preliminary analysis, the SRM recoveries were within the control limits and the data agreed very well with the data in this report, and in fact it was almost invariably within 20 to 30 %.

Using the General Provisions at the bottom of Table 1, that the CCVs and either the SRMs or spiked matrix had to be within the control limits, the data sets passed QA/QC for accuracy.

Overall, the accuracy QA/QC checks were very good and the out of control measurements were rare and not thought to affect data quality.

Arsenic, Selenium, Silver, Cadmium, Copper, Chromium, Nickel, Lead and Zinc

All SRMs for copper, chromium, lead, nickel, selenium, silver and zinc were within control limits. Both arsenic and cadmium had one SRM below control limits (72.8 and 67.4% respectively). For both of these elements all the matrix spike samples were within control limits.

Matrix spike samples were within control limits for 69 of 74 spiked samples. The five out of control spiked samples, one selenium in Batch 3 and two selenium and zinc in Batch 5, were all above 72% recovery (Table 2). The corresponding SRMs for all of these batches were within control limits. Therefore, the out of control samples should not affect the data quality.

Precision

The QA/QC parameters for precision, sample, SRM, and spiked matrix duplicates, relative percent differences (RPDs), were within control limits (<25%) in almost every data set. Sample duplicate RPDs were within control limits 46 of 49 times.

SRM duplicate RPDs were within control limits 33 of 36 times. These were not required in our agreed upon QA/QC parameters, but makes the data quality better.

Spiked matrix duplicate RPDs were within control limits in every batch except for one mercury value in Batch 4. The large difference between duplicates in the mercury spiked sample was caused by slightly differing amounts of tissue being added to the two spikes.

There were no batches where both sample and matrix spike out of control limit. Overall, the precision QA/QC checks were very good and the out of control measurements were rare and not thought to affect data quality.

Continuing Calibration Verification

The continuing calibration verifications were all within the control limits (90-110 for trace metals other than mercury, 80-120 % for mercury).

Frequency of analysis of QA/QC parameters

The requirements for frequency of analysis outlined in Table 1 have been met for all the parameters listed.

Completeness

The samples were analyzed for all the contaminants required and all the data sets were analyzed for the appropriate QA/QC parameters.

Summary of QA/QC

Overall, all data sets passed QA/QC. There was one SRM in data set 1 for mercury that was substantially out of control, but, because the other SRM, spiked matrices, and duplicates were in control it was thought to be a rare contamination or sample aliquoting error and was not thought to affect quality of the data from this data set. The other data sets were considered valid and passed QA/QC since they contained only a few minor out of control QA/QC measurements.

List of Abbreviations

CCV	Continuing Calibration Verification (one independent standard)
DFG	Department of Fish and Game
EPA	Environmental Protection Agency
ICV	Initial Calibration Verification (one independent standard)
Matrix Spikes (MS)	Also called Spiked Matrix. Composite tissue homogenate of field sample to which known amounts of target analytes have been added.
Matrix Spike Replicate	Also called (MSD). Replicate aliquots of Matrix Spike samples
MDL	Method of Detection
MQL	Method Quantitation Limit
NOAA	National Oceanographic and Atmospheric Admistration
OEHHA	Office of Environmental Health Hazard Assessment
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
Sample Duplicate	Also called Laboratory Replicate. Replicate aliquot of composite tissue homogenate of field sample.
SOPs	Standard Operating Procedures
SRM or CRM	Standard Reference Material or Certified Reference Material
SWRCB	State Water Resources Control Board

Appendix A

Year 1 Coastal Fish Contamination Program Station Information and Trace Metal Data

Appendix B

Mercury Batch Numbers and Associated Samples

Appendix C

Trace Metal Batch Numbers and Associated Samples