



# Surface Water Ambient Monitoring Program (SWAMP) Bioaccumulation Monitoring Program Data Validation Standard Operating Procedures

**Please note that this document is intended to complement the tissue validation procedures referenced in Group D Elements of the Bioaccumulation Monitoring Program’s Quality Assurance Project Plan (QAPP).**

**It is not intended for any other use.**

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## ACRONYMS AND ABBREVIATIONS

Acronym	Abbreviation
CCV	Continuing Calibration Verification
COM	Compliant
CRM	Certified Reference Materials
DMT	Data Management Team
EUM	LCS is outside of control limits
GB	MS recovery not within control limits
GBC	CRM analyte recovery not within control limits
GC-MS	Gas Chromatography Mass Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IP	Analyte detected in field or lab generated blank
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MDL	Method Detection Limit
ML	Minimum Level (Puckett, 2000)
MQO	Measurement Quality Objective
MS	Matrix Spike
MSD	Matrix Spike Duplicate
N/A	Not Applicable
ND	Not Detected
QA	Quality Assurance
QA Code	Quality Assurance Code ( <a href="#">Complete list of all QA Codes</a> )
QC	Quality Control
QUAL	Qualified
REJ	Rejected
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SWAMP	Surface Water Ambient Monitoring Program
VIL	RPD exceeds control limit
VIP	Analyte detected in field or lab generated blank
VIU	Percent recovery exceeds laboratory control limit
VQCA	QA/QC protocols were not met for accuracy
VQCP	QA/QC protocols were not met for precision
VRIL	Data rejected - RPD exceeds control limit
VRIP	Data rejected - Analyte detected in field or lab generated blank
VRIU	Data rejected - Percent recovery exceeds laboratory control limit

## BLANK CONTAMINATION CHECK

Blank verification samples identify if the target analyte has contaminated field samples via lab contamination from any part of sample preparation and analysis. One method blank (laboratory derived) sample is run with each analytical batch ( $\leq 20$  samples). The method blanks will be processed through the entire analytical procedure in a manner identical to the field samples. The ideal scenario is that method blank samples are non-detects. If a field sample is contaminated from laboratory procedures and the analytical quantification of that field sample is low, then a high proportion of the field sample value could be from laboratory contamination which results in that value being uncertain and not usable. Laboratory blank contamination could result in a false positive when field sample results are low. There is less concern of blank contamination affecting a field sample if field samples are some multiple higher than the method blank result (in this case 3 times (x) the method blank concentration).

In order to determine if field samples have been contaminated, the following data validation method is applied:

1. If there is more than 1 method blank in a batch, use the method blank with the highest concentration.
2. Compare the highest method blank concentration to the method blank MDL  
Note: SWAMP has a method blank MQO of  $< RL$  for all targeted analytes. If the method blank concentration is greater than the RL then corrective action needs to be taken by the lab prior to submitting data to the DMT. For the data validation exercise any quantitation of the method blank above the MDL is considered a detection and therefore the data validation exercise uses the MDL as the threshold for assessing blank contamination:
  - a. If the Method Blank concentration is less than ( $<$ ) the Method Blank MDL then there is no detection of that analyte in the blank sample. This suggests that there was no laboratory contamination of field samples and no further action for that analyte, in that batch, is required.
  - b. If the Method Blank concentration is greater than ( $>$ ) the Method Blank MDL then the method blank sample has been contaminated with the targeted analyte and there is possible contamination of associated field samples. For those cases where the method blank result is greater than the MDL, compare the field sample results to the highest Method Blank result for each batch. Be sure that the Method Blank results, MDLs, and field sample results are all in the same units and basis (wet weight or dry weight).
    - i. If the field result is less than ( $<$ ) 3x highest Method Blank concentration, then flag that field sample with QACode "VRIP". This

sample is considered a censored result (the blank contamination is likely too large a component of the field result to be differentiated). The compliance code is “REJ”.

- ii. If the field result is greater than ( $>$ ) 3x highest Method Blank, then the sample should be flagged with QACode “VIP” if not already “IP” flagged. The compliance code is “QUAL”.

## ACCURACY CHECK

Accuracy is the degree of agreement of a measurement with a known value and is utilized to assess the degree of closeness of field samples to their real value. Using the bull's-eye analogy (Figure 1), accuracy is the degree of closeness to the bull's-eye (which represents the true value). Over/under estimation of analytical quantification is important in this project. If the QA elements indicate overestimation of the field sample result than this could lead to false positives above particular human health consumption thresholds and potentially limit human consumption of particular sport fish species. If the QA elements indicate underestimated analytical quantification, then low field sample values could falsely suggest that fish are below human health thresholds when they may actually be above the thresholds. Good accuracy in a data set increases the confidence and certainty that the field sample value is close to the true value. Accuracy is determined by such QC elements as: CRM, LCS, blind spikes, MS, and performance samples.



Figure 1: Demonstration of target accuracy (black marks) to a known value (bull's-eye). The figure shows very good accuracy but poor precision.

For the accuracy data validation, SWAMP follows a multiple failure rule. The possible QC elements for the accuracy check are: CRM, Reference Material, LCS, and MS/MSD.

MS/MSD, preferably, alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, these QA elements should be used in conjunction with other available QC information.

Only samples in a quantitative range should be used for evaluation of accuracy, as non-quantitative results may be lucky passes or unlucky fails rather than true indications of the ability for the analysis to accurately determine concentrations:

- For any of the accuracy QC samples, Expected Value must be at least 1x RL, otherwise it shouldn't be used.

- For MS/MSDs, the MS Expected Value should be greater than or equal to 3x the Native Field Result.

## Data Validation for Accuracy

If there are no valid QC elements available based on the quantitative range screening from above, then apply QACode “VQCA” to all of the related results in that batch.

For the remaining QC samples in a quantitative range, the following apply where there is more than one usable measure.

1. Following SWAMP MQOs, one QC element is allowed to be outside the MQO for accuracy (occurs when the QC element is less than or greater than the MQO target range (see Tables 1 and 2) but less than 2x the MQO range (see method for determining this “2x” range in item 3 below) in a batch and still be compliant. If one QC element in a batch is outside the MQO, then the individual QC sample is given QACode “EUM”, “GBC”, or “GB”. The compliance code for the associated field samples is “COM”.
2. When more than one QC element is outside of the MQO, each QC element is given QACode “EUM”, “GBC”, or “GB”. The compliance code for the associated field samples is “QUAL”. In these cases, QACode “VIU” is applied to the field samples.
3. **Rejection Point:** The QACode “VRIU” is applied to the field samples when the percent recovery is more than 2x outside the MQO target range (see Tables 1 and 2) or when the lower rejection limit is < 10%, in 2 or more QC elements (CRM, Reference Material, LCS, MS/MSD). In these cases, the compliance code is changed to “REJ”. The QACode is applied to all field samples in the affected batch including those that are not quantifiable (flagged with ND in ResQualCode). Below is the method for determining the upper and lower rejection limits:
  - a. Lower Rejection Limit =  $100 - (2 * (100 - \text{lower limit of the range}))$
  - b. Upper Rejection Limit =  $100 + (2 * (\text{upper limit of the range} - 100))$

As an example, the acceptable range for certified reference material for organics is percent recovery 70-130%. The lower rejection limit would be  $100 - (2 * (100 - 70)) = 40$  and the upper rejection limit would be  $100 + (2 * (130 - 100)) = 160$ . Recoveries less than 40% and greater than 160% are more than 2x outside the MQO target range which would result in a compliance code of “REJ” and QACode “VRIU”.

If there is only one usable QC sample for accuracy evaluation, the individual QC sample is flagged as appropriate, and the following applies to the batch:

1. In the case where there is only one QC element reported in the batch and the percent recovery is more than 1 time outside the MQO target range (see Tables 1 and 2) but less than 2x the target range then the compliance code would be “QUAL” and QACode “VIU” is applied to the field samples in that batch.
2. **Rejection Point:** In the case where there is only one QC element reported in the batch and the percent recovery was more than 2x outside the MQO target range (see Tables 1 and 2) or when the lower rejection limit is < 10%, then the compliance code would be “REJ” and QACode “VRIU” is applied to the field samples in that batch.

*Table 1. General Measurement Quality Objectives\* for inorganic analytes in tissues. ML = minimum level (Puckett, 2000); N/A = Not Applicable*

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer’s specifications	Per analytical method or manufacturer’s specifications
Continuing Calibration Verification	Per 10 analytical runs	80-120% recovery
Laboratory Blank	Per 20 samples or per batch, whichever is more frequent	Blanks < ML for target analyte
Reference Material	Per 20 samples or per batch, whichever is more frequent	75-125% recovery
Matrix Spike	Per 20 samples or per batch, whichever is more frequent	75-125% recovery
Matrix Spike Duplicate	Per 20 samples or per batch, whichever is more frequent	75-125% recovery, RPD ≤ 25%
Laboratory Duplicate	Per 20 samples or per batch, whichever is more frequent	RPD ≤ 25%, N/A if concentrations of either sample < ML
Internal Standard	Accompanying every analytical run when method appropriate	75-125% recovery

\* Unless method specifies more stringent requirements

*Table 2. General Measurement Quality Objectives\* for synthetic organic analytes in tissues. MDL = Method Detection Limit (to be determined according to the SWAMP QA Management Plan; N/A = Not Applicable*

<b>Laboratory Quality Control</b>	<b>Frequency of Analysis</b>	<b>Measurement Quality Objective</b>
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 10 analytical runs	75-125% recovery
Laboratory Blank	Per 20 samples or per batch, whichever is more frequent	Blanks < ML for target analyte
Reference Material	Method validation: as many as required to assess accuracy and precision of method before routine analysis of samples  Routine accuracy assessment: per 20 samples or per batch (preferably blind)	70-130% recovery if certified; otherwise, 50-150% recovery
Matrix Spike	Per 20 samples or per batch, whichever is more frequent	50-150% recovery or control limits based on 3x the standard deviation of laboratory's actual method recoveries
Matrix Spike Duplicate	Per 20 samples or per batch, whichever is more frequent	50-150% recovery, RPD ≤ 25%
Laboratory Duplicate	Per 20 samples or per batch, whichever is more frequent	RPD ≤ 25%, N/A if concentrations of either sample < ML
Internal Standard	As specified in method	50-150% recovery

\* Unless method specifies more stringent requirements

Table 3 summarizes the application of QACodes for the accuracy check scenarios above.

Table 3. Accuracy Data Validation Rules – where there are more than 2 quantitative (usable) measures, A & B are the two quantitative measures with the worst performance for any given analyte

Measure A Range	Measure B Range	QA Code	Comment
> $\pm 2x$ range or when the lower rejection limit is < 10%	> $\pm 2x$ range or when the lower rejection limit is < 10%	VRIU	Both badly fail
> $\pm 2x$ range or when the lower rejection limit is < 10%	> $\pm 1x$ range - < $\pm 2x$ range	VIU	One badly, one marginally fail
> $\pm 2x$ range or when the lower rejection limit is < 10%	Within range	None	One badly fail, remainder pass
> $\pm 2x$ range or when the lower rejection limit is < 10%	Null	VRIU	One badly fail
> $\pm 1x$ range - < $\pm 2x$ range	> $\pm 1x$ range - < $\pm 2x$ range	VIU	Both marginally fail
> $\pm 1x$ range - < $\pm 2x$ range	Within range	None	One marginally fail, remainder pass
> $\pm 1x$ range - < $\pm 2x$ range	Null	VIU	One marginally fail
Within range	Within range	None	Both pass

## PRECISION CHECK

Precision is the degree to which repeated measurements under unchanged conditions show the same result (usually reported as a RSD or RPD). The repeatability measure indicates the variability observed within a laboratory, over a short time, using a single operator, item of equipment, etc. These QA elements also show the reproducibility of an analytical measurement. Good precision provides confidence that the analytical process is consistently measuring the target analyte in a particular matrix.

The possible QC elements in the precision check are: Lab duplicates, MS/MSD, and LCS/LCSD. See Tables 1 and 2 above for MQOs.

Similar to the case for evaluating accuracy, only results in a usable quantitative range should be used to calculate precision.

- Check for each sample (pair or set) analyzed in replicate that the average result is greater than (>) 1x the RL. If the average result is greater than (>) 1x the RL then include RPD or RSD in lab tests submission evaluation. Otherwise that set of sample replicates is not quantitative and thus not usable.



## Data Validation for Precision

If there are no valid precision QC elements available based on the quantitative range screening from above, then apply QACode “VQCP” to all of the related results in that batch.

For the remaining QC samples in a quantitative range, the following apply where there is more than one set of replicates.

1. When one or more QC elements for precision (e.g. lab duplicate or MS/MSD) is greater than 1 time to less than 2x the target (for organics and metals RPD or RSD greater than 25% to less than 50%, Tables 1 and 2 above) then the field samples within that batch are flagged with QACode “VIL”. The compliance code is “QUAL”.
2. If one QC elements fails badly ( $> 50\%$  RPD), then consider the RPD/RSD of the other QC elements (e.g. MS/MSD, LCS/LCSD) for that analyte. If other QC elements pass ( $\leq 25\%$ ), or marginally fail ( $25\% < \text{RPD} < 50\%$ ), and there are no other indications of ongoing QA problems, then assign the samples within that batch, for that analyte, with QACode “VIL”. The compliance code is “QUAL”.
3. **Rejection Point:** If more than one QC element fails badly ( $> 50\%$  RPD), then assign QACode “VRIL” to the samples for that analyte in the batch and a compliance code of REJ.

If there is only one usable quantitative measure, the following apply:

1. If there is only one QC element reported in the batch and the RPD is greater than 1 time to less than 2x the target (for organics and metals greater than 25% to less than 50%) then the field samples within that batch are flagged with QACode “VIL”. The compliance code is “QUAL”.
2. **Rejection Point:** If there is only one QC element reported in the batch and the RPD was more than 2x outside the MQO target ( $> 50\%$ ) then the compliance code would be “REJ” and the QACode “VRIL” is applied to the associated field samples in that batch

Table 4 summarizes the application of QACodes for the precision check scenarios described above.

*Table 4. Precision Data Validation Rules – where there are more than two usable measures, use the two worst as A & B.*

<b>Measure A</b>	<b>Measure B</b>	<b>QA Code</b>	<b>Comment</b>
> 50%	> 50%	VRIL	Both bad fail
> 50%	> 25%	VIL	One bad, one marginal fail
> 50%	< 25%	VIL	One bad fail, rest pass
> 50%	Null	VRIL	One usable, bad fail
> 25%	> 25%	VIL	Both marginal fail
> 25%	< 25%	VIL	One marginal fail, one pass
> 25%	Null	VIL	One usable, marginal fail
< 25%	< 25%	None	Both good

For analytes where RPD or RSD limits are not 25%, substitute 1x those limits for 25% and 2x those limits instead of 50%

Assumptions:

Measure A and B (Table 4) can be either different types of elements (duplicates, MS/MSD) or pairs of the same type of measure. Each measure is treated separately and not averaged when there are multiple pairs of the same measure (e.g. do not average RPD if there are 2 sets of replicates).

## GLOSSARY

**Calibration Standard:** Calibration standards are the measurement of an absolute value of a target analyte and in many cases, the standards are traceable back to standards at the National Institute for Standards and Technology. A calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. A calibration curve is one approach to the problem of instrument calibration.

**Certified Reference Material (CRM):** CRMs are similar in matrix and concentration range to the samples being prepared and analyzed. The accuracy of an analytical method can be assessed using CRMs only when certified values are provided for the target analytes.

**Continuing Calibration Verification (CCV):** Calibration verification solutions traceable to a recognized organization are inserted as part of the sample stream. The sources of the calibration verification solutions are independent from the standards used for the calibration. Calibration verification solutions used for the CCV will contain all the analytes of interest.

**Expected Value:** the concentration of the analyte in a reference standard, laboratory control sample (LCS) or matrix spike sample (MS), or the value expected to be obtained from analysis of the QC sample. This consists of the native sample result concentration plus the spike amount.

**Internal (or Surrogate) Standard:** To optimize Gas Chromatography Mass Spectrometry (GC-MS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses, internal standards (also referred to as “injection internal standards”) may be added to field and QC sample extracts prior to injection. Use of internal standards is particularly important for analysis of complex extracts subject to retention time shifts relative to the analysis of standards. The internal standards can also be used to detect and correct for problems in the GC injection port or other parts of the instrument.

**Laboratory Control Sample (LCS):** An LCS is a specimen of known composition prepared using contaminant-free reagent water or an inert solid spiked with the target analyte at the midpoint of the calibration curve or at the level of concern. The LCS must be analyzed using the same preparation, reagents, and analytical methods employed for regular samples.

**Laboratory Duplicate:** In order to evaluate the precision of an analytical process, a field sample is selected and digested or extracted in duplicate and analyzed according to the method.

**Matrix Spike (MS):** A MS is prepared by adding a known concentration of the target analyte to a field sample (spike amount), which is then subjected to the entire analytical

procedure. If the ambient concentration of the field sample is known, the amount of spike added is within a specified range of that concentration. MSs are analyzed in order to assess the magnitude of matrix interference. Because MSs are analyzed in pairs, the second spike is called the matrix spike duplicate (MSD).

**Method Blank:** A laboratory blank prepared to represent the sample matrix as closely as possible and analyzed exactly like the calibration standards, samples, and quality control (QC) samples. Results of method blanks provide an estimate of the within-batch variability of the blank response.

**Method Detection Limit (MDL) or Method Limit:** EPA defines the MDL as, "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." Any sample that is not quantifiable is considered to be not detected and below the MDL.

**Measurement Quality Objectives (MQO):** Numerical acceptance criteria for the quality attributes measured by project data quality indicators. During project planning, MQOs are established as quantitative measures of performance against selected data quality indicators, such as precision, bias, representativeness, completeness, comparability, and sensitivity.

**Native Sample:** the original sample to which a known spike amount is added. The native sample plus spike becomes a Matrix Spike (MS).

**Reference Material:** The distinction between a reference material and a certified reference material (CRM) does not involve how the two are prepared, rather with the way that the reference values were established. Certified values are determined through replicate analyses using two independent measurement techniques for verification. The certifying agency may also provide "non-certified or "reference" values for other target analytes. Such values are determined using a single measurement technique that may introduce bias.

**Reporting Limit (RL):** A RL is the minimum value below which chemistry data are documented as detected but not quantified.

## REFERENCES

Puckett, M. *Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program*; California Department of Fish and Game, Monterey, CA, 2002.