



# Specifying And Evaluating Analytical Chemistry Quality Requirements for Ecological Risk Assessments

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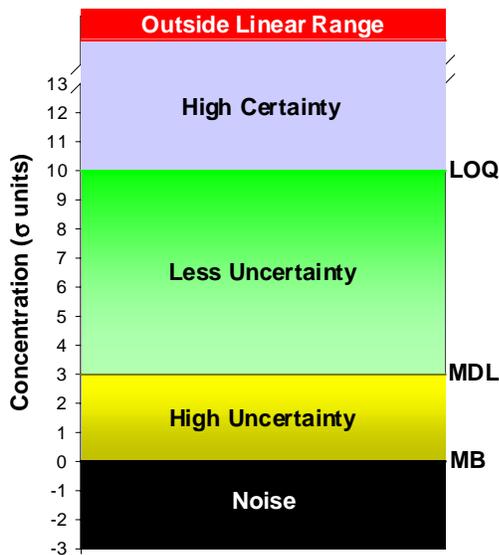
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# 1. EXECUTIVE SUMMARY

To achieve the goal of assessing risk to ecological systems, scientifically sound analytical chemistry data are needed. This document defines the quality assurance and quality control (QA/QC) procedures that will assure analytical chemistry data are capable of meeting the data quality objectives required for ecological risk assessments. For analysis of parts-per-billion levels of organic and inorganic contaminants in samples of water, sediment, and wildlife tissues (fish, birds, mammals, invertebrates, and plants) collected from estuarine and marine ecosystems, specialized methodologies are required that are more “research” oriented than routine methods that are generally available. A performance-based quality assurance program is described that requires the performing laboratory to demonstrate proficiency through routine analysis of certified or well documented reference materials. The laboratory is required to initiate corrective actions if their performance falls below minimal standards.

Any analytical chemistry data produced for an ecological risk assessment must be of sufficient quality to satisfy the intended use of the data. The philosophy of the performance-based approach presented in this guide is that as long as proper QA/QC requirements are implemented and comparable analytical performance on standard materials is demonstrated, multiple procedures for the analysis of different compound classes used by different laboratories should yield comparable results. Performance-based QA/QC requirements are defined which require the use of accuracy materials (e.g., certified or standard reference materials and laboratory control materials), calibration standards, method blanks, matrix spike samples, laboratory duplicates, internal standards, injection standards, and interlaboratory calibrations.

This guide is applicable to low parts-per-billion analyses of water, sediment, and tissue samples, unless otherwise noted. If implemented in a consistent manner, this protocol will provide the information necessary to verify the quality of the data, validate the raw data, and assess the comparability of data generated by different laboratories with different analytical procedures. The QA/QC requirements specified in this guide are the minimum requirements for any given analytical method. Additional method-specific requirements should always be followed, as long as the minimum requirements have been met.

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## 2. PURPOSE

To achieve the goal of assessing risk to ecological systems, scientifically sound analytical chemistry data are needed. Ecological risk assessments require analytical methods (1) that are capable of detecting chemicals below levels that can cause ecological effects as well as levels associated with background or naturally occurring concentrations, (2) that are capable of differentiating chemical levels from interferences due to sample matrices, and (3) that can be reliably reproduced and verified. The analytical methods must provide data that are scientifically sound and which can meet the representativeness, completeness, comparability, accuracy, and precision required to meet the data quality objectives of ecological risk assessments (Table 1). The purpose of this document is to define quality assurance and quality control (QA/QC) procedures that will provide the information necessary to verify the quality of the data, validate the raw data, and assess the comparability of data generated by different laboratories with different analytical procedures.

## 3. BACKGROUND

For analysis of parts-per-billion levels of organic and inorganic contaminants in estuarine and marine sediments and wildlife tissues (fish, birds, mammals, invertebrates, and plants), no procedure has been officially approved by regulatory authorities. For these types of samples, specialized methodologies are required that are more “research” oriented than routine methods available for monitoring soils, ground water, drinking water, hazardous wastes, and effluents (U.S. EPA 1979, 1994a, 1994b, 1996). Examples of analytical methods that have been proven to provide scientifically sound data are those used by the Environmental Protection Agency's (EPA) Environmental Monitoring and Assessment Program (EMAP, Strobel et al. 1995), the National Oceanic and Atmospheric Administration's National Status and Trends Program (NS&T, Lauenstein and Cantillo 1993), the Puget Sound Estuary Program (U.S. EPA and PSWQAT 1997a, b), and ecological risk assessment case studies conducted by the Navy and EPA (Mueller et al. 1992, Munns et al. 1991, Johnston et al. 1994).

These programs do not require that laboratories use particular analytical methods, but rather that each participating laboratory demonstrate proficiency through routine analysis of standard or certified reference materials (SRMs or CRMs) or similar types of reference materials. Certified Reference Materials are samples of environmental matrices (water, sediment, tissue, etc.) that have certified concentrations of chemicals, accurately determined by more than one valid method. A certificate or document issued by a certifying body (agencies such as the National Research Council of Canada (NRC), USEPA, US Geological Survey, etc.) is provided with the sample. Standard Reference Materials (SRMs) are CRMs issued by the National Institute of Standards and Technology (NIST). The performing laboratory is required to conduct ongoing performance evaluation exercises throughout the project, to demonstrate initial capability (i.e., prior to the analysis of actual samples) and on a continuous basis. If performance falls below minimum standards explicitly defined in the quality assurance plan, the laboratory is required to initiate corrective actions. In order to benefit from EPA's existing technical and administrative experience, this document has been adapted from the QA/QC guidance developed for the EMAP Near Coastal Demonstration Project (Valente et al. 1992, Reifsteck et al. 1993).

## 4. DEFINING THE QA/QC REQUIREMENTS

The data quality objectives for analytical chemistry analyses performed for ecological risk assessments (Table 1) require that the data produced will be of sufficient quality to satisfy the intended use of the data in a scientifically sound manner (Stanely and Verner 1985, US EPA 1994c). Because high-quality low-detection limits are required and the nature of the work is nonroutine, a quality assurance plan is needed that will expand on areas not addressed by the U.S. EPA Contract Laboratory Program (CLP). Accordingly, the procedures outlined in this document should be viewed as additions and expansions to CLP protocols. In all other areas, not explicitly addressed by this document (instrument tuning, chain-of-custody, data validation, etc.), standard CLP protocols will apply (U.S. EPA 1994a, 1994b, 1996.)

The philosophy of the performance-based approach is that as long as proper QA/QC requirements are implemented and comparable analytical performance on standard materials is demonstrated, multiple procedures for the analysis of different compound classes used by different laboratories should yield comparable results. Based on this assumption, performance-based QA/QC requirements are defined which require the use of accuracy materials (e.g., certified or standard reference materials and laboratory control materials), calibration standards, method blanks, matrix spike samples, laboratory duplicates, internal standards, injection standards, and interlaboratory calibrations (Table 2). The conceptual basis for the use of these quality control samples is presented below.

This guide is applicable to low parts-per-billion analyses of water, sediment, and tissue samples unless otherwise noted. If implemented in a consistent manner, this protocol will provide the information necessary to verify the quality of the data, validate the raw data, and assess the comparability of data generated by different laboratories with different analytical procedures. The QA/QC requirements specified in this guide are the minimum requirements for any given analytical method. Additional method-specific requirements should always be followed, as long as the minimum requirements presented in this document have been met.

As part of the data package, the laboratory must submit data for all QA/QC variables. Program managers and project coordinators must verify that requested QA/QC data are included in the data package as supporting information for the raw data. Qualified QA personnel overseeing the project should conduct a detailed review of the entire data package. The QA/QC data can be used initially to document the accuracy and precision of individual measurement processes and provide the ability to assess comparability among different laboratories.

The analytical laboratory should use the results obtained for the QA/QC samples to determine when warning and control limits have been exceeded and when corrective actions must be taken. Warning limits are numerical criteria that serve as flags to data reviewers and data users. When a warning limit is exceeded, the reported data may be qualified. Control limits are numerical data criteria that, when exceeded, require specific corrective action by the laboratory before the analyses may proceed. Warning and control limits and recommended frequency of analysis for each QA/QC element or sample type are summarized in Table 2. The use, frequency of analysis, type of information obtained, warning and control limits, and corrective actions required for each of these QA/QC elements are described below.

## 4.1 Performance Evaluation

An initial demonstration of the laboratory's capability is required before the laboratory can begin analyzing field samples (Table 2). The performance evaluation consists of evaluating the laboratory's capability for analyzing the analytes in the matrices required by the project. It includes a review of the standard operating procedures to be used, the initial calibration of the analytical instrumentation, whether the method detection limits are capable of meeting the target detection limits (Table 3), and whether the laboratory can demonstrate their proficiency on actual field samples.

### 4.1.1 Initial Calibration

Equipment must be calibrated before any samples are analyzed, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended control limit criteria (Table 2). Data documenting initial calibration and any events requiring recalibration and the corresponding recalibration data must be included with the analytical results. All standards used for initial calibration of a particular analyte must be obtained from a single source and should be traceable to a recognized organization for the preparation of QA/QC materials (e.g., National Institute of Standards and Technology, Environmental Protection Agency, etc.). Calibration curves must be established for each compound or element to be analyzed as well as any internal or calibration standards required by the method. For each batch of samples a calibration blank and a minimum of three analytical standards of increasing concentration, covering the range of expected sample concentrations should be used. The calibration curve must be established prior to the analysis of samples. Only data which results from quantification within the demonstrated working calibration range may be reported by the laboratory; samples outside the calibration range should be diluted or concentrated, as appropriate, and reanalyzed.

### 4.1.2 Initial Documentation of Detection Limits

For the purpose of clarity, this document will distinguish between two kinds of "limits" of detectability: the Method Detection Limit (MDL) and the Limit of Quantitation (LOQ) (Figure 1). The MDL represents a quantitative estimate of low-level response detected at the maximum sensitivity of a method. The MDL "... is 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" (See Appendix B of Code of Federal Regulations [40 CFR Part 136](#)). Confidence in the apparent analyte concentration increases as the analyte signal increases above the MDL (Figure 1).

The level above which quantitative results may be obtained with a specified degree of confidence is the LOQ (Keith 1991a). In practice, the LOQ usually represents a reported concentration level above which there is a high technical confidence in the quantified result (i.e., there is a low probability of either a false positive or false negative result at or above the LOQ, Figure 1). The LOQ is different from, and more difficult to reach than, simply measuring the presence or absence of an analyte (Keith 1991b). For each analyte, the recommended LOQ should be set equal to 10 times the standard deviation ( $\sigma$ ) used in calculating the MDL (Keith 1991a and 1919b). Sample concentrations that are less than the LOQ should be "flagged" to indicate the uncertainty associated with the result. Because sample concentrations equal to or greater than the LOQ are within the range of high certainty (Figure 1), the result can be reported without qualifying the uncertainty.

For the initial documentation of detection limits, the analytical laboratory must establish and report an MDL for each analyte in each matrix of interest (water, sediment or tissue) and analytical method (including the specific instrumentation that will be used) prior to the analysis of field samples. The laboratory is required to follow the procedures specified in Appendix B of [40 CFR Part 136](#) to calculate the MDL for each analytical method employed. Target MDL values have been established (Table 3) to ensure that the laboratory will be capable of detecting chemicals below levels that can cause ecological effects as well as levels associated with background or naturally occurring concentrations. The initial MDL reported by the laboratory should be equal to or less than the target values before the analysis of field samples may proceed. It should be recognized that the MDL is a statistically-derived, empirical value that subsequently may vary in actual samples as a function of sample size, matrix, concentration of chemical present, instrument sensitivity, etc. Therefore the laboratory should periodically (i.e. at least once a year) recalculate the MDLs for the analytical methods used and the sample matrices typically encountered.

#### 4.1.3 Blind Analysis of Sample Matrix Material

A representative sample matrix that is homogenous and contains known concentrations of the analytes of interest should be provided to the analytical laboratory to evaluate laboratory performance prior to the analysis of field samples. The laboratory must not know the concentrations of the analytes. The laboratory's performance will be considered acceptable if its submitted values are within  $\pm 30\%$  (for organic analyses) and  $\pm 15\%$  (for inorganic analyses) of the actual or certified concentration of each analyte in the blind sample. If any of the values resulting from the initial analysis are outside the control limit, the laboratory will be required to repeat the analysis until the control limit is met, prior to the analysis of real samples. Final acceptance is subject to review by the Project Managers and QA Officer. This requirement can be waived, if the laboratory can adequately demonstrate their capability by other means (e.g. participation in ongoing laboratory intercomparison programs, previous projects, etc.).

#### 4.2 Analysis of SRMs, CRMs, and LCM

Reference Materials (SRMs or CRMs) are generally considered one of the most useful QC samples for assessing the accuracy of a given analysis (Valente et al. 1992, Strobel et al. 1995, Lauenstein and Cantillo 1993, U.S. EPA and PSWQAT 1997a, b, Johnston et al. 1994). This is because the results obtained from the reference material are a measure of how close the analysis came to its true value. Reference Materials can be used to assess accuracy because they have "certified" concentrations of the analytes of interest, as determined through replicate analyses by a reputable certifying agency using two independent measurement techniques for verification. In addition, the certifying agency may provide "noncertified" or "informational" values for other analytes of interest. Such values are determined using a single measurement technique, which may introduce unrecognized bias. Therefore, non-certified values must be used with caution in assessing the accuracy of a laboratory method that differs from the one used by the certifying agency.

A laboratory control material (LCM) is similar to a CRM. A LCM is a homogeneous matrix that closely matches the samples being analyzed and the concentrations of certain analytes of interest are known with reasonable accuracy (i.e., as a result of a statistically valid number of replicate analyses by one or several laboratories). Sometimes a laboratory will be required to prepare a LCM because a suitable SRM or CRM is not available. In practice, the LCM is not officially certified, but it can be used by the laboratory to assess both accuracy and precision (i.e., batch-to-batch consistency).

Continuous analysis of laboratory control materials or certified reference materials is a vital aspect of the "performance-based" philosophy.

At least one SRM, CRM or LCM should be analyzed along with each batch of samples (Table 2). The concentrations of the target analytes should be known to the analyst and should be used to provide an immediate check on accuracy for each batch of samples. If the values are outside the control limits (Table 2), the entire batch of data are suspect. Calculations and instruments should be checked and the SRM or CRM should be reanalyzed to confirm the results. If the values are still outside the control limits in the repeated analysis, the laboratory is required to determine the source(s) of the problem and reprep and repeat the analysis of that batch of samples until control limits are met, before continuing with further sample analyses.

Analysis results for reference materials and laboratory control materials also should be recorded on control charts to monitor laboratory precision from batch to batch. This is particularly important in situations where certified or "true" concentrations are not available for all the analytes of interest in a particular control material, or where reference material concentrations are given only as "non-certified" values. In the latter case, a laboratory may find that a "method bias" prevents it from meeting the 70 to 130 percent recovery control limit for one or more analytes of interest in a particular SRM (or CRM/LCM). In such instances, the laboratory should be able to demonstrate (through the use of control charts) that its results are consistent from batch-to-batch for each analysis of a particular reference material or laboratory control material (i.e., wildly fluctuating results are not acceptable). The results of the reference material or laboratory control material analysis should never be used by the laboratory to "correct" the data for a given sample batch. Instead, a special data qualifier code "p" (see Table 4) may be used in those instances where the laboratory is able to demonstrate a consistent method bias in quantifying one or more analytes having non-certified concentrations in the SRM or CRM.

### **4.3 Calibration Check**

The initial instrument calibration is checked through the analysis of a calibration check standard. The standard used to prepare the calibration check standard should be obtained from a different source, if possible, than the initial calibration standards, so that it can provide an independent check both on the calibration and the accuracy of the standard solutions. Analysis of the calibration check standard should occur at the beginning of a sample set, once every 10 samples or every two hours during a run, and after the last analytical sample (Table 2). The calibration check should be used to evaluate calibration linearity, intercept drift, minimum response level, or any other control level that may be required by the method.

If the control limit for analysis of the calibration standard (Table 2) is not met, the initial calibration will have to be repeated. If possible, the samples analyzed before the calibration check that failed the control limit criteria should be reanalyzed following the re-calibration. The laboratory should begin by reanalyzing the last sample analyzed before the calibration standard that failed. If the relative percent difference (RPD) between the results of this reanalysis and the original analysis exceeds 30 percent, the instrument is assumed to have been out of control during the original analysis. If possible, reanalysis of samples should progress in reverse order until it is determined that there is less than 30 RPD between initial and reanalysis results. If it is not possible or feasible to perform reanalysis of samples, all earlier data (i.e., since the last successful calibration control check) should be

flagged. In this case, the laboratory should prepare a narrative explanation to accompany the submitted data.

#### 4.4 Method Blank

Method Blanks (MB, sometimes referred to as “laboratory reagent blanks” or “procedural blanks”) are used to assess laboratory contamination during all stages of sample preparation and analysis. For both organic and inorganic analyses, one method blank should be run in every sample batch or for every 12-hour shift, whichever is more frequent. Warning and control limits for blanks (Table 2) are based on the laboratory's method detection limits that were documented prior to the analyses of samples (Table 3). A reagent blank concentration between the MDL and 3 times the MDL should serve as a warning limit that requires further investigation based on the best professional judgement of the analyst(s). A reagent blank concentration equal to or greater than 3 times the MDL requires definitive corrective action to identify and eliminate the source(s) of contamination.

#### 4.5 Matrix Spike

A matrix spike (MS, also referred to as a “laboratory fortified sample matrix”) will be used to evaluate the effect of the sample matrix on the recovery of the compound(s) of interest. A minimum of one sample per batch must be selected at random for analysis as an MS sample (Table 2). The compounds used to spike the samples should include a wide range of representative analyte types. Care must be taken to spike the samples within the appropriate range for the analytes of concern. An attempt should be made to spike the samples such that the spike is no less than four times and no more than ten times the sample value.

The recovery data for each compound spiked in to the MS sample, which should be reported along with the rest of the data for each sample, will provide a basis for determining the prevalence of matrix effects in the samples analyzed during the project. If the percent recovery for any analyte is less than the recommended warning limit of 50 percent, the chromatograms and raw data quantitation reports should be reviewed. If an explanation for a low percent recovery value is not discovered, the instrument response should be checked using a calibration standard. Low recoveries for matrix spike may be caused by matrix interference and further instrument response checks may not be warranted, especially if the other laboratory QC samples indicate that the analysis for that batch of samples was in control. An explanation for low percent recovery values for matrix spike results should be discussed in the case narrative accompanying the data package. Corrective actions taken and verification of acceptable instrument response must be included.

#### 4.6 Laboratory Duplicates

One sample per batch should be split in the laboratory and analyzed in duplicate to provide an estimate of analytical precision. The sample should be thoroughly homogenized prior to splitting. Duplicate analyses also are useful in assessing potential sample heterogeneity and matrix effects. The recommended control limit for analysis of laboratory duplicates is a relative percent difference (RPD) of  $\pm 30\%$  for each analyte of interest (Table 2) calculated as follows:

$$\text{RPD} = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2)/2}$$

where  $C_1$  = the larger of the duplicate results for a given analyte  
and  $C_2$  = the smaller of the duplicate results for a given analyte

If results for a significant number of analytes are outside the control limit, calculations and instruments should be checked. A replicate analysis may be required to confirm the results. If results continue to exceed the control limit, subsequent corrective action is at the discretion of the program manager or QA officer, because matrix effects or incomplete homogenization (either in the field or laboratory) may be contributing factors. A discussion of the results of duplicate sample analysis should include probable sources of laboratory error, evidence of matrix effects, and an assessment of natural sample variability. Data outside the control limit may be flagged pending QA review of the probable laboratory or field sources of variation.

#### **4.7 Internal Standards**

Internal standards (commonly referred to as “surrogate spikes” or “surrogate analytes”) are compounds chosen to simulate the analytes of interest. The internal standard represents a reference against which the signal from the analytes of interest is compared directly for the purpose of quantification. Internal standards must be added to each sample, including QA/QC samples, prior to extracting, purging, or digesting. The reported concentration of each analyte should be adjusted to correct for the recovery of the internal standard (Strobel et al. 1995, Lauenstein and Cantillo 1993, U.S. EPA and PSWQAT 1997a, Mueller et al. 1992). The internal standard recovery data therefore should be carefully monitored; the laboratory should report the absolute amounts and the percent recovery of the internal standards along with the target analyte data for each sample. If possible, isotopically labeled analogs of the analytes should be used as internal standards.

Recommended control limits for internal standard recoveries are not specified. Instead, the laboratory must set its own warning and control limits based on the experience and best professional judgement of the analyst. It is the responsibility of the analyst to demonstrate that the analytical process is always “in control” (i.e., highly variable internal standard recoveries for repeat analyses of the same reference material, or for laboratory duplicates, are not acceptable).

#### **4.8 Injection Standards**

For gas chromatography (GC) analysis, injection standards (also termed “GC standards” or “injection internal standards”) are added to each sample just prior to injection to enable optimal quantification, particularly of complex extracts subject to retention time shifts relative to the analysis of standards. Injection standards are essential if the actual recovery of the internal standards added prior to extraction is to be calculated. The injection standards can be used to detect and correct for problems in the GC injection port or other parts of the instrument. The injection standards used must be different from those already used as internal standards. The analyst must monitor injection standard retention times and recoveries to determine if instrument maintenance or repair, or changes in analytical procedures, are indicated. Corrective action should be initiated based on the experience of the analyst and not because warning or control limits were exceeded (Table 2). Instrument problems that may have affected the data or resulted in the reanalysis of the sample must be documented in the analyst's logbook, on the raw data report, and in the case narrative submitted with the data package.

#### **4.9 Interlaboratory Calibration**

Interlaboratory calibrations should be conducted to provide an independent check on the accuracy of the analysis, identify any laboratory bias that may be present, and assure the comparability of the results reported by the different laboratories. This is especially important in projects where more

than one laboratory will be involved in analyzing samples. It is highly recommended that the laboratory participate in intercomparison programs offered by various agencies (such as NOAA's National Status and Trends Program or EPA's EMAP program). The intercalibration samples should be within a factor of four with that less than 20% of analytes outside the desired limit (Table 2). Variations between laboratories, inhomogeneity of the samples, and the relatively low concentrations of many of the analytes (below the LOQ and MDL) can contribute to differences in sample results obtained by participating laboratories. Gross differences between the laboratories will be subject to review by the Project Managers and the QA Officers to determine if corrective action is necessary.

## 5. Sample Analysis

An example of the minimum (5%) QA/QC samples required for the analysis of a hypothetical batch of 16 field samples is provided in Table 5. In addition to extracting the 16 field samples an additional four samples consisting of one reference material sample (SRM/CRM/LCM), one Laboratory Duplicate sample (DUP), one Matrix Spike sample (MS), and one Method Blank (MB) must also be extracted. These additional samples are treated exactly the same as the field samples during the analysis. Prior to actual analysis Calibration Check (CC) samples are added to the batch; one at the beginning of the batch, one after every tenth analysis, and one at the end of the batch resulting in a total of 23 analysis. Results from all analysis are included in the data report for the batch.

## 6. Sample Storage and Handling

The procedures for field collection of samples and transfer to the analytical chemistry laboratory should be documented in the project work plan. Sediments and tissue samples are to be kept frozen (-10° C) until just prior to analysis. For the determination of analytes listed in Table 3, with the exception of VOCs, no specific holding time limitation is necessary for samples stored in this manner (Gleason and Mueller 1989). Sample handling requirements for other samples to be analyzed (eg. water samples for metals, water samples for VOCs, and dried algal samples for metals, etc.) should be documented in the work plan and provided to the laboratory as required.

When sediments and tissues are to be analyzed they will be thawed to room temperature and homogenized. Any split samples required for interlaboratory calibration will be subsampled from the homogenate. The split samples will then be refrozen and held frozen until delivery to the participating laboratory(ies). Aliquots of the homogenized matrix will be selected for analysis and any remaining homogenate should be immediately refrozen and archived for future analysis. Extractions of the aliquots should be performed within 24 hr of thawing. The extracts can be stored up to six months, if they are kept at 4°C (Gleason and Mueller 1989), before analysis. Special instructions for homogenizing tissue samples (whole or dissected) and any other special sample handling procedure will be provided in accordance with the work plan. All sample inventory, sample information, and status will be maintained in a database system and documented on chain-of-custody logs in accordance with CLP guidance (US EPA 1994a, b. 1996).

## 7. Analytical Chemistry Data Reporting Requirements

Data for all QA/QC elements (e.g., SRMs or CRMs, calibration check samples, blanks, laboratory duplicates, etc.) must be submitted by the laboratory as part of the data package for each batch of samples analyzed. The laboratory must provide a case narrative that, at the minimum, provides notification to the Project Manager that data are being submitted, identifies what samples

were received, what methods and analytical procedures were performed, how the quality of the data was evaluated, any problems that had to be overcome, and the raw data produced for the field and QA/QC samples. The raw data for the field and QA/QC samples must be provided in an electronic format that will allow the data to be verified, validated, and loaded into the project database. (See Appendix A for a Data Deliverable Specification for analytical chemistry).

The QA/QC results and associated data will be subject to review by the Project Managers, QA Officer, or their designee(s). The laboratory is responsible for assigning data qualifier codes (i.e. "flags") to the data prior to submission; allowable codes are given in Table 4. This list of codes is consistent with that used in the NOAA National Status and Trends Program and EPA EMAP Program. Any other qualifications of the data which the laboratory feels are not covered by the allowable codes (e.g., minor excursions outside of control limits where sample re-analysis was not justified or not possible) should be explained in the case narrative accompanying the data. In these instances, the QA Officer will decide if additional qualification of the data is needed in the project database.

## **8. Miscellaneous Recommendations**

Care should be taken during the processing of all tissue samples that enough material is extracted so that the dry-weight sample size is comparable (if enough tissue is available) to the sample size used to determine the method detection limit (MDL). This will insure that the MDLs are as low as possible for the sample analysis. In addition, care should be taken to assure that sufficient sample material is available to prepare duplicate and matrix spike samples as required.

Samples to be used to determine the MDL should be subject to review and acceptance of the Project Manager and QA Officer.

Records should be kept of dry:wet ratios of the various tissue matrices. These should be consulted before determining the amount of material to be analyzed.

In cases where there is not enough material for the analysis, the Project Manager should be consulted to determine if it is possible to pool the samples (from appropriate replicates) to obtain enough material for a valid analysis.

For inorganic analyses where the instrument detection limit (IDL) is determined from repeated analysis of a clean blank, a flag (f) should be used for reporting results obtained between the IDL and the MDL. This will provide the data user with the maximum flexibility for data usage, while maintaining CLP-style, standard procedures for data verification (see Table 4).

## **9. Summary**

This guide provides the rationale, conceptual basis, and technical approach for implementing quality assurance and quality control (QA/QC) procedures to assure that analytical chemistry data are capable of meeting the data quality objectives required for ecological risk assessments. Scientifically sound analytical chemistry data are needed to achieve the goal of assessing risk to ecological systems. Through the application of the performance-based quality assurance program described in this document, the performing laboratory is required to demonstrate proficiency through routine analysis of certified or well documented reference materials and is required to initiate corrective actions if their performance falls below minimal standards. The application of this protocol will provide the

information necessary to verify the quality of the data, validate the raw data, and assess the comparability of data generated by different laboratories with different analytical procedures.

## 10. Points of Contact

For more information on these and related issues, please contact:

The Marine and Environmental Support Office  
 MARINE ENVIRON SUPPORT OFC  
 SPAWARSYSCEN D3621  
 53475 Strothe Rd Rm 258  
 San Diego, CA 92152-6326  
 Voice: 619.553.5330 or 619.553.5331; DSN 553.5330 or 5331  
 POC: Ms. Sandra Harrell, D3621, Head (619) 553-2906

For technical information, please contact:

Dr. Robert Johnston 619.553.2213 (johnston@spawar.navy.mil)

## 11. Where to Find Further Information

Site/Topic	Link
American Society for Quality!	<a href="http://www.asqc.org/">http://www.asqc.org/</a>
EPA Chesapeake Bay Program Homepage	<a href="http://www.epa.gov/chesapeake/">http://www.epa.gov/chesapeake/</a>
EPA Data Quality Related Documents	<a href="http://www.epa.gov/superfund/programs/clp/quality.htm#qag5">http://www.epa.gov/superfund/programs/clp/quality.htm#qag5</a>
EPA EMAP Reports	<a href="http://www.epa.gov/emap/html/pubs/browseI.html">http://www.epa.gov/emap/html/pubs/browseI.html</a>
EPA EMAP Homepage	<a href="http://www.epa.gov/emap/">http://www.epa.gov/emap/</a>
EPA link to EMAP QA	<a href="http://www.epa.gov/emap/html/qc/qs.html">http://www.epa.gov/emap/html/qc/qs.html</a>
EPA Region X's Quality Assurance References	<a href="http://www.epa.gov/region10/www/offices/oea/qaindex.htm">http://www.epa.gov/region10/www/offices/oea/qaindex.htm</a>
EPA Contract Laboratory Program	<a href="http://www.epa.gov/oerrpage/superfund/programs/clp/index.htm">http://www.epa.gov/oerrpage/superfund/programs/clp/index.htm</a>
EPA Search the U.S. EPA Internet Site	<a href="http://www.epa.gov/epahome/search.html">http://www.epa.gov/epahome/search.html</a>
Federal Geographic Data Committee Content standards for digital spatial metadata (CSDGM Version 2 - FGDC-STD-001-1998) Washington, D.C.	<a href="http://www.fgdc.gov/metadata/constan.html">http://www.fgdc.gov/metadata/constan.html</a>

GAO Policy and Guidance Materials	<a href="http://www.gao.gov/policy/guidance.htm">http://www.gao.gov/policy/guidance.htm</a>
GLOSSARY OF WATER RESOURCES TERMS	<a href="http://vger.eng.clemson.edu/dc_glossary.html">http://vger.eng.clemson.edu/dc_glossary.html</a>
ISO 14000 Training. EARA ACCREDITED!	<a href="http://www.yankee.com/iso14001.htm">http://www.yankee.com/iso14001.htm</a>
National Research Council of Canada (NRC)	<a href="http://www.nrc.ca/corporate/english/index.html">http://www.nrc.ca/corporate/english/index.html</a>
NIST Certified Standard for marine sediment	<a href="http://ois.nist.gov/srmcatalog/certificates/view_cert2.cfm?certificate=1941a">http://ois.nist.gov/srmcatalog/certificates/view_cert2.cfm?certificate=1941a</a>
NIST National Institute of Technology 1999. Standard Reference Material (SRM) Program, U.S. Department of Commerce, Gaithersville, MD.	<a href="http://ts.nist.gov/ts/htdocs/230/232/232.htm">http://ts.nist.gov/ts/htdocs/230/232/232.htm</a>
NIST Standard Reference Material	<a href="http://dolphin.nist.gov/ts/htdocs/230/232/232/232.html">http://dolphin.nist.gov/ts/htdocs/230/232/232/232.html</a>
Quality Engineering & Manufacturing Association is dedicated to Aerospace, Military, Automotive and Commercial business professionals (ISO/QS/AS 9000 & ISO 14000).	<a href="http://www.tqm.com/">http://www.tqm.com/</a>
Quality Progress Magazine	<a href="http://qualityprogress.asqc.org/">http://qualityprogress.asqc.org/</a>
Stanford University's Data Administration Plan for Quality Assurance of Data, Process and Object Models	<a href="http://www.stanford.edu/group/da/QAPlan_WWW.html">http://www.stanford.edu/group/da/QAPlan_WWW.html</a>
The Community Quality Electronic Network aims to assist Community Quality Efforts by facilitating electronic communication.	<a href="http://deming.eng.clemson.edu/pub/cqen/files/">http://deming.eng.clemson.edu/pub/cqen/files/</a>
The Public Sector Network Hotlist	<a href="http://deming.eng.clemson.edu/pub/psci/psn/hotlist.html">http://deming.eng.clemson.edu/pub/psci/psn/hotlist.html</a>
Uncertainty Analysis Of Ecological Models	<a href="http://www.anl.gov/LabDB/Current/Ext/H076-text.001.html">http://www.anl.gov/LabDB/Current/Ext/H076-text.001.html</a>

US Govt. Search - United States  
Government Documents

<http://www.gpo.ucop.edu/search/cfr.html>

## 12. Glossary of Terms

(Unless otherwise noted, definitions of these terms were obtained from U.S. EPA and PSWQAT 1997a)

**Accuracy** - The agreement between an analytical result and the true value. The difference between a measured value and the true or expected value represents an estimate of systematic error or net bias.

**Analyte** - That which is analyzed.

**Assessment** - The evaluation process used to measure the performance or compliance of sampling and analysis activities.

**Audit** - A systematic and independent examination to determine whether sampling and analysis activities and related results comply with planned practices, whether these practices are implemented effectively, and whether the nature and extent of these practices are suitable for the sampling and analysis activities they support.

**Batch** - The number of samples that are prepared or analyzed with associated laboratory QC samples at one time. A typical batch size is 20 samples and may be dependent on the method.

**Bias** - The systematic or persistent distortion of a measurement process that causes errors in one direction.

**Blank-corrected Result** - Refers to an analytical result that has been corrected (mathematically or through analytical procedures) for the contribution of the method blank. The method blank should be processed concurrently. Any correction should account mathematically for all relevant weights, volumes, dilutions and other similar sample processing elements.

**Calibration** - The determination of the relationship between analytical response and concentration (or mass) of the analyte.

**Certified Reference Material** - A reference material accompanied by, or traceable to, a certificate stating the concentration of chemicals contained in the material. The certificate is issued by an organization, public or private, that routinely certifies such material (e.g., National Institute of Standards and Technology, American Society for Testing and Materials).

**Chain of Custody** - An unbroken trail of accountability that ensures the physical security of samples, data and records.

**Check Standard** - A QC sample prepared independently of calibration standards, analyzed exactly like the samples, and used to estimate analytical precision and indicate bias due to calibration.

**Coefficient of Variation** - The standard deviation expressed as a percentage of the mean. Also termed relative standard deviation or RSD.

**Comparability** - An indication of the confidence with which one data set can be compared to another.

**Completeness** - A measure of the amount of valid data obtained from sampling and analysis activities compared to the amount that was expected to be obtained.

**Control Limit(s)** - A value or range of values against which results of QC sample analyses are compared in order to determine whether the performance of a system or method is acceptable. Control limits are typically statistically derived. When QC results exceed established control limits, appropriate corrective action should be taken to adjust the performance of the system or method.

**Corrective Action** - Measures taken to remove, adjust, remedy or counteract a malfunction or error so that a standard or required condition is subsequently met.

**Data Quality Objectives (DQOs):** Qualitative and quantitative statements that clarify study objectives, define the appropriate type of data, and specify the tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (US EPA 1994c).

**Defensible** - the ability to withstand any reasonable challenge related to the veracity, integrity, or quality of the logical, technical, or scientific approach taken in a decision making process (US EPA 1994c).

**Duplicate Analysis** - Analysis performed on a second subsample in the same manner as the initial analysis, used to provide an indication of measurement precision.

**Elutriate** - A standard test used to predict the release of contaminants in sediment to a water column resulting from open water disposal of the sediment.

**False Negative Decision Error** - a false negative decision error occurs when the decision-maker does not reject the null hypothesis when the null hypothesis is actually false. In statistical terminology, a false negative decision error is also called a Type II error. The measure of the size of the error is expressed as a probability, usually referred to as "beta ( $\beta$ )"; this probability is also called the complement of power (US EPA 1994c).

**False Positive Decision Error** - a false positive decision error occurs when a decision-maker rejects the null hypothesis when the null hypothesis is actually true. In statistical terminology, a false positive decision error is also called a Type I error. The measure of the size of the error is expressed as a probability, usually referred to as "alpha ( $\alpha$ )," the "level of significance," or "size of the critical region" (US EPA 1994c)

**Field Blank** - A simulated sample (usually consisting of laboratory pure water) that is taken through all phases of sample collection and analysis. Results of field blank analyses are used to assess the positive contribution from sample collection and analysis procedures to the final result.

**Field (matrix) spike** — A sample prepared at the sampling point (i.e., in the field) by adding a known mass of the target analyte to a specified amount of the sample. Field matrix spikes are used, for example, to determine the effect of the sample preservation, shipment, storage, and preparation on analyte recovery efficiency (the analytical bias) (US EPA 1998b).

**Field split samples** — Two or more representative portions taken from the same sample and submitted for analysis to different laboratories to estimate interlaboratory precision (US EPA 1998b).

**Guideline** - A suggested practice that is non-mandatory.

**Holding time** - The period of time a sample may be stored prior to its required analysis. While

exceeding the holding time does not necessarily negate the veracity of analytical results, it causes the qualifying or “flagging” of any data not meeting all of the specified acceptance criteria (US EPA 1998b).

**Hypothesis** - A tentative assumption made to draw out and test its logical or empirical consequences. In hypothesis testing, the hypothesis is labeled "null" or "alternative", depending on the decision-maker's concerns for making a decision error.

**Isotope Dilution Technique** - An internal standard technique for quantification of organic compounds that uses a large number of stable isotopically labeled compounds spiked into the sample before extraction to provide recovery correction (i.e., to correct for compound loss during sample workup on a sample-specific basis). The labeled compounds are analogs of the target compounds and are assumed to behave similarly. The isotopic labels typically involve replacement of hydrogen atoms with deuterium or replacement of carbon-12 atoms with carbon-13 atoms.

**Laboratory split samples** - Two or more representative portions taken from the same sample and analyzed by different laboratories to estimate the interlaboratory precision or variability and the data comparability (US EPA 1998b).

**Limit of Quantitation (LOQ)** - The minimum concentration of an analyte or category of analytes in a specific matrix that can be identified and quantified above the method detection limit and within specified limits of precision and bias during routine analytical operating conditions (US EPA 1998b).

**Matrix** - The sample material in which the analytes of interest are found (e.g., water, sediment, tissue).

**Matrix Spike** - A QC sample created by adding known amounts of analytes of interest to an actual sample, usually prior to extraction or digestion. The matrix spike is analyzed using the normal analytical procedures. The result is then corrected for the analyte concentration determined in the unspiked sample and expressed as a percent recovery. This provides an indication of the sample matrix effect on the recovery of target analytes.

**Must** - A requirement that has to be met.

**Method** - A body of procedures and techniques for performing an activity that is systematically presented in the order in which they are to be executed.

**Method Blank** - A QC sample intended to determine the response at zero concentration of analyte. A clean matrix (generally water) known to be free of target analytes that is processed through the analytical procedure in the same manner as associated samples.

**Method Detection Limit** - The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing the analyte Code of Federal Regulations (40 CFR Part 136).

**Normalize** - Perform a data calculation in order to express results in terms of a reference parameter or characteristic.

**Precision** - The statistical agreement among independent measurements determined from repeated applications of a method under specified conditions. Usually expressed as RPD, RSD or

coefficient of variation.

**Project** - An organized set of activities within a program.

**Quality Assurance** - An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item or service is of the type and quality needed and expected by the customer.

**Quality Control** - The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process. Quality Control is an element of quality assurance. Analyses of QC samples and auditing/assessment are common quality control activities.

**Qualified Data** - Data to which data qualifiers have been assigned. Data qualifiers provide an indication that a performance specification in the qualified sample or an associated QC sample was not met.

**Quality Assurance Project Plan** - A formal planning document describing in comprehensive detail the necessary QA, QC and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

**Quantification** - The process of calculating the value of an analyte in a particular sample.

**Recovery** - The percentage difference between two measurements, before and after spiking, relative to the concentration spiked.

**Replicate** - One of several identical experiments, procedures or samples.

**Reproducibility** - The ability to produce the same results for a measurement. Often measured by determining the RPD, RSD or coefficient of variation for an analysis.

**Representativeness** - A measure of the degree to which data accurately and precisely represent an environmental characteristic or condition.

**Reproducibility** - The precision, usually expressed as variance, that measures the variability among the results of measurements of the same sample at different laboratories (US EPA 1998b).

**Requirement** - A formal statement of a need and the expected manner in which it is to be met (US EPA 1998b).

**Reference Material** - A material of known analyte composition which can be used for comparison of analytical results. The reported analyte concentrations have not been certified (see Certified Reference Material).

**Relative Percent Difference (RPD)** - Difference of two measurements  $x_1$  and  $x_2$ , divided by the mean of the measurements, multiplied by 100.

**Percent RSD** - Calculated by dividing the standard deviation by the mean and multiplying by 100.

**Relative Standard Deviation** - see coefficient of Variation.

**Semivolatile Organic Compounds** - Gas chromatographable organic compounds with moderate or low vapor pressures that can be extracted from samples using organic solvents.

**Should** - Refers to a highly recommended practice. The practice may be mandatory, depending on the exact conditions of data generation.

**Spike** - A substance that is added to an environmental sample to increase the concentration of target analytes by known amounts; used to assess measurement accuracy (spike recovery). Spike duplicates are used to assess measurement precision (US EPA 1998b).

**Split samples** - Two or more representative portions taken from one sample in the field or in the laboratory and analyzed by different analysts or laboratories. Split samples are quality control (QC) samples that are used to assess analytical variability and comparability (US EPA 1998b).

**Standard** - A substance or material, the properties of which are believed to be known with sufficient accuracy to permit its use to evaluate the same property of a sample. In chemical measurements, standard often describes a solution of analytes used to calibrate an instrument.

**Standard Reference Material** - A material with known properties produced and distributed by the U. S. National Institute of Standards and Technology (NIST).

**Standard Operating Procedure (SOP)** - A written document that details the method for an operation, analysis, or action with thoroughly prescribed techniques and steps and that is officially approved as the method for performing certain routine or repetitive tasks (US EPA 1998b).

**Surrogate Spike Compound** - A compound that has characteristics similar to that of a compound of interest, is not expected to be found in environmental samples, and is added to a sample prior to extraction. The surrogate compound can be used to estimate the recovery of chemicals in the sample.

**Target Analytes** (or Target Compounds) - One or more elements or compounds which are intended to be determined by an analytical procedure (in contrast to tentatively identified compounds).

**Tentatively Identified Compounds** - Chemicals identified in a sample on the basis of mass spectral characteristics held in common with a reference mass spectra of a known chemical. These compounds cannot be more confidently identified unless a reliable standard of the compound is obtained and is confirmed to co-elute with the tentatively identified compound and generate similar mass spectra using the same GC/MS.

**Type I error** - A Type I error occurs when a decision-maker rejects the null hypothesis when it is actually true. See false positive decision error (US EPA 1994c).

**Type II error** - A Type II error occurs when the decision-maker fails to reject the null hypothesis when it is actually false. See false negative decision error (US EPA 1994c).

**Validation** - Confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. Can refer to a process whereby environmental data are determined by an independent entity to be complete and final (i.e., subject to no further change), and to have their value for the intended use described by both qualitative and quantitative statements.

**Volatile Organic Compounds** - Organic compounds with high vapor pressures that tend to evaporate readily from a sample.

Table 1. Data quality objectives for analytical chemistry analyses performed for ecological risk assessments.

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**Step 1 – State the problem.** The analysis goals of an ecological risk assessment require analytical methods (1) that are capable of detecting chemicals below levels that can cause ecological effects as well as levels associated with background or naturally occurring concentrations, (2) that are capable of differentiating chemical levels from interferences due to sample matrices, and (3) that can be reliably reproduced and verified. The analytical methods must provide data that are scientifically sound and which can meet the representativeness, completeness, comparability, accuracy, and precision required for the risk assessment.

**Step 2 – Identify the decision.** Define quality assurance and quality control (QA/QC) procedures that will allow the data to be evaluated, to the extent possible, for representativeness, completeness, comparability, accuracy, and precision.

**Step 3 – Identify inputs to the decision.** A performance-based QA/QC procedure will be implemented that will allow the analytical data to be evaluated and verified for representativeness, completeness, comparability, accuracy, and precision. The procedure should be independent of laboratory, analytical instrumentation, and samples to be processed. A quality assurance plan will be developed to document the procedures to be used.

**Step 4 – Define boundaries.** Field samples will be organized into batches of samples, organized by sample matrix and analyte(s) to be measured. A predefined set of QA/QC samples will be included in the batch and subjected to the same procedures as that of the field samples with regard to sample prep, extraction/digestion, and instrument analysis. The QA/QC samples to be used will be defined in the quality assurance plan.

**Step 5 – Develop decision rule.** The results obtained from the QA/QC samples will be used to judge the quality and usability of the data. If results indicate deviation from the expected accuracy and precision, corrective action must be taken. Appropriate corrective action will be defined in the quality assurance plan.

**Step 6 – Specify tolerable limits on decision errors.** Laboratories conducting the analyses will be required to demonstrate proficiency through routine analysis of accuracy-based materials. Ongoing performance evaluation exercises will be conducted to demonstrate initial capability (i.e., prior to the analysis of actual samples) and on a continuous basis throughout the project. The laboratory will be required to initiate corrective actions if their performance falls below certain predetermined minimal standards defined in the quality assurance plan.

**Step 7 – Optimize the design.** Based on the results obtained, the quality assurance plan will be updated to reflect realized performance criteria and allow for improvements in analytical methods and instrumentation.

Table 2. The Quality Assurance and Quality Control (QA/QC) elements, warning and control limits, and frequency of use for analytical chemical analysis of samples for ecological risk assessments.

QA/QC Element	Limit <sup>a</sup>			
	Warning	Control	Frequency	
<b>1. Performance Evaluation<sup>b</sup></b>				
Initial Calibration	NA <sup>c</sup>	NA	Initial	
Documentation of Detection Limits	NA	See Table 3	Once per year for every analyte and each matrix	
Blind Analysis of Sample Matrices <sup>d</sup>				
Organic	80%-120% <sup>e</sup>	70%-130%	Initial	
Inorganic	90%-110%	85%-115%	Initial	
<b>2. Ongoing Demonstration of Capability Analysis of SRMs, CRMs or LCMs<sup>f</sup></b>				
	Recovery of Each Analyte <sup>g</sup>	Percent Allowed Out <sup>h</sup>	Overall Average Recovery <sup>i</sup>	Frequency
PAH fraction	±40%	<35%	±35%	1 per Batch
PCB/Pesticide fraction	±40%	<35%	±35%	1 per Batch
Metals (excluding Hg)	±20%	<15%		1 per Batch
Hg	±25%			1 per Batch
<b>3. Calibration Check (CC)</b>				
	Warning	Control	Frequency	
Organic	80%-120% <sup>j</sup>	75%-135%	Beginning and end of each batch and every 10 samples	
Inorganic (excluding Hg)	90%-110%	85%-115%		
Hg	80%-120%	80%-120%		
<b>4. Method Blank (MB)</b>				
	Warning	Control	Frequency	
All analytes	MDL ≤ 3MDL	≥ 3MDL	one per batch	
<b>5. Matrix Spike (MS)<sup>k</sup></b>				
	Warning	Control	Frequency	
All analytes	±50%	NA <sup>l</sup>	one per batch	
<b>6. Laboratory Duplicate (DUP)<sup>m</sup></b>				
	Control	Percent Allowed Out	Frequency	
Organic	±30% RPD <sup>n</sup>	35%	one per batch	
Inorganic (excluding Al and Fe)	±30% RPD	35%	one per batch	
Al and Fe	±50% RPD	NA	one per batch	

Continued next page.

Table 2. Continued.

QA/QC Element	Limit		
	Warning	Control	Frequency
7. Internal Standards <sup>o</sup>	Warning	Control	Frequency
Organics <sup>p</sup>	Outside of 30-130% recovery	>50% difference between CRM and sample recoveries	each sample
8. Injection Standards	Warning	Control	Frequency
Organics <sup>q</sup>	Lab Develops Own	Lab Develops Own	each sample
9. Interlaboratory Calibration <sup>r</sup>	Warning	Allowed Out	Frequency
all matrices all analytes	greater than a factor of 4	20%	5% of samples by matrix

<sup>a</sup> If there is a sufficient body of data available from laboratory experience and control charts, the recommended warning and control limits provided in this table may be refined and replaced. The warning and control limits will be subject to review and approval by the Project Manager and Project QA/QC Officers.

<sup>b</sup> Demonstration of Laboratory's capability before analysis of field samples.

<sup>c</sup> Not applicable (NA),

<sup>d</sup> Blind samples containing a known quantity of target compounds for each matrix to be analyzed should be sent to the laboratory to demonstrate capability prior to analyzing any field samples. Final acceptance is subject to review by the Project Managers and QA Officer. This requirement can be waived, if the laboratory can adequately demonstrate their capability.

<sup>e</sup> Percent of true value.

<sup>f</sup> In reporting results from the analysis of standard reference materials (SRMs) certified reference materials (CRMs) or laboratory control materials (LCMs) any data obtained which are below the LOQ are not to be used for computing control limits. However, it is necessary to report all the results obtained from the SRM analysis (even those below the LOQ). These data will make it possible to identify matrix problems and evaluate method performance.

<sup>g</sup> Percentage of "True" value. The "True" values from the CRM may be either "certified" or "noncertified." Absolute accuracy can only be evaluated using certified values, but relative accuracy can be evaluated with noncertified values. The laboratory's value should be compared to the 95% confidence interval reported by the certifying agency. The laboratory's value must be within  $\pm 40\%$  of either the upper or lower bound of that interval. Control limits are only applied to analytes with concentrations above the Limit of Quantification (LOQ).

<sup>h</sup> The number of individual compounds, isomers or elements of a particular fraction that are allowed to be out of control. Warning flags are issued (see Table 5) for the analytes that were out of control. In determining the percent of analytes allowed out, fractions may be rounded up to the nearest whole number.

<sup>i</sup> The average recovery of all the compounds or isomers of a particular fraction.

<sup>j</sup> Percent of true value.

<sup>k</sup> Care must be taken to spike the samples within the appropriate range for the analytes of concern. An attempt should be made to spike the samples such that the spike is no less than 4 times and no more than 2 times the sample value.

<sup>l</sup> No control limits are specified for matrix spike samples. If analytes fall outside of the  $\pm 50\%$  recovery they should be flagged accordingly and explained in the case narrative. If more than 30% of the analytes fail to meet the  $\pm 50\%$  recovery criteria, the batch must be considered for reprepping based on the other control criteria.

<sup>m</sup> Both the sample and duplicate must be above the LOQ before the relative percent difference (RPD) can be calculated. It is understood that there will be a higher amount of variability in RPDs calculated for analytes near the LOQ (at  $10\sigma$ ). Therefore discretion should be used in evaluating the control criteria for those cases.

<sup>n</sup> Relative Percent Difference (RPD)

<sup>o</sup> Internal standard recoveries are advisory limits. The laboratory must set its own warning and control limits based on the data obtained from control charts documenting recoveries. It is the responsibility of the analyst to demonstrate that the analytical process is always "in control". However, extremely low or high recoveries for the internal standards for any sample in the batch, or large differences ( $>50\%$ ) between the recoveries obtained for the SRM and individual samples would be grounds for reprepping the batch, based on the results of the other control criteria.

<sup>p</sup> It is recommended that d10-phenanthrene, d12-benzo(a)anthracene, and d12-perylene for the PAHs and PCB 103 and PCB 198 for the PCBs be used for internal standards, if possible, to improve method accuracy and precision.

<sup>q</sup> The Laboratory must monitor the performance of injection standards with control charts to verify that the analysis is in control.

<sup>r</sup> The purpose of the interlaboratory calibration is to provide an independent check on the accuracy of the analysis. Variations between laboratories, inhomogeneity of the samples, and the relatively low concentrations of many of the analytes will interfere with the results. Gross differences between the laboratories will be subject to review by the Project Managers and the Project QA/QC Officers to determine if corrective action is necessary.

Table 3. Target method detection limits (MDLs) for analytes of concern. Wet weight or dry weight (DW) of the MDL is specified. (A) The analytes, matrices, and target MDLs for organic compounds. (B) The elements, matrices, target MDLs, and "typical" marine minimum concentrations for the inorganic analytes.

<b>A. Organic Compounds<sup>a</sup></b>					
Analyte	Sample Matrix	Target MDL		Basis	
Volatile Organics (VOCs)	water	6.0	µg/L	wet volume	
Polycyclic Hydrocarbons (PAHs)	water	5.0	µg/L	wet volume	
	sediment	5.0	ng/g	dry weight	
	tissue	20.0	ng/g	dry weight	
Chlorinated Pesticides	water	0.6	µg/L	wet volume	
	sediment	0.6	ng/g	dry weight	
	tissue	0.6	ng/g	dry weight	
Polychlorinated Biphenyl Congeners (PCBS)	water	1.0	µg/L	wet volume	
	sediment	0.5	ng/g	dry weight	
	tissue	0.5	ng/g	dry weight	
Butyltins	water	0.2	ng/L	wet volume	
	monobutyltin (MBT)	sediment	2.0	ng/g	dry weight
	dibutyltin (DBT)	tissue	2.0	ng/g	dry weight
	tributyltin (TBT)				

(Continued Next Page)

Table 3. Continued.

**B. Inorganic Elements<sup>b</sup>**

Analyte	Sample Matrix	Target MDL <sup>c</sup>	Typical Concn. <sup>d</sup>	Basis
Aluminum (AL)	water	75.0 µg/L	2.0 µg/L	wet volume
	sediment	NS <sup>e</sup>	43.4 mg/g <sup>f</sup>	dry weight
	tissue	NS	76.0 µg/g <sup>g</sup>	dry weight
Arsenic (As)	water	3.0 µg/L	3.7 µg/L	wet volume
	sediment	1.1 µg/g	0.98 µg/g	dry weight
	tissue	4.3 µg/g	4.97 µg/g	dry weight
Cadmium (Cd)	water	0.2 µg/L	0.1 µg/L	wet volume
	sediment	0.35 µg/g	0.031 µg/g	dry weight
	tissue	0.055 µg/g	0.81 µg/g	dry weight
Chromium (Cr)	water	3.0 µg/L	0.3 µg/L	wet volume
	sediment	3.16 µg/g	1.8 µg/g	dry weight
	tissue	0.28 µg/g	0.66 µg/g	dry weight
Copper (Cu)	water	0.7 µg/L	0.1 µg/L	wet volume
	sediment	1.25 µg/g	2.35 µg/g	dry weight
	tissue	5.0 µg/g	6.3 µg/g	dry weight
Iron (Fe)	water	20.0 µg/L	2.0 µg/L	wet volume
	sediment	NS	22.6 mg/g <sup>h</sup>	dry weight
	tissue	NS	209.0 µg/g <sup>i</sup>	dry weight
Lead (Pb)	water	3.0 µg/L	0.5 µg/L	wet volume
	sediment	1.2 µg/g	1.8 µg/g	dry weight
	tissue	0.6 µg/g	0.43 µg/g	dry weight
Manganese (Mn)	water	0.5 µg/L	0.2 µg/L	wet volume
	sediment	NS	0.392 mg/g <sup>j</sup>	dry weight
	tissue	NS	6.0 µg/g <sup>k</sup>	dry weight
Mercury (Hg)	water	5.0 µg/L	0.03 µg/L	wet volume
	sediment	0.007 µg/g	0.004 µg/g	dry weight
	tissue	0.036 µg/g	0.02 µg/g	dry weight
Nickel (Ni)	water	3.0 µg/L	1.7 µg/L	wet volume
	sediment	1.08 µg/g	1.7 µg/g	dry weight
	tissue	0.73 µg/g	0.56 µg/g	dry weight
Tin (Sn)	water	3.0 µg/L	0.01 µg/L	wet volume
	sediment	1.75 µg/g	0.12 µg/g	dry weight
	tissue	NS		
Zinc (Zn)	water	0.1 µg/L	0.5 µg/L	wet volume
	sediment	2.15 µg/g	1.8 µg/g	dry weight
	tissue	11.65 µg/g	70.1 µg/g	dry weight

<sup>a</sup> For the organic compounds the MDL obtained should be within a factor of two of the target MDL. Final acceptance of the MDLs is subject to review by the Project Officer and the Project QA/QC officers. Specific analytes will be evaluated on a case-by-case basis.

<sup>b</sup> For inorganic compounds the MDL obtained should be within a factor of two of the target MDL, or alternatively, within a factor of two of the "typical" marine minimum concentrations. Final acceptance of the MDLs is subject to review by the Project Officer and the Project QA/QC officers. Specific elements should be evaluated on a case-by-case basis.

<sup>c</sup> The target MDLs for water samples were obtained from the detection limits reported for the NCBC Davisville risk assessment pilot study (Munns et al. 1991).

<sup>d</sup> The "typical" marine minimum concentrations for waters are those found in oceanic seawater (Brown et al. 1989). Unless otherwise specified, the "typical" marine minimum concentrations for sediments are the median of the detection limits reported for sediments from the Virginian Province (Strobel et al. 1995), and the "typical" marine minimum concentrations for tissues are the 5th percentile of the mussel watch data reported by the NOAA Status and Trends Program (O'Connor 1992).

<sup>e</sup> Not specified (NS) by this requirement.

<sup>f</sup> The median concentration of Al reported for sediments from the Virginian Province (Strobel et al. 1995).

<sup>g</sup> The minimum concentration of Al reported for mussels from the Great Bay Estuary, NH and ME (Johnston et al. 1994).

<sup>h</sup> The median concentration of Fe reported for sediments from the Virginian Province (Strobel et al. 1995).

<sup>i</sup> The minimum concentration of Fe reported for mussels from the Great Bay Estuary, NH and ME (Johnston et al. 1994).

<sup>j</sup> The median concentration of Mn reported for sediments from the Virginian Province (Strobel et al. 1995).

<sup>k</sup> The minimum concentration of Mn reported for mussels from the Great Bay Estuary, NH and ME (Johnston et al. 1994).

Table 4. Example data flags. The final determination of the data flags and when they are to be used is subject to review and approval by the Project Manager and the Project QA officer.

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A. ORGANICS and INORGANICS.

Code	Description
a	analyte was not detected below the MDL shown
b	reported value is below the LOQ
c	not reported due to matrix interference
d	not quantified
e	not reported
f	reported value is below the MDL
h	quantification based on alternate internal standard
j	analysis performed with selected ion monitoring
p	value shown may be biased as determined by recovery of analyte in reference material

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B. INORGANICS Additional flags allowed:

Code	Description
n	the spike recovery is out of control
s	the sample was analyzed by method of standard addition
w	the analytical spike was outside of 85-115% recovery
*	the duplicate was out of control
+	the correlation of 0.995 was not met for the method of standard addition

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Table 5. Recommended batch size of 16 field samples. Example of the minimum (5%) QA/QC samples required for the analysis of a hypothetical batch of 16 field samples.

Sample Prep		
Sample	Number	Description
S1, S2, S3, ..., S16	16	Field Samples
SRM	1	Standard Reference Material <sup>a</sup>
DUP	1	Laboratory Duplicate
MS	1	Matrix Spike
MB	1	Method Blank
Total ES1, ..., ES20	20	Samples to be Extracted or Digested
Sample Extraction/Digestion		
Sample	Number	Description
SEQUENCE OF ANALYSIS		
CC1	1	Calibration Check
ES1, ..., ES10	10	Extracted Samples
CC2	1	Calibration Check
ES11, ..., ES20	10	Extracted Samples
CC3	1	Calibration Check
Total	23	Analytical Analyses

<sup>a</sup> If appropriate, the SRM can be substituted with a CRM or LCM sample.

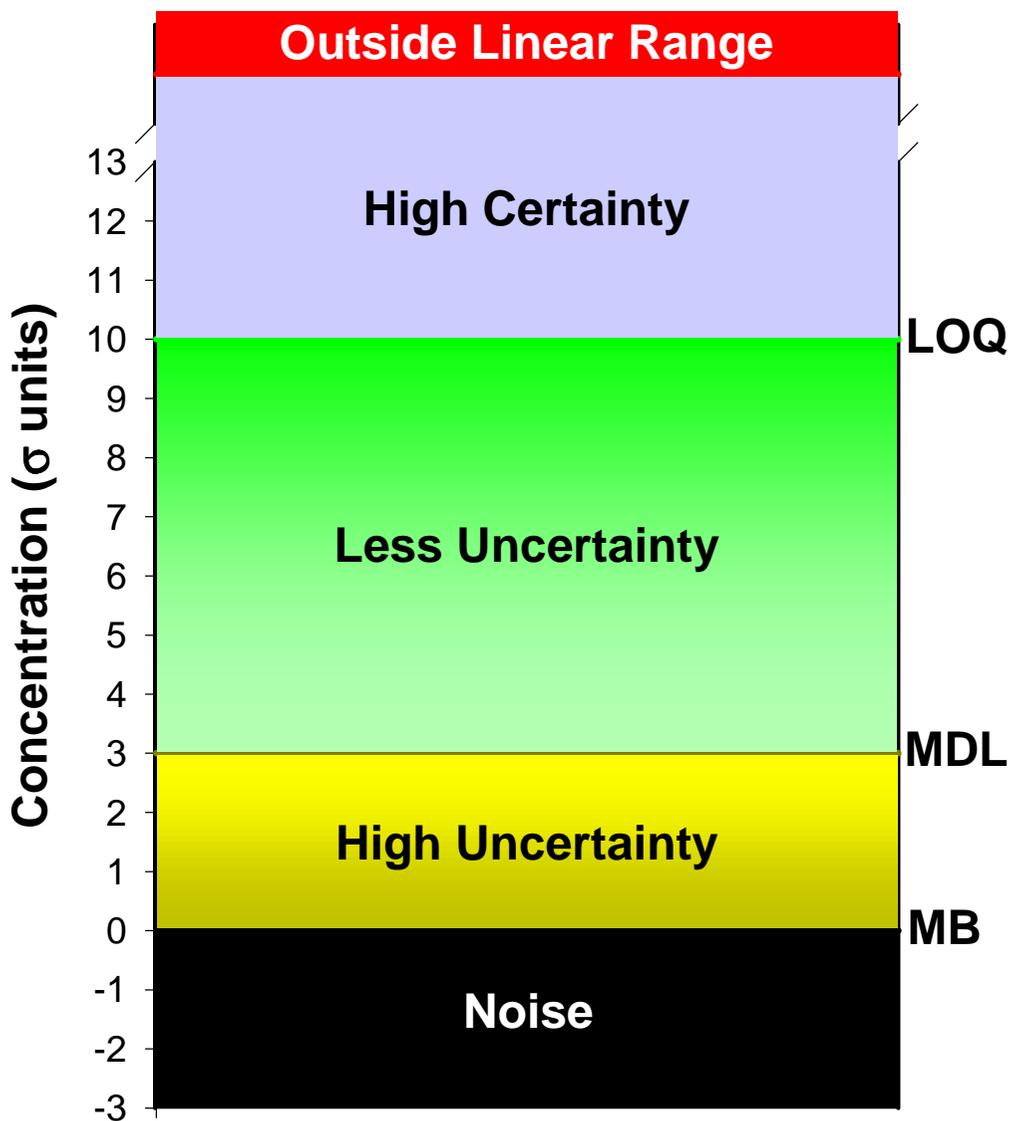


Figure 1. The relationship of the Method Blank (MB), Method Detection Limit (MDL), and the Limit of Quantification (LOQ) to certainty associated with the concentration of the analyte measured. The y-axis represents signal strength in units of the standard deviation ( $\sigma$ ) used to determine the MDL. Measurement results obtained below the MB are not distinguishable from noise. Results that are above the MB but less than the MDL are highly uncertain, while there is less uncertainty for results between the MDL and LOQ. Results above the LOQ and within the linear range (not off scale) are highly certain. Adapted from Keith 1991b.

## 15. Appendix

### 15.1 Data Deliverable Specification

#### DATA DELIVERABLE

##### 1. INTRODUCTION

This specification identifies the data deliverable required for reporting the results of routine chemical analysis conducted according to the QA/QC specifications of MESO Technical Memorandum MESO99-01.

##### 2. DATA REPORT -- HARDCOPY

The Data Report contains a hardcopy documentation of the final results and appropriate flags for each sample analyzed, along with all supporting data validation information. Data validation information includes instrument tuning and calibration, blank and spike recoveries, and all other quality control data, developed on a batch-by-batch basis. A narrative will be prepared for each batch which describes the key performance criteria evaluated to validate the batch as well and any discrepancies or deviations from the QA/QC plan. Any corrective measures taken during the analysis will also be documented in the narrative. The data report will also contain hardcopies of the contents of the Data Diskettes.

##### 3. DATA DUMP -- DATA DISKETTE

The Data Dump will consist of information provided on a 3.5 inch, PC-compatible diskette. The following information will be contained on the diskette:

A. Data Files (\*.DAT). ASCII text files with column or comma delimited fields. Data files should not contain any tabs or other control characters. Missing values should be entered as blanks for column-delimited files, or null values for comma delimited files.

- (1) DATA RECORD. A data record, which provides all the information for one sample, shall consist of an explicitly defined number of rows and columns in the file and shall be consistent through out the data file. The minimum information required per record includes:
  - (a) All pertinent sample identification and tracking information (e.g. field sample ID, lab sample ID, batch ID number, sample replicate or duplicate number, date sampled and received, etc.) and should be cross-referenced to the appropriate chain-of-custody information;
  - (b) Sample information (sample matrix, weight/volume, moisture/solid content, units of measure, color, texture, etc.);
  - (c) Analytical results (in concentration per dry weight or volume) and analytical flag (if applicable). Nondetected results should be reported as values and flagged according to the QA/QC plan.

(2) DATA FILES may be arranged according to the analysis type (e.g. metals, PAHs, PCBs, Pesticides, etc.)

(3) DATA FILES must contain unique identifier, or combination of identifiers, to uniquely identify each record.

(4) DATA FILES must be fully documented with a corresponding VARIABLE FILE (see below).

(5) DATA FILES prepared shall include the following:

- (a) **SAMPLE RESULTS.** A data file which contains the validated results of all field and duplicate samples. Each record should contain the concentration and QA/QC flag obtained for each analyte measured for the analysis type being reported.
- (b) **BLANK RESULTS.** A data file which contains the validated concentrations obtained from analysis of blanks. Nondetected values should be reported as either background or zero, which ever is more appropriate for the analyte of the analysis type being reported. Each record for the blanks must be cross-referenced to the sample results for which the blank results apply (eg. by batch ID number).
- (c) **REFERENCE STANDARD RESULTS.** A data file which contains the validated concentrations obtained from the analysis of SRM or CRMs. The first record of the file should contain the ID and certified and noncertified concentrations of the SRM/CRM used for the analytes of the analysis type being reported. Nondetected values should be reported as either the instrument detection limit (IDL) or method detection limit (MDL) and flagged accordingly. Each record for the Reference Standard Results must be cross-referenced to the corresponding sample results (eg. by batch ID number).
- (d) **SPIKE RECOVERIES.** A data file which contains the validated concentrations obtained from analysis of spiked matrices. The first record of the file should contain identification of the spike and the known concentrations of the spike used. Nondetected values should be reported as IDL or MDL concentrations and flagged accordingly. Each record for the spikes must be cross-referenced to the corresponding sample results (eg. by batch ID number).
- (e) **OTHER CONTROL DATA.** A data file which contains the validated results obtained from the analysis of laboratory control materials which are used to validate the sample results. Laboratory control materials are those which are used by the performing laboratory on a routine basis to validate sample results. Each record must be cross-referenced to the corresponding sample results (eg. by batch ID number).

B. VARIABLE FILES (\*.VAR). An ASCII text file created for each data file (\*.DAT) which documents the contents of the data file. The variable file contains the following minimum number fields:

1. HEADER:

FILENAME - variable file name (\*.VAR)

DATA FILENAME - data filename (\*.DAT)

AUTHOR/PI - author or principal investigator who created the file, affiliation, address and phone number.

COMMENT - describes the nature of the data and identified the performing laboratory

QA Check: Identifies person (and date) who verified the accuracy of the information contained in both the data and variable files.

2. DATA TYPES and RECORD LENGTH: Documents record length and data types (integer, character, fixed decimal, etc.) used in the file.

3. VARIABLE LIST. Presents the variable names, column positions, data type, and descriptions in a tabular format. The description should include units of measure, allowable ranges, and any other information necessary to understand the data values.

4. DATA FLAGS. Documents data qualifier codes used to flag variables.

5. META DATA: As identified in Federal Register 48 (191): 30503

(a) INTENDED USE: The intended use of the data and the associated acceptance criteria for data quality (precision, accuracy, representativeness, completeness, comparability)

(b) CORRECTNESS: Project requirements for precision, accuracy, representativeness, completeness, comparability, and how these will be determined.

(c) SAMPLE COLLECTION/PREPARATION: Procedures for selection of samples or sampling sites and collection or preparation of samples.

(d) SAMPLE HANDLING AND STORAGE: Procedures for sample handling, identification, preservation, transportation, and storage.

(e) MEASUREMENT METHOD AND PERFORMANCE CHARACTERISTICS: Description of measurement methods or test procedures with a statement of performance characteristics if methods are nonstandard.

(f) QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES: Standard quality assurance / quality control procedures (e.g. American Society for Testing Materials, American Public Health Association standard procedures) to be followed. Non-standard procedures must be documented.

(g) DATA REDUCTION AND REPORTING: Data reduction and reporting

procedures, including description of statistical analyses to be used.

6. OTHER. Other information deemed appropriate by the investigator. (Could include ASCII text versions of the hardcopy case narratives, if appropriate).

#### 4. EXAMPLES.

Examples of properly formatted and documented data deliverables can be provide upon request.

## 5. EQUIVALENT DATA DELIVERABLE.

The performing laboratory may develop its own data deliverable if:

- A. The proposed data deliverable contains the information and data according to the minimum reporting requirements identified above, in an equivalent format; and
- B. The proposed data deliverable format is approved by the Technical Coordinator prior to submission. The Technical Coordinator will work with the performing laboratory to assure that the data deliverable meets the specifications of this requirement in the most cost-effective manner.