EPA/540/G-90/004
OSWER Directive 9360.4-01
April 1990

QUALITY ASSURANCE/QUALITY CONTROL GUIDANCE FOR REMOVAL ACTIVITIES

SAMPLING QA/QC PLAN
and
DATA VALIDATION PROCEDURES

Interim Final

Environmental Response Team
Emergency Response Division

Office of Emergency and Remedial Response
U.S. Environmental Protection Agency
Washington, DC 20460

Disclaimer

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Preface

This document, Quality Assurance/Quality Control Guidance for Removal Activities, consists of two parts: Part I - Sampling QA/QC Plan and Part II - Data Validation Procedures. The purpose of the Sampling QA/QC Plan is to provide guidance in establishing, implementing, and using QA/QC protocols for data collection activities performed under the Removal Program. The purpose of the Data Validation Procedures is to provide guidance in reviewing laboratory data packages according to the guidance established by the Sampling QA/QC Plan.

The policies and procedures established in this document are intended solely for the guidance of government personnel. They are not intended, and cannot be relied upon, to create any rights, substantive or procedural, enforceable by any party in litigation with the United States. The Agency reserves the right to act at variance with these policies and procedures and to change them at any time without public notice.

Questions, comments, and recommendations are welcomed regarding the QA/QC Guidance for the Removal Program. Send remarks to :

Mr. William A. Coakley
Removal Program QA Coordinator
U.S. EPA - ERT
Raritan Depot - Building 18, MS-101
2890 Woodbridge Avenue
Edison, NJ 08837-3679

Quality Assurance/Quality Control Guidance for Removal Activities EPA Work Group

EPA Headquarters

Office of Emergency and Remedial Response	William Coakley Duane Geuder Tom Kady

EPA Regional

Region 6:	Bob Forrest
Region 8:	Rick Edmonds John Geidt Peter Stevenson
Region 10:	Jim Everts

Other Organizations

ICF Kaiser Engineers	Peter Mavraganis Regina Prevosto Joann Sabak Joseph Tang
Roy F. Weston	Christine Andreas Kenda Layne John Mateo
Ecology and Environment	Michael Bray Bill Carberry Bob Marguccio Glenn Scherb

In addition to the work group members, helpful suggestions and comments on the draft document were provided by the following as well as other EPA and contractor staff.

Carla Dempsey (Hazardous Response Support Division, OERR)
Anibal Diaz (Region 2 TAT, Roy F. Weston)
Owen Douglass (Zone 1 ZPMO, Roy F. Weston)
Donnissa Duvic (Region 4 TAT, Roy F. Weston)
David Friedman (Office of Solid Waste)
John Geidt (Region 8, Environmental Services Division)
Jerry McKenna (Region 2, Environmental Services Division)
Tim Ott (Region 1 TAT, Roy F. Weston)
Diane Terry (ZPMO, Roy F. Weston)
Donald Zelazny (Zone II ZPMO, Ecology and Environment)

TABLE OF CONTENTS

PART I: SAMPLING QA/QC PLAN

LIST OF TABLES

TABLE OF CONTENTS

PART II: DATA VALIDATION PROCEDURES

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

PART I

SAMPLING QA/QC PLAN

1.0 Introduction

Part I provides a detailed description of each section to be contained in a "Sampling QA/QC Plan." The development of the Sampling QA/QC Plan is the responsibility of the On-Scene Coordinator (OSC). The OSC reviews and approves the site-specific plan and may obtain assistance from the Regional QA Officer. This guidance will help ensure that reliable, accurate, and quality data are obtained through field sampling efforts as well as field and laboratory analytical services. The document to be produced from this guidance is neither intended to supersede nor replace the QA Project Plan; however, it is intended to augment the project plan by detailing site-specific information regarding sampling, analysis, and QA protocols.

Note: QA/QC and QA are interchangeable terms used throughout the guidance document.

1.1 Purpose

The purpose of this document is to provide guidance in establishing, implementing, and using quality assurance/quality control (QA/QC) protocols for data collection activities performed under the Removal Program.

1.2 Background

Agency policy requires that all EPA organizational units, including program offices, EPA regional offices, and EPA laboratories, that perform environmentally related measurements, participate in a centrally managed quality assurance (QA) program, as stated in the Administrator's Memorandum of May 30, 1979. This requirement applies to all environmental monitoring and measurement efforts mandated or supported by EPA through regulations, grants, contracts, or other formal means not currently covered by regulation. The responsibility for developing, coordinating, and directing the implementation of this program has been delegated to the Office of Research and Development (ORD), which has established the Quality Assurance Management Staff (QAMS) for this purpose. As stated in EPA Executive Order 5360.1, "Policy and Program Requirements to Implement the Mandatory Quality Assurance Program," the primary goal of the QA program is to ensure that all environmentally related measurements performed or supported by EPA produce data of **known quality**. *The quality of data is known when all components associated with its derivation are thoroughly documented, with such documentation being verifiable and defensible.*

As part of their participation in the Agency-wide QA program, program offices are required to establish their own "QA Program Plan." This plan is to be prepared and annually updated based on guidelines established by QAMS. It specifies the quality of data required from environmentally related measurements and provides sufficient resources to assure that an adequate level of QA is performed. The program plan is established at the Headquarters EPA level. For the Removal Program, the responsibility for the program plan lies with the Office of Emergency and Remedial Response (OERR). In addition to program plans, plans need to be developed for each regional office. These plans are similar to the program plans, but are tailored to the specific operational needs of the regional office. The program and regional plans are both broad in scope and merely provide the objectives and resources for undertaking environmentally-related measurements.

The most specific element of QA documentation is the QA Project Plan (see Figure 1). A QA Project Plan specifies

the policies, organization (where applicable), objectives, functional activities, and specific QA and QC activities designed to achieve the data quality goals of a specific project(s) or continuing operation(s). The QA Project Plan is required for each specific project or continuing operation (or group of similar projects or continuing operation(s)). Guidance for preparing such plans is contained in "Guidelines and Specifications for Preparing Quality Assurance Project Plans" (also known as QAMS-005), which was developed by QAMS. This document describes sixteen elements that must be considered for inclusion in all QA Project Plans.

To meet the requirement for a QA Project Plan in the removal program, the Emergency Response Division of OERR established a QA Workgroup to provide guidance. The workgroup decided that the QA Project Plan would be divided into two functional documents: a generic "Branch QA Project Plan," and a site-specific "Sampling QA/QC Plan." When combined, both documents address the sixteen elements described in QAMS-005. The Branch QA Project Plan will be prepared by each regional removal branch and will address only those elements generic to all activities occurring within the Region; the Sampling QA/QC Plan will be prepared for each site where sampling will be performed and address those elements specific to the site, such as sample collection and analysis. The Branch Plan should be updated periodically to reflect any operational changes in the Region. The Sampling QA/QC Plan should be prepared for each site and updated (amended) when the scope of work changes significantly from the scope of work described in any previous plan. Elements that are not addressed in the Sampling QA/QC Plan are included in the Branch Plan. For emergency responses, a Sampling QA/QC Plan is required to be submitted no later than 30 days after the response date for documentation purposes.

The intent of this document is to provide guidance on developing a site specific "Sampling QA/QC Plan" and assessing and substantiating data for various data users. The guidance is not intended to address field and lab QC practices. It is assumed and expected that field samplers and analytical labs will follow approved methods (with their inherent QC checks) and adhere to generally accepted "good laboratory practices."

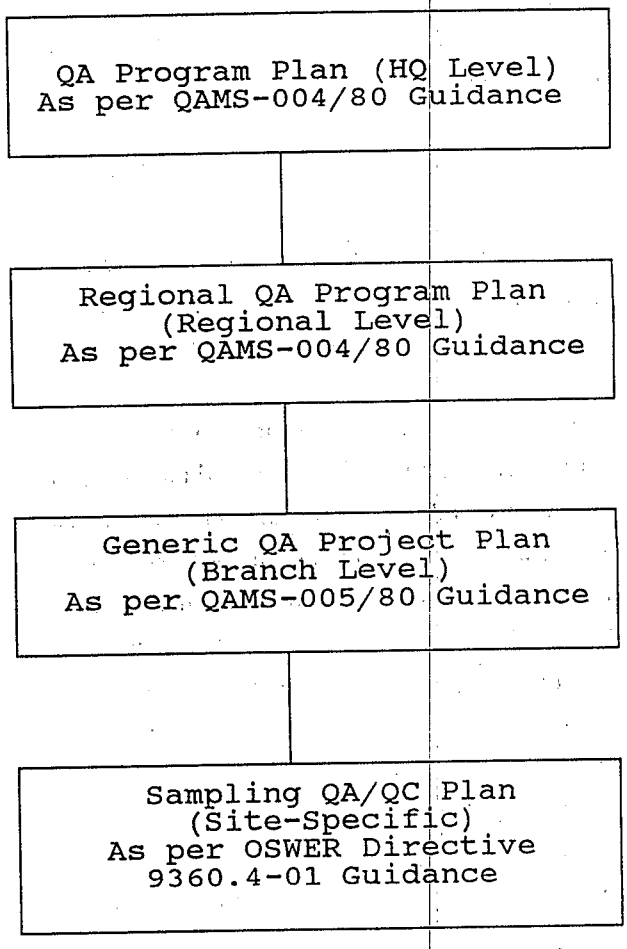

Figure 1: EPA Quality Assurance Documentation

This guidance has been designed to allow for the greatest possible variation in monitoring strategies. However, it is

recognized that occasionally certain quality assurance requirements cannot be met. In such cases, the reason for the deviation should be stated in the Sampling QA/QC Plan along with the expected or observed impact on the data.

1.3 Analytical Methods and Data Quality

The quality of data is determined by its accuracy and precision against prescribed requirements or specifications, and by its usefulness in assisting the user to make a decision or answer a question with confidence. The use of any one particular analytical method or instrument, therefore, cannot determine the quality of data obtained without an evaluation of the analytical accuracy (qualitative and quantitative) of the data and of the relevance (representativeness) of the data to user needs. Likewise, certain analytical methods may provide more information than other methods, but not necessarily better quality data.

To illustrate, a gas chromatograph/mass spectrometer method provides more information than a gas chromatograph method, which in turn provides more information than a spectrophotometer method. *However more information is not synonymous with accurate or useful data.* Analytical quality is dependent on analytical accuracy; that is to say that there is a degree of confidence associated with the data. The term accuracy refers to both the correctness of the concentration value and the qualitative certainty that an analyte is present.

This guidance is based on the idea that the use of any one particular analytical method or instrument does not determine the quality of data obtained. This guidance prompts the data collector to define the data quality within a framework that also incorporates the intended use of the data.

The guidance is structured around three quality assurance objectives. Each quality assurance objective is associated with a list of minimum requirements. Therefore, any method or analytical instrument that can meet the quality requirements can be used for any one of the objectives.

For example, if a spot test method was able to meet the requirements for QA3 (i.e., identify the specific analyte, determine the true concentration, and determine the error), then the spot test would not only be a valid method but it would give the same quality of data of a mass spectrometer (assuming the mass spectrometer method met all the QA3 requirements). It is anticipated that QA1 and QA2 will satisfy most data quality requirements for the Removal Program. QA3 is expected to be used only in those cases where an error determination is needed to identify false negative or false positive values for critical decision level concentrations.

2.0 Elements of a Sampling QA/QC Plan

The Sampling QA/QC Plan should contain the following sections:

- Title page
- Background
- Data Use Objectives
- Quality assurance objectives
- Approach and sampling methodologies
- Project organization and responsibilities
- Quality assurance requirements
- Deliverables
- Data validation

2.1 Title Page

The title page should include the name of the site/project, the contract and work order numbers (if the plan is being prepared by contractors), the contractor name, the date, key project personnel, and the approval signatures of the OSC and other appropriate persons. (Although it is recommended that the QA Sampling Plan be reviewed by Regional QA staff, it is not necessary that the plan be approved by the Regional QA officer.)

2.2 Background

This section should provide a brief description of the events or occurrences that led to the initiation of the sampling activity. This section may list chemicals which possibly contributed to the suspected contamination, including the suspected range of contamination, the sampling area size and proximity to local residents, or any other information that may be useful in an assessment of the situation and determination of QA, sampling, or analytical needs, possible contacts and existence of access agreements. Sources of such data include inventories, manifests, or other records; prior sampling data, such as that generated by an RI/FS; geological surveys; and incidents of exposure.

2.3 Data Use Objectives

Before any sampling activity is conducted, the intended use of the data must be determined. Careful consideration of intended data use is critical because it will affect the QA objective chosen and thereby maximize the probability of making a correct decision based on the analytical results. The decisions to be made, questions to be addressed, or both, should be listed in this section.

2.4 Quality Assurance Objectives

For each data collection activity, the QA/QC objective must be specified to correspond to the data use objectives. Three equally important QA/QC objectives have been defined for assessing and substantiating the collection of data to support its intended use. The three QA/QC objectives, hereafter referred to as QA1, QA2, and QA3, are described below. Evaluate the characteristics of the following QA objectives to determine which one or combination fits your data usage. All three objectives provide useful and valid data for enforcement purposes, disposal and/or treatment, responsible party identification, and cleanup verification. The QA characteristics are based on the Agency QA objectives for precision, accuracy (both quantitative and qualitative), representativeness, completeness, comparability, and detection level.

QA1: Rationale for QA1 objective:

QA1 is a screening objective to afford a quick, preliminary assessment of site contamination. This objective for data quality is available for data collection activities that involve rapid, non-rigorous methods of analysis and quality assurance. These methods are used to make quick, preliminary assessments of types and levels of pollutants. The primary reason for this objective is to allow for the collection of the greatest amount of data with the least expenditure of time and money. The user should be aware that data collected for this objective have neither definitive identification of pollutants nor definitive quantitation of their concentration level.

Although there is no quality assurance data collected with the data at this objective, a calibration or performance check of the method is required along

with verification of the detection level. Methods will be applied as per standard operating procedures and equipment manufacturer's specifications.

The QA1 objective does not preclude the adherence to prescribed quality control checks given in EPA methods and SOPs or the manufacturer's recommendations. The QA1 objective is generally applied to but not limited to the following activities: physical and/or chemical properties of samples; extent and degree of contamination relative to concentration differences; delineation of pollutant plume in ground water (head space or soil gas analysis techniques); monitor well placement; waste compatibility; preliminary health and safety assessment; hazardous categorization; and preliminary identification and quantitation of pollutants (determination of pH, flammability, chlorine presence, etc.).

QA1 Characteristics:

- Non-analyte or analyte specific (may also be specific for a chemical class, i.e., PCBs, total hydrocarbons, total organic halides, total ionizable organics, radiation).
- Non-definitive (i.e., unconfirmed) identification; non-qualitative to semi-qualitative.
- Non-definitive quantitation; no error determination (no precision and accuracy determination).
- Representative, comparable, complete[1].
- QA requirements for objective "QA1" are specified in Section 2.7, "Quality Assurance Requirements."

QA2: Rationale for QA2 objective:

QA2 is a verification objective used to verify analytical (field or lab) results. A minimum of 10% verification of results is required. This objective for data quality is available for data collection activities that require qualitative and/or quantitative verification of a "select portion of sample findings" (10% or more) that were acquired using non-rigorous methods of analysis and quality assurance. This quality objective is intended to give the decision-maker (OSC) a level of confidence for a select portion of preliminary data. This objective allows the OSC to focus on specific pollutants and specific levels of concentration quickly, by using field screening methods and verifying at least 10% by more rigorous analytical methods and quality assurance. The results of the 10% of substantiated data gives an associated sense of confidence for the remaining 90%. However, QA2 is not limited to only verifying screened data. The QA2 objective is also applicable to data that are generated by any method which satisfies all the QA2 requirements and thereby incorporates any one or a combination of the three verification requirements.

Generally the methods used for verification are more rigorous, as to analytical methodology and quality assurance. Only those verification methods that are analyte specific can be considered for this quality objective. When required, the analytical error is determined for all analytes that are of interest to the decision-maker (OSC) on at least 10% of samples.

[1] Representative: The degree to which sample data accurately and precisely represent the characteristic of the population. Comparable: An evaluation of the similarity of conditions under which different set of data are produced. Complete: The percentage of measurements made which are judged to be valid.

The QA2 objective is generally applied, but not limited to the following activities: physical and/or chemical properties of samples; extent and degree of contamination; verification of pollutant plume definition in ground water; verification of health and safety assessment; verification of pollutant identification; and verification of cleanup.

QA2 Characteristics:

- Analyte specific (i.e., benzene, cyanide, 2,3,7,8-TCDD, chromium).
- VERIFICATION of analyte identity and/or concentration. Choose any one or any combination of the following three:

  1. Definitive identification (choose one):

  Note: Except for X-ray fluorescence (XRF), confirmation of identity applies to organic analytes only. Confirm XRF determined analytes by an EPA-approved method.

  a. Screened data - confirm analyte identification by an EPA-approved method, different from the screening method, on at least 10% of preliminary screened samples.
  b. Unscreened data - confirm analyte identification by an EPA-approved method on all unscreened environmental samples (field or lab).

  2. Non-definitive quantitation (choose one):

  a. Screened data - verify analyte concentration on at least 10% of preliminary screened samples (field or lab) using an EPA-approved method, different from the screening method.
  b. Unscreened data - determine analyte concentration on all unscreened environmental samples (field or lab) using an EPA-approved method.

  3. Definitive quantitation/analytical error (choose one): Also, see Section 2.8 - Part I and Error Determination - Part II.

  Note: Error determination is advised if data are being evaluated against a critical action level.

  a. Screened data - determine the analytical error by calculating the precision, accuracy, and coefficient of variation for a subset (at least 10%) of the verified data using an EPA-approved method.
  b. Unscreened data - determine the analytical error by calculating the precision, accuracy, and coefficient of variation for all of the quantitative results using an EPA-approved method.

  Note: If definitive quantitation is chosen along with definitive identification for all the data, then your data meet the QA3 objective.

- Representative, comparable, complete.
- QA requirements for objective "QA2" are specified in Section 2.7, "Quality Assurance Requirements."

QA3: Rationale for QA3 objective:

QA3 is a definitive objective used to assess the accuracy of the concentration level as well as the identity of the analyte(s) of interest. This objective for data quality is available for data collection activities that require a high degree of qualitative and quantitative accuracy of all findings using rigorous methods of analysis and quality assurance for "critical samples" (i.e., those samples for which the data are considered essential in making a decision). This quality objective is intended to give the decision maker (OSC) a level of confidence for a select group of "critical samples" so he/she can make a decision based on an action level with regard to: treatment; disposal; site remediation and/or removal of pollutants; health risk or environmental impact; cleanup verification; pollutant source identification; delineation of contaminants; and other significant decisions where an action level is of concern. Only those methods that are analyte specific can be used

for this quality objective. Error determinations are made for all analytes that are of interest to the decision maker (OSC) for each critical sample that is of interest.

QA3 Characteristics:

- Analyte specific.
- Definitive identification - confirm analyte identification by a second method, such as mass spectroscopy, on 100% of the "critical samples" collected; applies only to organic analytes.

  Note: Except for X-ray fluorescence (XRF), confirmation of identity applies to organic analytes only. Confirm XRF determined analytes by an EPA-approved method.
- Non-definitive quantitation (choose one):
  a. Screened data - verify analyte concentration on at least 10% of preliminary screened samples (field or lab) using an EPA-approved method, different from the screening method.
  b. Unscreened data - determine analyte concentration on all unscreened environmental samples (field or lab) using an EPA-approved method.
- Definitive quantitation/analytical error - (determine the analytical error by calculating the precision, accuracy, and coefficient of variation) on 100% of the "critical samples" collected using an EPA-approved method.
- Representative, comparable, complete.
- QA requirements for objective "QA3" are specified in Section 2.7, "Quality Assurance Requirements."

2.4.1 Methods

It should not be assumed that an analytical method imparts a certain degree of quality to the results it provides. Quality is a matter of degree and can only be assessed against specific criteria. Therefore, one can choose any analytical method to use for any one of the three quality assurance objectives in Section 2.4, provided all of the quality assurance requirements are met for that objective as specified in Section 2.7. The methods that can be used for any of these three objectives include, but are not limited to, spot tests; paper strip tests; indicator tubes; chemical reactions producing colors, gases, or precipitates; electronic meters such as Geiger counters, pH meters, conductivity meters; electronic detectors such as photoionization, electron capture, flame ionization, flame photometric, electrolytic, and infrared; gas chromatography; mass spectroscopy; atomic absorption; inductively coupled plasma (ICP), and X-ray fluorescence. These methods may respond to either groups of analytes or specific analytes or both.

2.5 Approach and Sampling Methodologies

This section should provide a description of the possible sample matrices, required equipment and fabrication, sampling design (reference SOPs and EPA procedures used for collecting samples), sample documentation, corrective action, sample analyses, and a schedule of work (see Table 1). Procedures for decontamination of equipment and materials should be outlined in this section. In addition, a field sampling summary table (see Table 2) should be completed. In this table, specify the number of samples required per parameter per matrix, the number of QA samples, the required preservatives, appropriate sample containers and sample volumes.

2.6 Project Organization and Responsibilities

This section should list the managers, coordinators, and field sampling personnel, along with their project duties and responsibilities. The name and type of the laboratory performing the analysis, if appropriate, should also be included in this section. In addition, the parameters of interest (BNAs, VOAs, metals) should be detailed.

2.7 Quality Assurance Requirements

This section should describe the appropriate data quality indicators and QA/QC protocols, based on the QA/QC objective determined in Section 3.0, which will be followed in the evaluation of lab data packages. A QA/QC Analysis and Objectives Summary, including references to analytical methods (see Table 3), should be completed. The data quality indicators of concern for each QA/QC objective are listed below.

QA1

The following requirements apply:

A. Sample documentation.
B. Instrument calibration data or a performance check of a test method (i.e., Draeger tubes, test strips, spot tests).
C. Detection limit should be determined, unless inappropriate.

Note: QC procedures prescribed in SOPs and methods must be followed.

QA2

The following requirements apply:

A. Sample documentation.
B. Chain of custody (optional for field screening locations).
C. Sample holding times (document sample collection and analysis dates).
D. Initial and continuing instrument calibration data.
E. Method blank, rinsate blank, trip blank data (refer to Table 2, footnotes 2 and 3).

F. Choose any one or any combination of the following three:

1. Definitive identification (choose one):

   a. Screened data - confirm the identification of analytes via an EPA-approved method different from the screening method (field or lab) on at least 10% of the preliminary screened samples collected; provide documentation such as gas chromatograms, mass spectra, etc.
   b. Unscreened data - confirm the identification of analytes via an EPA-approved method on all unscreened environmental samples; provide documentation such as gas chromatograms, mass spectra, etc.

2. Non-definitive quantitation (choose one):

   a. Screened data - provide documentation of quantitative results from both the screening method and the EPA-approved verification method.
   b. Unscreened data - provide documentation of quantitative results.

(Documentation includes information and/or evidence on calculation procedures, calibration data, sample weight or volume, dilution factor, etc.)

3. Definitive quantitation/analytical error (choose one):

   a. Screened data - determine the analytical error by calculating the precision, accuracy, and coefficient of variation* by preparing and analyzing eight (8) QA replicates from the subset of samples used to verify screening results using an EPA-approved method. (See error determination Section 2.8.)
   b. Unscreened data - determine the analytical error by calculating the precision, accuracy, and coefficient of variation* by preparing and analyzing eight (8) QA replicates from all of the samples analyzed using an EPA-approved method.

G. Performance Evaluation Sample (optional) and where available.
H. Detection limit should be determined, unless inappropriate.

QA3:

The following requirements apply:

A. Sample documentation.
B. Chain of custody.
C. Sample holding times (document sample collection and analysis dates).
D. Initial and continuing instrument calibration data.

E. Definitive identification:

Confirm the identification of analytes by an EPA-approved method on 100% of the "critical" samples collected; and provide documentation such as gas chromatograms, mass spectra, etc.

F. Non-definitive quantitation (choose one):

a. Screened data - provide documentation of quantitative results from both the screening method and the EPA-approved verification method.
b. Unscreened data - provide documentation of quantitative results.

(Documentation includes information and/or evidence on calculation procedures, calibration data, sample weight or volume, dilution factor, etc.)

G. Definitive quantitation/analytical error

Determine the analytical error by an EPA-approved method on 100% of the "critical" samples collected. Calculate the precision, accuracy, and coefficient of variation* by preparing and analyzing eight (8) QA replicates from the critical samples collected. (See error determination Section 2.8.)

H. Method blank, rinsate blank, and trip blank data (refer to Table 2, Footnotes 2 and 3).

* Note: See data validation protocols for determining precision, accuracy, and coefficient of variation.

I. Performance Evaluation Samples, where available.
J. Detection limit should be determined, unless inappropriate.

Reference must be made to standard QA/QC protocols (i.e., SOPs, EPA reference procedures) for generating the above data quality indicator information.

2.8 Error Determination (Analytical and Total Error)

Any one of the following options can be used when determing error for QA2 or QA3:

2.8.1 Matrix Spike Samples

Spike and analyze at least eight (8) replicate samples with a concentration level equal to the level of interest. Use samples whose unspiked concentrations are less than or equal to the level of interest. Samples should be homogeneous. Determine bias (percent recovery) and precision (coefficient of variation) according to Section 3.5 of Part II - Data Validation Procedures.

2.8.2 Site Background Samples

Spike and analyze at least eight (8) replicate samples with a concentration level equal to the level of interest. These samples are from the site of interest (or nearby proximity). The analyte of interest is not detectable in the sample for the method used. Samples should be made homogeneous. Determine bias (percent recovery) and precision (coefficient of variation) according to Section 3.5 of Part II - Data Validation Procedures.

2.8.3 Site Action Level Samples (Total Error)

Collect and analyze at least 8 replicate samples whose analyte concentrations are equal to the level of interest. (Do this by collecting one sample with sufficient material to divide into the required number of replicates. Except for VOA samples, homogenize the sample thoroughly before dividing into replicates.) These samples are from the selected site and contain the target analyte at or near the level of interest. Determine bias (percent recovery) and precision (coefficient of variation) according to Section 3.5 of Part II - Data Validation Procedures. Bias can not be determined unless these samples are spiked first and percent recovery is calculated.

Note: This procedure (2.8.3) is useful in determining the total (sampling and analytical) error as well as the analytical error since it evaluates the sample collection, sample preparation, and the analysis. Sampling error determination is being addressed in representative sampling guidance documents for each media. These documents are under development for removal activities.

2.9 Deliverables

This section should provide a description of the reports and other deliverables (e.g., field activities, trip reports, status reports, maps/figures, analysis, data review, analytical reports, and draft final reports) to be generated as a result of the sampling activity.

2.10 Data Validation

This section details the criteria used to ensure that the analytical results received from a laboratory are valid and accurate for the QA objective chosen. Consult the "Data Validation Procedures" in this guidance document for the appropriate evaluation criteria. These procedures have been developed mainly from the "Laboratory Data Validation Functional Guidelines for Evaluation of Organic, Inorganic, and Dioxin Analyses" used in the Agency's Contract Laboratory Program.

QA1

- QA1 data need only be evaluated for calibration and detection limits criterion.

QA2

- The results of 10% of the samples in the analytical data packages should be evaluated for all of the elements listed in Section 2.7, "QA Requirements" of the Sampling QA/QC Plan. The holding times, blank contamination, and detection capability will be reviewed for all remaining samples.

QA3

- This objective, the most stringent of all the objectives, requires that at least 10% of the samples in a lab data package be evaluated for all of the listed elements in Section 2.7 "QA Requirements" of the Sampling QA/QC Plan. Of the remaining samples, holding times, blank contamination, precision, accuracy, error determination, detection limits, and confirmed identification data will be reviewed.This objective also requires review of all elements for all samples in each analyte category (i.e., VOAs and PCBs) in every 10th data package received from an individual lab.

Table 1: Example Proposed Schedule of Work

Item	(time period) ___/___	___/___	___/___	___/___
1. Laboratory Procurement				
2. Phase 1 Site Work				
3. Drilling Subcontract Procurement				
4. Phase 2 Site Work				
5. Laboratory Analysis				
6. Data Review				
7. Draft Report				
8. Final Report				

Table 2: Field Sampling Summary

Analytical Parameter	Level of Sensitivity[1]	Matrix*	Container Type and Volume (# container rq'd)	Preservative	Holding Times	Subtotal Samples	QC Extras				Total Field Samples
							Rinsate Blanks[2]	Trip Blanks[3] (VOAs)	QC Positives[4]	Matrix Spikes[5]	
VOA		S	40ml vial (1)	4°C	7 day						
VOA		W	40ml vial (3)	4°C**	7 day						
BNA		S	8oz glass (1)	4°C	7/40 d						
BNA		W	32oz amber glass (2)	4°C	7/40 d						
PESTICIDE		S	8oz glass (1)	4°C	7/40 d						
PESTICIDE		W	32oz amber glass (2)	4°C**	7/40 d						
PCB		S	8oz glass (1)	4°C	7/40 d						
PCB		W	32oz amber glass (2)	4°C**	7/40 d						
P.P. METALS		S	8oz glass (1)	4°C	6 mos						
P.P. METALS		W	1 liter glass or polyethylene (1)	NO_3 ph<2 4°C	6 mos						
CYANIDE		S	8oz glass (1)	4°C	14 day						
CYANIDE		W	1 liter polyethylene (1)	NaOH to pH > 12 4°C	14 day						

* Matrix: S-Soil, W-Water, O-Oil, DS-Drum Solid, DL-Drum Liquid, TS-Tank Solid, TL-Tank Liquid, X-Other, A-Air

** If residual chlorine is present, preserve with 0.008% $Na_2S_2O_2$.

1. The concentration level, specific or generic, that is needed in order to make an evaluation. This level will provide a basis for determining the analytical method to be used.
2. Only required if dedicated sampling tools are not used. For QA2 and QA3, one blank required per parameter per 20 samples. For QA1, enter "N/A".
3. For QA2 and QA3, one trip blank required per cooler used to ship VOA samples. Each trip blank consists of two 40ml vials filled with distilled/deionized water. For QA1, enter "N/A".
4. Performance check samples; optional for QA2, mandatory for QA3 at one per parameter per matrix. For QA1, enter "N/A".
5. For QA2 (optional) and for QA3 (mandatory): Determine bias (% recovery) using a minimum of 2 matrix spikes. Determine precision using a minimum of 8 matrix spikes. Ensure that sufficient environmental sample is collected for lab spiking. For QA1, enter "N/A".

Table 2: Field Sampling Summary (continued)

Analytical Parameter	Level of Sensitivity[1]	Matrix*	Container Type and Volume (# container rq'd)	Preservative	Holding Times	Subtotal Samples	QC Extras				Total Field Samples
							Rinsate Blanks[2]	Trip Blanks[3] (VOAs)	QC Positives[4]	Matrix Spikes[5]	
PHENOLS		S	8oz glass (1)	4°C	28 day			[redacted]			
PHENOLS		W	1 liter amber glass (1)	H_2SO_4 to pH < 2 4°C	28 day			[redacted]			

*
** Matrix: S-Soil, W-Water, O-Oil, DS-Drum Solid, DL-Drum Liquid, TS-Tank Solid, TL-Tank Liquid, X-Other, A-Air
If residual chlorine is present, preserve with 0.008% $Na_2S_2O_2$.

1. The concentration level, specific or generic, that is needed in order to make an evaluation. This level will provide a basis for determining the analytical method to be used.
2. Only required if dedicated sampling tools are not used. For QA2 and QA3, one blank required per parameter per 20 samples. For QA1, enter "N/A".
3. For QA2 and QA3, one trip blank required per cooler used to ship VOA samples. Each trip blank consists of two 40ml vials filled with distilled/deionized water. For QA1, enter "N/A".
4. Performance check samples; optional for QA2, mandatory for QA3 at one per parameter per matrix. For QA-1, enter "N/A".
5. For QA2 (optional) and for QA3 (mandatory): Determine bias (% recovery) using a minimum of 2 matrix spikes. Determine precision using a minimum of 8 matrix spikes. Ensure that sufficient environmental sample is collected for lab spiking. For QA1, enter "N/A".

Table 3: QA/QC Analysis and Objectives Summary

Analytical Parameter	Matrix*	Analytical Method Ref.	Spikes		QA/QC	
			Matrix[1]	Surrogate[2]	Detection Limits[3]	QA Objective[4]
VOA	S	8240/SW-846				
VOA	W	624/CLP				
BNA	S	8250 or 8270/ SW-846				
BNA	W	625/CLP				
PESTICIDE	S	8080/SW-846				
PESTICIDE	W	608				
PCB	S	8080/SW-846				
PCB	W	608				
P.P. METALS	S	SW-846				
P.P. METALS	W	EPA-600/CFR 40				
CYANIDE	S	SW-846				
CYANIDE	W	SW-846				

* Matrix: S-Soil, W-Water, O-Oil, DS-Drum Solid, DL-Drum Liquid, TS-Tank Solid, TL-Tank Liquid, X-Other, A-Air

1. For QA2 (optional) and for QA3 (mandatory): Determine bias (% recovery) using a minimum of 2 matrix spikes. Determine precision using a minimum of 8 matrix spikes. Ensure that sufficient environmental sample is collected for lab spiking. For QA1, enter "N/A".
2. For QA2 and QA3, surrogate spike analysis is to be run for each sample; therefore, enter "yes". For QA-1, enter "N/A".
3. To be determined by the person arranging the analysis. Should be equal to or less than the level of sensitivity.
4. Enter the QA Objective desired: QA1, QA2, or QA3.

Table 3: QA/QC Analysis and Objectives Summary (continued)

Analytical Parameter	Matrix*	Analytical Method Ref.	Spikes		QA/QC	
			Matrix[1]	Surrogate[2]	Detection Limits[3]	QA Objective[4]
PHENOLS	S	8040/SW-846		[redacted]		
PHENOLS	W	604/CFR 40		[redacted]		

* Matrix: S-Soil, W-Water, O-Oil, DS-Drum Solid, DL-Drum Liquid, TS-Tank Solid, TL-Tank Liquid, X-Other, A-Air

1. For QA2 (optional) and for QA3 (mandatory): Determine bias (% recovery) using a minimum of 2 matrix spikes. Determine precision using a minimum of 8 matrix spikes. Ensure that sufficient environmental sample is collected for lab spiking. For QA1, enter "N/A".
2. For QA2 and QA3, surrogate spike analysis is to be run for each sample; therefore, enter "yes". For QA-1: enter "N/A".
3. To be determined by the person arranging the analysis. Should be equal to or less than the level of sensitivity.
4. Enter the QA Objective desired: QA1, QA2, or QA3.

PART II

DATA VALIDATION PROCEDURES

1.0 Introduction

Part II provides guidance in the validation of laboratory data packages, according to the guidelines established by the Sampling QA/QC Plan. It is a compilation of those procedures used in the Contract Laboratory Program (CLP) and those found in the "Laboratory Data Validation Functional Guidelines for Evaluating Organic, Inorganics, Pesticides, and Dioxin Analysis." This guidance was developed for the Emergency Response Divisions' (ERD) use and is not intended to supercede the guidance documents developed for CLP data validation used for Remedial activities.

Items reviewed during the data validation process are dependent upon the QA objectives previously established by the data user in the Sampling QA/QC Plan. According to the tiered approach implemented in the Sampling QA/QC Plan each QA objective requires the following review:

QA3 - This objective, the most stringent of all the objectives, requires that at least 10% of the samples in a lab data package be reviewed for all of the elements. Of the remaining samples, holding times, blank contamination, precision, accuracy, error determination, detection limits, and confirmed identification data will be reviewed. This level also requires the review of all the elements for all samples in each analyte category in every 10th data package received from an individual lab.

QA2 - This objective requires that the results of 10% of the samples reported in the analytical data package should be evaluated for all of the elements listed in Section 7, QA Requirements, of the Sampling QA/QC Plan. The holding times, blank contamination, and detection limits will be reviewed for the remaining.

QA1 - This objective requires review of only the calibration and detection limits for all data.

Included in the section on Matrix Spike/Matrix Spike Duplicates are formulas for calculating confidence limits and the coefficient of variation. Confidence limits should be determined for all data generated under QA3 and may be calculated for QA2 if a sufficient number of spiked samples are collected. Although not stated in the following data validation procedures, the reviewer must examine the data packages for transcription/calculation errors that may have been overlooked by the lab.

2.0 Data Validation Qualifiers

J	The associated numerical value is an estimated quantity because the reported concentrations were less than the required detection limits or quality control criteria were not met.
N	Presumptive evidence of presence of material.
NJ	Presumptive evidence of the presence of the material at an estimated quantity.
PND	Precision Not Determined.
R	The sample results are rejected (analyte may or may not be present) due to gross deficiencies is quality control criteria. Any reported value is unusable. Resampling and/or reanalysis is necessary for verification.
RND	Recovery Not Determined.
U	The material was analyzed for, but not detected. The associated numerical value is the sample detection limit or adjusted sample detection limit.
UJ	The material was analyzed for, but not detected. The reported detection limit is estimated because Quality Control criteria were not met.

3.0 Metallic Inorganic Parameters

3.1 Sample Holding Times

1. Were any of the sample holding times exceeded?*

   Sample Holding Times:
   Metals - 6 months
   Cyanide - 14 days
   Mercury - 28 days
   Chromium^{+6} - 24 hours

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL). Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

*Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

3.2 Initial and Continuing Calibration Verification

1. Are values outside the range of 90% to 110% of the mean value, except for tin and mercury, for which the range is 80% to 120%, and cyanide, for which the range is 85% to 115%?

ACTION: If values are between 75-89% or 112-125% (65-79% and 121-135% for Hg and Sn, 70-84% and 116-130% for cyanide), flag as estimated (J).

If values are outside of the above windows, reject (R) as unacceptable data between calibration standard outside of above windows and nearest adjacent acceptable calibration standard(s).

2. Was a calibration standard and blank analyzed at the beginning of the analysis and after every 10 samples?

ACTION: If no, flag as estimated (J) all values not analyzed within 5 samples of a calibration standard or blank.

3. Were any sample results greater than 110% of the highest calibration standard?

ACTION: If yes, flag result reported as estimated (J).

3.3 Blanks

1. Do the concentrations of all blanks fall below the IDL for all parameters?

ACTION: If no, flag as undetected (U) all reported positive data that has a concentration less than 5 times the blank value.

NOTE: In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

2. Was one method blank analyzed for each 20 samples?

ACTION: If no, flag as estimated (J) all data for which a method blank was not analyzed. If only one blank was analyzed for more than 20 samples, the first 20 samples analyzed do not have to be flagged as estimated (J).

3.4 **ICP Interference Check Sample**

1. If all ICP Interference Check Sample (ICS) results are not inside of control limits (± 20% of mean value), are concentrations of Al, Ca, Fe, or Mg lower in the sample than in the ICS?

ACTION: If no, flag as estimated (J) those sample results for which ICS recovery is between ± 50% of mean value. For those sample results in which ICS recovery is above 150% or 50%, reject (R) all results.

2. Was ICS analyzed at the beginning and end of each run or at least twice every 8 hours, whichever is more frequent?

ACTION: If no, flag as estimated (J) all samples for which Al, Ca, Fe, or Mg concentration is higher than in ICS.

3.5 **Error Determination**

See Part I - Section 2.8 for QA Samples to be used for error determination.

3.5.1 Determination of Bias (% Recovery - Optional for QA-2; Mandatory for QA-3)

3.5.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc.} - \text{Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%, the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered whenever there is consistent evidence of bias.

3.5.1.2 Adjustment of Sample Value for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample values. % bias is the reciprocal value of % recovery (i.e., for 70% recovery you have a negative 30% bias). Use the average % recovery from the total number of matrix spikes analyzed. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

3.5.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

3.5.2.1 Replicate Analysis

1. Was a minimum of eight replicates analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

3.5.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision or standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

   Determine the coefficient of variation using the following equation:

   $$CV = \frac{s \times 100}{x_{DL}}$$

   where:

   x_{DL} = the decision level concentration

   s = the sample standard deviation given by the equation:

   $$s^* = [(x_i - x)^2/(n - 1)]^{1/2}$$

*Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (σ) rather than the sample standard deviation (s).

Apply the CV to the decision level to determine the false negative or false positive value as follows:

False positive value = Decision level value + (CV x decision level)

False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)
= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)
= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable. Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

3.6 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

3.7 Optional Additional Instrument QC (for elevated concentrations)

3.7.1 ICP Serial Dilution (if recovery is outside acceptable range)

1. Was serial dilution performed on one of each 20 samples of similar matrix where concentrations exceed 50 times IDL?

ACTION: If no, flag associated data as estimated (J).

2. If analyte concentration after a five fold dilution is greater than 10 times IDL, did analysis of diluted sample agree to within 10% of original determination for each parameter?

ACTION: If no, flag associated data as estimated (J).

3.7.2 Atomic Absorption Analysis Specific QC

1. Is any furnace result flagged with an (E) by the laboratory to indicate interference?

   If yes, is any associated post-digestion spike recovery less than 10% for any result flagged with an (E).

ACTION: If yes, reject (R) affected data.

2. When the method of standard addition was required, is the coefficient of correlation less than 0.995 for any sample?

ACTION: If yes, flag the associated data as estimated (J).

3.8 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

4.0 BNAs by GC/MS Analysis

4.1 Sample Holding Times

1. Were any of the sample holding times exceeded?*

   Sample Holding Times from date of sample collection:

   Water - 7 days to extract
   Soil, sediment, sludges - 14 days to extract

   Water/soil - analyze within 40 days after extraction

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL). Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

*Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

4.2 GC/MS Tuning Criteria

1. Has decafluorotriphenylphosphine (DFTPP) been run for every 12 hours of sample analysis per instrument?

ACTION: If no, reject (R) all associated data for that instrument which fall outside an acceptable 12-hour time interval.

2. Have the DFTPP ion abundance criteria been met for each instrument used?

m/z	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
69	(reference only)
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

ACTION: If no, evaluate against expanded ion abundance criteria.

3. Have the appropriate expanded ion abundance criteria been met for each instrument used?

m/z	Expanded ion abundance criteria
51	22-75% of mass 198
68	Less than 2% of mass 69
69	(reference only)
70	Less than 2% of mass 69
127	30-75% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	7-37% of mass 198
365	Greater than 0.75% of mass 198
441	Present, but less than mass 443
442	Greater than 30% of mass 198
443	17-23% of mass 442

ACTION: It is up to the reviewer's discretion, based on professional judgement, to flag data associated with tunes meeting expanded criteria, but not basic criteria. If only one element falls within the expanded criteria, no qualification may be needed. On the other hand, if several data elements are in the expanded windows, all associated data may merit an estimated flag (J). Note that the data reviewer may still choose to flag all data associated with a tune not meeting contract criteria as rejected (R) if it is deemed appropriate.

The most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z 198/199 and 442/443 ratios are critical. These ratios are based on the natural abundances of Carbon 12 and Carbon 13 and should always be met. Similarly, the m/z 68, 70, 197 and 441 relative abundances indicate the condition of the instrument and the suitability of the resolution adjustment and are very important. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile. For the ions at m/z 51, 127, and 275, the actual relative abundance is not critical. For instance, if m/z 275 has a 40% relative abundance (criteria 10-30%) and other criteria are met, the deficiency is minor. The

relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If m/z 365 relative abundance is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 1% minimum abundance criteria, the deficiency is not as serious.

4.3 Initial and Continuing Calibration Verification

1. Do any compounds have an average response factor equal to zero?

ACTION: If yes, reject (R) sample data for associated compounds.

2. Verify that all BNA compounds have Relative Response Factors of at least 0.05.

ACTION: If any BNA compound has a Relative Response Factor of less than 0.05, flag positive results for that compound as estimated (J). Flag non-detects for that compound as rejected (R).

3. Verify that all BNA compounds have a percent Relative Standard Deviation (%RSD) of $\leq 30\%$ for the initial calibration.

$$\%RSD = \frac{s \times 100}{x}$$

where:

s = standard deviation of 5 response factors
x = mean of 5 response factors

ACTION: If any BNA compound has a %RSD of greater than 30%, flag positive results for that compound as estimated (J). Non-detects may be qualified (J) using the reviewer's professional judgement.

4. Verify that the percent difference (%D) is $\leq 25\%$ for all BNA compounds in the continuing calibration.

ACTION: If any BNA compound has a %D between the initial and continuing calibration of greater than 25%, flag all positive results for the compound as estimated (J). Non-detects may be qualified (J) using the reviewer's professional judgement.

4.3.1 Internal Standards

1. Verify that all retention times and Internal Standard (IS) areas are acceptable.

ACTION: If an IS area is outside -50% or +100% of the associated standard, flag the positive results as estimated (J) for that sample fraction. Non-detects for compounds quantitated using that IS are flagged with the sample quantitation limit flagged as estimated (J) for that sample fraction. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. Non-detects should then be flagged as rejected (R).

If an IS retention time varies by more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection (R) of the data for that sample fraction.

4.4 Error Determination

See Part I - Section 2.8 for QA samples to be used for error determination.

4.4.1 Determination of Bias (% Recovery- Optional for QA-2; Mandatory for QA-3)

4.4.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc. - Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%, the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered whenever there is consistent evidence of bias.

4.4.1.2 Adjustment of Sample Values for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample values. % bias is the reciprocal value of % recovery (i.e., for 70% recovery you have a negative 30% bias). Use the average % recovery from the total number of matrix spikes analyzed.

This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

4.4.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

4.4.2.1 Replicate Analysis

1. Was a minimum of eight replicates analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

4.4.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision of standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

Determine the coefficient of variation using the following equation:

$$CV = \frac{s \times 100}{x_{DL}}$$

where:

x_{DL} = the decision level concentration

s = the sample standard deviation given by the equation:

$$s^* = [(x_i - x)^2/(n - 1)]^{1/2}$$

*Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (o) rather than the sample standard deviation (s).

Apply the CV to the decision level to determine the false negative or false positive value as follows:

False positive value = Decision level value + (CV x decision level)

False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)
= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)
= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable. Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

4.5 Blanks

1. Was a method blank extracted and analyzed for each set of samples or every 20 samples of similar matrix and similar extraction technique?

ACTION: If no, flag as estimated (J) all data for which a method blank was not analyzed. NOTE: If only one blank was analyzed for more than 20 samples, the first 20 samples analyzed do not have to be flagged as estimated (J).

2. Has the method blank for BNAs been run on the same GC/MS or GC system as the sample?

ACTION: If no, flag as estimated (J) all results that do not have an associated blank.

3. Are the concentrations of blank contaminants for BNAs greater than the Required Detection Limit (RDL) of any BNA compound?

ACTION: For sample values reported at less than 10 times the blank contamination level for common phthalate esters and 5 times the blank contamination level for other BNA compounds, flag as undetected (U).

NOTE: In instances where more than one blank is associated with a given sample, quantification should be based upon a comparison with the associated blank having the highest concentration of a

contaminant. The results must not be corrected by subtracting any blank value.

4.6 Compound Identification

1. Verify the following:

   -the Relative Retention Time (RRT) of reported compounds is within 0.06 RRT units of the standard RRT.

   -all ions present in the standard mass spectrum at a relative intensity greater than 10% are also present in the sample mass spectrum.

   -all ions present in the sample, but not present in the standard are accounted for.

   -relative intensities of the ions specified above as present in the sample and at a relative intensity greater than 10% in the standard, agree within 20% between the sample and the standard spectra.

ACTION: Use professional judgement to determine acceptability of the data if the above criteria were not all met. If it is determined that incorrect identifications were made, all such data should be reported as not detected with an estimated (J) quantitation limit. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for.

4.6.1 Tentatively Identified Compounds

1. Verify the following:

   -all ions presenting the reference mass spectrum with a relative intensity greater than 10% are present in the sample mass spectrum.

   -relative intensities specified above agree within 20% between the sample and the reference spectra.

   -molecular ions present in the reference spectrum are present in the sample spectrum.

   -all tentatively identified compounds are reported with estimated quantitation and detection limits.

ACTION: Use professional judgement to determine acceptability of the data if the above criteria are not all met. If data are considered to be unacceptable, the tentative ID should be changed to "unknown".

4.7 Compound Quantitation and Reported Detection Limits

1. Verify that the reported values, both positives and non-detects, have been correctly adjusted to reflect all dilutions, concentrations, splits, cleanup procedures, dry weight factors, an any other adjustments that have not been accounted for by the method.

   BNA for waters: $ug/L = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_s)(V_i)}$

   BNA for soils: $ug/kg = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(W_s)(D)(V_i)}$

A_x = area of characteristic ion for compound being measured
A_{is} = area of characteristic ion for the internal standard
I_s = amount of internal standard added (ng)
RF = daily response factor for the compound being measured
V_t = volume of total extract (ul)
V_i = volume injected (ul)
V_s = volume of sample (ml)
W_s = weight of sample extracted (g)
D = (100 - % moisture)/100

ACTION: If incorrect values have been reported, it is essential that the correct values be determined.

The reviewer should contact the laboratory to verify any corrections made to the data.

4.8 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

4.9 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

4.10 Optional QC Checks

4.10.1 Surrogate Recovery

1. If either two or more base neutral or acid surrogates were outside of specifications for any sample or blank, were the appropriate samples reanalyzed?

ACTION: If initial analysis and reanalysis both have two or more surrogates outside of specifications for samples or blanks, estimate (J) all quantitation results, including detection limits.

2. Does any one surrogate have less than 10% recovery?

ACTION: If yes, flag as estimated (J) positive results for that fraction; flag negative results as rejected (R).

5.0 VOAs by GC/MS Analysis

5.1 Sample Holding Times

1. Were any of the sample holding times exceeded?*

Sample Holding Times from date of sample collection:

Aromatic (for water) - 7 days (unpreserved), 14 days (preserved)

All other compounds - 14 days

Soil, sludge, sediments - 14 days

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL). Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

*Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

5.2 GC/MS Tuning Criteria

1. Has bromofluorobenzene (BFB) been run for every 12 hours of sample analysis per instrument?

ACTION: If no, reject (R) all associated data for that instrument which fall outside an acceptable 12-hour time interval.

2. Have the BFB ion abundance criteria been met for each instrument used?

m/z	Ion abundance criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5-9% of mass 174
176	95-101% of mass 174
177	5-9% of mass 176

ACTION: If no, evaluate against expanded ion abundance criteria.

3. Have the appropriate expanded ion abundance criteria been met for each instrument used?

m/z	Ion abundance criteria
50	11-50% of mass 95
75	22-75% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	Less than 2% of mass 95
174	Greater than 50% of mass 95
175	5-9% of mass 174
176	95-101% of mass 174
177	5-9% of mass 176

ACTION: It is up to the reviewer's discretion, based on professional judgement, to flag data associated with tunes meeting expanded criteria, but not basic criteria. If only one element falls within the expanded criteria, no qualification may be needed. On the other hand, if several data elements are in the expanded windows, all associated data may merit an estimated flag (J). Note that the data reviewer may still choose to flag all data associated with a tune not meeting contract criteria as rejected (R) if it is deemed appropriate.

For BFB, the most important factors to consider are the empirical results that are relatively insensitive to location on the chromatographic profile and the type of instrumentation. Therefore, the critical ion abundance criteria for BFB are the m/z 95/96 ratio, the 174/175 ratio, the 176/177 and the 174/176 ratio. The relative abundances of m/z 50 and 75 are of lower importance.

5.3 Initial and Continuing Calibration Verification

1. Do any compounds have an average response factor equal to zero?

ACTION: If yes, reject (R) sample data for associated compounds.

2. Verify that all VOA compounds have Relative Response Factors of at least 0.05.

ACTION: If any VOA compound has a Relative Response Factor of less than 0.05, flag positive results for that compound as estimated (J). Flag non-detects for that compound as rejected (R).

3. Verify that all VOA compounds have a percent Relative Standard Deviation (%RSD) of $\leq$ 30% for the initial calibration.

$$\%RSD = \frac{s \times 100}{x}$$

where:

s = standard deviation of 5 response factors

x = mean of 5 response factors

ACTION: If any VOA compound has a %RSD of greater than 30%, flag positive results for that compound as estimated (J). Non-detects may be qualified (J) using the reviewer's professional judgement.

4. Verify that the percent difference (%D) is $\leq$ 25% for all VOA compounds in the continuing calibration.

ACTION: If any VOA compound has a %D between the initial and continuing calibration of greater than 25%, flag all positive results for the compound as estimated (J). Non-detects may be qualified (J) using the reviewer's professional judgement.

5.3.1 Internal Standards

1. Verify that all retention times and Internal Standard (IS) areas are acceptable.

ACTION: If an IS area is outside -50% or +100% of the associated standard, flag the positive results as estimated (J) for that sample fraction. Non-detects for compounds quantitated using that IS are flagged with the sample quantitation limit flagged as estimated (J) for that sample fraction. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. Non-detects should then be flagged as rejected (R). If an IS retention time varies by more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection (R) of the data for that sample fraction.

5.4 Error Determination

See Part I - Section 2.8 for QA samples to be used for error determination.

5.4.1 Determination of Bias (% Recovery - Optional for QA-2; Mandatory for QA-3)

5.4.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc. - Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%, the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered whenever there is consistent evidence of bias.

5.4.1.2 Adjustment of Sample Values for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample

values. % bias is the reciprocal value of % recovery (i.e., for 70% recovery you have a negative 30% bias). Use the average % recovery from the total number of matrix spikes analyzed. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

5.4.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

5.4.2.1 Replicate Analysis

1. Was a minimum of eight replicates analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

5.4.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision of standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

   Determine the coefficient of variation using the following equation:

$$CV = \frac{s \times 100}{x_{DL}}$$

   where:

   x_{DL} = the decision level concentration

   s = the sample standard deviation given by the equation:

$$s^* = [(x_i - x)^2/(n - 1)]^{1/2}$$

*Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (σ) rather than the sample standard deviation (s).

Apply the CV to the decision level to determine the false negative or false positive value as follows:

False positive value = Decision level value + (CV x decision level)

False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)
= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)
= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable.

Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

5.5 Blanks

1. Was a method blank prepared and analyzed for each set of samples or every 20 samples of similar matrix and similar preparation technique?

ACTION: If no, flag as estimated (J) all data for which a method blank was not analyzed. NOTE: If only one blank was analyzed for more than 20 samples, the first 20 samples analyzed do not have to be flagged as estimated (J).

2. Has the method blank for VOAs been run on the same GC/MS or GC system as the sample?

ACTION: If no, flag as estimated (J) all results that do not have an associated blank.

3. Are the concentrations of any blank contaminants for VOAs greater than the RDL of any VOA compound?

ACTION: For sample values reported at less than 10 times the blank contamination level for methylene chloride, acetone, toluene and 2-butanone and 5 times the blank contamination level for other VOA compounds, flag as undetected (U).

NOTE: In instances where more than one blank is associated with a given sample, quantification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

5.6 Compound Identification

1. Verify the following:

-the Relative Retention Time (RRT) of reported compounds is within 0.06 RRT units of the standard RRT.

-all ions present in the standard mass spectrum at a relative intensity greater than 10% are also present in the sample mass spectrum.

-all ions present in the sample, but not present in the standard are accounted for.

-relative intensities of the ions specified above as present in the sample and at a relative intensity greater than 10% in the standard, agree within 20% between the sample and the standard spectra.

ACTION: Use professional judgement to determine acceptability of the data if the above criteria were not all met. If it is determined that incorrect identifications were made, all such data should be reported as not detected with an estimated (J) quantitation limit. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for.

5.6.1 Tentatively Identified Compounds

1. Verify the following:

-all ions presenting the reference mass spectrum with a relative intensity greater than 10% are present in the sample spectrum.

-relative intensities specified above agree within 20% between the sample and the reference spectra.

-molecular ions present in the reference spectrum are present in the sample spectrum.

-all tentatively identified compounds are reported with estimated quantitation and detection limits.

ACTION: Use professional judgement to determine acceptability of the data if the above criteria are not all met. If data are considered to be unacceptable, the tentative ID should be changed to "unknown".

5.7 Compound Quantitation and Reported Detection Limits

1. Verify that the reported values, both positives and non-detects, have been correctly adjusted to reflect all dilutions, concentrations, splits, cleanup procedures, dry weight factors, an any other adjustments that have not been accounted for by the method.

VOA for waters: $ug/L = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$

Low level VOA for soils:

$ug/kg = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)(D)}$

High level VOA for soils:

$ug/kg = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(W_s)(D)(V_i)}$

A_x = area of characteristic ion for compound being measured

A_{is} = area of characteristic ion for the internal standard

I_s = amount of internal standard added (ng)

RF = daily response factor for compound being measured

V_o = volume of water purged (ml)

W_s = weight of sample extracted (g)

D = (100 - % moisture)/100 or 1 on wet weight basis

V_t = volume of total extract (ul)

V_i = volume of extract added (ul) for purging

ACTION: If incorrect values have been reported, it is essential that the correct values be determined. The reviewer should contact the laboratory to verify any corrections made to the data.

5.8 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

5.9 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality

and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

5.10 Optional QC Checks

5.10.1 Surrogate Recovery

1. If either one or more VOA surrogates were outside of specifications for any sample or blank, were the appropriate samples reanalyzed?

ACTION: If initial analysis and reanalysis both have two or more surrogates outside of specifications for samples or blanks, estimate (J) all quantitation results, including detection limits.

2. Does any surrogate have less than 10% recovery?

ACTION: If yes, flag as estimated (J) positive results for that fraction; flag negative results as rejected (R).

6.0 Pesticides/PCBs

6.1 Sample Holding Times

1. Were any of the sample holding times exceeded?

Sample Holding Times from date of sample collection:

Water - 7 days to extraction
Soil, sludge, sediment - 14 days to extract

All - analyze within 40 days after extraction

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL), based on the reviewers professional judgement and the nature of the sample and analyte. Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

6.2 Instrument Performance

1. Check the raw data to verify that DDT retention time is greater than 12 minutes on the standard chromatogram and that there is adequate resolution (> 25%) between peaks of other pesticide standard compounds.

ACTION: If the retention time of DDT is less than 12 minutes (except on OV-1 and OV-101), a close examination of the chromatography is necessary to ensure that adequate separation of individual components is achieved. If adequate separation is not achieved, flag all affected compound data as rejected (R).

2. Check raw data to verify that retention time windows are reported and that all pesticide standards are within the established retention time windows.

ACTION: If the standards do not fall within the retention time windows, professional judgement should be used in the evaluation of associated sample results.

3. Check the raw data to verify that the percent breakdown for endrin and 4,4'-DDT, or the

combined percent breakdown, does not exceed 20% in all Evaluation Standard Mix B analysis.

ACTION: If the DDT breakdown is greater than 20%, beginning with the last in-control standard, flag all results for DDT as estimated (J). If DDT was not detected,but DDD and DDE are positive, then flag the quantitation limit for DDT as rejected (R). Flag results for DDD and/or DDE as presumptively present at an estimated quantity (NJ).

If the endrin breakdown is greater than 20%, flag all quantitative results for endrin as estimated (J). If endrin was not detected, but endrin aldehyde and endrin ketone are positive, then flag the quantitation limit for endrin as rejected (R). Flag results for endrin ketone as presumptively present at an estimated quantity (NJ).

4. Check the raw data to verify that the percent difference in retention time for the surrogate dibutylchlorendate (DBC) in all standards and samples in $\leq$ 2.0% for packed column analysis, $\leq$ 0.3% for capillary column analysis, and $\leq$ 1.5% for wide-bore capillary column analysis.

ACTION: If any of the percentages are greater than indicated, the analysis may be flagged as rejected (R) for that sample. Qualification of the data is left up to the professional judgement of the reviewer.

6.3 Initial and Continuing Calibration Verification

1. Verify that the %RSD of the calibration factor for aldrin, endrin, DBC and DDT are less than or equal to 10% for the initial calibration linearity check.

ACTION: If criteria for linearity is not met, flag all associated quantitative results as estimated (J).

$$\%RSD = \frac{s \times 100}{x}$$

where:

s = standard deviation of 5 response factors
x = mean of 5 response factors

2. If toxaphene or DDT series was identified and quantitated, verify that a three-point calibration was established.

ACTION: If no, flag as estimated (J) positive results for toxaphene or DDT.

3. Verify the proper 72-hour analytical sequence as follows:

   Standard Mix A, Standard Mix B, Standard Mix C (individual standard mix A, individual standard mix B, may be one mix), Toxaphene, Aroclors 1016/1260, (Aroclor 1221, Aroclor 1232, once per month), Aroclor 1242, Aroclor 1248, Aroclor 1254, 5 samples, Standard Mix B, 5 samples, Individual Standard Mix A or B, 5 samples, repeat starting from Standard Mix B, must end with individual Standard Mix A and B.

ACTION: If the proper standards have not been analyzed and the sequence followed, use professional judgement to determine the severity of the effect and qualify the data accordingly.

4. Review the pesticide sample data to verify whether the standard was used as a quantitation standard or as a confirmation standard.

ACTION: If the %D for standard analysis is greater than 15% on the quantitation column or greater than 20% on the confirmation column, flag all associated positive sample results as estimated (J).

6.4 Error Determination

See Part I - Section 2.8 for QA samples to be used for error determination.

6.4.1 Determination of Bias (% Recovery - Optional for QA-2; Mandatory for QA-3)

6.4.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc. - Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%, the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered whenever there is consistent evidence of bias.

6.4.1.2 Adjustment of Sample Values for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample values. % bias is the reciprocal value of % recovery (i.e., for 70% recovery you have a negative 30% bias). Use the average % recovery from the total number of matrix spikes analyzed. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

6.4.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

6.4.2.1 Replicate Analysis

1. Was a minimum of eight replicates analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

6.4.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision of standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

Determine the coefficient of variation using the following equation:

$$CV = \frac{s \times 100}{x_{DL}}$$

where:

x_{DL} = the decision level concentration

s = the sample standard deviation given by the equation:

$$s^* = [(x_i - x)^2/(n - 1)]^{1/2}$$

*Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (σ) rather than the sample standard deviation (s).

Apply the CV to the decision level to determine the false negative or false positive value as follows:

False positive value = Decision level value + (CV x decision level)

False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)
= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)
= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable. Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

6.5 Blanks

1. Verify that method blank analysis has been reported per matrix, per concentration level, at the proper frequency, for each GC system used to analyze samples, for each extraction batch.

ACTION: If the proper type and frequency of method blank have not been analyzed, use professional judgement to determine the effect on the data.

2. Verify that all blank analyses contain less than the Required Detection Limits (RDL) of any pesticide or interfering peak.

ACTION: Any pesticide detected in the sample and also detected in any associated blank, must be qualified as non-detect (U) when the sample concentration is less than 5X the blank concentration.

NOTE: In instances where more than one blank is associated with a given sample, quantification should

be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

6.6 Compound Identification

1. Verify that positive identifications have GC/MS confirmation or dissimilar column analysis (the 3% OV-1 column cannot be used for confirmation if both dieldrin and DDE are identified).

ACTION: If the qualitative criteria for dual column or GC/MS confirmation were not met, all reported positive results should be flagged as presumptively present at an estimated quantity (NJ).

2. If multipeak pesticides (chlordane and toxaphene)/PCBs were reported, were the retention times and relative peak height ratios of major component peaks compared against the appropriate standard chromatograms.

ACTION: If multipeak pesticides/PCBs exhibit marginal pattern-matching quality professional judgement should be used to establish whether the differences are attributable to environmental "weathering". If the presence of a multipeak pesticide/PCB is strongly suggested, results should be reported as presumptively present (N).

3. Verify that the sample chromatogram agree with the correct daily standard chromatogram, and that the retention time windows match.

ACTION: If the chromatograms do not agree, and the retention time windows vary significantly, the reviewer must use professional judgement to determine the flags that should be applied and the usefulness of the data.

6.7 Compound Quantitation and Reported Detection Limits

1. Verify that the reported values, both positives and non-detects, have been correctly adjusted to reflect all dilutions, concentrations, splits, cleanup procedures, dry weight factors, an any other adjustments that have not been accounted for by the method.

Pesticide/PCBs for waters: $ug/L = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_s)(V_i)}$

Pesticide/PCBs for soils: $ug/kg = \frac{(A_x)(I_s)(V_t)}{(A_s)(W_s)(D)(V_i)}$

A_x = area of quantitation peak(s)
I_s = amount of standard injected (ng)
V_t = volume of total extract (ul)
V_i = volume injected (ul)
V_s = volume of sample (ml)
W_s = weight of sample extracted (g)
D = (100 - % moisture)/100 or 1 for wet weight basis
A_s = Area of external standard

ACTION: If incorrect values have been reported, it is essential that the correct values be determined. The reviewer should contact the laboratory to verify any corrections made to the data.

6.8 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

6.9 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

6.10 Optional QA Checks

6.10.1 Surrogate Recovery

1. Verify that the recoveries are within the control limits.

ACTION: If not, check the raw data for possible interferences.

2. If recoveries are out of control limits, use professional judgement to determine the appropriate action.

ACTION: If zero surrogate pesticide recovery is reported, determine whether the surrogate is outside its retention time window. If yes, use professional judgement in the evaluation of this data. If the surrogate is not present, flag all negative results as rejected (R).

7.0 PCBs

7.1 Sample Holding Times

1. Were any of the sample holding times exceeded?

Sample Holding Times from date of sample collection:

Water - 7 days to extract
Soil, sediment, sludges - 14 days to extract

All - analyze within 40 days after extraction

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL), based on the reviewers professional judgement and the nature of the sample and analyte. Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

7.2 Instrument Performance

1. Examine standard chromatograms to assure adequate quantitation peak resolution.

ACTION: If there is inadequate peak separation (<25% quantitation peak resolution), flag the data as rejected (R).

2. Examine raw data and spot check the surrogate compound retention times.

ACTION: If the retention time shift for the surrogate compound exceeds 2.0% for packed columns, 0.3% for capillary columns, 1.5% for wide-bore capillary columns, the data may be rejected (R), but the qualification is left up to the professional judgement of the reviewer.

7.3 Initial and Continuing Calibration Verification

1. Verify that the Aroclors of interest have been analyzed at a minimum of three different concentrations (e.g., Aroclor 1260 analyzed at 1.0, 5.0 and 10.0 ppm).

ACTION: If no, flag data as estimated (J).

2. Verify that the %RSD of the calibration factor for all Aroclors is less than or equal to 10% for the initial linearity check.

$$\%RSD = \frac{s \times 100}{x}$$

where:

s = standard deviation of 5 response factors
x = mean of 5 response factors

ACTION: If criteria for linearity is not met, flag all associated quantitative results as estimated (J).

3. Verify that the continuing calibration for each Aroclor of interest was analyzed daily.

ACTION: If no, flag all associated sample results as estimated (J).

4. Verify %D between calibration factors.

ACTION: If the %D for standard analysis is greater than 15% on the quantitation column or greater than 20% on the confirmation column, flag all associated positive sample results as estimated (J).

7.4 Error Determination

See Part I - Section 2.8 for QA samples to be used for error determination.

7.4.1 Determination of Bias (% Recovery - Optional for QA-2; Mandatory for QA-3)

7.4.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc. - Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%,the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered whenever there is consistent evidence of bias.

7.4.1.2 Adjustment of Sample Values for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample values. % bias is the reciprocal value of % recovery (i.e., for 70% recovery you have a negative 30% bias). Use the average % recovery for the total number of matrix spikes analyzed. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

7.4.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

7.4.2.1 Replicate Analysis

1. Was a minimum of eight replicates analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

7.4.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision of standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

   Determine the coefficient of variation using the following equation:

$$CV = \frac{s \times 100}{x_{DL}}$$

where:

x_{DL} = the decision level concentration

s = the sample standard deviation given by the equation:

$$s^* = [(x_i - x)^2/(n - 1)]^{1/2}$$

*Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (σ) rather than the sample standard deviation (s).

Apply the CV to the decision level to determine the false negative or false positive value as follows:

False positive value = Decision level value + (CV x decision level)

False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)
= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)
= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect

and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable. Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

7.5 Blanks

1. Verify that method blank analysis has been reported per matrix, per concentration level, at the proper frequency, for each GC system used to analyze samples, for each extraction batch.

ACTION: If the proper type and frequency of method blank have not been analyzed, use professional judgement to determine the effect on the data.

2. Verify that all blank analyses contain less than the Required Detection Limits (RDL) of any PCB or interfering peak.

ACTION: Any PCB detected in the sample and also detected in any associated blank, must be qualified as non-detect (U) when the sample concentration is less than 5 times the blank concentration.

NOTE: In instances where more than one blank is associated with a given sample, quantification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

7.6 Compound Identification

1. Review the data to confirm that positive results were identified using the correct retention time window, peak height ratio, and "fingerprint" pattern. Determine which peak(s) were used to quantitate each Aroclor and verify that the finger-print pattern matches the standard chromatogram.

ACTION: If the reported positive results were not identified correctly, professional judgement should be used to qualify the data.

2. Verify that dual column confirmation of positive results identify the same Aroclor or that the lab performed GC/MS confirmation of PCB results that were greater than 10 ng/ul.

ACTION: If the qualitative criteria for dual column or GC/MS confirmation were not met, all reported positive results should be flagged as presumptively present at an estimated quantity (NJ).

7.7 Compound Quantitation and Reported Detection Limits

1. Verify that the reported values, both positives and non-detects, have been correctly adjusted to reflect all dilutions, concentrations, splits, cleanup procedures, dry weight factors, and any other adjustments that have not been accounted for by the method.

PCBs for waters: $ug/L = \frac{(A_x)(I_s)(V_t)}{(A_{is})(V_s)(V_i)}$

PCBs for soils: $ug/kg = \frac{(A_x)(I_s)(V_t)}{(A_s)(W_s)(D)(V_i)}$

A_x = area of quantitation peak(s)
I_s = amount of standard injected (ng)
V_t = volume of total extract (ul)
V_i = volume injected (ul)
V_s = volume of sample (ml)
W_s = weight of sample extracted (g)
D = (100 - % moisture)/100
A_s = Area of external standard

ACTION: If incorrect values have been reported, it is essential that the correct values be determined. The reviewer should contact the laboratory to verify any corrections made to the data.

7.8 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

7.9 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

7.10 Optional QC Checks

7.10.1 Surrogate Recovery

1. Verify that the recoveries are within the control limits.

ACTION: If not, check the raw data for possible interferences.

2. If recoveries are out of control limits, use professional judgement to determine the appropriate action.

ACTION: If zero surrogate pesticide recovery is reported, determine whether the surrogate is outside its retention time window. If yes, use professional judgement in the evaluation of this data. If the surrogate is not present, flag all negative results as rejected (R).

8.0 2,3,7,8-TCDD

8.1 Sample Holding Times

1. Were any of the sample holding times exceeded?*

   To extract - 6 months from sample collection

   To analysis - 40 days from extraction

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL). Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

*Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

8.2 Instrument Performance

1. Verify that a performance check solution was run at the beginning of each 8-hour shift and at the end of the final 8-hour period.

ACTION: If no, use professional judgement to qualify data.

2. Have the ion abundance criteria been met for each instrument used?

m/z	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
69	(reference only)
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

ACTION: If no, use professional judgement to flag all associated data.

3. Is the resolution of the valley between 2,3,7,8-TCDD and the peak representing all other TCDD isomers $\leq$ 25%? (where, Valley (%) = X/Y × 100 and X is measured from the valley of the least resolved adjacent isomer to the baseline, Y = peak height of 2,3,7,8-TCDD).

ACTION: If no, use professional judgement to qualify all positive sample data associated with the standard.

8.3 Initial Calibration

1. Verify the following:

-the five 2,3,7,8-TCDD standards have been run.

-the ratios of ions 320 to 322 for 2,3,7,8-TCDD and 332 to 334 for $^{13}C_{12}$-2,3,7,8-TCDD is $\geq$ 0.67 and $\leq$ 0.87.

-signal-to-noise ratios for ions 257, 320, 322 and 328 is $\geq$ 2.5 and the signal to noise ratios for ions 332 and 334 is $\geq$ 10.

-the ions 257, 320, 322 for 2,3,7,8-TCDD reached a maximum within three seconds of $^{13}C_{12}$-TCDD ions 332 and 334.

-during the unlabeled 2,3,7,8-TCDD calibration the percent Relative Standard Deviation (%RSD) of relative response factors for the five calibration concentrations is less than or equal to 15%.

-during the $^{37}Cl_4$-2,3,7,8-TCDD calibration the %RSD of relative response factors for the three calibration concentrations is less than or equal to 15%.

ACTION: If the calibration curve standards fail the acceptance criteria, use professional judgement to qualify associated data.

8.4 Continuing Calibration

1. Verify the following:

-the calibration standard has been run for every eight hour shift.

-the ratios of ions are 320 to 322 for 2,3,7,8-TCDD and 332 to 334 for $^{13}C_{12}$-2,3,7,8-TCDD $\geq$ 0.67 and $\leq$ 0.87.

-the signal to noise ratios for ions are 257, 320, 322 and 328 $\geq$ 2.5 and the noise ratios for ions 332 and 334 $\geq$ 10.

-the ions are 257, 320, 322 for 2,3,7,8-TCDD reached a maximum within three seconds of $^{13}C_{12}$-TCDD ions 332 and 334.

-the percent difference of the relative response factor is $\pm$ 30% of the initial calibration.

ACTION: If the calibration standard fails the above acceptance criteria, use professional judgement to qualify associated data.

8.5 Error Determination

See Part I - Section 2.8 for QA samples to be used for error determination.

8.5.1 Determination of Bias (% Recovery - Optional for QA-2; Mandatory for QA-3)

8.5.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc. - Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%, the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered whenever there is consistent evidence of bias.

8.5.1.2 Adjustment of Sample Values for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample values. % bias is the reciprocal value of

% recovery (i.e., for 70% recovery you have a negative 30% bias). Use the average % recovery from the total number of matrix spikes analyzed. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

8.5.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

8.5.2.1 Replicate Analysis

1. Was a minimum of eight replicates analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

8.5.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision of standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

   Determine the coefficient of variation using the following equation:

$$CV = \frac{s \times 100}{x_{DL}}$$

where:

x_{DL} = the decision level concentration

s = the sample standard deviation given by the equation:

$$s^* = [(x_i - x)^2/(N - 1)]^{1/2}$$

*Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (σ) rather than the sample standard deviation (s).

Apply the CV to the decision level to determine the false negative or false positive value as follows:

False positive value = Decision level value + (CV x decision level)

False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)
= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)
= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives

have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable. Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

8.6 Blanks

1. Has a method blank, spiked with the internal standards, been analyzed with each case?

ACTION: If the method blank contains contaminants at the method detection limit of the matrix of interest, the blank must be reanalyzed. If the contaminated method blank was extracted along with a batch of samples the associated positive samples must be reanalyzed. If the samples were not reanalyzed or if contamination is present in the second analysis, all positive sample results less than 5 times the concentration in the blank are flagged as non-detects (U).

2. Has a reagent blank been analyzed along with each case?

ACTION: The reagent blank should be free of contamination. If the level is > 0.10 ppb, use professional judgement to qualify associated data.

8.7 Internal Standard Requirements

1. Did ion 332 or 334 fail the relative ion intensity criteria ($\geq$ 0.67 and $\leq$ 0.87)? If yes, was the sample reanalyzed?

ACTION: If initial analysis and reanalysis both have ions 332 or 334 outside the relative ion intensity criteria, reject all quantitation results, including detection limits.

8.8 Identification of 2,3,7,8-TCDD

1. Verify the following:

-the retention time of the sample component is within three seconds of the retention time of the $^{13}C_{12}$ - 2,3,7,8-TCDD.

-the integrated ion currents detected for m/z 257, 320, and 322 maximize simultaneously.

-the ion ratio of 320 to 322 and 332 to 334 is $\geq$ .67 and $\leq$ .87.

-the integrated ion current for each analyte and surrogate compound (m/z 257, 320, 322 and 328) are at least 2.5 times background noise.

-internal standard ions are at least 10 times background noise. (The integrated ion current or the internal standard ions must not saturate the detector.)

-if the above requirements were not met, then reanalyze the samples.

ACTION: If initial analysis and reanalysis both have the sample outside the above limits, 2,3,7,8-TCDD was not qualitatively identified, reject (R) all positive results.

ACTION: If no, reject all quantitation results, including detection limits.

8.9 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

8.10 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

8.11 Optional QC Checks

8.11.1 Surrogate Recovery

1. Was surrogate outside of specifications for any samples? If yes, were the appropriate samples reanalyzed?

ACTION: For $^{37}Cl_4$-2,3,7,8-TCDD the ion 328 must have a signal to noise ratio of $\geq$ 2.5. The surrogate recovery must be $\geq$ 60 and $\leq$ 140 percent. If the signal to noise ratio for ion 328 does not meet acceptance criteria, reject positive and ND data. If surrogate recovery is outside acceptance limits, use professional judgement to qualify associated data.

9.0 Generic Data Validation Procedures

9.1 GC Analyses (i.e., Herbicides, Organophosphate, Pesticides)

9.1.1 Sample Holding Times

1. Were any of the sample holding times exceeded?*

   Sample holding times can generally be found in the analytical method, or in the appropriate reference, such as the 40CFR Part 136, MCAWW, or SW846.

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL). Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

*Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

9.1.2 Instrument Performance

1. Check the raw data to verify that there is adequate resolution (> 25%) between peaks of the standard compounds.

ACTION: If adequate separation is not achieved, flag all affected compound data as rejected (R).

2. Check raw data to verify that retention time windows are reported and that all standard compounds are within the established retention time windows.

ACTION: If the standard compounds do not fall within the retention time windows, professional judgement should be used in the evaluation of associated sample results.

9.1.3 Initial and Continuing Calibration Verification

1. Verify that the %RSD of the calibration factor for the calibration compounds are less than or equal to 10% for the initial calibration linearity check.

ACTION: If criteria for linearity is not met, flag all associated quantitative results as estimated (J).

2. Verify the proper analytical sequence was run as required.

ACTION: If the proper standards have not been analyzed and the sequence followed, use professional judgement to determine the severity of the effect and qualify the data accordingly.

3. Review the sample data to verify whether a standard was used as a quantitation standard or as a confirmation standard.

ACTION: If the %D for standard analysis is greater than 15% on the quantitation column or greater than 20% on the confirmation column, flag all associated positive sample results as estimated (J).

9.1.4 Error Determination

See Part I - Section 2.8 for QA samples to be used for error determination.

9.1.4.1 Determination of Bias (% Recovery - Optional for QA-2; Mandatory for QA-3)

9.1.4.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc.} - \text{Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%, the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered

whenever there is consistent evidence of bias.

9.1.4.1.2 Adjustment of Sample Values for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample values. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

9.1.4.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

9.1.4.2.1 Replicate Analysis

1. Was a minimum of four replicates for QA-2 or eight replicates for QA-3 analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

9.1.4.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision of standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

Determine the coefficient of variation using the following equation:

$$CV = \frac{s \times 100}{x_{DL}}$$

where:

x_{DL} = the decision level concentration

s = the sample standard deviation given by the equation:

$$s^* = [(x_i - x)^2/(n - 1)]^{1/2}$$

*Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (σ) rather than the sample standard deviation (s).

Apply the CV to the decision level to determine the false negative or false positive value as follows:

False positive value = Decision level value + (CV x decision level)

False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)

= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)

= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable. Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

9.1.5 Blanks

1. Verify that method blank analysis has been reported per matrix, per concentration level, at the proper frequency, for each GC system used to analyze samples, for each extraction batch.

ACTION: If the proper type and frequency of method blank have not been analyzed, use professional judgement to determine the effect on the data.

2. Verify that all blank analyses contain less than the Required Detection Limits (RDL) of any compound or interfering peak.

ACTION: Any compound detected in the sample and also detected in any associated blank, must be qualified as non-detect (U) when the sample concentration is less than 5X the blank concentration.

NOTE: In instances where more than one blank is associated with a given sample, quantification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

9.1.6 Compound Identification

1. Verify that positive identifications have dissimilar column analysis.

ACTION: If the qualitative criteria for dual column were not met, all reported positive results should be flagged as presumptively present at an estimated quantity (NJ).

2. If multipeak compounds were reported, were the retention times and relative peak height ratios of major component peaks compared against the appropriate standard chromatograms.

ACTION: If multipeak compounds exhibit marginal pattern-matching quality professional judgement should be used to establish whether the differences are attributable to environmental "weathering". If the presence of a multipeak compound is strongly suggested, results should be reported as presumptively present (N).

3. Verify that the sample chromatogram agree with the correct daily standard chromatogram, and that the retention time windows match.

ACTION: If the chromatograms do not agree, and the retention time windows vary significantly, the reviewer must use professional judgement to determine the flags that should be applied and the usefulness of the data.

9.1.7 Compound Quantitation and Reported Detection Limits

1. Verify that the reported values, both positives and non-detects, have been correctly adjusted to reflect all dilutions, concentrations, splits, cleanup procedures, dry weight factors, an any other adjustments that have not been accounted for by the method.

For waters: $ug/L = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_s)(V_i)}$

For soils: $ug/L = \frac{(A_x)(I_s)(V_t)}{(A_s)(W_s)(D)(V_i)}$

A_x = area of quantitation peak(s)
I_s = amount of standard injected (ng)
V_t = volume of total extract (ul)
V_i = volume injected (ul)
V_s = volume of sample (ml)
W_s = weight of sample extracted (g)
D = (100 - % moisture)/100 or 1 for wet weight basis
A_s = Area of external standard

ACTION: If incorrect values have been reported, it is essential that the correct values be determined. The reviewer should contact the laboratory to verify any corrections made to the data.

9.1.8 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

9.1.9 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

9.2 Non-Metal Inorganic Parameters (i.e., anions, pH, TOC, nutrients)

9.2.1 Sample Holding Times

1. Were any of the sample holding times exceeded?*

Sample Holding Times can generally be found in the analytical method, or in the appropriate reference, such as the 40CFR Part 136, MCAWW, or SW846.

ACTION: If yes, flag as estimated (J) those values above the Instrument Detection Limit (IDL). Values that are less than the IDL can be flagged as estimated (UJ) or rejected (R) based on the reviewers professional judgement and the nature of the sample and analyte.

*Because of their long shelf lives, performance evaluation samples do not have any associated holding times.

9.2.2 Initial and Continuing Calibration Verification

1. Verify that the %RSD of the calibration factor for the calibration compounds are less than or equal to 10% for the initial calibration linearity check.

ACTION: If criteria for linearity is not met, flag all associated quantitative results as estimated (J).

2. Verify the proper analytical sequence was run as required.

ACTION: If the proper standards have not been analyzed and the sequence followed, use professional judgement to determine the severity of the effect and qualify the data accordingly.

9.2.3 Error Determination

See Part I - Section 2.8 for QA samples to be used for error determination.

9.2.3.1 Determination of Bias (% Recovery - Optional for QA-2; Mandatory for QA-3)

9.2.3.1.1 Percent Recovery

1. Were at least eight spiked sample replicates for the matrix of interest analyzed at the required frequency?

ACTION: If no, flag as recovery not determined (RND) all data for which spiked samples were not analyzed.

2. Determine the average recovery of the eight spiked replicates. Is the average recovery within the applicable control limits (80% to 120%)?

% recovery for a single spiked sample =

$$\frac{\text{Spiked sample conc. - Sample conc.}}{\text{Spike conc. added}} \times 100$$

ACTION: If recoveries are within applicable control limits, no bias is considered. If % Recovery is less than 80% or greater than 120%, the sample data should be flagged with a (J) estimate and a corresponding (-) or (+) sign to show direction of the bias. Adjustment of sample values should be considered whenever there is consistent evidence of bias.

9.2.3.1.2 Adjustment of Sample Values for Bias

1. Depending on bias direction, add or subtract the value (% Bias x spike concentration) to or from the sample values. % bias is the reciprocal value of % recovery (i.e., for 70% recovery you have a negative 30% bias). Use the average % recovery from the total number of matrix spikes analyzed. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

9.2.3.2 Determination of Precision (Optional for QA-2; Mandatory for QA-3)

9.2.3.2.1 Replicate Analysis

1. Was a minimum of eight replicates analyzed? If yes, determine coefficient of variation. If no, flag data with precision not determined (PND), for which replicate samples were not analyzed.

9.2.3.2.2 Coefficient of Variation (Percent Relative Standard Deviation)

1. The coefficient of variation (CV) is used in determining the precision of standard deviation. The CV expresses the standard deviation as a percentage of the mean (average) value of the replicate values. The CV is used to determine a false positive or false negative value for results that are respectively greater than or less than a decision level concentration.

   Determine the coefficient of variation using the following equation:

   $$CV = \frac{s \times 100}{x_{DL}}$$

   where:

   x_{DL} = the decision level concentration

   s = the sample standard deviation given by the equation:

   $$s^* = [(x_i - x)^2/(n - 1)]^{1/2}$$

   *Note: When using a programmable calculator or computer statistics software, be sure the above equation with (n - 1) is used and not (n) by itself. The equation using (n) is to determine the population standard deviation (σ) rather than the sample standard deviation (s).

   Apply the CV to the decision level to determine the false negative or false positive value as follows:

   False positive value = Decision level value + (CV x decision level)

   False negative value = Decision level value - (CV x decision level)

Example:

For an decision level = 50 ppm and CV = 20%

False positive value = 50 ppm + (20% x 50 ppm)
= 50 ppm + (10 ppm)
= 60 ppm

False negative value = 50 ppm - (20% x 50 ppm)
= 50 ppm - (10 ppm)
= 40 ppm

For the above false positive example, any value between 50 ppm and 60 ppm are considered suspect and should be reanalyzed. Values above 60 ppm are considered actionable. In many cases, false positives have been considered actionable by the Agency for safety reasons. However, depending on the action to be taken, this can be costly and unjustifiable.

Consult the QA plan for intended use of data and data quality objectives.

For the above false negative example, any values between 40 ppm and 50 ppm are considered suspect and should be reanalyzed. Values below 40 ppm are considered non-actionable. In most cases, the decision maker will be using the false negative value as his decision level and not be concerned about the false positive value. Whenever sample values need to be corrected for both bias and precision, first correct the value for bias, then correct the biased value for precision.

9.2.4 Blanks

1. Verify that method blank analysis has been reported per matrix, per concentration level, at the proper frequency, for analytical system used to analyze samples, for each extraction batch.

ACTION: If the proper type and frequency of method blank have not been analyzed, use professional judgement to determine the effect on the data.

2. Verify that all blank analyses contain less than the Required Detection Limits (RDL) of any compound or interfering peak.

ACTION: Any compound detected in the sample and also detected in any associated blank, must be qualified as non-detect (U) when the sample concentration is less than 5X the blank concentration.

NOTE: In instances where more than one blank is associated with a given sample, quantification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

9.2.5 Compound Quantitation and Reported Detection Limits

1. Verify that the reported values, both positives and non-detects, have been correctly adjusted to reflect all dilutions, concentrations, splits, cleanup procedures, dry weight factors, and any other adjustments that have not been accounted for by the method.

ACTION: If incorrect values have been reported, it is essential that the correct values be determined. The reviewer should contact the laboratory to verify any corrections made to the data.

9.2.6 Performance Evaluation Samples

1. Were recovery limits within those set by the EMSL lab?

ACTION: If outside the limits, review on a compound by compound basis. If 50% of the compounds are outside of confidence limits or were misidentified, all sample results should be rejected (R).

9.2.7 Overall Assessment of Data

It is appropriate for the data reviewer to use professional judgment and express concerns and comments on the validity of the overall data package for a case. This is particularly appropriate for cases in which there are several QC criteria out of specification. The additive nature of QC factors which are out of specification is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user about data quality and data limitations. This helps the user to avoid using data inappropriately, while not precluding consideration of the data. The data reviewer would be greatly assisted in this endeavor if the data quality objectives were provided.

* U.S. Government Printing Office: 1990-748-159/00488